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## Chế tạo màng sợi nano lõi/vỏ từ chitosan, carrageenan, polyvinyl alcohol, và curcumin bằng phương pháp quay điện đồng trục hai lớp

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### TÓM TẮT

Phương pháp quay điện đồng trục đã được sử dụng để chế tạo thành công màng sợi nano lõi/vỏ làm từ chitosan (CS), carrageenan (CG), polyvinyl alcohol (PVA), và curcumin (CCM). Các yếu tố ảnh hưởng đến quá trình chế tạo sợi đã được khám phá, bao gồm tỷ lệ PVA/CS/CG là 8:1:1, nồng độ CG là 0,5%, khoảng cách từ đầu kim đến chất nền là 15 cm, điện áp là 18 kV và tốc độ dòng chảy là 0,1/0,1 mL/h. Các sợi nano thu được cho thấy cấu trúc lõi/vỏ rõ ràng (được quan sát thông qua ảnh TEM), với phân bố đường kính đồng đều trong phạm vi 100-600 nm, tập trung nhiều nhất trong phạm vi 100-300 nm và đường kính trung bình là  $274,35 \pm 19,57$  nm. Dữ liệu FTIR cho thấy màng sợi PVA/CCM@PVA/CS/CG chứa các nhóm chức năng đặc trưng của CG và CCM. Kết quả giải phóng CCM trong màng sợi chứng minh rằng lượng CCM được giải phóng nhanh trong vòng 6 giờ đầu tiên. Bắt đầu từ 12 giờ, lượng CCM được giải phóng có xu hướng giảm tốc và dần ổn định; đến 96 giờ, hàm lượng CCM được giải phóng đã đạt 83,96%. Kết quả nghiên cứu này chứng minh tiềm năng sử dụng màng nano sợi PVA/CCM@PVA/CS/CG trong quá trình lành vết thương hở.

**Từ khóa:** Màng sợi nano, cấu trúc lõi/vỏ, chữa lành vết thương, chitosan, carrageenan.

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# Fabrication of core/shell nanofiber membrane from chitosan, carrageenan, polyvinyl alcohol, and curcumin by two-layer coaxial electrospinning

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## ABSTRACT

Coaxial electrospinning was used to successfully construct a core/shell nanofiber membrane made from chitosan (CS), carrageenan (CG), polyvinyl alcohol (PVA), and curcumin (CCM). Factors influencing fiber fabrication were explored, including the PVA/CS/CG ratio of 8:1:1, CG concentration of 0.5%, distance from the needle tip to the substrate to 15 cm, voltage of 18 kV, and flow rate of 0.1/0.1 mL/h. The obtained nanofibers show a distinct core/shell structure (observed by TEM image), with a uniform diameter distribution in the range of 100-600 nm, most concentrated in the range of 100-300 nm, and an average diameter of  $274.35 \pm 19.57$  nm. The FTIR data show that the PVA/CCM@PVA/CS/CG fiber membrane contains CG and CCM-specific functional groups. The results of CCM release in the fiber membrane demonstrate that the amount of CCM released is rapid within the first 6 hours. Beginning at 12 hours, the amount of CCM released tends to decelerate and progressively stabilize, and by 96 hours, the CCM content released has reached 83.96%. This finding demonstrates the possible use of a PVA/CCM@PVA/CS/CG nanofiber membrane in open wound healing.

**Keywords:** *Nanofiber membrane, core/shell structure, wound healing, chitosan, carrageenan.*

## 1. INTRODUCTION

The majority of the body's structure is made up of skin, which serves as the primary protective barrier that keeps hazardous substances out. Healthy skin regulates body temperature and keeps substances in balance. However, the skin is extremely sensitive, experiencing both light touches and heavy blows. Damage to the skin affects all skin functions. The speed with which the wound heals is determined by its severity.<sup>1</sup>

Wound dressings play an important role in the therapy phase; selecting the proper wound

dressing can save time and money. Furthermore, recent research have indicated that nanomaterials are becoming increasingly popular, with one example being wound dressings made of nanofiber membranes. Nanofibers offer several essential properties, including a tiny diameter, controllable pore size, a high surface area to volume ratio, and controlled drug release rate and time by altering the fiber structure and morphological size, resulting in excellent wound healing. As a result, nanofibers are perfect for medical applications, particularly in the fabrication of wound dressings.<sup>2-4</sup>

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Many research initiatives have been carried out to fabricate chitosan (CS) nanofibers using the electrospinning process. Dhurai et al.<sup>5</sup> used electrospinning to create nanofibers from polylactic acid (PLA) and CS that included curcumin (CCM) as a medicine. In this investigation, the CS/PLA ratio was 5.5% (w/v), CCM was 11% (w/v), and the voltage applied was 20 kV. SEM examination revealed that the average fiber diameter was 66 nm. CCM incorporated onto CS/PLA nanofilm improved antioxidant capacity while being toxicity-free.<sup>5</sup> In 2017, Goonoo et al. electrospun nanofibers from kappa-carrageenan ( $\kappa$ -CG) and fucoidan with poly(ester-ether) polydioxanone at varying ratios and solvents. The fiber mats were employed for cell culture research and tissue engineering.<sup>6</sup> In 2020, Madruga et al. investigated and developed biocompatible nanofibers made from a combination of polyvinyl alcohol (PVA) and carboxymethyl-kappa-carrageenan (CMKC). The aqueous solution had ratios of 1:0, 1:0.25, 1:0.4, 1:0.5, and 1:0.75 (w/w PVA:CMKC). They employed a 15 kV electric field in the electrospinning process, a 15 cm distance from the tip to the collector, and a 1 mL/h pump rate to produce nanofibers with a diameter of less than 300 nm. CMKC is anticoagulant and antibacterial against *Escherichia coli* and *Staphylococcus aureus*, as well as effective at absorbing fluids and retaining moisture. The combination of CMKC enhances cytocompatibility, biodegradability, and cell proliferation.<sup>7</sup> Gouda et al. effectively manufactured nanofiber membranes for wound healing and skin regeneration using electrospinning of PVA, iota-carrageenan ( $\iota$ -CG), and graphene oxide. The combination of graphene oxide and nanofibers enhances skin regeneration. Graphene-based materials have several functions, including a large surface area, protein adsorption capacity, and antibacterial qualities, hence they are utilized as wound dressings to prevent infection in diverse wounds.

Many studies have shown that a tiny quantity of graphene oxide improves the attributes of polymer membranes, including mechanical strength, wound healing speed, and tissue regeneration. The membranes were examined for *Escherichia coli* and *Staphylococcus* infection. The results revealed that the membranes have good wound healing, reduce scar formation, and are antibacterial. Biopolymer-based electrospun nanofibers are extremely useful for biomedical applications.<sup>8</sup> In 2022, Vargas-Osorio et al. created electrospun nanofibers from polycaprolactone (PCL), CS, and  $\kappa$ -CG utilizing a safe solvent mixture of formic and acetic acid. The interactions of positively and negatively charged hydrophilic polysaccharides resulted in high polymer stability. All fiber mats exhibited morphological traits that indicated an average fiber diameter at the nanoscale. Investigations on living cells revealed no harmful effects; the cells multiplied and spread over time.<sup>9</sup>

In this study, a PVA/CCM@PVA/CS/CG nanofibrous membrane was electrospun to promote wound dressing orientation. Coaxial electrospinning was employed as a simple, one-step method for manufacturing uniformly shaped polymer fibers with core-shell structure. PVA is a promising synthetic polymer for wound dressing applications because to its biocompatibility, strong tensile and hydrophilic qualities, and fiber forming capabilities.<sup>9-12</sup> CS is a positively charged biopolymer produced via deacetylation of chitin.<sup>13</sup> CS is biodegradable, biocompatible, bactericidal, hemostatic, and has minimal toxicity, making it useful in a variety of medical applications.<sup>14-15</sup> CG is an anionic sulfated polysaccharide composed of galactose and anhydrogalactose units linked by glycoside linkages.<sup>16</sup> CG is a stabilizer, thickener, and gelling agent having numerous desired qualities in biological applications such as antiviral, anticancer, and immunomodulatory actions.<sup>17</sup> The combination of two oppositely charged

polymers, CS and CG, was designed to optimize the nanofiber production process.<sup>18</sup> In addition, CCM was added to boost the membrane's antibacterial capabilities and expedite wound healing on the skin.<sup>19-21</sup>

## 2. EXPERIMENT

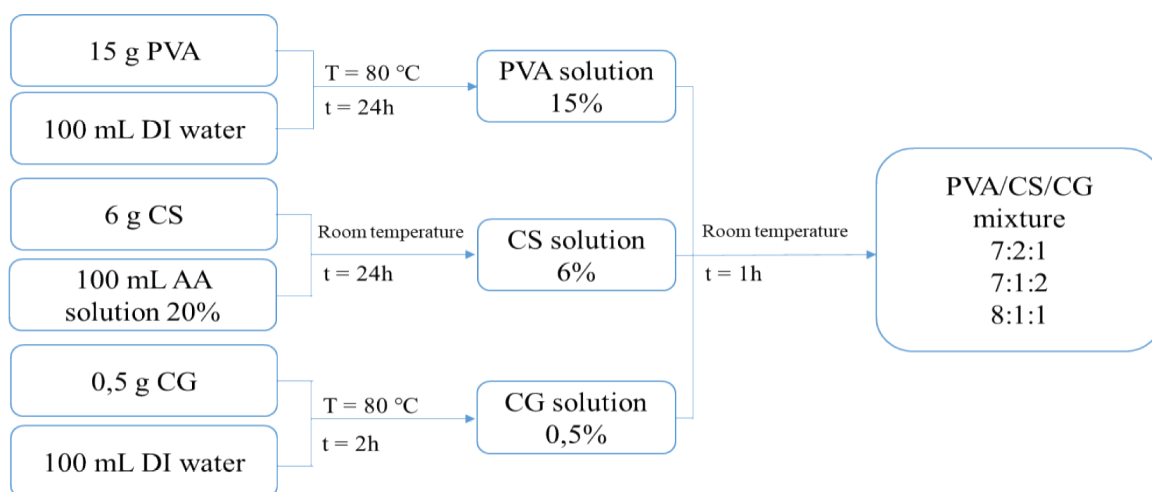
### 2.1. Chemicals

The chemicals used in this work include chitosan (CS, 92% deacetylation, Viet Nam), carrageenan (CG, Kappa-CG, Philippines), polyvinyl alcohol (PVA, 99.5%, hydrolysis degree 87 – 89%, Shanghai Zhanyun Chemical Co., China), curcumin (CCM, >90%, Viet Nam), acetic acid (AA, 90%, Xilong, China), ethanol (95%, Chemsol, Viet Nam), phosphate buffered saline (PBS, Himedia, India), Tween 20 (Guangdong, China). All other materials and reagents applied in this work were of analytical grade unless otherwise noted.

### 2.2. Synthesis of PVA/CCM@PVA/CS/CG nanofiber membrane

#### 2.2.1. The shell mixture preparation

The steps to prepare CS/PVA/CCM mixture are shown in Figure 1. Firstly, to prepare a homogenous 15% PVA solution, 15 g of PVA was mixed with 100 mL of distilled water in a glass beaker and swirled on a magnetic stirrer at 80°C for 24 hours. To make a 6% CS solution, 6 g of CS was added to a glass beaker holding 100 mL of 20% AA and stirred on a magnetic stirrer at room temperature for 24 hours. A 0.5% CG solution was obtained by adding 0.5 g of CG to a glass beaker holding 100 mL of distilled water and stirring on a magnetic stirrer at 80°C for 2 hours. Finally, the PVA/CS/CG shell solution was prepared by combining PVA, CS, and CG solutions in various ratios (7:2:1, 7:1:2, and 8:1:1) and stirring for 1 hour to produce a homogenous mixture.<sup>22-23</sup>

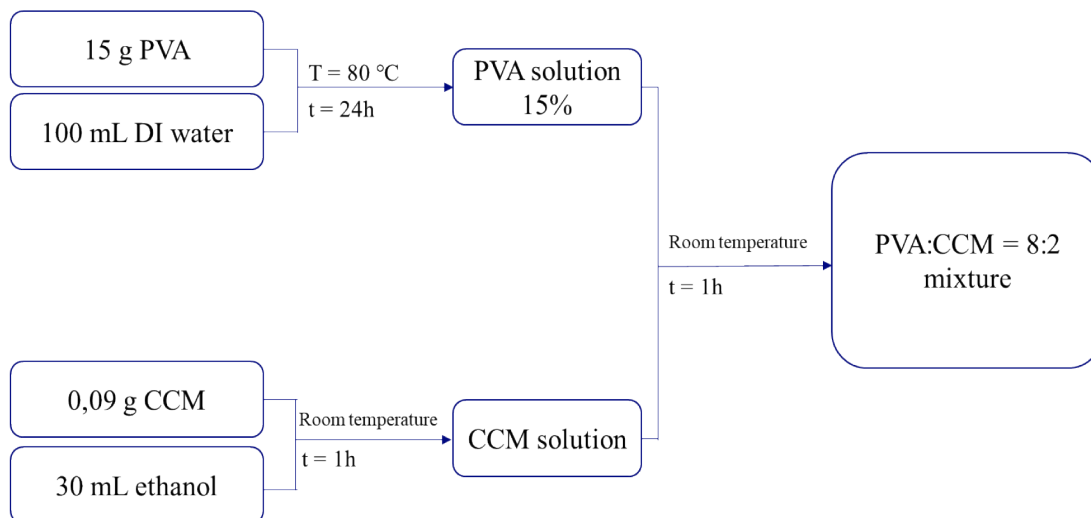


**Figure 1.** Flow chart of shell solution preparation process.

#### 2.2.2. The core mixture preparation

Figure 2 depicts the processes for preparing a PVA/CCM mixture. To create a 15% homogenous PVA solution, mix 15 g of PVA with 100 mL of distilled water in a glass beaker and stir with a magnetic stirrer at 80°C for 24

hours. Next, add 0.09 g of CCM to 30 mL of ethanol and stir for 1 hour at room temperature to create a CCM solution. The core solution was created by mixing the PVA and CCM solutions in an 8:2 ratio and stirring on a magnetic stirrer at room temperature for 1 hour.<sup>22-23</sup>



**Figure 2.** Flow chart of core solution preparation process.

### 2.2.3. Nanofiber membrane processing by coaxial electrospinning

The prepared core and shell solutions were injected into two 1 mL syringes, each attached to a double-layer concentric needle, and then placed in the electrospinning equipment. The concentric needles included an outer tube with an inner diameter of 1.01 mm and an outside diameter of 1.49 mm, as well as an inner tube with an inner diameter of 0.41 mm and an outer diameter of 0.72 mm. The sample collection board was protected with aluminum foil and a voltage generator.<sup>24-26</sup> During the electrospinning process, the parameters were set with the sample injection flow rate at 0.1/0.1 mL/h, 0.2/0.2 mL/h, the voltage at 17 kV, 18 kV, 19 kV, and the distance from the needle tip to the sample collection was 14 cm, 15 cm, and 16 cm.

## 2.3. Characterisation

### 2.3.1. The morphology, diameter, and size distribution of nanofibers

During the pre-tests, the diameter of the nanofibers was measured using an optical microscope (Nikon EPIPHOT 200, Japan). The nanofibers accumulated immediately on the aluminum layer and were seen using a Hitachi S-4800 scanning electron microscope made in

Japan. To better their observation, the nanofibers were sputter-coated with a platinum coating before being measured. The average fiber size and fiber size distribution were calculated using ImageJ software and SEM image data. The core/shell structure of the membranes was examined using TEM (JEM-1400 Flash Jeol, Japan) in a vacuum environment. A drop of diluted sample was placed on a cellulose stub for observation.

### 2.3.2. Fourier transform infrared spectroscopy (FTIR)

The PVA/CCM@PVA/CS/CG nanofibrous membrane's specific functional groups were described using an FTIR instrument (Nicolet 6700, Thermo, USA). The FTIR spectra was obtained under nitrogen flow with a total of 32 scans and a 4 cm<sup>-1</sup> resolution in the 4000-400 cm<sup>-1</sup> wavenumber band.

### 2.3.3. Survey of curcumin content in fiber membrane

*Establishing a standard curve for quantifying curcumin in ethanol solution*

Weigh precisely 0.005 g of curcumin standard in a 100 mL volumetric flask containing ethanol solution. Pipet exactly 1 mL, 2 mL, 3 mL, 4 mL, and 5 mL of this standard solution into a 25 mL volumetric flask, filling to the mark with



the same solvent. The equivalent concentrations for the five solutions above are 0.002; 0.004; 0.006; 0.008; and 0.01 mg/mL, respectively. The absorbance of solution A is measured at the wavelength  $\lambda_{\max}$ . A graph is created using the measured values to show the connection between A and C, which yields the linear equation of A in relation to C. The equation above is used to calculate the concentration of CCM in the sample at the following stages.<sup>22-23</sup>

#### *Determination of curcumin content of nanofiber membranes in ethanol solution*

First, 0.005 g of the nanofiber membrane was cleaned with alcohol to remove any CCM that had adhered to the membrane's surface. The membrane was then placed in a glass beaker holding 10 mL of ethanol solution. The beaker was sonicated at predefined time intervals (15, 30, 45, and 60 minutes). At these time points, 2 mL of the sample was removed for analysis, and 2 mL of fresh ethanol was added. The 2 mL of extracted material was combined with 8 mL of ethanol before UV-Vis analysis to quantify the amount of CCM released.

#### *2.3.4. Investigation of curcumin release process*

##### *Establishing a standard curve for quantifying curcumin in buffer solution*

Weigh exactly 0.005 g of curcumin standard in a 100 mL volumetric flask containing a 4:1 mixture of ethanol solution and PBS buffer solution. Pipette exactly 1 mL, 2 mL, 3 mL, 4 mL, and 5 mL of this standard solution into a 25 mL volumetric flask, filling to the mark with the same solvent. The equivalent concentrations for the five solutions above are 0.002; 0.004; 0.006; 0.008; and 0.01 mg/mL, respectively. The absorbance of these solutions is measured at the maximum wavelength ( $\lambda_{\max}$ ). A graph is created using the measured values to show the connection between A and C, which yields the linear equation of A in relation to C. The equation above is used to calculate the concentration of CCM in the sample at each stage. The amount

of CCM released for each survey period can be calculated using the standard curve equation described above.

#### *Experimental release of curcumin in buffer solution*

To imitate the animal serum environment, 0.005 g of nanofiber membrane was cleaned with alcohol before being placed in a glass beaker with 10 mL of PBS solution (pH 7.4) and 1% tween 20. The beakers were kept at a temperature of  $37 \pm 1^\circ\text{C}$  using a thermostat. Next, at certain time intervals (5 minutes, 10 minutes, 15 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, 4 hours, 6 hours, 12 hours, 24 hours, 48 hours, 72 hours, and 96 hours), 2 mL of sample was removed for analysis and 2 mL of new buffer was added. 2 mL of the analyzed sample was mixed with 8 mL of ethanol solution before being analyzed using a UV-Vis spectrometer to determine the amount of released CCM. Therefore, the percentage of CCM drug released from the fiber membrane can be calculated.<sup>22</sup>

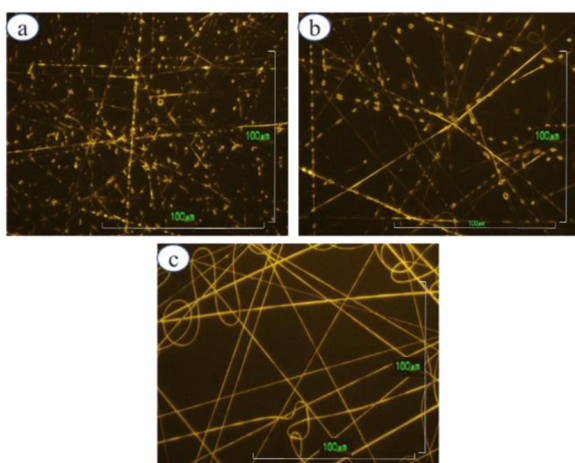
### **3. RESULTS AND DISCUSSION**

#### **3.1. Results on the influence of some factors on the electrospinning process**

##### *3.1.1. Effect of PVA/CS/CG ratio*

PVA, CS, and CG solutions were made and combined in the following ratios: 7:2:1, 7:1:2, and 8:1:1 to study the effect of the PVA/CS/CG ratio. Figure 3 depicts the survey results as observed via an optical microscope. The results demonstrate that in Figure 3a, there are many individual particles and fiber particles, but no full fibers are created. When the CG ratio is increased in the solution in Figure 3b, it is noted that there are less individual particles, more fiber particles, and fibers without particles; however, these fibers are not continuous but rather fractured. Furthermore, the PVA ratio utilized in the electrospinning solution is insufficient to draw full fibers, so adding more CG to the fiber does not result in continuous formation. In Figure 3c, the PVA ratio is raised, and no more particles or fiber particles occur;

instead, the fiber is created continuously and without breaking. The addition more amount of CG (ratios of 7:1:2 and 7:2:1) increases the conductivity of electrospun solutions<sup>27</sup>, resulting in stronger repulsive forces between the charged polymer groups, which enhances the elongation forces during eletrospinning, resulting in thinner fiber with breaking formation. These findings indicate that the 8:1:1 PVA/CS/CG ratio produces a desirable fiber morphology, making it the optimized proportion for incorporating CG into the nanofiber system.

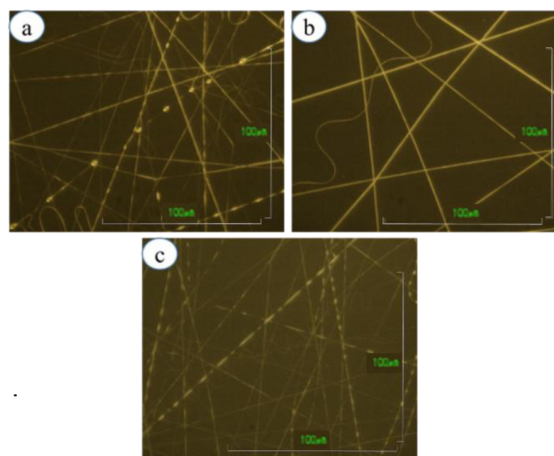


**Figure 3.** Optical microscope images of polymer fibers corresponding to PVA:CS:CG ratios of (a) 7:2:1, (b) 7:1:2, and (c) 8:1:1.

### 3.1.2. Effect of carrageenan concentration

Optical microscopy photos (Figure 4) reveal that CG at a concentration of 0.3% forms fibrils, however the fibrils are intermingled with particles, resulting in the creation of granular fibers. When the CG concentration is increased to 0.5%, the resulting fibers are more homogeneous, straight, and continuous. At a CG concentration of 0.7%, the fibers generated have a smaller diameter due to enhanced conductivity in the solution; however, the fibers are not continuous and are fragmented into pieces, resulting in granular fibers. Chitosan is a polycation, which can form ion complexes with a variety of natural or manufactured anions, including the polymer carrageenan. Because the presence of amino groups in the CS structure increases the surface

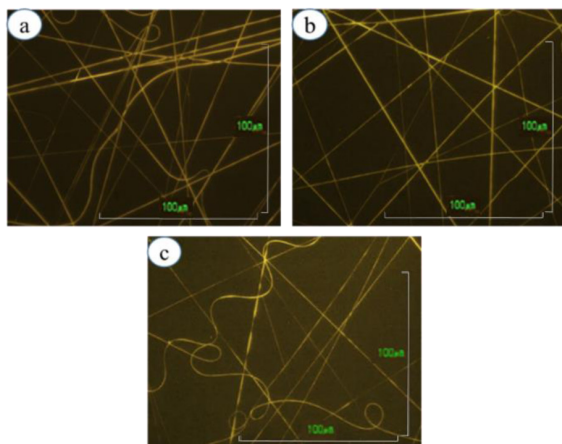
tension of the solution, the use of two types of polymers with opposite charges has resulted in positive charges in the CS structure and negative charges in the CG structure interacting with each other, and at a CG concentration of 0.5%, these charges are neutralized, resulting in straight and smooth nanofibers. Therefore, the electrospinning process uses a CG concentration of 0.5%.



**Figure 4.** Optical microscope images of polymer fibers corresponding to CG concentrations: (a) 0.3%, (b) 0.5%, and (c) 0.7%.

### 3.1.3. Effect of sampling distance

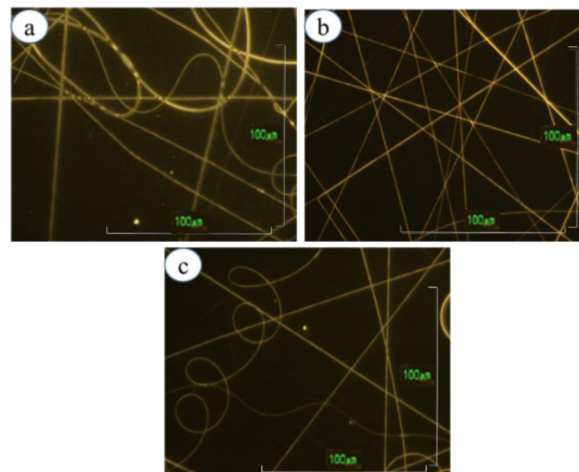
Figure 5 depicts the optical microscope results, which demonstrate clear changes in the fibers at distances of 14 cm, 15 cm, and 16 cm. At a distance of 14 cm, the fibers generated are relatively big, discontinuous, and frequently curved. When the distance between the nozzle tip and the sample collector is increased to 15 or 16 cm, the fiber size decreases. This can be explained by the fact that at a greater distance, the solvent has more time to evaporate, resulting in fibers with smaller diameter. The longer the distance, the more evenly distributed the fibers on the sample collector. Furthermore, particles will be created at both too close and too far away distances. The fibers have generally consistent diameters, are straight, and continuous over a distance of 15 cm, therefore this is the ideal distance for the electrospinning process.



**Figure 5.** Optical microscope images of polymer fibers corresponding to fiber forming distances of: (a) 14 cm, (b) 15 cm, and (c) 16 cm.

#### 3.1.4. Effect of applied voltage

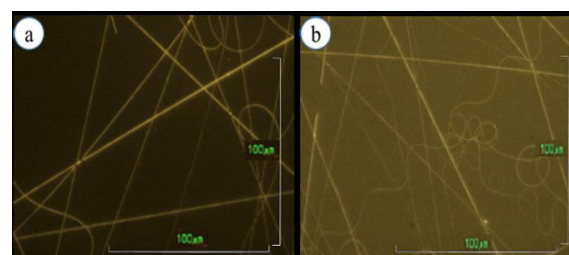
Voltage is critical in the electrospinning process because it regulates the electric field intensity between the needle tip and the sample collection. Figure 6 illustrates how voltage affects the electrospinning process for voltage values of 17 kV, 18 kV, and 19 kV. In general, fiber size reduces as voltage increases; at 17 kV, the fibers generated have a rather wide diameter, are irregular, and tend to cling together. This is because, at low voltage, the primary droplet's electrostatic repulsion is insufficient to overcome the solution's surface tension. Furthermore, at low voltage values, the solvent in the solution evaporates slowly, preventing the fibers from drying before reaching the sample collector. When the voltage is increased to 18 kV, the fibers form with a reasonably homogeneous and smaller diameter, and they are straight and continuous. When the voltage was increased to 19 kV, the fiber diameter reduced, but it was fractured and not uniform. Because of the high voltage, the solvent molecules rubbed fast, causing the solution to dry quickly at the primary drop at the nozzle tip. The dry main drop interrupted the electrospinning process, causing the fibers to break and bend, perhaps leading to a complete cessation of the electrospinning process.



**Figure 6.** Optical microscope images of polymer fibers corresponding to the voltages: (a) 17 kV, (b) 18 kV, and (c) 19 kV.

#### 3.1.5. Effect of injection flow

Figure 7 depicts the results of the inquiry into the effect of injection flow rate on the electrospinning process. It was discovered that when the injection flow rate was 0.1/0.1 mL/h, the fibers developed constantly. When the injection flow rate was increased to 0.2/0.2 mL/h, the fibers condensed and bent, forming beads. Because of the increased injection flow rate, more solution was pushed out, leaving insufficient time for the solvent to evaporate, resulting in the primary droplet at the injection tip progressively growing larger over time and eventually dripping down to the sample collector. Droplet dripping interrupts the electrospinning process, resulting in fibers with irregular diameters and even beads. As a result, the flow rate used for the electrospinning operation was 0.1/0.1 mL/h.



**Figure 7.** Optical microscope images of polymer fibers corresponding to injection flow rates of: (a) 0.1/0.1 mL/h and (b) 0.2/0.2 mL/h.

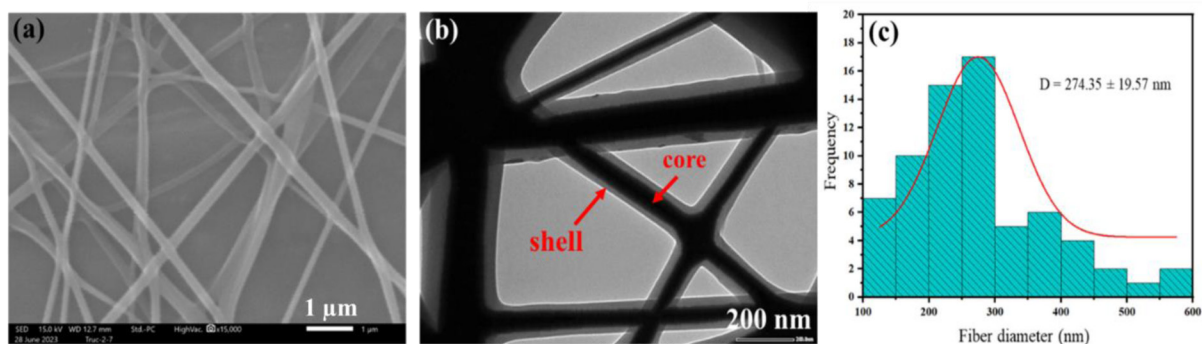


### 3.2. Physiochemical characteristics of nanofiber membrane

#### 3.2.1. Fiber morphology results by SEM and TEM analysis

Figure 8 depicts a SEM picture of the PVA/CCM@PVA/CS/CG membrane under optimum circumstances. The PVA/CS/CG ratio is 8:1:1, the CG concentration is 0.5%, the distance between the needle tip and the sample collector is 15 cm, the electrospinning voltage is 18 kV, and the spray flow rate is 0.1/0.1 mL per hour. The SEM image results demonstrate that there are no particles on the fiber surface, indicating that the substances have completely dissolved and the polymer solution mixture is homogeneous. Moreover, the TEM images revealed obvious core-shell structure of the nanofibers, with a light shell layer coating around the dark core. The core/shell structure of nanofiber structures aids in the controlled release of healing agents (curcumin), promoting effective wound healing compared

to single-layer nanofibers. Additionally, ImageJ software is used to determine the size of the fibers in the SEM picture, and a fiber diameter distribution chart is created from this information. The graph illustrates the distribution of fiber diameter, which is in the range of 100 - 600 nm, with the highest concentration in the range of 100 - 300 nm and an average diameter of  $274.35 \pm 19.57$  nm. In addition, when compared with the nanofibers prepared by Cao-Luu et al. (2024), the PVA/CCM@PVA/CS/CC fiber has an average diameter of  $301.55 \pm 76.77$  nm, indicating that the PVA/CCM@PVA/CS/CG nanofiber has a smaller diameter.<sup>22</sup> The combination of two types of charged polymers helps increase the conductivity of the solution, contributing to the fiber diameter reduction. This has demonstrated the efficiency of combining two types of polymers with opposite charges to produce nanofibers using the electrospinning technique.<sup>23</sup>

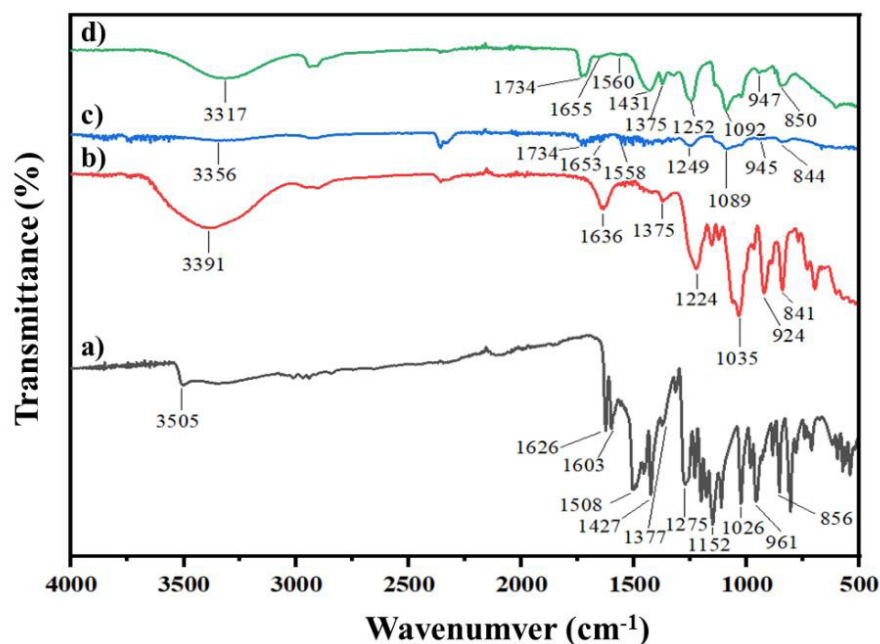


**Figure 8.** Morphology of nanofiber membranes through (a) SEM image, (b) TEM image, and (c) fiber diameter distribution histogram.

#### 3.2.2. FTIR results of the nanofiber membrane

The chemical properties of PVA/CCM@CS/PVA/CC nanofibrous membrane were determined using FTIR analysis, which revealed interactions between functional groups present in the nanofibers (Figure 9). The absorption peak at  $3505\text{ cm}^{-1}$  in CCM's FTIR spectrum corresponds to the stretching vibration of (O-H). The range from  $3100$  to  $2800\text{ cm}^{-1}$  corresponds to the stretching vibration of (C-H), specifically the asymmetric stretching vibration of (C-H) in

( $-\text{CH}_2-$ ), as demonstrated by the peak at  $2945\text{ cm}^{-1}$ . The peak at  $1626\text{ cm}^{-1}$  arises owing to the stretching vibration of (C=O) and (C=C), whereas the peak at  $1603\text{ cm}^{-1}$  is due to the stretching vibration of (C=C) and the benzene ring. The peak at  $1508\text{ cm}^{-1}$  corresponds to a stretching vibration within the benzene ring. The peaks at  $1427\text{ cm}^{-1}$  and  $1377\text{ cm}^{-1}$  represent the bending and stretching vibrations of (C-H), respectively. The peaks at  $1275\text{ cm}^{-1}$ ,  $1152\text{ cm}^{-1}$ ,  $1026\text{ cm}^{-1}$ ,  $961\text{ cm}^{-1}$ , and  $856\text{ cm}^{-1}$  represent the stretching vibration of (C-O).



**Figure 9.** FTIR spectra of (a) CCM, (b) CG, (c) PVA/CS/CG, and (d) PVA/CCM@PVA/CS/CG.

The FTIR spectrum of CG displays a large region in the range of  $3600\text{--}3100\text{ cm}^{-1}$ , with the peak at  $3391\text{ cm}^{-1}$  representing the stretching vibration of (O-H) from the hydroxyl group of the polysaccharide, which corresponds to the hydrophilic nature. The spectra reveals a peak at  $2903\text{ cm}^{-1}$ , which corresponds to the symmetric stretching vibration of C-H. The  $1636\text{ cm}^{-1}$  peak corresponds to the stretching of (C=O) and (C=C). The characteristic peak at  $1375\text{ cm}^{-1}$  is caused by the stretching vibration of (C-H), whilst the high absorption peak at  $1224\text{ cm}^{-1}$  is caused by the presence of (S=O) bonds in the sulfate ester groups. The CG spectrum displays a strong absorption peak in the range of  $1020\text{--}1050\text{ cm}^{-1}$ , which is characteristic of polysaccharides, with the peak at  $1035\text{ cm}^{-1}$  corresponding to the stretching vibration of (C-O). The peak at  $922\text{ cm}^{-1}$  represents the (C-O-C) bond of 3,6-anhydro-D-galactose. The signal at  $841\text{ cm}^{-1}$  indicates the presence of (C-O-SO<sub>3</sub>-)-D-galactose-4-sulfate. This shows the presence of  $\kappa$ -CG.

The FTIR spectrum of the PVA/CS/CG film shows a peak at  $3356\text{ cm}^{-1}$ , which corresponds to the stretching vibration of two

groups: hydroxyl (O-H) in PVA, CS, and CG and amino group (N-H) in CS. They have changed to lower wavenumbers, indicating that cross-linking has occurred between the groupings. The absorption peak at  $2908\text{ cm}^{-1}$  corresponds to the symmetric stretching vibration of (C-H) in (-CH<sub>2</sub>-). The peak at  $1734\text{ cm}^{-1}$  represents the stretching vibration of the (C=O) group in amide I; its appearance is related to bond overlap when compared to the peak at  $1626\text{ cm}^{-1}$  (C=O) group of CCM and the peak at  $1636\text{ cm}^{-1}$  (C=O) of CG. The peak at  $1653\text{ cm}^{-1}$  corresponds to the stretching vibration of the (C=O) group in amide I, while the bending vibration (N-H) of the N acetyl group in amide II has a characteristic peak at  $1558\text{ cm}^{-1}$  associated with CS. The peak at  $1375\text{ cm}^{-1}$  indicates the stretching vibration of (C-H), whereas the peak at  $1224\text{ cm}^{-1}$  in the CG spectrum moves to the peak at  $1249\text{ cm}^{-1}$ , which corresponds to the (S=O) bond in the sulfate ester groups. The peak at  $1089\text{ cm}^{-1}$  is caused by the stretching of the (C-O) bond and the bending of the (O-H); also, this peak demonstrates the merging and overlap of the (C-O) bond when compared to the peak at  $1035\text{ cm}^{-1}$  (of CG). Furthermore, the signal at  $1089\text{ cm}^{-1}$  corresponds to the free amino groups at the C2 position of

glucosamine. The peaks at 922 cm<sup>-1</sup> and 841 cm<sup>-1</sup> that correspond to the (C-O-C) bond and the presence of (C-O-SO<sub>3</sub><sup>-</sup>) in CG shifted to the peaks at 945 cm<sup>-1</sup> and 844 cm<sup>-1</sup>.

The peak 3317 cm<sup>-1</sup> in the FTIR spectrum of the PVA/CCM@PVA/CS/CG film is the merger of the peaks 3505 cm<sup>-1</sup> (in CCM), 3391 cm<sup>-1</sup> (in CG), and 3356 cm<sup>-1</sup> (in PVA/CS/CG film), which is caused by the stretching of the (O-H in PVA, CS, and CG) and amino groups (N-H in CS). The peak 2910 cm<sup>-1</sup>, which has shifted from the peak 2908 cm<sup>-1</sup> in PVA/CS/CG, is a merger of the peaks 2945 cm<sup>-1</sup> (in CCM) and 2903 cm<sup>-1</sup> in CG, both of which are indicative of the stretching vibration of (C-H). The amide group shifts the peak 1653 cm<sup>-1</sup> (of the PVA/CS/CG membrane) to 1655 cm<sup>-1</sup>, and the peak 1558 cm<sup>-1</sup> shifts to 1560 cm<sup>-1</sup>. Furthermore, the 1427 cm<sup>-1</sup> peaks, which correspond to the bending vibration of (C-H) in (-CH<sub>3</sub>), migrated to 1431 cm<sup>-1</sup> and 1375 cm<sup>-1</sup>. The peaks 1427 cm<sup>-1</sup> and 1377 cm<sup>-1</sup> in CCM, as well as the peak 1375 cm<sup>-1</sup> in CG, merged to form the peak 1375 cm<sup>-1</sup> characteristic of the alkane group (C-H). The change in intensity of this band is caused by PVA and CG's tendency to bind with water and hydroxyl groups present in CS and CCM, resulting in the shift of these peaks. The PVA/CS/CG membrane's peaks at 1249 cm<sup>-1</sup> and 1089 cm<sup>-1</sup> changed to 1252 cm<sup>-1</sup> and 1092 cm<sup>-1</sup>,

respectively. The typical peaks for the presence of CG in the PVA/CS/CG membrane were 945 cm<sup>-1</sup> and 844 cm<sup>-1</sup>, which were shifted to 947 cm<sup>-1</sup> and 850 cm<sup>-1</sup>, respectively, and the shifts of these peaks were likewise connected to the CCM (C-O) groups. The movements of the hydroxyl, amide, and sulfate groups revealed bond overlap and the development of polyanion-cation complexes.

FTIR research revealed a successful combination of PVA, CS, CG, and CCM in the electrospinning process for fiber membranes. The spectrum revealed the presence of specific functional groups in the fiber membranes, particularly CG's sulfate group. These findings demonstrated the creation of nanofibers between two polysaccharides with opposing charges, CS and CG.

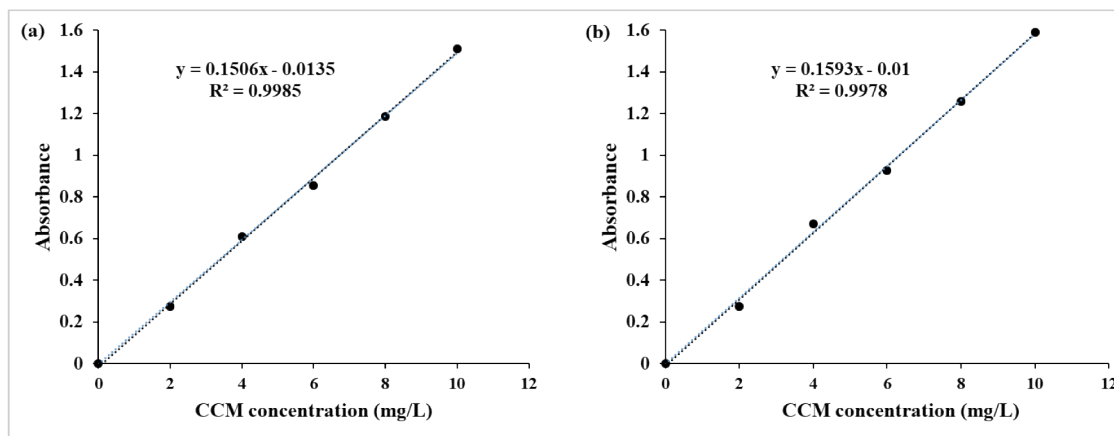
### 3.3. Results of CCM content in fiber membrane

#### 3.3.1. Establish the CCM standard curve in ethanol solution

First, the maximum absorption spectrum of CCM in ethanol was set to estimate the maximum absorption wavelength of CCM, and then create the absorption standard curve for CCM. The UV-Vis spectrum data indicate that CCM's maximum absorption wavelength in ethanol solution is 426 nm.

**Table 1.** Absorption of CCM in ethanol solution with different concentrations.

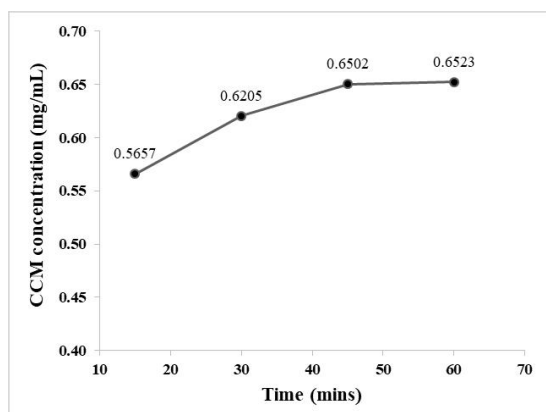
| CCM content (mg/L) | Absorbance<br>in ethanol solution | Absorbance<br>in PBS buffer solution |
|--------------------|-----------------------------------|--------------------------------------|
| 0                  | 0                                 | 0                                    |
| 2                  | 0.2736                            | 0.2741                               |
| 4                  | 0.6098                            | 0.6727                               |
| 6                  | 0.8557                            | 0.9257                               |
| 8                  | 1.1878                            | 1.2585                               |
| 10                 | 1.5112                            | 1.5896                               |



**Figure 10.** Standard curve of CCM (a) in ethanol solution, and (b) in PBS buffer solution.

Based on the results in Table 1, a CCM standard curve in ethanol solution was created and shown in Figure 10.

The standard equation for CCM in ethanol solution is  $y = 0.1506x - 0.0135$ , where  $y$  is the absorbance and  $x$  is the CCM content (mg/L). This equation is used to calculate the CCM content released based on the ultrasonic time. Results of the ultrasonic time survey to determine the curcumin content.



**Figure 11.** Ultrasonic time survey chart for determining CCM content.

The CCM content released at varied ultrasonication durations of 15, 30, 45, and 60 minutes was estimated using the UV-Vis analysis results and the standard curve equation, and is shown in Figure 11. The results showed that the CCM content released was 0.5657 mg within the first 15 minutes and 0.6205 mg after 30 minutes. When the period was extended to 45 minutes, the CCM content released was 0.6502 mg. There was no substantial difference in the CCM content

released at 45 and 60 minutes. As a result, the best time for ultrasonic testing was 60 minutes.

### 3.4. Results of curcumin release process

#### Establish the standard curve equation for curcumin in buffer solution.

According to the UV-Vis spectrum measurements, the maximum absorption wavelength of CCM in buffer solution is 426 nm. The standard curve equation for CCM in buffer solution is  $y = 0.1593x - 0.01$ , where  $y$  is absorbance and  $x$  is the CCM concentration in ethanol solution (mg/L). The standard curve equation can be used to compute the CCM content released throughout the *in vitro* process, as well as the percentage of CCM released with time.

#### Curcumin release results

Table 2 and Figure 12 show the results of the CCM release process in the buffer solution of the PVA/CCM@PVA/CS/CG fiber membrane. Because PVA, CS, and CG can all absorb water, causing the fibers to inflate, the solution from the release media quickly reaches the core of the fiber, resulting in fast diffusion of CCM molecules within the first 6 hours after placing the membrane in the release medium. Starting at 12 hours, the amount of CCM released tends to slow and eventually settle. By 96 hours, 83.96% of the CCM content has been released. CCM released early in the process aids in anti-inflammation, whereas CCM released later aids in anti-oxidation and wound healing.



Table 2. Percentage of CCM released in buffer solution.

| Time (hours) | Percentage of CCM released |
|--------------|----------------------------|
| 0.08         | 18.48 ± 1.92               |
| 0.17         | 24.99 ± 2.47               |
| 0.25         | 31.60 ± 2.34               |
| 0.50         | 41.46 ± 2.26               |
| 1            | 51.19 ± 2.09               |
| 2            | 62.26 ± 1.01               |
| 3            | 72.12 ± 1.48               |
| 6            | 77.56 ± 1.43               |
| 12           | 78.83 ± 2.19               |
| 24           | 81.54 ± 2.29               |
| 48           | 82.55 ± 2.16               |
| 72           | 83.89 ± 2.26               |
| 96           | 83.96 ± 2.29               |

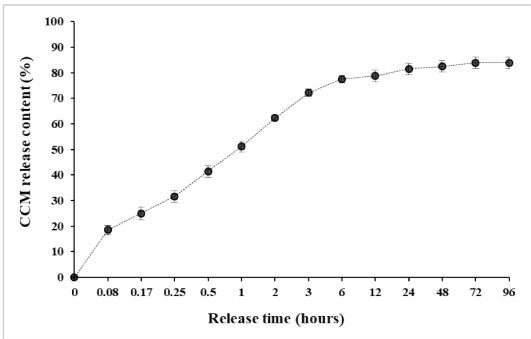


Figure 12. CCM release results of PVA/CCM@PVA/CS/CG fibers in 96 hours.

#### 4. CONCLUSION

PVA/CCM@PVA/CS/CG nanofiber membranes were produced using the following optimum ratios: The PVA:CS:CG ratio was 8:1:1, the CG concentration was 0.5%, the distance between the needle tip and the sample collector was 15 cm, the electrospinning voltage was set at 18 kV, and the spray flow was 0.1/0.1 mL/h. The produced fibers were relatively consistent in size, with diameters ranging from 100 to 300 nm and an average diameter of  $274.35 \pm 19.57$  nm. The FTIR data revealed the presence of PVA, CS, CG, and CCM in the fiber membrane, as well as the fact that the connection between CG and CS and the structure of CCM did not change during the electrospinning process used to create nanofiber membranes. The drug release data showed that CCM was released in substantial levels in the first 6 hours, then steadily dropped

after 12 hours, and by 96 hours, the amount of CCM released was 83.96%.

#### Acknowledgements

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# Nghiên cứu thiết kế hệ thống thủy lực nâng hạ cửa đập ngăn mặn tại tỉnh Bình Định

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*Ngày nhận bài: 05/01/2025; Ngày sửa bài: 02/04/2025;*

*Ngày nhận đăng: 11/04/2025; Ngày xuất bản: 28/06/2025*

## TÓM TẮT

Hiện nay, các đập ngăn mặn chủ yếu sử dụng cơ cấu quay tay trực vít me bằng tay hoặc sử dụng động cơ điện để vận hành nâng hạ, ở các phương pháp này có nhiều hạn chế như phụ thuộc tính chủ quan con người, quá trình đóng mở không phù hợp, dễ gây biến dạng trục chính dẫn đến hỏng các cơ cấu hộp số vít me. Để khắc phục vấn đề trên, giải pháp sử dụng xi lanh thủy lực đã được tác giả đề xuất trong bài báo này. Dựa trên các số liệu thực tế, tác giả đã thiết kế hệ thống vận hành đóng mở các đập ngăn mặn tại tỉnh Bình Định bằng hệ thống thủy lực. Kết quả mô phỏng cho thấy hệ thống vừa bảo đảm về mặt kỹ thuật vừa hiệu quả tính kinh tế, khắc phục các hạn chế vận hành trước đây. Giải pháp này không chỉ cải thiện chất lượng vận hành mà còn mở ra khả năng ứng dụng công nghệ mới để tự động hoá và giám sát từ xa trong quá trình vận hành cho các đập thủy lợi tương tự.

**Từ khóa:** Đập ngăn mặn, thủy lực, vít me, đập thủy lợi, Bình Định.

\*Tác giả liên hệ chính.

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# Research and design of the hydraulic system for raising and lowering the saltwater barrier gates in Binh Dinh province

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## ABSTRACT

Currently, the majority of saltwater barrier dams use manual ball screw mechanisms or electric motors for dam gate raising and lowering operations. These methods have several limitations, such as dependence on human subjectivity, improper dam gate raising and lowering processes, and the risk of main shaft deformation, leading to damage to the ball screw gearbox mechanisms. To address these issues, the use of hydraulic cylinders has been proposed by the author in this paper. Based on actual data, the author has designed a hydraulic system for operating the dam gate raising and lowering of saltwater barrier dams in Binh Dinh province. Simulation results demonstrate that the system not only meets technical requirements but is also economically efficient, overcoming previous operational limitations. This solution not only improves operational quality but also paves the way for adopting new technologies to automate and enable remote monitoring during the operation of similar irrigation dams.

**Keywords:** *Saltwater barrier dams, hydraulic, ball screw, irrigation dams, Binh Dinh.*

## 1. INTRODUCTION

The coastal area of Binh Dinh frequently faces challenges such as flooding and saltwater intrusion, which have a severe impact on freshwater resources, agricultural production, and the livelihoods of local residents. To address saltwater intrusion, saltwater barrier dams have been constructed. However, water regulation still largely depends on human control and tidal fluctuations along the coast, leading to difficulties in efficient management and operation. This results in frequent flooding and saltwater contamination in the inland areas of Binh Dinh's coastal region. The saltwater barrier gates

typically have the following characteristics: they are not large in size, the lifting load is moderate, and they are not subjected to the high pressures found in hydropower dams. The water level difference between the inside and outside of the gates usually fluctuates by a few meters, they handle large flow rates, and the flow currents are slow. These gates require high water-tightness, timely operation to prevent flooding and saltwater intrusion into the inland areas, and are exposed to harsh weather conditions. They are located far from residential areas, and the dam gate raising and lowering times vary according to tides and seasonal needs.

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Binh Dinh province currently manages 39 gates on embankments, 11 dams on embankments, 17 spillways on embankments, and 12 saltwater barrier dams.<sup>1</sup>

Currently, the most common method for opening and closing dam gates is manual operation due to the lack of electricity at the 17 spillways on the East Embankment (Figure 1a); the use of manual ball screw mechanisms at saltwater barrier gates (Figure 1b); or motorized control for opening and closing at saltwater barrier dams (Figure 1c, Lai Giang dam); and the use of winches, pulleys, and hoists (Figure 1d, Ha Gach dam). According to the report from the Institute of Irrigation Management and Economics, most saltwater barrier dams in Binh Dinh province use two lifting solutions: hoists and pulleys, and ball screw mechanisms. With pulleys, there are difficulties in pressure difference when lowering the dam. The ball screw mechanism allows for manual or motorized operation to raise or lower the dam gates. This is a simple and cost-effective drive mechanism. The ball screw mechanism is easy to integrate into gate operation systems, with a compact design and minimal installation space requirements.

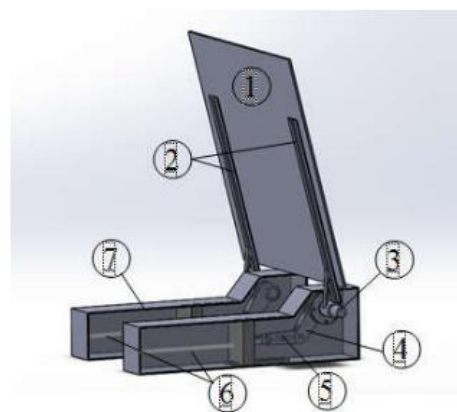


**Figure 1.** The manual lifting and lowering operating mechanism is through a Vitme.

Although ball screws have many advantages, they also have certain limitations, such as being prone to wear, requiring frequent lubrication, operating slowly, and being difficult to apply for dams with significant water level differences or requiring rapid raising and lowering. They are also susceptible to overloading during improper operation, often resulting in shaft bending and joint damage. Therefore, ball screws are typically used for smaller structures, such as field sluice gates, and they are expected to be replaced by more modern systems in the future.

In the document automatic flap gates operate based on the principle of changes in upstream water pressure and the equivalent stiffness of the spring system  $F=f(Kx)$ . When the moment generated by hydrodynamic pressure, combined with the gate's own weight and the friction at the pivot, exceeds the stiffness of the spring system, the gate will open to a state of equilibrium with the compressive (or tensile) force of the spring system.<sup>2</sup>

If the pressure remains unchanged and the compressive (or tensile) force of the spring system remains constant, the gate's opening angle will also remain unchanged. When the moment caused by hydrodynamic pressure continues to exceed the compressive (or tensile) force of the spring system, the gate will fully open (reaching a horizontal position). Conversely, when the compressive (or tensile) force of the spring system surpasses the moment generated by hydrodynamic pressure, the gate's weight, and frictional force, the gate will automatically close (returning to a vertical position).



**Figure 2.** Structure of automatic flap valve.<sup>2</sup>

This system is only suitable for dams designed for automatic flood discharge, it is not suitable for saltwater barrier dams. The hydraulic solution is also proposed in the article, featuring a system of cylinders arranged in a rather complex manner, which reduces the reliability of the operation process.<sup>3</sup> The curved gate principle used in this system is suitable for hydropower dams that require very high lifting forces.

Smart dam gate raising and lowering control monitoring solution is included in the application.<sup>4</sup> This dam system helps increase the accuracy of the dam gates opening and closing system which in turn helps the economy and saves lives. It also reduces the chances of human error.

The operation of opening and closing dam gates using pulleys is commonly applied to gates with significant weight, slow flow rates, and low water level differences, making them easy to operate.<sup>5</sup> However, this method is unsuitable when dealing with strong water currents, as gravity alone is insufficient to overcome the resistance pressure of the water to achieve full closure.

The radial gate mechanism controlled by a hydraulic system is typically used in hydropower dams with steep water gradients, high water pressure, and complex control systems. These mechanisms are commonly employed in dams with significant water level differences but are not suitable for saltwater barrier dams.<sup>6,7</sup>

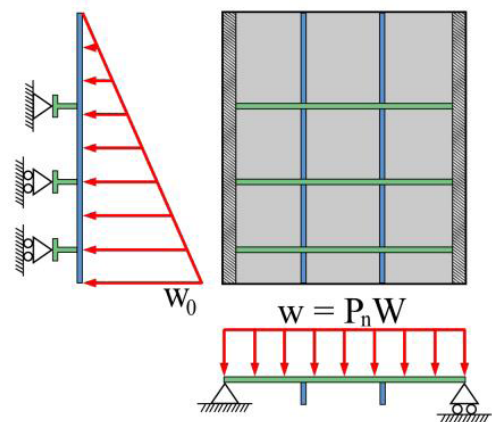
Hydraulic cylinders can generate very high thrust with stable pressure, making them suitable for applications that require large forces, such as opening and closing dam gate valves. The hydraulic system can adjust the oil flow to control the opening and closing speed flexibly. It is less affected by friction compared to the screw-nut system, helping to extend operational lifespan. Hydraulic cylinders can operate stably in wet conditions and are more resistant to corrosion. While hydraulic cylinders have a high initial investment cost, their low operating

costs are beneficial for long-term operations, such as dam operations. Due to their low friction coefficient, high efficiency, and lower energy consumption compared to the screw-nut system, hydraulic cylinders experience less wear and tear, offering higher durability and reducing component replacement costs.

## 2. IMPLEMENTATION CONTENT

### 2.1. Structural design criteria

All the saltwater barrier dams currently in use in Binh Dinh province are of the vertical panel type; therefore, the calculation of the force distribution on the gates is based on this design. The load case considered when structurally analyzing the dam gate is that of the hydrostatic pressure, with two edges simply supported. In particular the case when the gate is fully closed and there is no flow.<sup>1</sup>



**Figure 3.** The structurally idealized gate;  $W$  is uniform distributed load [N/m];  $W_0$  linearly varying load [N/m]; Girder reaction force [N].

There are many methods of defining the deflection of a beam due to bending. However, the method chosen for calculating deflection is Castaglianos theorem which is a relatively simple way of determining beam deflection. Castigliano's theorem is defined in equation (1).

$$\delta_i = \frac{\partial U}{\partial F_i} \quad (1)$$

Where  $U$  is the strain energy, and  $F_i$  is the force in the direction of the displacement. Strain energy due to bending can be defined in equation (2)

$$U = \int_0^L \frac{M^2}{2EI} \quad (2)$$

Where  $M$  is the equation of bending moment along the beam,  $E$  is the elastic modulus,  $I$  is the second moment of area and  $L$  is the length of the beam. Equation (2) can be combined with equation (1) to form an equation for Castagliano's theorem for bending, as seen in equation (3)

$$\delta_i = \int_0^L \frac{1}{EI} \left( M \frac{\partial M}{\partial F_i} \right) \quad (3)$$

A method used to determine the deflection at a point where a force  $F_i$  is not present is to introduce a fictitious force  $F_*$  at  $i$ . This force can be set to zero after calculating the partial derivative  $\frac{\partial M}{\partial F_i}$

The vertical stiffeners will be analyzed first. They are idealized as beams supported at the positions of the main girders. Since the number of main girders often exceeds two, the vertical stiffeners will in those cases be statically indeterminate. The superposition method can be utilized to simplify the indeterminate system into a determinate one. To achieve this the vertical stiffener can be idealized as a beam with two supports and point loads equal to the support reactions in the redundant supports ( $n > 2$ ). The deflection of the main girders is simpler to find, since it is idealized as a simply supported beam under uniformly distributed load, see Figure 3. This is a common standard load/support case where the deflection at point  $x$  along the beam can be defined in equation

$$\delta(y) = \frac{w_n y (W^3 - 2Wy^2 + y^3)}{24EI} \quad (4)$$

Thus, the option of selecting vertical steel gates with reinforced frames is suitable for installation in saltwater barrier dams.

## 2.2. Calculation of forces acting on the dam gate

The forces acting on the dam gate include weight  $F_m$ , hydrodynamic force  $F_{hd}$ , sediment force  $F_s$ ,

wave force  $F_w$ , friction force  $F_{ms}$ , and reaction force  $F_n$  ... These forces are categorized into two directions: vertical and horizontal.<sup>8</sup>

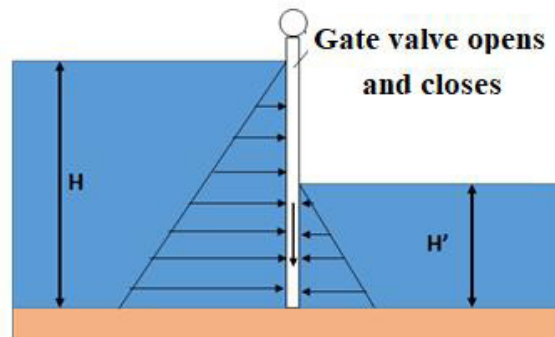


Figure 4. Door system to prevent salinity.

$$\begin{aligned} \sum F_x &= F_{hd} + F_w + F_s + F_{ms} - x \\ \sum F_y &= F_m - F_n - F_{ms} - y \end{aligned} \quad (5)$$

Neglecting minor impacts on the dam gate, equation (5) is rewritten as:

$$\begin{aligned} \sum F_x &= F_{hd} - x \\ \sum F_y &= F_m - F_n - y \end{aligned} \quad (6)$$

In a static state, gravity and the reaction force are balanced, with only water pressure acting on the dam gate. This value depends on the pressure difference between the water levels inside and outside the gate. Thus, to calculate the lifting force required for the hydraulic dam gate, two main forces must be overcome:

- The weight of the dam gate is  $G$ (kg), which is converted to gravitational force in the vertical direction as:

$$F_m = G \cdot g \quad (7)$$

Where:

$F_m$ : Gravitational force (N)

$G$ : Weight of the dam gate (kg)

$g$ : Acceleration due to gravity ( $\approx 9.81 \text{ m/s}^2$ )

- The frictional force between the gate and the dam wall depends on the normal (contact) force between the gate and the wall, as well as the coefficient of friction  $f$ , which is determined by the materials used for the gate and the dam wall. The frictional force can be calculated as:



$$F_{ms} = f.N \quad (8)$$

Where:

$F_{ms}$  : Frictional force (N)

$f$  : Coefficient of friction (depends on the materials)

$N$  : Normal force (N), which is the contact force between the gate and the dam wall.

$$N = \rho.g.H.A \quad (9)$$

$\rho$  : Density of water (typically around 1000 kg/m<sup>3</sup>)

$H$  : Water level difference

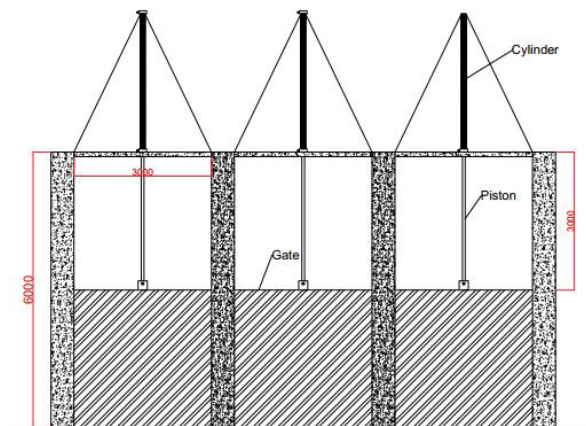
$A$  : Area of the gate surface in contact with the water.

Thus, the total lifting force acting on the dam gate is:

$$\sum F = F_m + F_{ms} \quad (10)$$

### 2.3. Propose a solution using hydraulic cylinders

There are several solutions when implementing the lifting and lowering of the dam gate using hydraulics: Hydraulic Cylinder System, Cable-Operated Hydraulic System, Hydraulic Screw System, etc. For saltwater barrier dams, which typically have low water levels and require frequent operation of opening and closing, the solution of choosing a Hydraulic Cylinder System is suitable.<sup>9</sup>



**Figure 5.** The opening and closing system of the salinity prevention dam is hydraulic.

The relevant quantities include weight  $F_m$ (N), water pressure  $F_n$ (N), frictional force  $F_{ms}$ (N), operating speed  $v$ (m/s), lifting stroke  $L$ (m), hydraulic pressure  $P$ (bar), piston diameter  $D$ (m), and cross-sectional area of the piston  $s$ (m<sup>2</sup>). The lifting force of the cylinder is determined by the formula.

$$F = P.s = P.\frac{\pi D^2}{4} \quad (11)$$

The L/D ratio should not exceed 20 to avoid the phenomenon of bending or deflection of the piston. The required hydraulic oil flow rate  $Q$ (m<sup>3</sup>/s) to operate the cylinder.

$$Q = v.s \quad (12)$$

Where:

$s$  : Piston cross-sectional area (m<sup>2</sup>)

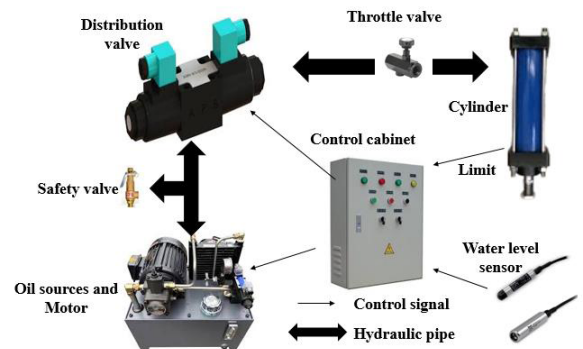
The power of the pump  $P_b$ (W) can be determined using the following formula

$$P_b = \frac{Q.P}{\eta} \quad (13)$$

Where:

$\eta$  : System efficiency (typically ranging from 0.8 to 0.9).

With the above characteristics, the proposed system for lifting and lowering the saltwater barrier gate is shown in Figure 6. The system includes: a oil supply source, an electric control mechanism, a hydraulic drive mechanism, and other measuring devices.



**Figure 6.** Hydraulic Cylinder System control diagram.

## 2.4. The problem of practical verification

Considering the data of Ha Gach Dam in Phuoc Thang Commune, Tuy Phuoc District, and given the diagram shown in Figure 5, the dam gate is made of sheet steel, with dimensions:  $3 \times 3 \times 0.1 \text{ m}^3$ , density  $\gamma = 7850 \text{ kg/m}^3$ , lifting speed  $v = 0.05 \text{ m/s}$ , friction coefficient  $f=0.3$ , and efficiency  $\eta=0.9$ .

The weight of the dam gate is calculated as:

$$F_m = V \times \gamma \times g = 0.9 \times 7850 \times 9.81 = 69307 \text{ N} \quad (14)$$

Assuming the maximum water level difference  $H$  is 3 meters:

$$N = \rho \times g \times H \times A = 264870 \text{ N} \quad (15)$$

$$F_{ms} = f \times N = 0.3 \times 264870 = 79461 \text{ N} \quad (16)$$

The force required to lift the dam gate is:

$$F = F_m + F_{ms} = 148768 \text{ N} \approx 14,9 \text{ kN} \quad (17)$$

Thus, a hydraulic cylinder with a capacity of 15 tons should be selected in order to lift the dam gate under maximum load conditions. Choose a cylinder with a stroke length  $L=3\text{ m}$ , and piston diameter  $D/d=150/250\text{ mm}$ .

The cross-sectional area is:

$$s = \pi \times 0.25^2 / 4 = 0.049 \text{ m}^2.$$

The hydraulic pressure on the piston surface is:

$$P = \frac{F}{s} = \frac{14,9}{0.049} = 304 \text{ kbar} \quad (18)$$

The required hydraulic oil flow rate to operate the cylinder is:

$$Q = v \times s = 0.00245 \text{ m}^3/\text{s} = 2450 \text{ cm}^3/\text{s} \quad (19)$$

The power of the pump is:

$$P_b = \frac{Q.P}{\eta} = \frac{0.00245 \times 3.036082}{0.9} = 8265 \text{ W} \quad (20)$$

Choose a motor with a maximum operating power of 11 kW. If the opening and closing occur when the water levels on both sides are balanced, the system load will only be the weight, neglecting the water pressure. The

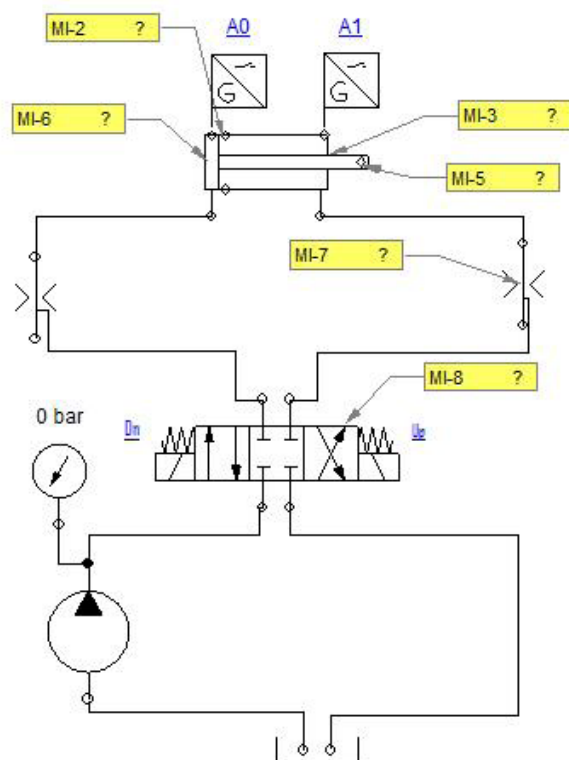
system has 3 gates operating non-synchronously,  
and the operating time for the entire system is:

$$t_{\Sigma} = 3.t_i = 3.\frac{L}{v} = 180 \text{ s} \quad (21)$$

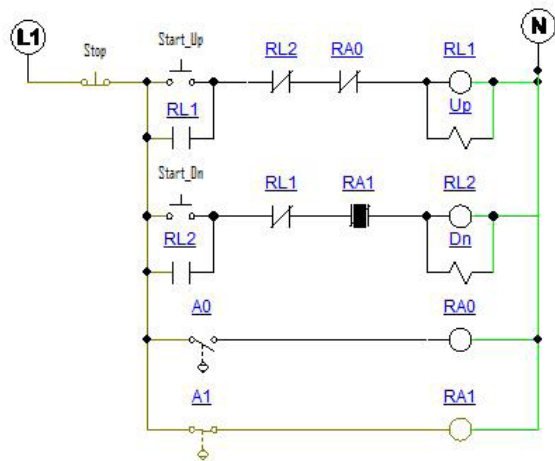
With the calculated parameters, the hydraulic equipment available on the market fully meets the requirements of the problem. The calculated power supply for the system is not too large, so for some saltwater barrier dams without access to the electrical grid, the solar energy power system is a suitable solution for operating the lifting and lowering of the saltwater barriers.

## 2.5. Simulation results and discussion

The author uses Automation Studio software to simulate the operation process of the gate-lifting system using a hydraulic cylinder based on the parameters provided in the problem above. The hydraulic system model (Figure 7) includes a double-acting cylinder with a 3-meter stroke arranged vertically to lift and lower the gate, a  $\frac{3}{4}$  directional control valve, a 300kbar hydraulic pump, an oil tank, a throttle valve, and a piping system.



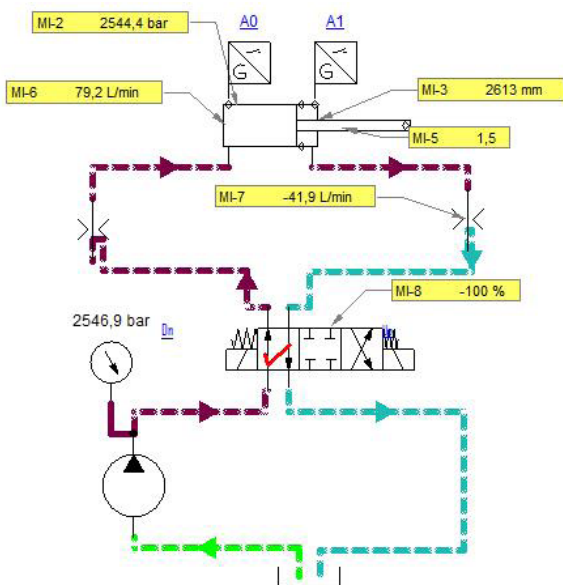
**Figure 7.** Hydraulic circuit model.



**Figure 8.** Logic control electrical diagram for the lifting and lowering of the saltwater barriers.

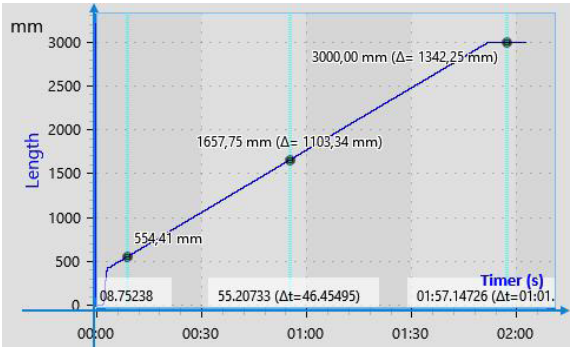
The electrical control system (Figure 8) comprises a solenoid coil for lifting (Up) and lowering (Dn), lift limit A0, lower limit A1, lift-lower-stop push buttons, and a control circuit power supply with a voltage of 220 V.

The process of hydraulic flow during the gate-lowering operation (Figure 9) shows that at a stroke of  $L = 2613$  mm, the measured pressure in the pipeline is 2.54 kbar. The directional control valve is fully open in the lowering position, and the parameters during the gate-lowering process fully comply with the design specifications.



**Figure 9.** Hydraulic diagram for the gate lowering process.

The time for the piston to lower from 0 to 3000 mm within 2 minutes (Figure 10) shows that during the startup phase from 0 to 4 seconds, the piston hardly moves. Starting from the 6<sup>th</sup> second, the piston must overcome two factors: inertia, friction, and the accumulation of hydraulic pressure.



**Figure 10.** Position diagram for gate lowering.

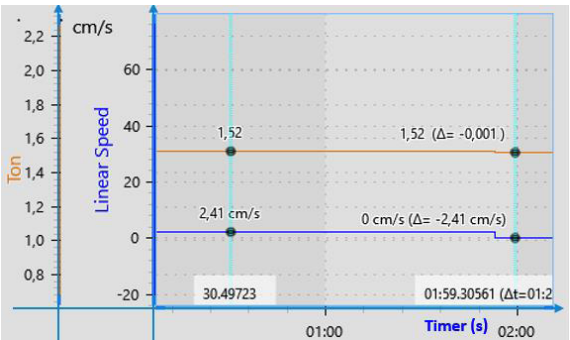
Throughout the motion, the velocity of the piston is nearly linear, which is consistent with a first-degree equation in the motion where only the piston component is involved. If the velocity varies over time, the piston movement can be described by a derivative equation:

$$v_{piston} = \frac{dx}{dt} \tag{22}$$

Where:

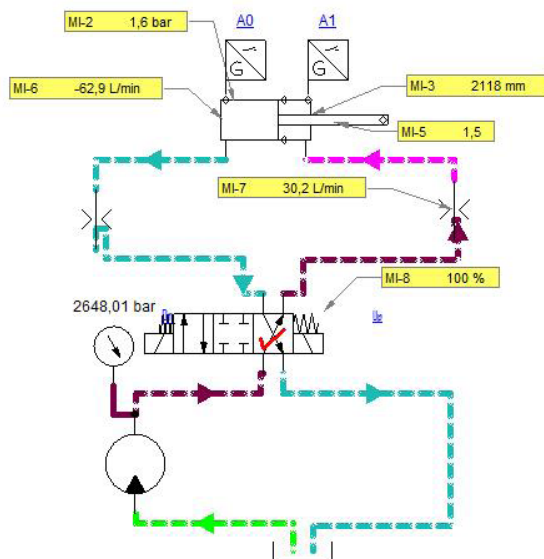
- $v_{piston}$ : Piston velocity over time (m/s)
- $x$ : Position of the piston (m)
- $t$ : Time (s)

Throughout the gate-lowering process, the velocity remains almost constant at 2.41 cm/s<sup>2</sup>, corresponding to a load force of 1.52 tons (Figure 11), which aligns with the calculated results.



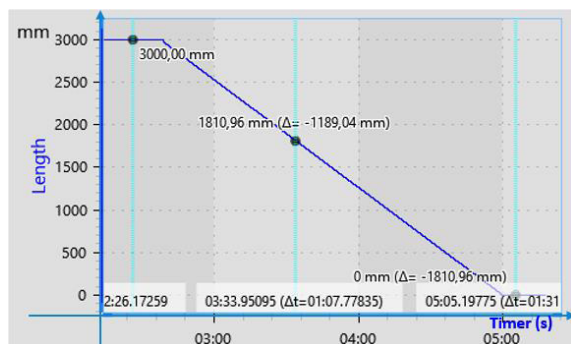
**Figure 11.** Velocity/force diagram for gate lowering.

In contrast to the gate-lowering process is the gate-lifting process (Figure 12). It is assumed that the maximum load and the lifting pressure are higher than during the lowering process due to the opposing gravitational force of the gate. The remaining values are equivalent.



**Figure 12.** Hydraulic diagram for the gate lifting process.

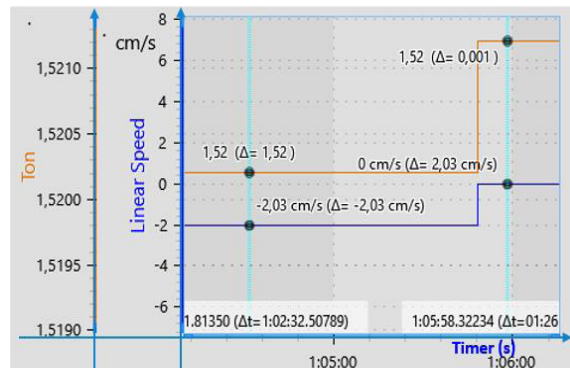
The gate-lifting time is 2.5 seconds (Figure 10), compared to the gate-lowering time of 2.0 seconds (Figure 13). With this result, the simulation time is longer than the ideal theoretical calculation, as it takes into account the gravitational force during lifting and the startup time of the piston. During the gate-lifting process, the piston also moves linearly for most of the stroke.



**Figure 13.** Position diagram for gate lifting.

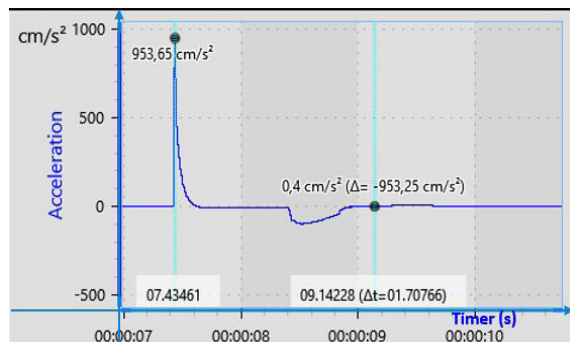
In the simulation diagram of velocity and force during the gate-lifting process (Figure 14),

similar to the gate-lowering process (Figure 11), the velocity remains constant at 2.14 cm/s throughout the stroke, corresponding to a load force of 1.52 tons. The simulation results are consistent with the experimental problem above.



**Figure 14.** Velocity/force diagram for gate lifting.

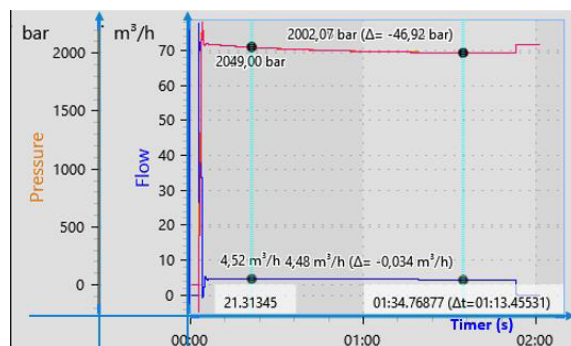
Thus, during the gate-lifting and gate-lowering processes, the system parameters remain nearly unchanged. The only differences are the time and force, with the lifting force being greater than the lowering force.



**Figure 15.** Piston acceleration process.

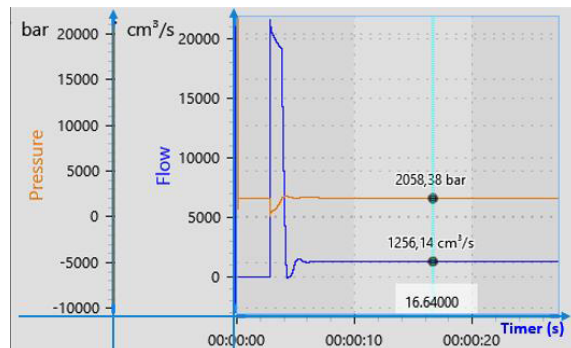
Although most of the piston's stroke involves linear motion, at certain moments, the piston's motion undergoes nonlinear acceleration (Figure 15). At the beginning of the gate-lowering process, the acceleration is higher compared to the gate-lifting process, which depends on the state of the piston, whether in the pushing or retracting mode. Based on these results, to increase the lifespan and reduce damage to the hydraulic systems, it is necessary to reduce the values associated with the acceleration process or the piston startup process.





**Figure 16.** Flow rate and pressure in/out of the throttle valve during the gate lowering process.

For the throttle valve and hydraulic piping, the simulation results show that the pressure remains relatively stable throughout both the lifting and lowering processes, indicating that the system operates stably, ensuring the flow rate and pressure stay within the allowable range. Similarly, for the pump, the acceleration process at the beginning occurs, with the transient period lasting for 2 seconds. To minimize the transient process, the author will propose a solution in another article.



**Figure 17.** Flow rate and Pressure of the pump.

### 3. CONCLUSION

The paper has achieved the following results:

The hydraulic system for lifting and lowering sluice gates in saltwater barriers in Binh Dinh province has been studied and designed.

Designing a system based on the actual data from the Ha Gach Dam demonstrates the feasibility of implementing the proposed hydraulic drive system, which is entirely compatible with the economic criteria and ensures technical reliability.

The simulation results using Automation Studio, based on actual data, are consistent with the theory and align with the calculated data presented above.

In addition to the results of the paper proposing the use of a hydraulic system for operating the gate lifting and lowering, the content also opens up the possibility of using solar energy to power saltwater barriers that currently do not have access to the electrical grid.

### Acknowledgment

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# Nâng cao hiệu suất cảm biến khí VOCs của màng mỏng ZnO thông qua biến tính bề mặt bằng hạt nano Au và chiếu bức xạ UV

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Ngày nhận đăng: 11/04/2025; Ngày xuất bản: 28/06/2025

## TÓM TẮT

Các hợp chất hữu cơ dễ bay hơi (VOCs), chẳng hạn như isopropanol (IPA), gây ra những rủi ro đáng kể cho sức khỏe và môi trường, làm nổi bật nhu cầu về các cảm biến khí có độ nhạy cao, chọn lọc và tiết kiệm năng lượng. ZnO là một vật liệu cảm biến đầy hứa hẹn do có dải cấm rộng, độ linh động electron cao và đặc tính hấp phụ khí mạnh. Tuy nhiên, các cảm biến ZnO tinh khiết thường yêu cầu nhiệt độ làm việc cao và thiếu tính chọn lọc. Công trình này nghiên cứu các màng mỏng ZnO được biến tính bằng hạt nano Au để tăng cường nhạy IPA dưới bức xạ UV 365 nm. Các màng ZnO và hạt nano Au được lắng đọng bằng phương pháp phún xạ. Các phân tích về cấu trúc và thành phần được thực hiện bằng kính hiển vi điện tử quét phát xạ trường (FE-SEM), nhiễu xạ tia X (XRD) và phổ tán xạ năng lượng tia X (EDS). Kết quả cho thấy các hạt nano Au hoạt động như các vị trí xúc tác, cải thiện quá trình truyền điện tích và quá trình oxy hóa khí, do đó tăng cường độ nhạy. Các hạt tải quang sinh do tia UV tạo ra giúp tăng hiệu suất của cảm biến. Các màng ZnO được biến tính bởi các hạt nano Au thể hiện khả năng hồi đáp vượt trội, với hiệu suất tối ưu ở mức hàm lượng Au vừa phải. Hoạt động hỗ trợ của tia UV cho phép phát hiện IPA hiệu quả ở nhiệt độ thấp hơn, giảm mức tiêu thụ điện năng. Những phát hiện này góp phần vào việc thiết kế các cảm biến VOCs thế hệ tiếp theo cho các ứng dụng trong môi trường và công nghiệp.

**Từ khóa:** Cảm biến khí VOC, ZnO, màng mỏng, isopropanol, hạt nano Au.

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# Enhancing VOCs gas sensing performance of ZnO thin films via Au nanoparticles surface modification and UV illumination

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## ABSTRACT

Volatile organic compounds (VOCs), such as isopropanol (IPA), pose significant health and environmental risks, highlighting the need for highly sensitive, selective, and energy-efficient gas sensors. Zinc oxide (ZnO) is a promising sensing material due to its wide bandgap, high electron mobility, and strong gas adsorption properties. However, pristine ZnO sensors often require high operating temperatures and lack selectivity. This study investigates Au nanoparticle-modified ZnO thin films for enhanced IPA sensing under 365 nm UV illumination. ZnO films were deposited via RF sputtering, with Au nanoparticles added using DC sputtering. Structural and compositional analyses were performed using field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDS). Results show that Au nanoparticles act as catalytic sites, improving charge transfer and gas oxidation, thereby enhancing sensitivity. UV-generated charge carriers boost sensor performance. Au-decorated ZnO films exhibit superior response characteristic, with optimal performance at moderate Au loading. UV-assisted operation enables efficient gas detection at lower temperatures, reducing power consumption. These findings contribute to the design of next-generation VOC sensors for environmental and industrial applications.

**Keywords:** VOCs gas sensing, ZnO, thin film, isopropanol, Au nanoparticles.

## 1. INTRODUCTION

Volatile organic compounds (VOCs), such as isopropanol (IPA), are widely used in industrial, medical, and household applications.<sup>1</sup> However, prolonged exposure to IPA vapors can cause serious health risks, including respiratory and neurological issues, as well as environmental harm.<sup>2</sup> Therefore, developing highly sensitive, selective, and energy-efficient gas sensors for IPA detection is essential for air quality monitoring

and workplace safety. Among various sensing materials, zinc oxide (ZnO) stands out due to its wide bandgap (~3.37 eV), high electron mobility, and strong adsorption-desorption properties.<sup>3</sup>

Zinc oxide (ZnO) is widely used in gas sensors due to its unique electronic properties and strong interaction with gas molecules.<sup>4,5</sup> Exposure to VOCs causes gas molecules to adsorb and react on the ZnO surface, altering charge carrier concentration and changing

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electrical conductivity.<sup>6</sup> ZnO nanomaterials, such as nanorods, nanowires, and nanosheets, show enhanced sensing performance due to their high surface-area-to-volume ratio, which promotes gas adsorption.<sup>7</sup> However, pristine ZnO sensors often lack selectivity and require high operating temperatures, necessitating material modifications for improved performance.<sup>8</sup>

ZnO-based gas sensors typically operate at elevated temperatures (200–400 °C) to enhance the adsorption and reaction of gas molecules on the surface. However, high-temperature operation not only increases power consumption but also accelerates material degradation, reducing the sensor's lifetime.<sup>8</sup> To address these limitations, researchers have explored two key strategies to enhance the gas sensing performance of ZnO at lower temperatures: (1) surface modification with noble metal nanoparticles (NPs) and (2) photoactivation using ultraviolet (UV) light.

Noble metal NPs, such as Au, Ag, and Pt, act as catalysts to improve the reaction kinetics of gas molecules, while UV illumination generates additional charge carriers, enhancing the sensor response at room temperature.<sup>9,10</sup> Gold (Au) nanoparticles, in particular, have been extensively studied for their excellent catalytic properties and ability to form Schottky junctions with ZnO, which modulate charge transport and improve sensor selectivity.<sup>11</sup> The catalytic effect of Au facilitates the oxidation of IPA molecules by promoting charge transfer between the gas and the semiconductor surface, leading to a more pronounced change in electrical conductivity.<sup>12</sup> The incorporation of Au NPs onto ZnO surfaces significantly enhances gas sensing performance through multiple mechanisms. Previous studies have demonstrated that Au-modified ZnO sensors exhibit superior performance in detecting VOCs such as ethanol, acetone, and toluene, making Au a promising dopant for IPA sensing applications.<sup>13</sup>

UV irradiation is an effective approach to lower the operating temperature of ZnO gas sensors by generating photogenerated electron-hole pairs that participate in gas sensing

reactions.<sup>14</sup> The energy of UV photons excites electrons from the valence band (VB) to the conduction band (CB) of ZnO, increasing charge carrier concentration and enhancing gas adsorption and/or desorption dynamics.<sup>15</sup> Studies have reported that UV-assisted ZnO sensors can operate efficiently at room temperature, making them suitable for low power and portable sensing applications.<sup>16,17</sup>

The combination of Au NPs and UV illumination in ZnO-based gas sensors has shown a synergistic enhancement in sensing performance. The catalytic activity of Au NPs accelerates gas oxidation, while UV-induced charge carrier generation further amplifies the sensor response.<sup>18</sup> This dual enhancement mechanism enables the detection of VOCs with higher sensitivity, lower detection limits, and improved response/recovery times. Recent studies have demonstrated that Au-ZnO hybrid sensors exhibit remarkable performance in detecting ethanol, formaldehyde, and acetone, but limited research has focused on IPA detection.<sup>19</sup>

In this study, we focus on the fabrication and characterization of ZnO thin films modified with Au nanoparticles for IPA sensing under 365 nm UV irradiation. The choice of ZnO thin films, rather than nanostructured ZnO powders, is motivated by their superior stability, uniformity, and compatibility with integrated sensor devices.<sup>20,21</sup> By combining the catalytic activity of Au nanoparticles with the photoactivation effect of UV light, we aim to achieve enhanced sensitivity, lower detection limits, and reduced operating temperature for IPA detection. The findings of this study will provide valuable insights into the design of next-generation gas sensors for VOCs monitoring in environmental and industrial applications.

## 2. EXPERIMENTAL

Substrates integrated with Au electrodes (5 mm × 5 mm × 0.1 mm) underwent sequential ultrasonic cleaning in acetone, methanol, and deionized water for 15 minutes each, followed by nitrogen blow-drying. Subsequently, thin ZnO films were deposited onto the pre-patterned substrates



via radio frequency (RF) sputtering of a high-purity (99.99%) ZnO target using a shadow mask. The deposition process was conducted at room temperature under an Ar pressure of 10 mTorr, with an input power of 50 W. To enhance structural integrity, the ZnO-coated substrates were thermally oxidized in ambient air at 400 °C for 1 hour, with a heating rate of 12.5 °C/min. During oxidation, the ZnO films underwent morphological evolution, exhibiting agglomeration into dome-like nanoparticles rather than maintaining planar surfaces.

The ZnO film substrates were further functionalized with Au nanoparticles via direct current (DC) sputtering of an Au target under identical deposition conditions: room temperature, 10 mTorr Ar pressure, and 50 W input power. The thicknesses of both the ZnO and Au layers were meticulously monitored using a quartz crystal microbalance sensor to ensure deposition precision. To promote structural stability and optimize surface dispersion, the samples were subjected to post-deposition annealing at 400 °C for 1 hour in ambient air, with a heating rate of 25 °C/min. It is expected that this process facilitated the uniform distribution of Au nanoparticles across the ZnO film surface.

To distinguish the samples, the ZnO films were labeled as ZnO25, ZnO50, ZnO100, and ZnO150, corresponding to their nominal thicknesses (monitored by the quartz microbalance sensor) of 25 nm, 50 nm, 100 nm, and 150 nm, respectively. After Au sputtering, the samples were further named based on the Au layer thickness, such as ZnO25/Au2.5, ZnO50/Au5, ZnO100/Au10, and ZnO150/Au15 for Au thicknesses of 2.5 nm, 5 nm, 10 nm, and 15 nm. However, cross-sectional SEM measurements indicated significant deviations from the intended thicknesses.

The surface morphology and structural characteristics of the sensing film were systematically analyzed using field-emission scanning electron microscopy (FE-SEM; HITACHI S-4800), X-ray diffraction (XRD; Bruker D2, equipped with Cu K $\alpha$ ,  $\lambda = 1.5406$

Å radiation) and energy-dispersive X-ray spectroscopy (EDS). The experimental setup for gas sensing measurements is schematically depicted in previous works.<sup>22,23</sup> The sensing performance was evaluated using a high-precision micro-ammeter/voltage source (Keithley 2601B). VOCs, generated through a bubble evaporator with an air carrier gas, served as the target analytes. The VOCs concentration was precisely regulated by diluting the vapor with dry air at a constant flow rate of 500 sccm before its introduction into the test chamber.

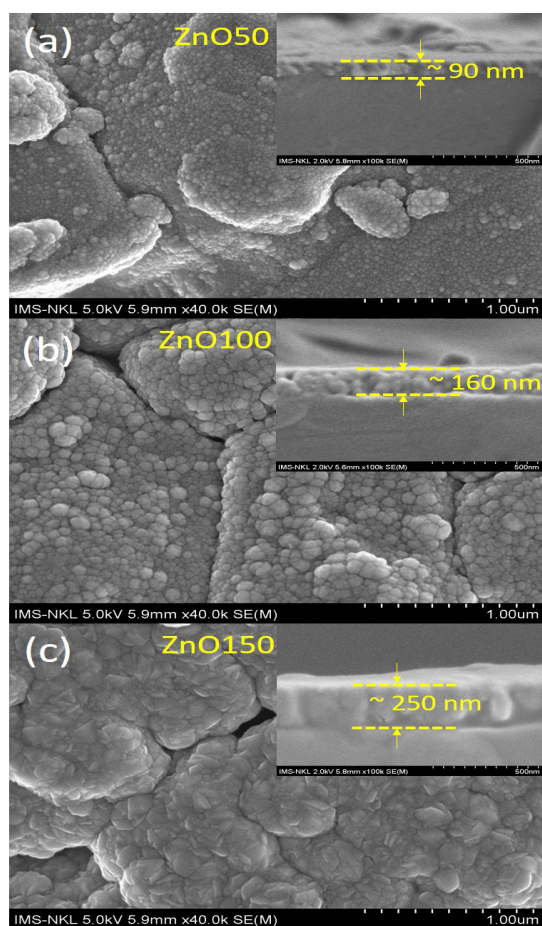
### 3. RESULTS AND DISCUSSION

#### 3.1. Morphology, structure, and chemical composition of the sensing film

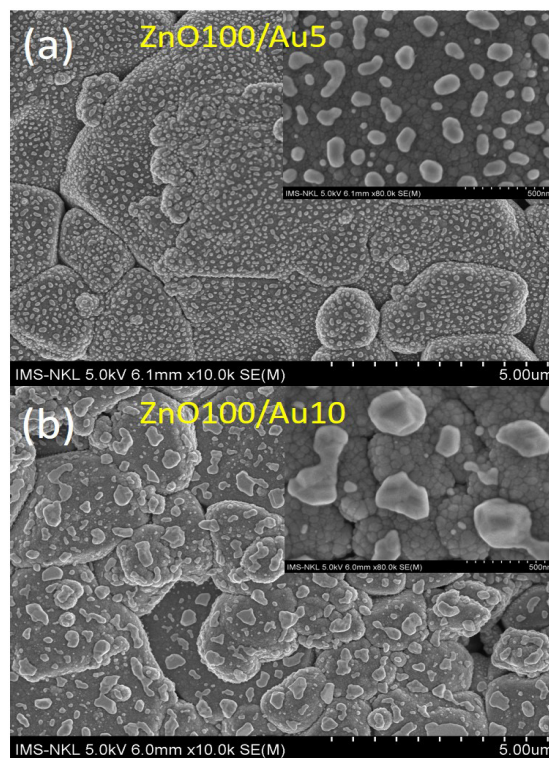
The FE-SEM images provide significant insights into the morphological properties of the ZnO and Au-decorated ZnO thin films. For the pure ZnO films (Figure 1), the FE-SEM images indicate the formation of ZnO nanoparticles, which agglomerate into dome-shaped particles during the oxidation process. The size of these nanoparticles increases with the initial thickness of the deposited film. This agglomeration is due to high-temperature annealing, which promotes grain growth and the coalescence of smaller particles. While the distribution of nanoparticles is relatively uniform, certain regions exhibit denser clustering, potentially affecting the film's overall homogeneity and surface area. Furthermore, the measured thicknesses of 160 nm for ZnO100 and 250 nm for ZnO150 (as shown in the insets of Figure 1) significantly deviate from their nominal values of 100 nm and 150 nm, respectively. This discrepancy suggests variations in the sputtering process, such as differences in deposition rates or post-deposition oxidation effects. The non-uniform thickness may impact the electrical and sensing properties of the films, underscoring the importance of precise control over deposition parameters.

In the case of Au-decorated ZnO films (Figure 2), the FE-SEM images demonstrate the successful deposition of Au nanoparticles on the ZnO surface. For ZnO100/Au5, the Au nanoparticles are uniformly distributed with

smaller sizes, while ZnO100/Au10 exhibits larger and more densely packed Au clusters. The increased Au thickness enhances the surface coverage, which could improve the catalytic activity and gas adsorption capabilities of the material. However, excessive clustering of Au nanoparticles might reduce the effective surface area, potentially impacting the sensor's performance. The presence of ZnO nanoparticles beneath the Au layer provides a high surface area substrate, which is beneficial for gas sensing applications. The interaction between the Au nanoparticles and the ZnO surface is crucial, as it can enhance the charge transfer processes and improve the sensitivity towards volatile organic compounds (VOCs). These findings underscore the importance of optimizing both the ZnO nanoparticle formation and Au thickness and distribution to achieve enhanced gas sensing properties.



**Figure 1.** Surface FE-SEM images of pure ZnO thin films: (a) ZnO50, (b) ZnO100, and (c) ZnO150. Insets show corresponding cross-sectional views.



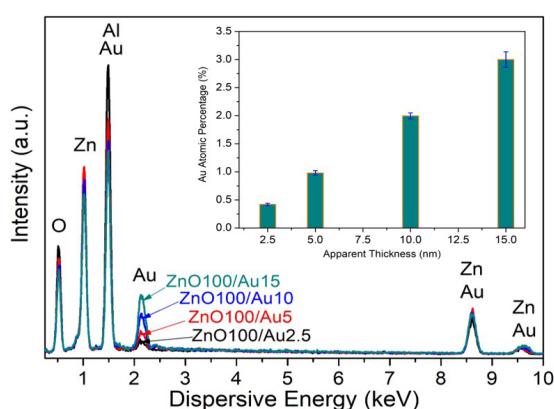
**Figure 2.** Surface FE-SEM images of Au-decorated ZnO thin films: (a) ZnO100/Au5 and (b) ZnO100/Au10. The insets show corresponding higher-magnification views.

The EDS spectra presented in Figure 3 confirm the elemental composition of the ZnO100/Au2.5, ZnO100/Au5, ZnO100/Au10, and ZnO100/Au15 samples. The spectra exhibit characteristic peaks corresponding to Zn (zinc), O (oxygen), and Au (gold), which validate the successful deposition of gold onto the ZnO surface. The intensity of the Au peaks increases progressively with the nominal thickness of the sputtered gold layer, indicating a systematic augmentation in gold content. Additionally, a minor Al (aluminum) signal is detected, which originates from the substrate.

The inset graph in Figure 3 quantitatively illustrates the atomic percentage of Au in relation to the nominal thickness of the deposited layer. A clear positive correlation is observed, with the Au content increasing as the nominal thickness rises from 2.5 nm to 15 nm. The error bars, which remain relatively small, indicate a high degree of measurement accuracy and reproducibility. The consistency between the EDS spectra and the

atomic percentage data further corroborates the uniform deposition of gold.

Overall, these findings confirm the controlled growth of Au layers on ZnO films, with elemental compositions aligning well with the expected deposition parameters. The presence of Zn and O peaks further verifies the integrity of the underlying ZnO layer. The data not only substantiate the effectiveness of the sputtering process but also establish a foundation for subsequent investigations into the physicochemical properties of these nanostructured materials.

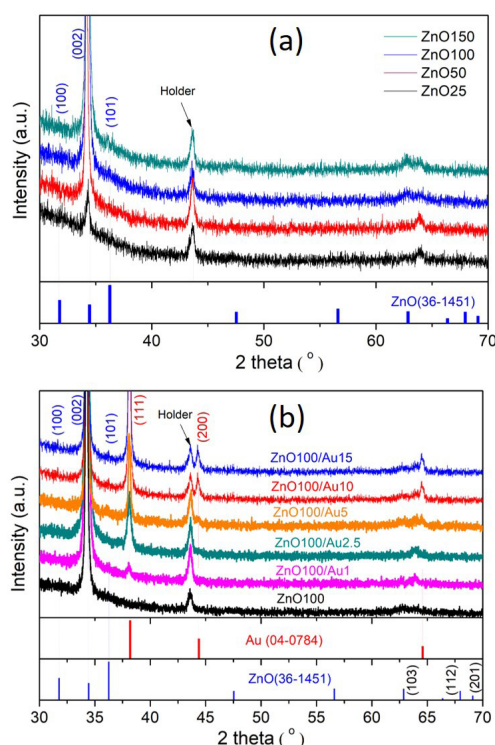


**Figure 3.** EDS spectra of the ZnO100/Au2.5, ZnO100/Au5, ZnO100/Au10, and ZnO100/Au15 samples. The inset shows the atomic percentage of Au element in the samples versus the nominal thickness.

Figure 4(a) presents the XRD patterns of ZnO thin films with varying thicknesses (ZnO25, ZnO50, ZnO100, and ZnO150), revealing the characteristic diffraction peaks of hexagonal wurtzite ZnO. The predominant peaks observed at  $2\theta \approx 31.8^\circ$ ,  $34.4^\circ$ , and  $36.6^\circ$  correspond to the (100), (002), and (101) crystal planes, respectively, in accordance with the JCPDS card No. 36-1451. Notably, as the film thickness increases, the intensity of these peaks strengthens, indicating an enhancement in crystallinity. The presence of a minor peak near  $2\theta \approx 43.5^\circ$  is attributed to the sample holder rather than the film itself.

Figure 4(b) illustrates the XRD spectra of ZnO100 before and after gold deposition with varying nominal thicknesses (1 nm, 2.5 nm, 5 nm, 10 nm, and 15 nm). The ZnO diffraction

peaks remain unchanged, suggesting that the deposition of Au does not significantly alter the ZnO crystal structure. However, the emergence of additional peaks at  $2\theta \approx 38.2^\circ$  and  $44.4^\circ$ , corresponding to the (111) and (200) planes of face-centered cubic (FCC) Au (JCPDS No. 04-0784), confirms the successful incorporation of gold onto the ZnO surface. The intensity of the Au(111) peak increases progressively with greater Au thickness, indicating a higher surface coverage and possible nanoparticle growth. Importantly, the absence of any noticeable shift in ZnO peak positions suggests that Au primarily forms a surface layer rather than diffusing into the ZnO lattice. These results validate the controlled deposition of Au on ZnO thin films, preserving the intrinsic wurtzite structure of ZnO while introducing a well-defined Au phase. This structural integrity is crucial for subsequent investigations into the functional properties of these Au-ZnO hybrid materials, particularly in applications.



**Figure 4.** XRD patterns of (a) ZnO films with varying thicknesses and (b) ZnO100 film before and after Au deposition at different thicknesses. Reference patterns for ZnO (JCPDS No. 36-1451) and Au (JCPDS No. 04-0784) are shown for comparison.

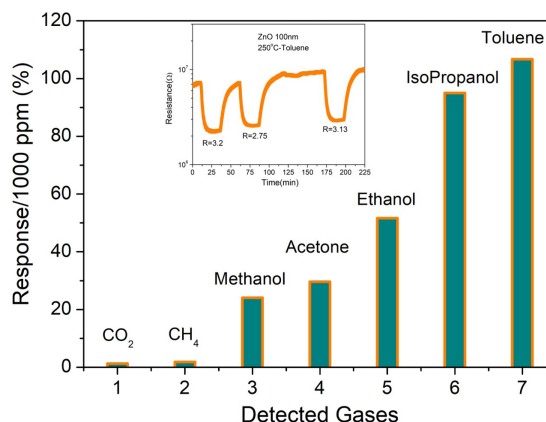


### 3.2. VOCs sensing performance

The bar chart (Figure 5) shows the ZnO100 sensor's response to various gases at 1000 ppm and 250 °C under dark conditions. The response of the sensor was defined by the  $R_a/R_g$  ratio, where  $R_a$  is the baseline resistance of the sensor in dry air and  $R_g$  is the resistance upon exposure to VOCs vapor at a given temperature. In this study, target gases were generated using a bubble evaporator system, in which dry air was passed through a glass bubbler containing the liquid analyte at room temperature. The saturated vapor was then mixed with a controlled flow of dry air using calibrated mass flow controllers to obtain the desired gas mixture. Based on the physical properties of the analytes (vapor pressure and density), the concentrations of the generated gases were calculated as follows: Toluene: 0.285% (2850 ppm), Acetone: 2.37% (23,700 ppm), Ethanol: 0.583% (5830 ppm), Methanol: 1.275% (12,750 ppm), Isopropanol (IPA): 0.635% (6350 ppm), CO<sub>2</sub>: 4% (40,000 ppm), CH<sub>4</sub>: 4% (40,000 ppm). These gas concentrations were used in the actual sensing tests. For comparative purposes, the response values were normalized to a reference concentration of 1000 ppm by assuming a near-linear response in the low-concentration range. This normalization allows for clearer discussion of the sensor's selectivity and sensitivity toward different analytes, independent of their initially tested concentrations.

The sensor responds most strongly to toluene, followed by IPA and ethanol, with moderate sensitivity to acetone and methanol. In contrast, CO<sub>2</sub> and CH<sub>4</sub> elicit negligible responses, indicating poor response to non-reactive gases. The inset graph in Figure 5 reveals the sensor's dynamic response to toluene, demonstrating excellent repeatability and stability across multiple cycles. The fabricated sensors exhibited n-type behavior of the semiconductor because of decreasing resistance of the sensor upon exposure to the reducing VOCs vapor. These results highlight the sensor's effectiveness in detecting aromatic and oxygenated VOCs,

particularly toluene and IPA, while showing selectivity against non-polar gases. This ZnO-based sensor holds promise for applications in air quality monitoring and VOC detection.



**Figure 5.** Response of the ZnO100 sensor to various VOCs vapors at 250 °C (relative to 1000 ppm). Inset shows resistance response to 2854.8 ppm toluene vapor over three measurement cycles at 250 °C.

The gas sensing performance of the ZnO100 sensor toward toluene is significantly influenced by both operating temperature and UV 365 nm irradiation, as illustrated in Figure 6(a). In the absence of UV illumination, the sensor's response gradually increases with temperature. However, under UV 365 nm irradiation, the sensor exhibits an enhanced response even at lower temperatures, demonstrating more stable and consistent behavior. Notably, at 200 °C, the sensor under UV irradiation achieves a response comparable to that observed at higher temperatures in the dark, underscoring the role of UV illumination in activating surface reactions and improving sensitivity.

The inset graph in Figure 6(a) provides further insight into the sensor's dynamic behavior at 200 °C. Without UV illumination, the sensor exhibits a high baseline resistance and incomplete recovery, as the resistance fails to return to its initial state after toluene exposure. This incomplete recovery suggests strong molecular adsorption on the ZnO surface, with insufficient thermal energy at 200 °C to facilitate desorption. Consequently, the sensor experiences signal drift and performance degradation over time. In contrast, under UV 365 nm irradiation,

the sensor demonstrates significantly improved recovery, with the resistance fully returning to its initial state after each exposure cycle. This behavior indicates that UV illumination enhances the desorption of adsorbed toluene molecules, due to the generation of photogenerated charge carriers that accelerate surface reactions. The increased electron-hole pairs promote the oxidation of hydrocarbons, effectively resetting the sensor to its baseline state. Additionally, the response magnitude ( $R \approx 2.65$ ) is notably higher under UV illumination compared to the dark condition, further highlighting the role of UV light in enhancing the sensor's sensitivity and stability. These findings emphasize the critical role of UV 365 nm irradiation in improving the ZnO sensor's gas sensing performance, reversibility, and operational efficiency at moderate temperatures. The combination of UV activation and optimized working temperature enables reliable and real-time detection of toluene, making this approach highly beneficial for practical gas sensing applications.

Interestingly, as shown in Figure 6(a), the response of the ZnO sensor at 225 °C under dark conditions was observed to be higher than that under UV 365 nm illumination. This counterintuitive result can be attributed to the thermal dominance at elevated temperatures, where thermally activated surface reactions are already highly efficient, rendering the additional contribution from UV-generated electron-hole pairs less significant. Moreover, UV irradiation may induce desorption of adsorbed oxygen species or VOC molecules, thereby reducing the density of reactive species on the surface. Additionally, UV light at high temperature could alter the reaction dynamics, possibly forming intermediate species that do not significantly contribute to charge transfer. These combined effects may lead to a decrease in sensing response under UV illumination at higher operating temperatures.

Figure 6(b) shows the response of ZnO sensors with different thicknesses (25–150 nm) to toluene at 200 °C under UV 365 nm irradiation.

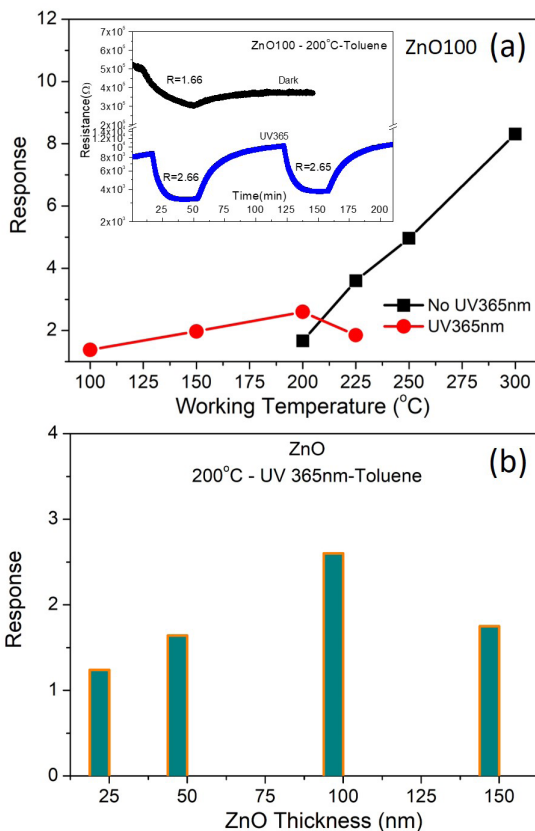
The response increases with thickness up to 100 nm, after which it decreases for the 150 nm sample. This non-monotonic trend can be attributed to the interplay between surface area and charge transport characteristics: (1) For thin films (ZnO25 and ZnO50 have thicknesses smaller than 90 nm, as estimated by FE-SEM (see Figure 1)), the limited active surface area results in lower gas molecule adsorption and, consequently, a weaker response; (2) For the optimal thickness (ZnO100 has a thickness of approximately 160 nm, as estimated by FE-SEM (see Figure 1)), a balance is achieved between surface reaction sites and efficient charge transport, leading to the highest response; (3) For thicker films (ZnO150 has a thickness of approximately 250 nm, as estimated by FE-SEM (see Figure 1)), the increased bulk volume promotes higher charge carrier recombination and reduced surface activity, thereby diminishing sensing performance. A 100 nm ZnO thickness is identified as the optimal condition under UV irradiation at 200 °C, striking a balance between surface reactivity and charge transport efficiency.

The sensing performance of metal oxide semiconductors depends critically on the interplay between surface reaction activity and charge transport efficiency. An optimal sensing layer morphology allows a balance between a sufficient number of active surface sites for gas adsorption and efficient transport of charge carriers generated during gas–solid interactions. If the film is too thin, the limited surface area reduces gas adsorption; if it is too thick or overly porous, carrier transport is hindered due to increased scattering and recombination at grain boundaries and defects, ultimately lowering the sensor response. Therefore, a moderate film thickness with a controlled nanostructure enhances the response by maximizing both surface reactivity and carrier mobility.<sup>4</sup>

Moreover, an excessive increase in bulk volume may lead to enhanced charge carrier recombination. As charge carriers generated from surface reactions travel through a thicker matrix, they are more to recombine before reaching the



electrode, especially in the presence of crystal defects or poor connectivity. This recombination reduces the effective modulation of electrical resistance and thus the sensing response.<sup>16,17,24,25</sup>

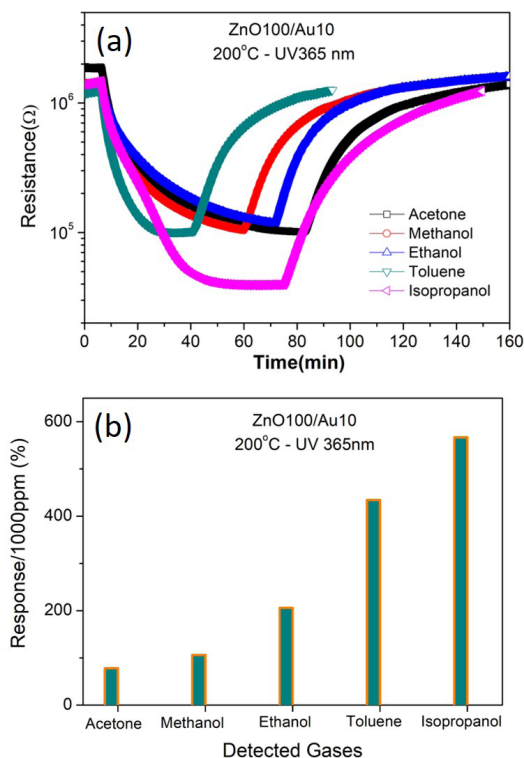


**Figure 6.** (a) Response of the ZnO100 sensor to 2854.8 ppm toluene vapor as a function of operating temperature under dark conditions (black squares) and UV365nm irradiation (red circles). The inset shows the dynamic resistance of ZnO100 sensor at 200°C in the dark and under UV illumination. (b) Response of ZnO100 sensors with different thicknesses to 2854.8 ppm toluene vapor at the optimized operating temperature of 200°C under UV365nm irradiation.

The sensing performance of the ZnO100/Au10 sensor toward various volatile organic compounds (VOCs) under UV 365 nm irradiation at 200 °C is illustrated in Figures 7(a) and 7(b). In Figure 7(a), the dynamic resistance curves exhibit a distinct decrease upon exposure to different VOC vapors, followed by a gradual recovery when the detected gas flow is stopped. Notably, the response and recovery characteristics vary significantly depending on the target gas. Among the tested VOCs, IPA induces the most pronounced resistance drop,

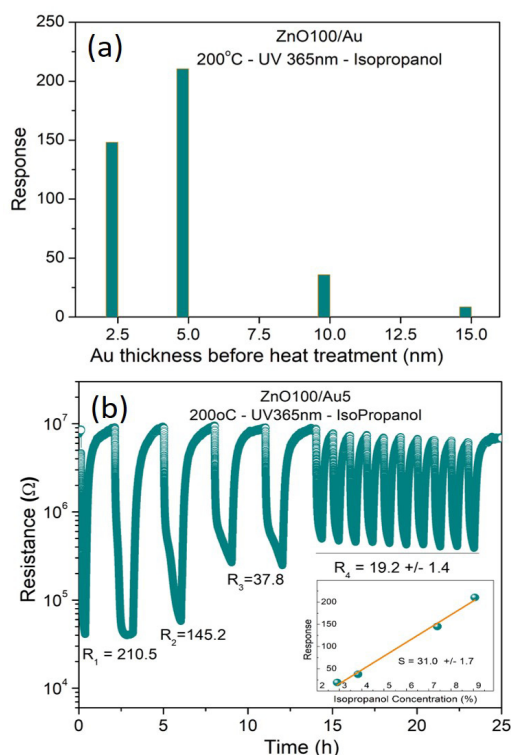
followed by toluene, ethanol, methanol, and acetone, highlighting the sensor's differential sensitivity. Furthermore, the complete recovery of resistance to its baseline after gas removal demonstrates the excellent reversibility of the ZnO100/Au10 sensor under UV irradiation, a critical feature for practical sensing applications.

Figure 7(b) quantifies the sensor's response, normalized per 1000 ppm of each gas. The results confirm the dynamic response trend observed in Figure 7(a), with IPA exhibiting the highest response, followed by toluene, ethanol, methanol, and acetone. The significantly enhanced response toward IPA and toluene suggests that the ZnO100/Au10 sensor has a strong affinity for these analytes, due to favorable surface interactions and catalytic effects induced by the Au nanoparticles. These findings highlight the sensor's capability for VOC detection with high selectivity, high response, and efficient recovery, making it a promising candidate for real-world gas sensing applications.



**Figure 7.** (a) Resistance response of the ZnO100/Au10 sensor to various VOCs and (b) the sensor's response normalized per 1000 ppm of each gas at 200 °C under UV365nm irradiation.

The gas sensing characteristics of Au-modified ZnO sensors toward IPA under UV 365 nm irradiation at 200 °C are illustrated in Figures 8(a) and 8(b), emphasizing the impact of Au nanoparticle size and the sensor's response across varying gas concentrations. Figure 8(a) depicts the sensor's response as a function of the Au nominal thickness (which was measured in real-time by the sensor throughout the gold deposition process), revealing that the ZnO100/Au5 sensor achieves the highest response, while thinner (nominal thickness of 2.5 nm) or thicker (The nominal thickness exceeds 10 nm) Au layers significantly diminish performance. This trend suggests that a 5 nm Au layer represents the optimal thickness, striking a balance between catalytic activity and charge transfer efficiency. Excessively thin Au layers may lack sufficient catalytic enhancement, whereas thicker layers are prone to agglomeration, reducing the active surface area and gas adsorption capacity.



**Figure 8.** (a) The sensor's response as a function of Au thickness before heat treatment to 9% IPA and (b) the dynamic response of the optimized ZnO100/Au5 sensor to different IPA concentrations at 200 °C under UV 365 nm irradiation. Inset in (b) illustrates a linear relationship between the sensor response and IPA concentration.

Figure 8(b) demonstrates the dynamic response of the optimized ZnO100/Au5 sensor to different IPA concentrations (9%, 7.4%, 3.8%, and 2.9%), with corresponding sensor responses of  $R_1 \approx 210.5$ ,  $R_2 \approx 145.2$ ,  $R_3 \approx 37.8$ , and  $R_4 \approx 19.2$ , respectively. The results reveal a strong correlation between gas concentration and sensor response, with higher IPA concentrations eliciting stronger responses. The consistent and reversible resistance variations underscore the sensor's stability and reliability for VOC detection. Additionally, the inset graph in Figure 8(b) illustrates a linear relationship between the sensor response and IPA concentration, with a calculated sensitivity of  $S = 31.0 \pm 1.7$ , highlighting the sensor's potential for accurate VOC quantification. The limit of detection (LOD) can be reasonably estimated by evaluating the standard deviation ( $\delta$ ) and sensitivity ( $S$ ) from the linear curve fitting of the sensor's response versus gas concentration (%). Using the formula  $LOD = 3\delta/S$ , with  $\delta = 1.4$  and  $S = 31.0 \pm 1.7$ , the LOD of sensor to IPA is estimated to be approximately 0.136%. This suggests that the sensor is capable of detecting IPA gas at low concentrations, making it suitable for practical applications.

### 3.3. Gas sensing mechanism of Au-decorated ZnO under UV365 nm illumination

The gas sensing performance of ZnO-based sensors relies on surface interactions between the target gas molecules and the semiconductor material. When ZnO is exposed to VOCs such as IPA, a series of adsorption, charge transfer, and reaction processes occur at the sensor surface, leading to measurable changes in electrical resistance. However, pristine ZnO often exhibits limitations in selectivity, response magnitude, and operating temperature, necessitating material modifications to enhance its sensing properties.

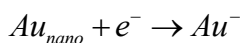
To address these challenges, Au NPs and UV 365 nm illumination are employed to improve sensor performance through Schottky barrier formation, catalytic effect (spillover), and localized surface plasmon resonance

(LSPR) enhancement. The Au NPs act as electron traps, facilitating charge transfer and promoting gas-surface interactions, while UV illumination generates additional charge carriers, accelerating adsorption-desorption dynamics. These synergistic effects lead to an enhanced response, improved selectivity, and reduced operating temperature compared to conventional ZnO sensors.

The gas sensing behavior of ZnO/Au under UV 365 nm illumination is governed by a series of surface reactions, including UV-induced charge carrier generation, oxygen species formation, IPA oxidation, and sensor recovery dynamics. These processes play a crucial role in modulating the sensor's electrical resistance, enabling sensitive and selective IPA detection. The detailed mechanistic steps are outlined below:

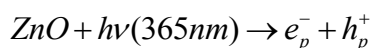
#### Step 1: Role of Gold Nanoparticles (AuNPs)

Au NPs function as electron traps, extracting electrons from ZnO and inhibiting their recombination with holes. This process results in the formation of a Schottky barrier at the Au-ZnO interface due to the work function difference ( $\Phi_{\text{Au}} \approx 5.1$  eV,  $\Phi_{\text{ZnO}} \approx 4.2$  eV),<sup>26</sup> which induces electron depletion in the ZnO region near the junction. Consequently, this barrier enhances charge separation, extends electron lifetime, and strengthens gas interactions by facilitating more efficient electron transfer during gas adsorption and reaction processes:



#### Step 2: UV Excitation and Charge Generation

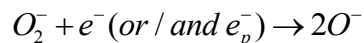
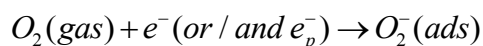
When ZnO absorbs UV 365 nm light, electrons in the VB gain energy and transition to the CB, creating electron-hole ( $e_p^- - h_p^+$ ) pairs:<sup>15</sup>



The photogenerated electrons ( $e_p^-$ ) play a crucial role in modulating gas adsorption and reaction dynamics on the sensor surface.

#### Step 3: Oxygen Adsorption and Formation of Reactive Oxygen Species

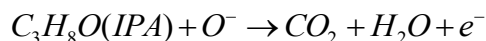
In ambient air, oxygen molecules ( $\text{O}_2$ ) adsorb onto the ZnO/Au surface and capture free or/and photogenerated electrons, forming reactive oxygen species that act as active sites for gas sensing:<sup>4,27</sup>



These oxygen species are highly reactive and play a key role in oxidizing IPA molecules upon exposure.

#### Step 4: Gas Interaction (IPA Oxidation) and Sensor Response

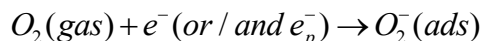
When IPA molecules interact with  $\text{O}^-$  species on the sensor surface, they undergo oxidation, releasing electrons back into the ZnO conduction band. This electron injection reduces the sensor's electrical resistance, leading to a strong sensing response:



The magnitude of this resistance change is directly correlated with the concentration of IPA molecules, making ZnO/Au an effective IPA sensor.

#### Step 5: Sensor Recovery after Gas Removal

Once the IPA vapor is removed, fresh oxygen molecules from air re-adsorb onto the ZnO/Au surface, restoring the baseline resistance of the sensor:



Under UV 365 nm irradiation, this desorption process is significantly accelerated, leading to faster recovery times and ensuring sensor stability over multiple detection cycles.

By leveraging UV-assisted charge carrier generation, Schottky barrier formation at Au-ZnO interfaces, and catalytic oxidation processes, the ZnO/Au sensor achieves high response and efficient recovery for IPA detection.

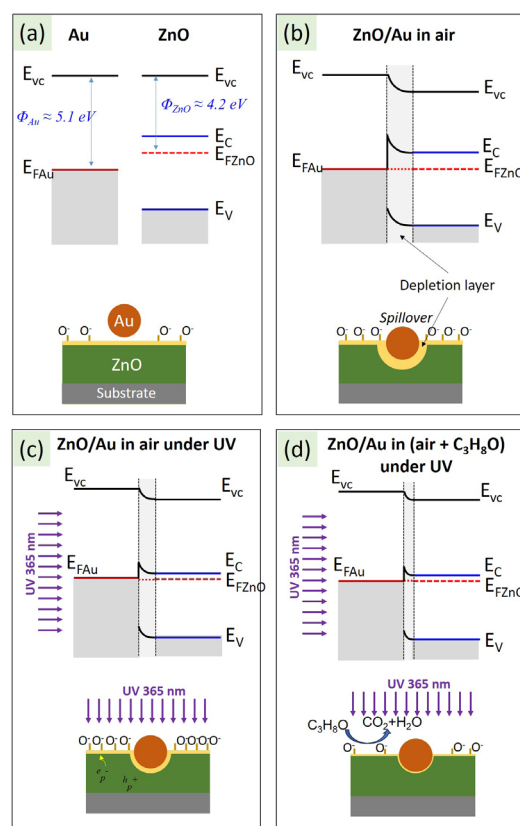
The size of Au NPs plays a critical role in determining the gas sensing performance of ZnO/Au hybrid sensors, particularly for IPA detection under UV 365 nm irradiation at 200 °C. If the Au NPs are small (ZnO100/Au2.5), they lack the ability to form well-defined Schottky barriers, resulting in weak electron trapping and lower sensor response. Conversely, larger Au NPs (ZnO100/Au10 and ZnO100/Au15) tend to agglomerate, reducing the density of Schottky junctions and limiting their impact on charge modulation. At an optimal size (ZnO100/Au5), Au NPs effectively trap and release electrons, maximizing the gas-induced resistance change and ensuring a strong, reversible sensor response.

In addition to Schottky barrier effects, LSPR enhancement further improves sensor performance. Under UV 365 nm irradiation, Au NPs exhibit plasmonic resonance, generating hot electrons that can be injected into ZnO's conduction band. This process increases free charge carrier concentration, suppresses recombination, and amplifies surface reactions. Smaller Au NPs exhibit weak plasmonic effects, whereas larger particles show broadened and less intense plasmonic peaks, reducing their effectiveness. For ZnO100/Au5, Au NPs exhibit strong LSPR effects, enhancing light absorption, accelerating electron-hole separation, and improving gas adsorption/desorption kinetics.

To gain deeper insight into the sensing mechanism of ZnO/Au structure - particularly under UV irradiation and in the presence of isopropanol (IPA) gas - we propose a model illustrating the energy band alignment and surface adsorption processes under various environmental conditions. These processes are illustrated in detail in Figure 9, which shows the corresponding energy band diagrams (top) and surface adsorption models (bottom) under each condition, highlighting the role of Au nanoparticles in enhancing oxygen adsorption and modulating the sensor response (Figure 9).

Before contact, the difference in work functions between Au and ZnO leads to a

misalignment in their Fermi levels (Figure 9a), which drives the formation of a Schottky junction upon contact (Figure 9b). Under dark conditions in air, charge redistribution occurs at the ZnO/Au interface, resulting in upward band bending in ZnO and the formation of a surface electron depletion layer. Additionally, Au nanoparticles facilitate the *spillover* effect, enhancing the adsorption of oxygen species on the ZnO surface (Figure 9b). Upon exposure to UV 365 nm, photogenerated electron-hole pairs further promote the formation of reactive oxygen species and narrowing the depletion region and decreasing the baseline resistance of the sensor (Figure 9c). When IPA gas is introduced, the reducing molecules react with the adsorbed oxygen species, releasing trapped electrons back into the ZnO conduction band. This reaction narrows the depletion layer and decreases the resistance, which serves as the basis for gas detection (Figure 9d).



**Figure 9.** Schematic energy band diagrams (top) and corresponding adsorption models (bottom) illustrating the interfacial and surface processes in



the ZnO/Au system under various environmental and optical conditions: (a) Isolated Au and ZnO before contact, where the difference in work function  $\Phi_{Au}$ ,  $\Phi_{ZnO}$  results in distinct Fermi levels ( $E_{FAu}$  and  $E_{FZnO}$ ); (b) ZnO/Au heterostructure in air under dark condition. Upon contact, electrons transfer from ZnO to Au until Fermi level equilibrium is achieved, leading to the upward band bending in ZnO and the formation of a depletion region near the interface. The presence of Au nanoparticles also facilitates the *spillover* effect, enhancing the adsorption of oxygen species on the ZnO surface; (c) ZnO/Au structure in air under UV (365 nm) illumination. UV excitation generates electron-hole pairs, where photogenerated holes ( $h^+$ ) participate in the formation of additional surface oxygen species, further narrowing the depletion layer and decreasing the sensor's baseline resistance; (d) ZnO/Au structure in a mixed atmosphere of air and isopropanol ( $C_3H_8O$ ) under UV illumination. Adsorbed oxygen species react with IPA, producing  $CO_2$  and  $H_2O$  and releasing trapped electrons back into the conduction band of ZnO. This reduces the width of the depletion region and leads to a measurable decrease in resistance, which serves as the sensing signal. The energy levels  $E_{VC}$ ,  $E_C$ ,  $E_V$ ,  $E_{FAu}$ , and  $E_{FZnO}$  represent the vacuum level, conduction band minimum, valence band maximum, Fermi level of Au, and Fermi level of ZnO, respectively.

#### 4. CONCLUSION

This study demonstrates the successful development of ZnO/Au nanostructured sensors for highly sensitive and selective IPA detection under UV365 nm irradiation at 200 °C. The optimized ZnO100/Au5 sensor exhibits outstanding gas sensing properties, with a response of 210.5 to 9% IPA, a high sensitivity of  $31.0 \pm 1.7$  (1%), and a low detection limit (LOD) of 0.136% IPA. The superior performance is attributed to the synergistic effects of Au-induced Schottky barrier modulation, plasmonic enhancement, and UV-assisted charge carrier generation, leading to improved adsorption-desorption kinetics and accelerated sensor recovery. Furthermore, the low operating temperature (200 °C) compared to conventional ZnO-based sensors (300 – 400 °C) makes this

system more energy-efficient and practical for real-world applications. Although 200 °C is not room temperature, it is still considered a relatively low operating temperature for metal oxide semiconductor gas sensors, particularly those based on ZnO. In many conventional systems, ZnO requires elevated temperatures in the range of 300 – 450 °C to achieve sufficient sensitivity to volatile organic compounds (VOCs) due to the need for thermal activation of surface reactions.<sup>28</sup> The ability of our ZnO-based sensor to exhibit a stable and enhanced response to isopropanol and toluene vapors at 200 °C demonstrates a significant improvement in reducing the thermal budget for sensor operation. Moreover, the application of UV irradiation further enhances sensor response and provides a promising direction for developing gas sensors capable of room-temperature operation in future designs. From an application standpoint, an operating temperature of 200 °C remains acceptable for a wide range of industrial and environmental monitoring systems, where heating elements are integrated and energy consumption is managed efficiently.<sup>29</sup> These findings suggest that our sensor structure has both scientific value and practical potential in real-world conditions.

Given these promising results, ZnO/Au hybrid sensors hold significant potential for real-time VOCs monitoring in various industries, including environmental air quality control, workplace safety, and smart sensor networks for industrial emissions monitoring. The ability to achieve high selectivity and sensitivity at relatively low temperatures positions these sensors as viable candidates for integration into portable and wearable gas detection devices.

However, a notable limitation of the current sensor is its relatively long response and recovery times, which may affect its real-time detection capability in dynamic environments. This delay in sensor reaction could be attributed to slow desorption kinetics of IPA molecules on



the ZnO/Au surface, even under UV irradiation. To address this challenge, future studies should focus on optimizing surface functionalization, tuning Au nanoparticle morphology, and exploring alternative catalytic materials to accelerate the gas adsorption-desorption process. Additionally, modifying ZnO with advanced nanostructured materials such as metal-organic frameworks (MOFs), 2D materials (graphene, MXenes), or heterostructures with p-type oxides could further enhance sensor performance by reducing response/recovery times while maintaining high sensitivity and selectivity.

For future research, several directions could further enhance the applicability of this sensor platform. First, optimizing the morphology and surface functionalization of ZnO/Au nanostructures could improve selectivity toward specific VOCs, such as toluene, acetone, and formaldehyde, which are critical pollutants in indoor air quality assessment. Second, integrating ZnO/Au sensors with flexible substrates and wireless communication modules could pave the way for next-generation IoT-based VOC sensing platforms. Third, exploring alternative noble metal catalysts (e.g., Pt, Pd, Ag) and multi-metallic hybrid nanostructures could provide further enhancements in sensor stability, lower detection limits, and multi-gas sensing capabilities.

Overall, this work provides a strong foundation for the design and application of advanced ZnO/Au-based gas sensors, offering a scalable, energy-efficient, and highly responsive solution for VOC detection. With continued optimization and material innovation, these sensors could play a crucial role in future smart sensing technologies for environmental and industrial applications.

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# Hiểu biết sâu sắc hơn về độ bền và đặc trưng của các liên kết hydrogen $O/C_{sp^2}-H\cdots Z$ trong các hệ phức tương tác giữa dẫn xuất của chalcogenoaldehyde acid và formamide

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## TÓM TẮT

Các cấu trúc bền của các phức tương tác giữa  $RCZOH$  và  $NH_2CHZ$ , với  $R = H, F, CH_3$  và  $Z = O, S, Se$  và  $Te$  đã được tìm thấy trong nghiên cứu này. Độ bền của các liên kết hydrogen  $O/C_{sp^2}-H\cdots Z$  có xu hướng giảm dần khi  $Z$  lần lượt là  $O, S, Se$ , và  $Te$ . Sự chuyển dời đỏ tần số dao động hóa trị của liên kết  $O-H$  trong các liên kết hydrogen  $O-H\cdots O$  lớn hơn so với các liên kết hydrogen  $O-H\cdots S/Se/Te$ , trong đó sự chuyển dời đỏ  $O-H$  rất lớn đạt đến  $958,0\text{ cm}^{-1}$  được phát hiện ở các liên kết hydrogen  $O-H\cdots O$ . Mức độ chuyển dời đỏ  $O-H$  càng tăng khi nhóm thế  $Z$  trong  $RCZOH$  đi từ  $O$  đến  $Te$  và  $R$  chuyển từ nhóm đẩy electron  $CH_3$  sang nhóm thế hút electron  $F$ . Đáng chú ý, sự chuyển dời xanh đáng kể của  $C_{sp^2}-H$  lên đến  $104,9\text{ cm}^{-1}$  trong liên kết hydrogen không cổ điển  $C_{sp^2}-H\cdots O$  đã được quan sát thấy. Tần số dao động hóa trị của  $C_{sp^2}-H$  trong các liên kết hydrogen  $C_{sp^2}-H\cdots S/Se/Te$  có xu hướng đi từ chuyển dời xanh sang chuyển dời đỏ khi nhóm thế  $Z$  trong  $NH_2CHZ$  dần được thay thế từ  $O$  đến  $Te$ . Đặc biệt, ái lực proton tại phần tử nhận proton  $Z$  và độ phân cực của phần tử cho proton  $O/C_{sp^2}-H$  càng tăng thì mức độ chuyển dời đỏ của  $O/C_{sp^2}-H$  càng rõ rệt và ngược lại.

**Từ khóa:** Liên kết hydrogen cổ điển, liên kết hydrogen không cổ điển, chuyển dời đỏ, chuyển dời xanh, NBO.

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# An insight into stability and characteristics of O/C<sub>sp2</sub>-H...Z hydrogen bonds in the binary systems of chalcogenocarboxylic acid and formamide derivatives

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## ABSTRACT

Forty-eight stable structures of complexes were identified for interaction of RCZOH and NH<sub>2</sub>CHZ, with R= H, F, CH<sub>3</sub> and Z= O, S, Se, Te. Strength of O/C<sub>sp2</sub>-H...Z hydrogen bonds decreases in the order of the Z acceptors: O > S > Se > Te. The O-H stretching frequency's red shifts of the O-H...O hydrogen bonds are larger than those of the O-H...S/Se/Te ones, in which the significant O-H red shift of 958.0 cm<sup>-1</sup> is detected in the O-H...O ones. There is an increase in the O-H red shift as Z in the RCZOH goes from O to Te, and R changes from the electron-donating CH<sub>3</sub> group to the electron-withdrawing F substituent. Remarkably, a substantial blue shift of the C<sub>sp2</sub>-H up to 104.9 cm<sup>-1</sup> in the nonconventional C<sub>sp2</sub>-H...O hydrogen bond is found, and an obvious trend from blue shift to red shift of C<sub>sp2</sub>-H stretching frequencies in the C<sub>sp2</sub>-H...S/Se/Te hydrogen bonds is also detected as Z in the NH<sub>2</sub>CHZ varying from the O to Te substituent. It is noteworthy that the proton affinity at the Z proton acceptors and the polarity of the O/C<sub>sp2</sub>-H proton donors increase along with the enhancement of the O/C<sub>sp2</sub>-H red shift, and *vice versa*.

**Keywords:** Conventional hydrogen bonds, nonconventional hydrogen bonds, red shift, blue shift, NBO.

## 1. INTRODUCTION

Hydrogen bond is one of the noncovalent interactions, playing essential roles in chemistry, physics, and biological systems such as DNA, RNA, or protein.<sup>1,2</sup> The importance of hydrogen bonds especially appears in biochemical reactions, supermolecule synthesis, and crystal design.<sup>2-4</sup> Therefore, a thorough understanding of hydrogen bonds can expand their application in various fields of life.

Up to now, the A-H...B hydrogen bonds have had two main types, including

conventional, and nonconventional hydrogen bonds. Therein, the A and B atoms in the conventional hydrogen bonds often possess high electronegativity or electron-rich regions. This type of hydrogen bonds is usually characterised by a stretching frequency red shift of the proton donor, which is displayed by an increase in the A-H bond length and a decrease of its stretching frequency.<sup>4,5</sup> By contrast, either or both A and B in the nonconventional hydrogen bonds have low electronegativity or lower electron density regions.<sup>5,6</sup> Notably, the nonconventional hydrogen bonds not only show the attributes of

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the red shift but also present the blue shift of stretching frequency, named the blue-shifting hydrogen bonds. The blue-shifting hydrogen bond is associated with a contraction of the proton donor bond length and an enhancement of its stretching frequency.<sup>7,8</sup>

The nature of hydrogen bonds, especially the blue-shifting ones, has been investigated both by experimental and theoretical methods.<sup>6,7,9,10</sup> Therein, some studies showed that attaching either electron-donating or electron-withdrawing groups to the C-H proton donors may change the electron density of the C-H bond,<sup>11–13</sup> affecting the strength and characteristics of hydrogen bonds. Noted that the blue shifts of the  $C_{sp^2}$ -H bonds are very large and even surpass those of the  $C_{sp^3}$ -H bonds.<sup>11,14</sup> Indeed, the increase in the  $C_{sp^2}$ -H bond's stretching frequency of the nonconventional  $C_{sp^2}$ -H...O/S hydrogen bonds in the range of 81 – 96  $cm^{-1}$  was reported for the complexes of HCOOH with XCHZ (X= H, F, Cl, Br,  $CH_3$ ,  $NH_2$ ; Z= O, S).<sup>11</sup> Besides, a huge blue shift of the  $C_{sp^2}$ -H bond up to 104.5  $cm^{-1}$  was obtained in the FCOOH... $CH_3CHO$  complex.<sup>15</sup> The characteristics of nonconventional  $C_{sp^2}$ -H...Se/Te, and O-H...Se/Te hydrogen bonds were also investigated in some recent studies. For instance, the nonconventional  $C_{sp^2}$ -H...Se/Te and O-H...Se/Te hydrogen bonds were found by Cuc *et al* in XCHZ... $nH_2O$  (X= H, F, Cl, Br,  $CH_3$ ; Z= O, S, Se, Te; n = 1-3) and XCHO... $nH_2Z$  (X= H, F, Cl, Br,  $CH_3$ ; Z= O, S, Se, Te; n = 1-2) complexes.<sup>16,17</sup> It is interesting that these nonconventional hydrogen bonds are characterized by the red shifts. Likewise, Quyen *et al* had observed the red shifts of the  $C_{sp^2}$ -H...Se/Te hydrogen bonds in the dimer of chalcogenoaldehyde derivatives and complexes of XCHZ...RCZOH (X= H, F; R= H, F, Cl, Br,  $CH_3$ ,  $NH_2$ ; Z= O, S, Se, Te) recently.<sup>18,19</sup> These reports pave the way for more studies on the stability and nature of nonconventional hydrogen bonds with heavy chalcogen atoms

playing as proton acceptors. Specially, Mishra *et al* discovered the existence and red shifts of nonconventional N-H...Se and O-H...Se hydrogen bonds both experimentally and computationally in the interactions of indole...dimethyl selenide, and phenol...dimethyl selenide.<sup>20</sup> Therefore, it is necessary to investigate the hydrogen bonds containing chalcogen atoms in various complexes to provide fundamental knowledge to exploit their applications in other fields.

Remarkably, Trung *et al* suggested that the strength and characteristics of nonconventional C-H...Z hydrogen bonds involve the inherent properties of the C-H proton donor, and the Z proton acceptor. In particular, the C-H stretching frequency's shift of these nonconventional hydrogen bonds can be predicted thanks to polarity of the proton donors, and proton affinity of the proton acceptors.<sup>21–24</sup> This model has provided a quick sign to detect characteristics of the hydrogen bonds. These observations lead to an idea of studying the interaction and characteristics of conventional and nonconventional hydrogen bonds in complexes between  $NH_2CHZ$  and  $RCZOH$  with R= H, F,  $CH_3$ ; Z= O, S, Se, Te by using quantum computational approach in order to have a more obvious understanding of origin of nonconventional hydrogen bonds. In addition, the system is chosen for investigation because as mentioned above some chalcogenoaldehydes substituted by electron-donating group and carboxylic acids replaced by electron-withdrawing one cause a blue shift of C-H bond involving in the hydrogen bond. Furthermore, studying different R and Z substituents can help to clarify their impact on the inherent properties of proton donors and proton acceptors which could be considered as one of the reasons for the various characteristics of nonconventional hydrogen bonds. The strength and nature of nonconventional O-H...Se/Te, and  $C_{sp^2}$ -H...Z (Z= O, S, Se, Te) hydrogen bonds are also highlighted in the present work.

## 2. COMPUTATIONAL METHODS

The geometrical structures of the monomers and investigated complexes were optimized using the second-order perturbation theoretical method (MP2)<sup>25</sup> with the pseudopotential basis set aug-cc-pVDZ-PP for Te,<sup>26</sup> and full-electron Pople basis set 6-311++G(3df,2pd) for the other atoms through the Gaussian 16 program.<sup>27</sup> The infrared spectra for both complexes and monomers were then calculated at the same level of theory. Interaction energies of the complexes were computed as the following expression:

$$\Delta E^* = (E + \text{ZPE})_{\text{complex}} - \sum (E + \text{ZPE})_{\text{monomer}} + \text{BSSE}$$

In which the single-point energy of the complex and monomer ( $E$ ), and the basis set superposition error (BSSE) correction were calculated using couple cluster CCSD(T) method. The zero-point vibrational energies (ZPE) were obtained at the optimized geometries of the molecule. The deprotonation enthalpy (DPE) and the proton affinity (PA) were respectively computed for the proton donors  $C_{\text{sp}^2}/\text{O-H}$  and the proton acceptors  $Z$  in the monomers using CCSD(T) method in combination with the 6-311++G(3df,2pd) basis set, except the aug-cc-pVDZ-PP applied for the Te atom. These parameters will be used to evaluate polarity of the proton donors  $C_{\text{sp}^2}/\text{O-H}$  and proton affinity of the proton acceptors  $Z$  in the isolated monomers.

Moreover, the formation and strength of hydrogen bonds in complexes were determined by the AIMall program<sup>28,29</sup> using MP2 method with the aug-cc-pVDZ-PP basis set for Te atom, and the 6-311++G(3df,2pd) for the remaining atoms. This analysis showed the bond critical

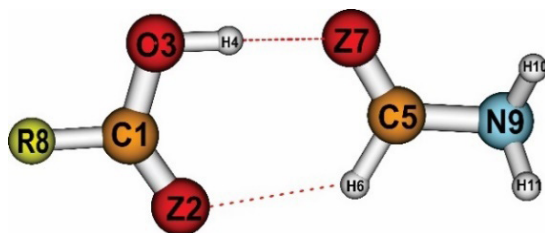
points (BCPs) which could explicitly prove the existence of hydrogen bonds. Some typical parameters at BCPs such as electron density  $\rho(r)$ , Laplacian electron density  $\nabla^2\rho(r)$ , and potential energy density  $V(r)$  were collected to evaluate for the strength of hydrogen bonds on the basis of the empirical formula:  $E_{\text{HB}} = 0.5V(r)$ ,<sup>30</sup> with  $E_{\text{HB}}$  being the energy of individual hydrogen bonds. Natural bond orbital (NBO) analysis<sup>31</sup> was also applied utilizing the same level of theory as for the AIM analysis. The NBO analysis provides data on intermolecular electron density transfer between two monomers, changes in electron density of a specific orbital and atomic charges.

## 3. RESULTS AND DISCUSSION

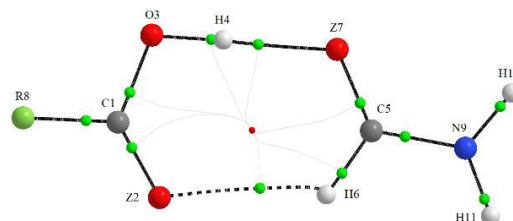
### 3.1. Geometrical structures and AIM analysis

Interaction of RCZOH with  $\text{NH}_2\text{CHZ}$  (with  $R = \text{H, F, CH}_3$ ;  $Z = \text{O, S, Se, Te}$ ) induces 48 stable complexes with the similar structures shown in Figure 1a. These structures are symbolized as **RZ2-Z7**, with  $R$  being  $\text{H, F, and CH}_3$ ; Z2 and Z7 being  $\text{O, S, Se, and Te}$  atoms in the RCZOH and  $\text{NH}_2\text{CHZ}$  monomers, respectively. All the complexes are stabilized by two intermolecular interactions  $\text{O-H}\cdots\text{Z7}$  and  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{Z2}$ . The topological features obtained from the AIM analysis point out the presence of bond critical points (BCPs) between  $\text{H}$  and  $\text{Z}$  atoms, and ring critical point (RCP) in complexes as displayed in Figure 1b. The intermolecular distances of  $\text{H}\cdots\text{O}$ ,  $\text{H}\cdots\text{S}$ ,  $\text{H}\cdots\text{Se}$ , and  $\text{H}\cdots\text{Te}$  contacts are smaller than their sum of Van der Waals radii, affirming the existence of the  $\text{O-H}\cdots\text{Z7}$  and  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{Z2}$  interactions and ring-shaped structures following the complexation.

(a)



(b)



**Figure 1.** (a) The stable geometrical structures and (b) their topological analysis of  $\text{RCZOH}\cdots\text{NH}_2\text{CHZ}$  complexes, with  $R = \text{H, F, CH}_3$ ;  $Z = \text{O, S, Se, Te}$ .

The data from AIM analysis in Tables S1a, and S1b of Supporting Information (SI) showed the values of electron density ( $\rho(r)$ ) and Laplacian of electron density ( $\nabla^2\rho(r)$ ) at the BCPs of the O-H $\cdots$ Z7 interactions being 0.022–0.068 au and 0.026–0.109 au, respectively. The  $\rho(r)$  and  $\nabla^2\rho(r)$  values for the C<sub>sp2</sub>-H $\cdots$ Z2 interactions are 0.009–0.017 au, and 0.021 – 0.063 au, respectively, which are smaller than those of the O-H $\cdots$ Z7 contacts. In general, these parameters belong to the range of the hydrogen bond formation.<sup>32</sup> Accordingly, the O-H $\cdots$ Z7, and C<sub>sp2</sub>-H $\cdots$ Z2 intermolecular interactions in the investigated complexes are tentatively assumed as hydrogen bonds, and the formers are much more stable than the latters. This is evidenced by the much more negative  $E_{HB}$  values of the O-H $\cdots$ Z7 hydrogen bonds (-16.0 to -101.3 kJ.mol<sup>-1</sup>) compared to the C<sub>sp2</sub>-H $\cdots$ Z2 ones (-5.3 to -16.4 kJ.mol<sup>-1</sup>) (cf. Tables S1a, and 1b). The negative values of the local electron energy density ( $H(r)$ ) at BCPs of the O-H $\cdots$ Z7 reflect their partially covalent character (cf. Table S1b). The larger strength of O-H $\cdots$ Z relative to C<sub>sp2</sub>-H $\cdots$ Z was also suggested in the RCZOH $\cdots$ CH<sub>3</sub>CHZ (R= H, F, CH<sub>3</sub>; Z= O, S)<sup>15</sup> and RCZOH $\cdots$ FCHZ (R= H, F, Cl, Br, CH<sub>3</sub>, NH<sub>2</sub>; Z= O, S, Se, Te) complexes.<sup>18</sup> The energies of the individual C<sub>sp2</sub>-H $\cdots$ O/S and O-H $\cdots$ O/S hydrogen bonds calculated at MP2/6-311++G(3df,2pd) in the RCZOH $\cdots$ CH<sub>3</sub>CHZ complexes were indeed in the ranges of -6.4 ÷ -13.5 kJ.mol<sup>-1</sup>, and -23.9 ÷ -71.8 kJ.mol<sup>-1</sup>, respectively.<sup>15</sup> This indicates that replacement of the CH<sub>3</sub> group in the CH<sub>3</sub>CHZ with a group that exerts a stronger electron-donating conjugation effect, such as NH<sub>2</sub>, induces an increase in the strength of the O/C<sub>sp2</sub>-H $\cdots$ Z hydrogen bonds.

For the nonconventional C<sub>sp2</sub>-H $\cdots$ Z2 hydrogen bonds, their strength decrease in the order of Z2 substituents O >> S > Se > Te upon fixing R and Z7 groups. This order agrees well with the less negative of  $E_{HB}$  when Z2 goes from O to S to Se and then to Te (cf. Table S1a). Indeed, the  $E_{HB}$  values of C<sub>sp2</sub>-H $\cdots$ S2/Se2/Te2 range from -5.3 to -9.7 kJ.mol<sup>-1</sup>, which are less negative than those of C<sub>sp2</sub>-H $\cdots$ O2 (from -11.2 to -16.4 kJ.mol<sup>-1</sup>). A similar observation was also obtained in the studies of Quyen *et al.*<sup>18</sup> and An *et al.*<sup>15</sup> This result emphasizes the importance of the oxygen compared to sulfur, selenium, and tellurium as Z2 in the stability of the nonconventional C<sub>sp2</sub>-H $\cdots$ Z2 hydrogen bonds. In contrast, for the same R and Z2, the strength of C<sub>sp2</sub>-H $\cdots$ Z2 tends to increase along with the shortening in intermolecular distance H $\cdots$ Z2 when Z7 turns from O via S via Se and then Te (cf. Figure S1a). The similar observation was found in the complexes of CYHNNH<sub>2</sub> with XH (Y= O, S, Se, Te; X= F, HO, NH<sub>2</sub>).<sup>12</sup> It is noteworthy that the DPE values of the C<sub>sp2</sub>-H bonds in the monomers decrease in the order NH<sub>2</sub>CHO > NH<sub>2</sub>CHS > NH<sub>2</sub>CHSe > NH<sub>2</sub>CHTe (cf. Table 1), implying the polarity of C<sub>sp2</sub>-H bonds in the NH<sub>2</sub>CHZ increase in the sequence of Z7 substituents O < S < Se < Te. Figure S1a also reflects the weakening of C<sub>sp2</sub>-H $\cdots$ Z2 hydrogen bonds in the order **CH<sub>3</sub>Z2-Z7** > **HZ2-Z7** > **FZ2-Z7** with Z2 and Z7 being O, S and Se, whereas the strength of C<sub>sp2</sub>-H $\cdots$ Te2 in the **HTe2-O7**, **FTe2-O7**, and **CH<sub>3</sub>Te2-O7** are almost similar. This comparison suggests that for the same Z2 and Z7, the stronger C<sub>sp2</sub>-H $\cdots$ Z2 hydrogen bonds are obtained for R being the electron-donating CH<sub>3</sub> substituent than the electron-withdrawing F one.

**Table 1.** Deprotonation enthalpy (DPE) of O/C<sub>sp2</sub>-H bond, and proton affinity at proton acceptors Z in NH<sub>2</sub>CHZ and RCZOH monomers with R= H, F, CH<sub>3</sub>; Z= O, S, Se, Te.

| Monomer               | PA(Z)<br>(kJ.mol <sup>-1</sup> ) | DPE(O/C-H)<br>(kJ.mol <sup>-1</sup> ) | Monomer              | PA(Z)<br>(kJ.mol <sup>-1</sup> ) | DPE(O/C-H)<br>(kJ.mol <sup>-1</sup> ) |
|-----------------------|----------------------------------|---------------------------------------|----------------------|----------------------------------|---------------------------------------|
| CH <sub>3</sub> COOH  | 823.7                            | 1495.1                                | FCOOH                | 736.9                            | 1406.9                                |
| CH <sub>3</sub> CSOH  | 840.6                            | 1433.0                                | FCSOH                | 780.8                            | 1351.6                                |
| CH <sub>3</sub> CSeOH | 840.0                            | 1406.0                                | FCSeOH               | 785.5                            | 1327.1                                |
| CH <sub>3</sub> CTeOH | 864.9                            | 1382.0                                | FTeOH                | 825.6                            | 1302.4                                |
| HCOOH                 | 780.1                            | 1480.4                                | NH <sub>2</sub> CHO  | 873.2                            | 1668.4                                |
| HCSOH                 | 805.8                            | 1421.4                                | NH <sub>2</sub> CHS  | 888.3                            | 1625.3                                |
| HCSeOH                | 806.2                            | 1396.5                                | NH <sub>2</sub> CHSe | 882.8                            | 1605.4                                |
| HCTeOH                | 839.0                            | 1374.2                                | NH <sub>2</sub> CHTe | 909.6                            | 1587.8                                |

Regarding the O-H...Z7 hydrogen bonds, for the same R and Z2, their strength decreases in the order of the Z7 groups: O > S > Se > Te. This result agrees with the observations of Biswal *et al*, and Das *et al* in previous reports.<sup>33,34</sup> The atomic charges at the Z7 atoms in the investigated complexes become less negative when Z7 goes from O to Te (*cf.* Table S2), leading to a descending in the electrostatic attraction of H4...Z7 in the sequence H4...O7 > H4...S7 > H4...Se7 > H4...Te7. This tendency is one of the reasons for the superior strength of O-H...O7 relative to O-H...S7/Se7/Te7. For the same R and Z7, the O-H...Z7 hydrogen bonds experience an enhancement in their strength when Z2 varies from O to S, to Se, and then to Te. This observation is consistent with the increase of O-H polarity in the order RCOOH < RCSOH < RCSeOH < RCTeOH (*cf.* Table 1). Thus, the polarity of O-H bonds and the strength of O-H...Z7 hydrogen bonds are affected by the Z7 atom in the RCZOH monomers, in which, Te7 is more influential than O7, S7 or Se7. Notably, the strength of O-H...Z7 goes down when R changes from F to H and then CH<sub>3</sub>, being opposite to the tendency observed for C<sub>sp2</sub>-H...Z2 hydrogen bonds (*cf.* Figures S1a, and S1b). This is reasonable because F surpasses CH<sub>3</sub> group in raising the polarity of O-H bonds (*cf.* Table 1) and the electrostatic attraction between H4 and Z7. Consequently, the electron-withdrawing substituent (F) induces stronger O-H...Z7 hydrogen bonds than the electron-donating

one (CH<sub>3</sub>). This effect was also reflected in the complexes of XCHZ...RCZOH (with X= H, F; R= H, F, Cl, Br, CH<sub>3</sub>, NH<sub>2</sub>; Z= O, Se, Se, Te).<sup>18</sup>

### 3.2. Interaction energy

The interaction energies corrected by both ZPE and BSSE (denoted by ΔE\*) of **RZ2-Z7** complexes are calculated at the CCSD(T)/6-311++G(3df,2pd)//MP26-311++G(3df,2pd) level of theory (except the aug-cc-pVDZ-PP basis set used for Te atom) to evaluate the stability of investigated complexes. The data in Table 2 shows the negative interaction energies of complexes ranging from -30.9 to -73.8 kJ.mol<sup>-1</sup>, indicating their certain stability on their potential energy surfaces.

For the same R and Z2, the individual interaction energies of **RZ2-O7**, **RZ2-S7**, **RZ2-Se7**, and **RZ2-Te7** are in the ranges -44.5 ÷ -73.8 kJ.mol<sup>-1</sup>, -34.8 ÷ -55.5 kJ.mol<sup>-1</sup>, -32.9 ÷ -55.8 kJ.mol<sup>-1</sup>, and -31.3 ÷ -47.0 kJ.mol<sup>-1</sup>, respectively. These values indicates that the stability of **RZ2-Z7** complexes decreases in the order of Z7 substituents: O > S > Se > Te, which is consistent with the lowering strength of O-H...Z7 in the sequence: O-H...O7 >> O-H...S7 > O-H...Se7 > O-H...Te7 as resulted from the AIM analysis. This observation emphasizes a predominant influence of the oxygen compared to sulfur, selenium, or tellurium as Z7 on the stability of **RZ2-Z7**. Besides, the superior role of the O-H...Z7 hydrogen bonds relative to C<sub>sp2</sub>-H...Z2 in stabilizing complexes is noticed.



**Table 2.** Interaction energies corrected by both ZPE and BSSE ( $\Delta E^*$ , kJ.mol<sup>-1</sup>) of complexes between NH<sub>2</sub>CHZ and RCZOH (R = H, F, CH<sub>3</sub>; Z = O, S, Se, Te) at CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) level of theory (except the aug-cc-pVDZ-PP basis set used for Te atom).

| Complex                | $\Delta E^*$ | Complex                | $\Delta E^*$ | Complex                 | $\Delta E^*$ | Complex                 | $\Delta E^*$ |
|------------------------|--------------|------------------------|--------------|-------------------------|--------------|-------------------------|--------------|
| CH <sub>3</sub> O2-O7  | -44.5        | CH <sub>3</sub> O2-S7  | -36.7        | CH <sub>3</sub> O2-Se7  | -35.3        | CH <sub>3</sub> O2-Te7  | -43.5        |
| CH <sub>3</sub> S2-O7  | -44.7        | CH <sub>3</sub> S2-S7  | -34.8        | CH <sub>3</sub> S2-Se7  | -32.9        | CH <sub>3</sub> S2-Te7  | -40.1        |
| CH <sub>3</sub> Se2-O7 | -46.3        | CH <sub>3</sub> Se2-S7 | -35.7        | CH <sub>3</sub> Se2-Se7 | -34.2        | CH <sub>3</sub> Se2-Te7 | -42.2        |
| CH <sub>3</sub> Te2-O7 | -55.3        | CH <sub>3</sub> Te2-S7 | -44.2        | CH <sub>3</sub> Te2-Se7 | -45.0        | CH <sub>3</sub> Te2-Te7 | -31.3        |
| HO2-O7                 | -46.3        | HO2-S7                 | -37.4        | HO2-Se7                 | -35.8        | HO2-Te7                 | -40.2        |
| HS2-O7                 | -47.6        | HS2-S7                 | -35.1        | HS2-Se7                 | -33.1        | HS2-Te7                 | -36.6        |
| HSe2-O7                | -47.2        | HSe2-S7                | -36.2        | HSe2-Se7                | -34.5        | HSe2-Te7                | -38.9        |
| HTe2-O7                | -55.2        | HTe2-S7                | -44.1        | HTe2-Se7                | -44.8        | HTe2-Te7                | -30.9        |
| FO2-O7                 | -58.9        | FO2-S7                 | -46.1        | FO2-Se7                 | -44.6        | FO2-Te7                 | -47.0        |
| FS2-O7                 | -60.0        | FS2-S7                 | -44.2        | FS2-Se7                 | -42.3        | FS2-Te7                 | -43.6        |
| FSe2-O7                | -63.2        | FSe2-S7                | -46.0        | FSe2-Se7                | -44.3        | FSe2-Te7                | -46.3        |
| FTe2-O7                | -73.8        | FTe2-S7                | -55.5        | FTe2-Se7                | -55.8        | FTe2-Te7                | -40.7        |

For the same R and Z7, the more negative interaction energies of **RZ2-O7**, **RZ2-S7**, and **RZ2-Se7** are observed for the Z2 being the Te atom rather than the O, S, and Se (*cf.* Table 2), in line with the decreasing strength of O-H...Z7 hydrogen bonds when Z2 goes from Te to O. However, an opposite trend is obtained for **RZ2-Te7** complexes, in which, **RO2-Te7** is more stable than **RSe2-Te7**, **RS2-Te7**, and **RTe2-Te7** (*cf.* Table 2).

Fixing Z2 and Z7, the interaction energies of **FZ2-Z7** are more negative than those of **HZ2-Z7** and **CH<sub>3</sub>Z2-Z7**. Indeed, the  $\Delta E^*$  values range from -40.7 to -73.8 kJ.mol<sup>-1</sup> for **FZ2-Z7**, from -30.9 to -55.2 kJ.mol<sup>-1</sup> for **HZ2-Z7**, and from -31.3 to -55.3 kJ.mol<sup>-1</sup> for **CH<sub>3</sub>Z2-Z7** (*cf.* Table 2). This implies that replacing R in the RCZOH with F can strengthen the stability of **RZ2-Z7** more than CH<sub>3</sub> which is also consistent with the larger strength of O-H...Z7 hydrogen bonds in **FZ2-Z7** compared to that of **CH<sub>3</sub>Z2-Z7**. Therefore, this observation affirms the crucial role of O-H...Z7 hydrogen bonds in the stability of the investigated complexes.

3.3. NBO analysis

To evaluate the electron density transfer between monomers upon the complexation, the NBO analysis is performed and the selected data are gathered in Tables 3a, and 3b. The total electron density transfer (EDT) of NH<sub>2</sub>CHZ monomers ranging from 0.036 to 0.091 indicates electron density transferring mainly from NH<sub>2</sub>CHZ to

RCZOH. This is proven by the intermolecular hyperconjugative energy ( $E_{inter}$ ) of electron transfer from nonbonding orbital n(Z7) to  $\sigma^*(O-H)$  antibonding orbital (*ca.* 85.3-252.0 kJ.mol<sup>-1</sup>) surpasses that from n(Z2) to  $\sigma^*(C_{sp^2}-H)$  (*ca.* 6.8-21.2 kJ.mol<sup>-1</sup>), confirming the larger strength of O-H...Z7 compared to that of  $C_{sp^2}-H...Z2$  hydrogen bonds.

For the same R and Z7, the  $E_{inter}$  values of the electron density transfer from n(Z2) to  $\sigma^*(C_{sp^2}-H)$  increase in the order of the Z2 substituents: O < S < Se < Te (*cf.* Tables 3a, and 3b), which is in a consistent with the enhancement of proton affinity at Z2 in the order RCOOH < RCOSeOH < RCTeOH (*cf.* Table 1). This order is opposite to the strength tendency of  $C_{sp^2}-H...Z2$  hydrogen bonds. Therefore, the higher strength of  $C_{sp^2}-H...O2$  compared to  $C_{sp^2}-H...S2/Se2/Te2$  hydrogen bonds is primarily determined by the electrostatic attraction rather than the intermolecular electron density transfer. The outstanding contribution of electrostatic attraction compared to the intermolecular electron density transfer on the strength of  $C_{sp^2}-H...Z$  hydrogen bonds was also pointed out in the XCHZ...RCZOH complexes (with X=H, F; R=H, F, Cl, Br, CH<sub>3</sub>, NH<sub>2</sub>; Z=O, S, Se, Te) by Quyen *et al.*<sup>18</sup> When fixing R and Z2, the  $E_{inter}$  values of the nonconventional  $C_{sp^2}-H...Z2$  hydrogen bonds go up as Z7 varies from O to Te, which is in line with the strength of  $C_{sp^2}-H...Z2$  hydrogen bonds.



**Table 3a.** Data from NBO analysis of **RZ2-Z7** complexes with R= H, F, CH<sub>3</sub>; Z= O, S.

| Complex                     | Hydrogen bond | EDT <sup>(a)</sup><br>(Electron) | E <sub>inter</sub><br>(kJ.mol <sup>-1</sup> ) | ΔE <sub>intra</sub> <sup>(b)</sup><br>(kJ.mol <sup>-1</sup> ) | Δσ <sup>*</sup> (C <sub>sp2</sub> /O-H)<br>(Electron) | Δ% <i>s</i> (C <sub>sp2</sub> ) |
|-----------------------------|---------------|----------------------------------|-----------------------------------------------|---------------------------------------------------------------|-------------------------------------------------------|---------------------------------|
| <b>CH<sub>3</sub>O2-O7</b>  | C5-H6...O2    | 0.036                            | 8.3                                           | -34.9                                                         | -0.0106                                               | 1.4                             |
|                             | O3-H4...O7    |                                  | 126.4                                         | 1.2                                                           | 0.0388                                                | 4.8                             |
| <b>CH<sub>3</sub>S2-O7</b>  | C5-H6...S2    | 0.037                            | 12.3                                          | -33.0                                                         | -0.0062                                               | 1.3                             |
|                             | O3-H4...O7    |                                  | 145.9                                         | 2.1                                                           | 0.0418                                                | 5.2                             |
| <b>CH<sub>3</sub>Se2-O7</b> | C5-H6...Se2   | 0.039                            | 13.5                                          | -34.4                                                         | -0.0059                                               | 1.3                             |
|                             | O3-H4...O7    |                                  | 157.0                                         | 0.3                                                           | 0.0441                                                | 5.3                             |
| <b>CH<sub>3</sub>Te2-O7</b> | C5-H6...Te2   | 0.040                            | 15.7                                          | -34.9                                                         | -0.0047                                               | 1.3                             |
|                             | O3-H4...O7    |                                  | 162.9                                         | 0.3                                                           | 0.0447                                                | 5.5                             |
| <b>HO2-O7</b>               | C5-H6...O2    | 0.039                            | 8.3                                           | -35.5                                                         | -0.0106                                               | 1.4                             |
|                             | O3-H4...O7    |                                  | 140.3                                         | 0.0                                                           | 0.0416                                                | 4.9                             |
| <b>HS2-O7</b>               | C5-H6...S2    | 0.039                            | 12.4                                          | -33.6                                                         | -0.0060                                               | 1.3                             |
|                             | O3-H4...O7    |                                  | 156.0                                         | -1.3                                                          | 0.0434                                                | 5.4                             |
| <b>HSe2-O7</b>              | C5-H6...Se2   | 0.041                            | 13.7                                          | -34.9                                                         | -0.0056                                               | 1.3                             |
|                             | O3-H4...O7    |                                  | 166.4                                         | -1.5                                                          | 0.0455                                                | 5.6                             |
| <b>HTe2-O7</b>              | C5-H6...Te2   | 0.040                            | 15.9                                          | -34.9                                                         | -0.0042                                               | 1.3                             |
|                             | O3-H4...O7    |                                  | 170.7                                         | -1.3                                                          | 0.0450                                                | 5.7                             |
| <b>FO2-O7</b>               | C5-H6...O2    | 0.052                            | 6.8                                           | -39.4                                                         | -0.0126                                               | 1.3                             |
|                             | O3-H4...O7    |                                  | 184.9                                         | 6.5                                                           | 0.0540                                                | 5.0                             |
| <b>FS2-O7</b>               | C5-H6...S2    | 0.055                            | 11.5                                          | -39.3                                                         | -0.0090                                               | 1.3                             |
|                             | O3-H4...O7    |                                  | 211.6                                         | -1.6                                                          | 0.0602                                                | 5.3                             |
| <b>FSe2-O7</b>              | C5-H6...Se2   | 0.059                            | 13.4                                          | -41.6                                                         | -0.0086                                               | 1.4                             |
|                             | O3-H4...O7    |                                  | 231.5                                         | 0.6                                                           | 0.0649                                                | 5.5                             |
| <b>FTe2-O7</b>              | C5-H6...Te2   | 0.061                            | 16.9                                          | -43.1                                                         | -0.0072                                               | 1.5                             |
|                             | O3-H4...O7    |                                  | 252.0                                         | -1.5                                                          | 0.0686                                                | 5.6                             |
| <b>CH<sub>3</sub>O2-S7</b>  | C5-H6...O2    | 0.049                            | 14.8                                          | -19.4                                                         | -0.0050                                               | 1.8                             |
|                             | O3-H4...S7    |                                  | 112.9                                         | 4.4                                                           | 0.0534                                                | 4.7                             |
| <b>CH<sub>3</sub>S2-S7</b>  | C5-H6...S2    | 0.051                            | 18.3                                          | -16.1                                                         | 0.0010                                                | 1.7                             |
|                             | O3-H4...S7    |                                  | 132.9                                         | 12.9                                                          | 0.0604                                                | 5.1                             |
| <b>CH<sub>3</sub>Se2-S7</b> | C5-H6...Se2   | 0.055                            | 19.3                                          | -16.3                                                         | 0.0016                                                | 1.7                             |
|                             | O3-H4...S7    |                                  | 143.3                                         | 8.6                                                           | 0.0642                                                | 5.3                             |
| <b>CH<sub>3</sub>Te2-S7</b> | C5-H6...Te2   | 0.057                            | 21.2                                          | -15.6                                                         | 0.0030                                                | 1.7                             |
|                             | O3-H4...S7    |                                  | 148.5                                         | 9.3                                                           | 0.0657                                                | 5.5                             |
| <b>HO2-S7</b>               | C5-H6...O2    | 0.055                            | 14.5                                          | -19.2                                                         | -0.0049                                               | 1.7                             |
|                             | O3-H4...S7    |                                  | 125.2                                         | 3.4                                                           | 0.0583                                                | 4.9                             |
| <b>HS2-S7</b>               | C5-H6...S2    | 0.055                            | 18.2                                          | -16.1                                                         | 0.0013                                                | 1.6                             |
|                             | O3-H4...S7    |                                  | 143.5                                         | 10.0                                                          | 0.0641                                                | 5.4                             |
| <b>HSe2-S7</b>              | C5-H6...Se2   | 0.059                            | 19.3                                          | -16.3                                                         | 0.0020                                                | 1.7                             |
|                             | O3-H4...S7    |                                  | 153.6                                         | 8.1                                                           | 0.0678                                                | 5.6                             |
| <b>HTe2-S7</b>              | C5-H6...Te2   | 0.059                            | 21.1                                          | -15.5                                                         | 0.0035                                                | 1.7                             |
|                             | O3-H4...S7    |                                  | 156.2                                         | 8.1                                                           | 0.0681                                                | 5.8                             |
| <b>FO2-S7</b>               | C5-H6...O2    | 0.075                            | 11.7                                          | -20.2                                                         | -0.0070                                               | 1.7                             |
|                             | O3-H4...S7    |                                  | 165.1                                         | -0.2                                                          | 0.0754                                                | 5.4                             |
| <b>FS2-S7</b>               | C5-H6...S2    | 0.078                            | 15.9                                          | -17.8                                                         | -0.0019                                               | 1.6                             |
|                             | O3-H4...S7    |                                  | 186.8                                         | 6.1                                                           | 0.0840                                                | 5.8                             |
| <b>FSe2-S7</b>              | C5-H6...Se2   | 0.083                            | 17.5                                          | -18.3                                                         | -0.0011                                               | 1.7                             |
|                             | O3-H4...S7    |                                  | 200.7                                         | 9.0                                                           | 0.0898                                                | 6.0                             |
| <b>FTe2-S7</b>              | C5-H6...Te2   | 0.086                            | 20.7                                          | -18.1                                                         | 0.0006                                                | 1.8                             |
|                             | O3-H4...S7    |                                  | 210.3                                         | 7.2                                                           | 0.0936                                                | 6.1                             |

(a) The total electron density transfer from NH<sub>2</sub>CHZ to RCZOH  
(b) The total intramolecular electron density transfer to the σ<sup>\*</sup>(C<sub>sp2</sub>/O-H) orbitals

Table 3b. Data from NBO analysis of **RZ2-R7** complexes, with R= H, F, CH<sub>3</sub>; Z= Se, Te.

| Complex                 | Hydrogen bond | EDT <sup>(a)</sup><br>(Electron) | E <sub>inter</sub><br>(kJ.mol <sup>-1</sup> ) | ΔE <sub>intra</sub> <sup>(b)</sup><br>(kJ.mol <sup>-1</sup> ) | Δσ <sup>*</sup> (C <sub>sp<sup>2</sup></sub> /O-H)<br>(Electron) | Δ% <i>s</i> (C <sub>sp<sup>2</sup></sub> ) |
|-------------------------|---------------|----------------------------------|-----------------------------------------------|---------------------------------------------------------------|------------------------------------------------------------------|--------------------------------------------|
| CH <sub>3</sub> O2-Se7  | C5-H6...O2    | 0.044                            | 15.1                                          | -16.3                                                         | -0.0031                                                          | 1.8                                        |
|                         | O3-H4...Se7   |                                  | 98.1                                          | 4.9                                                           | 0.0494                                                           | 4.4                                        |
| CH <sub>3</sub> S2-Se7  | C5-H6...S2    | 0.048                            | 17.7                                          | -12.8                                                         | 0.0026                                                           | 1.7                                        |
|                         | O3-H4...Se7   |                                  | 119.2                                         | 11.5                                                          | 0.0574                                                           | 5.0                                        |
| CH <sub>3</sub> Se2-Se7 | C5-H6...Se2   | 0.052                            | 18.5                                          | -12.7                                                         | 0.0032                                                           | 1.7                                        |
|                         | O3-H4...Se7   |                                  | 129.3                                         | 12.7                                                          | 0.0617                                                           | 5.2                                        |
| CH <sub>3</sub> Te2-Se7 | C5-H6...Te2   | 0.060                            | 20.5                                          | -10.8                                                         | 0.0051                                                           | 1.7                                        |
|                         | O3-H4...Se7   |                                  | 149.1                                         | 12.9                                                          | 0.0692                                                           | 5.6                                        |
| HO2-Se7                 | C5-H6...O2    | 0.051                            | 14.7                                          | -16.1                                                         | -0.0031                                                          | 1.7                                        |
|                         | O3-H4...Se7   |                                  | 110.0                                         | 6.3                                                           | 0.0546                                                           | 4.7                                        |
| HS2-Se7                 | C5-H6...S2    | 0.052                            | 17.5                                          | -12.8                                                         | 0.0028                                                           | 1.7                                        |
|                         | O3-H4...Se7   |                                  | 129.4                                         | 11.5                                                          | 0.0616                                                           | 5.3                                        |
| HSe2-Se7                | C5-H6...Se2   | 0.057                            | 18.3                                          | -12.8                                                         | 0.0035                                                           | 1.7                                        |
|                         | O3-H4...Se7   |                                  | 139.0                                         | 11.7                                                          | 0.0655                                                           | 5.5                                        |
| HTe2-Se7                | C5-H6...Te2   | 0.063                            | 20.4                                          | -10.6                                                         | 0.0055                                                           | 1.7                                        |
|                         | O3-H4...Se7   |                                  | 155.9                                         | 9.5                                                           | 0.0716                                                           | 5.9                                        |
| FO2-Se7                 | C5-H6...O2    | 0.072                            | 11.6                                          | -16.7                                                         | -0.0050                                                          | 1.7                                        |
|                         | O3-H4...Se7   |                                  | 146.4                                         | 0.3                                                           | 0.0717                                                           | 5.3                                        |
| FS2-Se7                 | C5-H6...S2    | 0.076                            | 14.9                                          | -13.8                                                         | -0.0001                                                          | 1.6                                        |
|                         | O3-H4...Se7   |                                  | 168.6                                         | 6.8                                                           | 0.0810                                                           | 5.7                                        |
| FSe2-Se7                | C5-H6...Se2   | 0.081                            | 16.4                                          | -14.1                                                         | 0.0007                                                           | 1.7                                        |
|                         | O3-H4...Se7   |                                  | 181.9                                         | 9.9                                                           | 0.0872                                                           | 6.0                                        |
| FTe2-Se7                | C5-H6...Te2   | 0.090                            | 19.6                                          | -12.6                                                         | 0.0029                                                           | 2.1                                        |
|                         | O3-H4...Se7   |                                  | 207.4                                         | 8.4                                                           | 0.0976                                                           | 6.3                                        |
| CH <sub>3</sub> O2-Te7  | C5-H6...O2    | 0.040                            | 14.6                                          | -12.0                                                         | -0.0018                                                          | 1.8                                        |
|                         | O3-H4...Te7   |                                  | 85.3                                          | 5.9                                                           | 0.0459                                                           | 4.1                                        |
| CH <sub>3</sub> S2-Te7  | C5-H6...S2    | 0.047                            | 16.2                                          | -8.8                                                          | 0.0035                                                           | 1.7                                        |
|                         | O3-H4...Te7   |                                  | 110.3                                         | 16.4                                                          | 0.0572                                                           | 4.7                                        |
| CH <sub>3</sub> Se2-Te7 | C5-H6...Se2   | 0.053                            | 18.4                                          | -8.7                                                          | 0.0048                                                           | 1.8                                        |
|                         | O3-H4...Te7   |                                  | 123.1                                         | 15.8                                                          | 0.0637                                                           | 5.1                                        |
| CH <sub>3</sub> Te2-Te7 | C5-H6...Te2   | 0.058                            | 18.1                                          | -7.5                                                          | 0.0054                                                           | 1.8                                        |
|                         | O3-H4...Te7   |                                  | 130.1                                         | 15.9                                                          | 0.0667                                                           | 5.3                                        |
| HO2-Te7                 | C5-H6...O2    | 0.047                            | 14.0                                          | -11.7                                                         | -0.0018                                                          | 1.7                                        |
|                         | O3-H4...Te7   |                                  | 96.1                                          | 7.8                                                           | 0.0516                                                           | 4.4                                        |
| HS2-Te7                 | C5-H6...S2    | 0.052                            | 15.7                                          | -13.2                                                         | 0.0036                                                           | 1.7                                        |
|                         | O3-H4...Te7   |                                  | 118.6                                         | 11.2                                                          | 0.0614                                                           | 5.1                                        |
| HSe2-Te7                | C5-H6...Se2   | 0.057                            | 18.0                                          | -8.7                                                          | 0.0049                                                           | 1.8                                        |
|                         | O3-H4...Te7   |                                  | 131.7                                         | 15.2                                                          | 0.0680                                                           | 5.4                                        |
| HTe2-Te7                | C5-H6...Te2   | 0.060                            | 17.7                                          | -7.5                                                          | 0.0056                                                           | 1.7                                        |
|                         | O3-H4...Te7   |                                  | 136.0                                         | 14.9                                                          | 0.0695                                                           | 5.6                                        |
| FO2-Te7                 | C5-H6...O2    | 0.071                            | 10.7                                          | -11.7                                                         | -0.0036                                                          | 1.6                                        |
|                         | O3-H4...Te7   |                                  | 132.1                                         | 5.4                                                           | 0.0704                                                           | 5.1                                        |
| FS2-Te7                 | C5-H6...S2    | 0.079                            | 13.1                                          | -9.0                                                          | 0.0010                                                           | 1.6                                        |
|                         | O3-H4...Te7   |                                  | 158.3                                         | 10.9                                                          | 0.0832                                                           | 5.7                                        |
| FSe2-Te7                | C5-H6...Se2   | 0.086                            | 15.7                                          | -9.2                                                          | 0.0023                                                           | 1.7                                        |
|                         | O3-H4...Te7   |                                  | 173.8                                         | 16.6                                                          | 0.0917                                                           | 6.0                                        |
| FTe2-Te7                | C5-H6...Te2   | 0.091                            | 16.6                                          | -8.3                                                          | 0.0033                                                           | 1.8                                        |
|                         | O3-H4...Te7   |                                  | 183.6                                         | 14.6                                                          | 0.0969                                                           | 6.3                                        |

(a) The total electron density transfer from NH<sub>2</sub>CHZ to RCZOH

(b) The total intramolecular electron density transfer to the σ<sup>\*</sup>(C<sub>sp<sup>2</sup></sub>/O-H) orbitals

Remarkably, Tables 3a, and 3b also figure out that the change in the electron density of the  $\sigma^*(C_{sp^2}-H)$  antibonding orbital ( $\Delta\sigma^*(C_{sp^2}-H)$ ) become less negative as Z7 goes from O to S to Se and then Te. Therein, the decrease in the electron density at the  $\sigma^*(C_{sp^2}-H)$  hits bottom when Z7 is O atom, which is explained by the intramolecular hyperconjugative energy ( $E_{intra}$ ) from  $n(O7)$  to  $\sigma^*(C_{sp^2}-H)$  overcoming the intermolecular hyperconjugative energy of electron density transfer from  $n(O2)$  to  $\sigma^*(C_{sp^2}-H)$ , resulting in a rearrangement of electron density throughout **RO2-O7**. Therefore, an increase in occupation of  $\sigma^*(C_{sp^2}-H)$  orbital causes a lengthening of the  $C_{sp^2}-H$  bond length and a decrease their stretching frequencies upon complexation. In other words, the stretching frequency of  $C_{sp^2}-H$  in the nonconventional  $C_{sp^2}-H\cdots Z2$  hydrogen bonds tends to turn from blue shift to red shift as Z7 changes from O to Te. For the same Z2 and Z7, the intermolecular transfer of electron density from  $n(Z2)$  to  $\sigma^*(C_{sp^2}-H)$  orbital witnesses an increase according to the substitution of R as the following order:  $F < H < CH_3$ . This is consistent with the increase in the proton affinity at Z2 in RCZOH in the order of R:  $F < H < CH_3$  (cf. Table 1). This implies that the intermolecular electron density transfer from  $n(Z2)$  to  $\sigma^*(C_{sp^2}-H)$  orbital can be promoted when R varies from an electron-withdrawing group (F) to an electron-donating one ( $CH_3$ ). When Z2 and Z7 are fixed, the lessening in occupation at  $\sigma^*(C_{sp^2}-H)$  becomes more pronounced as R changes from H to  $CH_3$  and then F (cf. Tables 3a, and 3b). This trend suggests that the characteristic of the nonconventional  $C_{sp^2}-H\cdots Z2$  hydrogen bonds shifts gradually from red shift to blue shift when R transitions from an electron-donating group to an electron-withdrawing one.

Regarding the  $O-H\cdots Z7$  hydrogen bonds, there is an increase in the intermolecular electron density transfer from  $n(Z7)$  to  $\sigma^*(O-H)$  orbitals when Z2 is replaced by O, S, Se, and Te, respectively. In contrast, for the same R and Z2, the  $E_{inter}$  values of  $O-H\cdots Z7$  hydrogen bonds

decrease in the sequence of Z7 substituents:  $O > S > Se > Te$ . These results agree with the strength tendency of  $O-H\cdots Z7$  as found in AIM analysis. Thus, the intermolecular electron density transfer also affects the strength of  $O-H\cdots Z7$ .

It is noted that that the increase in the electron density at  $\sigma^*(O-H)$  in complexes compared to the corresponding monomers ( $\Delta\sigma^*(O-H)$ ) (ca. 0.0388-0.0969 e) lengthens the O-H bond length and decreases its stretching frequency, which can induce the red shift of  $O-H\cdots Z7$  hydrogen bonds. For the same Z2 and Z7, the changing of R from  $CH_3$  via H via F results in an improvement in the electron density transfer from  $n(Z7)$  to the  $\sigma^*(O-H)$  orbitals, and an increase in the  $\Delta\sigma^*(O-H)$  values (cf. Tables 3a, and 3b). Therefore, the larger strength and red shift of  $O-H\cdots Z7$  hydrogen bonds are gained for R being the electron-withdrawing group (F).

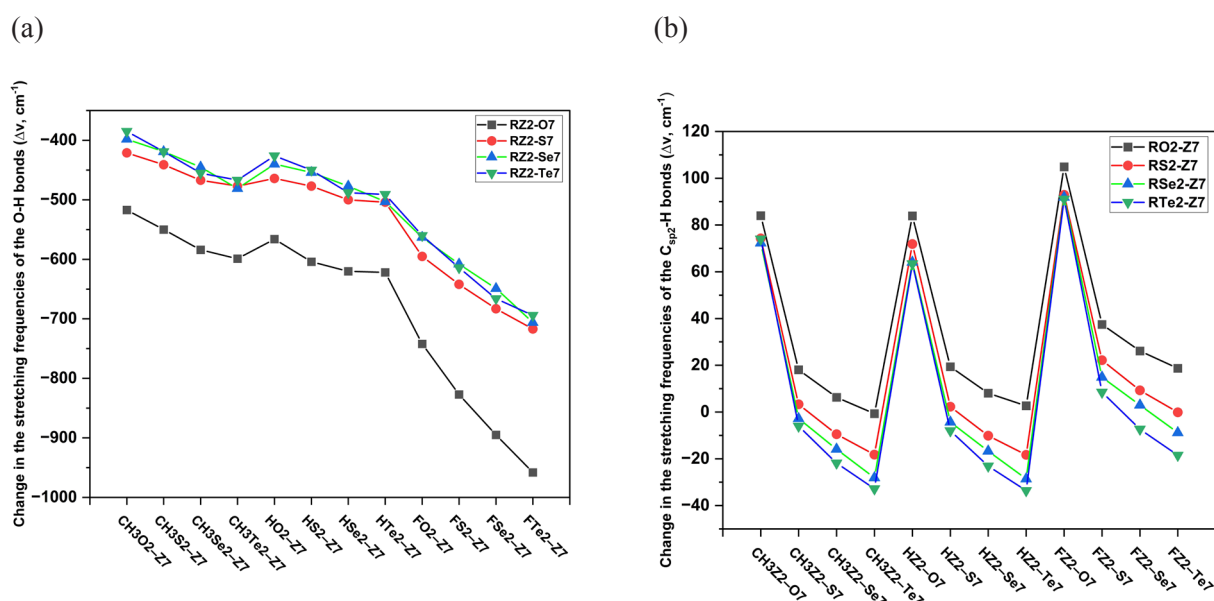
### 3.4. Changes in bond length and stretching frequency of the O-H and $C_{sp^2}-H$

The change in the bond length ( $\Delta r$ ) and stretching frequency ( $\Delta\nu$ ) of the O-H and  $C_{sp^2}-H$  bonds in the **RZ2-Z7** complexes compared to the corresponding monomers are collected in Tables S3a, and S3b and Figures 2a, and 2b.

The results show the elongation of the O-H bond length and the decrease of its stretching frequency in  $O-H\cdots Z7$  hydrogen bonds following the complexation. Indeed,  $\Delta r(O-H)$  and  $\Delta\nu(O-H)$  values range from 0.0180 to 0.0482 Å, and from -385.0 to -958.0  $cm^{-1}$ , respectively. This validates the red shift of  $O-H\cdots Z7$  hydrogen bonds as predicted in the NBO analysis above. For the same R and Z2,  $\Delta\nu(O-H)$  values in the **RZ2-O7** are more negative than those in the **RZ2-S7**, **RZ2-Se7**, and **RZ2-Te7** (cf. Figure 2a), implying a larger red shift of  $O-H\cdots O7$  hydrogen bonds compared to  $O-H\cdots S/Se/Te$  ones. This is in line with the larger intermolecular electron density transfer from  $n(O7)$  to  $\sigma^*(O-H)$  than from  $n(S7/Se7/Te7)$  to  $\sigma^*(O-H)$  orbitals (cf. Tables 3a, and 3b).

This observation, however, differs from the result collected in the complexes of RCZOH with FCHZ. Therein, the O-H red shift of O-H...O hydrogen bonds in the FCHO...RCOOH was less than that of O-H...S hydrogen bonds in the FCHS...RCOOH.<sup>18</sup> Besides, the O-H red shift increases significantly as the F atom in FCHZ monomer is substituted by the NH<sub>2</sub> group. This is due to a strong electron-donating group such as NH<sub>2</sub> surging the electron density at the Z sites in NH<sub>2</sub>CHZ. As a result, the Z sites in NH<sub>2</sub>CHZ exhibit a higher proton affinity compared to those in FCHZ, and the intermolecular electron density transfers from n(Z) to  $\sigma^*(\text{O-H})$  orbital in the RCZOH...NH<sub>2</sub>CHZ are larger than those in the RCZOH...FCHZ. Notably, the red shift of O-H...Z hydrogen bonds in the RCZOH...NH<sub>2</sub>CHZ complexes is even more significant than that in the RCZOH...CH<sub>3</sub>CHZ.<sup>15</sup> This substantially large shift affirms the outstanding influence of a strong electron-donating substituent (NH<sub>2</sub>) in NH<sub>2</sub>CHZ on the O-H red shift. Figure 2a points out that for the same R and Z7, the O-H red shift in investigated complexes increases in the order of Z2: O < S < Se < Te. This agrees well with

the rise in the occupation at the  $\sigma^*(\text{O-H})$  orbitals (*cf.* Tables 3a, and 3b) and the polarity of O-H bond in RCZOH (*cf.* Table 1) when Z2 shifts from O to S to Se and then Te. In the case of fixing Z2 and Z7, the red shift of O-H...Z7 hydrogen bonds witness a decline in the sequence **FZ2-Z7** > **HZ2-Z7** > **CH<sub>3</sub>Z2-Z7** (*cf.* Figure 2a), being consistent with the decrease in the  $E_{\text{inter}}$  values of O-H...Z7 hydrogen bonds when R changes from F to CH<sub>3</sub> (*cf.* Tables 3a, and 3b). This trend emphasizes the more dominant role of the electron-withdrawing group (F) relative to the electron-donating one (CH<sub>3</sub>) in promoting the O-H red shift. Such observation was once determined in the interaction between XCHZ and YCOOH, where X= H, CH<sub>3</sub>, NH<sub>2</sub>, and Y= H, F, Cl, Br, CH<sub>3</sub>, NH<sub>2</sub> calculated at the same level of theory.<sup>24</sup> The polarity of the O-H bonds in FCZOH is also better than that in HCZOH and CH<sub>3</sub>CZOH (*cf.* Table 1). Accordingly, the red shift of O-H...Z7 hydrogen bonds is closely related to the increase in the polarity of the O-H bond in the RCZOH monomers, and the strong intermolecular electron density transfer from n(Z7) to  $\sigma^*(\text{O-H})$  orbitals upon complexation.



**Figure 2.** (a) Change in the stretching frequency of the O-H bond in the **RZ2-Z7** complexes compared to the RCZOH monomers, with R= H, F, CH<sub>3</sub>; Z (Z2, Z7) = O, S, Se, Te. (b) Change in the stretching frequency of the C<sub>sp2</sub>-H in the **RZ2-Z7** complexes compared to the NH<sub>2</sub>CHZ monomers, with R= H, F, CH<sub>3</sub>; Z (Z2, Z7)= O, S, Se, Te.

On the other hand, Figure 2b shows that for the same R and Z7, the stretching frequency of  $C_{sp^2}$ -H involving nonconventional  $C_{sp^2}$ -H $\cdots$ O2 hydrogen bonds increases during the formation of **RO2-Z7** complexes ( $\Delta\nu(C_{sp^2}\text{-H}) = 2.7 - 104.9$   $\text{cm}^{-1}$ ), indicating the  $C_{sp^2}$ -H blue shift in  $C_{sp^2}$ -H $\cdots$ O2 hydrogen bonds. This blue shift can be attributed to a reduction of the electron density at the  $\sigma^*(C_{sp^2}\text{-H})$  orbital following the **RO2-Z7** complexation (*cf.* Tables 3a, and 3b) that leads to a contraction in the bond length and an increase in the stretching frequency of the  $C_{sp^2}$ -H bond in the  $C_{sp^2}$ -H $\cdots$ O2. When Z2 is replaced with S, Se, and Te, the  $C_{sp^2}$ -H stretching frequencies in  $C_{sp^2}$ -H $\cdots$ S2/Se2/Te2 hydrogen bonds in most complexes tend to be red-shifted, except for **RS2-O7**, **RS2-S7**, **RSe2-O7**, **RSe2-S7**, **RTe2-O7**, and **RTe2-S7**. Therefore, the  $C_{sp^2}$ -H stretching frequencies of  $C_{sp^2}$ -H $\cdots$ Z2 hydrogen bonds turn from blue- to red shift as Z2 varies from O to S to Se and then Te. This tendency is proportional to the enhancement of the proton affinity at Z2 in the order  $O < S < Se < Te$  (*cf.* Table 1). For the same R and Z2, there is a growth in the  $C_{sp^2}$ -H red shift upon the substitution of Z7 from O to Te which accords with the rise in the  $C_{sp^2}$ -H polarity of the  $\text{NH}_2\text{CHZ}$  monomers in the order  $\text{NH}_2\text{CHO} < \text{NH}_2\text{CHS} < \text{NH}_2\text{CHSe} < \text{NH}_2\text{CHTe}$  (*cf.* Table 1). Therefore, the  $C_{sp^2}$ -H red shift in  $C_{sp^2}$ -H $\cdots$ Z2 is closely related to the increase in the proton affinity at the Z sites and the polarity of the  $C_{sp^2}$ -H donor fragment. This observation was also suggested in some previous reports.<sup>15,16,19,24</sup> When fixing Z2 and Z7, the magnitude of the  $C_{sp^2}$ -H blue shift in  $C_{sp^2}$ -H $\cdots$ O2 significantly increases in the order of the R substituents:  $\text{CH}_3 < \text{H} < \text{F}$ , corresponding to the decrease in the proton affinity at Z site according to the trend above. Hence, the blue shift of  $C_{sp^2}$ -H bond can be observed along with the decline in the proton affinity at the proton acceptor Z. In comparison with the complexes of the RCZOH with the  $\text{CH}_3/\text{FCHZ}$ , the blue shift of  $C_{sp^2}$ -H $\cdots$ O is presented more obvious when an electron-donating atom (F) or a weaker electron-donating group ( $\text{CH}_3$ ) in the chalcogenoaldehyde derivatives is replaced with a strong electron-

donating substituent ( $\text{NH}_2$ ).<sup>15,18</sup> This trend relates to the decrease in the polarity of the  $C_{sp^2}$ -H bonds in the order of chalcogenoaldehyde derivatives:  $\text{FCHZ} > \text{CH}_3\text{CHZ} > \text{NH}_2\text{CHZ}$ . Besides, the  $C_{sp^2}$ -H stretching-frequencies in  $C_{sp^2}$ -H $\cdots$ S2/Se2/Te2 hydrogen bonds turn from red shift to blue shift when R changes from H to  $\text{CH}_3$  and then F. This observation suggests that the electron-donating group can urge forward the red shift of  $C_{sp^2}$ -H $\cdots$ Z hydrogen bonds more than the electron-withdrawing one.

#### 4. CONCLUSIONS

There are 48 stable complexes formed between RCZOH and  $\text{NH}_2\text{CHZ}$  (**RZ2-Z7**) (with  $\text{R} = \text{H}$ , F,  $\text{CH}_3$ ;  $\text{Z} = \text{O}$ , S, Se, Te) whose structures are stabilized by  $\text{O-H}\cdots\text{Z7}$  and  $C_{sp^2}\text{-H}\cdots\text{Z2}$  hydrogen bonds, in which the formers play a predominant role in the stability of the complexes. The increase in the stability of **RZ2-Z7** is observed when R changes from the electron-donating  $\text{CH}_3$  group to the electron-withdrawing F one, and Z2 turns from O to Te. For Z7 being O, S, and Se, **RTe2-Z7** is higher in stability than **RS2-Z7**, **RSe2-Z7**, and **RO2-Z7** while the **RO2-Te7** is more stable than the **RSe2-Te7**, **RS2-Te7**, and **RTe2-Te7**.

The strength of  $\text{O-H}\cdots\text{Z7}$  hydrogen bonds (*ca.*  $-16.0 \div -101.3$   $\text{kJ}\cdot\text{mol}^{-1}$ ) is larger than those of  $C_{sp^2}\text{-H}\cdots\text{Z2}$  ones (*ca.*  $-5.3 \div -16.4$   $\text{kJ}\cdot\text{mol}^{-1}$ ). The O-H stretching frequencies in the  $\text{O-H}\cdots\text{Z7}$  are characterised by the red shift. The strength and the red shift of  $\text{O-H}\cdots\text{Z7}$  decrease in the order of Z7 substituents:  $\text{O} > \text{S} > \text{Se} > \text{Te}$ . In contrast, the change of Z2 from O to Te, and R from  $\text{CH}_3$  to F leads to an increase in the O-H red shift. Remarkably, the O-H red shift agrees well with the rise in the O-H polarity, and the proton affinity at the proton acceptors Z. The very strong intermolecular transfer of electron density from  $n(\text{Z7})$  to  $\sigma^*(\text{O-H})$  orbitals also contributes significantly to the strength and the red shift of  $\text{O-H}\cdots\text{Z7}$  hydrogen bonds.

The nonconventional  $C_{sp^2}\text{-H}\cdots\text{Z2}$  hydrogen bonds experience a decrease in their stability as Z2 in RCZOH goes from O to Te, and R changes



from CH<sub>3</sub> to F. The substitution of the O atom in NH<sub>2</sub>CHZ with S, Se, and Te results in the larger strength of C<sub>sp<sup>2</sup></sub>-H...Z2 hydrogen bonds. In addition, the stretching frequencies of the C<sub>sp<sup>2</sup></sub>-H bond turn from blue shift to red shift as Z2 and Z7 vary from O to Te, in which the C<sub>sp<sup>2</sup></sub>-H blue shift of C<sub>sp<sup>2</sup></sub>-H...O2 reaching 104.9 cm<sup>-1</sup>. The magnitude of the C<sub>sp<sup>2</sup></sub>-H red shift becomes more obvious when R goes from F to CH<sub>3</sub> substitution. The increase in the C<sub>sp<sup>2</sup></sub>-H stretching frequencies occurs along with the decrease in both the proton affinity at Z2 sites and the polarity of C<sub>sp<sup>2</sup></sub>-H bonds, and *vice versa*. Interestingly, this work highlights the remarkable impact of NH<sub>2</sub> relative to CH<sub>3</sub>/F substitute in chalcogenoaldehydes on the increase in the stretching frequency O-H red- and C<sub>sp<sup>2</sup></sub>-H blue shift involving hydrogen bond.

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## Supporting information

### An insight into stability and characteristics of O/C<sub>sp2</sub>-H...Z hydrogen bonds in the binary systems of chalcogenocarboxylic acid and formamide derivatives

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**Table 1a.** The H6...Z2 interaction distance ( $r_{\text{H6}\cdots\text{Z2}}$ ), selected parameters at BCPs of H6...Z2 interactions, and individual energies ( $E_{\text{HB}}$ ) of the nonconventional C<sub>sp2</sub>-H...Z2 hydrogen bonds in NH<sub>2</sub>CHZ...RCZOH complexes (with R= H, F, CH<sub>3</sub>; Z= O, S, Se, Te).

| Complex                | $r_{\text{H6}\cdots\text{Z2}}$<br>(Å) | $\rho(r)$<br>(au) | $\nabla^2(\rho)$<br>(au) | $H(r)$<br>(au) | $E_{\text{HB}}$<br>(kJ.mol <sup>-1</sup> ) |
|------------------------|---------------------------------------|-------------------|--------------------------|----------------|--------------------------------------------|
| CH <sub>3</sub> O2-O7  | 2.29                                  | 0.014             | 0.050                    | 0.0015         | -12.4                                      |
| CH <sub>3</sub> S2-O7  | 2.78                                  | 0.011             | 0.030                    | 0.0009         | -7.3                                       |
| CH <sub>3</sub> Se2-O7 | 2.90                                  | 0.010             | 0.026                    | 0.0008         | -6.4                                       |
| CH <sub>3</sub> Te2-O7 | 3.08                                  | 0.009             | 0.022                    | 0.0006         | -5.4                                       |
| HO2-O7                 | 2.31                                  | 0.014             | 0.048                    | 0.0014         | -11.9                                      |
| HS2-O7                 | 2.79                                  | 0.011             | 0.029                    | 0.0009         | -7.1                                       |
| HSe2-O7                | 2.91                                  | 0.010             | 0.026                    | 0.0008         | -6.2                                       |
| HTe2-O7                | 3.08                                  | 0.009             | 0.021                    | 0.0006         | -5.3                                       |
| FO2-O7                 | 2.34                                  | 0.013             | 0.045                    | 0.0014         | -11.2                                      |
| FS2-O7                 | 2.80                                  | 0.010             | 0.029                    | 0.0010         | -7.0                                       |
| FSe2-O7                | 2.90                                  | 0.011             | 0.026                    | 0.0009         | -6.3                                       |
| FTe2-O7                | 3.06                                  | 0.010             | 0.022                    | 0.0007         | -5.6                                       |
| CH <sub>3</sub> O2-S7  | 2.17                                  | 0.017             | 0.061                    | 0.0016         | -15.8                                      |
| CH <sub>3</sub> S2-S7  | 2.65                                  | 0.013             | 0.034                    | 0.0008         | -9.3                                       |
| CH <sub>3</sub> Se2-S7 | 2.77                                  | 0.012             | 0.030                    | 0.0007         | -8.1                                       |
| CH <sub>3</sub> Te2-S7 | 2.95                                  | 0.012             | 0.025                    | 0.0005         | -6.7                                       |
| HO2-S7                 | 2.19                                  | 0.016             | 0.059                    | 0.0016         | -15.2                                      |
| HS2-S7                 | 2.66                                  | 0.013             | 0.034                    | 0.0008         | -9.1                                       |
| HSe2-S7                | 2.78                                  | 0.012             | 0.030                    | 0.0007         | -8.1                                       |
| HTe2-S7                | 2.96                                  | 0.011             | 0.024                    | 0.0005         | -6.6                                       |
| FO2-S7                 | 2.22                                  | 0.015             | 0.056                    | 0.0017         | -13.9                                      |

| Complex                 | $r_{H6\cdots Z2}$<br>(Å) | $\rho(r)$<br>(au) | $\nabla^2(\rho)$<br>(au) | $H(r)$<br>(au) | $E_{HB}$<br>(kJ.mol <sup>-1</sup> ) |
|-------------------------|--------------------------|-------------------|--------------------------|----------------|-------------------------------------|
| FS2-S7                  | 2.68                     | 0.012             | 0.033                    | 0.0009         | -8.6                                |
| FSe2-S7                 | 2.79                     | 0.012             | 0.030                    | 0.0008         | -7.6                                |
| FTe2-S7                 | 2.95                     | 0.011             | 0.025                    | 0.0006         | -6.6                                |
| CH <sub>3</sub> O2-Se7  | 2.15                     | 0.017             | 0.063                    | 0.0017         | -16.3                               |
| CH <sub>3</sub> S2-Se7  | 2.65                     | 0.013             | 0.035                    | 0.0007         | -9.5                                |
| CH <sub>3</sub> Se2-Se7 | 2.76                     | 0.013             | 0.030                    | 0.0007         | -8.2                                |
| CH <sub>3</sub> Te2-Se7 | 2.94                     | 0.012             | 0.025                    | 0.0005         | -6.9                                |
| HO2-Se7                 | 2.17                     | 0.017             | 0.060                    | 0.0016         | -15.6                               |
| HS2-Se7                 | 2.65                     | 0.013             | 0.034                    | 0.0007         | -9.3                                |
| HSe2-Se7                | 2.77                     | 0.012             | 0.032                    | 0.0006         | -8.3                                |
| HTe2-Se7                | 2.94                     | 0.012             | 0.025                    | 0.0005         | -6.9                                |
| FO2-Se7                 | 2.20                     | 0.015             | 0.057                    | 0.0018         | -14.2                               |
| FS2-Se7                 | 2.68                     | 0.012             | 0.033                    | 0.0009         | -8.7                                |
| FSe2-Se7                | 2.78                     | 0.012             | 0.030                    | 0.0008         | -7.7                                |
| FTe2-Se7                | 2.94                     | 0.012             | 0.025                    | 0.0006         | -6.8                                |
| CH <sub>3</sub> O2-Te7  | 2.15                     | 0.017             | 0.063                    | 0.0017         | -16.4                               |
| CH <sub>3</sub> S2-Te7  | 2.63                     | 0.013             | 0.035                    | 0.0007         | -9.7                                |
| CH <sub>3</sub> Se2-Te7 | 2.72                     | 0.013             | 0.032                    | 0.0007         | -8.9                                |
| CH <sub>3</sub> Te2-Te7 | 2.93                     | 0.012             | 0.025                    | 0.0005         | -7.0                                |
| HO2-Te7                 | 2.17                     | 0.017             | 0.061                    | 0.0016         | -15.7                               |
| HS2-Te7                 | 2.64                     | 0.013             | 0.034                    | 0.0007         | -9.5                                |
| HSe2-Te7                | 2.73                     | 0.013             | 0.032                    | 0.0007         | -8.7                                |
| HTe2-Te7                | 2.94                     | 0.012             | 0.025                    | 0.0005         | -6.9                                |
| FO2-Te7                 | 2.20                     | 0.015             | 0.058                    | 0.0018         | -14.1                               |
| FS2-Te7                 | 2.67                     | 0.012             | 0.034                    | 0.0009         | -8.8                                |
| FSe2-Te7                | 2.75                     | 0.0123            | 0.031                    | 0.0008         | -8.2                                |
| FTe2-Te7                | 2.94                     | 0.011             | 0.025                    | 0.0006         | -6.7                                |

**Table 1b.** The H4 $\cdots$ Z7 interaction distance ( $r_{H6\cdots Z2}$ ), selected parameters at BCPs of H4 $\cdots$ Z7 interactions, and individual energies ( $E_{HB}$ ) of the O-H $\cdots$ Z7 hydrogen bonds in NH<sub>2</sub>CHZ $\cdots$ RCZOH complexes (with R= H, F, CH<sub>3</sub>; Z= O, S, Se, Te).

| Complex                | $r_{H6\cdots Z2}$<br>(Å) | $\rho(r)$<br>(au) | $\nabla^2(\rho)$<br>(au) | $H(r)$<br>(au) | $E_{HB}$<br>(kJ.mol <sup>-1</sup> ) |
|------------------------|--------------------------|-------------------|--------------------------|----------------|-------------------------------------|
| CH <sub>3</sub> O2-O7  | 1.689                    | 0.047             | 0.102                    | -0.011         | -61.8                               |
| CH <sub>3</sub> S2-O7  | 1.655                    | 0.050             | 0.106                    | -0.013         | -68.1                               |
| CH <sub>3</sub> Se2-O7 | 1.638                    | 0.052             | 0.108                    | -0.014         | -71.8                               |
| CH <sub>3</sub> Te2-O7 | 1.627                    | 0.053             | 0.109                    | -0.015         | -74.2                               |
| HO2-O7                 | 1.668                    | 0.049             | 0.103                    | -0.012         | -66.2                               |
| HS2-O7                 | 1.640                    | 0.052             | 0.106                    | -0.014         | -71.7                               |
| HSe2-O7                | 1.626                    | 0.054             | 0.107                    | -0.015         | -75.0                               |
| HTe2-O7                | 1.622                    | 0.054             | 0.109                    | -0.015         | -75.7                               |

| Complex                 | $r_{\text{H6} \cdots \text{Z2}}$<br>(Å) | $\rho(\mathbf{r})$<br>(au) | $\nabla^2(\rho)$<br>(au) | $H(\mathbf{r})$<br>(au) | $E_{\text{HB}}$<br>(kJ.mol <sup>-1</sup> ) |
|-------------------------|-----------------------------------------|----------------------------|--------------------------|-------------------------|--------------------------------------------|
| FO2–O7                  | 1.605                                   | 0.057                      | 0.108                    | -0.018                  | -81.4                                      |
| FS2–O7                  | 1.571                                   | 0.062                      | 0.109                    | -0.021                  | -89.9                                      |
| FSe2–O7                 | 1.550                                   | 0.065                      | 0.109                    | -0.023                  | -95.9                                      |
| FTe2–O7                 | 1.533                                   | 0.068                      | 0.109                    | -0.025                  | -101.3                                     |
| CH <sub>3</sub> O2–S7   | 2.216                                   | 0.029                      | 0.046                    | -0.005                  | -27.0                                      |
| CH <sub>3</sub> S2–S7   | 2.192                                   | 0.031                      | 0.046                    | -0.005                  | -28.8                                      |
| CH <sub>3</sub> Se2–S7  | 2.176                                   | 0.032                      | 0.046                    | -0.006                  | -30.1                                      |
| CH <sub>3</sub> Te2–S7  | 2.169                                   | 0.032                      | 0.046                    | -0.006                  | -30.8                                      |
| HO2–S7                  | 2.193                                   | 0.031                      | 0.045                    | -0.005                  | -28.9                                      |
| HS2–S7                  | 2.173                                   | 0.032                      | 0.045                    | -0.006                  | -30.5                                      |
| HSe2–S7                 | 2.159                                   | 0.033                      | 0.045                    | -0.006                  | -30.1                                      |
| HTe2–S7                 | 2.156                                   | 0.033                      | 0.045                    | -0.007                  | -31.9                                      |
| FO2–S7                  | 2.129                                   | 0.035                      | 0.044                    | -0.008                  | -34.5                                      |
| FS2–S7                  | 2.109                                   | 0.037                      | 0.042                    | -0.009                  | -36.3                                      |
| FSe2–S7                 | 2.094                                   | 0.038                      | 0.041                    | -0.009                  | -37.9                                      |
| FTe2–S7                 | 2.085                                   | 0.039                      | 0.040                    | -0.010                  | -38.9                                      |
| CH <sub>3</sub> O2–Se7  | 2.358                                   | 0.025                      | 0.039                    | -0.003                  | -21.6                                      |
| CH <sub>3</sub> S2–Se7  | 2.331                                   | 0.027                      | 0.039                    | -0.004                  | -23.2                                      |
| CH <sub>3</sub> Se2–Se7 | 2.315                                   | 0.028                      | 0.038                    | -0.004                  | -24.3                                      |
| CH <sub>3</sub> Te2–Se7 | 2.278                                   | 0.030                      | 0.039                    | -0.005                  | -26.8                                      |
| HO2–Se7                 | 2.334                                   | 0.027                      | 0.039                    | -0.004                  | -23.2                                      |
| HS2–Se7                 | 2.312                                   | 0.028                      | 0.038                    | -0.005                  | -24.6                                      |
| HSe2–Se7                | 2.298                                   | 0.030                      | 0.038                    | -0.005                  | -26.0                                      |
| HTe2–Se7                | 2.267                                   | 0.031                      | 0.038                    | -0.006                  | -27.7                                      |
| FO2–Se7                 | 2.269                                   | 0.031                      | 0.037                    | -0.006                  | -27.8                                      |
| FS2–Se7                 | 2.249                                   | 0.032                      | 0.036                    | -0.007                  | -29.3                                      |
| FSe2–Se7                | 2.234                                   | 0.033                      | 0.035                    | -0.007                  | -30.5                                      |
| FTe2–Se7                | 2.199                                   | 0.036                      | 0.034                    | -0.008                  | -33.3                                      |
| CH <sub>3</sub> O2–Te7  | 2.562                                   | 0.022                      | 0.030                    | -0.002                  | -16.0                                      |
| CH <sub>3</sub> S2–Te7  | 2.524                                   | 0.024                      | 0.030                    | -0.003                  | -17.8                                      |
| CH <sub>3</sub> Se2–Te7 | 2.501                                   | 0.025                      | 0.030                    | -0.003                  | -18.9                                      |
| CH <sub>3</sub> Te2–Te7 | 2.490                                   | 0.026                      | 0.030                    | -0.004                  | -19.5                                      |
| HO2–Te7                 | 2.539                                   | 0.023                      | 0.030                    | -0.003                  | -17.1                                      |
| HS2–Te7                 | 2.509                                   | 0.025                      | 0.030                    | -0.003                  | -18.6                                      |
| HSe2–Te7                | 2.486                                   | 0.026                      | 0.029                    | -0.004                  | -19.8                                      |
| HTe2–Te7                | 2.480                                   | 0.026                      | 0.029                    | -0.004                  | -20.1                                      |
| FO2–Te7                 | 2.463                                   | 0.027                      | 0.029                    | -0.004                  | -21.1                                      |
| FS2–Te7                 | 2.435                                   | 0.029                      | 0.028                    | -0.005                  | -22.8                                      |
| FSe2–Te7                | 2.416                                   | 0.030                      | 0.026                    | -0.006                  | -24.0                                      |
| CH <sub>3</sub> O2–Te7  | 2.406                                   | 0.031                      | 0.026                    | -0.006                  | -24.6                                      |



**Table S2.** NBO charge at H4, H6, Z2, and Z7 atoms in **RZ2-Z7** complexes with R= H, F, CH<sub>3</sub>; Z2(Z7) = O, S, Se, Te.

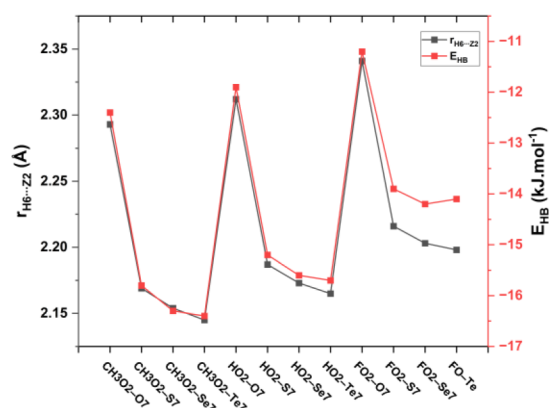
|              | CH <sub>3</sub> O-O | CH <sub>3</sub> S-O | CH <sub>3</sub> Se-O | CH <sub>3</sub> Te-O |              | CH <sub>3</sub> O-Se | CH <sub>3</sub> S-Se | CH <sub>3</sub> Se-Se | CH <sub>3</sub> Te-Se |
|--------------|---------------------|---------------------|----------------------|----------------------|--------------|----------------------|----------------------|-----------------------|-----------------------|
| <b>q(H4)</b> | 0.540               | 0.547               | 0.551                | 0.554                | <b>q(H4)</b> | 0.517                | 0.524                | 0.528                 | 0.528                 |
| <b>q(Z7)</b> | -0.770              | -0.770              | -0.773               | -0.776               | <b>q(Z7)</b> | -0.231               | -0.215               | -0.214                | -0.204                |
| <b>q(H6)</b> | 0.149               | 0.138               | 0.140                | 0.140                | <b>q(H6)</b> | 0.213                | 0.201                | 0.201                 | 0.202                 |
| <b>q(Z2)</b> | -0.762              | -0.264              | -0.238               | -0.166               | <b>q(Z2)</b> | -0.759               | -0.245               | -0.215                | -0.139                |
|              | HO-O                | HS-O                | HSe-O                | HTe-O                |              | HO-Se                | HS-Se                | HSe-Se                | HTe-Se                |
| <b>q(H4)</b> | 0.541               | 0.545               | 0.549                | 0.553                | <b>q(H4)</b> | 0.515                | 0.520                | 0.523                 | 0.522                 |
| <b>q(Z7)</b> | -0.772              | -0.771              | -0.774               | -0.777               | <b>q(Z7)</b> | -0.227               | -0.211               | -0.170                | -0.201                |
| <b>q(H6)</b> | 0.147               | 0.138               | 0.139                | 0.138                | <b>q(H6)</b> | 0.211                | 0.199                | 0.173                 | 0.200                 |
| <b>q(Z2)</b> | -0.748              | -0.254              | -0.225               | -0.147               | <b>q(Z2)</b> | -0.744               | -0.233               | -0.128                | -0.119                |
|              | FO-O                | FS-O                | FSe-O                | FTe-O                |              | FO-Se                | FS-Se                | FSe-Se                | FTe-Se                |
| <b>q(H4)</b> | 0.552               | 0.559               | 0.562                | 0.566                | <b>q(H4)</b> | 0.524                | 0.531                | 0.534                 | 0.532                 |
| <b>q(Z7)</b> | -0.775              | -0.774              | -0.776               | -0.780               | <b>q(Z7)</b> | -0.216               | -0.200               | -0.199                | -0.189                |
| <b>q(H6)</b> | 0.147               | 0.140               | 0.143                | 0.145                | <b>q(H6)</b> | 0.208                | 0.198                | 0.200                 | 0.202                 |
| <b>q(Z2)</b> | -0.751              | -0.275              | -0.254               | -0.195               | <b>q(Z2)</b> | -0.747               | -0.252               | -0.226                | -0.161                |
|              | CH <sub>3</sub> O-S | CH <sub>3</sub> S-S | CH <sub>3</sub> Se-S | CH <sub>3</sub> Te-S |              | CH <sub>3</sub> O-Te | CH <sub>3</sub> S-Te | CH <sub>3</sub> Se-Te | CH <sub>3</sub> Te-Te |
| <b>q(H4)</b> | 0.516               | 0.524               | 0.527                | 0.529                | <b>q(H4)</b> | 0.516                | 0.523                | 0.526                 | 0.528                 |
| <b>q(Z7)</b> | -0.259              | -0.246              | -0.246               | -0.246               | <b>q(Z7)</b> | -0.160               | -0.137               | -0.135                | -0.133                |
| <b>q(H6)</b> | 0.211               | 0.199               | 0.200                | 0.199                | <b>q(H6)</b> | 0.210                | 0.197                | 0.198                 | 0.198                 |
| <b>q(Z2)</b> | -0.759              | -0.246              | -0.215               | -0.138               | <b>q(Z2)</b> | -0.760               | -0.244               | -0.207                | -0.135                |
|              | HO-S                | HS-S                | HSe-S                | HTe-S                |              | HO-Te                | HS-Te                | HSe-Te                | HTe-Te                |
| <b>q(H4)</b> | 0.515               | 0.519               | 0.522                | 0.524                | <b>q(H4)</b> | 0.514                | 0.518                | 0.520                 | 0.522                 |
| <b>q(Z7)</b> | -0.256              | -0.243              | -0.243               | -0.244               | <b>q(Z7)</b> | -0.154               | -0.132               | -0.130                | -0.129                |
| <b>q(H6)</b> | 0.210               | 0.197               | 0.198                | 0.197                | <b>q(H6)</b> | 0.208                | 0.195                | 0.196                 | 0.196                 |
| <b>q(Z2)</b> | -0.743              | -0.234              | -0.202               | -0.119               | <b>q(Z2)</b> | -0.744               | -0.231               | -0.193                | -0.115                |
|              | FO-S                | FS-S                | FSe-S                | FTe-S                |              | FO-Te                | FS-Te                | FSe-Te                | FTe-Te                |
| <b>q(H4)</b> | 0.522               | 0.530               | 0.532                | 0.533                | <b>q(H4)</b> | 0.523                | 0.530                | 0.531                 | 0.532                 |
| <b>q(Z7)</b> | -0.247              | -0.234              | -0.234               | -0.235               | <b>q(Z7)</b> | -0.138               | -0.115               | -0.113                | -0.112                |
| <b>q(H6)</b> | 0.207               | 0.197               | 0.199                | 0.200                | <b>q(H6)</b> | 0.204                | 0.194                | 0.196                 | 0.197                 |
| <b>q(Z2)</b> | -0.746              | -0.253              | -0.227               | -0.161               | <b>q(Z2)</b> | -0.747               | -0.251               | -0.218                | -0.157                |

**Table S3a.** The change in the bond length ( $\Delta r$ , Å) and stretching frequency ( $\Delta \nu$ ,  $\text{cm}^{-1}$ ) of  $\text{C}_{\text{sp}^2}\text{-H}$  and  $\text{O-H}$  bonds in the **RZ2-Z7** complexes compared to their corresponding monomers, with  $\text{R} = \text{H, F, CH}_3$ ;  $\text{Z2} = \text{O, S, Se, Te}$ ;  $\text{Z7} = \text{O, S}$ .

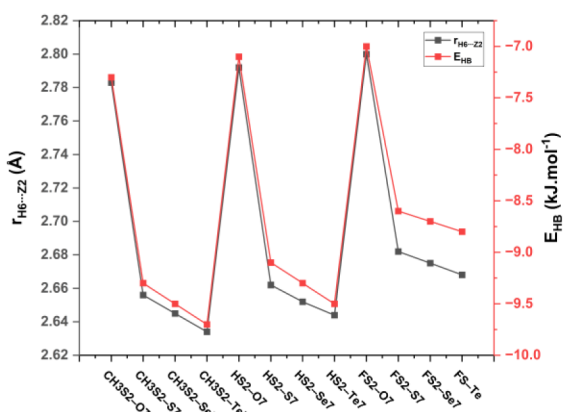
|                                               | <b>CH<sub>3</sub>O2-O7</b> | <b>CH<sub>3</sub>S2-O7</b> | <b>CH<sub>3</sub>Se2-O7</b> | <b>CH<sub>3</sub>Te2-O7</b> |
|-----------------------------------------------|----------------------------|----------------------------|-----------------------------|-----------------------------|
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | -0.0060                    | -0.0059                    | -0.0060                     | -0.0063                     |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 84                         | 74.3                       | 72.3                        | 74.0                        |
| $\Delta r(\text{O-H})$                        | 0.0256                     | 0.0273                     | 0.0291                      | 0.0300                      |
| $\Delta \nu(\text{O-H})$                      | -517                       | -550                       | -584                        | -599                        |
|                                               | <b>HO2-O7</b>              | <b>HS2-O7</b>              | <b>HSe2-O7</b>              | <b>HTe2-O7</b>              |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | -0.0059                    | -0.0059                    | -0.0058                     | -0.0060                     |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 83.9                       | 71.9                       | 64.1                        | 63.4                        |
| $\Delta r(\text{O-H})$                        | 0.0283                     | 0.0295                     | 0.0311                      | 0.0311                      |
| $\Delta \nu(\text{O-H})$                      | -566                       | -604                       | -620                        | -622                        |
|                                               | <b>FO2-O7</b>              | <b>FS2-O7</b>              | <b>FSe2-O7</b>              | <b>FTe2-O7</b>              |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | -0.0069                    | -0.0071                    | -0.0072                     | -0.0075                     |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 104.9                      | 92.9                       | 91.9                        | 91.1                        |
| $\Delta r(\text{O-H})$                        | 0.0368                     | 0.0411                     | 0.0447                      | 0.0482                      |
| $\Delta \nu(\text{O-H})$                      | -742                       | -827                       | -895                        | -958                        |
|                                               | <b>CH<sub>3</sub>O2-S7</b> | <b>CH<sub>3</sub>S2-S7</b> | <b>CH<sub>3</sub>Se2-S7</b> | <b>CH<sub>3</sub>Te2-S7</b> |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | -0.0005                    | -0.0002                    | 0.0000                      | -0.0002                     |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 18.1                       | 3.3                        | -2.8                        | -6.0                        |
| $\Delta r(\text{O-H})$                        | 0.0202                     | 0.0212                     | 0.0225                      | 0.0231                      |
| $\Delta \nu(\text{O-H})$                      | -421                       | -441                       | -467                        | -477                        |
|                                               | <b>HO2-S7</b>              | <b>HS2-S7</b>              | <b>HSe2-S7</b>              | <b>HTe2-S7</b>              |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | -0.0006                    | -0.0002                    | 0.0001                      | -0.0001                     |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 19.4                       | 2.3                        | -4.3                        | -8.0                        |
| $\Delta r(\text{O-H})$                        | 0.0224                     | 0.0231                     | 0.0244                      | 0.0247                      |
| $\Delta \nu(\text{O-H})$                      | -464                       | -477                       | -500                        | -504                        |
|                                               | <b>FO2-S7</b>              | <b>FS2-S7</b>              | <b>FSe2-S7</b>              | <b>FTe2-S7</b>              |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | -0.0019                    | -0.0016                    | -0.0013                     | -0.0013                     |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 37.5                       | 22.2                       | 14.9                        | 8.5                         |
| $\Delta r(\text{O-H})$                        | 0.0288                     | 0.0308                     | 0.0328                      | 0.0346                      |
| $\Delta \nu(\text{O-H})$                      | -595                       | -642                       | -683                        | -717                        |

**Table S3b.** The change in the bond length ( $\Delta r$ , Å) and stretching frequency ( $\Delta \nu$ ,  $\text{cm}^{-1}$ ) of  $\text{C}_{\text{sp}^2}\text{-H}$  and  $\text{O-H}$  bonds in the **RZ2-Z7** complexes compared to their corresponding monomers, with  $\text{R} = \text{H, F, CH}_3$ ;  $\text{Z2} = \text{O, S, Se, Te}$ ;  $\text{Z7} = \text{Se, Te}$ .

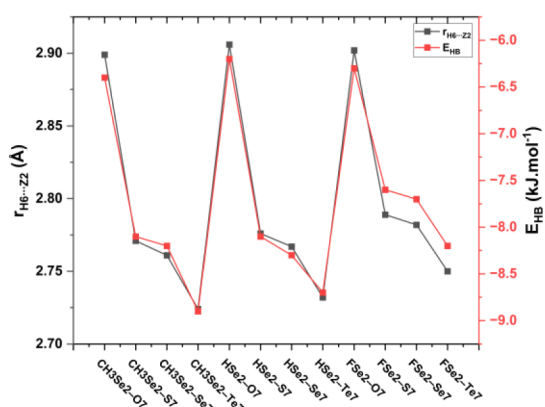
|                                               | <b>CH<sub>3</sub>O2-Se7</b> | <b>CH<sub>3</sub>S2-Se7</b> | <b>CH<sub>3</sub>Se2-Se7</b> | <b>CH<sub>3</sub>Te2-Se7</b> |
|-----------------------------------------------|-----------------------------|-----------------------------|------------------------------|------------------------------|
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | 0.0004                      | 0.0007                      | 0.0009                       | 0.0009                       |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 6.3                         | -9.5                        | -15.9                        | -21.8                        |
| $\Delta r(\text{O-H})$                        | 0.0190                      | 0.0201                      | 0.0214                       | 0.0233                       |
| $\Delta \nu(\text{O-H})$                      | -398                        | -419                        | -445                         | -481                         |
|                                               | <b>HO2-Se7</b>              | <b>HS2-Se7</b>              | <b>HSe2-Se7</b>              | <b>HTe2-Se7</b>              |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | 0.0002                      | 0.0007                      | 0.0010                       | 0.0010                       |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 8.1                         | -10.1                       | -16.7                        | -23.1                        |
| $\Delta r(\text{O-H})$                        | 0.0212                      | 0.0219                      | 0.0232                       | 0.0247                       |
| $\Delta \nu(\text{O-H})$                      | -440                        | -454                        | -477                         | -503                         |
|                                               | <b>FO2-Se7</b>              | <b>FS2-Se7</b>              | <b>FSe2-Se7</b>              | <b>FTe2-Se7</b>              |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | -0.0011                     | -0.0006                     | -0.0003                      | -0.0001                      |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 26.1                        | 9.3                         | 3.0                          | -7.3                         |
| $\Delta r(\text{O-H})$                        | 0.0272                      | 0.0290                      | 0.0310                       | 0.0341                       |
| $\Delta \nu(\text{O-H})$                      | -563                        | -608                        | -649                         | -706                         |
|                                               | <b>CH<sub>3</sub>O2-Te7</b> | <b>CH<sub>3</sub>S2-Te7</b> | <b>CH<sub>3</sub>Se2-Te7</b> | <b>CH<sub>3</sub>Te2-Te7</b> |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | 0.0009                      | 0.0013                      | 0.0018                       | 0.0017                       |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | -0.7                        | -18.2                       | -28.1                        | -32.8                        |
| $\Delta r(\text{O-H})$                        | 0.0180                      | 0.0196                      | 0.0214                       | 0.0220                       |
| $\Delta \nu(\text{O-H})$                      | -385                        | -419                        | -455                         | -467                         |
|                                               | <b>HO2-Te7</b>              | <b>HS2-Te7</b>              | <b>HSe2-Te7</b>              | <b>HTe2-Te7</b>              |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | 0.0006                      | 0.0013                      | 0.0018                       | 0.0018                       |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 2.7                         | -18.3                       | -28.6                        | -33.6                        |
| $\Delta r(\text{O-H})$                        | 0.0200                      | 0.0212                      | 0.0232                       | 0.0234                       |
| $\Delta \nu(\text{O-H})$                      | -426                        | -450                        | -488                         | -491                         |
|                                               | <b>FO2-Te7</b>              | <b>FS2-Te7</b>              | <b>FSe2-Te7</b>              | <b>FTe2-Te7</b>              |
| $\Delta r(\text{C}_{\text{sp}^2}\text{-H})$   | -0.0005                     | 0.0001                      | 0.0006                       | 0.0008                       |
| $\Delta \nu(\text{C}_{\text{sp}^2}\text{-H})$ | 18.7                        | -0.1                        | -8.8                         | -18.5                        |
| $\Delta r(\text{O-H})$                        | 0.0264                      | 0.0288                      | 0.0312                       | 0.0327                       |
| $\Delta \nu(\text{O-H})$                      | -560                        | -614                        | -666                         | -694                         |



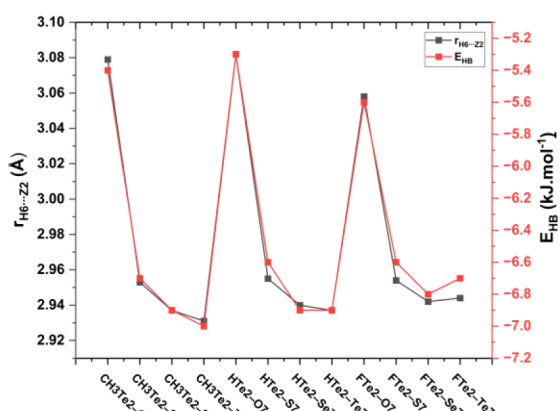
RO2-Z7



RS2-Z7

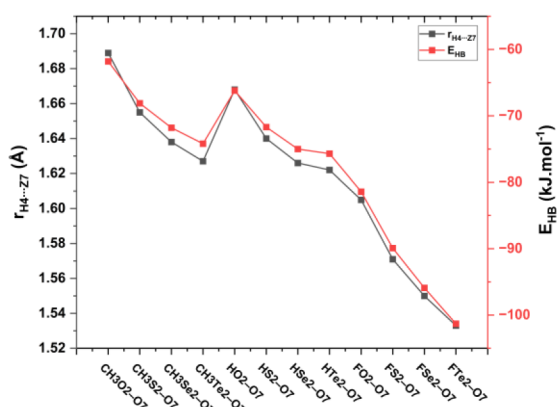


RSe2-Z7

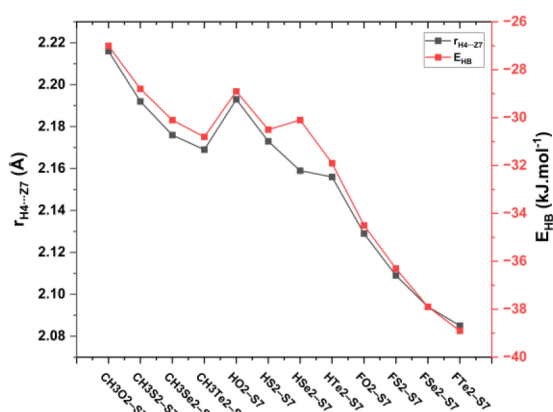


RTe2-Z7

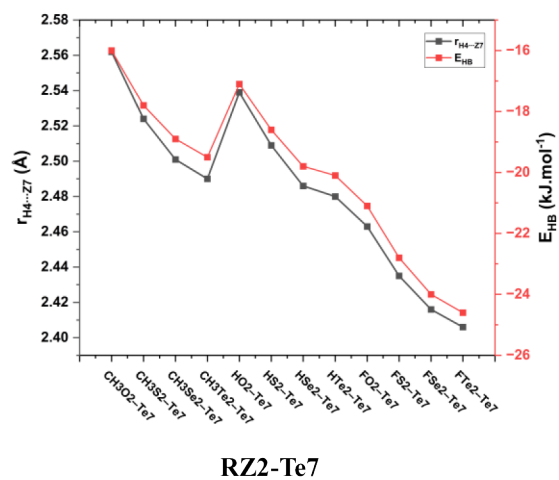
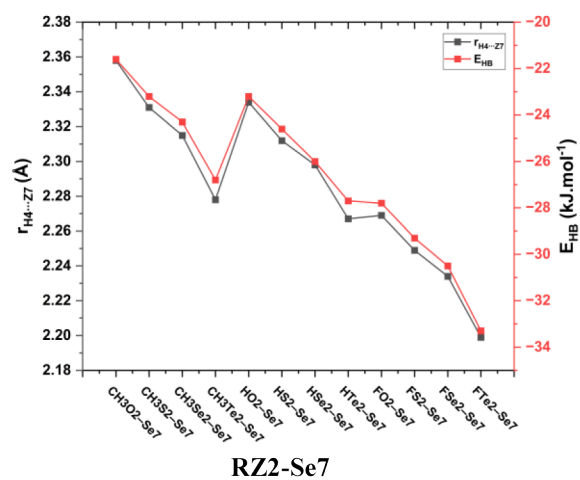
**Figure S1a.** The relationship between the H6...Z2 interaction distance and individual energy ( $E_{HB}$ ) of  $C_{sp^2}-H\cdots Z2$  hydrogen bond in **RZ2-Z7** complexes (with R = H, F, CH<sub>3</sub>; Z2(Z7) = O, S, Se, Te).



RZ2-O7



RZ2-S7



**Figure S1b.** The relationship between the H4...Z7 interaction distance and individual energy ( $E_{HB}$ ) of O-H...Z7 hydrogen bond in **RZ2-Z7** complexes (with R= H, F, CH<sub>3</sub>; Z2(Z7) = O, S, Se, Te).



# Phân tích và xây dựng danh mục tương tác thuốc tim mạch ở bệnh nhân ngoại trú tại Trung tâm Y tế huyện Long Mỹ, tỉnh Hậu Giang, năm 2023

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Ngày nhận bài: 18/01/2025; Ngày sửa bài: 12/04/2025;

Ngày nhận đăng: 07/05/2025; Ngày xuất bản: 28/06/2025

## TÓM TẮT

Tương tác thuốc-thuốc là các biến cố bất lợi thường xảy ra trong thực hành lâm sàng. Đáng chú ý, tỷ lệ tương tác thuốc liên quan đến thuốc tim mạch được ghi nhận cao hơn so với các loại thuốc khác. Tương tác thuốc có thể dẫn đến các hậu quả nghiêm trọng, bao gồm tăng độc tính, giảm hiệu quả điều trị, cũng như làm tăng nguy cơ nhập viện và tử vong. Mục tiêu của nghiên cứu này là đánh giá tỷ lệ, mức độ nghiêm trọng, cơ chế dược lý của tương tác của thuốc tim mạch với các thuốc khác và xây dựng danh sách các tương tác thuốc tim mạch tại bệnh nhân ngoại trú Trung tâm Y tế Long Mỹ, Hậu Giang, trong năm 2023. Chúng tôi đã tiến hành một nghiên cứu cắt ngang, hồi cứu trên tất cả các đơn thuốc liên quan đến tim mạch tại bệnh nhân ngoại trú Trung tâm Y tế Long Mỹ, Hậu Giang từ ngày 01 tháng 01 năm 2023 đến hết ngày 31 tháng 03 năm 2023. Tiêu chí đánh giá tương tác thuốc được thực hiện dựa trên ba cơ sở dữ liệu: Drugs.com ([www.drugs.com/drug\\_interactions.html](http://www.drugs.com/drug_interactions.html)), Medscape ([reference.medscape.com/drug-interactionchecker](http://reference.medscape.com/drug-interactionchecker)), và Micromedex ([www.micromedexsolutions.com](http://www.micromedexsolutions.com)). Nghiên cứu đã xây dựng thành công danh sách gồm 23 cặp tương tác thuốc liên quan đến thuốc tim mạch có ý nghĩa lâm sàng, tạo nền tảng cho các can thiệp lâm sàng trong tương lai nhằm giảm thiểu các tương tác thuốc, đặc biệt là ngăn ngừa các trường hợp có mức độ nghiêm trọng cao.

**Từ khóa:** Tương tác thuốc, thuốc tim mạch, bệnh nhân ngoại trú, Trung tâm y tế huyện Long Mỹ.

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# Assessment of cardiovascular drug-drug interactions and development of a drug-drug interactions list among outpatients at Long My Health Center, Hau Giang, in 2023

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## ABSTRACT

Drug-drug interactions (DDIs) are adverse events that frequently occur in clinical practice. Notably, the incidence of cardiovascular DDIs has been observed to be higher compared to other drugs. DDIs may result in severe outcomes, including increased toxicity, diminished therapeutic efficacy, and an elevated risk of hospitalization and mortality. The purpose of this research was to assess the prevalence, severity, pharmacological mechanisms of cardiovascular DDIs and develop a cardiovascular DDIs list among outpatients at Long My Health Center, Hau Giang, in 2023. We conducted a cross-sectional, retrospective study of all cardiovascular prescriptions among outpatients at Long My Health Center, Hau Giang from January 1<sup>st</sup>, 2023, to March 31<sup>st</sup>, 2023. Criteria for evaluating DDIs involve using three databases: drugs.com ([www.drugs.com/drug\\_interactions.html](http://www.drugs.com/drug_interactions.html)), medscape ([reference.medscape.com/drug-interactionchecker](http://reference.medscape.com/drug-interactionchecker)), and micromedex ([www.micromedexsolutions.com](http://www.micromedexsolutions.com)). The study has successfully built a practical list of clinically significant cardiovascular DDIs using three databases, including 23 pairs, which will be the foundation for future clinical interventions aimed at minimizing the prevalent drug interactions, especially to prevent the occurrence of major severity.

**Keywords:** *Drug-drug interactions, cardiovascular medicines, outpatients, Long My health center, Hau Giang.*

## 1. INTRODUCTION

Drug-drug interactions (DDIs) refer to alterations in the concentration of medications in the bloodstream due to the concurrent presence of additional pharmaceuticals, which could potentially impact therapeutic efficacy or elevate adverse events. DDIs may result in severe outcomes, including increased toxicity, diminished therapeutic efficacy, and an elevated risk of hospitalization and mortality.<sup>1</sup> DDIs are events that frequently occur in clinical practice.<sup>2</sup> Notably, the incidence of cardiovascular DDIs

has been observed to be higher compared to other drugs.<sup>3</sup> Indeed, clinicians frequently prescribe cardiovascular medications to the elderly, who typically have multiple comorbidities that required complex drug regimens, known as polypharmacy, which could increase the risk of DDIs.<sup>4,5</sup> DDIs are preventable clinical events that can be mitigated through the utilization of popular medication interaction monitoring databases, including Drug Interaction Checker, Medscape Drug Interaction Checker, and Micromedex Drug Interaction Checker.

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Assessment of the prevalence, mechanism, and severity of cardiovascular DDIs may inform clinical pharmacological strategies to reduce the rate of DDIs in the future.

Consequently, this study was conducted to identify cardiovascular DDIs among outpatients at Long My Health Center, Hau Giang, Vietnam and thereby develop a list of clinically relevant cardiovascular DDIs.

## 2. METHODS

### 2.1. Method

Cross-sectional, retrospective study of all cardiovascular prescriptions among outpatients from January 1<sup>st</sup>, 2023, to March 31<sup>st</sup>, 2023, satisfying the inclusion and exclusion criteria.<sup>6</sup>

- Inclusion criteria: Prescriptions, including cardiovascular medication.

- Exclusion criteria:

- +The prescription only has one medication.

- +The prescription contains two drugs, of which one is a functional food or an external drug or an herbal medicinal product.

### 2.2. Assessment criteria

#### 2.2.1. Drug interaction checker databases

Lookup drug interactions based on comprehensive, professional websites, including:

- Drug Interaction Checker-DI ([https://www.drugs.com/drug\\_interactions.html](https://www.drugs.com/drug_interactions.html)),

- Medscape Drug Interaction Checker-MDI (<https://reference.medscape.com/drug-interactionchecker>),

- Micromedex Drug Interaction Checker-MMDI (<https://www.micromedexsolutions.com/micromedex2/librarian/>).

This study recorded interactions between cardiovascular medications and other drugs.

#### 2.2.2. Assessment criteria of clinically relevant drug interactions

According to the European Medicines Agency, a clinically relevant drug interaction is one

that results in therapeutic or toxic changes that require dose adjustment or medical intervention.<sup>7</sup> Therefore, this study recorded interactions between cardiovascular medications and other drugs documented in the three aforementioned databases with a moderate to severe interactive severity.

#### 2.2.3. Development a list of clinically relevant drug interactions

Identify clinically relevant drug interactions that were reported in at least two of the three above databases with a moderate to major severity or in at least one database with a major severity.

#### 2.2.4. Data analysis

Data were analyzed using SPSS (version 16.0) software and expressed in percentage.

## 3. RESULTS AND DISCUSSION

During the 3-month study period, 468 prescriptions that met both inclusion and exclusion criteria were utilized for this study.

### 3.1. Demographic characteristics

The 468 prescriptions of the study population had nearly equal proportions of male and female participants. The mean age of included patients was  $64.5 \pm 12.0$  years, and those aged 60 years and older accounted for the highest proportion (63.7%). There were seven types of cardiovascular diseases diagnosed among patients, of which hypertension had the highest rate (87.4%), followed by dyslipidemia (12.6%); angina pectoris and cardiomyopathy had almost the same rates (7.26% versus 6.62%); the remaining ones, such as old myocardial infarction, acute myocardial infarction and heart failure, constituted approximately 1%. This study was similar the reseach conducted by Sharma S. et al. with hypertension being the most prevalent condition. The research at Phulbari Hospital, Pokhara, Nepal, regarding cardiovascular drug interactions in outpatients revealed that over fifty percent of patients with cardiovascular disease presented with hypertension.<sup>8</sup> Table 1 following described patient characteristics.

3.2. Characteristics of cardiovascular medications

The average number of medications prescribed per patient was  $4.76 \pm 1.60$  medications. A total of 256 (54.7%) of patients were prescribed five or more (known as polypharmacy). Polypharmacy is prevalent among the elderly due to the presence of multimorbidity. Notably, polypharmacy increases the risk of appearing drug interactions, which can increase the hazard of hospitalization and death if the drug interaction is contraindicated.<sup>4,5</sup> This study found that more than half of patients were received polypharmacy during treatment. The most frequently prescribed cardiovascular medication in this study was calcium channel blockers (60.5%), followed by angiotensin II receptor blockers-ARBs (roughly 20%); the statin and diuretic groups were approximately equivalent (around 13%); the remaining pharmaceuticals, such as angiotensin-converting enzyme inhibitors (ACEIs), organic nitrates, and  $\beta$ -blockers, comprised about 10%. Table 2 following showed numbers and classes of cardiovascular medications.

Table 1. Patient characteristics.

|                                         | N=468 (%)   |
|-----------------------------------------|-------------|
| <b>Gender</b>                           |             |
| Females                                 | 229 (48.9)  |
| Males                                   | 239 (51.1)  |
| <b>Age (years)</b>                      |             |
| ≤ 40                                    | 14 (3.00)   |
| 41-60                                   | 156 (33.3)  |
| ≥ 60                                    | 298 (63.7)  |
| Mean ± SD                               | 64.5 ± 12.0 |
| <b>Types of cardiovascular diseases</b> |             |
| Hypertension                            | 409 (87.4)  |
| Dyslipidemia                            | 59 (12.6)   |
| Angina pectoris                         | 34 (7.26)   |
| Cardiomyopathy                          | 31 (6.62)   |
| Old myocardial infarction               | 8 (1.71)    |
| Acute myocardial infarction             | 1 (0.21)    |
| Heart failure                           | 1 (0.21)    |

Table 2. Number and classes of cardiovascular medications.

|                                                  | N=468 (%)   |
|--------------------------------------------------|-------------|
| <b>Number of medications</b>                     |             |
| ≤ 4                                              | 212 (45.3)  |
| ≥ 5                                              | 256 (54.7)  |
| 5-7                                              | 235 (50.2)  |
| 8-10                                             | 21 (4.50)   |
| Mean ± SD                                        | 4.76 ± 1.60 |
| <b>Classes of cardiovascular medications</b>     |             |
| Calcium channel blockers (CCBs)                  | 283 (60.5)  |
| Angiotensin II receptor blockers (ARBs)          | 92 (19.6)   |
| Statin                                           | 64 (13.7)   |
| Diuretics                                        | 62 (13.2)   |
| Angiotensin-converting enzyme inhibitors (ACEIs) | 21 (4.49)   |
| Organic nitrates                                 | 10 (2.14)   |
| β-blockers                                       | 9 (1.92)    |

Amlodipine was the only medication that belonged to calcium channel blockers (CCBs). ARBs had two medications prescribed frequently: Telmisartan and irbesartan. Atorvastatin and rosuvastatin were anti-dyslipidemia drugs prescribed among the patients. In the diuretics, hydrochlorothiazide was documented to have the highest rate. Table 3 following indicated cardiovascular medications.

Table 3. Cardiovascular medications.

| Cardiovascular medications | N=468 (%)  |
|----------------------------|------------|
| <b>CCBs</b>                |            |
| Amlodipin                  | 283 (60.5) |
| <b>ARBs</b>                |            |
| Telmisartan                | 52 (11.1)  |
| Irbesartan                 | 43 (9.18)  |
| Candesartan                | 1 (0.22)   |
| <b>Statin</b>              |            |
| Atorvastatin               | 36 (7.69)  |
| Rosuvastatin               | 28 (5.99)  |

|                                    |                  |
|------------------------------------|------------------|
| <b>Diuretics</b>                   | <b>62 (13.2)</b> |
| Hydrochlorothiazide                | 58 (12.4)        |
| Furosemide                         | 4 (0.80)         |
| <b>ACEIs</b>                       | <b>21 (4.49)</b> |
| Perindopril                        | 14 (2.99)        |
| Enalapril                          | 4 (0.85)         |
| Captopril                          | 3 (0.65)         |
| <b>Organic nitrates</b>            | <b>10 (2.14)</b> |
| Isosorbide mononitrate             | 10 (2.14)        |
| <b><math>\beta</math>-blockers</b> | <b>9 (1.92)</b>  |
| Bisoprolol                         | 5 (1.06)         |
| Atenolol                           | 4 (0.86)         |

### 3.3. Characteristics of DDIs

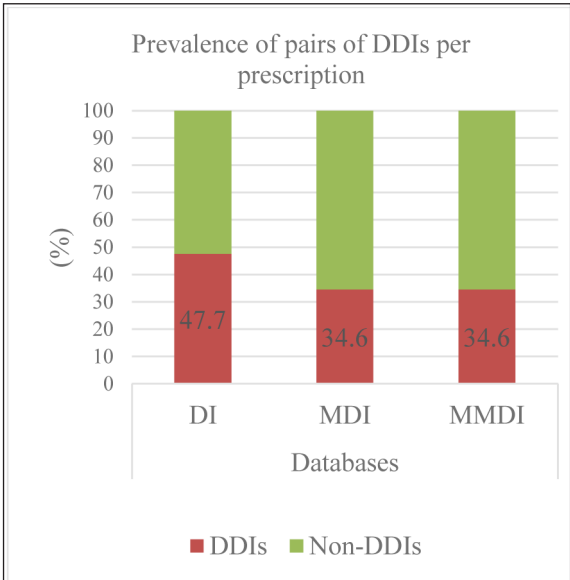
#### 3.3.1. Prevalence of DDIs

In DI database, approximately half of prescriptions (n=468) were recorded DDIs; the number of DDIs in the MDI and MMDI was equivalent to one-thirds of prescriptions. The findings of our study regarding the prevalence of drug interactions in prescriptions were closely proportional to those of a survey conducted in Puducherry, India, which reported that 48% of prescriptions for outpatients with hypertension contained drug interactions.<sup>9</sup> Figure 1 illustrated the frequency of DDIs in three databases.

#### 3.3.2. Frequency of pair of interacting drugs

The total number of drug interaction pairs in the three databases DI, MDI, and MMDI were 338, 194, and 188 pairs, respectively.

Approximately one-third of prescriptions with one pair of DDI were recorded in all three databases. In DI, there were 12.2% of prescriptions that had two pairs of DDIs per prescription; in MDI and MMDI, both were below 3%. The percentage of prescriptions with 4 or more pairs was quite low, it was below 1% across all 3 databases. Table 4 demonstrated frequency of number of drug interactions pairs.



**Figure 1.** The prevalence of drug interaction pairs per prescription.

**Table 4.** The prevalence of the number of drug interaction pairs per prescription.

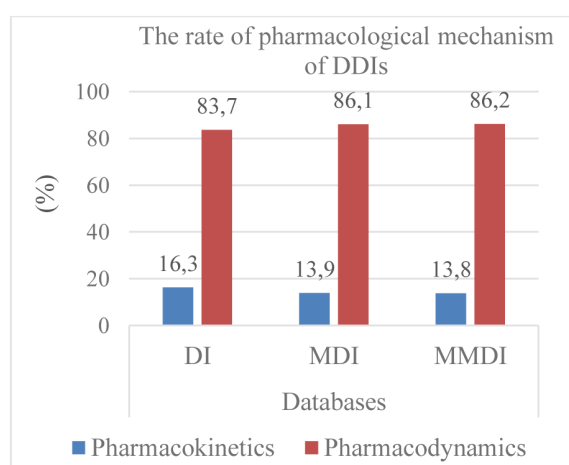
| Number of drug interaction pairs | N=468 (%)  |            |           |
|----------------------------------|------------|------------|-----------|
|                                  | DI         | MDI        | MMDI      |
| 1                                | 146 (31.2) | 142 (30.3) | 145 (31)  |
| 2                                | 57 (12.2)  | 12 (2.56)  | 12 (2.56) |
| 3                                | 12 (2.56)  | 4 (0.85)   | 3 (0.64)  |
| 4                                | 4 (0.85)   | 4 (0.85)   | 1 (0.21)  |
| 5                                | 2 (0.43)   | -          | -         |
| 6                                | -          | -          | 1 (0.21)  |
| 7                                | -          | -          | -         |
| 8                                | 2 (0.43)   | -          | -         |

#### 3.3.3. Pharmacological mechanism of DDIs

In all 3 databases, the pharmacodynamic mechanism accounted for a higher proportion than the pharmacokinetic mechanism. In which the pharmacodynamic mechanism was higher than 83% among the pairs of interacting drugs, the pharmacokinetic mechanism was lower than 17%. A study was conducted in Ethiopia that also indicated that pharmacodynamic mechanism interactions were predominant (73.1%).<sup>3</sup> The



drug interaction pairs based on pharmacodynamic mechanisms estimated for the majority, including: amlodipine-methocarbamol, amlodipine-methylprednisolone, amlodipine-metformin, and hydrochlorothiazide-metformin. Most of these drug interaction pairs involve antagonistic effects. Specifically, methylprednisolone increases salt and water retention and raises sympathetic receptor expression, leading to hypertension. Therefore, methylprednisolone can reduce the antihypertensive effect of amlodipine. Figure 2 showed the pharmacological mechanism of DDIs.

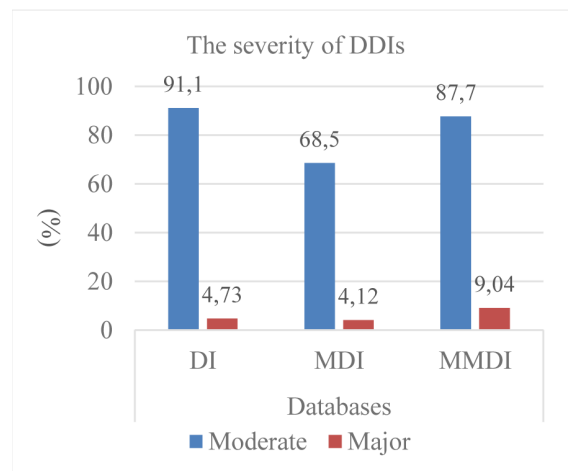


**Figure 2.** The rate of pharmacological mechanism of DDIs.

### 3.3.4. Clinically relevant DDIs

Of the 338 drug interaction pairs in DI, 324 pairs were clinically significant. There were 133 and 182 clinically relevant pairs among 194 and 188 pairs in MDI and MMDI, respectively. A study performed on cardiac patients at Ayub Teaching Hospital, Abbottabad, Pakistan, found a high incidence of clinically significant drug interactions of 84.5%.<sup>10</sup>

The most clinically relevant DDI was moderate interactions, accounting for 91.1% of all interactive pairs in DI. Similarly, moderate DDI constituted 68.5% and 87.7% in MDI and MMDI, respectively. Major interactions were 4.73%, 4.12%, and 9.04% in DI, MDI, MMDI, respectively. A study conducted among outpatients similarly demonstrated these results of our study.<sup>11</sup> Figure 3 signified the severity of clinically relevant DDIs.



**Figure 3.** The frequency of clinically relevant drug interactions.

### 3.3.5. Pharmaceutical pairs of clinically relevant DDIs

Within the DI database, three clinically relevant drug interaction pairs, all of those were moderate in severity, were identified as having the highest prevalence among the total prescriptions analyzed (n=468), namely amlodipine-methocarbamol, amlodipine-methylprednisolone, and hydrochlorothiazide-metformin, with corresponding proportions of 12.8%, 10.5%, and 8.55%, respectively. There were 3.41% of all prescriptions with major level, including the interactions involving clopidogrel (with rosuvastatin, esomeprazole, and omeprazole), irbesartan-methocarbamol, notably the drug interaction pairs between ACEIs with ARBs. Table 5 demonstrated the most frequent clinically relevant drug interaction pairs; lookup the DI website.

For the MDI database, amlodipine-metformin was the most frequent drug interaction pair (roughly 18% of all prescriptions), with moderate in severity. Major drug interactions accounted for 1.71%, including interaction involving clopidogrel (with esomeprazole and omeprazole), celecoxib (with enalapril and captopril), and ACEIs-ARBs. Table 6 presented the details of clinically relevant DDI pairs on the MDI.

According to the MMDI website, amlodipine-metformin exhibited the highest proportion of clinically significant drug interactions, accounting for nearly 18%. A similar result was observed when this interaction was analyzed using the MDI database. Hydrochlorothiazide-metformin ranked second (8.55%). In addition, both of these interactions were classified as having moderate severity. The major drug interaction pairs with 3.63% included hydrochlorothiazide (interacting with tenoxicam, etoricoxib, and etodolac), clopidogrel (interacting with esomeprazole, omeprazole, diclofenac, and etoricoxib), rosuvastatin-antacids, and ACEIs-ARBs. Table 7 provided a comprehensive overview of clinically significant DDI pairs identified on the MMDI.

Amlodipine was the drug with the highest incidence of drug interactions across all three databases, which may be attributed to its highest frequency prescription. All identified drug interactions involving amlodipine were classified as moderate in severity. For major severity, clopidogrel-PPIs (such as omeprazole, esomeprazole), and ACEIs-ARBs pairs were consistently identified across all three databases. For clopidogrel-PPIs, these interactions have been regularly discussed among the medical experts. Mechanistically, PPIs inhibit the CYP2C19 isoform, a crucial enzyme responsible for biotransformation clopidogrel into its active metabolite, thereby potentially reducing its antiplatelet efficacy. Multiple studies have reported that the concomitant use of PPIs and clopidogrel may elevate the risk of adverse cardiovascular events.<sup>12-14</sup> However, the prescription of PPIs in patients receiving

clopidogrel is sometimes necessary, especially for those at high risk of gastrointestinal bleeding (e.g., patients over 75 years of age, those with a history of gastrointestinal bleeding, those taking NSAIDs, and so forth). This combination has the benefit of preventing the risk of gastrointestinal bleeding but the disadvantage of increasing the adverse cardiovascular events. Therefore, the additional prescription of PPIs should be tailored, only prescribed when the patient is at high risk of gastrointestinal bleeding, and another drug in the PPI group, such as pantoprazole, should be chosen.<sup>15</sup> For ACEIs-ARBs, the concurrent use of both may result in increased risk of adverse events including hypotension, syncope, hyperkalemia, changes in renal function, acute renal failure. The concomitant use of those should therefore be avoided.

3.4. Development a list of clinically relevant drug interactions

The drug interaction list was developed utilizing data from three aforementioned databases. This list serves as a foundation for clinical interventions aimed at improving outcomes related to drug interactions in the future. To ensure practicality, the study included interaction pairs that achieved a consensus of at least two-thirds of the databases with a classification of moderate or those with major severity in each database. This list provides comprehensive information on drug interaction pairs, including warn patients, clinical management strategies, levels of consensus, and severity classifications. Table 8 showed a comprehensive list of clinically relevant cardiovascular drug-drug interactions across the three databases.

Table 5. Pharmaceutical pairs of clinically relevant DDI in DI database.

| Pharmaceutical pairs of clinically relevant DDI | Interactive level | Frequency | Percentage (%) |
|-------------------------------------------------|-------------------|-----------|----------------|
| Amlodipine-methocarbamol                        | Moderate          | 60        | 12.8           |
| Amlodipine-methylprednisolone                   | Moderate          | 49        | 10.5           |
| Hydrochlorothiazide-metformin                   | Moderate          | 40        | 8.55           |
| Amlodipine-atorvastatin                         | Moderate          | 14        | 2.99           |

| Pharmaceutical pairs of clinically relevant DDI | Interactive level | Frequency | Percentage (%) |
|-------------------------------------------------|-------------------|-----------|----------------|
| Amlodipine-calcium carbonate                    | Moderate          | 14        | 2.99           |
| Hydrochlorothiazide-esomeprazole                | Moderate          | 11        | 2.35           |
| Atorvastatin-esomeprazole                       | Moderate          | 10        | 2.14           |
| Atorvastatin-clopidogrel                        | Moderate          | 9         | 1.92           |
| Amlodipine-etodolac                             | Moderate          | 9         | 1.92           |
| Perindopril-metformin                           | Moderate          | 7         | 1.49           |
| Irbesartan-celecoxib                            | Moderate          | 6         | 1.28           |
| Hydrochlorothiazide-methocarbamol               | Moderate          | 5         | 1.07           |
| Hydrochlorothiazide-bisoprolol                  | Moderate          | 5         | 1.07           |
| Hydrochlorothiazide-lansoprazole                | Moderate          | 5         | 1.07           |
| Hydrochlorothiazide-magnesium hydroxide         | Moderate          | 5         | 1.07           |
| Rosuvastatin-Aluminum hydroxide                 | Moderate          | 5         | 1.07           |
| Others (*)                                      | Moderate          | 54        | 11.5           |
| Irbesartan-methocarbamol                        | Major             | 7         | 1.49           |
| Clopidogrel-rosuvastatin                        | Major             | 3         | 0.64           |
| Clopidogrel-esomeprazole                        | Major             | 3         | 0.64           |
| Clopidogrel-omeprazole                          | Major             | 1         | 0.21           |
| Irbesartan-enalapril                            | Major             | 1         | 0.21           |
| Telmisartan-perindopril                         | Major             | 1         | 0.21           |

(\*) others included drug interaction pairs that had prevalence less than 1.00 percent.

Table 6. Pharmaceutical pairs of clinically relevant DDI in MDI database.

| Pharmaceutical pairs of clinically relevant DDIs | Interactive level | Frequency | Percentage (%) |
|--------------------------------------------------|-------------------|-----------|----------------|
| Amlodipine-metformin                             | Moderate          | 84        | 17.9           |
| Perindopril-metformin                            | Moderate          | 7         | 1.50           |
| Irbesartan-celecoxib                             | Moderate          | 6         | 1.28           |
| Others (*)                                       | Moderate          | 28        | 5.98           |
| Clopidogrel-esomeprazole                         | Major             | 3         | 0.64           |
| Clopidogrel-omeprazole                           | Major             | 1         | 0.21           |
| Irbesartan-enalapril                             | Major             | 1         | 0.21           |
| Telmisartan-perindopril                          | Major             | 1         | 0.21           |
| Enalapril-celecoxib                              | Major             | 1         | 0.21           |
| Captopril-celecoxib                              | Major             | 1         | 0.21           |

(\*) others included drug interaction pairs that had prevalence less than 1.00 percent.

**Table 7.** Pharmaceutical pairs of clinically relevant DDI in MMDI database.

| Pharmaceutical pairs of clinically relevant DDIs | Interactive level | Frequency | Percentage (%) |
|--------------------------------------------------|-------------------|-----------|----------------|
| Amlodipine-metformin                             | Moderate          | 84        | 17.95          |
| Hydrochlorothiazide-metformin                    | Moderate          | 40        | 8.55           |
| Clopidogrel-atorvastatin                         | Moderate          | 9         | 1.92           |
| Perindopril-metformin                            | Moderate          | 7         | 1.50           |
| Irbesartan-celecoxib                             | Moderate          | 6         | 1.28           |
| Others (*)                                       | Moderate          | 19        | 4.06           |
| Hydrochlorothiazide-tenoxicam                    | Major             | 3         | 0.64           |
| Rosuvastatin-antacid                             | Major             | 3         | 0.64           |
| Clopidogrel-esomeprazole                         | Major             | 3         | 0.64           |
| Clopidogrel-omeprazole                           | Major             | 1         | 0.21           |
| Hydrochlorothiazide-etoricoxib                   | Major             | 2         | 0.43           |
| Hydrochlorothiazide-etodolac                     | Major             | 1         | 0.21           |
| Telmisartan-perindopril                          | Major             | 1         | 0.21           |
| Irbesartan-enalapril                             | Major             | 1         | 0.21           |
| Clopidogrel-diclofenac                           | Major             | 1         | 0.21           |
| Clopidogrel-etoricoxib                           | Major             | 1         | 0.21           |

(\*) *others included drug interaction pairs that had prevalence less than 1.00 percent.*

**Table 8.** A comprehensive list of clinically relevant of cardiovascular DDIs across the three databases.

| Drug-drug interactions                          | Databases |       |       | Warnings                                                                                                                                                                  | Clinical management                                                                                                                                                       |
|-------------------------------------------------|-----------|-------|-------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                 | DI        | MDI   | MMDI  |                                                                                                                                                                           |                                                                                                                                                                           |
| Clopidogrel-omeprazole/<br>esomeprazole         | Major     | Major | Major | Concurrent use of clopidogrel and omeprazole/esomeprazole may result in reduced clopidogrel's active metabolite exposure and reduced antiplatelet activity.               | Consider the use of alternative medications: <i>Rabeprazole</i> (given 4 hours after clopidogrel), <i>lansoprazole</i> , <i>dexlansoprazole</i> , and <i>ranitidine</i> . |
| Irbesartan-enalapril<br>Telmisartan-perindopril | Major     | Major | Major | Concurrent use of ACEIs and ARBs may result in increased risk of adverse events (ie, hypotension, syncope, hyperkalemia, changes in renal function, acute renal failure). | Concomitant use should generally be avoided; however, should coadministration be necessary, closely monitor blood pressure, renal function, and electrolytes.             |

| Drug-drug interactions          | Databases |          |          | Warnings                                                                                                                                     | Clinical management                                                                                                                                                                                                                                                                                                                                                                                                           |
|---------------------------------|-----------|----------|----------|----------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                 | DI        | MDI      | MMDI     |                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                               |
| Hydrochlorothiazide-etodolac    | Moderate  | Moderate | Major    | Concurrent use of NSAIDs and thiazide diuretics may result in reduced diuretic effectiveness and possible nephrotoxicity.                    | During concomitant use of NSAIDs and diuretics, monitor for signs of worsening renal function and assure diuretic efficacy, including appropriate effects on blood pressure.                                                                                                                                                                                                                                                  |
| Clopidogrel-diclofenac          | Moderate  | Moderate | Major    | Concurrent use of antiplatelet agents and NSAIDs may result in an increased risk of bleeding.                                                | Use caution and monitor the patient for signs of bleeding with concomitant use of antiplatelet agents and NSAIDs.                                                                                                                                                                                                                                                                                                             |
| Rosuvastatin-aluminum hydroxide | Moderate  | Moderate | Major    | Concurrent use of rosuvastatin and antacids may result in reduced rosuvastatin exposure and reduced efficacy of rosuvastatin.                | In patients taking antacids, administer rosuvastatin at least 2 hours after the antacid.                                                                                                                                                                                                                                                                                                                                      |
| Captopril/enalapril-celecoxib   | Moderate  | Major    | Moderate | Concurrent use of ACEIs/ARBs and NSAIDs may result in reduced antihypertensive effect and renal dysfunction and/or increased blood pressure. | When concomitant use is required, determine the need to monitor renal function at initiation of treatment, monitor for antihypertensive efficacy, and assess renal function periodically for signs of renal deterioration or failure, especially in patients who are elderly, during treatment initiation, in the volume-depleted, or those with preexisting renal dysfunction. Ensure that patients are adequately hydrated. |
| Irbesartan-celecoxib/etodolac   | Moderate  | Moderate | Moderate |                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                               |
| Enalapril/perindopril-metformin | Moderate  | Moderate | Moderate | Concurrent use of ACEIs and antidiabetic agents may result in an increased risk of hypoglycemia.                                             | If concomitant use is required, conduct more frequent glucose monitoring, both during treatment and after withdrawal of an ACE inhibitor.                                                                                                                                                                                                                                                                                     |



| Drug-drug interactions         | Databases |          |          | Warnings                                                                                                                                                                                                               | Clinical management                                                                                                                                                       |
|--------------------------------|-----------|----------|----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                | DI        | MDI      | MMDI     |                                                                                                                                                                                                                        |                                                                                                                                                                           |
| Atenolol-diclofenac            | Moderate  | Moderate | Moderate | Concurrent use of beta blocker and NSAIDs may result in reduced antihypertensive effect.                                                                                                                               | Monitor blood pressure when coadministration is required.                                                                                                                 |
| Irbesartan-methocarbamol       | Major     | Moderate | None     | Concurrent use of irbesartan and methocarbamol may result in increased hypotension.                                                                                                                                    | Close monitoring for development of hypotension is advised during coadministration of these agents                                                                        |
| Clopidogrel-pantoprazole       | Moderate  | Moderate | None     | Concurrent use of clopidogrel and pantoprazole may result in reduced clopidogrel's active metabolite exposure and reduced antiplatelet activity.                                                                       | Consider the use of alternative medications: <i>Rabeprazole</i> (given 4 hours after clopidogrel), <i>lansoprazole</i> , <i>dexlansoprazole</i> , and <i>ranitidine</i> . |
| Bisoprolol-amlodipine          | Moderate  | Moderate | None     | Additive reductions in heart rate, cardiac conduction, and cardiac contractility may occur when CCBs are used concomitantly with beta blockers, particularly in patients with ventricular or conduction abnormalities. | Close clinical monitoring of patient hemodynamic response and tolerance                                                                                                   |
| Bisoprolol-furosemide          | Moderate  | Moderate | None     | Diuretics and beta-blockers may increase the risk of hyperglycemia and hypertriglyceridemia in some patients.                                                                                                          | Monitoring of serum potassium levels, blood pressure, and blood glucose is recommended during coadministration.                                                           |
| Hydrochlorothiazide-furosemide | Moderate  | Moderate | None     | The combination of a thiazide and loop diuretic may produce additive or synergistic effects on diuresis and excretion of electrolytes including sodium, potassium, magnesium, and chloride.                            | Dosages should be titrated slowly and carefully, and electrolytes, fluid status, blood pressure, and renal function should be monitored regularly.                        |

| Drug-drug interactions          | Databases |          |          | Warnings                                                                                                                                                                             | Clinical management                                                                                                                                                                                                                                                                                                                                                                                                           |
|---------------------------------|-----------|----------|----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                 | DI        | MDI      | MMDI     |                                                                                                                                                                                      |                                                                                                                                                                                                                                                                                                                                                                                                                               |
| Hydrochlorothiazide-perindopril | Moderate  | None     | Moderate | Concurrent use of ACEI and thiazide diuretics may result in reduction of blood pressure.                                                                                             | Before starting ACEI therapy, decreasing or discontinuing the diuretic or increasing salt intake may minimize the risk of hypotensive effects. If these measures are not possible, reduce the ACE inhibitor starting dose.                                                                                                                                                                                                    |
| Telmisartan-etodolac            | Moderate  | None     | Moderate | Concurrent use of ACEIs/ARBs and NSAIDs may result in reduced antihypertensive effect and renal dysfunction and/or increased blood pressure.                                         | When concomitant use is required, determine the need to monitor renal function at initiation of treatment, monitor for antihypertensive efficacy, and assess renal function periodically for signs of renal deterioration or failure, especially in patients who are elderly, during treatment initiation, in the volume-depleted, or those with preexisting renal dysfunction. Ensure that patients are adequately hydrated. |
| Clopidogrel-atorvastatin        | Moderate  | None     | Moderate | Concurrent use of clopidogrel and CYP3A4 metabolized statins may result in decreased formation of clopidogrel active metabolites resulting in high on-treatment platelet reactivity. | If a patient develops high on-treatment platelet reactivity during treatment with clopidogrel and a statin metabolized by CYP3A4 (ie, atorvastatin, lovastatin, or simvastatin), discontinue the statin and substitute a statin that is not metabolized by CYP3A4 (ie, pravastatin or rosuvastatin).                                                                                                                          |
| Amlodipin-metformin             | None      | Moderate | Moderate | Concurrent use of metformin and CCBs may result in an increased risk of hyperglycemia and potential loss of glycemic control.                                                        | Observe the patients for loss of blood glucose control when such drugs are administered to a patient receiving metformin. When such drugs are withdrawn from a patient receiving metformin, the patient should be observed closely for hypoglycemia.                                                                                                                                                                          |

#### 4. CONCLUSION

The study has built a quietly comprehensive list of clinically significant drug interactions using three databases, which will be the foundation for future clinical interventions aimed at minimizing the prevalent drug interactions, especially to prevent the occurrence of major drug interactions. In the future, we will intervene clinically by implementing workshops and then re-evaluate the effectiveness of the intervention in subsequent studies.

This is a retrospective cross-sectional study, which included prescriptions collected at a single time point, without taking into account laboratory data or clinical interpretations by physicians. These limitations may have led to overestimation of the findings.

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## Phát triển và đặc trưng vật liệu composite bentonite - than hoạt tính từ vỏ trấu nhằm tăng cường khả năng hấp phụ khí $H_2S$

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### TÓM TẮT

Hydro sulfua ( $H_2S$ ) là tạp chất chính trong biogas cần được loại bỏ hiệu quả để ngăn ngừa ăn mòn và ô nhiễm môi trường. Nghiên cứu này đánh giá quá trình tổng hợp và khả năng hấp phụ  $H_2S$  của vật liệu composite giữa bentonite và carbon hoạt tính từ vỏ trấu (SRH@Ben). Các vật liệu composite được chế tạo dưới các điều kiện hoạt hóa nhiệt và hóa học khác nhau, đồng thời được phân tích đặc trưng về cấu trúc, hình thái và thành phần hóa học bằng phương pháp hiển vi quang học, kính hiển vi điện tử quét phát xạ trường (FE-SEM), phổ tán xạ năng lượng tia X (EDS) và nhiễu xạ tia X (XRD). Kết quả cho thấy nhiệt độ hoạt hóa và hàm lượng vỏ trấu ảnh hưởng đáng kể đến khả năng hấp phụ, trong đó mẫu tối ưu (SRH@Ben 50%-450°C) đạt dung lượng hấp phụ  $H_2S$  là 2,23 mg/g. Quá trình hoạt hóa hóa học bằng KOH tiếp tục cải thiện dung lượng hấp phụ lên 2,34 mg/g nhờ tăng cường độ xốp và nhóm chức bề mặt. Phân tích so sánh cho thấy vật liệu SRH@Ben có hiệu suất hấp phụ vượt trội so với vật liệu hấp phụ gốc carbon thương mại (1,18 mg/g) và đạt hiệu quả tương đương với vật liệu gốc oxit sắt (2,46 mg/g). Kết quả này khẳng định tiềm năng của SRH@Ben như một giải pháp hấp phụ  $H_2S$  chi phí thấp và bền vững cho quá trình làm sạch biogas.

**Từ khóa:**  $H_2S$ , bentonit, trấu, vật liệu composite, khả năng hấp phụ.

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# Development and characterization of bentonite - activated carbon composite from rice husk for enhanced H<sub>2</sub>S gas adsorption

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## ABSTRACT

Hydrogen sulfide (H<sub>2</sub>S) is a major impurity in biogas that must be efficiently removed to prevent corrosion and environmental pollution. This study investigates the synthesis and adsorption performance of bentonite-rice husk activated carbon (SRH@Ben) composites for H<sub>2</sub>S removal. The composites were prepared under varying thermal and chemical activation conditions, and their structural, morphological, and chemical properties were characterized using optical microscopy, field-emission scanning electron microscopy (FE-SEM), Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray diffraction (XRD). The results indicate that both activation temperature and rice husk content significantly influence adsorption capacity, with the optimal composite (SRH@Ben 50%-450°C) achieving an H<sub>2</sub>S adsorption capacity of 2.23 mg/g. Further chemical activation with KOH enhanced the adsorption capacity to 2.34 mg/g due to increased porosity and surface functionality. Comparative analysis demonstrated that SRH@Ben composites outperformed commercial carbon-based adsorbents (1.18 mg/g) and exhibited comparable efficiency to iron oxide-based materials (2.46 mg/g). These findings highlight the potential of SRH@Ben composites as a cost-effective and sustainable alternative for biogas purification.

**Keywords:** *H<sub>2</sub>S, bentonite, rice husk, composites, adsorption capacity.*

## 1. INTRODUCTION

Hydrogen sulfide (H<sub>2</sub>S) is a major contaminant in biogas, posing serious environmental and operational challenges. Even at low concentrations, H<sub>2</sub>S is highly toxic and corrosive, leading to severe damage to pipelines, gas storage systems, and energy conversion units such as internal combustion engines and fuel cells.<sup>1</sup> Moreover, the emission of H<sub>2</sub>S contributes to air pollution and acid rain formation, necessitating its effective removal from biogas before utilization. Various H<sub>2</sub>S removal techniques

have been developed, including chemical scrubbing, catalytic oxidation, and biological filtration. However, these methods often suffer from high operational costs, complex maintenance, and secondary waste generation. Adsorption-based methods, particularly those utilizing low-cost, biomass-derived materials, have gained significant attention due to their cost-effectiveness, ease of operation, and environmental sustainability.<sup>2</sup> Activated carbon (AC) is widely employed in H<sub>2</sub>S adsorption due to its high surface area, well-developed porosity, and tunable surface chemistry.<sup>3</sup> Among

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biomass-based precursors, rice husk-derived activated carbon (RHAC) is of particular interest due to its abundance, renewability, and ease of modification.

Rice husk-derived activated carbon has demonstrated excellent adsorption properties, attributed to its unique pore structure and ease of surface modification.<sup>4</sup> However, while activated carbon offers significant adsorption potential, its efficiency can be further improved by incorporating other materials that provide additional functional sites and structural stability. In one study, biochar produced from rice hulls through pyrolysis at 500°C exhibited a notable H<sub>2</sub>S adsorption capacity of 382.7 mg/g. The adsorption kinetics aligned with the Yoon-Nelson model, suggesting a consistent mass transfer mechanism during the adsorption process.<sup>5</sup> Another investigation synthesized a triethylenetetramine (TETA)-grafted activated rice husk ash (TRI-A-RHA) to assess its efficacy in removing CO<sub>2</sub> and H<sub>2</sub>S from biogas. The modified material demonstrated adsorption capacities of approximately 0.34 mmol/g for CO<sub>2</sub> and 0.14 mmol/g for H<sub>2</sub>S at room temperature, attributed to its high surface area and effective amine functionalization.<sup>6</sup> These studies underscore the potential of rice husk-derived activated carbon as a cost-effective and efficient material for H<sub>2</sub>S adsorption in biogas applications. Modifications such as amine grafting, hydrogel composite formation, and optimization of pyrolysis conditions can significantly enhance adsorption performance, offering valuable insights for developing sustainable biogas purification technologies.

Bentonite, a naturally occurring clay mineral, has been extensively studied for gas and liquid adsorption due to its high cation exchange capacity, layered structure, and strong affinity for polar molecules.<sup>7,8</sup> Bentonite based materials have been extensively studied for their potential in adsorbing hydrogen sulfide (H<sub>2</sub>S) from biogas. Recent research has focused on enhancing the adsorption capacity of bentonite through various modifications. One study employed molecular simulations to investigate the adsorption of H<sub>2</sub>S

onto bentonite doped with cations such as Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>. The findings indicated that these doped bentonites exhibit selectivity towards H<sub>2</sub>S, suggesting their suitability for natural gas sweetening applications.<sup>8</sup> Another investigation explored the modification of bentonite using carbide slag, followed by high-temperature activation. The results demonstrated that the carbide slag-modified bentonite achieved a breakthrough adsorption capacity of 0.92 mg/g, significantly outperforming unmodified bentonite, which had a capacity of 0.06 mg/g. The enhanced performance is attributed to the active groups formed upon introducing Ca(OH)<sub>2</sub> from the carbide slag.<sup>9</sup> Collectively, these studies highlight that doping bentonite with specific cations or modifying it with industrial by-products like carbide slag can substantially improve its H<sub>2</sub>S adsorption capabilities, making it a promising material for biogas purification.

Rice husk-derived activated carbon (RHAC) and bentonite are promising, cost-effective, and sustainable adsorbents for H<sub>2</sub>S removal. RHAC provides high surface area and porosity, while bentonite offers structural stability and ion-exchange capacity. However, both materials have limitations. RHAC suffers from limited chemical stability, low affinity for acidic gases, rapid saturation, poor regeneration, moisture sensitivity, and sulfur deposition, reducing its long-term effectiveness. Similarly, bentonite has low surface area, limited adsorption capacity, susceptibility to moisture, mechanical instability, slow kinetics, and weak H<sub>2</sub>S affinity, requiring modifications for improved performance.

To overcome these limitations, researchers have developed bentonite-activated carbon composites, which enhance adsorption capacity, improve mechanical strength, and reduce moisture sensitivity by combining the high porosity of activated carbon with the structural stability of bentonite.<sup>10</sup> Moreover, the modification of these materials through chemical activation or metal impregnation can significantly improve their selectivity and capacity for H<sub>2</sub>S removal.<sup>10,11</sup> Investigating the adsorption behavior of

H<sub>2</sub>S on this composite can provide valuable insights into optimizing adsorbent performance for practical applications in air purification, biogas upgrading, and industrial gas treatment. Therefore, this study aims to: (1) Synthesize and characterize bentonite–rice husk activated carbon (SRH@Ben) composites under varying thermal and chemical activation conditions; (2) Evaluate their H<sub>2</sub>S adsorption capacity through breakthrough curve analysis and (3) Compare their performance with commercial adsorbents to assess their practical applicability. The findings of this research will provide valuable insights into the development of cost-effective and environmentally sustainable adsorbents for biogas purification and industrial gas treatment applications.

## 2. EXPERIMENTAL

### 2.1. Materials

Commercial bentonite powder (Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>·H<sub>2</sub>O), sourced from India, was procured from Viet My Binh Dinh Co., Ltd. (655 Hung Vuong, Nhon Phu, Quy Nhon, Binh Dinh, Vietnam). Potassium hydroxide (KOH, 85 %), manufactured by Xilong, was imported from China. Finely milled rice husk, with a particle size of less than 1 mm, was obtained from a local rice milling facility located in Quang Hy Hamlet, Phuoc Loc Commune, Tuy Phuoc District, Binh Dinh, Vietnam. In addition, large rice husks (1–3 mm particle size) and rice bran were also collected from the same facility for comparative purposes.

### 2.2. Material fabrication

A total of 350 mL of distilled water was introduced into 200 g of a bentonite-milled rice husk mixture, with the proportions of the components varied systematically. The mixture was homogenized through continuous mechanical mixing for 15 minutes. The resulting bentonite/rice husk composite was subsequently molded into cylindrical pellets, each measuring approximately 6 mm in diameter and 1.5 cm in height. To evaluate the compressive strength of the SRH@Ben composite pellets, a uniaxial compression test was conducted using a manual cylindrical piston with a 2 cm diameter. The

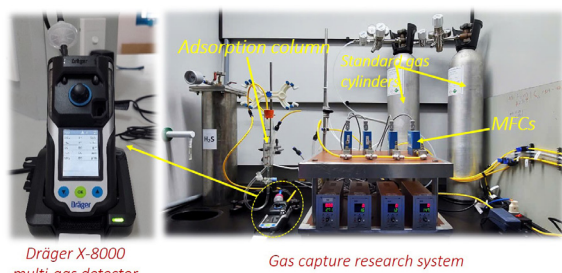
pellets, shaped as cylinders with a diameter of 0.6 cm and a height of 1.5 cm, were placed centrally beneath the piston. The applied force was gradually increased until a compressive stress of approximately 2 MPa was reached, which is sufficient for assessing the mechanical integrity of the pellet without inducing premature fracture. These pellets were initially air-dried under natural sunlight for a period of 2 days and 3 nights, followed by oven-drying at 90 °C for 12 hours. The dried composite was then subjected to anaerobic pyrolysis at 450 °C for 1.5 hours using a loosely covered ceramic crucible, which allowed the release of gaseous byproducts and prevented pressure buildup during the carbonization process. The pyrolysis was conducted in a Nabertherm LT3/12/B180 muffle furnace with a heating rate of 15 °C/min. Notably, no inert carrier gas such as nitrogen (N<sub>2</sub>) or vacuum system was employed, in order to reduce operational complexity and cost. The final product was designated as SRH@Ben (SRH = Small Rice Husk, Ben = Bentonite). Following the same procedure, composite materials were fabricated using bentonite combined with larger rice husk (1–3 mm particle size) and rice bran. These samples were labeled as LRH@Ben and Bran@Ben, respectively. To optimize the H<sub>2</sub>S adsorption capacity, the SRH@Ben composite was further activated by treatment with 0.15 M KOH at 90 °C for 1 hour. After activation, the material was dried at 90 °C and underwent anaerobic pyrolysis at 650 °C for 30 minutes.

### 2.3. Characterization and gas adsorption measurements

The surface morphology, chemical composition, and structural properties of the synthesized materials were comprehensively characterized using optical imaging, field-emission scanning electron microscopy (FE-SEM; HITACHI S-4800), Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray diffraction (XRD; Bruker D2, equipped with Cu K $\alpha$  radiation). A schematic representation of the experimental setup for H<sub>2</sub>S gas adsorption measurements is provided in Figure 1. The H<sub>2</sub>S gas concentration was precisely regulated using mass flow controllers



(MFCs), with a certified  $\text{H}_2\text{S}$  gas cylinder (10,000 ppm, diluted in nitrogen) and high-purity  $\text{N}_2$  (99.99 %) serving as the carrier gas. The  $\text{H}_2\text{S}$  concentration was quantified before and after passage through the filtration column using a Dräger X-8000 multi-gas detector.



**Figure 1.** Experimental setup for  $\text{H}_2\text{S}$  gas adsorption study. The system comprises standard gas cylinders for controlled gas supply, mass flow controllers (MFCs) for precise gas flow regulation, an adsorption column containing the tested sorbents, and a Dräger X-8000 multi-gas detector for real-time monitoring of  $\text{H}_2\text{S}$  concentration at the outlet.

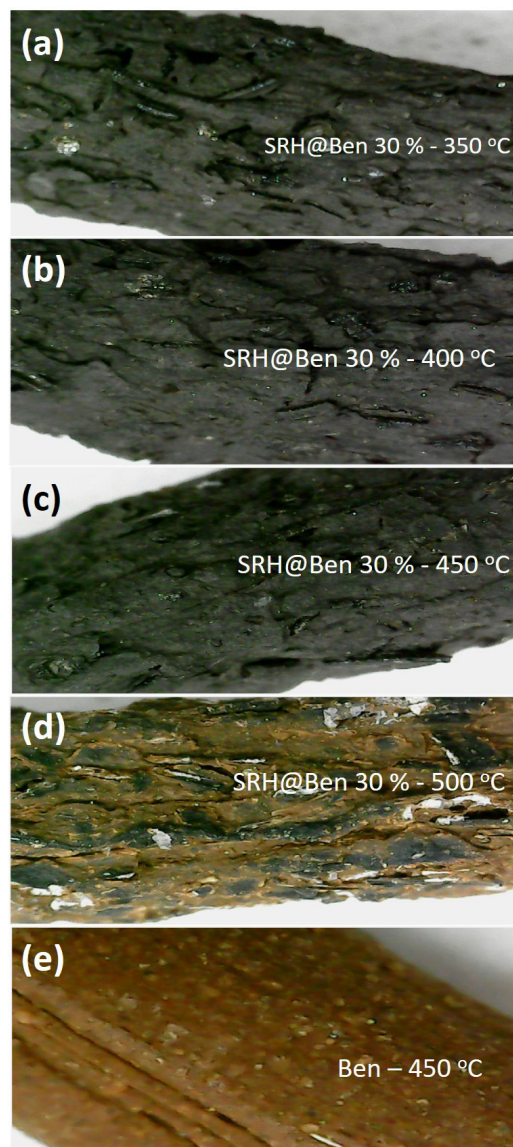
### 3. RESULTS

#### 3.1. Morphology, structure, and chemical composition of composite materials

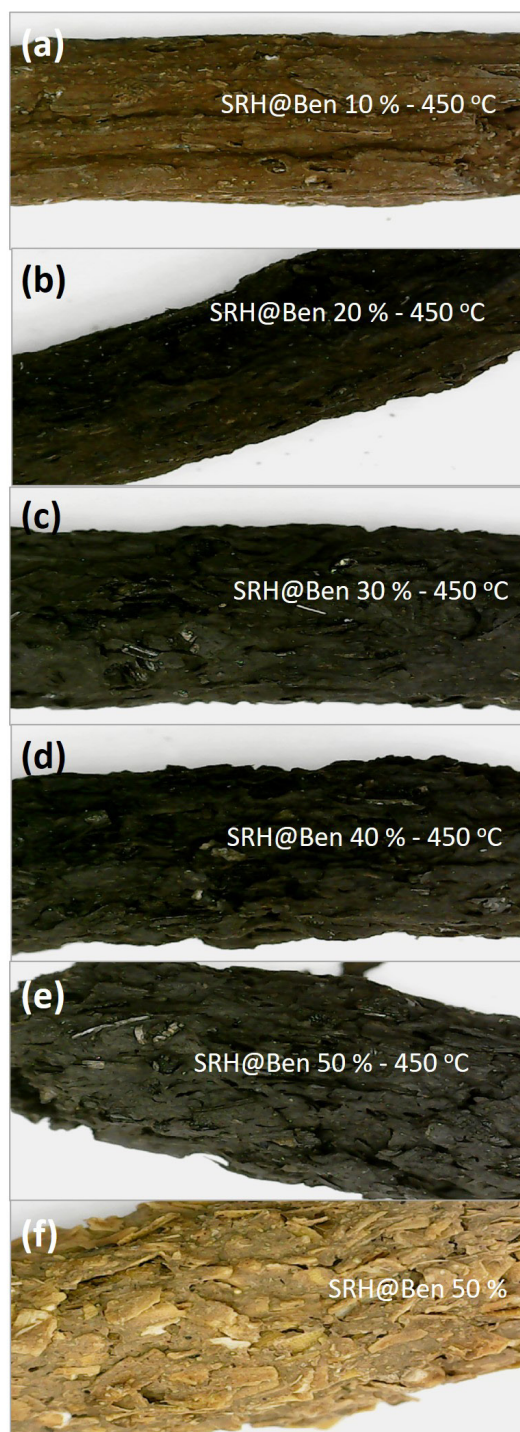
The optical images (Figure 2 and 3) provide a comparative analysis of SRH@Ben composites with varying rice husk (SRH) content subjected to different thermal treatments under anaerobic conditions. In the Figure 2, samples containing 30 % SRH were thermally treated at 400 °C, 450 °C, and 500 °C. Notably, the material undergoes significant morphological and color changes as the temperature increases.

Figure 2a shows the surface morphology of the SRH@Ben 30 % composite material after anaerobic pyrolysis at 350 °C. The sample exhibits a relatively rough surface with minimal shrinkage or structural damage, indicating that the temperature was sufficient to initiate carbonization without causing thermal degradation. The dark color suggests the beginning stages of carbon formation. However, the structure remains partially preserved, and no significant cracking or pore development is observed at this stage, implying that further increases in temperature may enhance the

porosity and carbon content of the material. The sample treated at 400 °C (Figure 2b) exhibits a dark and compact appearance, while the sample treated at 450 °C (Figure 2c) retains a similar structure but displays a more developed texture. At 500 °C (Figure 2d), the surface becomes rougher and more porous, indicating potential structural degradation at elevated temperatures. In contrast, the pure bentonite sample treated at 450 °C (Figure 2e) demonstrates a distinctly different morphology, characterized by a lighter color and a denser structure.



**Figure 2.** Optical images of SRH@Ben composites with 30 % rice husk content treated under anaerobic conditions at different temperatures: (a) 350 °C (b) 400 °C, (c) 450 °C, (d) 500 °C. Image (e) shows the pure bentonite sample treated at 450 °C.



**Figure 3.** Optical images of SRH@Ben composites with varying rice husk content treated at 450 °C: (a) 10 %, (b) 20 %, (c) 30 %, (d) 40 %, (e) 50 %. Image (f) represents the SRH@Ben 50 % sample before thermal treatment.

Figure 3 illustrates the effect of SRH content on the composite structure at a fixed temperature of 450 °C. As the SRH ratio increases from 10 % to 50 % (Figures 3a-e), the

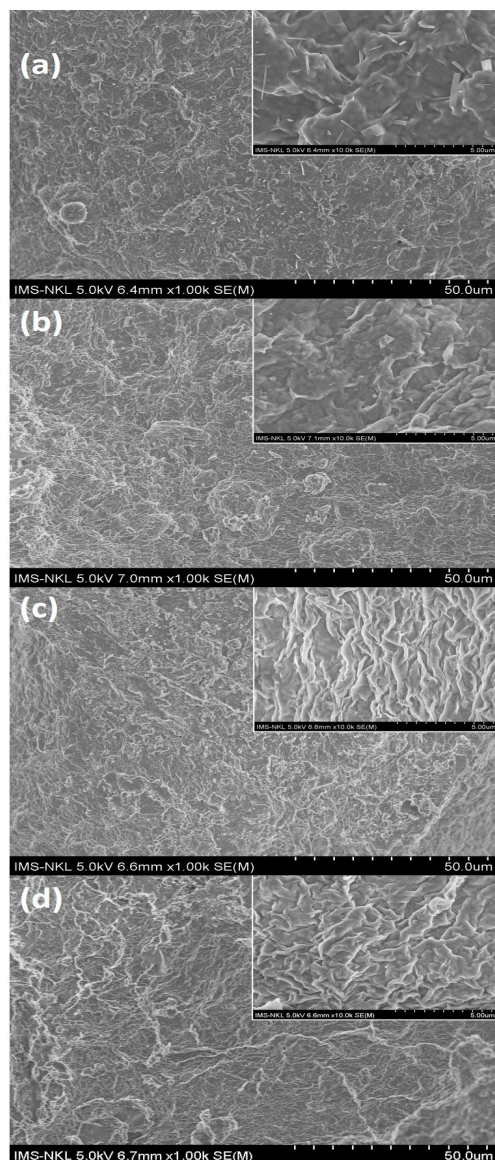
material progressively darkens and develops a more compact texture, likely due to enhanced carbonization. The SRH@Ben 50 % sample treated at 450 °C (Figure 3e) exhibits the most uniform and dense structure, consistent with its highest H<sub>2</sub>S adsorption efficiency observed in the study. Importantly, the non-thermally treated SRH@Ben 50 % sample (Figure 3f) appears significantly lighter in color with a more fibrous structure, underscoring the substantial transformation induced by thermal treatment. These observations demonstrate that both the thermal treatment temperature and the SRH content critically influence the final morphology and textural properties of the composite materials, which in turn directly affect their adsorption performance.

The SEM images provide a comparative analysis of the morphological evolution of SRH@Ben composites subjected to different thermal treatments under anaerobic conditions. At 350 °C (Figure 4a), the material exhibits a relatively compact and smooth surface with minimal porosity, indicating that thermal decomposition has not yet progressed significantly. As the temperature increases to 400 °C (Figure 4b), surface roughness becomes more pronounced, accompanied by the emergence of microvoids, suggesting the onset of structural modification and partial volatilization of organic components.

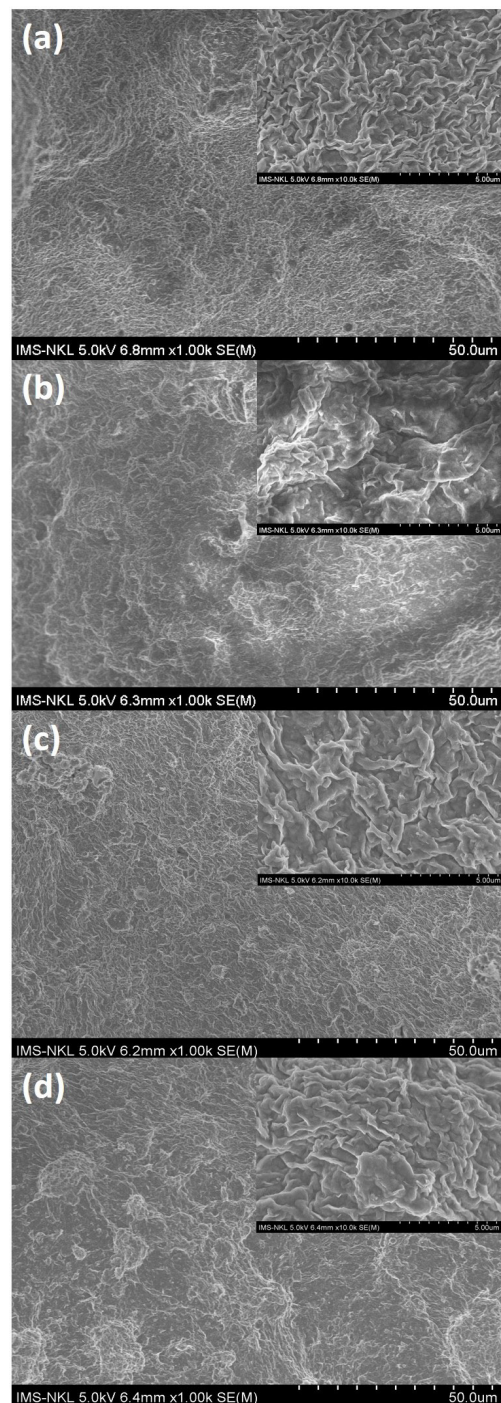
At 450 °C (Figure 4c), the material displays a well-developed porous structure with enhanced surface roughness, indicative of effective carbonization and increased surface area. The formation of interconnected pore networks at this temperature likely facilitates improved adsorption capacity, making this condition optimal for gas adsorption applications. However, at 500 °C (Figure 4d), noticeable structural degradation is observed, with the material exhibiting a more fragmented and brittle morphology. The excessive thermal treatment may have led to the collapse of microporous structures and potential carbon burnout, reducing its mechanical integrity and adsorption efficiency.



The progressive morphological transformations observed in the SEM images highlight the critical role of thermal treatment in tailoring the physicochemical properties of the composite. 450 °C appears to be the optimal temperature, striking a balance between structural stability and porosity enhancement, thereby maximizing the material's suitability for gas adsorption applications such as H<sub>2</sub>S removal. Conversely, excessive heating at 500 °C may lead to undesirable material degradation, compromising its functional performance.



**Figure 4.** SEM images of SRH@Ben composites with 30 % rice husk treated at different temperatures: (a) 350 °C, (b) 400 °C, (c) 450 °C, and (d) 500 °C. The inset images display higher magnification views ( $\times 10.0k$ ) of each sample.



**Figure 5.** SEM images of SRH@Ben composites treated at 450 °C with varying rice husk contents: (a) 10 %, (b) 20 %, (c) 40 %, and (d) 50 %. The inset images (magnified at  $\times 10.0k$ ) provide a closer view of the surface morphology.

The SEM images illustrate the influence of rice husk content on the morphological characteristics of SRH@Ben composites pyrolyzed at 450 °C. At a low rice husk content (10 %, Figure 5a), the surface appears relatively

compact with limited porosity. The material maintains a somewhat dense structure, indicative of incomplete structural transformation and insufficient development of porous networks.

As the rice husk content increases to 20 % (Figure 5b), a noticeable change in morphology is observed, with the emergence of microvoids and enhanced surface roughness. This suggests a higher degree of decomposition and carbonization, leading to an increase in available adsorption sites. At 40 % rice husk content (Figure 5c), the porous structure becomes more pronounced, characterized by a well-interconnected network of micro- and mesopores. This transformation significantly enhances the material's surface area, which is beneficial for adsorption-based applications, particularly in gas capture.

At the highest rice husk content of 50 % (Figure 5d), the composite exhibits the most developed porous structure, with an intricate network of wrinkles and voids. The increased textural complexity suggests an optimal balance between carbonization and porosity formation, enhancing the material's adsorption potential. However, excessive porosity may compromise mechanical stability, making the material more fragile under certain operational conditions.

Overall, the 40-50 % rice husk content range appears to be optimal for achieving a well-structured porous network while maintaining material integrity. This suggests that a higher proportion of biomass precursor facilitates effective porosity development, thereby improving the composite's adsorption capacity, particularly for applications such as  $H_2S$  gas removal.

The EDS results in Figure 6 provide insights into the elemental composition of SRH@Ben composites and its variation with processing conditions. In Figure 6a, the elemental composition of SRH@Ben 30 % composite subjected to anaerobic pyrolysis at 350 °C, 400 °C, 450 °C, and 500 °C is shown. The major detected elements include C, O, N,

Al, Si, Na, Mg, Ca, and Fe. Figure 6b illustrates the effect of rice husk content (10 %, 20 %, 30 %, 40 %, and 50 %) on the elemental composition of SRH@Ben composites pyrolyzed at 450 °C. To enhance the reliability of the analysis, EDS measurements were conducted at three distinct locations on each sample. The average atomic percentages of key elements (C, O, N, Al, and Si) were calculated and are presented in Figures 6c and 6d.

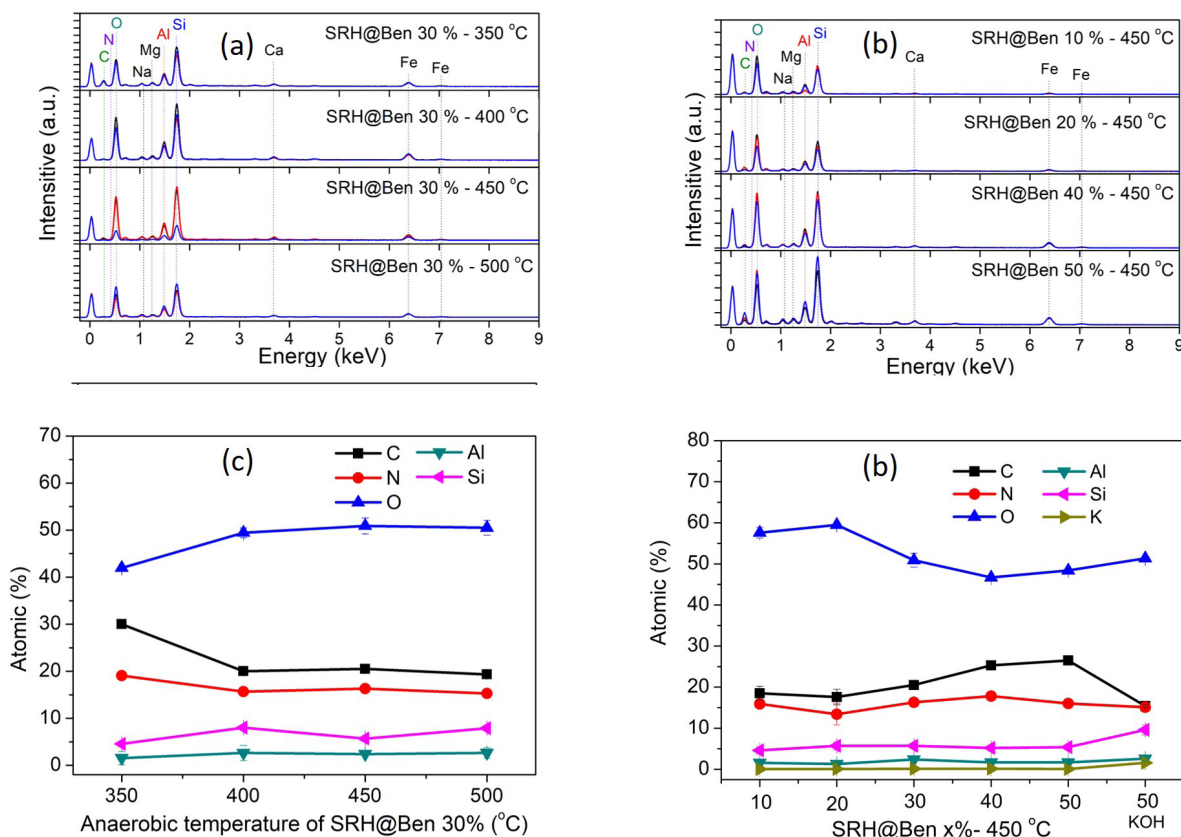
In Figure 6c, the elemental composition of SRH@Ben (30 % rice husk) is analyzed as a function of carbonization temperature (350-500 °C). Oxygen (O) remains the dominant element, with its content increasing slightly with temperature before stabilizing around 450 °C. This trend suggests the progressive oxidation of carbonaceous species or the retention of oxygenated functional groups. In contrast, the carbon (C) content decreases slightly with increasing temperature, likely due to thermal decomposition and gasification processes. The nitrogen (N) content remains relatively stable, indicating minimal nitrogen loss within the investigated temperature range. Silicon (Si) and aluminum (Al), originating from the bentonite structure, are present in minor quantities, with their concentrations remaining nearly unchanged across the temperature range. These results suggest that 450 °C is an optimal carbonization temperature, as it maintains a balanced elemental composition favorable for adsorption applications.

Figure 6d examines the influence of varying rice husk content (10-50 %) at a fixed carbonization temperature of 450 °C. The oxygen content shows a decreasing trend as the rice husk percentage increases, which can be attributed to the higher degree of carbonization of organic matter. Conversely, the carbon content increases with higher rice husk content, consistent with the expectation that a greater amount of organic precursor leads to enhanced carbon deposition. The concentrations of Si and Al remain relatively stable, confirming that the bentonite matrix is not significantly affected



by the rice husk content. The final sample in Figure 4d represents SRH@Ben with 50 % rice husk, which was activated using a 0.15 M KOH solution followed by thermal treatment at 650 °C for 30 minutes. This sample exhibits a notable change in elemental composition, with a significant increase in potassium (K) content. The higher K concentration indicates the successful incorporation of KOH-derived residues into

the material, which can enhance porosity and catalytic properties. Additionally, the oxygen content increases slightly compared to non-activated samples, likely due to the formation of oxygen-containing surface functionalities during activation. The enhanced porosity and modified surface chemistry of this KOH-activated sample suggest its potential for improved adsorption and catalytic performance.



**Figure 6.** EDS spectra and atomic composition of SRH@Ben composites: (a) EDS spectra of SRH@Ben 30 % pyrolyzed at different temperatures (350, 400, 450, and 500 °C), (b) EDS spectra of SRH@Ben composites with varying rice husk content (10-50 wt%) pyrolyzed at 450 °C, (c) Atomic percentages of main elements (C, N, O, Al, Si) as a function of pyrolysis temperature for SRH@Ben 30 % and (d) Atomic percentages of elements (C, N, O, Al, Si, K) as a function of rice husk content for composites pyrolyzed at 450 °C.

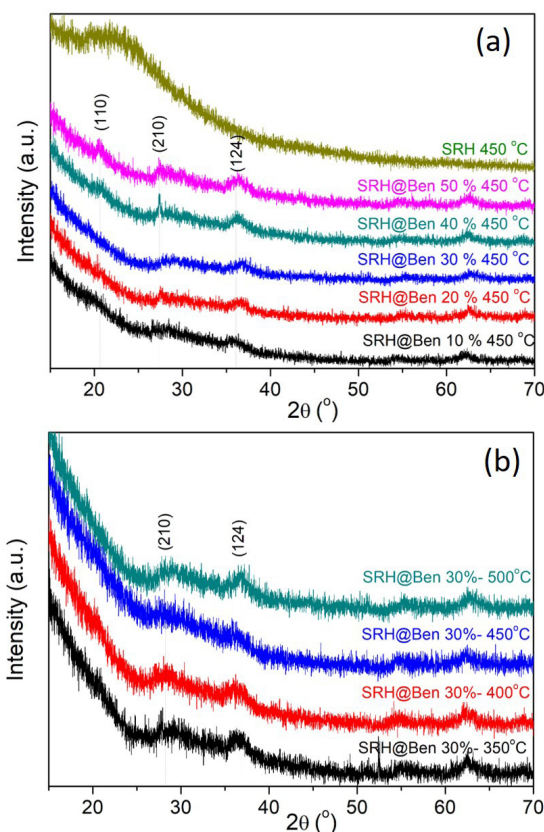
Overall, these results demonstrate the significant influence of carbonization temperature, rice husk content, and chemical activation on the structural and elemental composition of SRH@Ben composites. These parameters can be systematically tailored to optimize the material for specific adsorption or catalytic applications.

The XRD patterns presented in Figure 7 provide insights into the structural evolution

of SRH@Ben composites as a function of rice husk content and carbonization temperature. Figure 7a illustrates the XRD spectra of SRH@Ben samples with varying rice husk content (10-50 %) carbonized at 450 °C. The broad diffraction humps centered around 20-30° (2θ) indicate the presence of amorphous silica and/or carbon, primarily derived from the rice husk phase. As the rice husk content increases, the intensity of this amorphous peak becomes more

pronounced, suggesting a higher concentration of silica within the composite. Notably, the absence of sharp crystalline peaks in the XRD patterns confirms the predominantly amorphous nature of the materials. Minor variations in peak intensity across different compositions indicate that the structural integrity of the bentonite matrix remains largely unaffected by the increasing rice husk content. The characteristic peaks at diffraction angle,  $2\theta = 20.7^\circ$ ,  $26.5^\circ$ ,  $36.3^\circ$  corresponds to the planes (110), (210) and (124) of the bentonite material. These XRD patterns are in good agreement with the standard JCPDS file (card no.01-088-0891).

Figure 7b depicts the XRD patterns of SRH@Ben composites with 30 % rice husk, subjected to anaerobic treatment at temperatures ranging from  $350^\circ\text{C}$  to  $500^\circ\text{C}$ . A progressive increase in the intensity of the broad peak around  $20\text{--}30^\circ$  ( $2\theta$ ) is observed with rising temperature, further confirming the presence of amorphous silica and/or carbon structures. The gradual disappearance of minor crystalline features at higher temperatures suggests enhanced decomposition of organic matter and structural reorganization of silica phases. Despite these changes, the overall amorphous nature of the samples remains consistent, underscoring the thermal stability of the composite framework. These results demonstrate that SRH@Ben composites exhibit predominantly amorphous characteristics due to the incorporation of rice husk-derived silica and bentonite. The extent of amorphous phase formation is influenced by both rice husk content and processing temperature, with higher rice husk content and elevated temperatures promoting increased silica enrichment. Importantly, the structural integrity of the bentonite matrix remains intact, making these composites promising candidates for adsorption and catalytic applications that require high-surface-area amorphous materials. The characteristic peaks at diffraction angle,  $2\theta = 26.5^\circ$ ,  $36.3^\circ$  corresponds to the planes (210) and (124) of the bentonite material.

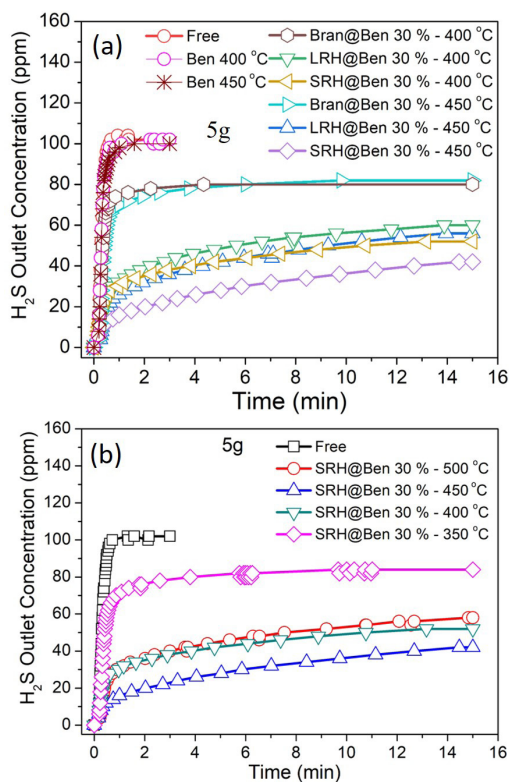


**Figure 7.** XRD patterns of SRH@Ben composites: (a) Effect of rice husk content (10-50 %) at  $450^\circ\text{C}$ ; (b) Effect of carbonization temperature ( $350\text{--}500^\circ\text{C}$ ) on SRH@Ben with 30 % rice husk.

The  $\text{H}_2\text{S}$  adsorption performance of the synthesized materials is systematically evaluated in Figure 6, which illustrates the temporal variation of  $\text{H}_2\text{S}$  outlet concentration under different experimental conditions.

In Figure 8a, the  $\text{H}_2\text{S}$  outlet concentration profiles are compared for various composites, including Bran@Ben 30 %, LRH@Ben 30 %, SRH@Ben 30 %, and pure bentonite (Ben), treated at  $400^\circ\text{C}$  and  $450^\circ\text{C}$ . The "Free" curve, representing the control experiment without any adsorbent, shows a rapid increase in  $\text{H}_2\text{S}$  concentration, reaching saturation within a short time. In contrast, all composite materials exhibit significantly lower  $\text{H}_2\text{S}$  outlet concentrations, indicating effective adsorption capabilities. Among the tested samples, SRH@Ben treated at  $450^\circ\text{C}$  demonstrates the lowest  $\text{H}_2\text{S}$  outlet concentration, suggesting superior adsorption efficiency. This can be attributed to its optimized

structural and textural properties, which enhance active site availability for  $H_2S$  capture. Notably, the adsorption performance of Bran@Ben and LRH@Ben composites is also commendable, though slightly inferior to SRH@Ben, likely due to differences in porosity and surface chemistry. Pure bentonite (Ben) treated at both 400 °C and 450 °C shows significantly higher  $H_2S$  outlet concentrations, reaching saturation quickly. This indicates that pure bentonite has limited adsorption capacity compared to the composites, highlighting the importance of incorporating rice husk-derived components to enhance adsorption performance.



**Figure 8.**  $H_2S$  outlet concentration profiles over time for (a) different composites (Bran@Ben 30 %, LRH@Ben 30 %, SRH@Ben 30 %, and pure bentonite) thermally treated at 400 °C and 450 °C, and (b) SRH@Ben 30 % composites subjected to carbonization at varying temperatures (350 °C to 500 °C).

Figure 8b further investigates the impact of carbonization temperature on SRH@Ben 30 %. The results reveal that increasing the carbonization temperature from 350 °C to 450 °C markedly enhances  $H_2S$  removal efficiency, likely due to the improved porosity and active

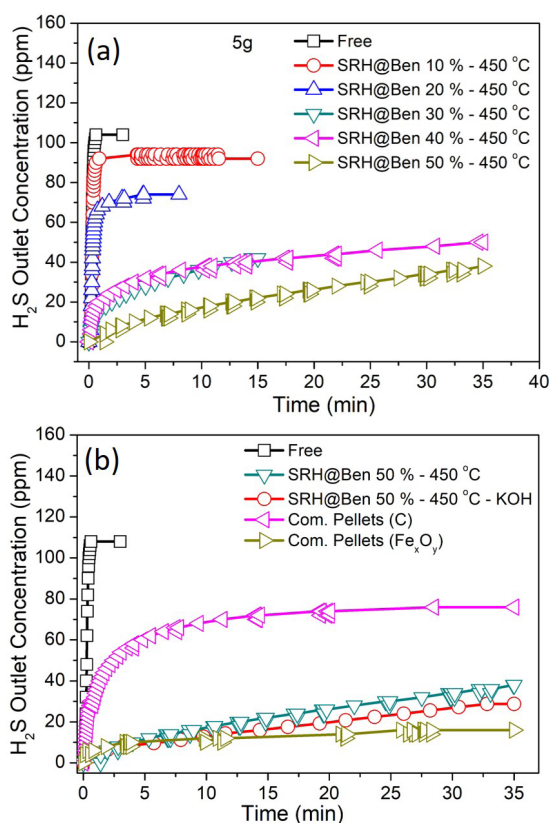
site availability. However, at 500 °C, a slight decline in performance is observed, possibly due to excessive thermal degradation leading to reduced surface functionality. Notably, SRH@Ben450 °C outperforms other samples, reinforcing the optimal thermal activation conditions for maximizing  $H_2S$  adsorption efficiency. These findings underscore the critical role of thermal treatment in tuning the physicochemical properties of the adsorbents for effective gas removal applications.

The  $H_2S$  adsorption performance, as illustrated in Figure 9 (using 5 g of material for each sample), offers critical insights into the impact of rice husk content and chemical activation on adsorption efficiency, along with a comparative evaluation against commercial adsorbents. Figure 9(a) highlights the effect of varying rice husk content on the  $H_2S$  adsorption performance of SRH@Ben composites. Among the tested samples, SRH@Ben 50 % exhibits the most efficient  $H_2S$  removal, maintaining the lowest outlet concentration over an extended duration. This superior adsorption performance can be attributed to the increased presence of carbonaceous material, which enhances pore development and active surface sites, leading to improved gas capture capability. In contrast, composites with lower rice husk content (10-20 %) show a rapid breakthrough, indicating limited adsorption capacity due to insufficient carbon content and surface area.

Notably, rice husk content beyond 50 % was not investigated in this study due to mechanical limitations in pellet formation. At higher rice husk ratios, the structural integrity of the composite pellets significantly deteriorates, making them prone to breakage and fragmentation. This mechanical instability compromises practical applicability, as fragile pellets would result in increased pressure drop and handling difficulties in industrial adsorption systems. Therefore, the 50 % rice husk composite was identified as the optimal formulation, balancing enhanced adsorption efficiency with sufficient mechanical strength for real-world applications.



Figure 9(b) compares the optimal composite, SRH@Ben 50 % - 450 °C, with its KOH-activated counterpart (0.15 M) and two commercial adsorbents: a carbon-based pellet (Com. Pellet C) and an iron oxide-based pellet (Com. Pellet  $\text{Fe}_x\text{O}_y$ ). The activation with KOH further improves  $\text{H}_2\text{S}$  adsorption, as evidenced by a lower breakthrough concentration and prolonged retention time, likely due to enhanced surface area and active functional groups. Comparatively, the commercial carbon pellet exhibits significantly weaker performance, with rapid saturation, while the iron oxide pellet demonstrates superior efficiency, approaching the adsorption behavior of the optimized SRH@Ben 50 % - 450 °C -KOH sample. These findings underscore the efficacy of tailored bentonite-carbon composites in  $\text{H}_2\text{S}$  removal applications, with potential competitiveness against commercial adsorbents.



**Figure 9.**  $\text{H}_2\text{S}$  adsorption performance of SRH@Ben composites: (a) Effect of rice husk content (10-50 %) on  $\text{H}_2\text{S}$  breakthrough behavior; (b) Comparison of the optimized SRH@Ben 50 % - 450 °C composite, with and without KOH activation, against commercial adsorbents (carbon-based and iron oxide-based pellets).

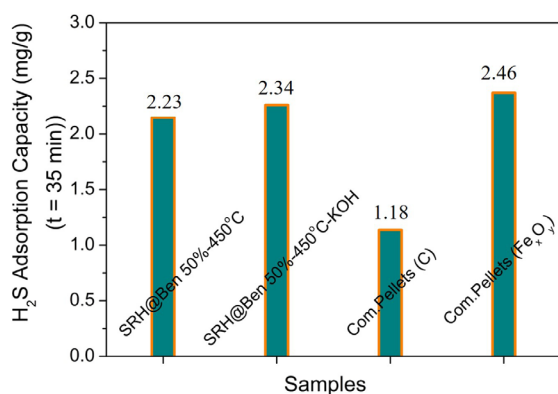
The adsorption capacity ( $C_s$ ) is one of the key factors for evaluating the adsorption performance of the filter material. The  $\text{H}_2\text{S}$  adsorption capacity is determined by integrating the area above the breakthrough curve, considering the inlet  $\text{H}_2\text{S}$  concentration, adsorbent mass, and flow rate. It is calculated using the following equation:<sup>12</sup>

$$C_s = 10^{-3} \frac{M_s F P}{m_a} C_{\text{Sin}} \int_0^{t_b} \left( 1 - \frac{C_{\text{Sout}}}{C_{\text{Sin}}} \right) dt$$

where:  $C_s$  is the  $\text{H}_2\text{S}$  adsorption capacity (mg/g);  $M_s$  is the molecular weight of sulfur (32 g/mol);  $m_a$  is the mass of the adsorbent (g);  $C_{\text{Sin}}$  is the inlet  $\text{H}_2\text{S}$  concentration (108 ppm  $\approx$  150.538 mg/m<sup>3</sup>);  $C_{\text{Sout}}$  is the outlet  $\text{H}_2\text{S}$  concentration (mg/m<sup>3</sup>);  $F$  is the total gas flow rate (0.2 L/min); and  $t_b$  is the adsorption time until the outlet concentration exceeds the breakthrough point (min). In this study, the  $\text{H}_2\text{S}$  capture capacity is evaluated at  $t = 35$  minutes to facilitate a comparative analysis of the performance of different samples.

The  $\text{H}_2\text{S}$  adsorption capacities of the synthesized materials, measured at  $t = 35$  minutes, are presented in the Figure 10. The results reveal significant variations in performance among the tested samples, highlighting the influence of composition and activation on adsorption efficiency.

The SRH@Ben 50 % sample treated at 450 °C demonstrates an  $\text{H}_2\text{S}$  adsorption capacity of 2.23 mg/g, reflecting moderate performance. This is attributed to its optimized rice husk content and carbonization temperature, which enhance porosity and active site availability. Further improvement is observed in the SRH@Ben 50% sample activated with KOH, which achieves a capacity of 2.34 mg/g. This enhancement is likely due to the chemical activation process, which increases surface area and introduces functional groups that facilitate  $\text{H}_2\text{S}$  capture.



**Figure 10.** H<sub>2</sub>S adsorption capacity (mg/g) of various materials, including SRH@Ben composites and commercial pellets, measured after 35 minutes of adsorption using 5 g of material for each sample. **Note:** Due to the time-consuming nature and complexity of the H<sub>2</sub>S adsorption measurements-requiring separate sample preparation, and precise quantification for each run-replicate experiments were not performed in this study. However, strict control of experimental conditions and careful instrument calibration were employed to ensure the reliability of the results. Further studies involving replicate measurements are planned to assess the statistical variations in adsorption performance.

When compared to commercial pellets, the synthesized SRH@Ben samples exhibit significantly superior performance. The commercial pellet Com.Pellets (C) shows a notably lower adsorption capacity of 1.18 mg/g, less than half that of the SRH@Ben materials. This stark difference underscores the effectiveness of the tailored composition and activation processes used in the fabrication of SRH@Ben composites. Additionally, the adsorption capacity of the SRH@Ben samples is comparable to that of the commercial pellet Com.Pellets (Fe<sub>3</sub>O<sub>4</sub>), which achieves 2.46 mg/g. This indicates that the synthesized materials are not only highly efficient but also competitive with commercially available alternatives.

The superior performance of the SRH@Ben samples can be linked to their enhanced structural properties, such as increased porosity and the presence of oxygen-containing functional groups, which are critical for H<sub>2</sub>S adsorption. These findings highlight the potential

of the synthesized materials as cost-effective and sustainable solutions for H<sub>2</sub>S capture, offering performance that rivals or exceeds that of commercial products.

## 4. DISCUSSION

### 4.1. Effect of thermal treatment and rice husk content on adsorption performance

The adsorption performance of the SRH@Ben composites was strongly influenced by thermal treatment temperature and rice husk content, as evidenced by the breakthrough curves and adsorption capacity measurements. The optimal composite, SRH@Ben 50% - 450 °C, exhibited the highest H<sub>2</sub>S adsorption capacity (2.23 mg/g), which can be attributed to a well-developed porous structure and enhanced surface reactivity. Increasing the carbonization temperature from 350 °C to 450 °C led to an improvement in adsorption performance due to the removal of volatile organic compounds and the formation of micropores and mesopores. However, at 500°C, a slight decline in adsorption capacity was observed, likely due to excessive structural degradation and reduced surface functionalities.

Similarly, the increase in rice husk content (10-50%) resulted in enhanced adsorption performance, with the highest efficiency observed at 50% rice husk content. This is likely due to the increased carbon content, which contributes to a higher surface area and greater availability of active sites for H<sub>2</sub>S adsorption. However, further increasing the rice husk content beyond 50% was not explored in this study due to structural instability, as composites with higher rice husk content tend to be mechanically weaker and more prone to disintegration during handling and testing.

### 4.2. Mechanism of H<sub>2</sub>S adsorption on SRH@Ben composites

The adsorption of H<sub>2</sub>S onto SRH@Ben composites is governed by a combination of physisorption, chemisorption, and catalytic oxidation mechanisms, facilitated by the

structural and chemical properties of both activated carbon (from rice husk) and bentonite.

#### 4.2.1. *Physisorption via porous structure*

The well-developed pore structure of the carbonized rice husk phase provides a high surface area and multiple adsorption sites for  $H_2S$  molecules. The presence of micropores enhances van der Waals interactions, allowing gas molecules to be retained within the porous network. Additionally, mesopores play a critical role in gas diffusion, facilitating the accessibility of active sites within the material. The increase in adsorption capacity after KOH activation (from 2.23 mg/g to 2.34 mg/g) further supports this, as KOH treatment is known to enhance porosity and improve the dispersion of functional groups on the adsorbent surface.

#### 4.2.2. *Chemisorption via functional groups*

The interaction between  $H_2S$  and SRH@Ben composites is also influenced by the oxygen-containing functional groups present on the activated carbon surface, such as carboxyl ( $-COOH$ ), hydroxyl ( $-OH$ ), and carbonyl ( $-C=O$ ) groups. These functional groups can react with  $H_2S$ , forming surface-bound sulfur species (e.g., elemental sulfur or polysulfides), thereby enhancing adsorption efficiency. The presence of bentonite further contributes to adsorption through its hydrophilic nature and cation exchange capacity, which facilitates the trapping of  $H_2S$  molecules via electrostatic interactions.

#### 4.2.3. *Catalytic oxidation and sulfur deposition*

A portion of the adsorbed  $H_2S$  is likely oxidized into elemental sulfur (S) or sulfate ( $SO_4^{2-}$ ) under ambient conditions. The presence of metal oxides in bentonite may serve as catalytic sites, accelerating this oxidation process. The sulfur species formed during adsorption may block adsorption sites over time, leading to gradual saturation. This explains why, after extended adsorption cycles, a reduction in breakthrough time was observed, indicating progressive deactivation of adsorption sites due to sulfur deposition.

### 4.3. Comparison with commercial adsorbents

To evaluate the practical applicability of SRH@Ben composites, their adsorption performance was compared with commercial adsorbents, including carbon-based (Com. Pellet C) and iron oxide-based (Com. Pellet  $F_xO_y$ ) materials. The results indicate that: (1) SRH@Ben 50 % - 450 °C (2.23 mg/g) outperformed commercial carbon-based adsorbents (1.18 mg/g), demonstrating the superior adsorption efficiency of the composite material; (2) KOH-activated SRH@Ben (2.34 mg/g) exhibited adsorption capacity comparable to iron oxide-based adsorbents (2.46 mg/g), suggesting that the composite material is a viable alternative to more expensive commercial sorbents.

These findings emphasize that the synergy between bentonite and activated carbon significantly enhances  $H_2S$  removal efficiency, making SRH@Ben a cost-effective and sustainable solution for biogas purification.

## 5. CONCLUSION

In conclusion, this study demonstrates the successful synthesis and optimization of SRH@Ben composites for  $H_2S$  adsorption, highlighting the critical role of tailored composition, thermal treatment, and chemical activation in enhancing adsorption performance. The SRH@Ben 50 % - 450 °C composite, with its uniform and dense structure, achieved an  $H_2S$  adsorption capacity of 2.23 mg/g, which increased to 2.34 mg/g after KOH activation. These values are more than double that of the commercial carbon-based pellet (1.18 mg/g) and comparable to the iron oxide-based pellet (2.46 mg/g), underscoring the superior performance of the synthesized materials. The enhanced adsorption capacity is attributed to the optimized porosity, surface area, and functional groups introduced through thermal and chemical activation. These findings position SRH@Ben composites as cost-effective, sustainable, and highly efficient alternatives for  $H_2S$  capture, with significant potential for industrial applications. Future work will focus

on scaling up production and evaluating long-term performance under real-world conditions.

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## Chất hấp phụ dạng hạt thân thiện môi trường từ than hoạt tính nguồn gốc bã cà phê ứng dụng xử lý nước thải

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### TÓM TẮT

Nghiên cứu này tạo ra chất hấp phụ dạng hạt thân thiện môi trường có nguồn gốc từ bã cà phê dùng cho xử lý nước thải. Than hoạt tính (AC) được tổng hợp từ bã cà phê và kết hợp với chitosan (CS) và alginate (AL) để tạo thành vật liệu composite, CAA, nhằm tăng cường khả năng loại bỏ thuốc nhuộm. Quá trình tổng hợp được tối ưu hóa bằng cách điều chỉnh các tham số chính, bao gồm khối lượng AC, nồng độ NaOH và thời gian ngâm, để tối ưu hóa hiệu quả hấp phụ. Hiệu năng của vật liệu được đánh giá bằng cách sử dụng thuốc nhuộm Malachite xanh (MG) làm chất ô nhiễm mô hình. Các đặc trưng cấu trúc và hóa học, bao gồm phân tích nhiệt trọng lượng (TGA) và quang phổ hồng ngoại biến đổi Fourier (FT-IR), xác nhận sự tổng hợp thành công của chất hấp phụ composite. Kính hiển vi điện tử quét (SEM) cho thấy phân bố kích thước hạt đồng đều, bề mặt thô và cấu trúc xốp phát triển tốt. Với diện tích bề mặt riêng là 11,231 m<sup>2</sup>/g và cấu trúc mao quản có đường kính lỗ 12,887 Å, chất hấp phụ này cho thấy tiềm năng mạnh mẽ trong xử lý nước thải. Những phát hiện này củng cố việc sử dụng than hoạt tính từ bã cà phê như một giải pháp bền vững và tiết kiệm chi phí để loại bỏ các chất ô nhiễm hữu cơ, đặc biệt là thuốc nhuộm, từ nước thải.

**Từ khoá:** Than hoạt tính, hấp phụ, chất hấp phụ dạng hạt, malachite xanh, bã cà phê.

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# Eco-friendly granular adsorbent based activated carbon from spent coffee grounds for wastewater treatment

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## ABSTRACT

This study discovers the development of an eco-friendly granular adsorbent derived from spent coffee grounds for wastewater treatment. Activated carbon (AC) was synthesized from spent coffee grounds and combined with chitosan (CS) and sodium alginate (AL) to form a composite material, CAA, for enhanced dye removal. The synthesis process was optimized by adjusting key parameters, including AC mass, NaOH concentration, and soaking time, to maximize adsorption efficiency. The effectiveness of the material was evaluated using Malachite Green (MG) dye as a model pollutant. Comprehensive structural and chemical characterizations, including thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR), confirmed the successful formation of the composite adsorbent. Scanning electron microscopy (SEM) revealed a uniform particle size distribution, rough surface morphology, and well-developed porous structure. With a specific surface area of 11.231 m<sup>2</sup>/g and a mesoporous structure featuring a pore diameter of 12.887 Å, the adsorbent demonstrates strong potential for wastewater treatment. These findings highlight the promising use of coffee-ground-derived activated carbon as a sustainable and cost-effective solution for the removal of organic pollutants, specifically dyes, from wastewater.

**Keywords:** *Activated carbon, adsorption, granular adsorbent, malachite green, spend coffee grounds.*

## 1. INTRODUCTION

As sustainability, resource efficiency, and economic viability continue to gain prominence, agricultural by-products are increasingly being utilized across various industries, offering innovative solutions to waste management challenges while promoting environmentally friendly alternatives to conventional materials.<sup>1</sup>

The growing focus on circular economy principles highlights the vital role of agricultural wastes in advancing environmental sustainability. Among these agricultural by-products, spent coffee grounds have emerged as a promising raw material for the production of activated carbon (AC), a highly effective adsorbent for environmental remediation, particularly in wastewater treatment.<sup>2</sup>

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Water pollution caused by synthetic dyes from industries such as textiles, leather, and paper manufacturing remains one of the most pressing environmental concerns. These dyes, often toxic, persistent, and non-biodegradable, pose a significant threat to aquatic ecosystems by blocking light penetration, disrupting photosynthesis, and depleting oxygen levels in water.<sup>3</sup> Furthermore, many synthetic dyes contain carcinogenic and mutagenic compounds that can bioaccumulate in aquatic organisms, causing long-term ecological and health risks. Traditional methods, including photocatalysis, biodegradation, membrane filtration, electrochemical oxidation, and coagulation, have been developed to address this issue, but each method comes with its own set of limitations, such as high energy demands, chemical usage, and slow processing times.<sup>4</sup>

Among these treatment methods, adsorption using activated carbon has proven to be one of the most effective, offering advantages like simplicity, high efficiency, low energy consumption, and the ability to remove a wide range of organic pollutants, including dyes.<sup>5</sup> However, the use of powdered or fine-grained activated carbon (AC) presents challenges in terms of recovery, reusability, and mechanical stability, limiting its widespread application in large-scale wastewater treatment.<sup>6</sup>

In response to these challenges, this study introduces an innovative solution by developing eco-friendly granular adsorbents derived from spent coffee grounds. By integrating activated carbon with biopolymers such as chitosan (CS) and sodium alginate (AL), this study enhances the adsorbent's structural stability and efficiency in dye removal. Chitosan, a biodegradable and non-toxic biopolymer, and sodium alginate, known for its gel-forming capabilities and high water stability, offer valuable functional groups that further improve the adsorptive properties of the material.<sup>7</sup> This approach not only provides a sustainable method for coffee ground waste utilization but also contributes to an effective,

environmentally friendly solution for wastewater treatment and the removal of organic pollutants.

## 2. Material and methods

### 2.1. Materials

In this study, spent coffee grounds were collected from Trung Nguyen coffee shops in Can Tho City, providing an abundant, sustainable raw material for the production of activated carbon. The chemicals used in the synthesis process included phosphoric acid, sodium hydroxide, sulfuric acid, acetic acid, and potassium chloride, all sourced from Xilong Scientific Co., Ltd., which played a crucial role in optimizing the activation and composite formation. Chitosan powder, a biodegradable and eco-friendly biopolymer, was supplied by S-Green Co., Jsc, while sodium alginate, known for its gel-forming properties and water stability, was obtained from Shanghai Zhanyun. Together, these materials were combined to create a granular composite adsorbent that integrates the sustainability of spent coffee grounds with the enhancing properties of natural biopolymers, paving the way for an efficient, eco-friendly solution to wastewater treatment.

### 2.2. Preparation of activated carbon from coffee grounds

The spent coffee grounds were carefully collected, washed with distilled water to remove surface impurities, and then dried at 50 °C to prepare them for further processing. After drying, the moisture content and mass of the coffee grounds were accurately measured using a moisture analyzer to ensure consistency. The dried grounds were then subjected to carbonization at 850 °C for 1 h in an oven, transforming them into raw activated carbon. To enhance the adsorptive properties, the resulting carbon was activated by soaking in a 1 M phosphoric acid ( $\text{H}_3\text{PO}_4$ ) solution at a ratio of 1:10 (w/v) for 2 h at room temperature. This activation process allowed the formation of a highly porous structure, ideal for pollutant adsorption. After activation, the carbon was meticulously washed with distilled water through ultrasonic waves

to remove any residual chemicals, continuing until a neutral pH was achieved. Finally, the activated carbon (AC) was dried, ground, and sieved to obtain fine particles with a diameter of less than 80  $\mu\text{m}$ , ensuring its suitability for effective wastewater treatment and adsorption applications. This process not only transforms spent coffee grounds into a valuable resource but also highlights the potential of sustainable materials for environmental remediation.

### 2.3. Synthesis of composite bead adsorbent on activated carbon base derived from coffee grounds

In this study, an eco-friendly granular composite adsorbent was developed by combining activated carbon (AC) derived from spent coffee grounds with biopolymers, chitosan (CS) and sodium alginate (AL), through a gel-ion self-association method. To begin, a CS solution was prepared by dissolving 1 gram of chitosan in 25 mL of 2% (v/v) acetic acid, creating a smooth gel. AC was then added to the chitosan solution at a specified mass ratio and stirred until a uniform dispersion was achieved. To form the granular composite adsorbent, the CS-AC suspension was carefully dispensed through a syringe into a sodium hydroxide (NaOH) solution, where the chitosan was rapidly condensed, shaping the material into granular particles within a set time. The adsorbent particles were then filtered, washed with distilled water, and adjusted to a near-neutral pH.

Next, the CS-AC adsorbent was functionalized by soaking it in a 2% (w/v) sodium alginate (AL) solution for 2 hours then continue to soak in 2.5% (w/v)  $\text{CaCl}_2$  solution for 2 hours at room temperature, shaking at 100 rpm, allowing the AL to bind with the material, further enhancing its adsorptive properties. After filtration and washing to neutral pH, the composite adsorbent was dried under vacuum conditions (600 mbar, 60  $^{\circ}\text{C}$ ) for 5 h to obtain the final granular adsorbent material—CAA—designed for the effective adsorption of organic dyes from aqueous solutions.

The synthesis process of the CAA composite adsorbent was optimized by investigating the adsorption of Malachite Green (MG) dye under controlled conditions: an initial concentration of 20 ppm, adsorbent mass of 0.2 g, dye solution volume of 25 mL, contact time of 24 h, and shaking speed of 150 rpm. The dye concentration at equilibrium was measured using UV-Vis molecular absorption spectroscopy at the maximum absorption wavelength of 617 nm. The adsorption capacity ( $q$ , mg/g) and the removal efficiency (%) of MG were calculated to evaluate the effectiveness of the adsorbent via equation (1) and (2), demonstrating the potential of this eco-friendly composite material as a sustainable solution for wastewater treatment and organic dye removal.

$$q = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

$$H = \left( \frac{C_0 - C_e}{C_0} \right) \cdot 100 \quad (2)$$

where,  $C_0$  (mg/L) is the initial concentration and  $C_e$  (mg/L) is the concentration at equilibrium.  $V$  (L) is the volume of the solution and  $m$  (g) is the mass of the adsorbent.

### 2.4. The characteristic properties of synthetic granular adsorbent materials

To fully understand the properties and performance of the developed eco-friendly granular composite adsorbent (CAA), a comprehensive set of characterization techniques was employed. The surface morphology of the composite material was analyzed using the Scanning Electron Microscope (SEM) by Horiba. This provided detailed insights into the structural features, including particle size distribution, surface roughness, and pore development, essential for understanding the material's potential in pollutant adsorption. Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability and mass changes of the adsorbent during processes such as decomposition, oxidation, and reduction. The analysis was carried out in a nitrogen atmosphere using the TGA-DSC3+ system

(Mettler Toledo), with temperatures ranging from 25 °C to 1000 °C and a heating rate of 5 °C/min, providing valuable information on the material's thermal behavior.

The specific surface area and porosity of the composite adsorbent were measured using the Brunauer-Emmett-Teller (BET) method, based on nitrogen adsorption-desorption isotherms, with the 201A apparatus from Porous Materials-America. These measurements are critical for understanding the material's capacity to adsorb pollutants, as a higher surface area and well-developed pores enhance its efficiency. Lastly, the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of the composite adsorbent was determined to understand its surface charge behavior in different pH environments. A 0.2 g sample of the AC-CS material was immersed in 25 mL of 0.1 M KCl solution in a 250 mL Erlenmeyer flask, and the pH was adjusted from 2 to 12 using 0.1 M NaOH and 0.1 M HCl. After 24 h, the final pH was recorded, and the  $\text{pH}_{\text{pzc}}$  value was determined graphically, providing further insights into the material's interaction with pollutants in wastewater.

Through these characterizations, this work was able to comprehensively evaluate the eco-friendly granular composite adsorbent's structural, thermal, and chemical properties, confirming its potential as an effective and sustainable solution for wastewater treatment and organic dye removal.

### 3. RESULT AND DISCUSSION

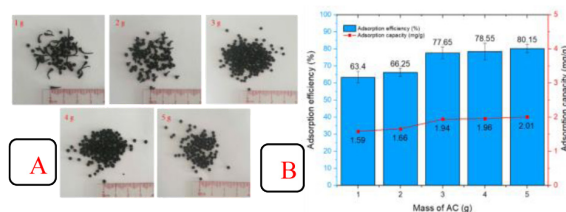
#### 3.1. Parameters influencing the synthesis of granular adsorbent CAA

##### 3.1.1. Influence of activated carbon (AC) content

The effect of activated carbon (AC) content on the fabrication and performance of the eco-friendly granular composite adsorbent is highlighted in Figure 1. The experimental results reveal that the AC content plays a crucial role in both the adsorption capacity and structural integrity of the composite material, directly influencing its effectiveness in removing Malachite Green (MG) dye from aqueous solutions.

As the AC mass increased from 1 g to 5 g, the adsorption efficiency of the composite material significantly improved, with removal efficiencies of  $63.40 \pm 3.51\%$ ,  $66.25 \pm 2.37\%$ ,  $77.65 \pm 3.45\%$ ,  $78.55 \pm 4.89\%$ , and  $80.15 \pm 2.88\%$ , respectively (Figure 1B). This trend demonstrates a clear correlation between the AC content and the material's ability to remove MG dye, suggesting that a higher concentration of AC enhances the adsorption capacity. The functional groups of AC, particularly  $-\text{OH}$  and  $-\text{COOH}$  groups, are key contributors to this improved performance.<sup>8</sup> The  $-\text{OH}$  groups facilitate the swelling of the material through hydrogen bonding with the nitrogen and oxygen atoms in MG molecules, while the  $-\text{COOH}$  groups ionize to form  $-\text{COO}^-$ , which further strengthens ionic interactions, attracting the oppositely charged regions of the dye molecules.<sup>8</sup>

However, the AC content also significantly impacts the granulation process of the composite adsorbent. As shown in Figure 1A, when the AC content was below 3 g, the resulting droplets failed to form stable, well-structured granules. These fragile formations lacked the mechanical strength required to withstand external forces during the granulation process, leading to structurally weak adsorbents that were unsuitable for practical applications. Hence, achieving an optimal balance of AC content is essential to ensure both high adsorption efficiency and robust structural stability.



**Figure 1.** Influence of activated carbon (AC) content on the formation of adsorbent (A) and the removal ability of Malachite Green (B).

##### 3.1.2. Influence of NaOH

In this study, NaOH solution was employed as the solvent for preparing the eco-friendly CAA granular adsorbents, utilizing a phase inversion



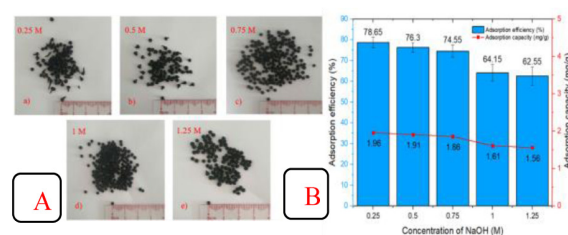
process to achieve stable granule formation. The phase inversion technique involves transforming CS from its gel phase back into a solid state through the modification of its glycosidic bonds.<sup>9</sup> This process occurs in two critical stages: gelation, where a gel structure is formed, and precipitation, where the structure solidifies. The precipitation is driven by an acid-base reaction, which begins when CS is dissolved in a 2% (v/v) acetic acid solution. In this acidic medium, the amine groups ( $-\text{NH}_2$ ) on the CS molecules accept protons, forming positively charged ammonium groups ( $-\text{NH}_3^+$ ). This protonation increases chitosan's polarity and solubility in water, allowing it to remain in solution.

The precipitation process is initiated when the CS-AC mixture is introduced into the NaOH solution. At the interface between the liquid droplets and the NaOH solution, the hydroxide ions ( $\text{OH}^-$ ) neutralize the ammonium groups ( $-\text{NH}_3^+$ ), reducing the polarity of the CS.<sup>10</sup> This rapid neutralization triggers chitosan's precipitation, initially forming a gel layer on the particle surface. Over time, the excess hydroxide ions further facilitate the transition from the gel phase to a solid precipitate, ultimately resulting in mechanically stable, granular adsorbents.<sup>10</sup>

The impact of NaOH concentration on the synthesis of CAA granules is depicted in Figure 2A. As the NaOH concentration increased, the stability of the precipitation process improved, resulting in more uniform-sized particles with a stable surface. This enhanced stability was observed to be beneficial for creating well-formed granules, ideal for practical applications. However, an excessively high NaOH concentration posed a challenge: it could completely neutralize the cations on the particle surface, disrupting electrostatic interactions. This disruption hindered the subsequent immersion in the sodium alginate solution, negatively affecting the material's adsorption capacity.<sup>11</sup>

Figure 2B at a NaOH concentration of 1.25 M, the granule formation process is rapid, but the adsorption efficiency is limited, reaching

only  $62.55 \pm 4.51\%$ . As the NaOH concentration decreases, the MG adsorption efficiency increases. At NaOH concentrations of 0.25 M, 0.5 M, and 0.75 M, the adsorption results were similar; however, granules formed at 0.75 M NaOH exhibited more uniformity and durability compared to those formed at 0.25 M and 0.5 M concentrations. Therefore, a NaOH concentration of 0.75 M was selected for synthesising the granules for subsequent investigations.



**Figure 2.** Influence of NaOH concentration on the formation of adsorbent (A) and the removal ability of Malachite Green (B).

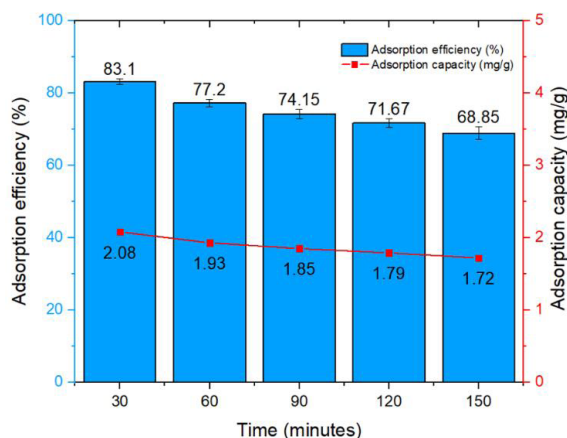
### 3.1.3. Influence of soaking time in NaOH

Figure 3 demonstrates the effect of soaking time in a 0.75 M NaOH solution on the adsorption efficiency of MG dye by the eco-friendly granular adsorbent. As the soaking time increased from 30 to 150 min, a noticeable decrease in MG adsorption efficiency was observed. The adsorbent soaked for 30 min exhibited the highest adsorption efficiency at  $83.10 \pm 0.73\%$ , but the granules were poorly shaped and fragile, making them prone to mechanical breakage. This highlights the challenge of balancing effective adsorption with the mechanical stability of the granules.

Based on the adsorption data, the optimal soaking time was found to be 60 min, where a balanced combination of high adsorption efficiency ( $77.20 \pm 1.05\%$ ) and well-formed granules was achieved. The granules produced at this soaking time exhibited good structural integrity, making them suitable for practical applications while maintaining relatively high dye removal performance. As the soaking time was extended beyond 60 min, the adsorption efficiency gradually decreased. Specifically, at

90 min, the efficiency dropped to  $74.15 \pm 1.35\%$ , and by 150 min, it reached  $68.85 \pm 1.72\%$ . This decline in adsorption performance can likely be attributed to the over-modification of the material's structure or degradation of adsorption sites as a result of prolonged exposure to the NaOH solution.<sup>12</sup> Prolonged soaking could also lead to a loss of functional groups essential for dye removal due to chitosan is susceptible to glycosidic bond cleavage and denaturation of amino groups  $-\text{NH}_2$ , leading to a decrease in the number of adsorption sites, further diminishing the material's efficiency<sup>13</sup>.

These findings emphasize that while NaOH treatment is crucial for enhancing the adsorption capacity of the adsorbent, excessive soaking can have detrimental effects. Therefore, a soaking time of 60 min is considered optimal, providing the ideal balance between adsorption performance and structural stability. This soaking time was selected as the standard condition for all subsequent experiments, ensuring the production of an efficient and durable adsorbent material for wastewater treatment applications.



**Figure 3.** Influence of soaking time in NaOH on the removal ability of Malachite Green.

### 3.2. The characteristic properties of synthetic granular adsorbent materials

#### 3.2.1. Surface morphology of CAA granular adsorbent

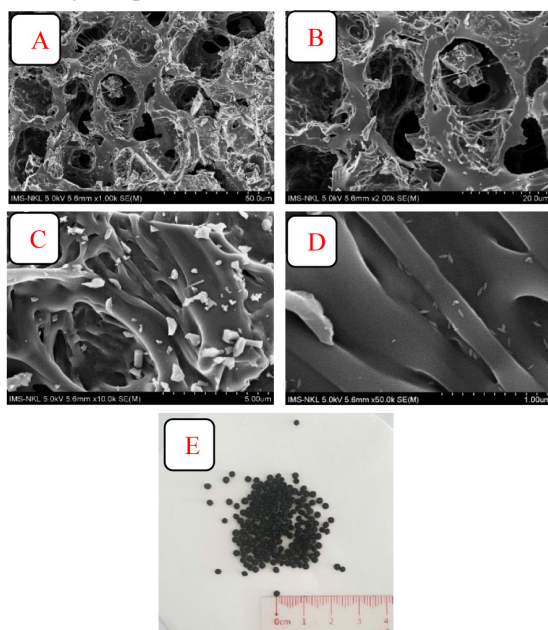
The surface morphology and internal structure of the eco-friendly CAA adsorbent particles

were thoroughly examined using scanning electron microscopy (SEM). The images presented in Figure 4A and 4B, captured at different resolutions, reveal the highly porous internal structure of the adsorbent. The material, composed of AC integrated with CS and AL, demonstrates well-developed capillary pores ranging from 13 to 18  $\mu\text{m}$  in size (Figure 4E). These uniform pores suggest that the adsorbent has an excellent capacity to adsorb and store molecules, which is crucial for its effectiveness in dye removal during wastewater treatment.

Further examination of the surface morphology in Figure 4C and 4D shows a distinctive combination of concave and convex surface features. The surface is characterized by grooves, cracks, and blocks of varying sizes, which not only contribute to the material's mechanical stability but also increase the surface area available for adsorption. These structural features, along with the porous capillary system, provide additional surface roughness and fractures, creating multiple potential adsorption sites for contaminants.<sup>13</sup> This unique surface architecture is expected to enhance the adsorbent's overall capacity to capture and retain organic pollutants, such as MG dye, from aqueous solutions.

Additionally, the white areas observed on the particle surface are likely a result of the AL component, formed after the cross-linking process. This suggests that the AL polymer plays a key role in the structural integrity and functionality of the adsorbent, likely contributing to its stability and enhancing its ability to interact with pollutants.

The SEM analysis highlights the exceptional design of the CAA adsorbent, which combines a porous internal structure with a rough and varied surface morphology. This makes the material highly effective for wastewater treatment applications, capable of adsorbing a wide range of contaminants while maintaining the necessary physical strength and stability for practical use.



**Figure 4.** Internal morphology of granular adsorbent material at different magnifications X1,000 (A), X2,000 (B); External surface morphology of the material at different magnifications X10,000 (C), X50,000 (D); Digital image of granular adsorbent material (E).

### 3.2.2. Thermogravimetric analysis (TGA)

The thermal stability of the granular adsorbent, was assessed through thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curves, as shown in Figure 5A. The thermal decomposition behavior of the AC, produced by a mechanical method, activated at 850 °C, and further treated with  $H_3PO_4$ , reveals three distinct stages of mass loss, each indicative of different material properties.

The first stage, occurring between 29 °C and 100 °C, is associated with the evaporation of both physical and chemically bound water and the decomposition of volatile organic materials. This phase results in a relatively small mass loss of 5.2%.<sup>14</sup> The peak observed at 82.76 °C in the differential scanning calorimetry (DSC) curve confirms the exothermic nature of water evaporation, highlighting the removal of moisture from the carbonized material.

The second stage, between approximately 200 °C and 410 °C, is marked by the decomposition

of hemicellulose, followed by the breakdown of cellulose at around 455 °C, accompanied by the degradation of the carbon skeleton.<sup>15</sup> This stage represents the most significant mass loss of 56.6%, highlighting the breakdown of the organic components in the material. The peak at 284.54 °C in the DSC curve emphasizes the endothermic nature of this decomposition process. As the material undergoes pyrolysis, the carbon structure begins to form, and volatile organic components are released.

The third stage, occurring between 500 °C and 600 °C, reflects the decomposition of the amorphous cellulose regions, oxidation of the cellulose carbon skeleton, and breakdown of lignin in the sample.<sup>15</sup> This stage produces carbon gases such as CO and CO<sub>2</sub>, as the high molecular weight compounds dissociate into lower molecular weight fragments. The DSC peak at 812.13 °C further corroborates the breakdown of hemicellulose and cellulose during pyrolysis, with the slow degradation of lignin evident in the extended tail of the DTG curve. This suggests passive pyrolysis beyond 550 °C, where slight volatilization occurs as C–C and C–H bonds are cleaved, contributing to the thermal carbonization of the biomass.<sup>14</sup>

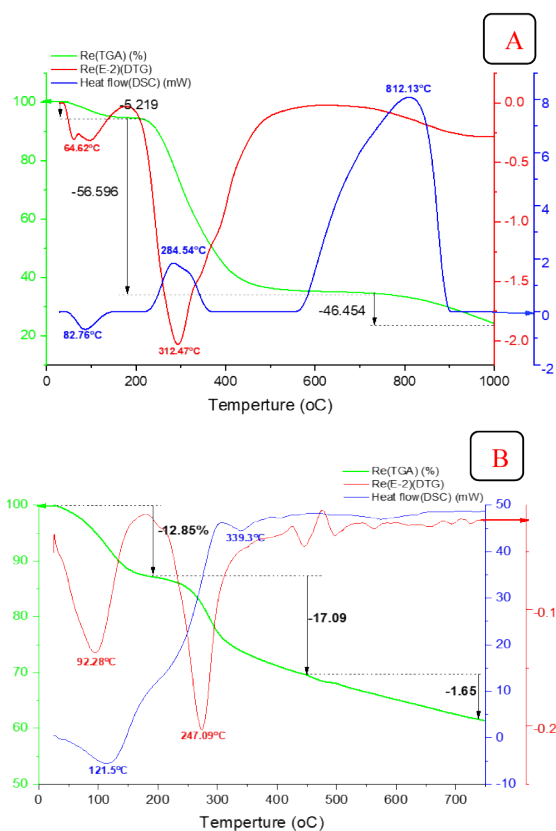
The thermal analysis of the composite granular adsorbent (CAA) is presented in Figure 5B, where the first stage, occurring between 25 °C and 185 °C, corresponds to initial mass loss due to both physical and chemical dehydration. During this phase, the vitrification transition of CS leads to a significant mass reduction of 12.86%, as indicated by the DSC peak at 121.5 °C, which confirms the exothermic phase change of the CS.

In the subsequent stages, CS and AL are progressively decomposed. This stage, occurring between 200 °C and 400 °C, results in the breakdown of AL and the formation of CaCO<sub>3</sub>, which is typical of the cross-linking process involving sodium alginate. The combined thermal behavior of all CS, AL, and AC is reflected in the DTG curve, showing the distinct



contributions of each component to the thermal stability and structural integrity of the CAA.

These findings underscore the complex thermal behavior of the CAA adsorbent, revealing the critical role of each component in determining the material's stability. The combination of AC derived from spent coffee grounds with biodegradable biopolymers like CS and AL results in a highly stable, environmentally friendly adsorbent, ideal for wastewater treatment applications. The thermal analysis further supports the feasibility of this material for practical use, demonstrating its robust structure and thermal resilience even under harsh conditions.



**Figure 5.** TGA/DTG and DSC diagrams of AC derived from coffee grounds (A) and CAA granular adsorbent (B).

### 3.2.3. Fourier Transform-infrared (FT-IR) spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was employed to analyze the functional groups and chemical changes in the material before and after

treatment. The FT-IR spectrum of AL exhibited characteristic peaks at  $1333\text{ cm}^{-1}$  and  $1032\text{ cm}^{-1}$ , corresponding to the C-H stretching vibration of glucose and the C-O stretching vibration of ether and alcohol groups, respectively,  $2824\text{ cm}^{-1}$  represents the aliphatic C-H stretching vibration ( $-\text{CH}_2-$ ,  $-\text{CH}-$ ) characteristic of the polyuronic backbone of alginate,  $2482\text{ cm}^{-1}$  the presence of this peak indicates that the alginate has been acidified and is typical of alginate's chemical structure.<sup>16</sup> These functional groups play an essential role in the adsorption process by providing active sites for interactions with pollutants.

The FT-IR spectrum of CS, a key component in the composite adsorbent, displayed a prominent peak at  $3577\text{ cm}^{-1}$ , corresponding to the N-H stretching vibration of the amino group, and another peak at  $1635.3\text{ cm}^{-1}$  related to the N-H bending vibration of the primary amide group within the CS.<sup>17</sup> These functional groups are crucial for the adsorption of pollutants, such as MG, through electrostatic and hydrogen bonding interactions.

The AC spectrum displayed peaks at  $1635\text{ cm}^{-1}$  and  $1385\text{ cm}^{-1}$ , which are indicative of C=O bonds found in carboxyl and aromatic groups on the AC surface. These peaks suggest that the carbonization process introduces oxygen-containing functional groups, which are key to enhancing the adsorbent's ability to interact with organic pollutants in wastewater.

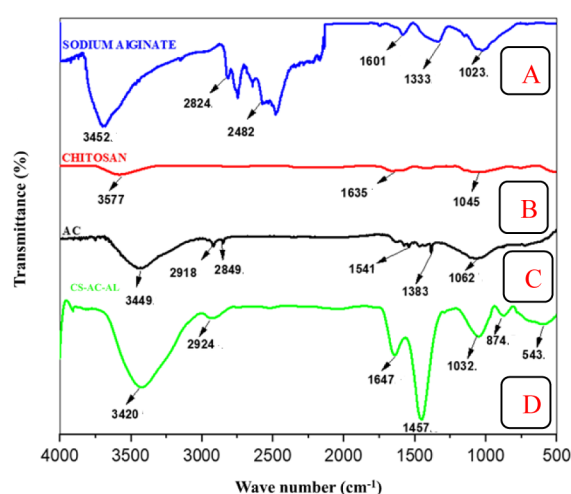
When comparing the FT-IR spectra of the CAA granular adsorbent, common functional groups such as O-H at  $3420\text{ cm}^{-1}$ ,  $3449\text{ cm}^{-1}$ , and  $3452\text{ cm}^{-1}$ , along with  $-\text{COO}$ , C=O, and C-O at  $1647\text{ cm}^{-1}$ ,  $1541\text{ cm}^{-1}$ , and  $1601\text{ cm}^{-1}$ , were observed in all materials.<sup>18</sup> These peaks are indicative of the successful incorporation of various components, including CS, AL, and AC, into the final composite material. The presence of these functional groups demonstrates the material's potential to interact with pollutants, particularly organic dyes like MG.

A small peak at  $534\text{ cm}^{-1}$  attributed to the vibration of the Ca-O bond, confirming

the formation of the gel network through ionic bonding between  $\text{Ca}^{2+}$  and the carboxylate group of alginate.<sup>19</sup> Moreover, the C-H bond at  $1457\text{ cm}^{-1}$  suggests the formation of hydrogen bonds between the functional groups, particularly between CS and AC, which further enhances the material's stability and adsorption capacity.<sup>20</sup>

Since MG is a positively charged ion in aqueous solutions, it interacts electrostatically with the negatively charged functional groups on the adsorbent, particularly  $-\text{COO}^-$  and  $\text{O-H}$ .<sup>21</sup> These functional groups act as adsorption sites, facilitating the effective removal of MG from wastewater. The FT-IR analysis confirms the key role of the functional groups in enhancing the material's adsorption efficiency, which is critical for wastewater treatment applications.

Briefly, the FT-IR spectra of the CAA granular adsorbent demonstrate the successful incorporation of CS, AL, and AC from spent coffee grounds, which contribute to the material's ability to effectively adsorb organic dyes like MG. The presence of multiple functional groups, including hydroxyl, carboxyl, and amino groups, underscores the material's potential as an eco-friendly and efficient adsorbent for wastewater treatment.



**Figure 6.** Fourier Transform-infrared (FT-IR) spectroscopy result of AL (A), CS (B), AC (C), The CAA granular adsorbent (D).

### 3.2.4. Adsorption/desorption $N_2$ isotherm (BET equation)

The specific surface area of the CAA granular adsorbent, derived from spent coffee grounds and AC using the BET (Brunauer-Emmett-Teller), BJH (Barrett-Joyner-Halenda) method, was analyzed to assess its potential for wastewater treatment applications. Nitrogen adsorption-desorption isotherms were used to evaluate the material's pore characteristics and adsorption capacity. The BET analysis revealed that the AC derived from spent coffee grounds exhibited a significantly higher adsorption compared to desorption, as shown in Figure 7. The surface area of the activated material was measured at  $300.842\text{ m}^2/\text{g}$ , indicating that the material possesses a relatively large surface area. This value is notably higher than many other adsorbents reported in previous studies, suggesting the material's superior adsorption potential.

The pore diameter of the AC was found to be  $10.628\text{ Å}$ , placing the material within the micropore category. This observation aligns with the SEM analysis, which showed the presence of a highly porous structure. The high surface area and micropore distribution are crucial for efficient adsorption, as they provide numerous sites for pollutant molecules to interact with the adsorbent. These findings highlight that the material's high adsorption capacity reinforced by the IUPAC-type I adsorption isotherms is largely attributed to the large surface area created during the activation process.<sup>20</sup>

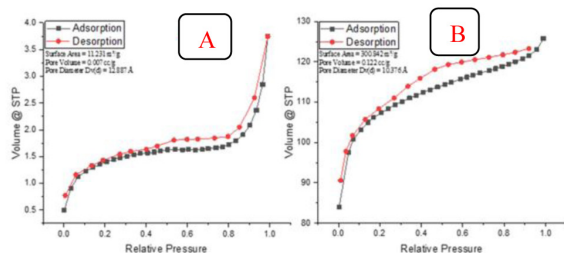
In contrast, the CAA granular adsorbent, prepared by incorporating CS and AL, showed a decrease in specific surface area to  $11.231\text{ m}^2/\text{g}$  compared to the raw AC. However, the pore diameter increased to  $12.887\text{ Å}$ . This shift in pore characteristics is likely due to the formation of a granular structure during the condensation of CS, which encapsulated the AC. While the surface area decreased, the enlarged pores still ensured effective adsorption, indicating that



the granular structure maintained sufficient adsorption sites for molecules.

Despite the increased pore size, the granular adsorbent still demonstrated significant adsorption potential. The 12.887 Å pore diameter is slightly larger than the size of MG dye molecules, which range from 0.8 to 1.58 nm. This suggests that the material can still effectively adsorb MG molecules, although the larger pore size might slightly hinder the diffusion of the dye into the adsorbent's structure. However, this slower diffusion is balanced by the material's long-term adsorption efficiency, as evidenced by the Type IV adsorption isotherm, which showed a relatively large pressure hysteresis region. This hysteresis is indicative of efficient adsorption, even for larger molecules, over an extended period.<sup>22</sup>

In brief, the BET analysis underscores the effectiveness of the activated carbon derived from spent coffee grounds and the CAA composite in wastewater treatment applications. The combination of a high surface area, microporosity, and a well-structured granular form makes this material an ideal candidate for adsorbing organic pollutants like MG from aqueous solutions.



**Figure 7.** Adsorption/Desorption  $N_2$  isotherm (BET equation) of CAA granular adsorbent (A); AC (B).

### 3.2.5. Point of zero charge of the CAA granular adsorbent

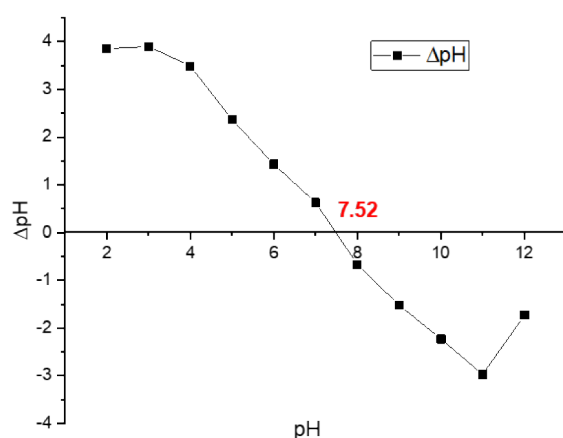
Understanding the point of zero charge ( $pH_{pzc}$ ) is crucial for optimizing adsorption processes, especially in industrial and environmental applications like wastewater treatment. The

$pH_{pzc}$  represents the pH at which the adsorbent surface carries no net charge, meaning it neither attracts nor repels charged species from the solution. Below this pH, the adsorbent surface tends to be positively charged, while above it, the surface becomes negatively charged.<sup>10</sup> This property plays a significant role in how the material interacts with different pollutants in aqueous solutions.

In this study, the  $pH_{pzc}$  of the CAA adsorbent was determined to be 7.52, as shown in Figure 8. This isoelectric point, where the surface charge is neutral, marks a key threshold in the material's ability to adsorb different ions. Specifically, below a pH of 7.52, the material's surface is positively charged, making it more likely to attract anions. Conversely, when the pH rises above 7.52, the surface becomes negatively charged, favoring the adsorption of cations.

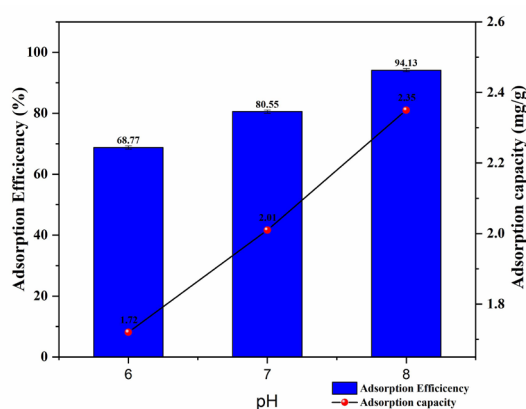
This finding is particularly significant for wastewater treatment applications. For example, the adsorption of MG, a cationic dye, is enhanced at pH values above 7.52, where the negative charge on the CAA surface attracts the positively charged dye molecules. This interaction promotes efficient adsorption of the dye, demonstrating how the  $pH_{pzc}$  plays a vital role in optimizing the removal of contaminants from wastewater.

The ability of the CAA material to efficiently adsorb both anions and cations at varying pH levels highlights its versatility as an eco-friendly adsorbent for wastewater treatment. By adjusting the pH of the solution, the adsorption efficiency of the material can be fine-tuned to target specific pollutants, providing a more adaptable and effective solution for real-world environmental applications. This underscores the significant impact of surface charge dynamics on the material's adsorption properties and its potential for treating wastewater in an eco-friendly and sustainable manner.



**Figure 8.**  $\text{pH}_{\text{pzc}}$  of granular adsorbent CAA.

The results presented in Figure 9 show that the adsorption efficiency and adsorption capacity increased significantly when the pH of the medium increased from 6 to 8.



**Figure 9.** Effect of pH on the adsorption capacity of MG dye from aqueous solution of CAA adsorbent.

Specifically, the adsorption efficiency increased from 68.77% to 94.13%, while the adsorption capacity increased from 1.72 mg/g to 2.35 mg/g. The  $\text{pH}_{\text{pzc}}$  value was determined to be 7.52. The change in the surface properties of the material with pH can explain the mechanism of increased adsorption through both the surface charge and the protonation state of the active functional groups. At pH lower than the isoelectric point ( $\text{pH} < 7.52$ ), the material surface is mainly positively charged because the functional groups such as the amine ( $-\text{NH}_2$ ) of chitosan are protonated to  $-\text{NH}_3^+$ . As pH increases, the  $-\text{NH}_3^+$  groups are gradually deprotonated back to  $-\text{NH}_2$

( $\text{pK}_a \approx 6.3\text{--}6.5$ ), reducing the positive surface charge and increasing the ability to adsorb cations through coordination interactions or ion exchange.<sup>23</sup> At the same time, the  $-\text{COOH}$  groups on alginate and  $-\text{OH}$  groups on activated carbon begin to be deprotonated at  $\text{pH} > 4\text{--}5$  ( $\text{pK}_a$  of  $-\text{COOH} \approx 3.5\text{--}4.5$ ;  $\text{pK}_a$  of  $-\text{OH} \approx 9\text{--}10$ ), resulting in an increasingly negative surface charge at  $\text{pH} > 7.5$ .<sup>24</sup> This facilitates the interaction with positively charged dye ions in solution.

#### 4. CONCLUSION

This study successfully developed an eco-friendly granular adsorbent, CAA, by combining AC from spent coffee grounds with CS and AL. The adsorbent features a uniform size, rough surface, and well-developed capillary system, enhancing its adsorption potential. AC, prepared at  $850^\circ\text{C}$ , showed a high degree of aromatic condensation, improving adsorption yield. The synthesis process was optimized with 3 g of AC, 0.75 M NaOH solution, 2% (w/v) AL concentration, and a 2-hour soaking period. FT-IR analysis confirmed successful integration of the components. The final adsorbent had an average diameter of  $1.05 \pm 0.04$  mm, specific surface area of  $11.231 \text{ m}^2/\text{g}$ , and a pore diameter of  $12.887 \text{ \AA}$ , making it ideal for dye removal. With a  $\text{pH}_{\text{pzc}}$  of 7.52, the CAA adsorbent demonstrates excellent potential for selectively adsorbing cationic dyes, such as MG, from wastewater. This study showcases the material's effectiveness and sustainability, offering a promising solution for environmentally-friendly wastewater treatment.

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## Đánh giá khả năng đối kháng của nấm *Trichoderma* spp. với nấm *Colletotrichum* spp. gây bệnh thán thư trên ớt chỉ thiên trong điều kiện *in vitro*

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### TÓM TẮT

*Colletotrichum* là một chi nấm gây bệnh thực vật quan trọng, lây nhiễm cho nhiều loại cây chủ. *Colletotrichum* spp. gây ra bệnh thán thư, dẫn đến tổn thất kinh tế nghiêm trọng trong nông nghiệp. *Trichoderma* spp. là một loại nấm đất phổ biến có hoạt tính đối kháng với nhiều loại mầm bệnh thực vật, bao gồm *Colletotrichum* spp., tác nhân gây bệnh thán thư trên ớt. Để xác định *Trichoderma* spp. có hoạt tính đối kháng cao với bệnh thán thư, ba mẫu đất đã được thu thập từ các vùng trồng ớt chỉ thiên tại huyện Phù Mỹ. Dựa trên các đặc điểm hình thái, bốn chủng *Trichoderma* spp. đã được phân lập và hai chủng có hoạt tính đối kháng cao với bệnh thán thư đã được chọn. Trong số đó, Tr.1 và Tr.2 thể hiện chỉ số đối kháng cao lần lượt là 74,78% và 85,44%, trong điều kiện *in vitro*. Phân tích trình tự ITS xác định Tr.1 là *T. viride* và Tr.2 là *T. asperellum*. Hai chủng đối kháng này có tiềm năng đầy hứa hẹn trong việc kiểm soát sinh học bệnh thán thư ở ớt chỉ thiên.

**Từ khóa:** Đối kháng, bệnh thán thư, tác nhân gây bệnh nấm, *Colletotrichum indemuthianum*, *Trichoderma*.

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# Evaluation of the antagonistic activity of *Trichoderma* spp. against *Colletotrichum* spp. causing anthracnose in chili pepper under *in vitro*

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## ABSTRACT

*Colletotrichum* is an important genus of plant-pathogenic fungi that infects a wide range of host plants. *Colletotrichum* spp. causes diseases such as anthracnose, leading to significant economic losses in agriculture. *Trichoderma* spp. is a common soil fungus with antagonistic activity against various plant pathogens, including *Colletotrichum* spp., the causal agent of anthracnose in chili pepper. To identify *Trichoderma* spp. with high antagonistic activity against anthracnose, three soil samples were collected from skyward pointing chili pepper growing areas in Phu My District. Based on morphological characteristics, four *Trichoderma* spp. strains were isolated, and two strains with high antagonistic activity against anthracnose were selected. Among them, Tr.1 and Tr.2, exhibited high antagonistic indices of 74,78% and 85,44%, respectively, under *in vitro* conditions. ITS sequence analysis identified Tr.1 as *T. viride* and Tr.2 as *T. asperellum*. These two antagonistic strains hold promising potential for biological control of anthracnose in skyward pointing chili pepper.

**Keywords:** Antagonistics, anthracnose, fungal pathogens, *Colletotrichum indemuthianum*, *Trichoderma*.

## 1. INTRODUCTION

Chili peppers (*Capsicum frutescens* L. var. *fasciculatum* (Sturt) Bailey), belonging to the Solanaceae family, are one of the most important and widely grown spice plants in the world.<sup>1,2</sup> Vietnam's chili growing areas span the country, from North to South, covering approximately 50.000 hectares.<sup>3</sup> Of which, Binh Dinh province (Phu My, Phu Cat, and Tay Son districts) is the largest producer. However, fungal diseases, particularly anthracnose, significantly impact yields and cause substantial economic losses.<sup>4</sup> Anthracnose is characterized by small, round

spots initially appearing on chili pepper leaves and fruits. These spots progress, causing infected areas to become sunken and dry.<sup>5</sup> The disease is caused by various *Colletotrichum* species. Previous studies believed that at least five species have been associated with anthracnose in peppers, including *C. gloeosporioides*, *C. acutatum*, *C. coccoides*, *C. dematium*, and *C. truncatum*.<sup>6</sup>

Chemical control of chili anthracnose presents significant drawbacks.<sup>7</sup> Pesticide use contributes to environmental pollution, poses risks to human health, and drives the

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development of pesticide-resistant fungal strains. Consequently, alternative and sustainable methods such as biological control have been studied and applied for creating a safer and cleaner agricultural system. Antagonists (also known as biological control agents) are often soil microorganisms. They can suppress fungal pathogens through various mechanisms including competition, antibiosis (antibiotic production), and parasitism.<sup>8</sup> *Trichoderma* spp., for example, is a well-established antagonist of soilborne pathogens, including *C. truncatum*, a causative agent of chili anthracnose.<sup>9</sup> *Trichoderma*-based biocontrol agents are increasingly utilized globally as a safer and more environmentally alternative to chemical pesticides.<sup>10</sup>

*T. viride* shows the strongest potentials for inhibiting mycelial growth and spore germination of *C. lindemuthianum*.<sup>11</sup> *T. asperellum*, in dual-culture studies, effectively inhibited various filamentous fungal pathogens. Furthermore, *T. asperellum* exhibits plant growth-promoting properties, including IAA production, phosphate solubilization, and positive impacts on seed germination, root and leaf development.<sup>12</sup>

This study aims to: (1) isolate and identify *Trichoderma* spp. species from skyward pointing chili pepper soil samples in Phu My, Binh Dinh; (2) select *Trichoderma* spp. strains with antagonistic activities against skyward pointing chili peppers' anthracnose.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Pathogenic fungal samples on chili fruits and soil samples from chili-growing areas in My Cat Commune, Phu My District, Binh Dinh Province.

Isolation of *Trichoderma* fungi from soil samples collected in chili-growing areas in My Cat Commune, Phu My District, Binh Dinh Province.

Fungal culture medium: Potato Dextrose Agar (PDA) medium.

Essential chemicals and materials for the research: Agar, glucose, petri dishes, test tubes, sample cutting knives, forceps, alcohol lamp, measuring cylinders, filter paper, glass slides, cover slips, pots, jars, inoculating loops, drying oven, autoclave, refrigerator, incubator, biosafety cabinet and microscope.

### 2.2. Methods

#### 2.2.1. Sample collection method

##### - Soil sample collection method

Soil samples were collected from the rhizosphere of healthy skyward pointing chili pepper plants in three communes (My Cat, My Tai, and My Trinh), Phu My, Binh Dinh.

Three soil samples (500g each) were collected and stored in sterile bags, and transported to the laboratory for analysis within one day (maximum one week at 2-4°C).<sup>13</sup>

##### - Collection of pathogenic fungal samples of skyward pointing chili peppers

Pathogenic fungal samples of chili fruits were collected at growing areas from My Cat commune. They were similarly stored and transported to the laboratory for analysis within one day (maximum one week at 2-4°C).

#### 2.2.2. Isolation methods

##### Isolation pathogenic fungi

Diseased chili fruits were thoroughly washed under running tap water. Small tissue pieces (0,5-1 cm), excised from the border between healthy and diseased tissue using a sterile blade, were surface-sterilized in NaCl 0,9% for one minute and rinsed with sterile distilled water. Sterilized tissue pieces were inoculated onto PDA (Potato Dextrose Agar) plates and incubated at  $28 \pm 2^\circ\text{C}$  for 48 hours. Putative *Colletotrichum* colonies on PDA were purified, and pure cultures were stored at 4°C for further analysis.<sup>14</sup>

##### - Isolation *Trichoderma*

One gram of soil from each sample was suspended in NaCl 0,9% and serially diluted to

$10^6$ . 0,1 ml of the  $10^{-4}$ ,  $10^{-5}$ ,  $10^{-6}$  dilutions were spread onto PDA plates and incubated at  $28 \pm 2^\circ\text{C}$  for 48 hours. Putative *Trichoderma* colonies on PDA were purified, and pure cultures were stored at  $4^\circ\text{C}$  for further analysis.<sup>15</sup>

### 2.2.3. Morphological identification method

Fungal colonies from the third generation of isolation were subcultured onto fresh PDA plates and incubated at  $28^\circ\text{C} \pm 2^\circ\text{C}$  for three days. Colony morphology was assessed daily, while spore and hyphal structures were examined using an optical microscope. The morphological characteristics were then compared with reference descriptions from previous for identification.<sup>16</sup>

### 2.2.4. Molecular identification method

Molecular identification method of fungi: Ribosomal RNA barcode gene region was used for identification. Total DNA was extracted from purified fungal samples by CTAB method.<sup>17</sup> Primer pair ITS1 (5'-TCCGTAGGTGAACCTGCGG-3', forward) and ITS4 (5'-TCCTCCGCTTATTGATATGC-3', reverse) were used to amplify the ITS region by PCR technique (2,5  $\mu\text{L}$  PCR buffer; 0,5  $\mu\text{L}$  total DNA; 0,5  $\mu\text{L}$  dNTP; 1  $\mu\text{L}$  each primer and 0,2  $\mu\text{L}$  Taq polymerase).<sup>18</sup> The thermal cycling conditions included an initial denaturation at  $94^\circ\text{C}$  for 3 min, followed by 35 cycles of denaturation at  $94^\circ\text{C}$  for 30 s, annealing at  $52^\circ\text{C}$  for 30 s, and extension at  $72^\circ\text{C}$  for 45 s, with a final extension at  $72^\circ\text{C}$  for 5 min. The PCR product was purified using PureLink Quick Gel Extraction Kit (Invitrogen, USA) for 2-way direct sequencing (NK Biotek Laboratory, Ho Chi Minh City, Vietnam).

### 2.2.5. Sequence Analysis

Sequencing data were analyzed using the BLAST algorithm available in the National Center for Biotechnology Information (NCBI) nucleic acid database. Phylogenetic relationships

were inferred using the Neighbor-Joining (NJ) method with the maximum composite likelihood substitution model in MEGA 7.0.<sup>16</sup> Tree reliability was assessed through 1000 bootstrap (BS) replicates.

### 2.2.6. Method for testing *Trichoderma* spp. antagonism against *Colletotrichum* spp. causing anthracnose in vitro.

- A symmetrical inoculation method was used on Petri dishes under laboratory conditions, employing two treatments:

+ Control (Ctrl): *Colletotrichum* spp. inoculation only

+ Experiment (Ex): Simultaneous inoculation of *Trichoderma* spp. and *Colletotrichum* spp.

- Fungal strains were inoculated onto PDA at  $28 \pm 2^\circ\text{C}$ . Colony diameter and growth were monitored.<sup>19</sup>

$$\text{Antagonistic ratio} = \frac{(R_{\text{ctrl}} - R_0) - (R_{\text{ex}} - R_0)}{(R_{\text{ctrl}} - R_0)} \times 100$$

In which:

Antagonistic ratio (T)

$R_{\text{ctrl}}$ : radius of the pathogenic fungal colony on the control plate;  $R_{\text{ex}}$ : radius of the pathogenic fungal colony on the treatment plates;  $R_0$ : radius of the initial fungal inoculum (3 mm).

Antagonistic efficiency (H):

- 75%: very high antagonism
- 60-75%: high antagonism
- 50-60%: medium antagonism
- $\leq 50\%$ : low antagonism

### 2.2.7. Data collection and processing methods

The reported data are the average values of 3 experimental repetitions. The data were processed using Statgraphics 19 - X64. The average values were analyzed by ANOVA using the Tukey test and the value of  $p < 0.05$  indicates a statistically significant difference.

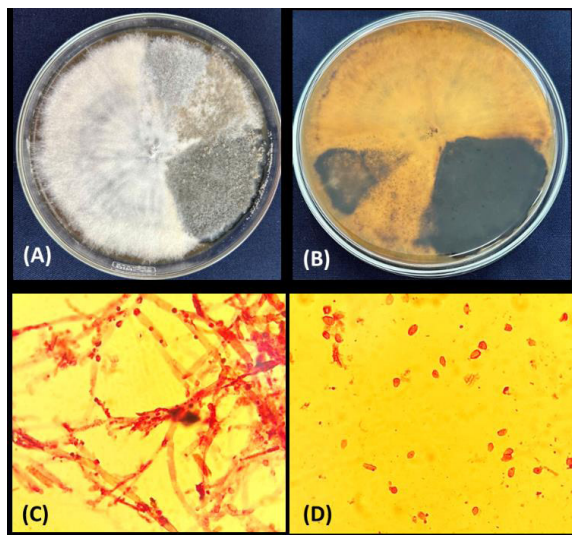
### 3. RESULT

#### 3.1. Isolation and morphological identification of anthracnose fungus on chili peppers

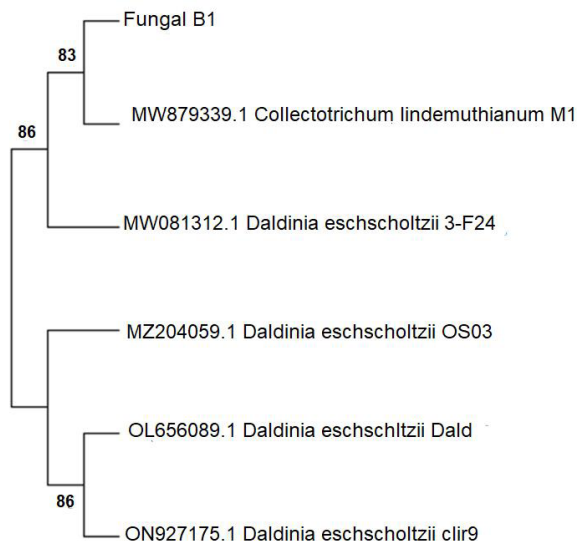
The diseased chili samples collected from chili fields of farmers in My Cat commune, Phu My District, Binh Dinh Province, were isolated on a PDA medium. The isolation results are presented in Figure 1.

The results of morphological observations showed that the isolated samples were *Colletotrichum* spp. with the characteristics of aerial mycelium growing loosely or close to the surface of the agar (QCVN 01-160:2014/ BNNPTNT). The fungal colony is concentrically circular, the upper surface is white then turns gray, the lower surface is pink-orange to black. The fungus has septa and branches. The transparent spores are cylindrical in shape, with two rounded ends or one rounded end and one pointed end. On PDA, spores appear after 96 hours. Sclerotia appear after 7 days.

Based on the morphological assessment of the isolated samples, we determined that the agent was *Colletotrichum* spp., although there was still not enough evidence to determine the exact species.



**Figure 1.** Morphological characteristics of fungal samples on PDA medium after 7 days, observed under an Olympus microscope with a magnification of 60X. (A): front of the mushroom disc, (B): back of the mushroom disc, (C): Mycelium, (D): Spore shape



**Figure 2.** Genetic tree of the Fungal B1 isolate with some samples in the gene bank.

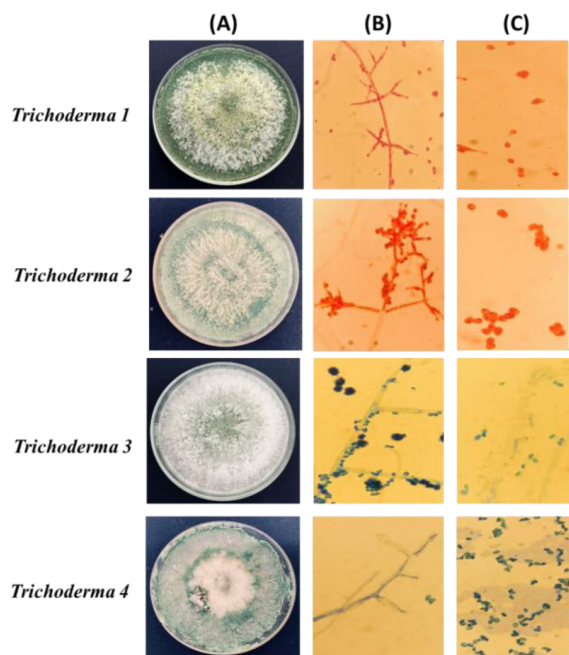
Therefore, the fungal samples were then identified by PCR technique with the primer pair ITS1 - ITS4. The results of the species clustering tree analysis showed that the Fungal B1 isolate was in the same branch as *Colletotrichum lindemuthianum* M1 with a Bootstrap value of 83% (Figure 2), the similarity level of the Fungal B1 isolate with *Colletotrichum lindemuthianum* M1 was 99.62%.

Based on the results of the identification of the agent causing anthracnose on chili plants as *Colletotrichum lindemuthianum*, this source of isolated samples was used to conduct further studies.

#### 3.2. Isolation and identification of *Trichoderma* spp. Fungi

Soil samples from chili fields were collected from many locations with different ecological environments in Phu My district, Binh Dinh, to isolate *Trichoderma* spp. The results isolated a total of 4 fungal strains with typical morphology of *Trichoderma* spp. (white, spongy fungal colonies, forming elliptical/spherical conidia, smooth surface). After 5 days of culture, the fungal colonies gradually turned green, forming many conidia, and the flask was cylindrical in shape (Figure 3).





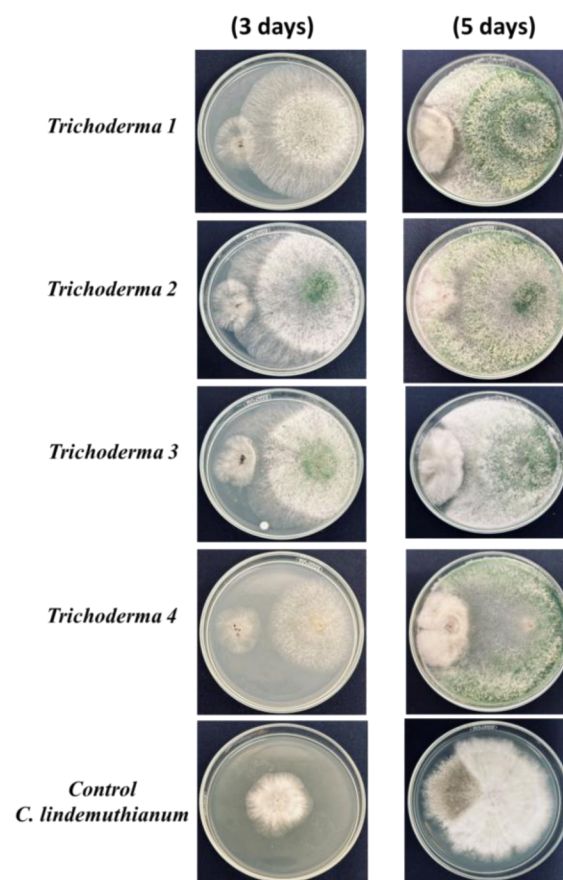
**Figure 3.** Morphology of colony (A), colonia (B) and Spore (C) of *Trichoderma* on PDA. Analysis performed at 60x.

### 3.3. Evaluation of antagonistic efficacy between *Trichoderma* spp. and anthracnose fungi on chili plants under *in vitro* conditions

Next, with the aim of evaluating the antagonistic ability against *Colletotrichum lindemuthianum*, the 4 isolated *Trichoderma* spp. strains were cultured symmetrically on both sides on PDA medium (Figure 4).

The results showed that the 4 *Trichoderma* spp. strains all showed the ability to antagonize the pathogen, with an efficacy of 54.66 - 85.88% (Table 1). Of which 2 strains of *Trichoderma* spp., Tr.1 and Tr.2, have the strongest antagonistic effect against *Colletotrichum lindemuthianum* causing anthracnose, with an inhibitory effect of 74,78 – 85,88% (Table 1). In previous studies, *Trichoderma* spp. have been noted to have good inhibitory ability against anthracnose pathogens in chili. Previous studies by other authors showed that preparations containing *Trichoderma* spp. have the ability to significantly limit anthracnose caused by *Colletotrichum* spp. on chili plants.<sup>20-22</sup> Spraying the preparation evenly on the plant combined with spreading the preparation

around the base is a feasible measure to limit anthracnose. Based on this result, 2 strains of *Trichoderma* spp., Tr.1 and Tr.2, were selected for scientific identification in order to potentially use them in the future to protect the plants.



**Figure 4.** Antagonism of *Trichoderma* spp. against *C. lindemuthianum* on PDA, at 28 °C ± 2 after 3 days and 5 days.

The result is consistent with previous studies on *Trichoderma* spp. Pham Thi Ly Thu selected *Trichoderma* spp. with high antagonistic activity against fungi causing anthracnose on mango trees in provinces of the Mekong area. The result recorded 6 strains Tr.X1, Tr.X2, Tr.X3, Tr.X4, T1, M2 with the highest antagonistic activity from 77,76-86,25% *in vitro*.<sup>23</sup> Nguyen Anh Dung examined the antagonistic ability of 14 *Trichoderma* strains isolated on agricultural land with the ability to antagonize the *Corticium samonicolor* fungus on rubber trees.<sup>7</sup> In addition, Aisha Saleh Alwadai isolated 48 *Trichoderma* spp. from the soil samples having antagonist



potential against the tested plant pathogenic fungi. There were three strains with highly effective in reducing the growth of tested plant pathogenic fungi. *Trichoderma* A (1) 2.1 T was highly effective against *F. oxysporum* (82%), *Trichoderma* A (6) 2.2 T prevented the maximal growth of *H. rostratum* (77%) according to the dual culture data.<sup>24</sup>

**Table 1.** Antagonistic efficiency between *Trichoderma* spp. and *C. lindemuthianum* on PDA, at 28 °C ±2.

| Tr.   | 3 days                     |        | 5 days                    |           |
|-------|----------------------------|--------|---------------------------|-----------|
|       | T (%)                      | H      | T (%)                     | H         |
| Tr. 1 | 57,22 ± 11,12 <sup>a</sup> | Medium | 74,78 ± 4,51 <sup>b</sup> | High      |
| Tr. 2 | 58,61 ± 7,67 <sup>a</sup>  | Medium | 85,44 ± 5,25 <sup>c</sup> | Very high |
| Tr. 3 | 55,04 ± 7,73 <sup>a</sup>  | Medium | 58,40 ± 2,17 <sup>a</sup> | Medium    |
| Tr. 4 | 58,62 ± 7,16 <sup>a</sup>  | Medium | 54,66 ± 2,34 <sup>a</sup> | Medium    |

Note: Numbers in the same column followed by one or more identical letters are not significantly different by Duncan's test.

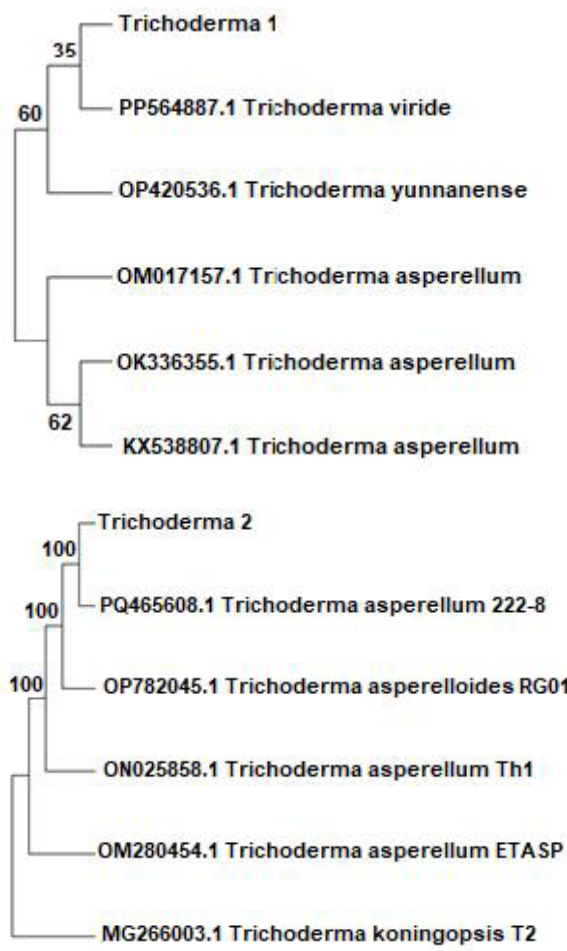
**3.4. Identification of *Trichoderma* spp. fungi antagonistic to anthracnose pathogens in chili plants**

To identify the *Trichoderma* spp. molecularly, this study sequenced the ITS region of the fungal strains and constructed a phylogenetic tree with known data on *Trichoderma* species based on the GeneBank database.

The results showed that the Tr.1 strain belonged to the *Trichoderma viride* T-VT-15 species with a similarity level of ITS sequence reaching 100% and a Bootstrap value of 35%, while the Tr.2 strain belonged to the *Trichoderma asperellum* Z228 species with a similarity level of ITS sequence reaching 100% and a Bootstrap value of 100% (Figure 5).

Previous studies have shown that the antagonistic ability of *Trichoderma* spp. against pathogens is explained by the exogenous cellulase,

protease and chitinase production properties to destroy the cell wall of pathogenic fungi.<sup>25</sup>



**Figure 5.** Genetic tree of the *Trichoderma* 1 and 2 with some samples in the gene bank.

**4. CONCLUSION**

From soil samples collected in chili growing areas in My Cat commune, Phu My District, Binh Dinh Province, the study isolated 4 strains of *Trichoderma* spp. Under *in vitro* conditions, 2 out of 4 strains of *Trichoderma* spp. showed a strong antagonism against *Colletotrichum lindemuthianum* causing anthracnose in chili plants with an efficacy ranging from 74,78 to 85,88%.

Based on morphological characteristics and ITS region sequencing, *Trichoderma* Tr. 1 strain was identified as belonging to the *Trichoderma viride* species and *Trichoderma* Tr. 2 to the *Trichoderma asperellum* species.

The study will continue to test the effectiveness of using *Trichoderma* Tr. 1 and Tr. 2 strains to produce biological products for application in controlling anthracnose on chili plants.

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# Phương pháp xanh và đơn giản để chế tạo graphene oxide từ graphite bằng phương pháp bóc tách điện hóa

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## TÓM TẮT

Trong nghiên cứu này, vật liệu graphene oxide chất lượng cao, kích thước lớn đã được chế tạo từ thanh graphite bằng phương pháp bóc tách điện hóa. Điện cực graphite được sử dụng là thanh graphite thương mại giá rẻ, dung dịch điện ly là  $(\text{NH}_4)_2\text{SO}_4$ . Các điều kiện của điện áp ảnh hưởng đến chất lượng graphene oxide đã được kiểm tra chi tiết. Điện áp được sử dụng trong phương pháp bóc tách điện hóa được thay đổi từ 4.5 đến 10 V. Các đặc trưng của graphene oxide đã được kiểm tra thông qua các phép đo như kính hiển vi điện tử quét (SEM), phổ tán sắc năng lượng tia X (EDX), Phổ hấp thụ hồng ngoại (FTIR) và quang phổ Raman. Bằng phương pháp thân thiện môi trường và đơn giản, graphene oxide đã được chế tạo thành công với chất lượng cao, diện tích bề mặt lớn và khả năng phân tán tốt trong nước. Với điều kiện thích hợp (từ 6 đến 8 V), graphene oxide thu được đạt hiệu suất cao (70%), tỷ lệ sai hỏng thấp với tỷ số C/O cao (4.3) và  $I_D/I_G$  thấp (0.47), khả năng phân tán tốt với thế Zeta = -39.4 mV. Graphene oxide thu được có tiềm năng ứng dụng cho xử lý môi trường và các vật liệu composite.

**Từ khóa:** Graphene oxide, bóc tách điện hóa, graphite, điện áp không đổi.

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# A simple green approach for synthesizing graphene oxide from graphite via electrochemical exfoliation

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## ABSTRACT

In this work, high-quality graphene oxide with large lateral dimensions was synthesized via a green and simple electrochemical exfoliation method from graphite rods. The graphite electrode utilized was a commercially available graphite rod, and the electrolyte mixture consisted of ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$ , which is both a readily accessible and cost-effective materials. The effects of various potential conditions on the quality of graphene were examined in detail. Graphene oxide materials were fabricated via an electrochemical exfoliation approach in ammonium sulfate, employing a constant voltage range of 4.5-10 V. The characteristics of the graphene oxide were confirmed by Scanning electron microscope (SEM), Energy dispersive X-ray (EDX), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy. Through this environmentally friendly and straightforward method, few-layer graphene oxide was successfully produced, exhibiting high quality, large surface areas, and excellent dispersion in water. At an appropriate voltage (from 6 to 8 V), the graphene oxide demonstrated a high yield (70%), larger surface areas, a high C/O ratio (4.3), low defect density ( $I_D/I_G=0.47$ ), and good dispersion in water (Zeta potential = -39.4 mV). The obtained graphene oxide holds potential for applications in environmental treatment and composite materials.

**Keywords:** *Graphene oxide, electrochemical exfoliation, graphite, constant voltage.*

## 1. INTRODUCTION

Graphene is a single-layer two-dimensional honeycomb lattice of carbon atoms with  $\text{sp}^2$  hybridization. Graphene possesses many remarkable properties such as high electrical and thermal conductivity, high mechanical strength, and high electron mobility.<sup>1-3</sup> Due to its unique properties, graphene has found applications in a wide range of fields, such as corrosion prevention,<sup>3</sup> composite materials,<sup>4</sup> supercapacitors and batteries,<sup>5</sup> sensors,<sup>2</sup> and environmental remediation.<sup>6</sup>

Currently, there are two main approaches to synthesize graphene: bottom-up and top-down. Bottom-up methods typically include chemical vapor deposition<sup>7</sup> and organic synthesis in solution.<sup>8</sup> Top-down methods are referred to as graphite exfoliation methods, including high energy milling, micromechanical cleavage, the Hummer's method (chemical), and electrochemical exfoliation.<sup>9,10</sup> The fabrication of graphene often faces a significant challenge in balancing two factors: the yield and the quality of the graphene material. While the

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chemical vapor deposition (CVD) method can produce single layer and large area films, it requires relatively complex conditions such as high-temperature, inert reaction chambers and expensive experimental equipment. Mechanical exfoliation (without chemical modification) generally high-yield quality but suffers from very low production efficiency.<sup>11</sup> On the other hand, chemical exfoliation methods for producing graphene oxide (GO) typically offer high yields and are commercially viable. However, the presence of oxygen-containing functional groups on the large surface area, resulting in a low C/O ratio, significantly reduces the properties of GO compared to pristine graphene. This significantly impacts the potential applications of the obtained product.

In recent years, the electrochemical method has emerged as a fast, simple, efficient, and environmentally friendly technique for graphene fabrication, attracting significant attention from scientists. Electrochemical exfoliation of graphene or GO from graphite involves applying a negative (cathodic) or positive (anodic) potential to one end of graphite electrode, with the other end connected to a counter electrode, typically platinum or graphite. Under the influence of the electric field within the electrolyte solution, positive ions ( $\text{Li}^+$ ) migrate and intercalate between the layers of the graphite cathode, separating the layers to form graphene (cathodic exfoliation). Conversely, negative ions ( $\text{SO}_4^{2-}$ ) can be attracted to the anode to exfoliate graphite into graphene (anodic exfoliation). Various forms of graphite materials are used for electrochemical graphene fabrication, including graphite sheets, rods, and highly oriented pyrolytic graphite. Several factors influence the yield and quality of electrochemically exfoliated graphene, with four primary factors being (1) the shape of the graphite electrode, (2) the applied voltage, (3) the electrolyte solution, and (4) the reduction method employed after graphene or GO synthesis.

Graphite electrodes used in electrochemical exfoliation are typically natural graphite in the form of foils, rods, or sheets, as well as highly oriented pyrolytic graphite (HOPG).<sup>12</sup> Munuera et al. demonstrated that using graphite foil can reduce the oxidation of graphene during electrochemical exfoliation compared to HOPG.<sup>11</sup> Fuertes et al. also indicated that graphite rods or sheets generally exhibit lower exfoliation rates than graphite foils. However, graphite rods produce graphene material with a thickness of about two layers and a high C/O ratio (11.7), with graphene sheet sizes around  $1\text{ }\mu\text{m}$ .<sup>13</sup> Green et al. showed that graphite rods can be used to produce high-quality graphene through electrochemical methods, but with the drawback of low efficiency when using a constant voltage.<sup>14</sup> Chen et al. utilized pencil cores containing a mixture of graphite and clay as graphite electrodes. After electrochemical exfoliation, the obtained graphene material floats on the surface of the solution while the clay settles to the bottom, allowing for easy collection of graphene after synthesis.<sup>15</sup> Natchanon et al. also fabricated graphene using pencil lead via an electrochemical method, resulting in graphene with low electrical resistance ( $1.86\text{ k}\Omega$ ).<sup>16</sup>

The quality and yield of graphene production also depend on the voltage applied to the graphite electrode, encompassing both anodic and cathodic exfoliation. Studies have shown that alternating current (AC) or direct current (DC) can be used in electrochemical methods for graphene fabrication. Yang et al. demonstrated the feasibility of using an AC source with  $[\text{TBA.HSO}_4]$  as the conductive medium to obtain graphene that meets both quality and yield criteria.<sup>17</sup> Their results showed that graphene (1-3 layers) accounted for over 75% of the obtained product with a high C/O ratio. Srivastava et al. also employed a constant voltage with varying values from 2-10 V to evaluate the quality and yield of graphene in electrochemical fabrication. The findings indicated that while higher voltages lead to increased yields, the quality of graphene decreases due to increased

defect density and higher oxygen content in the graphene.<sup>18</sup> Eredia et al. further highlighted that longer electrochemical exfoliation times result in lower C/O ratios, significantly impacting the quality of graphene.<sup>19</sup> To enhance graphene quality, several research groups have introduced equipment modifications. For instance, Xu et al. proposed limiting the contact between the graphite rod and the electrolyte surface during electrochemical exfoliation by continuously replenishing the electrolyte solution as the graphite rod is consumed,<sup>20</sup> this approach yielded graphene with fewer than three layers and sizes ranging from 3-5  $\mu\text{m}$ . Additionally, other groups have introduced innovative techniques such as pressing graphite powder into rods using filter membranes or combining it with an electric field to cut graphite layers within the electrolyte solution for higher efficiency.<sup>14,21</sup>

The electrolyte solution significantly influences the quality and yield of graphene in electrochemical fabrication. The ions in the electrolyte solution must have a size compatible with the interlayer spacing in the graphite structure (0.35 nm). Commonly used electrolytes include  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaBr}$ ,  $\text{NaI}$ , and  $\text{KOH}$ , as their dissociated ions have sizes comparable to the interlayer spacing of graphite.<sup>11</sup> After electrochemical graphene synthesis, the oxygen content can vary depending on the experimental conditions, leading to the formation of GO. While GO exhibits good dispersion in organic solvents and finds applications in various fields, it has limitations due to altered physicochemical properties compared to pristine graphene. Typically, GO is converted to reduced graphene oxide (rGO) through thermal reduction at high temperatures (500 - 800  $^{\circ}\text{C}$ ) under suitable conditions.<sup>22,23</sup>

## 2. EXPERIMENTAL

### 2.1. Materials

An electrode for fabricating graphene is a cheap, commercially cylindrical graphite rod (carbon; 99.9%) with a length of 100 mm and a diameter

of 10 mm which acts as the positive electrode. The negative electrode is the other same graphite rod. The power supply is a programmable control source (IT6832A) manufactured by ITECH (Taiwan). This power supply can adjust the DC voltage from 0 to 32 V and the maximum current up to 6 A. The programmable source can be adjusted using buttons or knobs, the voltage or current values can be held at constant values or varied arbitrarily with different pulse modes dependent on time and amplitude. Ammonium sulfate solution  $(\text{NH}_4)_2\text{SO}_4$  was bought from Sigma Aldrich. Filtration film MCE (Mixed Cellulose Ester, Advantec) with a pore size of 0.45  $\mu\text{m}$  and a diameter of 47 mm.

In this experiment, an electrolyte solution of  $(\text{NH}_4)_2\text{SO}_4$  0.5 M (200 mL) is placed in a heat-resistant glass beaker, and constant voltages are applied, including 4.5 V, 6 V, 8 V, and 10 V. The samples are labeled as GO4, GO6, GO8 and GO10, respectively. Initial temperature conditions are measured using a thermometer, indicating a range of 25-27 $^{\circ}\text{C}$ , and the currents are 0.6 A, 1.1 A, 1.9 A, and 2.8 A, respectively (Table 1).

**Table 1.** Constant voltages applied with 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  electrolyte solution.

| Voltage (V)                                | 4.5 | 6   | 8   | 10   |
|--------------------------------------------|-----|-----|-----|------|
| Sign                                       | GO4 | GO6 | GO8 | GO10 |
| Initial temperature ( $^{\circ}\text{C}$ ) | 26  | 25  | 26  | 27   |
| Initial current (A)                        | 0.6 | 1.1 | 1.9 | 2.8  |

### 2.2. Characterizations

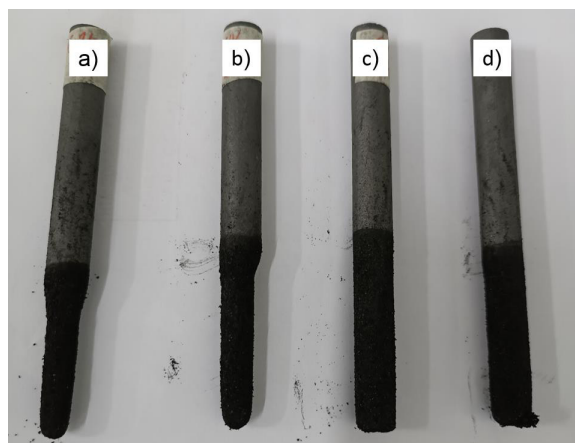
The surface morphologies, structure and electro-physical measurements of the fabricated materials were investigated using scanning electron microscopy (SEM, Hitachi S-4800, Japan) with X-ray energy dispersive spectrometry (EDS), Raman spectroscopy (Horiba, Japan) with 532 nm excitation source, Fourier transform infrared spectroscopy (FTIR) spectroscopy (Bruker,

Germany) was used to investigate the functional groups of the nanocomposite, Zeta potential of nanoparticle samples was investigated by Zeta potential analyzer (SZ-100, Horiba).

### 3. RESULT AND DISCUSION

#### 3.1. The efficiency of graphite electrode exfoliation

The structure of graphite is an arrangement of graphene sheets through  $\pi$ - $\pi^*$  bonds with a distance of approximately 0.35 nm between the layers. Under the influence of a positive potential, the anions in the electrolyte solution ( $\text{SO}_4^{2-}$ ) with a diameter of approximately 0.46 nm are dissociated and move toward the anode electrode. Due to the expansion of the electrodes in the electrolyte solution along with the appropriate size of  $\text{SO}_4^{2-}$  ions, these ions can easily intercalate into the layers of graphite leading to the electrochemical exfoliation process. Graphite rod electrodes with a mass of 11.2 g ( $\pm$  0.1 g) after being exfoliated in an  $(\text{NH}_4)_2\text{SO}_4$  0.5 M for 2 hours at several voltages of 4.5 V, 6 V, 8 V, and 10 V are depicted in Figure 1.



**Figure 1.** Images of the graphite electrode after erosion at different voltages: (a) 10 V, (b) 8 V, (c) 6 V, and (d) 4.5 V.

The results show the extent of graphite electrode erosion depends on the applied voltage across the electrodes. With a voltage of 10 V (Figure1a), the mass of the sample GO10 obtained is 3.36 g and represents the highest value among the surveyed voltages. Upon decreasing the voltage to 8 V (Figure 1b),

the mass of the exfoliated GO8 decreased to 2.69 g. Figure 1c, d illustrate the relatively low levels of electrode erosion for the graphite electrode corresponding to voltages of 4.5 V and 6 V, yielding 0.45 g (sample GO4) and 0.85 g (sample GO6), respectively. Thus, as the voltage increases, the mass of exfoliation also increases within the same experimental duration. To assess the efficiency of obtaining GO from graphite, the solution after electrochemical exfoliation was filtered, washed, sonicated for 1 hour, and centrifuged at 5000 rpm for 10 minutes. The ratio of the mass of the graphene obtained after centrifugation to the mass of exfoliated graphite was determined as the efficiency of graphene synthesis (Table 2).

**Table 2.** Effect of applied voltage on electrode exfoliation level and yield.

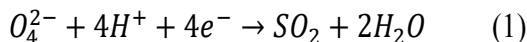
| Voltage             | 10 V | 8 V  | 6 V  | 4.5 V |
|---------------------|------|------|------|-------|
| Exfoliated mass (g) | 3.36 | 2.69 | 0.85 | 0.45  |
| Yield (%)           | 55   | 61   | 70   | 80    |
| Sample sign         | GO10 | GO8  | GO6  | GO4   |

Although GO10 exhibits significant exfoliation mass, the obtained efficiency is low (55%) due to the high voltage applied to the electrolyte solution, which not only generates small-sized graphene due to intense oxidation but also results in the presence of a large quantity of large-sized graphite particles created by the high voltage. In contrast, with a voltage of 8 V, the obtained GO8 shows an increased efficiency of 61%, representing a 6% improvement. This result also demonstrates that GO8 exhibits more uniform size due to reduced oxidation compared to the 10 V. As the voltage is further reduced to 6 V and 4.5 V, the efficiencies of GO6 and GO4 increase to 70% and 80%, respectively, indicating a more uniform size distribution in the obtained graphene materials.

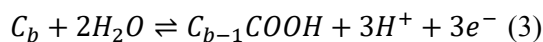
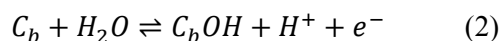
The mechanism of the electrochemical exfoliation of graphite rods can be described



as follows: when a sufficiently high voltage is applied across the electrodes, water reduction reactions occur at the cathode producing hydroxyl ions ( $\text{OH}^\bullet$ ) that act as strong nucleophiles in the electrolyte solution. These strong nucleophiles migrate to the graphite anode and undergo initial reactions in the vicinity of the graphite rod. Oxidation occurs in the electrode vicinity, leading to changes in the charge and expansion of the graphite layers. This creates favorable conditions for sulfate ions ( $\text{SO}_4^{2-}$ ) to intercalate into the layers of graphite. During this process, water molecules can also intercalate simultaneously with the  $\text{SO}_4^{2-}$  ions. The reduction of sulfate ions and the auto-oxidation of water produce gases such as  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , etc., observed as gas bubbles emitted at the electrodes during the electrochemical exfoliation. At the positive electrode, the reduction of sulfate ions to form  $\text{SO}_2$  may exert a force large enough to separate the graphite layers into thinner sheets, with the reaction equation taking the form:



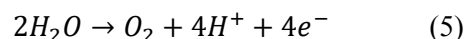
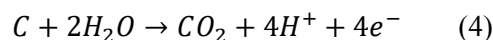
During the electrochemical exfoliation process, under the application of an applied voltage across the two electrode ends, electrons flow out from the anode and several reactions take place, including carboxylation, carbonylation, and water oxidation. These reactions can be described as follows: <sup>24</sup>



The reactions can be explained as follows: when a sufficiently high voltage is applied to the graphene electrode, hydroxide ions ( $\text{OH}^\bullet$ ) generated from water attack the  $\text{sp}^2$  carbon bonds in the graphite, leading to the formation of hydroxyl groups and carboxyl groups. Additionally, other functional groups such as epoxy and carbonyl groups may also form during the electrochemical process.

The oxidation process is associated with gas bubbling at the negative electrode.

The appearance of gas bubbles is due to the formation of  $\text{O}_2$  gas through the self-oxidation of water and  $\text{CO}_2$  gas formation through the C-O bond formation at the electrode, following the reactions:<sup>24</sup>



The change in electrolyte solution temperature was monitored during the electrochemical exfoliation process (Table S1). The results demonstrate that as the exfoliation time increases, the solution temperature also rises. This indicates that the dynamic processes occurring within the solution continuously move ions, resulting in an increase in the system's thermal energy and, consequently, the solution temperature.

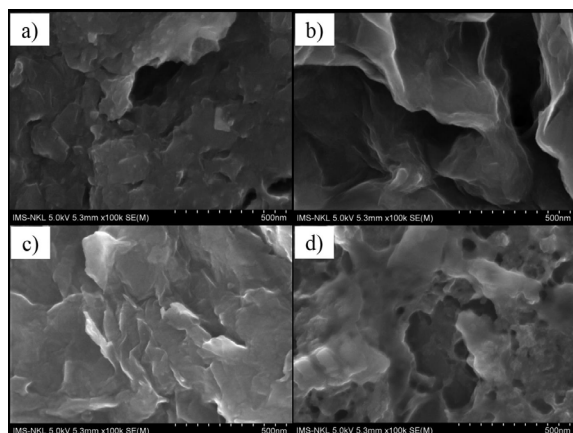
To assess the impact of GO after exfoliation and immersion in an electrolyte solution, we also measured the current passing through the circuit, and the results obtained are shown in Figure S1. The obtained results indicate that the current through the circuit with different constant voltages tends to slightly increase, then gradually decrease towards the initial value at the end of the experiment. The detailed analysis results are presented in Table S2.

### 3.2. Morphology of graphene

The surface morphology of the GO material synthesized at constant voltages of 4.5 V, 6 V, 8 V, and 10 V is illustrated in the SEM image of Figure 2. The results indicate that at a voltage of 4.5 V (Figure 2a), the GO4 material exhibits exfoliation into small layers with relatively smooth surfaces and considerable thickness, suggesting minimal oxidation occurred in the GO4 samples. Upon increasing the voltage to 6 V (Figure 2b), the GO6 sample shows the formation of thinner layers, larger-sized GO, and evident folds, indicating that oxidation occurred during the electro-exfoliation process, signifying a significant ion intercalation process leading to the formation of thin layers of graphene with larger sizes. Upon further increasing the voltage



to 8 V (Figure 2), the obtained results also illustrate the exfoliation of the GO8 material into easily observable thin layers, with a reduction in the lateral size compared to the 6 V voltage. This indicates a significant increase in the ion intercalation into the graphene layers, making the obtained GO8 layers thinner. However, higher voltage also signifies a stronger oxidation process, making it easier to break the larger graphene layers into smaller ones. With a voltage of 10 V (Figure 2d), it is observable that the lateral size of GO10 is smaller compared to the 6 V and 8 V voltages, displaying fragmentation due to intense oxidation, signifying significant damage in the GO10 sample. Thus, a voltage too low (<6 V) may lead to minimal electrode oxidation and increased ion insertion rate, resulting in small lateral size and low efficiency of GO. Conversely, a voltage too high (>10 V) may induce intense oxidation and material damage.

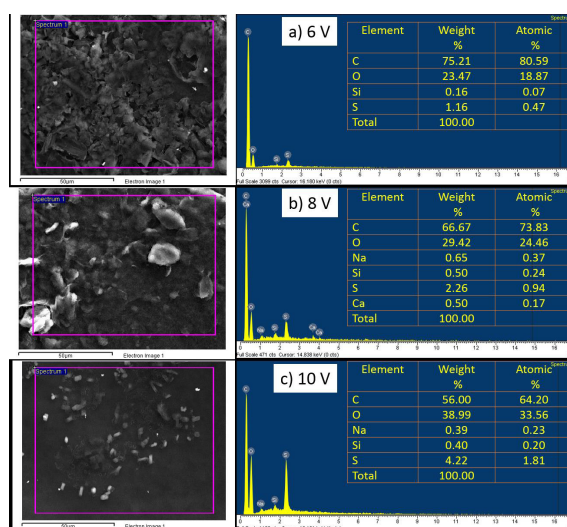


**Figure 2.** SEM images of GO at different applied voltages: (a) 4.5 V, (b) 6 V, (c) 8 V, and (d) 10 V.

### 3.3. Content of oxygen in graphene material

Based on the analysis provided, the 4.5 V voltage resulted in a non-ideal GO sample, leading to its exclusion from further studies. Figure 3 illustrates the chemical composition analysis of graphene at constant voltages of 6 V, 8 V, and 10 V. At 6 V, the GO6 sample exhibited a carbon content of 80.59%, oxygen content of 18.87%, and a corresponding C/O ratio of 4.3. This result reaffirms that the 6 V voltage induced electrode oxidation, although the degree of oxidation was not significant, as evidenced by the high

C/O ratio. At 8 V, the GO8 sample displayed carbon and oxygen contents of 75.21% and 23.47%, respectively, resulting in a C/O ratio of 3.0. This indicates a substantial increase in the oxygen content, signifying a stronger oxidation process. Upon increasing the voltage to 10 V, the carbon and oxygen contents were 56.00% and 38.99%, with a corresponding C/O ratio of 1.9. This signifies a high oxygen content in the sample, indicating an intense oxidation process. Therefore, as the voltage increases, the oxidation process becomes more pronounced, leading to higher oxygen content, indicating an increase in sample damage.

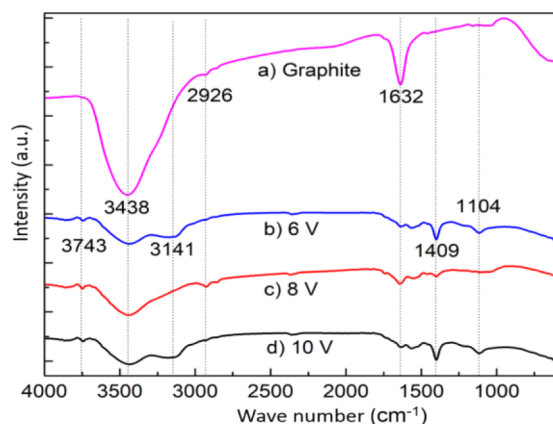


**Figure 3.** EDX analysis of GO under different voltages.

### 3.4. FTIR analysis

In FTIR analysis, the absorption of infrared radiation occurs when a photon encounters a molecule and excites it to a higher energy state. The excited state generates molecular bond vibrations (stretching, bending, twisting, etc.) occurring at different wavelengths (or frequencies) in the infrared region of the electromagnetic spectrum. The wavelength of each absorption peak is determined by the inherent physicochemical properties of the corresponding molecules, characterized by functional groups such as C-H, O-H, C-O, C=O, etc. FTIR spectroscopy is a powerful tool for determining the presence of functional groups in GO, especially oxygen-containing groups,<sup>25</sup> recorded in the wavenumber range from 4000-

400  $\text{cm}^{-1}$  (Figure 4), and the peak positions are indicated in Table S3. The FTIR spectrum in Figure 4a of graphite shows two characteristic peaks corresponding to OH bonds (3438  $\text{cm}^{-1}$ ) and C=C bonds (1632  $\text{cm}^{-1}$ ). The stretching vibration of the O-H functional group appears due to absorbed water molecules in graphite, which can be attributed to the electrode strip being exposed to high humidity conditions in the laboratory, resulting in a large peak intensity and width. The characteristic infrared absorption peak around the position of 1632  $\text{cm}^{-1}$  is confirmed to be the stretching vibration of the C=C bond in the aromatic ring of carbon atoms network,<sup>26</sup> which is indicative of the  $\text{sp}^2$  structure of the carbon atom network.<sup>27</sup>

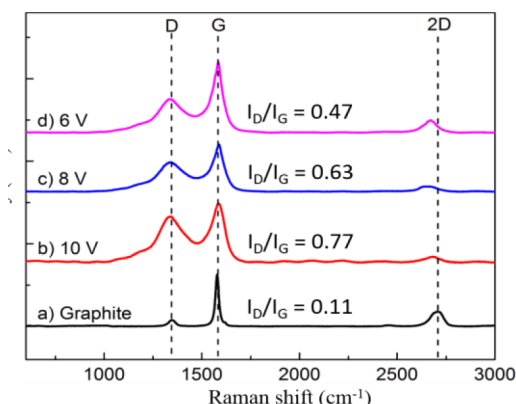


**Figure 4.** FTIR spectroscopy of exfoliated GO under different voltages.

After the electrochemical exfoliation process, the presence of an absorption peak at a wavenumber of 2926  $\text{cm}^{-1}$  indicates the stretching vibration of C-H bonds, which is a hydrocarbon group inherited from the graphene rod and thus still present in the graphene samples. Peaks appearing at wavenumbers of 1104  $\text{cm}^{-1}$  indicate the stretching vibration of C-O bonds, and 1409  $\text{cm}^{-1}$  indicates the stretching vibration of COO-H and/or CO-H bonds, which are carboxyl groups<sup>28</sup>. This suggests that oxidation reactions have occurred at the graphite electrode, leading to the formation of oxygen-containing functional groups. These functional groups play an important role in improving the dispersibility of GO in organic solvents.

### 3.5. Raman spectra

The Raman spectra in the wavenumber range of 600-3000  $\text{cm}^{-1}$  for graphite, GO6, GO8, and GO10 samples are shown in Figure 5. The results indicate that both graphite and GO samples exhibit three characteristic peaks: D (1335-1345  $\text{cm}^{-1}$ ), G (1578-1589  $\text{cm}^{-1}$ ), and 2D (2646-2703  $\text{cm}^{-1}$ ) related to the graphite lattice structure. The D peak represents the presence of disordered carbon and the loss of hexagonal structure in the graphite lattice. The G peak corresponds to the ordered structure in the graphite lattice with  $\text{sp}^2$  hybridization, indicating the high-energy  $E_{2g}$  phonon vibration at the Brillouin zone center, and the  $I_D/I_G$  ratio reflects the degree of lattice defects.<sup>29</sup> The 2D peak describes the vibration mode of two second-order phonons and strongly depends on the excitation laser energy frequency. Figure 5a illustrates the structure of the graphite material with characteristic peaks of D, G, and 2D, and an  $I_D/I_G$  ratio of 0.11. Observations show a slight downshift of the 2D peak towards lower wavenumbers, confirming the presence of multilayered graphene in the electrochemically exfoliated samples.<sup>30</sup> With a voltage of 10 V, the structural analysis of the GO10 material reveals significant defects with an  $I_D/I_G$  ratio of 0.77 (Figure 5b). With higher voltages, the ions move at a faster rate, resulting in thinner exfoliated layers and increased defects. When applying a voltage of 8 V, the  $I_D/I_G$  ratio of 0.63 indicates a significant reduction in the level of defects within the material. Further reducing the voltage to 6 V leads to a greater reduction in the level of defects, with an  $I_D/I_G$  ratio of 0.47.



**Figure 5.** Raman spectra of graphite and exfoliated GO at different applied voltages.

Furthermore, the positions of the D, G, and 2D peaks for the graphite, GO6, GO8, and GO10 samples are also evaluated as shown in Table S4. Observations of increased peak widths for D and 2D peaks, as well as the downshift and increased intensity of these peaks, are indicative of structural changes, defect levels, and the formation of graphene structures in the obtained samples.

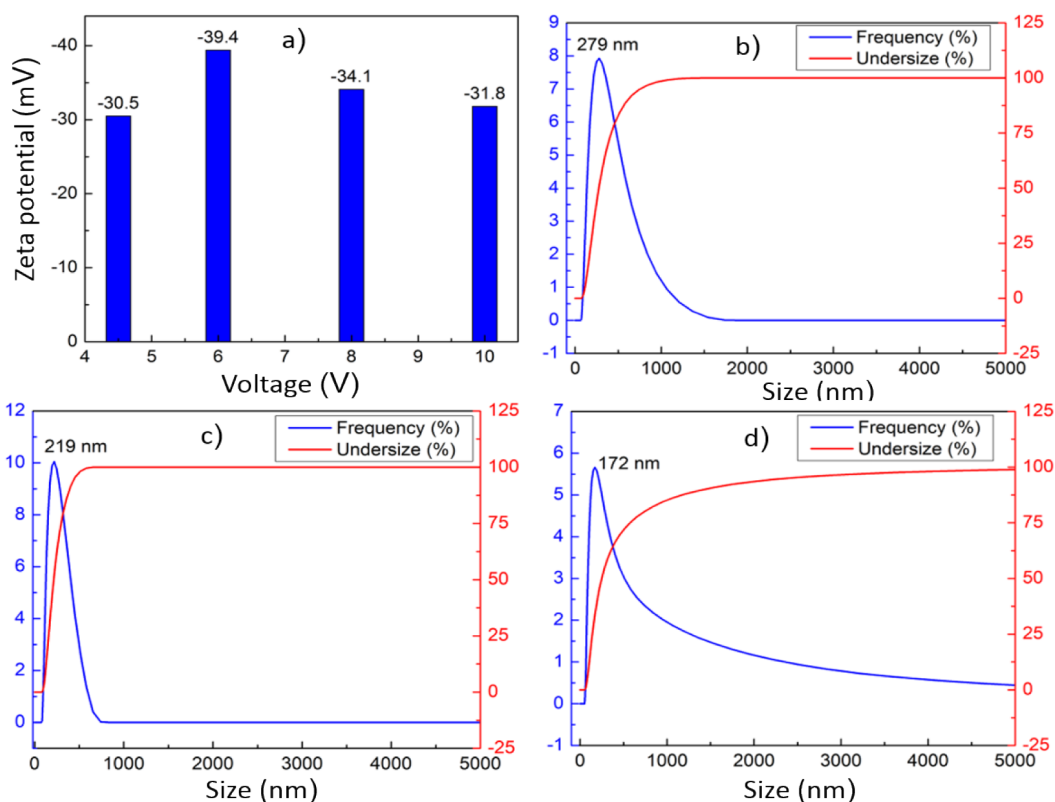
As the applied voltage across the two electrode ends increases, the D and 2D peak spectra become broader and shifted to lower wavenumbers compared to the graphite material. Therefore, through Raman spectroscopy analysis, we can observe a greater degree of material damage as the voltage increases. Consequently, the ideal research results for a constant voltage are determined to be in the range of from 6 to 8 V, with the optimal value being 8 V.

### 3.6. Effective dispersion of exfoliated graphene in water

Zeta potential is used to determine the dispersibility and stability of colloidal

suspensions and provides information about the sign and magnitude of the effective surface charge of graphene sheets. Samples with a Zeta potential more negative than -30 mV or more positive than +30 mV are considered to have good dispersibility and stability in the environment. If the Zeta potential is more negative than -45 mV or more positive than +45 mV, it indicates excellent dispersibility and long-term stability<sup>31</sup>. The GO samples obtained in this study all show good dispersibility and stability in water. This stability is attributed to the negative charges on the surface and edges of the graphene sheets, resulting from the ionization of different functional groups present on graphene, such as C-OH, C-O-C, C=O.

The Zeta potential of GO in water at different voltages was determined as shown in Figure 6a. Overall, the GO6, GO8, and GO10 samples all exhibit good dispersibility in water, as their respective Zeta potentials are lower than -30 mV.



**Figure 6.** Zeta potential and size distributions of GO samples at different applied voltages.

Detailed evaluations reveal that the Zeta potential of GO6 is -39.4 mV, which is the highest value among the samples, indicating better dispersibility and stability. This can be explained by the lower applied voltage, resulting in a smaller current being generated. As a result, the exfoliation process produces thin graphene sheets with a larger lateral area, leading to a higher density of surface charges. For the GO8 sample, the obtained Zeta potential is around -34.1 mV, also indicating good dispersibility in the solution. This suggests that the obtained graphene sheets are smaller in size due to a higher applied voltage, but not large enough to undergo significant oxidation. With a voltage of 10 V, the GO10 sample shows a reduced Zeta potential of approximately -31.8 mV. The lower value indicates a reduction in lateral size of the graphene sheets due to strong oxidation, leading to the breaking of C-C bonds between carbon atoms. Additionally, the number of layers obtained is relatively thin.

The evaluation results of the size distribution of graphene in solution at different constant voltages are shown in Figure 6b, c, d. Although the measured particle size distribution does not accurately reflect the thickness or boundary size of GO in the solution, it reflects the uniformity level of the graphene as a thin nano-film material, influenced by its shape when dispersed in water. For a voltage of 6 V (Figure 6b), the GO6 particle size is concentrated in the range of 0 to 1000 nm, with no occurrence of graphene particles larger than 1000 nm. The most frequent size is at 279 nm, indicating a relatively even distribution of the obtained graphene sample. In Figure 6c, the size distribution of GO8 ranges from 0 to 600 nm, with almost no graphene particles larger than 600 nm. The most frequent size is at 172 nm, indicating a uniform distribution of GO in the solution. Figure 6d shows that GO10 in the solution has an uneven size distribution, ranging from 100 to 3000 nm. Although the size density is concentrated around 172 nm, it also exhibits large-sized GO particles

due to changes in the electrical resistance in the electrolyte solution over prolonged exfoliation time. This suggests that with a higher applied voltage, GO10 is exfoliated into thin layers and smaller sizes, while also producing large-sized GO particles when the exfoliation time becomes sufficiently long. On the other hand, at 8 V, a lower-quality sample like GO8 can be produced, but the exfoliation yield is three times higher compared to the 6 V condition. Therefore, the appropriate voltage should be selected based on the quality requirements and the desired exfoliation yield for further application-oriented research.

#### 4. CONCLUSION

Graphene oxide materials were fabricated via an electrochemical exfoliation approach in ammonium sulfate, using a constant voltage range of from 4.5 to 10 V. The characteristics of the graphene were confirmed by SEM, EDX, FTIR, and Raman spectroscopy. Through this green and simple method, few-layer graphene oxide was successfully produced with high quality, large surface areas, and excellent dispersion in water. At an appropriate voltage (from 6 to 8 V), the graphene oxide exhibited a high yield (70%), larger surface areas, a high C/O ratio (4.3), low defect density ( $I_D/I_G=0.47$ ), and good dispersion in water (Zeta potential = -39.4 mV). The obtained graphene could be used as a material for environmental treatment and composite applications.

#### Acknowledgements

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Supporting information

A simple green approach for synthesizing graphene oxide from graphite via electrochemical exfoliation

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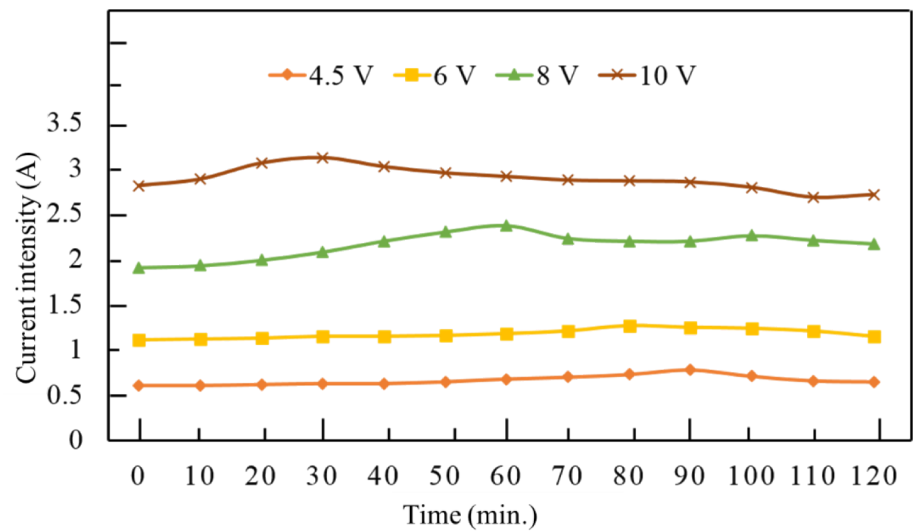


Figure S1. The current change in electrolyte solution.

Table S1. Change of temperature into electrolyte solution in electrochemical exfoliated process (supplementary).

| <div>Time</div> <div>Voltage</div> | 0 min | 30 mins | 60 mins | 90 mins | 120 mins |
|------------------------------------|-------|---------|---------|---------|----------|
| 4.5 V                              | 26°C  | 30°C    | 32°C    | 33°C    | 33°C     |
| 6 V                                | 25°C  | 28°C    | 30°C    | 32°C    | 34°C     |
| 8 V                                | 26°C  | 33°C    | 35°C    | 39°C    | 42°C     |
| 10 V                               | 27°C  | 43°C    | 51°C    | 54°C    | 55°C     |

**Table S2.** The current change in electrolyte solution.

| Time (min.) | 4.5 V | 6 V  | 8 V  | 10 V |
|-------------|-------|------|------|------|
| 0           | 0.60  | 1.10 | 1.90 | 2.80 |
| 10          | 0.60  | 1.11 | 1.92 | 2.87 |
| 20          | 0.61  | 1.12 | 1.98 | 3.05 |
| 30          | 0.62  | 1.14 | 2.07 | 3.11 |
| 40          | 0.62  | 1.14 | 2.19 | 3.01 |
| 50          | 0.64  | 1.15 | 2.29 | 2.94 |
| 60          | 0.67  | 1.17 | 2.36 | 2.90 |
| 70          | 0.69  | 1.20 | 2.22 | 2.86 |
| 80          | 0.72  | 1.26 | 2.19 | 2.85 |
| 90          | 0.77  | 1.24 | 2.19 | 2.84 |
| 100         | 0.70  | 1.23 | 2.25 | 2.78 |
| 110         | 0.65  | 1.20 | 2.20 | 2.67 |
| 120         | 0.64  | 1.14 | 2.16 | 2.70 |

**Table S3.** Functional groups on graphene.

| Functional groups | Wave number (cm <sup>-1</sup> ) |
|-------------------|---------------------------------|
| C = C             | 1632                            |
| – OH              | 3438                            |
| C – O             | 1102                            |
| COO – H           | 1409                            |
| C – H             | 2926                            |

**Table S4.** The characteristics peaks D, G, 2D of graphite and graphene.

| Materials | D (cm <sup>-1</sup> ) | G (cm <sup>-1</sup> ) | 2D (cm <sup>-1</sup> ) |
|-----------|-----------------------|-----------------------|------------------------|
| GP        | 1345                  | 1578                  | 2703                   |
| GR-6      | 1337                  | 1586                  | 2680                   |
| GR-8      | 1339                  | 1589                  | 2657                   |
| GR-10     | 1339                  | 1584                  | 2671                   |

## Nghiên cứu đặc trưng cấu trúc và hoạt tính quang xúc tác phân hủy dung dịch RhB của vật liệu màng C/g-C<sub>3</sub>N<sub>4</sub>/PVDF

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### TÓM TẮT

Vật liệu composite carbon/graphit carbon nitride/polyvinylidene fluoride (C/g-C<sub>3</sub>N<sub>4</sub>/PVDF) có cấu trúc dị thể được tổng hợp thành công bằng phương pháp đảo pha đơn giản. Hình thái, cấu trúc và hoạt tính quang xúc tác của các hạt C/g-C<sub>3</sub>N<sub>4</sub> và màng composite đã được đánh giá. Nhờ hiệu ứng hiệp trợ giữa carbon và g-C<sub>3</sub>N<sub>4</sub> được phân tán trên màng PVDF đóng vai trò là chất xúc tác đã cải thiện một cách đáng kể khả năng phân hủy chất màu rhodamine B trong dung dịch. Cụ thể, vật liệu C/g-C<sub>3</sub>N<sub>4</sub>/PVDF thể hiện hiệu suất quang xúc tác cao nhất (H = 89%) so với các vật liệu g-C<sub>3</sub>N<sub>4</sub>/PVDF (H = 45,92%) sau 160 phút chiếu sáng dưới vùng ánh sáng khả kiến. Với phương pháp đưa vật liệu lên màng đã khắc phục được những nhược điểm vốn có của các loại xúc tác truyền thống như khó thu hồi và khả năng tái sử dụng xúc tác với hiệu suất thấp sau nhiều chu kỳ. Vì vậy, nghiên cứu này dự kiến sẽ được mở rộng một cách triển vọng trong lĩnh vực xúc tác quang.

**Từ khóa:** Composite, polyvinylidene fluoride, C/g-C<sub>3</sub>N<sub>4</sub>/PVDF, rhodamine B, chất xúc tác quang.

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# Study on structure characteristics and the photocatalytic activities degradation of RhB solution on C/g-C<sub>3</sub>N<sub>4</sub>/PVDF membrane material

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## ABSTRACT

Heterogeneous carbon/graphite carbon nitride/polyvinylidene fluoride (C/g-C<sub>3</sub>N<sub>4</sub>/PVDF) composite materials were successfully synthesized by a simple phase inversion method. The morphology, structure, and photocatalytic activity of C/g-C<sub>3</sub>N<sub>4</sub> particles and composite films were evaluated. Thanks to the synergistic effect between carbon and g-C<sub>3</sub>N<sub>4</sub> dispersed on the PVDF membrane acting as a catalyst, the ability to decompose rhodamine B dye in solution was significantly improved. Specifically, the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF material exhibited the highest photocatalytic efficiency (H = 89%) compared to the g-C<sub>3</sub>N<sub>4</sub>/PVDF material (H = 45,92%) after 160 minutes of illumination under visible light. The method of putting materials on the membrane has overcome the inherent disadvantages of traditional catalysts, such as difficulty in recovery and the ability to reuse the catalyst with low efficiency after many cycles. Therefore, this study is expected to be prospectively extended in photocatalysis for the treatment of polluted water.

**Keywords:** Composite, polyvinylidene fluoride, C/g-C<sub>3</sub>N<sub>4</sub>/PVDF, rhodamine B, photocatalyst.

## 1. INTRODUCTION

Photocatalysis has emerged as one of the most promising green technologies thanks to its environmental benefits, cost-effectiveness, and high efficiency. It has found widespread applications in environmental management and energy conversion.<sup>1,2</sup> A crucial aspect of advancing photocatalytic technology lies in developing new photocatalysts that efficiently harness solar energy, addressing the pressing need for environmental remediation today.

Rhodamine B (RhB) is one of the most popular dyes for the printing, textile, and leather industries, which could cause environmental pollution if not treated appropriately. Various technologies have been explored recently to develop effective methods for completely removing pharmaceutical and dye compounds from water.<sup>3,4</sup> Among these, advanced oxidation processes (AOPs) have been identified as a promising solution for treating difficult-to-degrade compounds. AOPs, remarkably

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heterogeneous photocatalysis, have received significant due to their high efficiency in removing pharmaceuticals.<sup>5,6</sup> Photocatalysts absorb photons from an external light source to generate electron-hole pairs, participating in redox reactions. Among the various photocatalysts, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) has emerged as a promising metal-free, layered material easily synthesized by thermal condensation using inexpensive and abundant organic precursors in soil, such as urea.<sup>7</sup>

As a narrow band gap semiconductor (2.7 eV),  $g\text{-C}_3\text{N}_4$  demonstrates stable physicochemical properties, excellent thermal stability, and remarkable photoelectron transfer capabilities. Additionally, it is non-toxic, easy to store, and can be obtained from various sources.<sup>8</sup> Recently,  $g\text{-C}_3\text{N}_4$  has become an optimal choice for forming heterostructured materials with wide-band gap semiconductors. For example, Wang et al. developed a unique in situ microwave-assisted synthesis method to fabricate  $\text{N-TiO}_2/g\text{-C}_3\text{N}_4$  composites, which showed significant improvements in photocatalytic activity.<sup>9</sup> Similarly, Miranda et al. successfully obtained  $g\text{-C}_3\text{N}_4/\text{TiO}_2$  composites with high photoactivity by combining hydrothermal and sintering methods, achieving a final phenol conversion rate of approximately 90%.<sup>10</sup> However,  $g\text{-C}_3\text{N}_4$  has shortcomings, such as a small specific surface area and a high recombination rate of photogenerated electron-hole pairs. To overcome this drawback, many methods have been applied to modify  $g\text{-C}_3\text{N}_4$ , such as preparing  $g\text{-C}_3\text{N}_4$  in capillary structures and modifying  $g\text{-C}_3\text{N}_4$  by doping techniques or grafting with other semiconductors to composite materials.<sup>11,12</sup>

Polyvinylidene fluoride (PVDF) is widely used for membrane fabrication due to its high mechanical strength, chemical resistance, and thermal stability.<sup>13,14</sup> Several  $g\text{-C}_3\text{N}_4$ -PVDF membranes have been developed and successfully applied in studies aimed at removing pollutants from water in continuous flow mode, with photocatalysts serving as self-cleaning materials that exhibit antifouling properties.<sup>15,16</sup>

The main objective of this study is to modify the surface of PVDF membranes with  $g\text{-C}_3\text{N}_4$ . The performance of the modified membranes was evaluated in the degradation of Rhodamine B dye.

## 2. EXPERIMENTAL

### 2.1. Material synthesis

**Chemicals:** All chemicals used for material synthesis include potassium hydroxide (KOH, 90%), hydrochloric acid (HCl, 37%), polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP) urea ( $\text{CO}(\text{NH}_2)_2$ ,  $\geq 99\%$ ) (Sigma-Aldrich) and rhodamine B ( $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$ ) Merck.

### 2.2. Materials synthesis

#### 2.2.1. Synthesis of $g\text{-C}_3\text{N}_4$

Ten grams of the precursor urea was finely ground and transferred into a ceramic cup. The cup was then heated in a furnace at 550 °C with a heating rate of 10 °C/min under an Ar atmosphere for one hour. The obtained powder was washed with water, dried, and ground. The sample denoted  $g\text{-C}_3\text{N}_4$ .

#### 2.2.2. Synthesis of $\text{C}/g\text{-C}_3\text{N}_4$ membrane material

A mixture of urea (15 g) and  $\text{C}^{17}$  (0.1 g) was dispersed in a water-alcohol solution (1:1 ratio) and then subjected to ultrasonic vibration for 30 minutes. The mixture was continuously stirred at 60 °C until the water and alcohol wholly evaporated. The resulting solid was ground and heated in Argon gas at 550 °C for 1 hour. The product was washed, filtered, and dried at 80 °C for 12 hours to obtain the final product,  $\text{C}/g\text{-C}_3\text{N}_4$ .

#### 2.2.3. Synthesis of $\text{C}/g\text{-C}_3\text{N}_4/\text{PVDF}$ membrane material

Add 0.1 grams of  $\text{C}/g\text{-C}_3\text{N}_4$  material to a glass jar with a lid, then add 5 mL of N-Methyl-2-pyrrolidone (NMP). Sonicate the mixture for 10 minutes, followed by stirring for 30 minutes. Afterward, continue sonicating for another 20 minutes and stir for 20 minutes. Next, add 0.646 grams of polyvinylidene fluoride (PVDF) and

stir the mixture at 40 °C for 4 hours. Allow the mixture to stand for 3 hours. Use a stainless steel knife (250  $\mu\text{m}$  x 15 cm) to evenly roll the mixture onto a glass surface to form a composite film. Quickly immerse the glass with the film into the water to perform the phase inversion process.<sup>17</sup> The resulting product is denoted as C/g-C<sub>3</sub>N<sub>4</sub>/PVDF.

The process for dispersing g-C<sub>3</sub>N<sub>4</sub> onto PVDF polymer is carried out similarly, and the product obtained is denoted as g-C<sub>3</sub>N<sub>4</sub>/PVDF.

### 2.3. Material characterization

The synthesized materials were characterized using several techniques. Infrared spectroscopy IR was performed on a Shimadzu IR Prestige-21. The crystal phase was analyzed by X-ray diffraction (XRD) using a Siemens D-500 Bruker system. Scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS) were conducted using a JSM-7600F device. Photoluminescence (PL) spectra were measured on a Hitachi F-7000 instrument with an excitation wavelength of 360 nm.

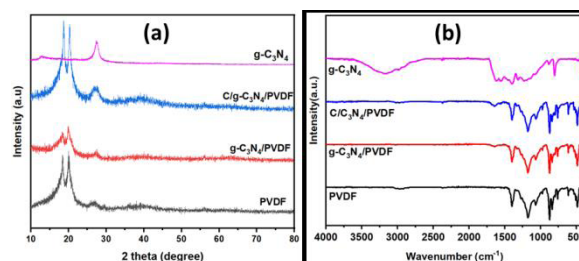
### 2.4. Photocatalytic evaluation

The photocatalytic activity of the obtained materials was evaluated by the decomposition of Rhodamine B (RhB) in an aqueous solution under visible light irradiation. Materials membrane containing 0.1 g of the photocatalyst was added to 100 mL of RhB solution with a concentration of 10 mg/L and stirred in the dark for 30 minutes to achieve adsorption-desorption equilibrium. The photocatalytic process was then initiated under a 30W LED light. Every 20 minutes, 5 mL of the solution was centrifuged to remove the solid part. The concentration of RhB in the solution was determined on a UV-Vis meter (CE-2011) at a wavelength of 553 nm.

## 3. RESULTS AND DISCUSSION

### 3.1. Material characteristics

XRD patterns were used to determine the crystalline phase of g-C<sub>3</sub>N<sub>4</sub>/PVDF and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composites, as shown in Figure 1a.



**Figure 1.** (a) XRD and (b) FT-IR patterns of PVDF, g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>/PVDF, and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF.

PVDF is a semi-crystalline polymer with two main crystalline phases,  $\alpha$  and  $\beta$ .<sup>18,19</sup> The results in Figure 1 indicate three characteristic peaks at 18.5°, 20.1° and 26.7°, which are assigned to the reflection planes of (020), (110), and (021), corresponding to the  $\alpha$  crystalline phase. When g-C<sub>3</sub>N<sub>4</sub> or C/g-C<sub>3</sub>N<sub>4</sub> were added to the PVDF polymer to form g-C<sub>3</sub>N<sub>4</sub>/PVDF and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composites, no significant change was observed compared to the pure PVDF sample. The three peaks attributed to the reflections of PVDF remain at nearly the same position but with varying intensities. The XRD pattern of g-C<sub>3</sub>N<sub>4</sub> (Figure 1a) shows two characteristic peaks at 27.6° and 13.1° corresponding to the (002) and (100) reflection planes of graphite-structured materials.<sup>20</sup> In addition, the characteristic peak at 27.6° corresponding to the (002) plane of g-C<sub>3</sub>N<sub>4</sub> appears in both the g-C<sub>3</sub>N<sub>4</sub>/PVDF and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF samples (Figure 1a). The peak at 27.6° corresponding to the (002) plane of g-C<sub>3</sub>N<sub>4</sub> is believed to result from the alternating stacking of conjugated aromatic units, similar to graphite structure.<sup>21</sup> The peak at 13.1° of g-C<sub>3</sub>N<sub>4</sub> was not seen in the XRD patterns of g-C<sub>3</sub>N<sub>4</sub>/PVDF and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF materials, possibly due to the small amount of g-C<sub>3</sub>N<sub>4</sub> in the sample. The diffraction peaks of the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite are more intense than those of the g-C<sub>3</sub>N<sub>4</sub> sample, likely due to carbon increasing the intensity of the peaks in this material sample.

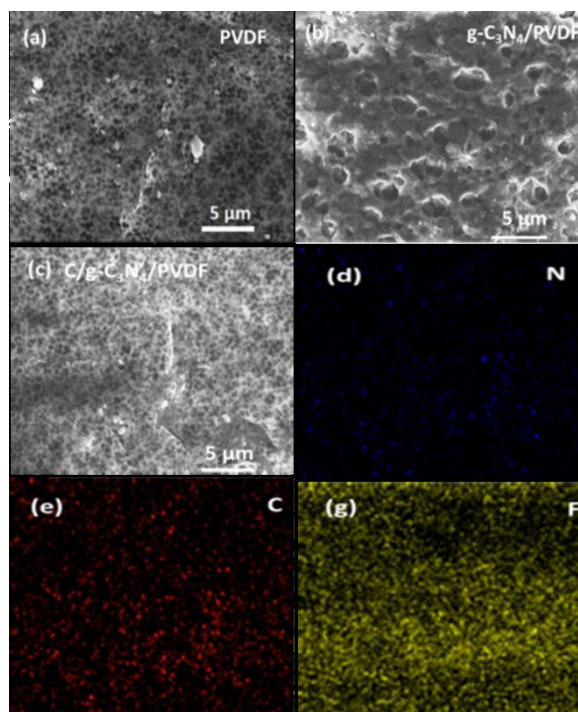
FT-IR spectra were employed to characterize the chemical bond characteristics of the samples, and the results are presented in Figure 1b. The FTIR spectrum of g-C<sub>3</sub>N<sub>4</sub>

shows broad shoulder absorption bands at  $3187\text{ cm}^{-1}$  corresponding to the stretching vibrational pattern of N-H in the incompletely condensed amine group or OH of the adsorbed water. In addition, there are some dominant, strong bands in the  $1100\text{--}1700\text{ cm}^{-1}$  region in the IR spectrum, corresponding to the characteristic vibrational pattern of CN heteroaromatic rings. Specifically, the peaks around  $1639\text{ cm}^{-1}$  and  $1574\text{ cm}^{-1}$  can be attributed to the characteristic vibrational pattern of C=N bonds, while the peaks at  $1247\text{ cm}^{-1}$  to  $1458\text{ cm}^{-1}$  are assigned to the stretching vibrational pattern of C-N bonds in conjugated aromatic rings. The bands at  $1325\text{ cm}^{-1}$  and  $1247\text{ cm}^{-1}$  correspond to the valence vibrations of the C-N(-C)-C bridging units with a fully condensed system or C-NH-C with a partially condensed system. In addition, a sharp absorption band at  $820\text{ cm}^{-1}$  is attributed to the deformation vibrations of the N-H groups of the triazine units.<sup>22,23</sup>

The FTIR spectrum of the PVDF membrane shows that the peak at  $763\text{ cm}^{-1}$  corresponds to the bending vibration of the  $\text{CF}_2$  group. The peaks at  $794$  and  $977\text{ cm}^{-1}$  are attributed to the shaking vibration of the  $\text{CF}_2$  group, while the peak at  $1170\text{ cm}^{-1}$  is associated with the valence vibration of the  $\text{CF}_2$  group.<sup>24,25</sup> The peak at  $1413\text{ cm}^{-1}$  is deemed to be the valence vibration of the C-H functional group. In addition, the PVDF sample exhibits peaks at  $875$ ,  $615$ ,  $531$ , and  $490\text{ cm}^{-1}$ , all of which correspond to PVDF's  $\alpha$  phase crystal structure.<sup>26</sup> For the composite membrane materials g- $\text{C}_3\text{N}_4$ /PVDF and C/g- $\text{C}_3\text{N}_4$ /PVDF, the peak appearing at  $1639\text{ cm}^{-1}$  is attributed to the valence vibration of the C=N group.<sup>27</sup> The peaks at  $2979$  and  $1411\text{ cm}^{-1}$  are assigned to the valence and deformation vibrations of the  $\text{CH}_2$  group, respectively. In addition, the peak at  $1181\text{ cm}^{-1}$  vibration is related to the valence vibration of the  $\text{CF}_2$  group.<sup>28</sup>

The SEM images reveal that the surface of pure PVDF (Figure 2a) exhibits a homogeneous

morphology. In comparison, the SEM image of g- $\text{C}_3\text{N}_4$ /PVDF (Figure 2b) shows numerous voids between g- $\text{C}_3\text{N}_4$  and polymer chains, which are formed due to the particle distribution during the sample preparation. The SEM image of the C/g- $\text{C}_3\text{N}_4$ /PVDF composite (Figure 2c) shows that many small particles are evenly dispersed on the PVDF substrate. These observations confirm that the presence of carbon in the composite sample influences the voids between particles and polymer chains.<sup>21</sup>

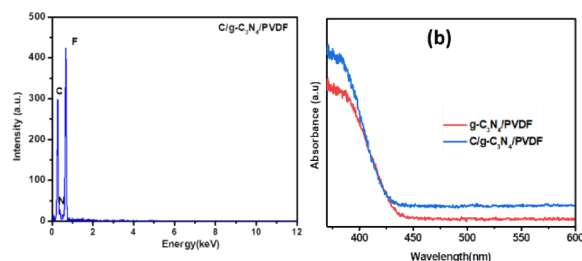


**Figure 2.** FE-SEM images of (a) PVDF, (b) g- $\text{C}_3\text{N}_4$ /PVDF, (c) C/g- $\text{C}_3\text{N}_4$ /PVDF, (d) mapping images of N, (e) C and (f) F elements.

The EDX spectrum in Figure 3 was used to identify the elements in the characterized C/g- $\text{C}_3\text{N}_4$ /PVDF composite membrane material.

The mapping images in Figures 2 d, e, f, and Figure 3a confirm the presence of C, F, and N elements in the C/g- $\text{C}_3\text{N}_4$ /PVDF composite. The results showed that the elements on the surface membrane were mainly C, F, and N, with contents of 39.61%, 56.44%, and 3.95%, respectively, indicating that the membrane agglomeration was a C/g- $\text{C}_3\text{N}_4$  catalyst.



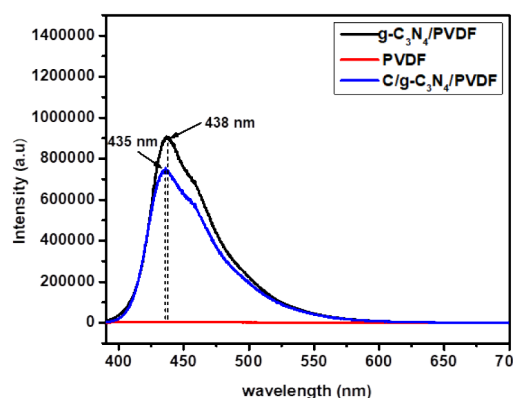


**Figure 3.** (a) EDX spectrum of C/g-C<sub>3</sub>N<sub>4</sub>/PVDF and (b) UV-Vis DRS spectra of g-C<sub>3</sub>N<sub>4</sub>/PVDF and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membrane.

The UV-Vis spectra of g-C<sub>3</sub>N<sub>4</sub>/PVDF and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membrane materials are shown in Figure 3b.

The results show that g-C<sub>3</sub>N<sub>4</sub>/PVDF and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membranes absorb in the ultraviolet region and extend into the visible. Compared with the g-C<sub>3</sub>N<sub>4</sub>/PVDF sample, the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membrane has a higher absorption intensity than the g-C<sub>3</sub>N<sub>4</sub>/PVDF in the visible region. This may be due to the presence of carbon in the composite.

As the photocatalytic activity of semiconductor materials is greatly affected by the recombination rate of photogenerated electron and hole pairs, the photoluminescence (PL) spectrum is used to evaluate this recombination ability. The photoluminescence spectra of PVDF, g-C<sub>3</sub>N<sub>4</sub>/PVDF, and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF materials are presented in Figure 4.



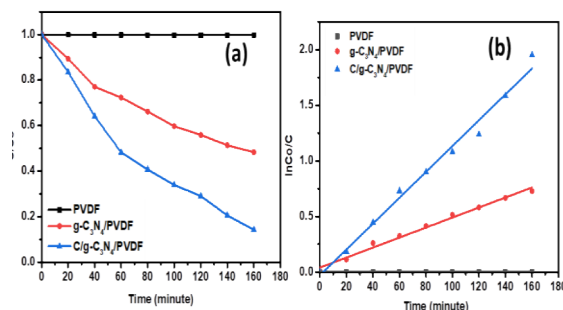
**Figure 4.** PL spectra of PVDF, g-C<sub>3</sub>N<sub>4</sub>/PVDF, and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF materials.

PL spectra of PVDF, g-C<sub>3</sub>N<sub>4</sub>/PVDF, and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF materials were conducted with an excitation wavelength of 390 nm. As shown

in Figure 4, the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF and C<sub>3</sub>N<sub>4</sub>/PVDF show peaks at 435 and 438 nm, respectively. However, the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membrane material exhibits lower emission intensity than g-C<sub>3</sub>N<sub>4</sub>/PVDF, which may be due to the addition of carbon helping improve the dispersion of the material. No significant PL intensity is observed across the entire measured PL spectrum for the PVDF membrane, indicating its limited adsorption properties. Consequently, the luminescence intensity is very low and nearly non-existent. Since PVDF does not have inherent luminescence, the observed PL shift is attributed to the excitation effect induced by adding g-C<sub>3</sub>N<sub>4</sub> and carbon.<sup>29</sup> The PL spectral results suggest that the recombination rate of electron-hole pairs in C/g-C<sub>3</sub>N<sub>4</sub>/PVDF is lower than in g-C<sub>3</sub>N<sub>4</sub>/PVDF. This enhanced electron separation in C/g-C<sub>3</sub>N<sub>4</sub>/PVDF creates favorable conditions for photogenerated electrons to diffuse to the catalyst surface, where they interact with adsorbed H<sub>2</sub>O or O<sub>2</sub> molecules to generate active free radicals, thus improving the efficiency of pollutant treatment.

### 3.2. Photocatalytic performance

The results of the photocatalytic evaluation for PVDF, g-C<sub>3</sub>N<sub>4</sub>/PVDF, and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF are shown in Figure 5a.



**Figure 5.** (a) RhB decomposition and (b) pseudo-first-order kinetic model under visible light of g-C<sub>3</sub>N<sub>4</sub>/PVDF, C/g-C<sub>3</sub>N<sub>4</sub>, and C/g-C<sub>3</sub>N<sub>4</sub>/PVDF materials.

After 160 minutes of illumination, the RhB decomposition efficiency of the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membrane reached 89%, which was higher than that of C<sub>3</sub>N<sub>4</sub>/PVDF, which achieved efficiencies of 45.92%. For the RhB solution of the PVDF fiber membrane without catalyst powder, the concentration remained

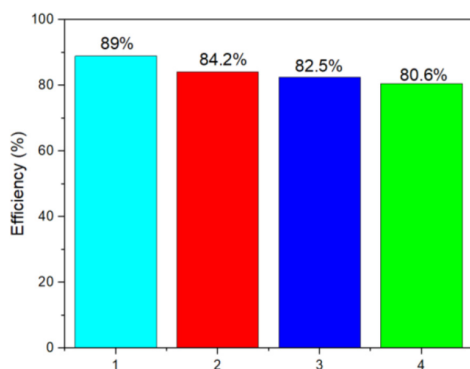
almost unchanged under dark adsorption and light conditions, and the adsorption of RhB in the dark was only 2.09%, which also shows that pure PVDF has no degradation ability for RhB under natural conditions. After the PVDF membrane was laminated with g-C<sub>3</sub>N<sub>4</sub> or C/g-C<sub>3</sub>N<sub>4</sub> composite, the adsorption capacity of RhB in the dark was enhanced, which also shows that part of the g-C<sub>3</sub>N<sub>4</sub> or C/g-C<sub>3</sub>N<sub>4</sub> catalyst was exposed on the membrane, thereby increasing the dark adsorption of RhB by the composite membrane. Therefore, the ability to decompose RhB will increase when exposed to light. This is consistent with the results discussed in PL and UV-Vis DRS spectra.

These results highlight the potential of g-C<sub>3</sub>N<sub>4</sub>/PVDF, C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite for practical membrane-based environmental treatment applications.

Furthermore, Figure 5b presents the fitting results of the photoreduction kinetic curves of RhB over different samples using the first-order reaction kinetics equation of  $-\ln(C/C_0)=kt$ . The maximum photoreduction rate constant of RhB over the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF photocatalysis membrane is 0.0116 min<sup>-1</sup>, which is about 2.6 times that of g-C<sub>3</sub>N<sub>4</sub>/PVDF (0.0045 min<sup>-1</sup>). These results demonstrate that the synergistic effect of C/g-C<sub>3</sub>N<sub>4</sub> and PVDF membrane improves the photoreduction performance of g-C<sub>3</sub>N<sub>4</sub>.<sup>30</sup>

### 3.3. Photocatalytic cycle experiment

The photocatalytic stability of the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membrane was analyzed by conducting a cycle stability experiment (Figure 6).



**Figure 6.** Reusability of C/g-C<sub>3</sub>N<sub>4</sub>/PVDF membrane materials.

The results showed that the removal rate of RhB was 89% when the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membrane was used for catalytic degradation once. After ultrasonic cleaning of the recovered composite membrane, the degradation efficiency of RhB was 84.2% (second time) after 160 min of illumination. After repeating twice, the removal rates of RhB were 82.5% (third time) and 80.6% (fourth time), respectively. This shows that the membrane can effectively photocatalytically degrade RhB and can be reused through water-washing regeneration. After regeneration three times, the membrane maintained a high efficiency, indicating that the prepared C/g-C<sub>3</sub>N<sub>4</sub>/PVDF membrane has efficient photocatalytic and excellent regeneration performance for RhB.

## 4. CONCLUSION

The phase inversion method successfully synthesized g-C<sub>3</sub>N<sub>4</sub>/PVDF, C/g-C<sub>3</sub>N<sub>4</sub>/PVDF materials. The C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membrane exhibits excellent photocatalytic activity under visible light with an efficiency of 89% after 160 min of illumination, which was superior to those of g-C<sub>3</sub>N<sub>4</sub>/PVDF and pure PVDF membranes (45.92% and 2.09%, respectively). At the same time, it has stable recycling performance. Even after 4<sup>th</sup> recycling, the degradation efficiency reaches 80.6%, indicating that the C/g-C<sub>3</sub>N<sub>4</sub>/PVDF composite membrane has broad application prospects in the photocatalytic degradation of organic dyes in wastewater.

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# Thiết kế mô hình dự báo chuỗi thời gian mờ tối ưu dựa trên đại số gia tử

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## TÓM TẮT

Dự báo chuỗi thời gian mờ đã thu hút được sự chú ý đáng kể nhờ khả năng xử lý sự không chắc chắn và thiếu chính xác trong dữ liệu chuỗi thời gian. Các mô hình chuỗi thời gian mờ truyền thống thường gặp hạn chế trong việc nắm bắt các mối quan hệ phức tạp giữa các biến. Để giải quyết thách thức này, chúng tôi đề xuất một mô hình tiếp cận mới gọi là mô hình dự báo chuỗi thời gian mờ dựa trên đại số gia tử (OHAM). Đầu tiên, chúng tôi giới thiệu khái niệm về đại số gia tử và ứng dụng của chúng trong phân tích chuỗi thời gian mờ. Sau đó, chúng tôi trình bày các bước xây dựng mô hình, bao gồm việc xác định các nhãn ngôn ngữ trong đại số gia tử, xây dựng các quan hệ mờ từ dữ liệu, chia đoạn cho không gian tham chiếu. Tiếp đó, chúng tôi đề xuất một thuật toán tối ưu hóa để tinh chỉnh các tham số của OHAM, nhằm đạt được hiệu quả dự báo tối ưu. Cuối cùng là thử nghiệm trên một số bộ dữ liệu cụ thể để đánh giá tính hiệu quả của mô hình. Kết quả thử nghiệm cho thấy mô hình mới đề xuất ít sai số hơn so với nhiều mô hình khác.

**Từ khóa:** Dự báo, chuỗi thời gian mờ, đại số gia tử, từ mờ, giá trị ngôn ngữ.

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# Design of optimal hedge-algebras-based model for fuzzy time series forecasting

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## ABSTRACT

Fuzzy time series forecasting has garnered significant attention due to its ability to handle uncertainty and imprecision in time series data. Traditional fuzzy time series models often face limitations in capturing complex relationships between variables. To address this challenge, we propose a novel approach called the Optimal Hedge-Algebras-based Model (OHAM). First, we introduce the concepts of hedge algebra and its application in fuzzy time series analysis. Subsequently, we present the model construction steps, including defining linguistic labels in hedge algebra, constructing fuzzy relations from data, and partitioning the universe of discourse. Following this, we propose an optimization algorithm to fine-tune the parameters of OHAM, aiming to achieve optimal forecasting performance. Finally, experiments are conducted on several specific datasets to evaluate the effectiveness of the model. The experimental results demonstrate that the newly proposed model exhibits better accuracy than many others.

**Keywords:** *Forecasting, fuzzy time series, hedge algebras, vague words, linguistic terms.*

## 1. INTRODUCTION

The proposed hedge algebra by N. C. Ho<sup>1-3</sup> has been tested in various applications, yielding positive results in problems such as fuzzy control, classification, fuzzy clustering, and fuzzy time series forecasting,<sup>4,5</sup> among others.

Forecasting plays a crucial role in numerous fields such as finance, weather prediction, and stock market analysis.<sup>6,7</sup> In recent years, fuzzy time series forecasting models have gained attention due to their ability to handle the uncertainty and vagueness present in real-world data. One such model is the hedge-algebras-based forecasting model.<sup>8</sup>

The hedge-algebras-based forecasting model utilizes an algebraic structure to capture the relationships between historical data and future predictions. However, the performance of this model heavily relies on parameter calibration. Determining optimal parameters is a challenging task that requires an efficient optimization algorithm.

In this paper, we propose the application of the Artificial Bee Colony (ABC) algorithm to optimize the parameters of the hedge-algebras-based forecasting model for fuzzy time series. The ABC algorithm is a metaheuristic optimization technique inspired by the foraging behavior of honey bees. It has been successfully applied to

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various optimization problems and showcases robustness and convergence efficiency.

By employing the ABC algorithm, this research aims to enhance the accuracy and reliability of the hedge-algebras-based forecasting model. The ABC algorithm will efficiently search the parameter space, finding the optimal combination of parameters for the model. This process will help in achieving improved forecast accuracy, reduced error rates, and enhanced decision-making capabilities in diverse applications.

To evaluate the proposed approach, extensive experiments will be conducted using real-world datasets from different domains. Comparative analyses will be carried out, comparing the performance of the optimized hedge-algebras-based forecasting model with other well-established optimization techniques. The results obtained will provide insights into the effectiveness and efficiency of the ABC algorithm in parameter optimization for fuzzy time series forecasting models.

## 2. PROBLEM OF FUZZY TIME SERIES FORECASTING

The problem in time series forecasting is to accurately predict future values or trends based on historical data. This involves addressing challenges such as identifying and modeling trends, handling seasonality and noise, accounting for non-linear relationships and non-stationarity, and choosing the optimal model and parameters. The goal is to develop a robust forecasting method that can generalize well beyond the training data and provide reliable predictions for effective decision-making. Overcoming these challenges requires a combination of statistical techniques, machine learning algorithms, and domain expertise to achieve accurate and meaningful forecasts.

Fuzzy time series, a concept derived from fuzzy set theory, is a powerful tool for modeling and forecasting time-dependent data with inherent uncertainty and imprecision.

Unlike traditional time series analysis, which assumes crisp values, fuzzy time series allows for the representation of vague and uncertain information through linguistic terms and membership functions. By incorporating fuzzy logic into the modeling process, fuzzy time series enables the handling of complex data, making it particularly suitable for real-world scenarios where uncertainty is prevalent. This approach has found applications in various domains, including finance, economics, weather prediction, and decision-making systems, providing valuable insights and accurate predictions in situations where conventional methods may fall short.

The problem is stated as follows: Given  $n$  values  $y(t_1), y(t_2), \dots, y(t_n)$  where  $t_1, t_2, \dots, t_n$  are point times. How to predict the next value?

### 2.1. Some basic definitions

The fuzzy time series model was first proposed by Q. Song and B. S. Chissom.<sup>9</sup> Then, it is improved by S.M Chen<sup>10,11</sup> to process some arithmetic calculations. From that point, they can get more exact forecasting results. In this session, we briefly review the concepts of fuzzy time series as in Q.Song.<sup>9</sup>

Let  $U$  be the universe of discourse, where  $U = \{u_1, u_2, \dots, u_n\}$ . A fuzzy set defined in the universe of discourse  $U$  can be represented as follows:  $A = f_A(u_1)/u_1 + f_A(u_2)/u_2 + \dots + f_A(u_n)/u_n$ , where  $f_A$  denotes the membership function of the fuzzy set  $A$ ,  $f_A : U \rightarrow [0, 1]$ , and  $f_A(u_i)$  denotes the degree of membership of  $u_i$  belonging to the fuzzy set  $A$ , and  $f_A(u_i) \in [0, 1]$ , and  $1 \leq i \leq n$ .

**Definition 1.**<sup>9</sup> Let  $Y(t)$  ( $t = \dots, 0, 1, 2, \dots$ ) be the universe of discourse and be a subset of  $R$ . Assume  $f_i(t)$  ( $i = 1, 2, \dots$ ) are defined on  $Y(t)$ , and assume that  $F(t)$  is a collection of  $f_1(t), f_2(t), \dots$ , then  $F(t)$  is called a fuzzy time series definition  $Y(t)$  ( $t = \dots, 0, 1, 2, \dots$ ).

**Definition 2.**<sup>9</sup> Assume that  $F(t)$  is caused by  $F(t-1)$  only, denoted as  $F(t-1) \rightarrow F(t)$ , then this relationship can be expressed as  $F(t) = F(t-1) \circ R(t, t-1)$ , where  $F(t) = F(t-1) \circ R(t, t-1)$  is called the first-order model of  $F(t)$ ,

$R(t, t-1)$  is the fuzzy relationship between  $F(t-1)$  and  $F(t)$ , and “ $\circ$ ” is the Max-Min composition operator.

**Definition 3.**<sup>9</sup> Assume that the fuzzified input data of the  $i^{\text{th}}$  year/month is  $A_j$  and the fuzzified input data of the  $i+1^{\text{th}}$  year/month is  $A_k$ , where  $A_j$  and  $A_k$  are two fuzzy sets defined in the universe of discourse  $U$ , then the fuzzy logical relationship can be represented by  $A_j \rightarrow A_k$ , where  $A_j$  is called the current state of the fuzzy logical relationship.

If we have  $A_i \rightarrow A_{j1}, A_i \rightarrow A_{j2}, \dots, A_i \rightarrow A_{jk}$  then we can write  $A_i \rightarrow A_{j1}, A_{j2}, \dots, A_{jk}$ .

## 2.2. Rules for calculating output value

Assume that  $A_j$  is the value of  $F(t-1)$ , the forecasted output  $F(t)$  be defined as in research:<sup>10</sup>

*If there exists a relation 1-1 within the group of the relations where  $A_j$  is on the left of the rule, suppose that  $A_j \rightarrow A_k$ , and the maximum membership value of  $A_k$  occurs at interval  $u_k$ , then the output of  $F(t)$  is the middle point of  $u_k$ .*

a) If  $A_k = \emptyset$ , that means  $A_j \rightarrow \emptyset$  and the maximum membership value of  $A_j$  occurs at interval  $u_j$ , then the output of  $F(t)$  is the middle point of  $u_j$ .

b) If we have  $A_j \rightarrow A_1, A_2, \dots, A_n$ , and the maximum membership values of  $A_1, A_2, \dots, A_n$  occur at intervals  $u_1, u_2, \dots, u_n$  respectively, then the output of  $F(t)$  is average of the middle points  $m_1, m_2, \dots, m_n$  of  $u_1, u_2, \dots, u_n$ , that is  $(m_1 + m_2 + \dots + m_n)/n$ .

## 3. THE MODEL OF FORECASTING TIME SERIES BASED ON HEDGE ALGEBRAS

In this section, we provide a brief overview of the algebraic approach to the semantics of vague words in natural languages, as explored in previous studies,<sup>1-4</sup> and introduce a new forecasting method based on hedge algebra theory.

### 3.1. Algebraic structure of vague term domain

Hedge algebras, denoted as  $AX = (\mathcal{X}, \mathbb{G}, \mathbb{C}, \mathcal{H}, \leq)$ , are a mathematical structure to handle

uncertainty and vagueness. In hedge algebras,  $\mathcal{X}$  represents a set of words  $\mathcal{H}$  is the set of linguistic hedges or modifiers considered as 1-ary operations of the algebra  $AX$ ;  $\mathbb{C} = \{0, W, 1\}$  is a set of special words which are, respectively, the least, the medium and the greatest elements of  $\mathcal{X}$  and regarded as constants of  $AX$  since they are fixed points;  $\mathbb{G} = \{c-, c+\}$  is a set of the primary or atomic words of the linguistic variable  $X$ , the first one is called the negative word, and the second, the positive one.  $\mathbb{G} \cup \mathbb{C}$  is the set of the generators of the algebra  $AX$  that is  $\mathcal{H}(\mathbb{G} \cup \mathbb{C}) = \mathcal{X} = \mathbb{C} \cup \mathcal{H}(\mathbb{G})$ , the underlying set of  $AX$  where for a subset  $Z$  of  $\mathcal{X}$ , the set  $\mathcal{H}(Z)$  denotes the set of all elements freely generated from the words in  $Z$ . I.e.  $\mathcal{H}(Z) = \{\sigma x : x \in Z \text{ and } \sigma \in \mathcal{H}^*\}$ , where  $\mathcal{H}^*$  is the set of all strings of hedges in  $\mathcal{H}$ , including the empty string  $\varepsilon$ . Note that for  $\sigma = \varepsilon$ ,  $\varepsilon x = x$  and, hence,  $Z \subseteq \mathcal{H}(Z)$ . In the case  $Z = \{x\}$  we shall write  $\mathcal{H}(x)$  instead of  $\mathcal{H}(\{x\})$ .  $\leq$  is a semantical order relation upon  $\mathcal{X}$ .

Consider a hedge algebra  $AX = (\mathcal{X}, \mathbb{G}, \mathbb{C}, \mathcal{H}, \leq)$  of an attribute  $X$  with numeric reference interval domain  $U$  normalized to be  $[0, 1]$ , for convenience in a unified presentation of the quantification of the hedge algebras. Formally, the numeric semantics of the words of  $\mathcal{X}$  can be determined by a so-called Semantically Quantifying Mapping (SQM),  $f: \mathcal{X} \rightarrow [0, 1]$ , defined as follows.

**Definition 4.**<sup>3</sup> A mapping  $f: \mathcal{X} \rightarrow [0, 1]$  is said to be an SQM of  $AX$ , if we have:

- $f$  is an *order isomorphism*, i.e. it is one-to-one and for  $\forall x, y \in \mathcal{X}$ ,  $x \leq y \Rightarrow f(x) \leq f(y)$ .

- The image of  $\mathcal{X}$  under  $f$ ,  $f(\mathcal{X})$ , is topologically dense in the universe  $[0, 1]$ .

**Definition 5.**<sup>3</sup> A function  $fm: \mathcal{X} \rightarrow [0, 1]$  is said to be a fuzziness measure of the hedge algebra  $AX$  associated with the given variable  $X$ , if it satisfies the following axioms, for any  $x \in \mathcal{X}$  and  $h \in \mathcal{H}$ :

- $fm(c-) + fm(c+) = 1$ .
- $\sum_{-q \leq j \leq p, j \neq 0} fm(h_j x) = fm(x)$ .

- $fm(hx) = \mu(h)fm(x)$ , where  $\mu(h)$  is called for convenience the fuzziness measure of  $h$  as well.
- For  $x = h_n h_{n-1} \dots h_1 c$ ,  $fm(x) = fm(h_n h_{n-1} \dots h_1 c) = \mu(h_n)\mu(h_{n-1}) \dots \mu(h_1)fm(c)$ ,  $c \in \mathbb{G} = \{c^-, c^+\}$ .
- Setting  $\sum_{-q \leq j \leq -1} \mu(h_j) = \alpha$  &  $\sum_{1 \leq j \leq p} \mu(h_j) = \beta$ , we have  $\alpha + \beta = \sum_{-q \leq j \leq p, j \neq 0} \mu(h_j) = 1$ .

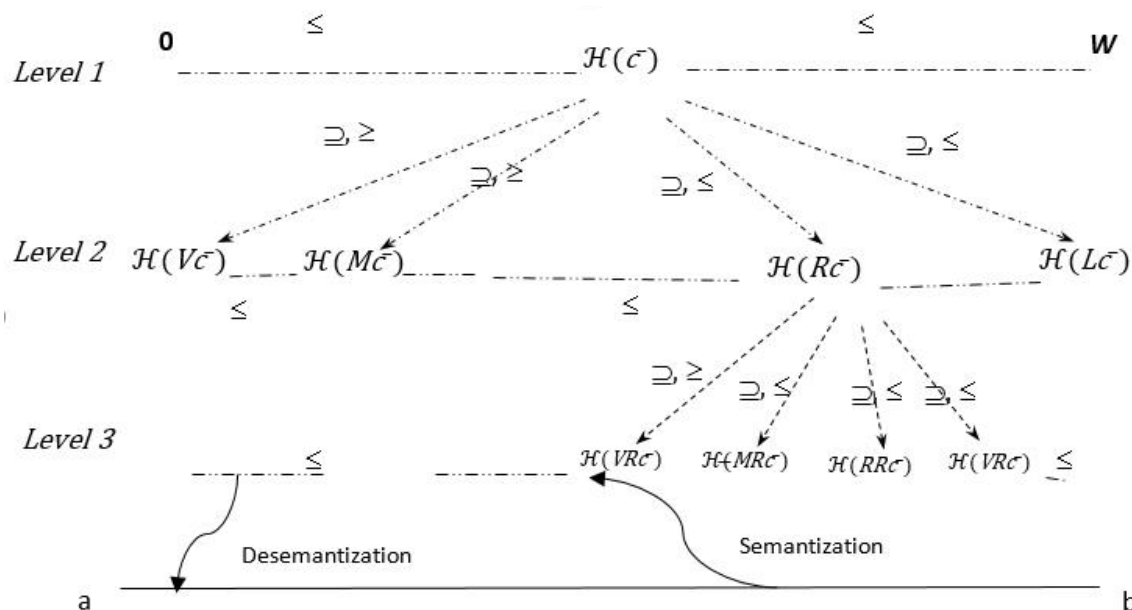
In the general case, for given values of the fuzziness parameters of  $X$ , we can establish a recursive expression to compute the SQM  $v_{fm}$ , called the SQM induced by the given  $fm$ , as follows:<sup>3</sup>

- $v_{fm}(W) = \kappa = fm(c^-)$ ,  $v_{fm}(c^-) = \kappa - \alpha fm(c^-) = \beta fm(c^-)$ ,  $v_{fm}(c^+) = \kappa + \alpha fm(c^+)$ ;
- $v_{fm}(h_j x) = v_{fm}(x) + sign(h_j x) \times (\sum_{i=sign(j)}^{j-1} \mu_i(h_i) + (1 - \omega(h_j x)) \mu(h_j)) fm(x)$

where

$\omega(h_j x) = \frac{1}{2} [1 + sign(h_j x) sign(h_p h_j x) (\beta - \alpha)] \in \{\alpha, \beta\}$ , for all  $j \in [-q \dots p]$ ,  $j \neq 0$ , and  $sign()$  function is defined as in research<sup>3,4</sup>.

### 3.2. Converting values between semantic and



**Figure 1.** A graph representation of  $\mathcal{H}(Z) \subseteq \mathcal{H}(c)$  and transform a value from  $[0, 1]$  to  $[a, b]$  and vice versa.

### reference domains

To convert the values from the reference domain to the semantic domain of a variable  $X$  and vice versa, we synthesize some transformations as: Assume that  $[a, b]$  is a reference domain of the variable  $X$ , and  $[a_s, b_s] \subseteq [0, 1]$  is the semantic domain. The conversion value  $x$  from  $[a, b]$  to  $[a_s, b_s]$  is called *semantization*, denoted  $S(x)$  and the conversion value  $y$  from  $[a_s, b_s]$  to  $[a, b]$  is called *desemantization*, denoted  $D(y)$ .

For flexibility in semantization or desemantization, we add some parameters  $sp, dp \in [-1, 1]$  then:  $S(x) = f(x, sp)$ , satisfy  $0 \leq f(x, sp) \leq 1$ ,  $f(x=a, sp) = 0$ ,  $f(x=b, sp) = 1$ . And,  $D(y) = g(y, dp)$ , satisfy  $a \leq g(y, dp) \leq b$ ,  $g(y=0, dp) = a$ ,  $g(y=1, dp) = b$ .

In this paper, we use the functions:  $S(x) = f(x, sp) = (sp \times x(1-x) + x)/(b-a)$  and  $D(y) = g(y, dp) = dp \times (f(y, sp) - a) \times (b - f(y, sp))/(b - a) + f(y, sp)$ .

Figure 1 illustrates the hedge algebra  $AX = (\mathcal{X}, \mathbb{G}, \mathbb{C}, \mathcal{H}, \leq)$  with the hedge set  $H = \{\text{Very-V, More-M, Rather-R, Less-L}\}$  and the transfer of values from the semantic domain to the reference domain and vice versa.

### 3.3. Hedge-Algebras-based Model (HAM) for time series forecasting

We consider each reference domain in the forecasting problem to correspond to a hedge algebra. Let PAR be a set of parameters, including the fuzzy measures of the hedges and the values sp and dp. Given that PAR has been determined, in this section, we present the fuzzy time series forecasting algorithm as follows.

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**Algorithm 1. HAM(PAR)**


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INPUT:

- $n$  values of data  $\{y(t_1), y(t_2), \dots, y(t_n)\}$  with  $t_1, t_2, \dots, t_n$  are point times.
- System of the parameters of hedge algebras and sp, dp for semantization and desementization, denoted PAR.

OUTPUT: the forecasted value  $F(t_i)$ .

Step 1. Define the discourse  $U$

Put  $U = [D_{\min}, D_{\max}]$  where  $D_{\min} = \min\{y(t_1), y(t_2), \dots, y(t_n)\}$  and  $D_{\max} = \max\{y(t_1), y(t_2), \dots, y(t_n)\}$ .

Step 2. Building the intervals upon  $U$  by using the fuzziness model of hedge algebra.

Based on an algebra  $AX = (\mathcal{X}, \mathbb{G}, \mathbb{C}, \mathcal{H}, \leq)$  we divide  $U$  into  $k$  intervals  $u_1, u_2, \dots, u_k$  w.r.t level  $l$  (see Figure 1). The interval  $u_i$  is labeled  $A_i$ ,  $i = 1, 2, \dots, k$  satisfying  $A_1 < A_2 < \dots < A_k$ . We calculate  $f_{ui} = fm(A_i) \times (D_{\max} - D_{\min})$ ,  $i = 1, 2, \dots, k$ . So we have  $u_1 = [u_{1d}, u_{1c}] = [D_{\min}, D_{\min} + f_{u1}]$ ,  $u_2 = [u_{2d}, u_{2c}] = [u_{1c} + 1, u_{1d} + f_{u2}]$ ,  $\dots$ ,  $u_k = [u_{kd}, u_{kc}] = [u_{(k-1)c} + 1, u_{kd} + f_{uk}]$ .

Step 3. Quantifying semantics of the linguistic values  $A_1, A_2, \dots, A_k$ .

To quantify the semantic of  $A_1, A_2, \dots, A_k$  we use SQM  $v_{jm}$  as  $SA_1 = v_{jm}(A_1)$ ,  $SA_2 = v_{jm}(A_2)$ ,  $\dots$ ,  $SA_k = v_{jm}(A_k)$ . By properties of hedge algebras, it is clear that  $SA_1 < SA_2 < \dots < SA_k$ .

Step 4. Constructing the relationships

Suppose that,  $F(t-1)$  is  $A_p$ ,  $F(t)$  is  $A_j$  and  $F(t)$  is caused by  $F(t-1)$ . Clearly, we have a relation between  $A_i$  and  $A_j$  denoted  $A_i \rightarrow A_j$ .

Step 5. Grouping relationships

If  $A_i \rightarrow A_{j1}$ ,  $A_i \rightarrow A_{j2}, \dots$ ,  $A_i \rightarrow A_{jm}$ , then we establish the relation by grouping all of them into a unique relation  $A_i \rightarrow A_{j1}, A_{j2}, \dots, A_{jm}$ .

---

Step 6. Calculating output value

From a group of the relations in Step 5, applying the rules as in Section 2.2 we get the results of  $F(t)$ , scilicet: If there is a relation  $A_i \rightarrow A_j$  then  $F(j) = D(SA_j)$  upon  $u_j = [u_{jd}, u_{jc}]$ . If  $A_i \rightarrow \emptyset$  then  $F(j) = D(\emptyset)$  upon  $u_i = [u_{id}, u_{ic}]$ . If  $A_i \rightarrow A_{j1}, A_{j2}, \dots, A_{jm}$  then  $F(j) = D(W_{ij1} \times SA_{j1} + W_{ij2} \times SA_{j2} + \dots + W_{ijm} \times SA_{jm})$  upon interval  $[\min\{u_{j1d}, u_{j2d}, \dots, u_{jmd}\}, \max\{u_{j1c}, u_{j2c}, \dots, u_{jmc}\}]$  where  $W_{ij}$  is the weights measured in the ratio number of times of real data in the interval  $u_i$  to sum of number of times of real data in the intervals  $u_{j1}, u_{j2}, \dots, u_{jm}$ .

Step 7. Return the values  $F(t_i)$ ,  $i = 1, \dots, n$ .

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## 4. THE OPTIMAL HEDGE-ALGEBRAS-BASED MODEL

In Step 2 of the HAM model above, we assume that each point at a time will belong to a word in the hedge algebra  $AX = (\mathcal{X}, \mathbb{G}, \mathbb{C}, \mathcal{H}, \leq)$ ,  $\mathbb{C} = \{c^-, c^+\}$ ,  $\mathcal{H} = \{h_{-q}, \dots, h_{-1}, h_1, \dots, h_p\}$  with given parameters  $\mu(h_i)$ ,  $h_i \in H$ . Obviously, all parameters to be used in HAM contain  $n = p + q + 2$  parameters, which are  $\mu(h_{-q}), \mu(h_{-q+1}), \dots, \mu(h_{-1}), \mu(h_1), \dots, \mu(h_p)$ , and sp, dp for semantization and desementization. So we can present that by the vector  $PAR = (x_1, x_2, \dots, x_n)$  where  $x_1 = \mu(h_{-q})$ ,  $x_2 = \mu(h_{-q+1}), \dots, x_{n-2} = \mu(h_p)$ ,  $x_{n-1} = sp$ ,  $x_n = dp$ . Vector PAR is also an artificial bee in the OHAM below.

To optimize the parameters, we choose the fitness function to be the Root Mean Square Error (RMSE), where a smaller value indicates better fitness. The root mean squared error can be expressed as follows:

$$RMSE = \sqrt{\frac{\sum_{t=1}^n (y_t - \hat{y}_t)^2}{n}}$$

where  $y_t$  is the actual data point at time  $t$ , and  $\hat{y}_t$  is the predicted value at time  $t$ .

The fitness function can be written:



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**Algorithm 2. Fitness(PAR)**

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INPUT: A system of parameters *PAR* represented for a bee; a real dataset  $\{y_t\}_{t=1}^n$ .

OUTPUT: Value of fitness of *PAR*.

*Step 1.* Generate language lattice of HA and quantify those values based on parameters in *PAR*.

*Step 2.* Calculate forecast values  $\hat{y}_t$  ( $t = 1, \dots, n$ ) by HAM(PAR).

*Step 3.* Set Err = 0.

*Step 4.* For each real value  $y_t$  and forecasted value  $\hat{y}_t$  at  $t$  time, we put:

$$\text{Err} = \text{Err} + (y_t - \hat{y}_t)^2.$$

*Step 5.*  $\text{RMSE} = \sqrt{\frac{\text{Err}}{n}}$ .

*Step 6.* Return value RMSE.

---

The model is built as:

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**Algorithm 3. OHAM()**

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INPUT:  $n$  values of data  $\{y(t_1), y(t_2), \dots, y(t_n)\}$  with  $t_1, t_2, \dots, t_n$  are point times.

OUTPUT: the best system of parameters for solving optimization forecast problems.

*Step 1.* Initialization

Start by randomly initializing a population of artificial bees, where each bee represents a potential solution to the optimization problem. The population size is typically defined beforehand.

*Step 2.* Employed Bees' Phase

Each employed bee explores a new solution by adjusting its current position based on information shared with a randomly selected neighbor bee. The new solution is generated by modifying the position using specific search operators or strategies. After generating the new solution, the fitness of both the current and new solutions is evaluated.

*Step 3.* Onlooker Bees' Phase

Onlooker bees probabilistically choose a solution to explore based on the fitness values of employed bees. The better the fitness value, the higher the probability of being chosen. This phase allows good solutions to be shared among the population and improves the overall search process.

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*Step 4.* Scout Bees' Phase

If an employed bee exhausts its exploration resources without finding a better solution, it becomes a scout bee. Scout bees generate a new random solution to diversify the search space and prevent the algorithm from getting stuck in local optima.

*Step 5.* Memorize the best solution (BestPAR) achieved so far.

*Step 6.* Termination

The algorithm will be stopped if a termination condition is satisfied. If not, go back to *Step 2*.

*Step 7.* Return *BestPAR*.

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**5. EXPERIMENTAL RESULTS**

In this section, the proposed approach is applied to forecast the price of State Bank of India (SBI) shares at BSE India from April 2008 to March 2010, the enrollments at the University of Alabama from years 1971 to 1992, and the TAIEX Index of November and December 2004. The result will then be compared with different published methods. To measure the accuracy of the forecasting methods, the following metrics are used for comparison with RMSE.

For each test dataset, we used hedge algebra consisting of four hedge operators: Very, More, Possible, and Little, along with two parameters, *sp* and *dp*, for semantization and desemantization. The OHAM model was implemented using the ABC optimization algorithm with a maximum of 3000 iterations, and the number of employed and onlooker bees was set to 50. The optimal parameters obtained correspond to the experimental datasets: the SBI price, student enrollment at the University of Alabama, and the TAIEX stock index, as presented in Table 1.

Using the RMSE metric to evaluate forecasting performance, it is evident that the OHAM model produces less error than other models (see the last column of Tables 2-4). Visually, from Figures 2-4, the forecasted data curves generated by the proposed method



follow the actual trend more closely compared to other models. Notably, at points with large amplitude variations, the OHAM model's predictions remain closer to the actual values, further demonstrating the high adaptability of the proposed model.

**Table 1.** The optimal parameters obtained by OHAM.

| Parameters<br>Forecasting problems | $\mu(Little)$ | $\mu(Possible)$ | $\mu(More)$ | $\mu(Very)$ | $sp$  | $dp$   |
|------------------------------------|---------------|-----------------|-------------|-------------|-------|--------|
| SBI                                | 0.316         | 0.286           | 0.204       | 0.194       | 0.467 | -0.457 |
| Enrollment                         | 0.205         | 0.213           | 0.395       | 0.187       | 0.066 | -0.167 |
| TAIEX                              | 0.194         | 0.239           | 0.149       | 0.418       | 0.113 | -0.449 |

5.1. SBI prices forecasting

**Table 2.** Results of the forecasting models for SBI data.

| Months       | Actual SBI Prices | Chen <sup>10</sup> (1996) | Huarng <sup>12</sup> (2001) | Pathak and Singh <sup>13</sup> (2011) | Joshi and Kumar <sup>14</sup> (2012) | Kumar and Gangwar <sup>15</sup> (2015) | Bisht and Kumar <sup>6</sup> (2016) | OHAM    |
|--------------|-------------------|---------------------------|-----------------------------|---------------------------------------|--------------------------------------|----------------------------------------|-------------------------------------|---------|
| April-08     | 1819.95           | -                         | -                           | -                                     | -                                    | -                                      | -                                   | -       |
| May-08       | 1840.00           | 1900                      | 1855                        | 1770.00                               | 1777.80                              | 1725.98                                | 1877.657                            | 1867.00 |
| June-08      | 1496.70           | 1900                      | 1855                        | 1832.50                               | 1865.71                              | 1725.98                                | 1877.657                            | 1583.00 |
| July-08      | 1567.50           | 1500                      | 1575                        | 1470.00                               | 1531.50                              | 1512.39                                | 1466.360                            | 1583.00 |
| August-08    | 1638.90           | 1500                      | 1505                        | 1570.00                               | 1531.50                              | 1512.39                                | 1466.360                            | 1583.00 |
| September-08 | 1618.00           | 1600                      | 1610                        | 1670.00                               | 1777.80                              | 1574.35                                | 1533.504                            | 1583.00 |
| October-08   | 1569.90           | 1600                      | 1610                        | 1603.33                               | 1531.50                              | 1574.35                                | 1533.504                            | 1583.00 |
| November-08  | 1375.00           | 1500                      | 1505                        | 1670.00                               | 1531.50                              | 1512.39                                | 1466.360                            | 1366.00 |
| December-08  | 1325.00           | 1433                      | 1482                        | 1382.50                               | 1504.23                              | 1305.52                                | 1520.652                            | 1366.00 |
| January-09   | 1376.40           | 1433                      | 1365                        | 1332.50                               | 1504.23                              | 1665.90                                | 1520.652                            | 1366.00 |
| February-09  | 1205.90           | 1433                      | 1482                        | 1332.50                               | 1504.23                              | 1305.52                                | 1520.652                            | 1192.00 |
| March-09     | 1132.25           | 1433                      | 1155                        | 1195.00                               | 1258.23                              | 1294.27                                | 1144.718                            | 1192.00 |
| April-09     | 1355.00           | 1300                      | 1365                        | 1145.00                               | 1258.23                              | 1294.27                                | 1322.446                            | 1366.00 |
| May-09       | 1891.00           | 1433                      | 1482                        | 1357.50                               | 1504.23                              | 1665.90                                | 1520.652                            | 1867.00 |
| June-09      | 1935.00           | 1900                      | 1890                        | 1882.50                               | 1865.71                              | 2006.51                                | 1877.657                            | 1867.00 |
| July-09      | 1840.00           | 1900                      | 1890                        | 1970.00                               | 1883.93                              | 2006.51                                | 1895.491                            | 1867.00 |
| August-09    | 1886.90           | 1900                      | 1855                        | 1470.00                               | 1865.71                              | 1725.98                                | 1877.657                            | 1867.00 |
| September-09 | 2235.00           | 1900                      | 1855                        | 1970.00                               | 1865.71                              | 2006.51                                | 1877.657                            | 2259.00 |
| October-09   | 2500.00           | 2300                      | 2485                        | 2245.00                               | 2142.04                              | 2520.00                                | 2311.382                            | 2498.00 |
| November-09  | 2394.00           | 2300                      | 2415                        | 2470.00                               | 2245.65                              | 2420.00                                | 2374.204                            | 2384.00 |
| December-09  | 2374.75           | 2300                      | 2345                        | 2395.00                               | 2191.75                              | 2365.99                                | 2352.723                            | 2384.00 |
| January-10   | 2315.25           | 2300                      | 2205                        | 2395.00                               | 2191.75                              | 2365.99                                | 2352.723                            | 2384.00 |
| February-10  | 2059.95           | 2300                      | 2205                        | 2295.00                               | 2142.04                              | 2020.00                                | 2311.382                            | 2083.00 |
| March-10     | 2120.05           | 2100                      | 2135                        | 2070.00                               | 1883.93                              | 2120.00                                | 2166.247                            | 2083.00 |
| RMSE         |                   | 187.26                    | 164.04                      | 205.96                                | 200.17                               | 131.28                                 | 179.03                              | 36.50   |

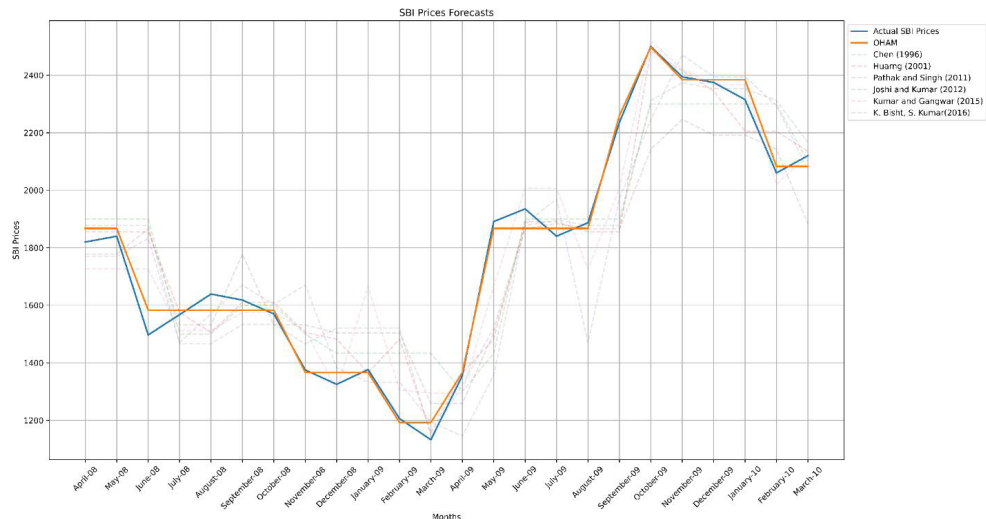


Figure 2. Line chart of forecast method results for SBI data.

5.2. Enrollment student forecasting

Table 3. Results of the forecasting models for enrollment student.

| Actual data | Song and Chissom <sup>9</sup> (1993) | Chen <sup>10</sup> (1996) | Huarng <sup>12</sup> (2001) | Lee and Chou <sup>16</sup> (2004) | SC_time variant <sup>17</sup> (1994) | Cheng et al. <sup>18</sup> (2006) | Cheng et al. <sup>19</sup> (2008) | Yolcu et al. <sup>20</sup> (2009) | Qiu et al. <sup>21</sup> (2011) | Joshi and Kumar <sup>14</sup> (2012) | Kumar and Gangwar <sup>15</sup> (2015) | Bisht and Kumar <sup>6</sup> (2016) | OHAM   |
|-------------|--------------------------------------|---------------------------|-----------------------------|-----------------------------------|--------------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|---------------------------------|--------------------------------------|----------------------------------------|-------------------------------------|--------|
| 13055       | -                                    | -                         | -                           | -                                 | -                                    | -                                 | -                                 | -                                 | -                               | -                                    | -                                      | -                                   | -      |
| 13563       | 14000                                | 14000                     | -                           | 14025                             | -                                    | 14230                             | 14242                             | 14031.35                          | 14195                           | 14250                                | -                                      | 13595.67                            | 13752  |
| 13867       | 14000                                | 14000                     | -                           | 14568                             | -                                    | 14230                             | 14242                             | 14795.36                          | 14424                           | 14246                                | 13693                                  | 13814.75                            | 13752  |
| 14696       | 14000                                | 14000                     | 14000                       | 14568                             | -                                    | 14230                             | 14242                             | 14795.36                          | 14593                           | 14246                                | 13693                                  | 14929.79                            | 14753  |
| 15460       | 15500                                | 15500                     | 15500                       | 15654                             | 14700                                | 15541                             | 15474.3                           | 14795.36                          | 15589                           | 15491                                | 14867                                  | 15541.27                            | 15341  |
| 15311       | 16000                                | 16000                     | 15500                       | 15654                             | 14800                                | 15541                             | 15474.3                           | 16406.57                          | 15645                           | 15491                                | 15287                                  | 15540.62                            | 15341  |
| 15603       | 16000                                | 16000                     | 16000                       | 15654                             | 15400                                | 15541                             | 15474.3                           | 16406.57                          | 15634                           | 15491                                | 15376                                  | 15540.62                            | 15341  |
| 15861       | 16000                                | 16000                     | 16000                       | 15654                             | 15500                                | 16196                             | 15474.3                           | 16406.57                          | 16100                           | 16345                                | 15376                                  | 15540.62                            | 16040  |
| 16807       | 16000                                | 16000                     | 16000                       | 16197                             | 15500                                | 16196                             | 16146.5                           | 16406.57                          | 16188                           | 16345                                | 15376                                  | 16254.5                             | 16879  |
| 16919       | 16813                                | 16833                     | 17500                       | 17283                             | 16800                                | 16196                             | 16988.3                           | 17315.29                          | 17077                           | 15850                                | 16523                                  | 17040.41                            | 16879  |
| 16388       | 16813                                | 16833                     | 16000                       | 17283                             | 16200                                | 17507                             | 16988.3                           | 17315.29                          | 17105                           | 15850                                | 16066                                  | 17040.41                            | 16040  |
| 15433       | 16789                                | 16833                     | 16000                       | 16197                             | 16400                                | 16196                             | 16146.5                           | 17315.29                          | 16369                           | 15850                                | 17519                                  | 16254.5                             | 15341  |
| 15497       | 16000                                | 16000                     | 16000                       | 15654                             | 16800                                | 15541                             | 15474.3                           | 16406.57                          | 15643                           | 15450                                | 16606                                  | 15540.62                            | 15341  |
| 15145       | 16000                                | 16000                     | 15500                       | 15654                             | 16400                                | 15541                             | 15474.3                           | 16406.57                          | 15648                           | 15450                                | 15376                                  | 15540.62                            | 15341  |
| 15163       | 16000                                | 16000                     | 16000                       | 15654                             | 15500                                | 15541                             | 15474.3                           | 16406.57                          | 15622                           | 15491                                | 15376                                  | 15541.27                            | 15341  |
| 15984       | 16000                                | 16000                     | 16000                       | 15654                             | 15500                                | 15541                             | 15474.3                           | 16406.57                          | 15623                           | 15491                                | 15376                                  | 15541.27                            | 16040  |
| 16859       | 16000                                | 16000                     | 16000                       | 16197                             | 15500                                | 16196                             | 16146.5                           | 16406.57                          | 16231                           | 16345                                | 15287                                  | 16254.5                             | 16879  |
| 18150       | 16813                                | 16833                     | 17500                       | 17283                             | 16800                                | 17507                             | 16988.3                           | 17315.29                          | 17090                           | 17950                                | 16523                                  | 17040.41                            | 18283  |
| 18970       | 19000                                | 19000                     | 19000                       | 18369                             | 19300                                | 18872                             | 19144                             | 19132.79                          | 18325                           | 18961                                | 17519                                  | 18902.3                             | 19291  |
| 19328       | 19000                                | 19000                     | 19000                       | 19454                             | 17800                                | 18872                             | 19144                             | 19132.79                          | 19000                           | 18961                                | 19500                                  | 19357.3                             | 19291  |
| 19337       | 19000                                | 19000                     | 19000                       | 19454                             | 19300                                | 18872                             | 19144                             | 19132.79                          | 19000                           | 18961                                | 19000                                  | 19168.56                            | 19291  |
| 18876       | -                                    | 19000                     | 19000                       | -                                 | 19600                                | 18872                             | 19144                             | 19132.79                          | 19000                           | 18961                                | 19500                                  | 19168.56                            | 19291  |
| RMSE        | 650.40                               | 880.73                    | 638.36                      | 476.97                            | 501.28                               | 511.04                            | 478.45                            | 805.17                            | 511.33                          | 433.76                               | 493.56                                 | 428.63                              | 178.21 |

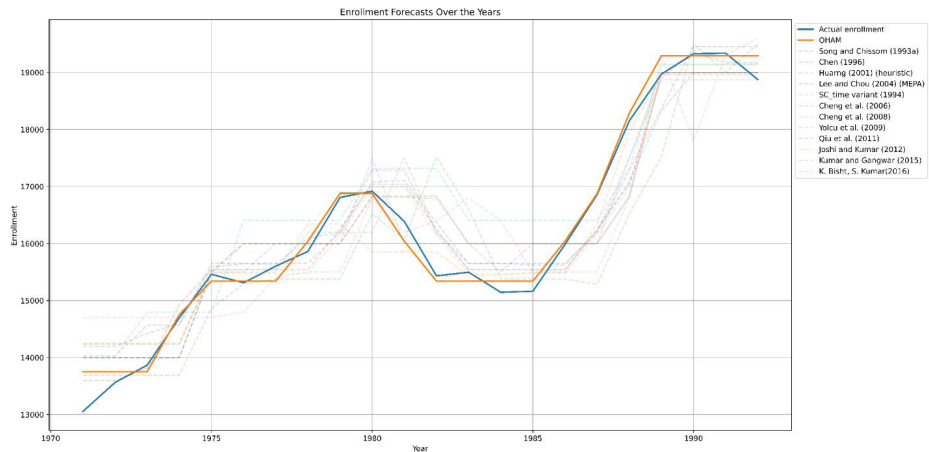


Figure 3. Line chart of forecast method results for enrollment student data.

5.3. TAIEX index forecasting

Table 4. Results of the forecasting models for TAIEX index.

| Date       | Actual Index | Chen' Forecasted Index <sup>10</sup> | Loc' Forecasted Index <sup>7</sup> (a) | Loc' Forecasted Index <sup>8</sup> (b) | OHAM    |
|------------|--------------|--------------------------------------|----------------------------------------|----------------------------------------|---------|
| 2/11/2004  | 5759.61      | 5674.81                              | 5743.00                                |                                        | 5768.00 |
| 3/11/2004  | 5862.85      | 5768.14                              | 5852.00                                | 5886.00                                | 5863.00 |
| 4/11/2004  | 5860.73      | 5854.81                              | 5876.04                                | 5886.00                                | 5863.00 |
| 5/11/2004  | 5931.31      | 5908.26                              | 5876.04                                | 5934.00                                | 5942.00 |
| 8/11/2004  | 5937.46      | 5934.81                              | 5912.05                                | 5934.00                                | 5942.00 |
| 9/11/2004  | 5945.2       | 5943.81                              | 5912.05                                | 5934.00                                | 5942.00 |
| 10/11/2004 | 5948.49      | 5934.81                              | 5912.05                                | 5978.00                                | 5942.00 |
| 11/11/2004 | 5874.52      | 5937.12                              | 5912.05                                | 5886.00                                | 5863.00 |
| 12/11/2004 | 5917.16      | 5908.26                              | 5919.27                                | 5934.00                                | 5903.00 |
| 15/11/2004 | 5906.69      | 5934.81                              | 5919.27                                | 5934.00                                | 5903.00 |
| 16/12/2004 | 5910.85      | 5934.81                              | 5919.27                                | 5934.00                                | 5903.00 |
| 17/11/2004 | 6028.68      | 5937.12                              | 5919.27                                | 5978.00                                | 6038.00 |
| 18/11/2004 | 6049.49      | 6068.14                              | 5979.18                                | 5978.00                                | 6038.00 |
| 19/11/2004 | 6026.55      | 6068.14                              | 5979.18                                | 5978.00                                | 6038.00 |
| 22/11/2004 | 5838.42      | 5976.47                              | 5979.18                                | 5886.00                                | 5833.00 |
| 23/11/2004 | 5851.10      | 5854.81                              | 5876.04                                | 5886.00                                | 5833.00 |
| 24/11/2004 | 5911.31      | 5934.85                              | 5876.04                                | 5934.00                                | 5903.00 |
| 25/11/2004 | 5855.24      | 5934.81                              | 5919.27                                | 5886.00                                | 5863.00 |
| 26/11/2004 | 5778.65      | 5854.81                              | 5876.04                                | 5768.00                                | 5768.00 |
| 29/11/2004 | 5785.26      | 5762.12                              | 5797.89                                | 5768.00                                | 5768.00 |
| 30/11/2004 | 5844.76      | 5762.12                              | 5852.00                                | 5886.00                                | 5833.00 |
| 1/12/2004  | 5798.62      | 5834.85                              | 5876.04                                | 5768.00                                | 5768.00 |
| 2/12/2004  | 5867.95      | 5803.26                              | 5797.89                                | 5886.00                                | 5863.00 |
| 3/12/2004  | 5893.27      | 5854.81                              | 5876.04                                | 5886.00                                | 5903.00 |
| 6/12/2004  | 5919.17      | 5854.81                              | 5919.27                                | 5934.00                                | 5903.00 |
| 7/12/2004  | 5925.28      | 5937.12                              | 5912.05                                | 5934.00                                | 5942.00 |
| 8/12/2004  | 5892.51      | 5876.47                              | 5912.05                                | 5886.00                                | 5903.00 |
| 9/12/2004  | 5913.97      | 5854.81                              | 5919.27                                | 5934.00                                | 5903.00 |
| 10/12/2004 | 5911.63      | 5934.81                              | 5919.27                                | 5934.00                                | 5903.00 |

|            |         |         |         |         |         |
|------------|---------|---------|---------|---------|---------|
| 13/12/2004 | 5878.89 | 5937.12 | 5919.27 | 5863.00 | 5863.00 |
| 14/12/2004 | 5909.65 | 5854.81 | 5919.27 | 5903.00 | 5903.00 |
| 15/12/2004 | 6002.58 | 5934.81 | 5919.27 | 5994.00 | 5994.00 |
| 16/12/2004 | 6019.23 | 6068.14 | 5979.18 | 6038.00 | 6038.00 |
| 17/12/2004 | 6009.32 | 6062.12 | 5979.18 | 5994.00 | 5994.00 |
| 20/12/2004 | 5985.94 | 6062.12 | 5979.18 | 5994.00 | 5994.00 |
| 21/12/2004 | 5987.85 | 5937.12 | 5979.18 | 5994.00 | 5994.00 |
| 22/12/2004 | 6001.52 | 5934.81 | 5979.18 | 5994.00 | 5994.00 |
| 23/12/2004 | 5997.67 | 6068.14 | 5979.18 | 5994.00 | 5994.00 |
| 24/12/2004 | 6019.42 | 5934.81 | 5979.18 | 6038.00 | 6038.00 |
| 27/12/2004 | 5985.94 | 6068.14 | 5979.18 | 5994.00 | 5994.00 |
| 28/12/2004 | 6000.57 | 5937.12 | 5979.18 | 5994.00 | 5994.00 |
| 29/12/2004 | 6088.49 | 6068.14 | 5979.18 | 6125.00 | 6125.00 |
| 30/12/2004 | 6100.86 | 6062.12 | 6119.36 | 6125.00 | 6125.00 |
| 31/12/2004 | 6139.69 | 6137.12 | 6143.57 | 6125.00 | 6125.00 |
| RMSE       |         | 56.86   | 48.02   | 26.88   | 12.73   |



Figure 4. Line chart of forecast method results for TAIEX index data.

6. CONCLUSIONS

In this study, we propose a new fuzzy time series forecasting method using hedge algebra. We also introduce a segmentation approach for the reference space based on *k-level* and the fuzziness measure of linguistic terms of hedge algebra.

The effectiveness of this fuzzy time series forecasting method is demonstrated by applying it to the benchmark problem of forecasting the enrollment numbers at the University of Alabama. The relatively small RMSE value indicates that the proposed model outperforms other methods. Moreover, financial time series exhibit intrinsic characteristics such as relatively

high volatility and frequent fluctuations in individual time series data over time, making forecasting more challenging compared to other types of time series data. Even well-established time series forecasting methods tend to produce high forecasting errors. However, the proposed OHAM model proves to be highly suitable and effective for forecasting financial time series, where nonlinearity, intrinsic characteristics, and fuzziness complicate the forecasting process.

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