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Mô phỏng đa vật lý và phân tích lỗi hệ thống khởi động ô tô bằng phần mềm Siemens Simcenter

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TÓM TẮT

Bài báo trình bày phương pháp mô phỏng và chẩn đoán sớm hư hỏng trong hệ thống khởi động ô tô thông qua mô hình tích hợp điện – cơ – nhiệt trên nền tảng phần mềm Simcenter Amesim. Các tình huống hư hỏng điển hình được mô phỏng để phân tích sự biến đổi của các thông số đặc trưng như dòng điện, điện áp, tốc độ trục khuỷu và nhiệt độ trong quá trình khởi động. Kết quả mô phỏng giúp làm rõ mối quan hệ giữa các thông số, từ đó phát hiện sớm các dấu hiệu về sự suy giảm hiệu suất hoặc khả năng khởi động. Nghiên cứu này cung cấp cơ sở kỹ thuật vững chắc cho việc phát triển các giải pháp chẩn đoán sớm, nhằm tối ưu hóa quá trình bảo dưỡng và nâng cao độ tin cậy của hệ thống khởi động trên ô tô.

Từ khóa: Hệ thống khởi động, điện trở phản ứng, simcenter amesim, chổi than, dòng điện.

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Multiphysics simulation and fault analysis of the automotive starting system using Siemens Simcenter software

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ABSTRACT

The paper presents a method for simulating and early diagnosing faults in the automotive starting system through an integrated electrical-mechanical-thermal model on the Simcenter Amesim platform. Typical fault scenarios are simulated to analyze the variation of characteristic parameters such as current, voltage, crankshaft speed, and temperature during the starting process. The simulation results help clarify the relationship between these parameters, enabling the early detection of signs of performance degradation or starting ability issues. This study provides a solid technical foundation for developing early diagnostic solutions to optimize the maintenance process and enhance the reliability of the automotive starting system.

Keywords: *Start system, armature resistance, simcenter amesim, brush, current.*

1. INTRODUCTION

The starter system plays an important role in the operation of vehicles using internal combustion engines employed for transitioning the engine from a static state to a stable operating state. With the widespread adoption of Start-Stop technology in modern vehicles, the frequency of starter system operation has increased significantly. This frequent operation imposes continuous electrical and mechanical loads on components such as the starter motor, battery, brushes, and drive mechanism.¹

However, unlike safety systems such as brakes, steering, or engine control, which are equipped with continuous monitoring sensors, the starter system typically lacks the dedicated sensors to monitor its operational status or

provide fault warnings. When the start system occurs failure, the user only detects it when the engine can't start. This results in impact on the engine's operation, prolongs the diagnosis and repair time, and increases maintenance costs.²

Nowadays, there is a strong need to develop a simulation model of the starter system capable of accurately replicating its electrical, mechanical, and thermal characteristics. In recent years, several studies have focused on analyzing electrical signals during the starting process – such as excitation current, rotational speed, and terminal voltage – with the aim of early fault detection using intelligent algorithms such as fuzzy logic or adaptive neuro-fuzzy inference systems^{3,4} or simply conducting assessments of the starter motor's service life.⁵

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However, these experimental studies often encounter significant limitations due to the simultaneous influence of various uncontrollable factors, such as ambient temperature, battery charge status, or load fluctuations. Additionally, signal acquisition on real vehicles requires specialized measurement systems, which complicates implementation and limits the ability to investigate specific fault scenarios proactively.

Based on this, the study adopts a simulation model approach for the starter system on the Simcenter Amesim software platform. The model is built for a 4-cylinder diesel engine, allowing for the proactive simulation of typical fault scenarios such as brush wear, increased mechanical resistance, or reduced starter motor efficiency—faults that significantly affect the electrical-mechanical signal characteristics. Thanks to the simulation environment that allows complete control of system parameters, the study aims to quantify the signal features in each fault scenario, thereby developing a set of criteria for early diagnosis and optimizing the maintenance of starter systems in modern vehicles. This approach not only enhances the understanding of fault behavior under various conditions but also contributes to the advancement of intelligent maintenance strategies for automotive electrical systems.

2. CONTENT

2.1. Theoretical basis and research methodology

2.1.1. Characteristics of the automotive starting system

The starter system in automobiles is important for starting the internal combustion engine. This system provides enough initial torque to rotate the crankshaft. When the crankshaft rotates, the intake-compression-power-exhaust cycle occurs in the cylinders, allowing the engine to operate. The operational principle of this system is demonstrated through the main processes:

When the driver turns on the ignition key (or presses the Start button for push-button start systems), the control circuit supplies power to the starter relay. This relay activates a high current from the battery to the starter motor. At the same time, the gear mechanism (usually Bendix) is pushed into engagement with the flywheel's gear ring. The starter motor rotates, turning the flywheel and crankshaft. When the crankshaft reaches sufficient speed, the ignition or fuel injection system is activated, and the engine begins to run independently through the combustion process. After that, the starter gear disengages, and the motor switches off.

During the starting phase, the torque generated by the starter motor must be large enough to overcome the total resisting torque acting on the crankshaft. If the starter torque is smaller than the resisting torque, the engine will not be able to reach the required rotational speed to sustain operation, resulting in a failed start. Therefore, understanding this torque interaction is a critical foundation for building simulation models and fault analysis of the starter system.

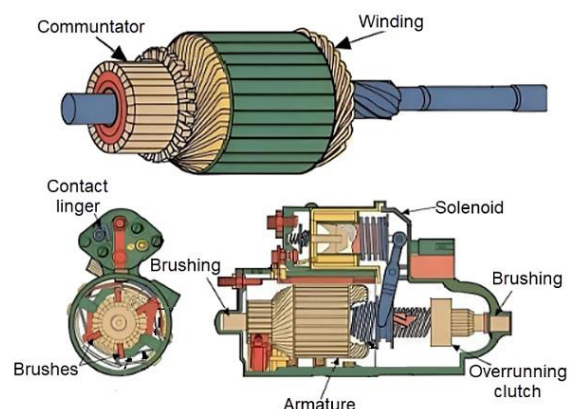


Figure 1. Automotive starter motor structure.

The main power source of the starter system is the series-wound DC motor, which generates high torque right at the moment of starting. This characteristic allows the starter motor to overcome significant initial resistances such as mechanical friction, air pressure in the cylinders, and the rotational inertia of the engine

components. Figure 1 illustrates the typical structure of the motor.

Common faults of the starter system:⁶

- Increased contact resistance or brush wear: Both of these phenomena lead to an increase in resistance in the power circuit to the starter motor, reducing the starting current and output torque. As a result, the motor rotates weakly, the crankshaft speed fails to reach the required level, and the starting process becomes slow or completely fails. Weak or intermittent starting sounds often accompany the phenomenon.

- Increased mechanical resistance: Causes such as lack of lubrication, worn bearings, seized shaft bearings, or dirt and foreign objects entering the mechanical system can significantly increase the resisting torque during the starting process. As the resisting torque increases, the starter motor must generate higher current to maintain the ability to rotate the crankshaft. In severe cases, especially when the ambient temperature is low or the battery is weak, the starter motor may not generate enough force to rotate, leading to a failed start.

2.1.2. Mathematical model of the series-wound DC motor:⁷

- Back electromotive force

$$bemf = K_t \cdot \omega_{dif} \quad (1)$$

Where

$bemf$: Back electromotive force (V)

K_t : Torque and electromotive force constant (Nm/A or V.s/rad)

ω_{dif} : Relative speed between rotor and stator (rad/s)

- Current through the armature winding

$$\frac{dI_s}{dt} = \frac{U_s - R_s \cdot I_s - bemf}{L_s} \quad (2)$$

Where

I_s : Current through the series-wound excitation coil (A)

U_s : Voltage across the coil (V)

R_s : Resistance of the coil (Ω)

L_s : Inductance of the coil (H)

- Electromagnetic torque generated

$$M_e = K_t \cdot I_s \quad (3)$$

Where

K_t : Torque constant

I_s : Starting current (A)

- Temperature compensation

Torque constant:

$$K_t = K_{t0} (1 + \alpha_{Kt} (Temp - T_0)) \quad (4)$$

Coil resistance:

$$R_s = K_{t0} (1 + \alpha_{Rs} (Temp - T_0)) \quad (5)$$

Where

K_{t0} : Torque constant at the reference temperature T_0

α_{kt} : Temperature coefficient of the torque constant

$Temp$: Current operating temperature

- Dynamics equation

During the starting process, the rotating system, including the crankshaft, flywheel, and pistons, has a moment of inertia that varies with the rotational angle. The general equation is as follows:⁸

$$\frac{dI}{d\phi_r} \cdot \frac{\omega_r^2}{2} + \frac{d\omega_r}{dt} \cdot I = M_e + M_{a-t} + M_{loss} \quad (6)$$

Where

I : Moment of inertia of the rotating mass ($\text{kg} \cdot \text{m}^2$)

$dI/d\phi_r$: Rate of change of the moment of inertia with respect to the crankshaft rotational angle (rad^{-1})

ω_r : Crankshaft angular velocity (rad/s)

M_e : Electromagnetic torque from the starter motor (Nm)

M_{a-r} : Torque due to compressed air in the cylinders (Nm)

M_{loss} : Mechanical loss torque (Nm)

From this model, signals such as starting current I_s , torque M_e , and crankshaft speed ω_r can be monitored and recorded. These signals will exhibit significant variations when system faults occur, allowing for early fault detection without dismantling the system.

2.1.3. Overview of Simcenter Amesim Software

Simcenter Amesim is a multi-domain physical modeling simulation software developed by Siemens Digital Industries Software. The software supports the design, analysis, and optimization of electrical, mechanical, thermal, and hydraulic systems in real time. With its intuitive drag-and-drop interface and extensive simulation block library, Simcenter Amesim allows users to quickly, accurately, and flexibly build complex system models across various fields, including mechatronics, automotive, energy, and automation.⁹

Quy Nhon University has been granted legal access to use Simcenter Amesim software through Siemens' official licensing program, serving the purposes of teaching, research, and the development of engineering simulation models. Owning the software license allows the university to access modern tools, enhancing the quality of education, particularly in mechanical engineering, electrical-electronics, and automotive engineering.

Some characteristic blocks used in simulating the starter system include:

- Motor DC: Simulates the electrical-mechanical characteristics of the series-wound starter motor.
- Friction: Describes the torque loss due to friction between rotating components.
- Shaft: Represents the rotating shaft that transmits motion between components like the motor, gears, and flywheel.

- Crankshaft: Simulates the crankshaft mechanism of an internal combustion engine.

- Battery: The main power source providing energy to the starter system.

- Transmission: The reduction gear between the starter motor shaft and engine crankshaft increases the starting torque.

- Load: The mechanical load block simulating resisting torque, which can be constant, time-varying, or speed-dependent.

2.2. Simulation model construction

2.2.1. Model structure

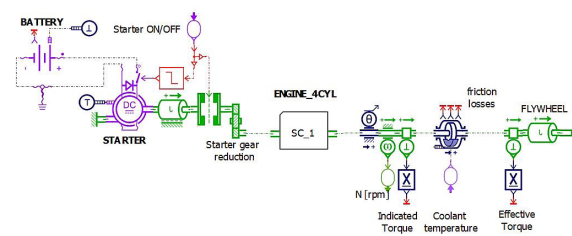


Figure 2. Engine starting model on Simcenter Amesim.

The starter system model for a 4-cylinder diesel engine is built on the Simcenter Amesim software (Figure 2). The model consists of the main blocks: battery, DC starter motor, reduction gearbox, engine crankshaft, and flywheel. The transmission process begins with the current that activates the starter motor, generating torque and transmitting it through the starter gearbox to the crankshaft. The system also integrates simulated sensors such as current measurement, rotational speed, coolant temperature, and adequate torque to accurately replicate the electrical-mechanical-thermal characteristics during the starting phase.

2.2.2. Input parameters for simulation

The model's input parameters were collected from the technical data of a Hyundai Avante CRDi vehicle using a 4-cylinder diesel engine. This data provides the foundation for the model to accurately reflect the operational characteristics and the system's actual starting process.

Table 1. Technical specifications of the engine and starter motor for the Hyundai Avante CRDi.¹⁰

Parameter	Value
ENGINE	
Piston diameter	77.2 mm
Piston stroke	84.5 mm
Compression ratio	17.3
Number of cylinders	4
Connecting rod length	143.5 mm
Engine displacement	1582 cc
STARTER MOTOR	
Motor type	DC electric motor
Rated voltage	12V
Power	1.8 kW
Minimum starting speed	≥ 150 rpm
Gear ratio	10:1
Manufacturer	Bosch

2.2.3. Simulation conditions

The model is set up for a 4-cylinder inline diesel engine with a displacement of 1.6 L. It uses a DC motor starter system and a gear reduction transmission. The power supply is a stable 12 VDC, and the simulation time is 1.6 seconds. The surrounding ambient temperature is assumed to be 30°C. At the same time, the compression pressure in the cylinders is considered uniform to simplify the calculations and focus on evaluating the system's electrical-mechanical characteristics during the starting process.

2.3. Simulation of starter motor characteristics and fault analysis on Simcenter Amesim

2.3.1. Normal operation of the starter motor

In the standard starter motor operation simulation scenario, all system parameters are set according to the manufacturer's standard values, ensuring no technical faults or performance degradation occur. In this case, the primary objective of the simulation is to test the system's ability to start reliably, while also analyzing the electrical-mechanical-thermal characteristics of the starter

motor, such as the consumption current, variation voltage, and crankshaft speed during operation.

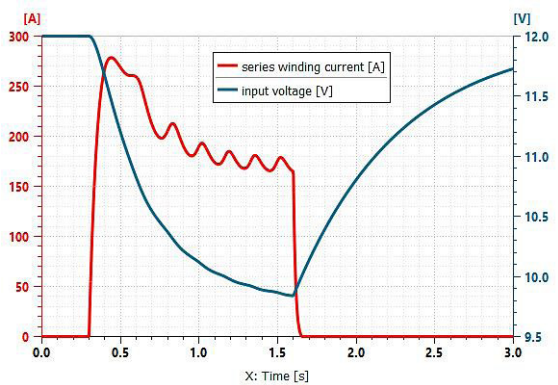


Figure 3. Variation of coil current and input voltage of the starter motor during the starting process.

The simulation results show that the initial starting current rapidly increases to a peak value of approximately 280A, then gradually decreases while the crankshaft speed increases. Simultaneously, the input voltage drops from 12V to about 10V before recovering progressively. The electromagnetic torque generated by the motor reaches a sufficient value to overcome the resisting torque due to compression and friction. This allows the crankshaft speed to get about 160–210 RPM after 1.0–1.5 seconds. This speed is sufficient for the diesel engine to begin the self-sustaining combustion.

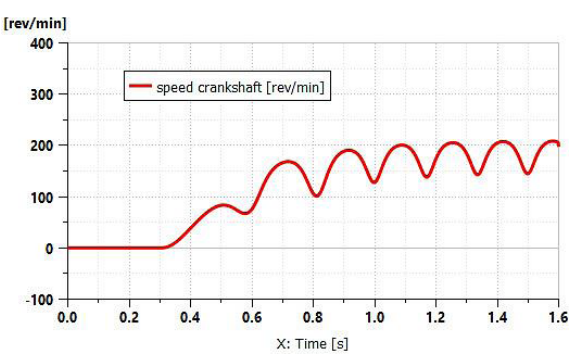


Figure 4. Crankshaft speed during normal starting conditions.

In addition, the crankshaft speed exhibits a characteristic periodic oscillation, reflecting the compression-expansion cycle in the cylinders. The obtained waveform reflects the normal starting process, with the system operating stably and no signs of abnormality.

The results from this simulation are essential in establishing the baseline for comparing and evaluating future fault scenarios.

2.3.2. Case of brush wear and inadequate contact at the commutator

One of the common faults of the starter motor is inadequate contact between the brushes and the commutator, typically arising from mechanical wear, oxidation of the commutator surface, or reduced elasticity of the brush holder. These factors increase the overall contact resistance, thereby reducing the starting current, causing voltage loss, and decreasing torque transmission efficiency to the engine crankshaft.

In this study, the phenomenon is simulated by increasing the armature resistance in the DC motor model to investigate the impact of various levels of wear on the electrical-mechanical characteristics during the starting phase.

Figure 5 shows the current variation through the starter motor winding at different simulated contact resistances. Under good contact conditions (solid line), the starting current rapidly increases to about 280 A, then gradually decreases over time, whereas the crankshaft speed increases. The engine speed reaches over 200 RPM after 1.1 seconds, sufficient for the diesel engine to start the self-sustaining combustion process. In this case, the motor's input voltage remains stable around 11.5–12 V, reflecting low voltage loss and high energy conversion efficiency.

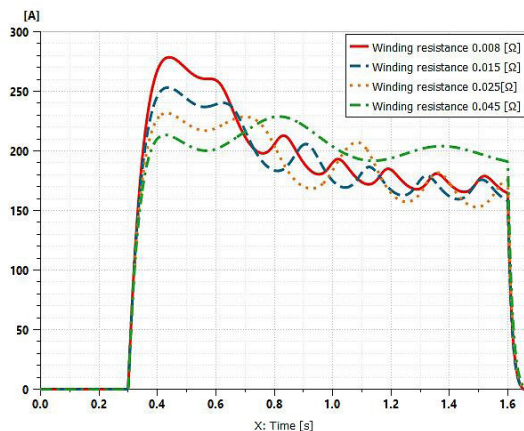


Figure 5. Variation of starting current for various contact resistances.

As the contact resistance increases (dashed line – corresponding to moderate wear or unstable contact), the starting current decreases to 150–250 A, and the crankshaft speed reaches only 150–190 RPM. The acceleration time is prolonged, and the amplitude of the speed oscillations decreases, indicating a decline in system efficiency. At the same time, the input voltage decreases slightly, fluctuating around 10–11 V.

In this case, the motor can still start the engine, but the problems such as slow starting, weak cranking, or instability during continuous cranking may occur.

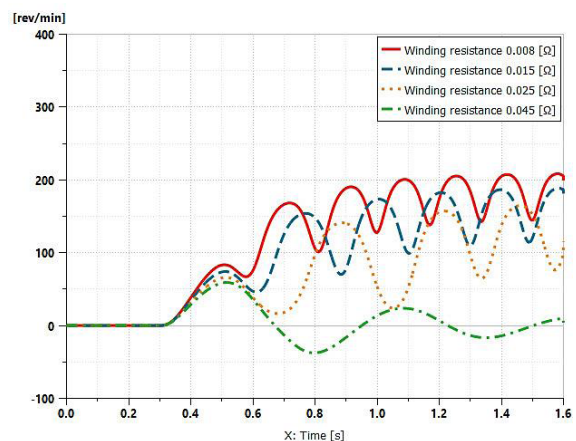


Figure 6. Variation of crankshaft speed for various contact resistances.

Notably, when the resistance reaches a high threshold (dash-dotted line – simulating heavy wear or severe damage at the commutator), the starting current decreases sharply to 130–210 A, and the crankshaft speed does not exceed 100 RPM, with a tendency for weak oscillations and occasional reverse rotation. The acceleration time is extended, but fails to reach the required threshold to maintain the compression-ignition process. In this scenario, the input voltage drops significantly to 9–10 V, indicating that electrical energy is consumed but not effectively converted into mechanical motion. The system enters a state where it cannot start, causing energy loss and serving as a warning sign for severe damage that requires maintenance intervention.

The simulation results suggest that electrical signals during the starting phase—especially a starting current below 150 A combined with a crankshaft speed not exceeding 100 RPM—can be used as early diagnostic indicators for brush wear or poor contact at the commutator. This opens the possibility of integrating early fault warning mechanisms in control systems, enabling proactive maintenance and preventing sudden failure of the starter system. Such integration not only enhances system reliability but also extends the operational lifespan of the starting components by addressing issues before they escalate.

2.3.3. Case of worn bearings, dust accumulation, dry lubrication, or seized motor shaft

In practical operation, mechanical faults such as bearing wear, dust accumulation, dried lubrication, or a seized rotating shaft can increase the resisting torque during the starting phase. These faults force the starter motor to work under greater mechanical load, significantly altering the electrical-mechanical signals, directly impacting the motor's ability to start the engine.

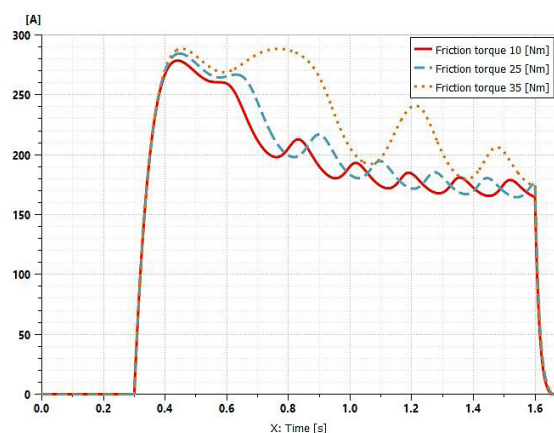


Figure 7. Variation of current for various starting friction torques.

Figure 7 shows the starting current variation at different friction torques. Under standard conditions (solid line), the current peaks at approximately 280 A and quickly decreases with time. When the resisting torque increases slightly (dashed line), the current remains high

for a more extended period (~280 A) with a larger oscillation amplitude – indicating a heavier mechanical load that forces the motor to increase its power to start. In the case of unusually high resisting torque (dotted line), the current stays at a high level continuously, without decreasing over time, indicating an overloaded operating condition that can easily lead to motor damage.

Figure 8 illustrates the variation in engine speed under the conditions mentioned above. Under standard conditions, the speed increases steadily, reaching approximately 210 RPM after about 1.1 seconds – sufficient for the diesel engine to complete the compression-ignition cycle. With light resistance, the speed only reaches about 180 RPM, with a longer acceleration time (~1.4 seconds) and stronger oscillations. In the case of unusually high resistance, the crankshaft speed fluctuates around ~120–130 RPM and experiences extreme oscillations, failing to meet the required conditions for starting.

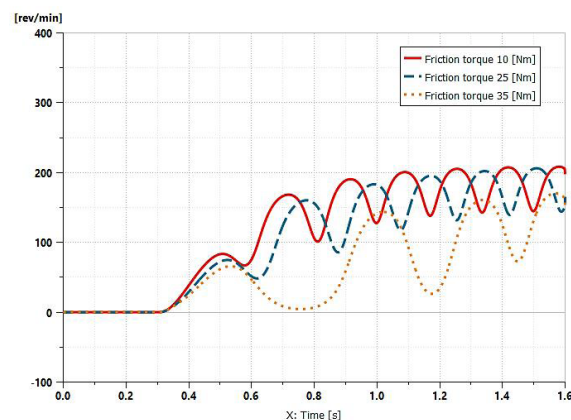


Figure 8. Engine speed for the various starting friction torques.

The results indicate that the combination of high current sustained over time and low crankshaft speed effectively indicates mechanical issues within the starter motor assembly or the starting drive system. Such symptoms can establish warning thresholds in early diagnostic systems, allowing for timely detection of signs of bearing wear, dry lubrication, or seized components before they cause severe damage or a complete loss of starting capability.

2.3.4. Effect of temperature on starting

The simulation results in Figures 9 and 10 show that the ambient temperature significantly impacts the performance and electrical-mechanical characteristics of the engine starter system. In the three conditions investigated (0°C, 30°C, 90°C), the current and crankshaft speed signals vary differently, reflecting the simultaneous change in mechanical load and electromagnetic efficiency.

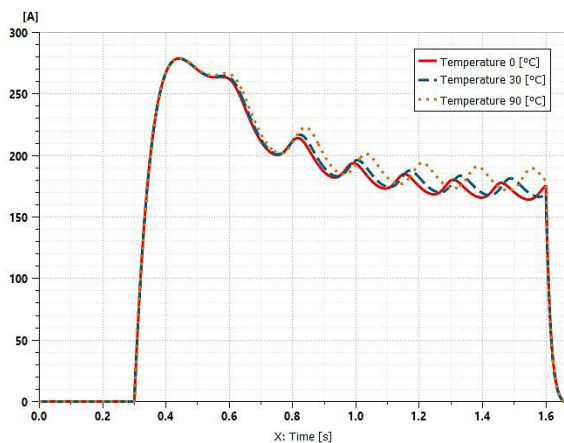


Figure 9. Variation of current for the various starting temperatures.

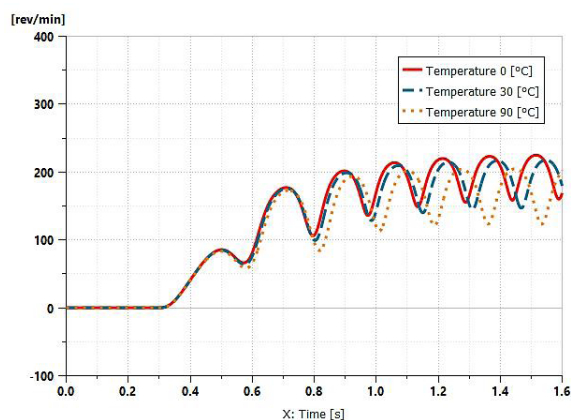


Figure 10. Engine speed for the various starting temperatures.

At 0°C, although the resisting torque increases due to thicker oil and higher friction, the engine still achieves a stable starting speed, thanks to the maintained electrical-mechanical efficiency due to the low coil resistance. In contrast, at 90°C, despite the reduced mechanical load, the increased coil resistance reduces the effective torque, leading to a lower starting speed

and stronger oscillations. The 30°C condition provides the most balanced results regarding current, speed, and oscillations, reflecting the optimal operating state of the starter system.

Figure 9 illustrates the variation of starting current over time at three different temperatures. Although the peak current is similar (~275–280 A), at higher temperatures, the current remains at a high level for longer and exhibits larger oscillations, indicating a decline in electrical-mechanical efficiency. Figure 10 clearly shows the separation of crankshaft speed at different temperatures: at 0°C, the speed reaches its highest peak, while at 90°C, the maximum speed is lower and the oscillations are stronger.

Additionally, under real operating conditions, if the engine is required to start multiple times consecutively within a short period, the temperature in the motor windings can increase rapidly. As a result, the coil resistance continuously increases, causing a decrease in output torque, even though the current remains high. This leads to a gradual reduction in rotational speed after each start, with the time to reach the required speed becoming longer and oscillations becoming stronger, which can result in a failed start if the load conditions increase or the battery weakens.

This indicates that the system is operating outside its optimal efficiency range. Therefore, it is necessary to integrate an algorithm that limits the number of consecutive start cycles or use temperature monitoring sensors to warn early about thermal overload risks and the degradation of starting efficiency.

3. CONCLUSION

The study successfully developed a simulation model of the diesel engine starting system on the Simcenter Amesim platform, accurately simulating the interaction between electrical, mechanical, and thermal factors throughout the starting cycle. The model reflects the standard operating condition and allows for the analysis of typical fault scenarios such as increased contact resistance, brush wear, increased mechanical

resistance, and the impact of ambient temperature on starting performance.

Through the simulation process, the research team identified several characteristic electrical-mechanical indicators that can be used to diagnose abnormalities in the starter system early. Specifically:

- An initial peak current exceeding the design threshold may indicate an abnormal starting load, possibly caused by mechanical jamming, increased friction, or excessive opposing torque.
- An extended cranking time beyond the standard limit reflects the potential presence of faults such as worn brushes or increased internal resistance of the winding.
- A low crankshaft speed within the first 0.5–1.0 seconds may signal degraded electrical contacts or elevated contact resistance, resulting in localized voltage drops during startup.
- Irregular current or rotational speed fluctuations throughout the starting cycle indicate electromechanical instability within the system.

Notably, the research results open up the possibility of applying existing measurement signals from the vehicle's electronic system, such as data from the ECU, current sensors, voltage sensors, and rotational speed, to develop a sensorless diagnostic solution for the starter system. This approach enables monitoring the operational status and early detection of performance degradation in the starter system through parameters already recorded by the vehicle's electronic system during operation.

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Nghiên cứu phân tán vật liệu $\text{SiO}_2/\text{g-C}_3\text{N}_4$ trên nền polyvinylidene fluoride và hoạt tính quang xúc tác phân hủy dung dịch RhB trong môi trường nước

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TÓM TẮT

Vật liệu $\text{SiO}_2/\text{g-C}_3\text{N}_4$ được phân tán lên màng polyvinylidene fluoride (PVDF) bằng phương pháp đảo pha thu được màng quang xúc tác phân hủy chất màu hữu cơ rhodamine B (RhB) trong môi trường nước dưới vùng ánh sáng khả kiến. Hình thái, cấu trúc và hoạt tính quang xúc tác của các vật liệu đơn và composite phân tán lên màng PVDF được đánh giá. Với vật liệu composite $\text{SiO}_2/\text{g-C}_3\text{N}_4$ có tính chất xốp hơn, có nhiều vị trí khuyết tật hơn so với các vật liệu SiO_2 hay $\text{g-C}_3\text{N}_4$ đơn chất khi phân tán lên màng làm cải thiện đáng kể hiệu quả quang xúc tác của vật liệu. Cụ thể, hiệu suất phân hủy RhB khỏi màng composite $\text{SiO}_2/\text{g-C}_3\text{N}_4/\text{PVDF}$ dưới tác động của ánh sáng khả kiến đạt 81,35% vượt trội hơn so với $\text{g-C}_3\text{N}_4/\text{PVDF}$ (46,07%) và SiO_2/PVDF (14,79%). Do đó, nghiên cứu này được kỳ vọng sẽ mở rộng triển vọng trong lĩnh vực công nghệ lọc màng.

Từ khóa: SiO_2 , $\text{g-C}_3\text{N}_4$, $\text{SiO}_2/\text{g-C}_3\text{N}_4$, PVDF.

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Study on dispersion of $\text{SiO}_2/\text{g-C}_3\text{N}_4$ on polyvinylidene fluoride substrate and photocatalytic activity in decomposing RhB solution in aqueous environment

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ABSTRACT

$\text{SiO}_2/\text{g-C}_3\text{N}_4$ material was dispersed onto polyvinylidene fluoride (PVDF) membrane by the phase inversion method to obtain a photocatalytic membrane for decomposing organic dye rhodamine B (RhB) in aqueous medium under visible light. The morphology, structure, and photocatalytic activity of single and composite materials deposited on PVDF membranes were evaluated. With $\text{SiO}_2/\text{g-C}_3\text{N}_4$ composite material having more porous properties and more defect locations than single SiO_2 or $\text{g-C}_3\text{N}_4$ materials when dispersed onto the membrane, the photocatalytic efficiency of the material is significantly improved. Specifically, the degradation efficiency of RhB from $\text{SiO}_2/\text{g-C}_3\text{N}_4/\text{PVDF}$ composite membrane under the influence of visible light reached 81.35%, which was superior to $\text{g-C}_3\text{N}_4/\text{PVDF}$ (46.07%) and SiO_2/PVDF (14.79%). Therefore, this study is expected to expand the prospects in the field of membrane filtration technology.

Keywords: SiO_2 , $\text{g-C}_3\text{N}_4$, $\text{SiO}_2/\text{g-C}_3\text{N}_4$, PVDF.

1. INTRODUCTION

Water pollution by persistent organic compounds – dyes, pesticides, and pharmaceutical residues – is becoming one of the most serious environmental challenges today. These compounds are often highly toxic, difficult to biodegrade, and accumulate in the environment for long, requiring effective and eco-friendly treatment methods.¹ Among modern treatment technologies, heterogeneous photocatalysis under visible light is a promising method due to its ability to completely decompose organic pollutants into non-toxic products such as CO_2 and H_2O without leaving secondary residues.^{2,3} In the field of photocatalytic materials, graphitic

carbon nitride ($\text{g-C}_3\text{N}_4$) is considered a potential candidate due to its narrow band gap (~2.7 eV), good visible light absorption, high chemical stability, and simple synthesis from precursors such as melamine or urea.⁴ However, $\text{g-C}_3\text{N}_4$ has limitations, typically low surface area, poor adsorption capacity, and a fast recombination rate of electron pairs.⁵ To improve the catalytic efficiency, forming composite materials between $\text{g-C}_3\text{N}_4$ and supporting materials is considered an effective strategy. Silicon dioxide (SiO_2) – a potential semi-doped material with a porous structure, large surface area, and high stability – not only enhances the dispersion of $\text{g-C}_3\text{N}_4$ but also improves the charge transfer process in

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the photocatalytic reaction.^{6,7} Similar to SiO_2 , several approaches have been taken to improve the photocatalytic activity of $\text{g-C}_3\text{N}_4$, including incorporating dopants and coupling with other semiconductors. Extensive efforts have been devoted to improving the photocatalytic activity of $\text{g-C}_3\text{N}_4$, and numerous novel $\text{g-C}_3\text{N}_4$ -based photocatalysts have been reported, such as $\text{ZnO/g-C}_3\text{N}_4$,⁸ $\text{SmVO}_4/\text{g-C}_3\text{N}_4$ and $\text{TaON/g-C}_3\text{N}_4$.⁹⁻¹¹ These photocatalysts were mainly developed based on the coupling effect. In addition, metal or non-metal element doping is typically used to improve the photoactivity of $\text{g-C}_3\text{N}_4$ (such as $\text{g-C}_3\text{N}_4$ and $\text{Fe-g-C}_3\text{N}_4$),^{12,13} which is based on energy band engineering. The hybridization of SiO_2 and $\text{g-C}_3\text{N}_4$ achieves a synergistic effect to overcome the major disadvantages of each material and create composite materials with good photocatalytic activity. In treating polluted water, the direct use of catalysts has the advantage of very high photocatalytic activity. However, these materials are still in powder form. Hence, they are challenging to recycle after the photocatalytic process.^{14,15} This causes significant waste of photocatalysts but also causes secondary pollution to the environment. Therefore, finding solutions to the problem of material recovery is of interest to researchers. Several methods for recovering inorganic photocatalysts have been reported, such as adding magnetic materials, forming rigid, recyclable, and flexible thin film materials, and loading them onto organic polymer materials.^{16,17} The major drawback of immobilizing the catalyst materials onto the substrate is the reduction of the active site, and the durability of the catalyst materials with the substrate is also of great concern. Poly (vinylidene fluoride) (PVDF) is a fluoropolymer with good chemical stability, good mechanical properties, and easy to process into films, which is very suitable as a substrate for membrane-based photocatalyst systems, which helps to improve the applicability and reusability.¹⁸ In this study, $\text{SiO}_2/\text{g-C}_3\text{N}_4$ composite materials loaded onto PVDF were synthesized by a simple phase inversion method.

This study focused on the synthesis, chemical characterization, and evaluation of the treatment performance of $\text{SiO}_2/\text{g-C}_3\text{N}_4/\text{PVDF}$ materials for typical organic compounds in wastewater such as RhB, enhancing the photocatalytic activity under visible light, and improving the stability and recovery of materials after treatment.

2. EXPERIMENTAL METHODS

2.1. Chemicals

All chemicals used for material synthesis include urea ($(\text{NH}_2)_2\text{CO}$), TEOS (Tetraethyl orthosilicate) ($\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$), CTAB (Hexadecyl trimethyl ammonium bromide), ($[(\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3]\text{Br}$), polyvinylidene fluoride (PVDF), N-Methy-2-pyrrolidone (NMP) 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 $\text{g-C}_3\text{N}_4$ material

$\text{g-C}_3\text{N}_4$ material was prepared by a simple method using urea as raw material. The first, 10 grams of finely ground urea then transferred into alumina crucible, sealed with aluminum foil and calcined at 550°C for 1 hour. The solid obtained was pale yellow, washed with distilled water and ethanol, then dried at 80°C for 12 hours. The product is finely ground and marked $\text{g-C}_3\text{N}_4$.

2.2.2. Synthesis of SiO_2 material

SiO_2 material is synthesized according to the following process: Add 0.16 g of hexadecyl trimethyl ammonium bromide (CTAB) to 50 mL of distilled water, then slowly add 15 mL of ethanol and 1 mL of solution. Stir for 0.5 hour, slowly add 1 mL tetraethyl orthosilicate (TEOS) dropwise into the solution, and stir for 24 hours. The obtained product was washed with deionized water and ethanol three times, dried for 24 h at 60°C , and denoted SiO_2 .

2.2.3. Synthesis of $\text{SiO}_2/\text{g-C}_3\text{N}_4$ composite material

Samples were prepared by a simple method using SiO_2 powder and urea as precursors. First, a mixture of 0.1g SiO_2 and 3g urea into an agate

mortar and grind finely. Then, the as-prepared mixtures were then transferred into an alumina crucible, sealed with aluminum foil, and heat it in an inert Ar gas environment at 550 °C for 1 hour. Cool to room temperature, grind and wash the sample with distilled water until neutral. The solid was dried at 80 °C for 12 hours and denoted as $\text{SiO}_2/\text{g-C}_3\text{N}_4$.

2.2.4. Synthesis of $\text{SiO}_2/\text{g-C}_3\text{N}_4/\text{PVDF}$ material

$\text{SiO}_2/\text{g-C}_3\text{N}_4/\text{PVDF}$ material was prepared using the following procedure. Firstly, put 0.1g of $\text{SiO}_2/\text{g-C}_3\text{N}_4$ material into a glass jar with a lid, add 5 mL of NMP solution, and sonicate for 10 minutes. Then stir well on a magnetic stirrer for 30 minutes. Continue ultrasonic vibration for another 20 minutes and stir evenly on a magnetic stirrer for 20 minutes. Continue ultrasonic vibration for another 20 minutes and stir evenly on a magnetic stirrer for 20 minutes. Then let the mixture sit for 3 hours. Using a stainless steel scraper (250 μm x 15 cm), roll the mixture evenly onto the glass to form a composite film, quickly put the glass with the film into water to perform the phase reversal process, and the material is denoted as $\text{SiO}_2/\text{g-C}_3\text{N}_4/\text{PVDF}$.

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 containing 0.1 g of the photocatalyst were added to 100 mL

of RhB solution with a concentration of 10 mg/L and stirred in the dark for 60 minutes to achieve adsorption-desorption equilibrium. The photocatalytic process was then initiated under a 40W LED light. Every 30 minutes, 7 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

The crystal structures and phase compositions of the synthesized SiO_2 , $\text{g-C}_3\text{N}_4$, $\text{SiO}_2/\text{g-C}_3\text{N}_4$ powders, and PVDF, SiO_2/PVDF , $\text{g-C}_3\text{N}_4/\text{PVDF}$, and $\text{SiO}_2/\text{g-C}_3\text{N}_4/\text{PVDF}$ films are shown in Figure 1.

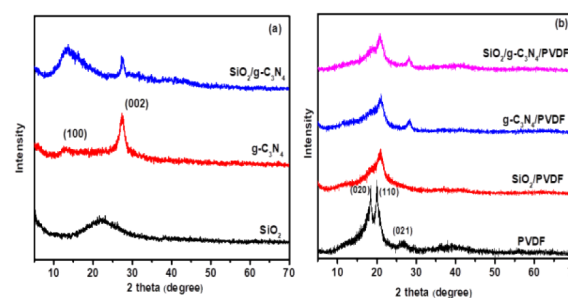


Figure 1. (a) XRD patterns of SiO_2 , $\text{g-C}_3\text{N}_4$, $\text{SiO}_2/\text{g-C}_3\text{N}_4$ and (b) PVDF, SiO_2/PVDF , $\text{g-C}_3\text{N}_4/\text{PVDF}$ and $\text{SiO}_2/\text{g-C}_3\text{N}_4/\text{PVDF}$.

Figure 1a shows that the SiO_2 material exhibits a broad peak at $2\theta \approx 23^\circ$ corresponding to the amorphous nature of SiO_2 .¹⁹ $\text{g-C}_3\text{N}_4$ shows typical diffraction peaks corresponding to the (002) and (100) planes of $\text{g-C}_3\text{N}_4$.²⁰ Specifically, the peak at $2\theta = 13.5^\circ$ can be attributed to the in-plane structural stacking motif in the tri-s-triazine (s-heptazine)-based structure of $\text{g-C}_3\text{N}_4$, while the strong diffraction peak located at $2\theta = 27.6^\circ$ is a result of the inter-plane stacking of the conjugated aromatic units of $\text{g-C}_3\text{N}_4$.²¹ XRD results of $\text{SiO}_2/\text{g-C}_3\text{N}_4$ composite material fully show the characteristic peaks of both $\text{g-C}_3\text{N}_4$ and SiO_2 . The SiO_2 peak at 23° is not clearly shown in the composite sample, possibly due to the amorphous SiO_2 structure and the

stacking of $g\text{-C}_3\text{N}_4$. Thus, the SiO_2 added to the $g\text{-C}_3\text{N}_4$ substrate does not change the crystal structure. The results in Figure 1b show that PVDF has 3 characteristic peaks at 18.5° , 20.1° , 26.7° corresponding to the planes (020), (110), (021). When dispersing $g\text{-C}_3\text{N}_4$, SiO_2 , $\text{SiO}_2/g\text{-C}_3\text{N}_4$ onto PVDF polymer matrix, the PVDF peaks still appear at almost the same position but the intensity is reduced. For the $g\text{-C}_3\text{N}_4/\text{PVDF}$ sample, a characteristic strong peak at 27.6° and a weak peak at 13.5° corresponding to the (002) and (100) reflection planes of graphite-structured materials appear.²²

Figure 2 shows the FT-IR spectrum of the synthesized material samples, demonstrating no change in the PVDF polymer structure.

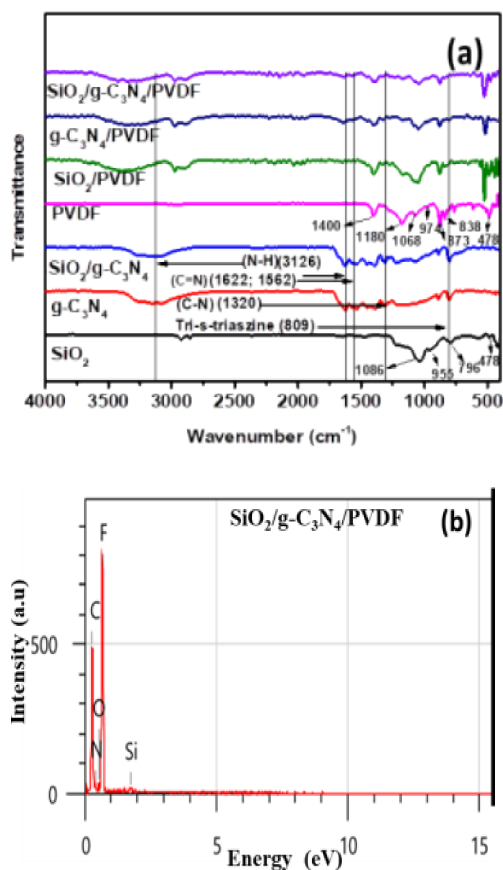


Figure 2. (a) FT-IR spectra of SiO_2 , $g\text{-C}_3\text{N}_4$, $\text{SiO}_2/g\text{-C}_3\text{N}_4$, PVDF, SiO_2/PVDF , $g\text{-C}_3\text{N}_4/\text{PVDF}$, $\text{SiO}_2/g\text{-C}_3\text{N}_4/\text{PVDF}$, and (b) EDX spectra of $\text{SiO}_2/g\text{-C}_3\text{N}_4/\text{PVDF}$.

The FT-IR spectrum of pure PVDF shows the combination of α and β phases. The

characteristic absorption bands for the α form are 1180 and 974 cm^{-1} , and for the β form are 1400, 1068, 873, and 838 cm^{-1} . The absorption bands at 1400, 873 cm^{-1} represent the valence vibration of the C-F bond, at 1180 and 487 cm^{-1} represent the C-C bond and the bending vibration of CF_2 . These absorption bands are present in all FT-IR spectra of the material films without any structural changes, which may be caused by chemical bonding. Furthermore, the FT-IR spectra of SiO_2/PVDF and $g\text{-C}_3\text{N}_4/\text{PVDF}$ materials showed characteristic absorption bands for $g\text{-C}_3\text{N}_4$ and SiO_2 . Typical absorption bands for $g\text{-C}_3\text{N}_4$ are located at 3126 cm^{-1} corresponding to N-H groups, at 1622 and 1562 cm^{-1} belonging to C=N bonds, at 1320 cm^{-1} corresponding to C-H bonds, and the absorption band at 809 cm^{-1} corresponding to tri-s-triazine units.²³

In the IR spectrum of SiO_2 , strong absorption bands appear at wave numbers 1086, 955, and 796 cm^{-1} corresponding to the bonds of Si-O-Si, the deformation vibration of Si-OH, and the symmetric valence vibration of the Si-O bond. The peak observed at 478 cm^{-1} in the composite film material is related to the Si-O-Si stretching vibration of SiO_2 .²⁴

SEM images show a clear difference in the distribution of materials on the polymer membrane. PVDF material (Figure 3a) has a reasonably smooth surface with a uniform surface structure and is applied as a good substrate membrane. Figure 3b shows that the SiO_2 particles are relatively uniformly distributed in the PVDF matrix. The surface of the material becomes more porous and increases the surface area. The $g\text{-C}_3\text{N}_4$ material is in sheet form, so when dispersed on the PVDF substrate (Figure 3c), it creates density heterogeneity, large particle clusters, uneven structure, and increases the material's porosity. The combination of SiO_2 and $g\text{-C}_3\text{N}_4$ (Figure 3d) shows a significantly more porous surface, showing dispersed phases and many defect sites. This improves the photocatalytic properties, mechanical strength, and membrane permeability.

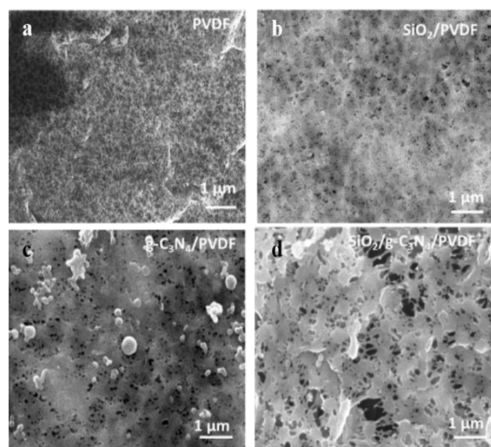


Figure 3. SEM images of PVDF (a), SiO₂/PVDF (b), g-C₃N₄/PVDF (c), SiO₂/g-C₃N₄/PVDF (d).

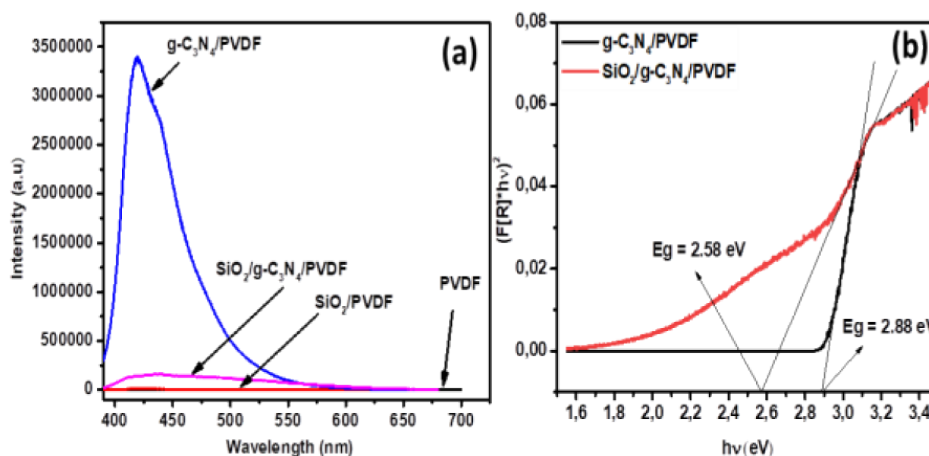


Figure 4. (a) PL spectra of g-C₃N₄/PVDF, SiO₂/PVDF, PVDF, SiO₂/g-C₃N₄/PVDF (a) and (b) Band gap energy of g-C₃N₄/PVDF, SiO₂/g-C₃N₄/PVDF.

For PVDF, no PL intensity was observed over the entire spectral range. The g-C₃N₄ particles dispersed on the PVDF membrane have a maximum intensity corresponding to a wavelength of 419 nm, where the molecules with amino groups, such as g-C₃N₄, the nucleophile attack of the amino group on the carbon atom will lead to the nucleophile substitution of fluorine to form a covalent bond between PVDF and g-C₃N₄. The observed PL intensity of g-C₃N₄ is higher, which indicates a faster recombination rate between photogenerated electrons and holes. As for the PL spectrum of SiO₂/PVDF, the emission intensity is very low, almost equivalent to the PL spectrum of PVDF. This is explained by the fact that SiO₂ has a significant band gap energy and poor

Energy dispersive X-ray (EDX) spectrum was characterized for the SiO₂/g-C₃N₄/PVDF composite sample (Figure 2b). The results from EDX images show the full presence of elements F, C, O, Si, and N in the sample, proving the successful synthesis of the material.

PL spectra of the materials were performed with an excitation wavelength of 390 nm at room temperature to study the photogenerated electron-hole recombination, and solid UV-Vis spectra determined the band gap energy of the materials, as shown in Figure 4.

photocatalytic activity in the visible light region. On the other hand, the PL spectrum of the SiO₂/g-C₃N₄/PVDF composite material has a reduced fluorescence emission intensity compared to g-C₃N₄/PVDF (Figure 4a) and the band gap energy of the SiO₂/g-C₃N₄/PVDF material (Eg = 2.58 eV) is lower than that of g-C₃N₄/PVDF (Eg = 2.88 eV) (Figure 4b). Therefore, when there is radiation, electrons move from g-C₃N₄ to the conduction band of SiO₂ and then quickly move to the catalyst's surface to perform a reduction reaction with oxygen molecules, limiting the ability to recombine.

3.2. Photocatalytic performance

The results of the photocatalytic evaluation for PVDF, g-C₃N₄/PVDF, and C/g-C₃N₄/PVDF are shown in Figure 5.

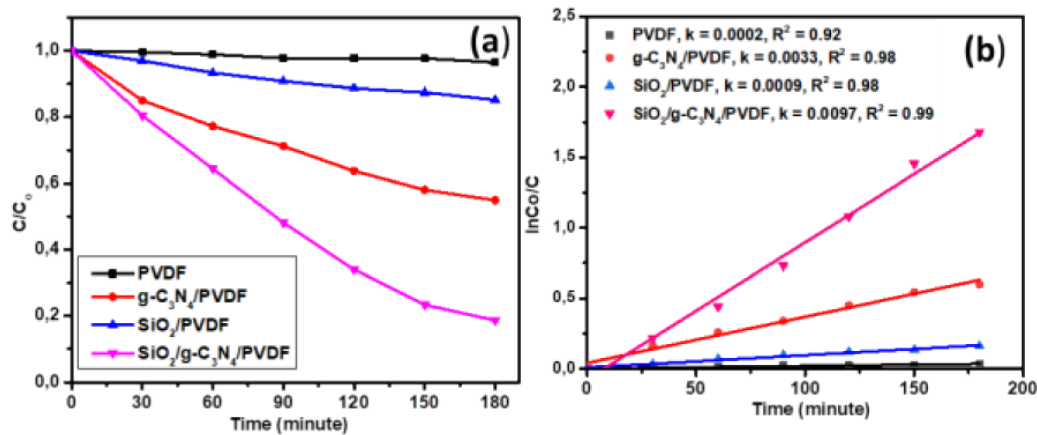


Figure 5. (a) RhB decomposition and (b) pseudo-first-order kinetic model under visible light of g-PVDF, C_3N_4 /PVDF, $SiO_2/g-C_3N_4$, and $SiO_2/g-C_3N_4/PVDF$.

The graph shows that after 180 minutes of illumination under a 40W LED lamp, the decomposition efficiency of RhB solution of $SiO_2/g-C_3N_4/PVDF$ sample is the highest at 81.35%, the materials $g-C_3N_4/PVDF$, $SiO_2/PVDF$ have decomposition efficiency of 46.07% and 14.79% respectively. This may be because the band gap energy of the $SiO_2/g-C_3N_4/PVDF$ material (2.58 eV) is lower than the band gap energy of the $g-C_3N_4$ material (2.88 eV), which makes the ability to separate and move photogenerated electrons and holes to the material surface to perform reactions faster, limiting the ability to recombine between charge carriers. $SiO_2/PVDF$ material works well in the ultraviolet region, which is understandable because the photocatalytic efficiency in the visible light region is only 14.79%. The PVDF membrane alone did not show photocatalytic activity, indicating that the photocatalytic activity was due to the composite material; the single dispersed materials were exhibited. The kinetic model of RhB degradation of $SiO_2/g-C_3N_4/PVDF$ material has a rate constant of 0.0097 (min⁻¹) which is much larger than that of $C_3N_4/PVDF$ and $SiO_2/PVDF$ materials (0.0033 and 0.0009 min⁻¹) (Figure 5b). A comparison of the rate constant of the present work with the previous works is listed in Table S1. However, the comparison is lame because the reaction

conditions are not the same. However, Table S1 shows that the rate constant of $SiO_2/g-C_3N_4/PVDF$ is relatively high compared to previous studies. This result confirms the potential application of $SiO_2/g-C_3N_4/PVDF$ material in the treatment of organic pollutants under visible light in aquatic environments.

4. CONCLUSION

In this study, PVDF composite films modified with SiO_2 and $g-C_3N_4$ were successfully synthesized. XRD and FT-IR results showed that the incorporation of fillers did not change PVDF's crystal structure and polymer framework. The surface morphology is significantly improved with the appearance of a porous structure and a uniformly dispersed phase. PL spectrum and band gap analysis showed that the $SiO_2/g-C_3N_4/PVDF$ sample can inhibit e^-/h^+ recombination, and the band gap is suitable for visible light absorption. Photocatalytic testing showed that the $SiO_2/g-C_3N_4/PVDF$ sample had the highest RhB degradation efficiency (81.35%), confirming its potential application in organic pollution treatment under visible light.

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Đặc điểm thích nghi về cơ quan sinh dưỡng của một số loài thực vật ven sông sống chủ yếu tại khu vực hạ lưu sông Côn, xã Phước Hòa, huyện Tuy Phước, tỉnh Bình Định

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TÓM TẮT

Hệ thực vật ven sông hạ lưu sông Côn có vai trò rất lớn trong việc điều hòa khí hậu, giữ đất, phòng hộ trong mùa mưa bão và đóng góp vào môi trường sống của các loài thủy sản. Nghiên cứu được tiến hành trên 4 loài thực vật, gồm thân cỏ và thân bụi nhỏ thuộc ngành Ngọc Lan (Magnoliophyta). Các phương pháp hình thái so sánh, vi phẫu, nhuộm kép, đo mẫu và chụp ảnh hiển vi rỗ, thân và lá cây được thực hiện để xác định các đặc điểm thích nghi về cơ quan sinh dưỡng của các đối tượng nghiên cứu. Kết quả nghiên cứu cho thấy, các loài thực vật tại khu vực nghiên cứu thích nghi với điều kiện ánh sáng mạnh: biểu bì lá phân bố nhiều lông che chở và mô giậu phát triển (chiếm đến 56,22% độ dày phiến lá). Mô khuyết phát triển mạnh, có nhiều khoang trống lớn trong rỗ và thân (chiếm đến 63,49% bán kính rỗ), số lượng mạch gỗ ít và đường kính mạch lớn ($25,00 \pm 4,00$ mạch/mm² và đường kính mạch $109,92 \pm 13,15$ μ m ở rỗ thứ cấp, $5,33 \pm 0,33$ mạch/mm² và đường kính mạch $114,83 \pm 20,08$ μ m ở thân sơ cấp) giúp cây thích nghi với điều kiện thiếu oxy và ngập nước trong mùa mưa. Mô cứng bao quanh các bó mạch ở rỗ, tạo thành dải bao quanh thân, rải rác tinh thể oxalate calcium và tế bào đá trong mô mềm thịt lá giúp các đối tượng nghiên cứu chịu được các tác động cơ học (gió, bão).

Từ khóa: Giải phẫu, hình thái, sông Côn, thích nghi, thực vật ven sông.

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Adaptive features of the vegetative organs of some common riparian plants in the lower Con river, Phuoc Hoa commune, Tuy Phuoc district, Binh Dinh province

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ABSTRACT

The riparian vegetation along the lower Con river plays a crucial role in regulating the microclimate, stabilizing soil, providing protection during the rainy and stormy season, and contributing to the aquatic ecosystem. This study was carried out on four herbaceous and undershrub species in Magnoliophyta. Morphological comparison, microsurgery, double-staining, microscopic measurements and imaging of roots, stems, and leaves were applied to identify adaptive features in the vegetative organs of the studied species. The results revealed that the plant species in the study area are adapted to high light conditions, as evidenced by the abundance of trichomes on the leaf epidermis and the well-developed palisade mesophyll (accounting for up to 56.22% of leaf thickness). Aerenchyma tissues were strongly developed, forming large air cavities in both roots and stems (up to 63.49% of root radius). These species also exhibited a low number of xylem vessels with large vessel diameters (25.00 ± 4.00 vessels/mm² and 109.92 ± 13.15 μm in secondary roots; 5.33 ± 0.33 vessels/mm² and 114.83 ± 20.08 μm in primary stems), facilitating adaptation to hypoxic and waterlogged conditions during the rainy season. The presence of sclerenchyma surrounding vascular bundles in roots and stems, scattered distribution of calcium oxalate crystals and sclereids in the leaf mesophyll support the species' tolerance to mechanical stress, such as wind and storms.

Keywords: *Anatomy, morphology, Con river, adaptation, riparian vegetation.*

1. INTRODUCTION

The Con river is the largest river in Binh Dinh province, originating from the eastern mountainous region of the Truong Son range, at an elevation of over 1000 meters. In its upper course, the river flows in a northwest-southeast direction; upon reaching Vinh Son, it shifts to a north-south orientation, and at Binh Thanh, it turns west-east before emptying into the Thi Nai lagoon. At Binh Thanh, the Con river bifurcates into two main distributaries: the

Tan An and Dap Da rivers. The Tan An river subsequently discharges into the Go Boi – Tan An estuary, representing the lower course of the Con river. The ecosystem in this area is highly diverse and is characteristic of riparian ecosystems within the province, with vegetation exhibiting numerous adaptive traits to the local environmental conditions. In addition to its crucial role in climate regulation, participation in essential biological processes, water provision, and serving as a vital habitat for aquatic species, the riparian ecosystem also contributes to

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soil retention and provides natural protection during the rainy and storm seasons.¹ Despite its significant ecological importance, this area has yet to receive adequate research attention and conservation efforts. The vegetation in the study area is primarily composed of shrub and herbaceous plant species. However, the number of species has been severely declining due to the construction of irrigation and civil infrastructure by local communities along the river basin. Given the urgent need to protect the downstream ecosystem of the Con river, it is essential to study the common adaptive characteristics of riparian plant species to establish a scientific basis for proposing effective restoration measures and promoting the sustainable development of the riparian ecosystem in this region.

2. SUBJECTS AND METHODS

2.1. Subjects

The research subjects include four common plant species found in the lower Con river, Binh Dinh province: *Ludwigia octovalvis* (Jacq.) Raven - Onagraceae and *Celosia argentea* L. - Amaranthaceae, both belonging to Eudicots; *Melinis repens* (Willd.) Zizka – Poaceae and *Commelina longifolia* Lam. - Commelinaceae, both belonging to Monocots.

2.2. Methods

2.2.1. Field study methods

The vegetative organs (roots, stems, and leaves) of the studied plant species were observed, described, and measured for morphological characteristics, root length, stem height, and leaf area, and were photographed under natural conditions. Subsequently, the vegetative organs were collected following the botanical survey method,² stored in plastic bags, and transported to the laboratory for preservation and further analysis.

2.2.2. Laboratory study methods

Sample sectioning and double staining method

After collection, the samples were rinsed with water, then fixed and preserved in a FAA

solution comprising ethyl alcohol 96%, acetic acid 40%, formalin, and distilled water.³ Samples were sectioned thinly with a razor blade, subjected to double staining, and prepared as temporary slides. The double-staining technique distinguishes cells with cellulose walls (stained red by carmine) and cells with lignified walls (stained blue by methylene blue).⁴ This method helps identify the presence and distribution of tissue types that enable plant adaptation to specific ecological factors.

Microscopy method

Samples were observed and photographed under a Kruss MBL 2000-T microscope (Germany). Staining allowed identification of lignified cell groups (fibers and sclereids), and collenchyma with cellulose walls which provide mechanical support for plant bodies;⁵ xylem vessels and tracheids also possess lignified secondary walls (stained blue), and the dense distribution of these conductive elements facilitates plant adaptation to drought conditions; the presence of aerenchyma with cellulose-based cell walls (stained red) enables plants to adapt to environments with oxygen deficiency.³

Sampling and Data Processing Methods

For each study species, six mature individuals were collected simultaneously to ensure that the observed samples shared similar size, morphology, and structure at the same developmental stage. Measurements of each vegetative trait were repeated six times across the six individuals of the same species ($n = 6$) to calculate the mean value ($\bar{X}$) and standard deviation (S) for each parameter.

The dimensions of structural components in roots, stems, and leaves were measured using the measurement tools integrated into the Microscope Manager software. The comparative proportions of these components are related to plant adaptation to environmental conditions. Adaptations to intense light and high temperatures are reflected in the well-developed palisade tissue in leaf blades, the presence of dense trichomes, and protective cutin layers,

while adaptation to oxygen-deficient conditions is indicated by the abundant occurrence of aerenchymatous tissue.³

Measurement data were statistically processed using Microsoft Excel 2016 to determine:

$$\text{Mean value: } \bar{X} = \frac{\sum_{i=1}^n x_i}{n} \quad (n = 6)$$

$$\text{Standard deviation: } S = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{X})^2}{n-1}} \quad (n < 30)$$

Comparative morphology method

Plant classification was based on morphological characteristics, especially those of reproductive organs, which are less affected by environmental changes compared to vegetative organs.⁶

Scientific identification method

Specimen identification was carried out using the references of Pham and Nguyen.^{7,8}

3. RESULTS AND DISCUSSION

3.1. Morphological adaptations

3.1.1. Roots

Melinis repens (Willd.) Zizka and *Commelina*

longifolia Lam. possess fibrous root systems that exhibit extensive growth, enabling them to effectively compete for water and mineral nutrients with other species by spreading horizontally.⁹ In contrast, *Ludwigia octovalvis* (Jacq.) Raven and *Celosia argentea* L. develop prominent taproot systems (Figure 2). Additionally, the nodes of *C. longifolia* and *L. octovalvis*, particularly along the creeping stems, produce adventitious roots that anchor the plant to the ground and facilitate horizontal expansion, thereby enhancing resistance to mechanical forces such as wind and flooding. Root diameters for *M. repens*, *C. longifolia*, *L. octovalvis*, and *C. argentea* were recorded as 1.72–1.78 mm, 1.84–1.87 mm, 4.28–4.34 mm, and 7.65–7.69 mm, respectively.

3.1.2. Stems

M. repens and *C. argentea* possess erect stems, with heights ranging from 77–105 cm and 90–110 cm, respectively. The height of *M. repens* in the present study area is lower than that reported by Corrales-Lerma et al. in Chihuahua, Mexico, likely due to different environmental conditions.¹⁰



Figure 1. Growth forms of the investigated plant species.

a. *Celosia argentea* L., b. *Ludwigia octovalvis* (Jacq.) Raven, c. *Melinis repens* (Willd.) Zizka, d. *Commelina longifolia* Lam.



Figure 2. Morphological characteristics of the investigated plant species.

a. *Celosia argentea*, b. and c. *Ludwigia octovalvis*, d. *Melinis repens*, e. *Commelina longifolia*

L. octovalvis exhibits a mostly erect stem or partially horizontal growth habit, whereas *C. longifolia* features a creeping stem morphology, with recorded heights of 90–130 cm and 22–61 cm, respectively (Figure 1). Most study species grow in dense clumps, with notable stem branching observed in *L. octovalvis*. These morphological characteristics are considered adaptive features that mitigate mechanical stress from environmental factors, such as strong winds and flood-induced water flow.¹¹ Secondary stems of *L. octovalvis* develop cork layers with longitudinal grooves, enhancing gas exchange during inundation seasons and high river water levels.⁵

3.1.3. Leaves

All investigated species exhibit small, elongated leaf blades, an adaptation believed to reduce wind impact during storms.¹² Leaf blade surface areas were recorded as follows: 6.72–11.55 cm² (*C. longifolia*), 9–15.68 cm² (*M. repens*), 7.8–16.8 cm² (*C. argentea*), and 7.82–14.4 cm² (*L. octovalvis*). The leaf area of *C. longifolia* is smaller than that reported by Tran *et al.* in Long An Province (16–30 cm²),¹¹ potentially due to more favorable climatic conditions and reduced storm frequency in that region, which may allow for better growth and larger leaf size.

Leaf thickness values were as follows: 348.37 ± 41.64 μm (*C. longifolia*), 233.27 ± 27.69 μm (*M. repens*), 392.37 ± 75.26 μm (*C. argentea*), and 244.10 ± 18.73 μm (*L. octovalvis*). The outer epidermal surfaces of all species, except *C. argentea*, are covered with protective trichomes, most abundant in *L. octovalvis*, which function to protect leaf tissue from heat stress and reduce water loss through stomatal transpiration.¹³

3.2. Adaptive anatomical characteristics

3.2.1. Roots

The roots of *M. repens* and *C. longifolia* exhibit a primary anatomical structure comprising four main components: epidermis, cortex, stele, and pith. The epidermis consists of 1–2 cell layers, with large cells accounting for 5.98% and 5.11% of the root radius in *M. repens* and *C. longifolia*, respectively (Table 1). The cortex in both species features well-developed aerenchyma (Figure 3), forming numerous large intercellular spaces that account for 63.49% and 62.49% of root radius in *M. repens* and *C. longifolia*, respectively. In *M. repens*, aerenchyma cells are radially arranged from the stele to the epidermis, while in *C. longifolia*, they are uniformly distributed, forming rhomboid-shaped spaces. These air spaces function in gas storage and facilitate

gas exchange under low-oxygen environmental conditions.¹³ In *C. longifolia*, 2–3 layers of lignified cells encircle the cortex region, and the stele in both species is reinforced with multiple layers of sclerenchyma surrounding the xylem vessels, enhancing the mechanical strength of the roots.⁵

The secondary roots of *C. argentea* and *L. octovalvis* consist primary components: bark and secondary xylem. Secondary xylem is dominant, comprising 83.88% and 75.15% of the root radius in *C. argentea* and *L. octovalvis*, respectively (Table 2). In *C. argentea*, secondary xylem is clustered and embedded within parenchyma tissue (Figure 4), similar to findings by Rajput on the genus *Celosia*.¹⁴ In *L. octovalvis*, well-developed xylem rays facilitate radial transport.¹² According to the

study by Bedoya and Madriñán on the genus *Ludwigia*, in mature plants, aerenchyma tissue is extensively developed from the phellogen.¹⁵

The xylem vessel density per mm² in the roots of *M. repens*, *C. longifolia*, *C. argentea*, and *L. octovalvis* are 44.33 ± 4.33 , 22.20 ± 1.12 , 23.33 ± 2.33 , and 25.00 ± 4.00 vessels/mm², respectively. These values are lower than those reported by Duong and Phan for species in arid environments - coastal rocky hills, where vessel densities exceed 100 vessels/mm².¹⁶ Vessel diameters in the studied species range from 52–118 µm. According to Thomas, the average vessel diameter in Angiospermatophyta is approximately 40 µm,¹⁷ indicating that the studied species have relatively wide vessels - an adaptive trait suitable for water-abundant environments.

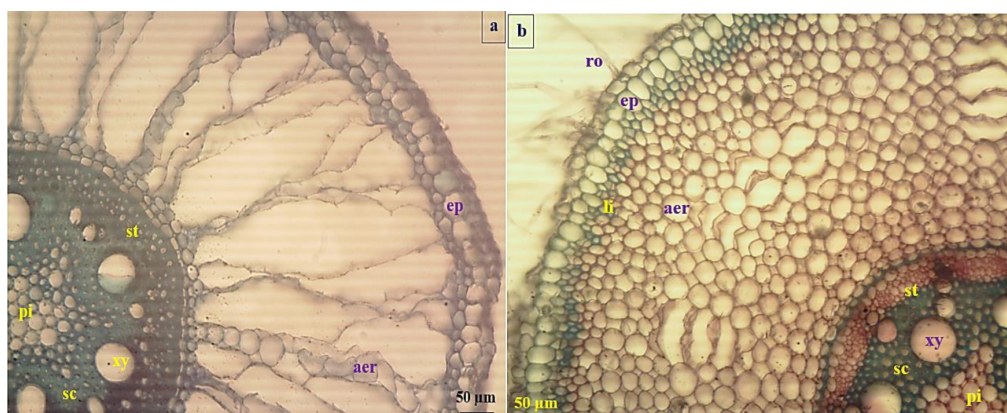


Figure 3. Anatomical features of the primary root structures in the investigated plant species.

a. *Melinis repens*, b. *Commelina longifolia*, ro: root hair, ep: epidermis, li: lignified cell, aer: aerenchyma, st: stele, sc: sclerenchyma, xy: xylem vessel, pi: pith

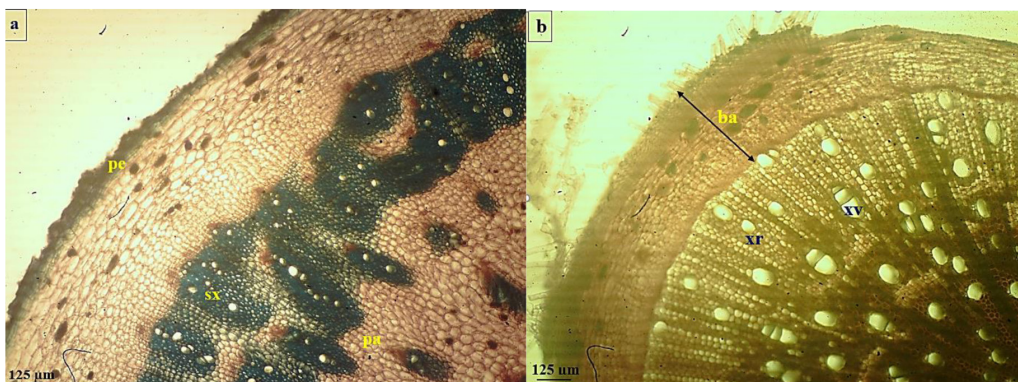


Figure 4. Anatomical features of the secondary root structures in the investigated plant species.

a. *Celosia argentea*, b. *Ludwigia octovalvis*, ba: bark, pe: periderm, sx: secondary xylem, pa: parenchyma, xr: xylem ray, xv: xylem vessel

Table 1. The dimensions of primary root structures in the studied plant species.

RR: root radius

Species	Primary root									
	Epidermis		Cortex		Stele			Pith		
	$\bar{X} \pm S$ (μm)	% RR	$\bar{X} \pm S$ (μm)	% RR	$\bar{X} \pm S$ (μm)	% RR	Vessel density ($\bar{X} \pm S$) (No. of vessels per mm^2)	Vessel diameter ($\bar{X} \pm S$) (μm)	$\bar{X} \pm S$ (μm)	% RR
<i>Melinis repens</i> (Willd.) Zizka	52.37 ± 1.12	5.98	555.70 ± 36.27	63.49	158.27 ± 16.96	18.08	44.33 ± 4.33	88.00 ± 1.00	108.93 ± 24.86	12.45
<i>Commelina longifolia</i> Lam.	47.27 ± 1.49	5.11	577.77 ± 27.26	62.49	192.17 ± 27.02	20.78	22.20 ± 1.12	72.13 ± 1.05	107.43 ± 16.96	11.62

Table 2. The dimensions of secondary root structures in the studied plant species.

RR: root radius

Species	Secondary root							
	Bark				Secondary xylem			
	Cork		Secondary phloem					
	$\bar{X} \pm S$ (μm)	% RR	$\bar{X} \pm S$ (μm)	% RR	$\bar{X} \pm S$ (μm)	% RR	Vessel density ($\bar{X} \pm S$) (No. of vessels per mm^2)	Vessel diameter ($\bar{X} \pm S$) (μm)
<i>Celosia argentea</i> L.	116.17 ± 15.08	3.03	502.08 ± 42.15	13.09	3217.50 ± 131.25	83.88	23.33 ± 2.33	51.92 ± 2.77
<i>Ludwigia octovalvis</i> (Jacq.) Raven	157.75 ± 16.00	7.32	377.92 ± 25.52	17.53	1620.33 ± 113.02	75.15	25.00 ± 4.00	109.92 ± 13.15

3.2.2. Stems

The primary stems of *M. repens* and *C. longifolia* exhibit aerenchyma development: 4–5 layers of aerenchymatous cells below the epidermis in *M. repens*, and throughout the stem in *C. longifolia*, forming large gas cavities (Figure 5) that enhance gas exchange.¹¹ A similar observation was made by Nguyen in *Panicum repens* L. (Poaceae), which also exhibits abundant

intercellular spaces.¹⁸ Inside the 4–5 layers of cortical parenchyma cells, a continuous band of sclerenchyma tissue is formed encircling the stem. Sclerenchyma also surrounds the vascular bundles, consistent with the findings of Wahua on *Commelina erecta* L..¹⁹ Oval-shaped calcium oxalate crystals are scattered within the aerenchyma of *C. longifolia* stem, collectively contributing to the mechanical reinforcement of the primary stems.⁵

C. argentea and *L. octovalvis* possess secondary stem structures. The cork layer is thin, accounting for 1.41% and 4.3% of the stem radius in *C. argentea* and *L. octovalvis*, respectively (Table 4), compared to herbaceous species living in coastal rocky areas.¹⁶ This is completely consistent with plant species adapted to moist environments. In *C. argentea*, the secondary xylem appears in clusters interspersed with parenchyma. In contrast, a study by Rajut on *Aerva sanguinolenta* (L.), a species belonging to the same family Amaranthaceae, reported that its secondary xylem forms a continuous ring.²⁰ In *L. octovalvis*, secondary xylem develops continuously below the vascular cambium and features abundant fibers, enhancing mechanical

strength, a pattern consistent with Scremin-Dias et al.²¹ Prominent xylem rays support radial transport of nutrients and gases (Figure 6), aiding adaptation to hypoxic conditions during seasonal flooding.³

Xylem vessel density in stems ranges from 5 to 32 vessels/mm², and vessel diameters range from 55 to 117 μ m (Table 3 and 4). Compared to the study by Duong and Phan on herbaceous species in mangrove swamps,²² the studied species have wider vessel diameters. This is consistent with their freshwater riparian habitat, whereas smaller vessel diameters in mangrove species may promote faster flow and limit salt toxicity.

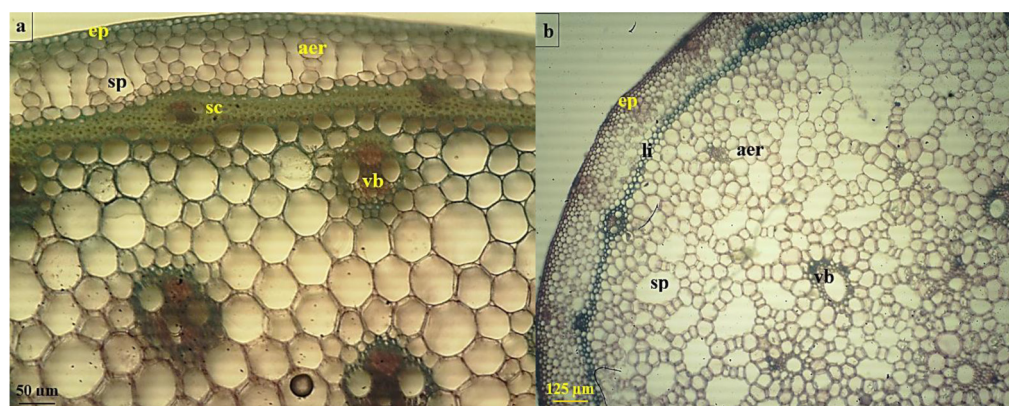


Figure 5. Anatomical features of the primary stem structures in the investigated plant species.

a. *Melinis repens* and b. *Commelina longifolia*, ep: epidermis, aer: aerenchyma, sp: intercellular space, sc: sclerenchyma ring, vb: vascular bundle, li: lignified cell

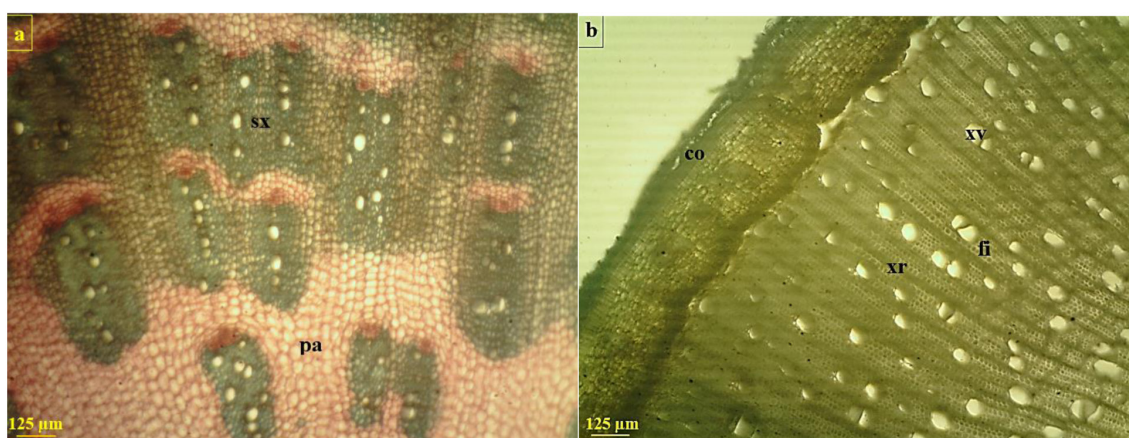


Figure 6. Transverse section through the secondary xylem of the secondary stem of *Celosia argentea* (a) and the secondary stem of *Ludwigia octovalvis* (b), sx: secondary xylem, pa: parenchyma, co: cork, xr: xylem ray, xv: xylem vessel, fi: fiber

Table 3. The dimensions of primary stem structures in the studied plant species.

SR: stem radius, "-": absent

Species	Primary stem							
	Epidermis		Parenchyma and vascular bundles				Pith cavity	
	$\bar{X} \pm S$ (μm)	% SR	$\bar{X} \pm S$ (μm)	% SR	Vessel density ($\bar{X} \pm S$) (No. of vessels per mm^2)	Vessel diameter ($\bar{X} \pm S$)	$\bar{X} \pm S$ (μm)	% SR
<i>Melinis repens</i> (Willd.) Zizka	12.58 ± 0.27	0.60	1365.00 ± 81.25	64.69	28.67 ± 4.33	55.42 ± 3.65	732.50 ± 25.00	
<i>Commelina</i> <i>longifolia</i> Lam.	21.17 ± 1.08	1.02	2053.33 ± 109.90	98.98	5.33 ± 0.33	114.83 ± 20.08	-	-

Table 4. The dimensions of secondary stem structures in the studied plant species.

ST: stem radius, "-": absent

Species	Bark				Secondary xylem				Pith parenchyma	
	Cork		Secondary phloem							
	$\bar{X} \pm S$ (μm)	% SR	$\bar{X} \pm S$ (μm)	% SR	$\bar{X} \pm S$ (μm)	% SR	Vessel density ($\bar{X} \pm S$) (No. of vessels per mm^2)	Vessel diameter ($\bar{X} \pm S$) (μm)	$\bar{X} \pm S$ (μm)	% SR
<i>Celosia</i> <i>argentea</i> L.	137.17 ± 40.90	1.41	1440.83 ± 127.08	14.80	8159.42 ± 742.90	83.79	15.33 ± 2.33	82.75 ± 1.31	-	-
<i>Ludwigia</i> <i>octovalvis</i> (Jacq.) Raven	265.58 ± 21.65	4.30	366.17 ± 34.08	5.93	3901.42 ± 372.90	63.18	32.67 ± 4.33	117.75 ± 18.81	1642.08 ± 113.02	26.59

3.2.3. Leaves

The leaf blades of *M. repens* and *C. longifolia* are characteristic of monocots. In *C. longifolia*, the epidermal cells are large, occupying 23.31%

(upper) and 15.07% (lower) of total leaf thickness (Table 5). These results are generally consistent with the findings of Tran *et al.*¹¹

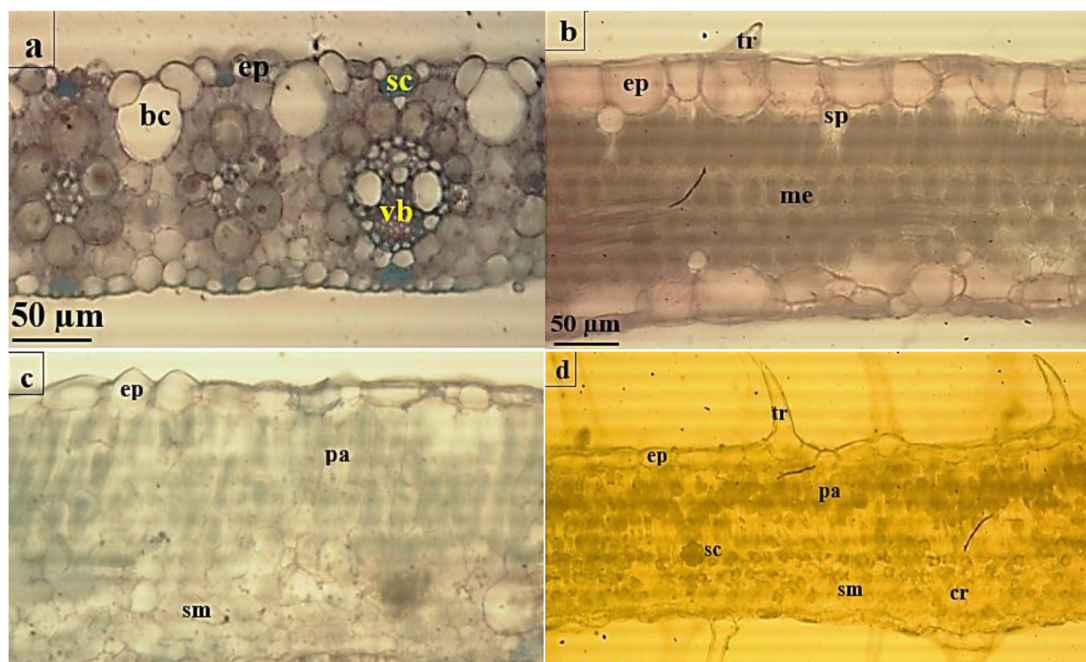


Figure 7. Anatomical features of the leaf blade structures in the investigated plant species.

a. *Melinis repens*, b. *Commelina longifolia*, c. *Celosia argentea*, d. *Ludwigia octovalvis*, tr: trichome, ep: epidermis, bc: bulliform cell, sc: sclerenchyma, vb: vascular bundle, sp: intercellular space, me: mesophyll, pa: palisade mesophyll, sm: spongy mesophyll, cr: crystal

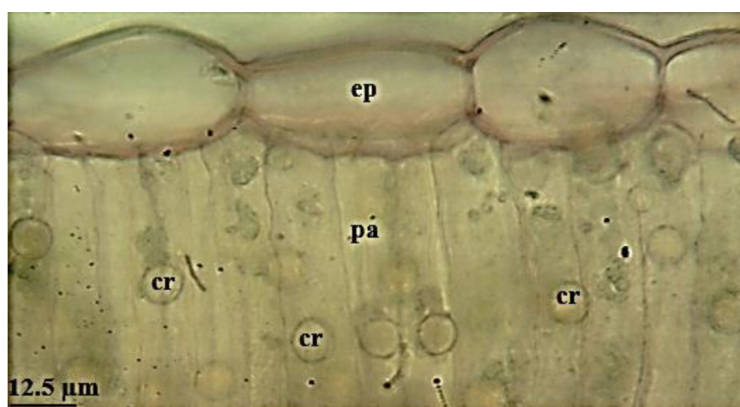


Figure 8. Transverse section through the palisade mesophyll of *Ludwigia octovalvis* leaf blade.

ep: epidermis, pa: palisade mesophyll, cr: crystal

The upper epidermis of both species possesses trichomes, with scattered intercellular spaces observed in the leaves of *C. longifolia* (Figure 7), which facilitate gas exchange.¹⁸ In the leaf blade of *M. repens*, the upper epidermis contains bulliform cells that enable the lamina to roll, thereby reducing water loss through stomata under hot or drought conditions.⁵ Sclerenchyma clusters beneath the epidermis in *M. repens* increase mechanical strength, the vascular bundles exhibit a Kranz anatomy.²³

In contrast, the leaf blades of *C. argentea* and *L. octovalvis* exhibit the anatomical structure characteristic of eudicots. The epidermis of *L. octovalvis* is densely covered with protective trichomes (Figure 7), and stomata are distributed on both surfaces of the leaf blade, though more abundantly on the abaxial side.²⁴ In the upper epidermis of *C. argentea*, epidermal cells exhibit considerable variation in size, whereas the lower epidermal layer is thinner and possesses an undulating surface.²⁵ In *C.*

argentea, the palisade and spongy mesophyll comprise 44.18% and 39.18% of the total leaf thickness, respectively (Table 5). Spherical crystals and sclereids are scattered throughout the mesophyll of *L. octovalvis* leaves (Figure 8),

consistent with findings by Scremin-Dias et al. in *Ludwigia grandiflora*,²¹ and contribute to increased mechanical resistance against wind and storm damage.

Table 5. The dimensions of leaf blade structures in the studied plant species.

TLT: total leaf thickness

Species	Leaf blade								
	TLT (µm)	Upper epidermis (µm)	% TLT	Lower epidermis (µm)	% TLT	Palisade mesophyll (µm)	% TLT	Spongy mesophyll (µm)	% TLT
	$\bar{X} \pm S$	$\bar{X} \pm S$		$\bar{X} \pm S$		$\bar{X} \pm S$		$\bar{X} \pm S$	
<i>Celosia argentea</i> L.	392.37 ± 75.26	42.23 ± 3.06	10.76	23.07 ± 1.21	5.88	173.33 ± 10.29	44.18	153.73 ± 12.41	39.18
<i>Ludwigia octovalvis</i> (Jacq.) Raven	244.10 ± 18.73	26.47 ± 2.12	10.84	15.53 ± 0.82	6.36	137.23 ± 23.12	56.22	64.87 ± 2.24	26.58
<i>Melinis repens</i> (Willd.) Zizka	233.27 ± 27.69	16.13 ± 1.22	6.92	22.13 ± 1.10	9.49	Mesophyll		% TLT	
						195.00 ± 12.96		83.60	
<i>Commelina longifolia</i> Lam.	348.37 ± 41.64	81.20 ± 4.21	23.31	52.50 ± 4.99	15.07	214.67 ± 25.33		61.62	

4. CONCLUSION

Riparian plant species are heliophilous, with features such as protective trichomes on the outer epidermis and highly developed palisade tissue (up to 56.22% of total leaf thickness).

These species are adapted to water-abundant, low-oxygen environments, as evidenced by low xylem vessel densities (lowest in *C. longifolia*: 22.20 ± 1.12 vessels/mm² in roots and 5.33 ± 0.33 vessels/mm² in stems) and wide vessel diameters (widest in *L. octovalvis*: 109.92 ± 13.15 µm in roots and 117.75 ± 18.81 µm in stems). Aerenchyma is well-developed in roots and stems (up to 63.49% of root radius in *M. repens*), and intercellular spaces are scattered throughout the leaves.

These species also exhibit adaptations to mechanical stress from wind and flooding:

growth in dense clumps, adventitious rooting from prostrate stems, presence of sclerenchyma bands or clusters surrounding xylem vessels or stems, and scattered calcium oxalate crystals in stem and leaf parenchyma.

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Đánh giá tiềm năng tái sử dụng bùn thải từ nhà máy nước để thay thế một phần xi măng trong vật liệu bê tông xây dựng

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*Ngày nhận bài: 16/06/2025; Ngày sửa bài: 05/09/2025;
Ngày nhận đăng: 24/09/2025; Ngày xuất bản: 28/02/2026*

TÓM TẮT

Sự gia tăng nhanh chóng của dân số và đô thị hóa trong những năm gần đây đã làm gia tăng lượng chất thải, bao gồm cả bùn thải từ các nhà máy xử lý nước sinh hoạt, nước thải và các quy trình công nghiệp. Theo phương pháp truyền thống, bùn thải thường được xử lý bằng cách chôn lấp tại các khu vực quy định, gây ra vấn đề môi trường và chi phí cao. Đồng thời, nhu cầu ngày càng lớn về vật liệu xây dựng, đặc biệt là bê tông – một trong những vật liệu xây dựng chủ đạo trên toàn cầu – đã làm gia tăng việc khai thác tài nguyên thiên nhiên và góp phần đáng kể vào lượng phát thải CO₂, nhất là từ sản xuất xi măng Portland. Những vấn đề trên cho thấy sự cần thiết phải tìm kiếm các vật liệu thay thế nhằm giảm thiểu tác động môi trường. Trong bối cảnh đó, việc sử dụng bùn thải từ nhà máy xử lý nước như một phần thay thế xi măng trong sản xuất bê tông nổi lên như một giải pháp tiềm năng. Cách tiếp cận này mang lại nhiều lợi ích: giảm chất thải, tiết kiệm tài nguyên, giảm tiêu thụ năng lượng và hạn chế phát thải CO₂ từ sản xuất xi măng. Nghiên cứu này nhằm đánh giá tiềm năng sử dụng bùn thải xử lý nước như một chất thay thế một phần cho xi măng trong các hỗn hợp bê tông. Kết quả cho thấy tính khả thi của giải pháp và đóng vai trò làm nền tảng cho các nghiên cứu tiếp theo, hướng đến ứng dụng thực tiễn và phát triển bền vững trong xây dựng.

Từ khóa: Bùn thải nhà máy nước, bê tông, thay thế xi măng, phát triển bền vững.

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Assessing the potential of water treatment sludge for cement replacement in concrete

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ABSTRACT

The rapid growth of population and urbanization in recent years has led to a significant increase in waste generation, including sludge produced from domestic water treatment plants, wastewater treatment facilities, and various industrial processes. Conventionally, the disposal of such sludge is carried out through landfilling at designated sites, which not only poses environmental challenges but also incurs substantial associated costs. Concurrently, the rising demand for construction materials, particularly concrete, which constitutes a major portion of global building materials, has escalated the consumption of natural resources and contributed to considerable CO₂ emissions, especially from the production of Portland cement. These concerns underscore the urgent need to explore alternative materials that can mitigate environmental impacts. In this context, the reuse of sludge from water treatment plants as a partial replacement for cement in concrete production emerges as a promising solution. This approach offers multiple benefits, including waste reduction, conservation of raw materials, energy savings, and a decrease in CO₂ emissions associated with cement production. This study aims to evaluate the potential of utilizing water treatment sludge as a partial substitute for cement in concrete mixtures. The results highlight the feasibility of this approach and serve as a foundation for further research toward its practical application, contributing to sustainable development in the construction sector.

Keywords: *Water sludge treatment, concrete, cement replacement, sustainable development.*

1. INTRODUCTION

The production of waste materials is an ever-increasing global challenge, particularly the large quantities of sludge generated by wastewater treatment processes and water treatment plants (WTPs).¹⁻³ In Danang city, the volume of municipal sewage sludge has been estimated at approximately 6 million m³/year.⁴ The direct disposal of this sludge, whether from wastewater or water treatment, poses serious environmental concerns due to the presence of pathogens, heavy metals, unstable organic

matter, and the limited landfill space.^{1,2,4,5} These issues necessitate a critical search to identify effective and environmentally safe management alternatives.

The construction industry, known for its high demand for resources and materials, presents a significant opportunity for the valorization and reuse of waste materials generated by its own activities and other sectors.⁶ Utilizing waste into construction can decrease energy consumption, conserve non-renewable natural resources, and reduce the volume of material

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sent to landfills.⁶ Given its substantial volume and potential environmental impact, sludge from water and wastewater treatment has been identified as a promising material for application in the construction sector.⁶⁻¹¹ However, the use of wastewater treatment sludge is limited by the presence of undesirable constituents, such as heavy metals and complex organic compounds, as well as the need for extensive pre-treatment.¹² Conversely, water treatment sludge (WTS) originating from drinking water treatment plants typically contains lower levels of these contaminants, rendering it more suitable and increasingly considered for use in construction materials. Various recycling and recovery options have been developed for sewage sludge, including its use in manufacturing ceramic tiles and bricks, synthesizing lightweight materials, producing cementitious binders, and serving as an alternative fuel in the clinkerization process. Water treatment sludge (WTS) has also been explored for use in ceramic materials and as a lightweight aggregate.^{3,7}

Previous research has explored the effects of incorporating WTS, in various forms and treatments, into concrete and cement-based materials. Using WTS as a partial replacement for aggregate in concrete has shown potential benefits for mechanical properties and durability.¹³ Investigations into replacing clinker or cement with WTS have yielded varying results.^{8,14} For example, studies on eco-cement produced with dry WTS as a partial replacement of raw materials indicated that chemical composition is comparable to ordinary Portland cement, although properties such as specific gravity, fineness, setting times, and workability are affected.^{2,15} Mechanical strengths can be comparable to control samples, particularly at later curing ages, but notable reductions might occur depending on the replacement level and water/cement ratio. The incorporation of raw or wet WTS has generally been found to reduce concrete strength, making it less suitable for

structural applications, though it remains viable for non-structural concrete at low replacement levels.^{7,9,10} The porous and irregular morphology of sludge particles can increase water demand and negatively affect workability. This variability underscores the importance of evaluating WTS in specific local contexts, considering both material properties and practical application requirements.

Despite its promising potential and environmental benefits, in Vietnam, research on the reuse of WTS in construction remains limited, despite the country facing growing urbanization, infrastructure demand, and environmental pressures from waste disposal. To address this gap, the present study investigates the potential of WTS sourced from the Cau Do Water Treatment Plant in Danang City as a partial replacement for Portland cement in concrete. Specifically, the study examines the effects of incorporating thermally treated WTS at different replacement levels on the compressive strength of concrete at various curing ages. By providing experimental evidence within the Vietnamese context, this work aims to assess the technical feasibility of WTS recycling, support sustainable waste management practices, and contribute to advancing circular economy approaches in the construction industry.

2. COLLECTION OF WATER TREATMENT SLUDGE FROM WATER TREATMENT

The water treatment sludge (WTS) utilized in this study was sourced from the Cau Do Water Treatment Plant, located in Cam Le District, Da Nang City, Vietnam. The facility, occupying an area of approximately 124,916 m², abstracts raw water from the Cam Le River and serves as a primary source of potable water for the urban population. Initially designed with a treatment capacity of 170,000 m³/day, the plant was upgraded in 2020 to increase its capacity to 290,000 m³/day. Future development plans aim to further expand this capacity to 390,000 m³/day by 2030 to meet the city's growing water

demand. The Cau Do Water Treatment Plant is a critical component of Da Nang's water supply infrastructure, accounting for approximately 82% of the city's total water treatment capacity.



Figure 1. Location of Cau Do water treatment plant.

During the treatment (Figure 2) of raw river water for domestic use at the Cau Do Water Treatment Plant, the processes of suspended solids and turbidity removal result in the generation of substantial quantities of sludge. The principal sources of this sludge are the sedimentation process-following by the dosing of coagulant chemicals, where flocculated particles aggregate and settle at the bottom of sedimentation basins, and the routine backwashing of sand filters, which removes accumulated particulates. Sludge from the sedimentation tanks, along with the solids-laden backwash water, is collected via an integrated system of pipelines and pumps, and subsequently conveyed to the plant's designated sludge treatment facility. At this stage, the sludge undergoes dewatering and is encapsulated in specialized containment bags to facilitate handling, transport, and subsequent disposal or further treatment.

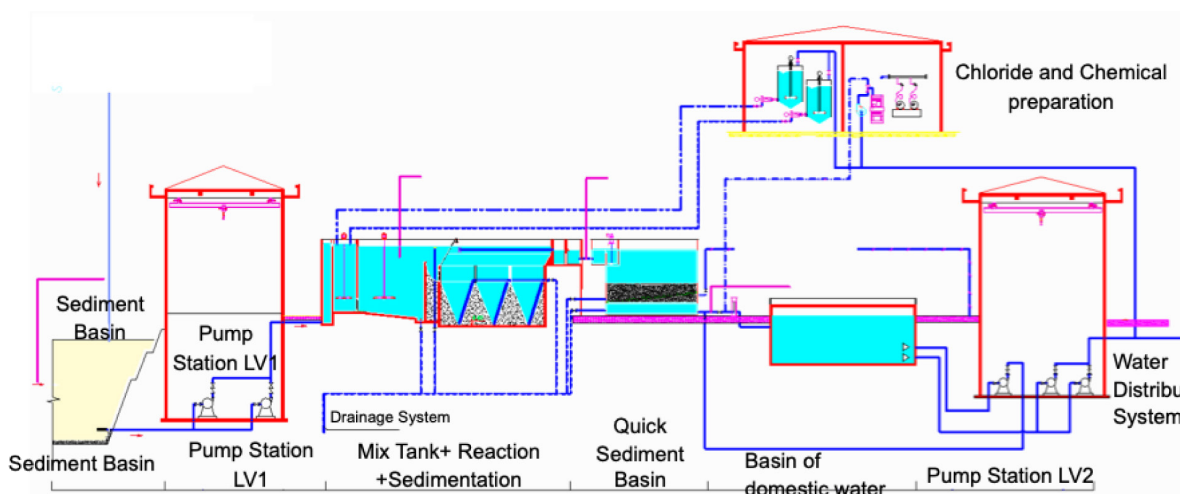


Figure 2. The process of a water treatment plant.

3. CONCRETE MIXTURE WITH WATER TREATMENT SLUDGE AS PARTIAL CEMENT SUBSTITUTE

Water treatment sludge collected from the treatment plant was subjected to thermal processing at temperatures of 300°C in a controlled heating chamber (Figure 3). This thermal treatment aimed to eliminate residual moisture content within the sludge. The process duration ranged from 2 to 3 days, depending

on the initial moisture content. The heating process was considered complete when the mass difference between two consecutive weight measurements became negligible, indicating the attainment of a constant weight.

Figure 4 presents the chemical compositions of WTS in its original state (sample M1) and after heating at 300°C (sample M2). Following thermal treatment, the Loss On Ignition (LOI) content decreased significantly,

from nearly 30% in the original state to approximately 5% at 300°C. This expected behavior reveals a possibility to remove unwanted moisture and organic matter from the WTS for further use as a cement substitute.

Following thermal treatment, the water treatment sludge (WTS) was allowed to cool to room temperature, then crushed and sieved to obtain particles with diameters smaller than 0.09 mm-comparable to the fineness of Portland cement. To prevent agglomeration caused by ambient moisture, the processed WTS was subsequently stored in sealed plastic bags and placed in a controlled dry chamber to maintain its stability before further use.



Figure 3. Heating chamber.

The concrete mixtures was designed for concrete of strength grade B15 according to The Vietnamese Standard (TCVN 5574:2018). Different mixtures were prepared corresponding to different replacement ratios of WTS for Portland cement: 0%, 5% and 10% at 300°C. The grade cement used in this study was PCB40, manufactured by Hoang Thach Company, and mixed with river sand and coarse aggregate with particle sizes ranging from 1 ÷ 2 cm (Table 1).

Cubic concrete specimens measuring 150mm x 150mm x 150mm were prepared, cured and tested for compressive strength in accordance with the Vietnamese Standard TCVN 3118:2022 (Figure 5, Figure 6). The mixtures were designed to achieve a target compressive strength of grade B15 following the Vietnamese Standard (TCVN 5574:2018). The experimental program included mixtures with varying replacement levels of Portland cement by water treatment sludge (WTS) calcined at 300°C, specifically at substitution rates of 0%, 5%, and 10% by mass.

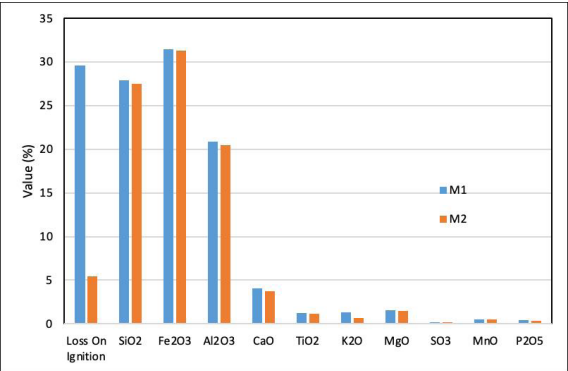


Figure 4. Chemical composition of WTS after thermal treatment.

Table 1. Mixture of concrete with partial replacement of cement by WTP.

No	Substitution Rate	Adhesive Aggregate (kg)		Stone (kg)	Sand (kg)	Water to Cement Ratio	Heating Temperature (°C)	Number of sample	Slump (cm)
		Cement	WTS						
1	0%	305.00	0	1120.9	728.3	0.69	0	3	9
2	5%	289.75	15.25	1120.9	728.3	0.69	300	3	8
3	10%	274.50	30.50	1120.9	728.3	0.69	300	3	6

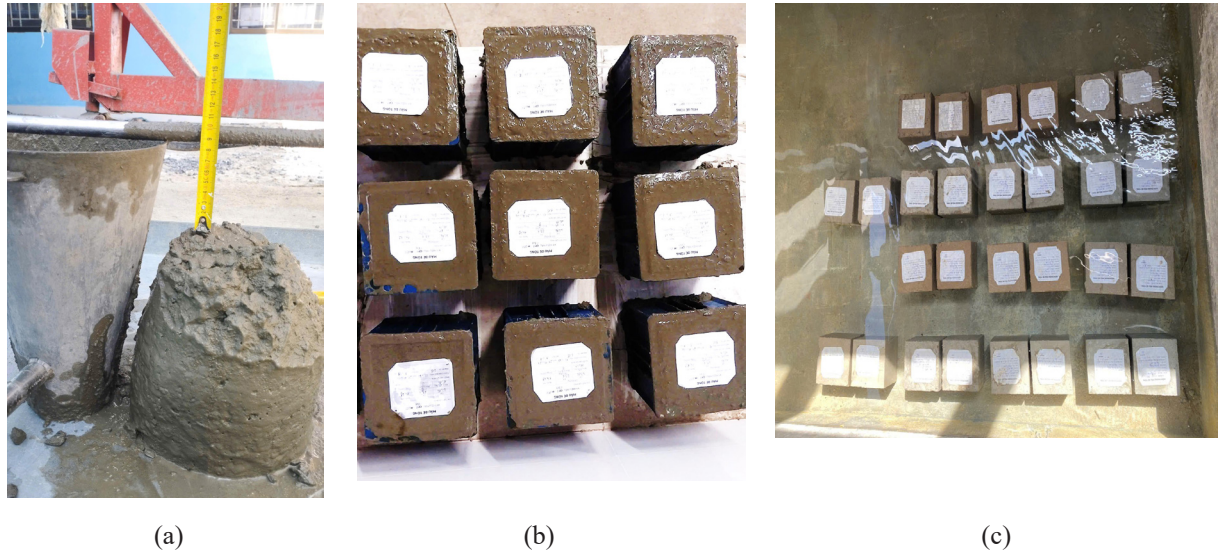


Figure 5. (a) Slump tests, (b) Concrete samples after casting and (c) Curing of concrete samples.

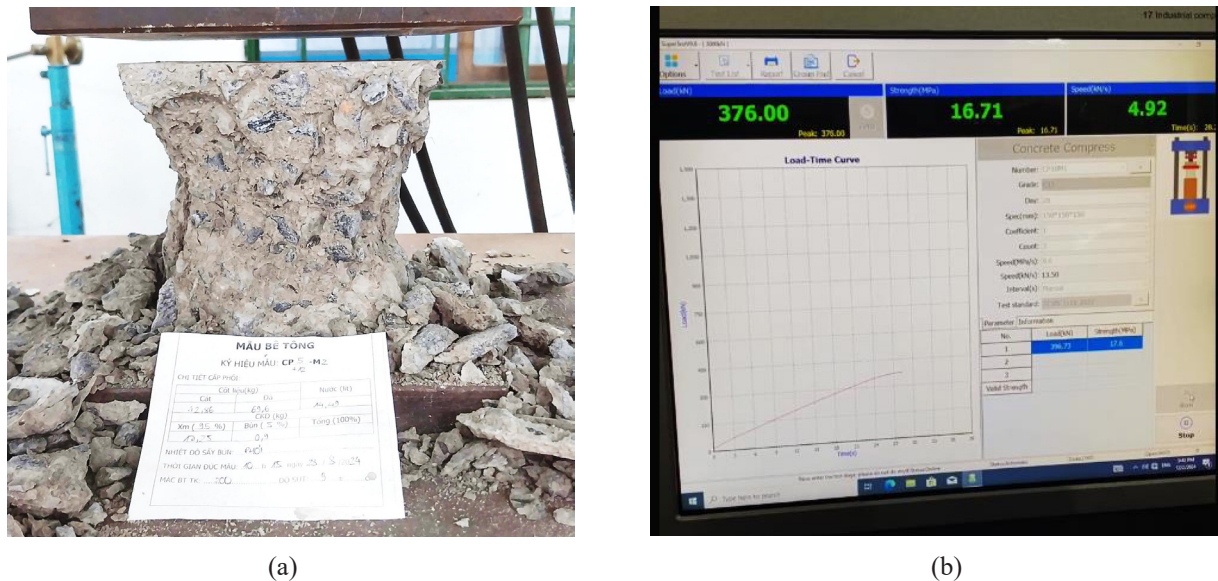


Figure 6. (a) Compressive test, (b) Monitoring the compressive result.

4. EVALUATION OF COMPRESSION STRENGTH OF CONCRETE USING WATER TREATMENT SLUDGE

This section presents the compressive strength results of various concrete mixtures incorporating water treatment sludge (WTS) as a partial replacement for cement. The WTS was collected from a municipal water treatment facility and subsequently dried at 300°C to eliminate residual moisture. Following this pre-treatment, the WTS was used to partially replace cement in different concrete mix designs, as detailed in Section 3.

Compressive strength tests were conducted at curing ages of 3, 7, and 28 days (Figure 7). For comparison, the compressive strength of a reference concrete mix without WTS was also evaluated at each corresponding age.

As illustrated in Figure 7, the compressive strength of concrete increased with curing time. However, achieving compressive strength comparable to the reference mixture proved challenging when incorporating WTS as a partial cement replacement. Across all tested mixtures, those without WTS consistently

exhibited higher compressive strength than those containing WTS. Nonetheless, the degree of compressive strength reduction varied with different replacement ratios. Among the investigated proportions, a 5% WTS replacement demonstrated the most favorable performance, consistently yielding higher compressive strength than 10% replacement level. Notably, at 28 days, the compressive strength of the 5% WTS mixture approached 91% of the reference value when dried at 300 °C. These findings suggest that a 5% WTS replacement may represent an optimal ratio for maintaining compressive strength comparable to conventional concrete formulations. This result is consistent with the findings of Gomes et al.^{3,7} who reported that the negative effect of WTS became more significant at replacement level higher than 5%.

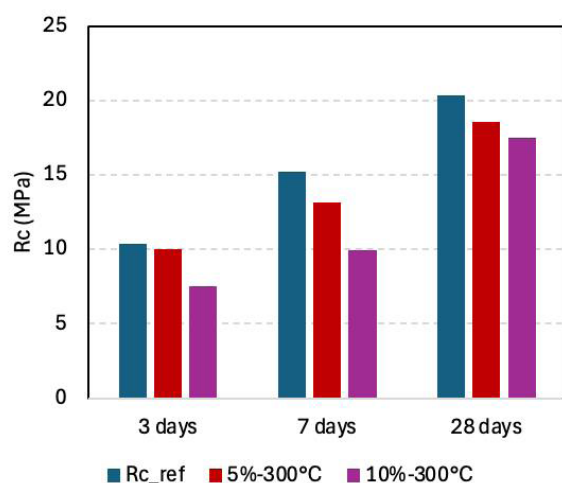


Figure 7. Compression Strength of different concrete mixture with WTS drying at 300 °C.

5. CONCLUSIONS

This study evaluated the use of thermally treated water treatment sludge (WTS) from the Cau Do Water Treatment Plant as a partial cement replacement in concrete. At a 5% replacement level, WTS treated at 300 °C retained up to 91% of the 28-day compressive strength, indicating improved pozzolanic activity. Although strength reductions were observed, results suggest WTS can be applied in non-structural concrete,

supporting waste valorization and sustainable construction. Further studies on durability, workability, and environmental impacts are recommended.

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Từ phản ứng pha rắn trong hơi nước đến vật liệu anode hiệu năng cao cho pin lithium-ion: một khảo sát ngoại trình (ex-situ) với vật liệu lithium vanadate

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TÓM TẮT

Phản ứng pha rắn truyền thống bộc lộ nhiều nhược điểm như khó khống chế hình thái và kích thước hạt của vật liệu, tiêu hao năng lượng lớn và nhiều rủi ro môi trường. Nhằm khắc phục những vấn đề này, một kỹ thuật tổng hợp pha rắn trong điều kiện thường dưới tác động của hơi nước đã được đề xuất để tổng hợp vật liệu ứng dụng làm điện cực anode cho pin lithium-ion. Trong nghiên cứu này, lithium vanadate (Li_3VO_4) được khảo sát như một thí dụ, trong đó tính năng điện hóa của vật liệu Li_3VO_4 tổng hợp bằng phản ứng pha rắn trong hơi nước thể hiện nhiều ưu điểm vượt trội hơn vật liệu tương tự theo phương pháp truyền thống với dung lượng riêng thuận nghịch đạt $590.8 \text{ mAh}\cdot\text{g}^{-1}$ ở cường độ dòng riêng $100 \text{ mA}\cdot\text{g}^{-1}$ sau 50 chu kỳ. Các kỹ thuật ngoại trình (ex-situ), như nhiễu xạ tia X, Raman và hiển vi điện tử quét, được sử dụng nhằm làm sáng tỏ cơ chế cũng như sự biến đổi hình thái của Li_3VO_4 tổng hợp bằng phản ứng pha rắn trong hơi nước.

Từ khóa: Pin lithium-ion, anode, phản ứng pha rắn, kỹ thuật ex-situ.

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From water vapor-assisted solid-state reaction to high-performance anode for lithium-ion batteries: an ex-situ investigation for a case study of lithium vanadate

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ABSTRACT

Conventional solid-state reactions (SSRs) suffer from uncontrollable morphology and particle size, massive energy consumption, and environmental risk. To address these problems, a novel approach involving ambient SSRs under water vapor has been proposed for the preparation of anode materials for lithium-ion batteries. In this work, a case study of lithium vanadate (Li_3VO_4) has been investigated in which the electrochemical properties of Li_3VO_4 from the vapor route are superior to those from conventional SSRs, delivering a reversible specific capacity of $590.8 \text{ mAh}\cdot\text{g}^{-1}$ at a specific current of $100 \text{ mA}\cdot\text{g}^{-1}$ after 50 cycles. Ex-situ techniques, such as X-ray diffraction, Raman, and scanning electron microscopy, have been employed to elucidate the mechanism of vapor-assisted SSRs in Li_3VO_4 synthesis.

Keywords: *Solid-state reaction, anode, lithium-ion batteries, ex-situ techniques.*

1. INTRODUCTION

Rising as a key component in the global race to develop electric vehicles and stationary energy storage, the advancement of lithium-ion batteries (LIBs) has been driven by the demand for high energy and power density, as well as the need for fast charging capabilities.¹ However, the preparation strategy of most active electrode materials, especially anode materials, has recently been based on conventional solid-state reactions (SSRs), which involve high energy consumption for high-temperature treatment, uncontrollable morphology, and particle size of the products due to severe aggregation. Meanwhile, wet chemistry preparations are conducted under mild conditions, but they carry the risk of releasing polluted solvents. Therefore,

mimicking the solvent role of water in wet chemistry routes, a vapor-assisted SSR has been proposed to perform materials synthesis at low temperatures with controllable morphology.^{2,3}

As an intercalation-type anode, lithium vanadate, Li_3VO_4 , has been studied as a promising alternative to carbon-based materials due to its advantages, such as a higher theoretical capacity ($591 \text{ mAh}\cdot\text{g}^{-1}$) and a safer operating voltage.⁴ However, the application of Li_3VO_4 as an anode for LIBs is hindered by its low intrinsic electronic conductivity, which becomes more serious due to the large particle size from conventional SSR synthesis. Following a prolonged research period on these materials, various efforts, which could be divided into three categories: (i) aliovalent doping, (ii) combining

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with a highly conductive network or coating layer, and (iii) particle size and morphology control, have been undertaken to address this issue. For the first strategy, the aliovalent such as $\text{In}^{3+}/\text{Ce}^{4+}$,⁵ Sm^{3+} ,⁶ W^{6+} ,⁷ Cr^{3+} ,⁸ Cl^- ,⁹ etc. Recently, the Sm has been introduced to the structure of Li_3VO_4 , inducing reduction of V^{5+} to V^{4+} and oxygen vacancy, which modified the electronic band structure of the host materials toward higher electrical conductivity.⁶ The conductive network and coating layer applied in Li_3VO_4 -based anode include N-doped porous carbon,¹⁰ carbon fiber,^{11,12} graphene,¹³ or LiNbO_3 .¹⁴ While the carbon-based networks provide an effective conductive pathway for electron transfer, the coating layer protects materials from side reactions with the electrolyte and minimizes solid electrolyte interphase evolution. To control the particle size and morphology of Li_3VO_4 , various methods have been applied, including spray drying,¹⁵ electrostatic spray,¹⁶ recrystallization,¹⁷ electrospinning,¹¹ etc. Among multiple strategies to address this issue, confining particle size to sub-microsize could reduce the electron transport pathway, hence improving its electrochemical performance.^{2,18,19}

In this work, the vapor-assisted SSR has been utilized to prepare Li_3VO_4 as sub-micrometer spherical-like particles. The mechanism of this reaction is clarified using ex-situ techniques, which indicate the rapid phase transition of the outer layer, followed by the slow process of the completed inner reaction. The variation of morphology during the vapor-assisted SSR is also elucidated. The vapor-produced Li_3VO_4 exhibits significantly improved electrochemical performance, including a reversible capacity of $590.8 \text{ mAh}\cdot\text{g}^{-1}$ at a specific current of $100 \text{ mA}\cdot\text{g}^{-1}$ after 50 cycles, which is 2.6 times higher than that of conventional SSR- Li_3VO_4 .

2. EXPERIMENTALS

Chemicals: All the chemicals in this work were purchased and used without further purification.

Lithium hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$, $\geq 98\%$) and vanadium pentoxide (V_2O_5 , $\geq 98\%$) were supplied by Sigma-Aldrich, Germany. Acetylene black and anhydrous N-methylpyrrolidone (NMP, 99.5%) were sourced from Sigma-Aldrich. The electrolyte, as a $1.0 \text{ mol}\cdot\text{L}^{-1}$ solution of lithium hexafluorophosphate (LiPF_6) in a 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), and poly (vinylidene fluoride) (PVDF, $\geq 99.5\%$) were obtained from MTI Corporation.

Materials preparation: Li_3VO_4 was prepared using both vapor-assisted SSR and conventional SSR. For vapor-assisted SSR, as shown in Scheme 1, a mixture of $\text{LiOH}\cdot\text{H}_2\text{O}$ and V_2O_5 in a molar ratio of 3:1 was ground in a mortar. The resulting orange solids were transferred to an alumina crucible covered with aluminum foil and heated to 600°C for 5 hours, as described by Li et al.²⁰ The final powder was reground and labeled as c-LVO. The precursor mixture was placed in a tea filter bag and suspended in a 20 mL vial containing 3 mL of deionized water. The sealed reactor was maintained at 80°C for 24 hours. The resulting humid solid was dried at 80°C for an additional 12 hours, reground, and labeled as v-LVO.

Materials characterization: The phase and crystal information of the as-prepared samples were investigated using X-ray diffraction (XRD) in a 2θ range of 10 – 80° , conducted on a Rigaku Miniflex-600 diffractometer with a $\text{Cu-K}\alpha$ tube at a voltage of 40 kV and a current of 15 mA. The morphology of these samples was analyzed using field-emission scanning electron microscopy (FE-SEM), conducted on a Nova Nano SEM 450.

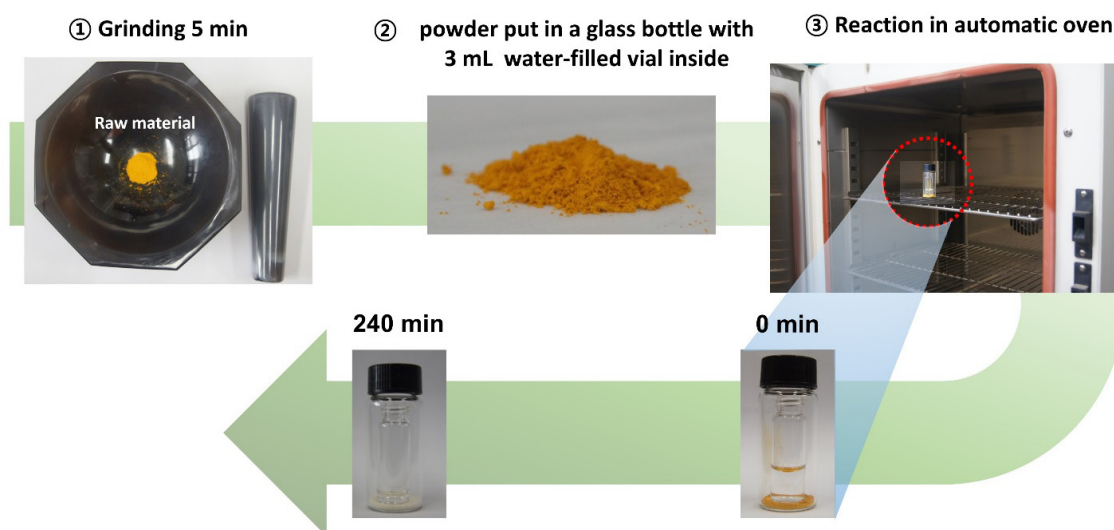
Ex-situ characterization: The vapor-assisted SSR was investigated at various reaction times, ranging from 30 minutes to 1, 2, 5, 12, and 24 hours. After these periods, the solid was collected and dried at 80°C for 12 hours. The individual solids were characterized using XRD, Raman spectroscopy, and FE-SEM. The Raman

spectroscopy of these v-LVOs was collected on a DXR 3xi (Thermo Fisher) under a 532-nm wavelength excitation with a laser power of 0.1 ~ 1mW, and an exposure time of 0.05 ~ 0.5s.

Electrochemical characterization: The lithium storage properties of c-LVO and v-LVO were investigated in a half-cell configuration, where a lithium metal disc served as both the reference and counter electrode. The working electrodes were fabricated using the slurry casting method. A mixture of active materials (c-LVO or v-LVO), acetylene black as a conductive agent, and PVDF as a binder, with a mass ratio of 7:2:1, respectively, was blended in NMP solvent until a uniform slurry was formed. The obtained slurry was cast on a copper foil using a doctor blade with a controlled thickness of 15 μm . The electrode was dried at 120 $^{\circ}\text{C}$ for 24 hours under vacuum, then punched into 10-mm diameter discs for further use. The CR-2032 coin cell was assembled in an Argon-Filled glovebox, with

oxygen and moisture content maintained below 1.0 ppm. Typically, the half-cell was constructed from a working electrode and a lithium metal foil, separated by a glass microfiber separator soaked in the electrolyte. The newly assembled coin-cells were rested for 12 hours before further experiments.

The galvanostatic properties of the half-cells were performed on the NAGANO-BTS-4000H battery station in a potential range of 0.10–3.00 V (vs. Li/Li^+) at a specific current of 100 $\text{mAh}\cdot\text{g}^{-1}$. The electrochemical behavior of lithium storage in these cells was clarified using cyclic voltammetry (CV) over the relevant potential range at a scan rate of 0.05 $\text{mV}\cdot\text{s}^{-1}$. The electrochemical impedance spectroscopy (EIS) results were obtained in a frequency range of 0.01 – 10^5 Hz under an alternating current amplitude of 5 mV. The CV and the EIS results were recorded on the MultiAutolab/M101 system.



Scheme 1. Illustration of vapor-assisted solid-state reaction for v-LVO preparation.

3. RESULTS AND DISCUSSION

Crystal structure analysis: The XRD patterns of the as-prepared c-LVO and v-LVO are exhibited in Figure 1a. Accordingly, the XRD pattern of c-LVO comprises the signals at 2θ of 16.3 $^{\circ}$, 21.5 $^{\circ}$, 22.8 $^{\circ}$, 21.3 $^{\circ}$, 28.1 $^{\circ}$, 32.7 $^{\circ}$,

35.9 $^{\circ}$, 36.3 $^{\circ}$, 50.2 $^{\circ}$, 58.6 $^{\circ}$, 66.2 $^{\circ}$, and 70.8 $^{\circ}$ corresponding to the (100), (110), (011), (111), (200), (002), (201), (202), (320), (203), and (322). Similarly, the observations from the XRD diffraction of v-LVO are almost the same as those of c-LVO, demonstrating that the sample

prepared via vapor-assisted SSR is crystallized in the orthorhombic phase. The illustration of the crystal structure of orthorhombic Li_3VO_4 is presented in Figure 1b. Therein, the lattice units of Li_3VO_4 are constructed from tetrahedra of LiO_4 and VO_4 connecting via oxygen atoms. However, the diffraction of the v-LVO is broadening compared to that of the c-LVO. As shown in the insets of Figure 1a, the full width at half maximum (FWHM, β) of the (111) peak in v-LVO is larger than that of c-LVO, demonstrating lower crystallinity and smaller crystallite size. To calculate the crystallite size, the Williamson-Hall (WH) approach was employed. According to Figure 1c and Table 1,

the plots of $(\beta\cos\theta)$ vs $(4\sin\theta)$ of the c-LVO and v-LVO indicate the intercepts of 0.046 and 0.0320, corresponding to crystallite sizes of 31.2 nm and 4.5 nm, respectively. In addition, the microstrain in the lattice structures of these samples is also derived from the slope of the WH plot. Therein, the higher slope of c-LVO induces a larger value of microstrain of 145, 2.8 times higher than that of the v-LVO. The crystal structure analysis indicates that vapor-assisted SSRs conducted in ambient conditions can produce more polycrystallite properties with lower lattice strain, which is favorable for lithium transport during lithiation/delithiation.

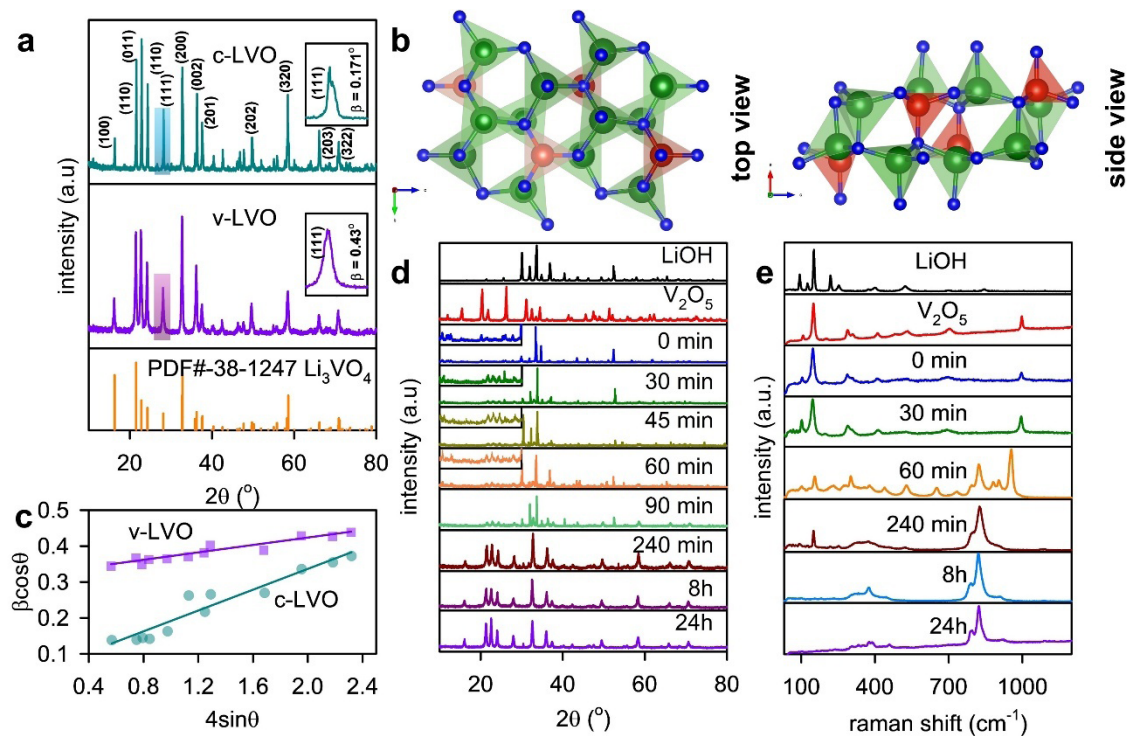


Figure 1. (a) XRD patterns of the c-LVO and v-LVO (the insets are the enlargement of XRD patterns in 2θ -range of $31\text{--}34^\circ$); (b) the illustration of top and side views of orthorhombic Li_3VO_4 , where red, green, and blue represent vanadium, lithium, and oxygen; (c) Williamson-Hall plots of c-LVO and v-LVO; (d) ex-situ XRD and (e) ex-situ Raman spectroscopy of the LiOH , V_2O_5 , and v-LVO after various reaction times from 0 min to 24 hours.

Table 1. Results derived from WH method for determining crystallite size and microstrain of c-LVO and v-LVO.

Sample	WH equation $\beta\cos\theta = 4\varepsilon\sin\theta + K\lambda/D$	Intercept ($K\lambda/D$)	Crystallite size (nm)	Slope (ε)	Microstrain ($\times 10^{-3}$)
c-LVO	$y = 0.14498x + 0.04643$	0.04643	31.190	0.14498	144.98
v-LVO	$y = 0.05167x + 0.32032$	0.32032	4.521	0.05167	51.67

Ex-situ investigation on vapor-assisted SSR The formation of the v-LVO was investigated using ex-situ XRD. According to Figure 1d, the diffractions of the $\text{LiOH}\cdot\text{H}_2\text{O}$ including peaks at $2\theta = 30.1, 31.1, 32.9, 34.9, 36.8, 40.3,$ and 52.5° , corresponding to the $(-111), (-201), (220), (130), (021), (-311),$ and (400) planes of monoclinic structure with a space group of C2/m ascribing to PDF#01-076-1073. Meanwhile, the XRD pattern of V_2O_5 comprises signals at $2\theta = 15.4, 20.3, 21.8, 26.4, 31.2, 32.4, 34.5, 41.4, 47.6,$ and 51.2° matching to the $(200), (001), (101), (110), (400), (011), (002), (600),$ and (020) plane of the orthorhombic lattice of $\alpha\text{-V}_2\text{O}_5$ ($\text{P2}_1/\text{m}$) according to PDF#41-1426. Those lattice diffractions are well-observed in the mixing solid's XRD pattern (0 min). After being exposed to water vapor for 30 minutes, the XRD pattern exhibits significant variation in the 2θ range of $20\text{--}30^\circ$, indicating the formation of a newly formed Li_3VO_4 phase at the interface of the precursors. However, this variation remains for the next two hours, as illustrated by the insignificant changes in the XRD patterns at 45, 60, and 90 minutes of reaction. After 240 minutes of reaction, the evolution of Li_3VO_4 is observable, while the precursor is indicated as an impurity with low content. After 8 hours of reaction, no impurity could be observed, indicating the complete reaction.

A similar phenomenon can be inferred from the ex-situ Raman data, as shown in Figure 1d. As shown in the Raman spectrum of LiOH , the strong peaks in the range of $60\text{--}300\text{ cm}^{-1}$ are assigned to the ionic bonds of Li^+ and OH^- , while the low-intensity bands at 401 and 533 cm^{-1} are ascribed to the libration motion of water molecules.²¹ The V_2O_5 Raman spectrum comprises the stretching modes of V=O located at 991.3 cm^{-1} , the vibration of bridging V-O-V at 702.5 cm^{-1} , the stretching motion of ladder V-O at 528.3 cm^{-1} , the in and out-of-phase oscillation of V and O atoms at 292.1 and 282.4 cm^{-1} , while the shearing distortion of these atoms is attributed to the lowest Raman shift bands at 201.1 and

147.5 cm^{-1} .²² Those signals of vanadium oxides are clearly observed in mixing precursors, while the LiOH -related peak is missing, which could be attributed to the high dissolution of LiOH . As shown in the Raman spectrum of the reaction mixture after 30 minutes, there is no significant variation compared to the original mixture, indicating a low product content and a slow reaction rate for the solid-state reaction. After 60 minutes of reaction, the Raman spectrum exhibits various new bands related to the interaction of LiOH and V_2O_5 . Therein, the vanishment of the 991.3 cm^{-1} peak along with the addition of new peaks at 966.1 and 946.2 cm^{-1} corresponding to the phase transition of $\alpha\text{-V}_2\text{O}_5$ to $\gamma\text{-Li}_x\text{V}_2\text{O}_5$,^{22,23} which could be formed by the intercalation of lithium-ion into the layered structure of V_2O_5 . Additionally, the newly emerging signals appeared at 830.1 and 780.4 cm^{-1} , assigned to the symmetric and asymmetric stretching vibrations of VO_4^{3-} units, indicating the formation of Li_3VO_4 . The vibration of VO_4^{3-} is also characterized by a band around 400 cm^{-1} , as reported in previous studies.^{14,24} However, the remaining signals below 200 cm^{-1} until 240 min demonstrate a slow rate and incomplete reaction. For a longer reaction time, the Raman spectra consist of only two bands at $300\text{--}450\text{ cm}^{-1}$ and $700\text{--}850\text{ cm}^{-1}$, characteristic of orthorhombic Li_3VO_4 , which confirms the pure phase of the products and is in good agreement with XRD data.

The morphology evolution of Li_3VO_4 prepared via vapor-assisted SSR is investigated using the FE-SEM technique. As shown in Figures 2a,b, the raw V_2O_5 exhibits polyhedrons of a few hundred micrometers, while the LiOH is observed as an aggregation of particles of a few tens of nanometers. After the precursors are mixed (Figure 2c), the surface of V_2O_5 polyhedrons is covered with LiOH nanoparticles, which could be explained due to (i) the different solubility of precursors: LiOH is hydrophilic and highly dissolved in water, but V_2O_5 is hydrophobic and performs low solubility, (ii) acid – base nature of precursors: LiOH is a strong base and V_2O_5 is

acidic surface, hence, under a vapor surrounding, LiOH tends to absorb water and etching to V_2O_5 surface by acid-base reaction. The etching behavior of LiOH is enlarged by the time of reaction, as shown in Figure 2d, and fully covers the polyhedrons. After 60 minutes of reaction, the coverage layer of the product tends to form as long streptococci-like particles (Figure 2e). These particles become larger and break down into nanorods after 120 minutes (Figure 2f). Due to the high solubility of Li_3VO_4 , the newly formed product continues to be etched by water vapor. According to Figures 2g,h, after longer reaction times, the long strings break into shorter rods, accumulate on a porous surface, and form

aggregated spherical particles. The morphology evolution of Li_3VO_4 is illustrated in Figure 2i. Compared to the v-LVO, the Li_3VO_4 particles synthesized by the conventional SSR have a larger size, reaching a few micrometers. The smaller size of v-LVO is preferable for improving electrochemical performance in lithium-ion storage due to shortening the electron and ion diffusion pathways, enhancing electrolyte/electrode contact, and alleviating lattice strain and stress caused by volume variation during lithiation/delithiation. Therefore, it is promising that the v-LVO could provide better electrode cycling performance compared to that of the c-LVO, as demonstrated in the following section.

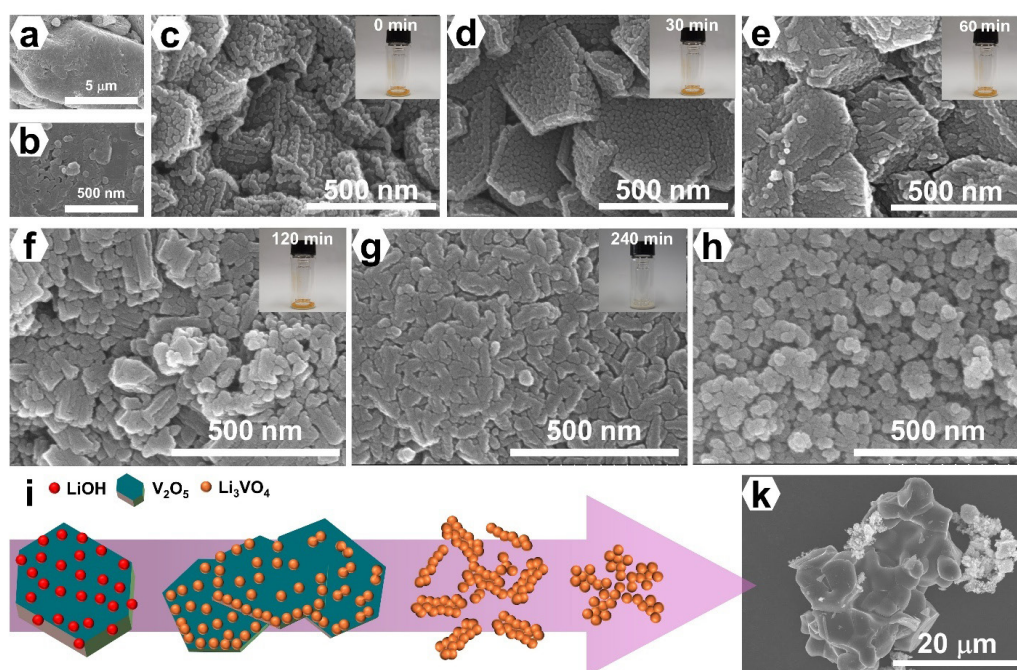


Figure 2. Morphology evolution of Li_3VO_4 synthesized via vapor-assisted solid-state reaction: FE-SEM images of (a) V_2O_5 ; (b) $LiOH \cdot H_2O$; (c) precursors after mixing (0 mins); and solids obtained after relevant reaction times of (d) 30 mins; (e) 60 mins; (f) 120 mins; (g) 240 mins; (h) 24 hours; (i) illustration of morphology evolution of Li_3VO_4 prepared via vapor-assisted solid-state reaction; (k) FE-SEM image of c-LVO.

Electrochemical performance: The lithium-ion storage mechanism of the obtained materials is studied using the CV curves, as shown in Figures 3a,b. As shown in Figure 3b, the first cathodic curve of the v-LVO exhibits two peaks at 0.76 and 0.51 V (vs. Li/Li^+). These peaks are attributed to the intercalation of lithium ions into Li_3VO_4 , resulting in $Li_{3+x}VO_4$, which is associated with the reduction of V^{5+} to V^{4+} and

V^{3+} .²⁵ The correlative behavior is also observed in the c-LVO with a signal at 0.72 V (vs. Li/Li^+) and a shoulder below 0.5 V (vs. Li/Li^+) (Figure 3a). The lower-potential peaks in both electrodes tend to broaden, which can be attributed to the formation of a solid electrolyte interface (SEI) layer resulting from the decomposition of electrolyte salts and solvents. In the anodic process, the v-LVO electrode exhibits a shoulder

signal comprising a lower-intensity peak at 1.15 V (vs. Li/Li^+) and a stronger peak at 1.31 V (vs. Li/Li^+), corresponding to the reversible delithiation from $\text{Li}_{3+x}\text{VO}_4$. Compared to c-LVO, the potential gap of the redox peaks related to the insertion and extraction of lithium ions in v-LVO is narrower (the inset of Figures 3a,b), indicating less polarization impedance of this electrode. This can be attributed to the nanosized particles of v-LVO compared to the microsize of c-LVO, which may accelerate lithium and electron transport, thereby improving the kinetics of the electrode reaction.²⁵⁻²⁷ In the subsequent

cycles, the reduction peaks shift to higher potentials, while the oxidation signals shift to lower potentials, indicating a further decrease in potential differences. Therein, the redox peak shift in v-LVO is more than what is observed in the c-LVO, resulting in a smaller gap of 0.22 V compared to 0.33 V, respectively. In addition, the fact that the CV curve forms a larger area, and the redox peaks are sharper for v-LVO, could demonstrate an improved kinetic behavior of this electrode, promising better electrochemical performance.^{28,29}

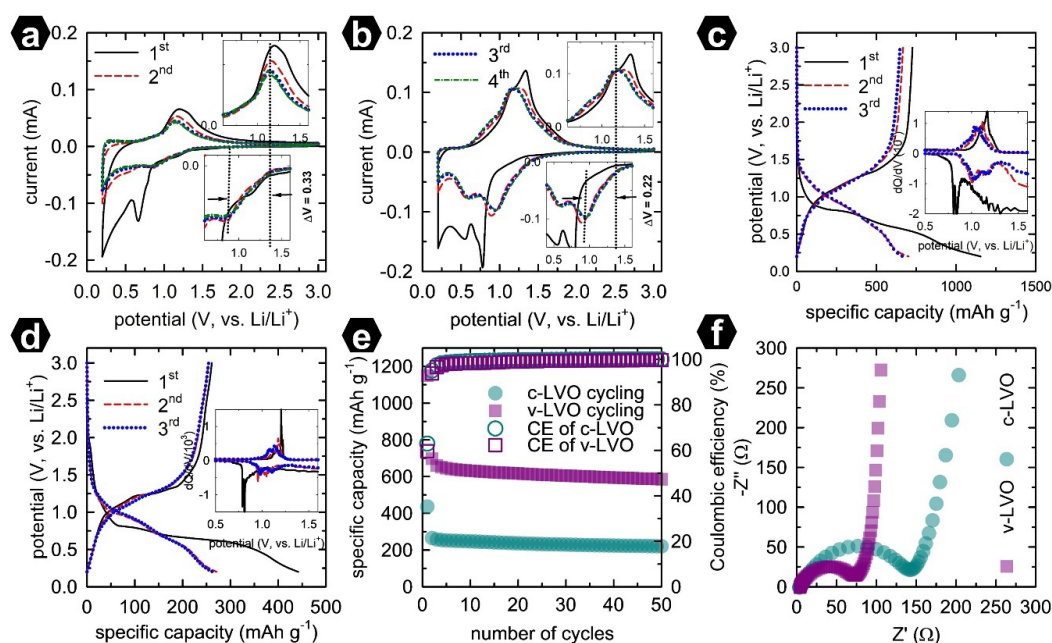


Figure 3. CV curves of the first four cycles of (a) c-LVO and (b) v-LVO electrodes, the insets are the enlargement of relevant data in the selected potential ranges; galvanostatic charge-discharge profile of the first three cycles of (c) v-LVO and (d) c-LVO, the insets are the dQ/dV plots of relevant data in the selected potential ranges; (e) cycling performance and Coulombic efficiency of the c-LVO and v-LVO electrodes; and the Nyquist plots of c-LVO and v-LVO electrodes. All of the experiments are conducted in the potential range of 0.2 – 3.0 V vs. Li/Li^+ , and at a scan rate of $0.5 \text{ mV}\cdot\text{s}^{-1}$ for CV and at a specific current of $100 \text{ mA}\cdot\text{g}^{-1}$ for cycling.

The galvanostatic charge-discharge profiles of the v-LVO and c-LVO electrodes are illustrated in Figures 3c and 3d. The initial discharge process can be categorized into three distinct regions: (i) a potential drop above 1.0 V (vs. Li/Li^+); (ii) two continuous plateaus around the potentials of 0.75 V and 0.60 V (vs. Li/Li^+); and (iii) a subsequent decline towards the low cut-off potential. The first plateau corresponds to the reduction of V^{5+} to V^{4+} , while the following

plateau is associated with the further reduction to V^{3+} , consistent with the results from CV. In the charge profile and subsequent cycles, the reversible plateaus are less discernible, which may be due to the nanosize effect that minimizes the potential gap between the two-phase transitions.^{30,31} However, as indicated in the inset, the dQ/dV plots effectively highlight these transition steps. The v-LVO electrode achieves a specific discharge capacity of $1153.9 \text{ mAh}\cdot\text{g}^{-1}$

and a specific charge capacity of 726.4 mAh·g⁻¹, yielding a Coulombic efficiency (CE) of 62.8%. In comparison, the first specific discharge and charge capacities for the c-LVO electrode are 441.8 mAh·g⁻¹ and 263.5 mAh·g⁻¹, respectively, resulting in a first CE of 59.6%. The relatively low CE observed in both electrodes can be attributed to the irreversible formation of the SEI layer. The lower CE of the c-LVO electrode is linked to its diminished kinetic characteristics, which contribute to a thicker SEI layer. In contrast, the v-LVO electrode demonstrates a higher specific capacity of 590.8 mAh·g⁻¹ - 2.6 times greater than that of the c-LVO electrode - and retains 81.3% of its capacity after 50 cycles. The impedance behavior of these electrodes was investigated using EIS techniques, and the obtained Nyquist plots are shown in Figure 3f.

Accordingly, the Nyquist plots perform a semi-circle characterized by the charge transport resistance, and a linear tail indicating diffusion properties. As shown in Figure 3f, the v-LVO electrode exhibits a semicircle with a smaller diameter, indicating improved charge transfer kinetics compared with the c-LVO electrode. This observation is correlated to the reduction in particle size, resulting in enhanced electrical contact and shortening the charge transport pathway, as mentioned above. The recent results of v-LVO are comparable with other publications, as shown in Table 2. The enhanced electrochemical performance of the v-LVO can be ascribed to improved kinetic properties resulting from the nanosize control achieved through the vapor-assisted SSR method.

Table 2. A comparison of the electrochemical performance of Li₃VO₄ nanorod-carbon composite and other related anode materials. (LVO = Li₃VO₄)

Materials	Synthesis method	Operating potential window (V, vs. Li/Li ⁺)	Specific current (mA·g ⁻¹)	Specific capacity (mAh·g ⁻¹) – cycle	Retention (%)	Ref.
LVO/rGO	solvothermal	0 – 3.0	150	410.7 – 200	69.3	32
Facet-controlled LVO	Rapid hydrothermal	0.2 – 3.0	25	315.0 – 50	-	33
LVO@C	Freeze drying, sintering and water etching	0.01 – 3.0	200	850.8 – 150	-	34
LVO@C	Sol-gel method	0.2 – 3.0	100	299.0 – 100	99	35
W ⁶⁺ -doped LVO	Spray-drying and sintering	0.2 – 3.0	40	305.8 – 200	91.4	7
Sm-doped LVO/C	Sol-gel and carbonization	0.2 – 3.0	100	379.5 – 50	93.7	6, 36
Ge-doped γ-LVO	Calcination	0.2 – 3.0	2000	383.0 – 1500	111.5	36
1D-LVO/Carbon fiber	Chemical vapor deposition	0 – 3.0	200	516.2 – 100	-	12
LiNbO ₃ -coated LVO	Sol-gel and calcination	0.05 – 2.5	40	481.0 – 100	90	14
LVO mesocube	Solid-state reaction and hydrothermal	0.02 – 3.0	200	262.6 – 500	97.5	17
LVO@C	Calcination	0.01 – 3.0	150	855.0 – 300	-	37
LVO nanoparticles	Vapor-assisted solid-state reaction	0.2 – 3.0	100	590.8 – 50	81.3%	This work

4. CONCLUSIONS

In this work, Li_3VO_4 is prepared using both conventional and vapor-assisted SSR methods. A comparative study has been conducted to demonstrate the ability of the vapor-assisted SSR in the synthesis of pure-phase Li_3VO_4 under ambient conditions. The phase transformation of Li_3VO_4 during vapor-assisted SSR progression has been investigated using ex-situ XRD and Raman spectroscopy, demonstrating that the product phase appears at a slow reaction rate at the beginning of the procedure, and the reaction does not complete until at least 240 minutes. Meanwhile, the morphological evolution of Li_3VO_4 throughout vapor-assisted SSR has been monitored using the FE-SEM technique, elucidating the slow etching of LiOH over the V_2O_5 surface, from polyhedrons to long strings, until the accumulation of nanospheres. The enhanced electrochemical properties of vapor-prepared materials are attributed to the nanosize effect, which is beneficial for both lithium-ion and electron transport, thereby accelerating the kinetics of electrode reactions.

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Tổng hợp composite $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ làm chất xúc tác quang hiệu năng cao phân hủy methylene blue

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TÓM TẮT

Trong nghiên cứu này, vật liệu composite $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ được tổng hợp bằng cách chuẩn bị riêng biệt hai thành phần $\text{g-C}_3\text{N}_4$ và $\text{Co}_2[\text{Fe}(\text{CN})_6]$, sau đó kết hợp chúng thông qua quá trình phân tán $\text{Co}_2[\text{Fe}(\text{CN})_6]$ lên bề mặt $\text{g-C}_3\text{N}_4$ ở 90 °C trong 1 giờ. Các vật liệu thu được được đặc trưng bằng các kỹ thuật nhiễu xạ tia X (XRD), phổ hồng ngoại biến đổi Fourier (FT-IR), phổ tán xạ năng lượng tia X (EDS), hiển vi điện tử quét (SEM), phổ phản xạ khuếch tán UV-Vis (UV-Vis DRS) và phổ phát quang (PL). Hiệu suất xúc tác quang của vật liệu composite được đánh giá thông qua quá trình phân hủy methylene blue (MB) trong dung dịch nước dưới chiếu xạ ánh sáng mặt trời. Vật liệu composite $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ cho thấy hoạt tính xúc tác quang vượt trội so với từng thành phần riêng lẻ là $\text{g-C}_3\text{N}_4$ và $\text{Co}_2[\text{Fe}(\text{CN})_6]$.

Từ khóa: $\text{Co}_2[\text{Fe}(\text{CN})_6]$, $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$, photocatalytic activity, methylene blue, sunlight.

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Synthesis of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite as an improved photocatalyst for degradation of methylene blue

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ABSTRACT

In this study, the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite was synthesized by first preparing $\text{g-C}_3\text{N}_4$ and $\text{Co}_2[\text{Fe}(\text{CN})_6]$ separately, followed by their coupling through the dispersion of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ onto $\text{g-C}_3\text{N}_4$ at 90°C for 1 hour. The resulting materials were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), energy-dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), and photoluminescence (PL) spectroscopy. The photocatalytic performance of the composite was evaluated via the degradation of methylene blue (MB) in aqueous solution under sunlight irradiation. The $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite exhibited superior photocatalytic activity compared to the individual components, $\text{g-C}_3\text{N}_4$ and $\text{Co}_2[\text{Fe}(\text{CN})_6]$.

Keywords: $\text{Co}_2[\text{Fe}(\text{CN})_6]$, $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$, photocatalytic activity, methylene blue, sunlight.

1. INTRODUCTION

Faced with the growing reality of seriously polluted water sources that threaten both public health and the environment, various technologies have been developed for wastewater treatment. However, conventional methods often fail to completely eliminate toxic contaminants and typically require substantial energy inputs.¹ To align with the principles of sustainable chemistry, it is essential to develop more efficient reaction conditions and advanced catalytic systems for pollutant removal, thereby ensuring water quality.² Photocatalysis is a light-driven chemical

process that occurs when a photocatalyst is activated under light irradiation. This technique has attracted considerable attention due to its simplicity, cost-effectiveness, non-toxicity, high degradation efficiency, and long-term stability. It is widely recognized as a promising strategy for wastewater treatment and environmental protection.³

In recent years, semiconductor materials such as TiO_2 , ZnO , SnO_2 , $\text{g-C}_3\text{N}_4$, and perovskites have been extensively investigated for photocatalytic applications in environmental remediation. Among emerging photocatalysts,

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$\text{Co}_x[\text{Fe}(\text{CN})_6]_y$ has attracted growing attention and is gradually demonstrating its potential in photocatalysis, showing promise as a candidate for broad environmental applications.

Despite its outstanding advantages—such as strong visible-light absorption, non-toxicity to humans and other organisms, absence of secondary pollution, and ease of recyclability— $\text{Co}_x[\text{Fe}(\text{CN})_6]_y$ exhibits a major limitation: its high solubility in aqueous media. This characteristic poses significant challenges for its synthesis and practical application.

In 2013, Dwivedi et al.⁴ employed gel beads containing cobalt hexacyanoferrate immobilized on micrometer-sized alginate beads (a salt of alginic acid, $(\text{C}_6\text{H}_8\text{O}_6)_n$) as an adsorbent material for the removal of radioactive contaminants—such as cesium, an element with a half-life spanning several decades—from aqueous solutions. In 2016, K. A. Lin et al.⁵ successfully synthesized a series of Prussian blue analogues with the general formula $\text{M}(\text{II})_3[\text{M}(\text{III})(\text{CN})_6]_2$ ($\text{M}^{2+} = \text{Co}, \text{Cu}, \text{Fe}, \text{Mn}, \text{Ni}$; $\text{M}^{3+} = \text{Co}, \text{Fe}$), which exhibited high photocatalytic activity. These materials were capable of efficiently degrading Rhodamine B (RhB) in aqueous solution when activated by peroxymonosulfate (PMS) under neutral conditions. Cobalt-based Prussian blue analogues (PBAs) have shown great potential as efficient catalysts for water-splitting reactions and the degradation of organic pollutants. Moreover, the Co–Fe PBAs retain their original crystalline structure even after multiple recycling cycles, indicating excellent structural stability.

Several studies have employed metal-containing complexes and their isomers as polymeric materials. These isomeric complexes often crystallize in cubic structures and feature metal ions in varying oxidation states.⁶ The frameworks of these complexes possess porous structures, which endow them with a high specific surface area, excellent adsorption capacity, and numerous catalytic active sites. As a result, such

complexes have been extensively studied across various fields, particularly in photocatalysis.⁷ Therefore, the modification of these complexes with semiconductors to develop novel materials exhibiting enhanced photocatalytic activity has attracted significant attention from researchers.

2. EXPERIMENTS

2.1. Chemicals

Chemicals were purchased from Sigma-Aldrich (Germany) with high purity, including cobalt sulfate (CoSO_4 , $\geq 99.0\%$), potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$, $\geq 98.5\%$), melamine ($\text{C}_3\text{H}_6\text{N}_6$, $\geq 99.0\%$), methylene blue hydrate ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot x\text{H}_2\text{O}$, $\geq 97.0\%$), and ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.9\%$). All chemicals were used without further purification.

2.2. Materials preparation

2.2.1. Synthesis of $\text{g-C}_3\text{N}_4$: Five grams of melamine were ground in an agate mortar and then transferred to a porcelain crucible. The crucible was tightly covered with aluminum foil to minimize sublimation and enhance the condensation efficiency of $\text{g-C}_3\text{N}_4$. The sample was heated in a muffle furnace at 550°C for 2 hours with a heating rate of $10^\circ\text{C}/\text{min}$. After natural cooling to room temperature, the resulting product—yellowish in color—was collected and labeled as $\text{g-C}_3\text{N}_4$.

2.2.2. Synthesis of $\text{Co}_2[\text{Fe}(\text{CN})_6]$: 5 milliliters of 0.2 M CoSO_4 solution were added to a 200 mL glass beaker. Then, 100 mL of $0.05\text{ M K}_4[\text{Fe}(\text{CN})_6]$ solution were gradually added at a rate of $5\text{ mL}/\text{min}$ under continuous stirring at room temperature. A precipitate formed during the addition. The mixture was stirred for an additional 60 minutes, followed by ultrasonic treatment at 90°C for 2 hours. The resulting solid was collected by centrifugation and washed repeatedly with distilled water until the pH of the filtrate reached 7. Finally, the sample was dried at 80°C for 48 hours. The final product was identified as $\text{Co}_2[\text{Fe}(\text{CN})_6]$.

2.2.3. Synthesis of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite: Cobalt sulfate (CoSO_4) was dissolved in deionized water under stirring until fully dissolved. A suitable amount of $\text{g-C}_3\text{N}_4$ powder was then added to the solution, followed by stirring and ultrasonication for 60 minutes at room temperature to promote the adsorption of Co^{2+} ions onto the $\text{g-C}_3\text{N}_4$ surface. The resulting suspension was centrifuged to collect the solid. Subsequently, a $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution (with a mass ratio of $\text{K}_4[\text{Fe}(\text{CN})_6]$ to $\text{g-C}_3\text{N}_4$ of 1:3) was added to the solid under continuous stirring at 90 °C for 60 minutes to allow in situ formation of the $\text{Co}_2[\text{Fe}(\text{CN})_6]$ framework on the $\text{g-C}_3\text{N}_4$ matrix. The product was separated by centrifugation, washed thoroughly, and dried at 80 °C for 48 hours to yield a blue solid of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer equipped with a Cu K α radiation source ($\lambda = 1.540 \text{ \AA}$), operating at 30 kV and 0.01 A. Fourier-transform infrared (FTIR) spectra were obtained using a PerkinElmer GX spectrometer. The morphology and elemental composition of the samples were examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a Nova Nano SEM 450 system. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were measured using a Jasco V-770 spectrophotometer, while photoluminescence (PL) spectra were recorded on a Horiba Jobin Yvon FL322 fluorescence spectrometer. The concentration of MB solution was determined by a photometric method using a Jenway 6800 UV–Vis spectrophotometer.

2.4. Photocatalytic activity

The adsorption equilibrium time of MB on the materials was investigated under dark conditions using the following procedure. A total of 0.07 g of the material sample was added to a 250 mL beaker containing 120 mL of MB solution (10 mg/L). The beaker was covered with a

wooden enclosure to prevent light exposure and continuously stirred using a magnetic stirrer. At 30-minute intervals, 8 mL of the suspension was withdrawn, centrifuged to separate the supernatant, and the resulting solution was transferred into a vial. The collected samples were labeled as $t_0, t_1, t_2, \dots, t_8$, corresponding to sampling times of 0, 30, 60, ..., and 240 minutes.

The adsorption capacity is calculated using the following equation:

$$q = \frac{(C_i - C_f) \cdot V}{m}$$

where q : adsorption capacity at a given time (mg/g); C_i : initial concentration of the solution (mg/L); C_f : concentration of the solution at the given time (mg/L); V : volume of the solution subjected to adsorption (L); m : mass of the adsorbent (g).

A plot of adsorption capacity versus time was drawn to determine the time required to reach adsorption equilibrium. Following the adsorption study, the sample was further exposed to sunlight to evaluate its photocatalytic activity. The degradation efficiency of MB by the materials was calculated using the following equation:

$$H = \frac{C_0 - C_t}{C_0} \times 100\%$$

where C_0 and C_t are the MB concentrations at the initial and selected t -times, respectively.

3. RESULTS AND DISCUSSIONS

3.1. Material characterization

The $\text{Co}_2[\text{Fe}(\text{CN})_6]$, $\text{g-C}_3\text{N}_4$, and $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ samples were characterized by XRD, FTIR, and SEM techniques.

As shown in Figure 1a, the XRD pattern of the $\text{Co}_2[\text{Fe}(\text{CN})_6]$ sample displays distinct diffraction peaks at $2\theta = 25.27^\circ, 35.92^\circ, 44.45^\circ, 51.53^\circ, 54.01^\circ, \text{ and } 58.38^\circ$, which correspond to the (220), (400), (422), (440), (620), and (622) crystal planes, respectively. These results

are in good agreement with previous reports on $\text{Co}_2[\text{Fe}(\text{CN})_6]$. $\text{Co}_2[\text{Fe}(\text{CN})_6]$ exhibits high crystallinity with characteristic diffraction peaks corresponding to the Prussian blue analogue (PBA) phase, in accordance with JCPDS card No. 77-1161.⁸⁻¹⁰ The formation of the PBA-type $\text{Co}_2[\text{Fe}(\text{CN})_6]$ material from its precursors can be represented by the following reaction equation:

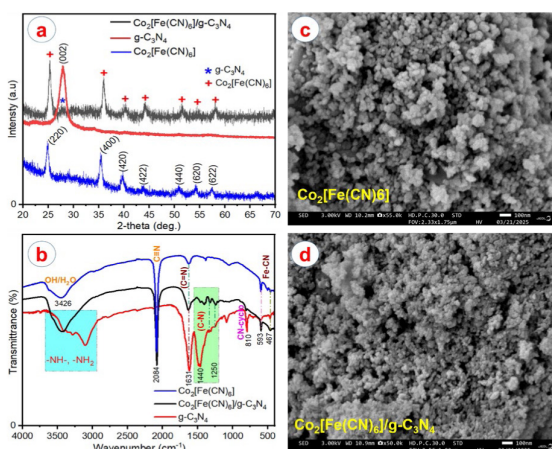
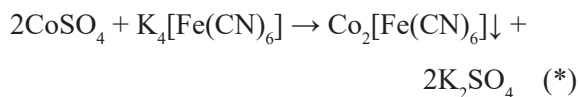


Figure 1. (a) XRD patterns; (b) FTIR spectra; (c, d) SEM images of $\text{Co}_2[\text{Fe}(\text{CN})_6]$, $\text{g-C}_3\text{N}_4$, and the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite.

The XRD pattern of pure $\text{g-C}_3\text{N}_4$ exhibits a prominent diffraction peak at $2\theta = 27.4^\circ$, which corresponds to the (002) crystal plane. This peak is attributed to the interlayer stacking of conjugated aromatic systems in the graphitic carbon nitride structure. The $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite clearly exhibits the characteristic diffraction peaks of both constituent materials, $\text{Co}_2[\text{Fe}(\text{CN})_6]$ and $\text{g-C}_3\text{N}_4$. Moreover, no additional crystalline phases are detected, indicating that the composite consists solely of these two components. This result is consistent with previously reported studies on PBA/ $\text{g-C}_3\text{N}_4$ materials.⁸

The FTIR spectra of the samples are presented in Figure 1b. The $\text{g-C}_3\text{N}_4$ sample exhibits a distinct absorption band at 810 cm^{-1} , which is attributed to the out-of-plane

bending vibration of C–N bonds within the tri-s-triazine (heptazine) units—the fundamental structural motifs of the graphitic carbon nitride framework.^{11,12} The sharp absorption bands in the region of $1250\text{--}1631\text{ cm}^{-1}$ are attributed to the stretching vibrations of C–N and C=N bonds within the aromatic rings of the heptazine-based structure.^{13,14} In addition, a broad absorption band in the range of $3100\text{--}3400\text{ cm}^{-1}$ is observed, which is attributed to the stretching vibrations of –NH– and –NH₂ groups originating from the incompletely condensed structure of $\text{g-C}_3\text{N}_4$. The FTIR spectrum of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ displays several characteristic absorption bands. A strong and sharp peak at 2084 cm^{-1} is attributed to the stretching vibration of the C≡N bond in the cyanide ligands, while a prominent band at 593 cm^{-1} corresponds to the bending vibration of the same group. Additionally, the absorption band at 467 cm^{-1} is ascribed to the stretching vibration of the Fe–CN bond,^{15,16} confirming the metal–ligand coordination typical of Prussian Blue analogues (PBAs). Furthermore, a broad absorption band centered around 3426 cm^{-1} is associated with the –OH stretching vibration of water molecules adsorbed on the material surface. For the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite, the characteristic peaks corresponding to both $\text{g-C}_3\text{N}_4$ and $\text{Co}_2[\text{Fe}(\text{CN})_6]$ were clearly observed, indicating the successful integration of the two components. In particular, the intense absorption band at 2084 cm^{-1} (assigned to the –C≡N stretching vibration) remained prominent, while the C–N and C=N stretching vibrations of $\text{g-C}_3\text{N}_4$ were also retained. These observations confirm that the key structural features of both phases were preserved in the composite. Moreover, the absence of new absorption bands or significant peak shifts suggests that the interaction between $\text{Co}_2[\text{Fe}(\text{CN})_6]$ and $\text{g-C}_3\text{N}_4$ is primarily physical in nature, possibly involving electrostatic attractions or hydrogen bonding. This result is in good agreement with the XRD data.

The SEM images of the $\text{Co}_2[\text{Fe}(\text{CN})_6]$ sample (Figure 1c) and the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite (Fig. 1d) reveal distinct

morphological characteristics. The pristine $\text{Co}_2[\text{Fe}(\text{CN})_6]$ exhibits a granular morphology composed of irregularly shaped, densely packed nanoparticles with a pronounced tendency toward agglomeration. The surface of the material appears relatively rough and compact, which may limit the accessibility of active sites for catalytic processes. In contrast, the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite exhibited a more porous architecture with significantly reduced particle agglomeration. The nanoparticles were more uniformly dispersed, with increased interparticle voids, likely attributed to the structural support provided by the $\text{g-C}_3\text{N}_4$ matrix. This morphology suggests enhanced textural properties, such as a larger specific surface area and improved accessibility to active sites-factors that are critical for adsorption and photocatalytic performance. The morphological differences between the two samples provide clear evidence for the successful incorporation of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ into the $\text{g-C}_3\text{N}_4$ matrix. This integration effectively suppresses excessive particle agglomeration, enhances interfacial contact, and facilitates charge transfer during the photocatalytic process. These observations are consistent with the XRD and FTIR analyses, further confirming the formation of a structurally and functionally synergistic composite material.

The EDS spectra in Figure 2 and Table 1 confirm the elemental composition of the samples.

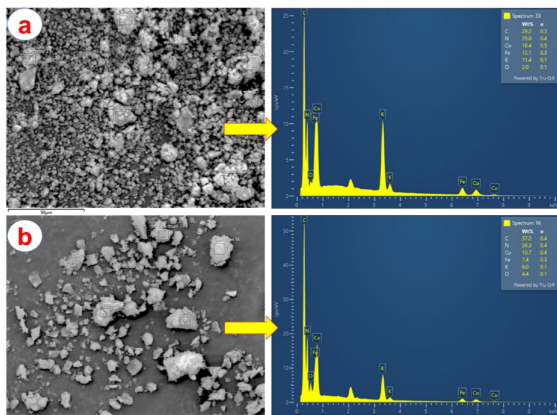


Figure 2. EDS spectra of (a) the $\text{Co}_2[\text{Fe}(\text{CN})_6]$ sample and (b) the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite.

Both the $\text{Co}_2[\text{Fe}(\text{CN})_6]$ and $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ samples exhibit characteristic peaks of Co, Fe, C, and N, consistent with the expected structure of Prussian Blue analogues (PBA). Additionally, minor signals of K and O are observed. The presence of K is attributed to residual $\text{K}_4[\text{Fe}(\text{CN})_6]$ precursor, while the O signal likely originates from surface-adsorbed moisture (H_2O). In the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite, the increased intensities of C and N peaks are ascribed to the contribution of the $\text{g-C}_3\text{N}_4$ matrix, while the decreased Co and Fe contents suggest effective dispersion of the PBA phase on the $\text{g-C}_3\text{N}_4$ surface. These findings confirm the successful formation of the composite material.

Table 1. Elemental composition of $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ and $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2/\text{g-C}_3\text{N}_4$.

$\text{Co}_2[\text{Fe}(\text{CN})_6]$		$\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$	
Element	Weight %	Element	Weight %
C	29.2	C	37.2
N	29.0	N	34.3
Co	16.4	Co	10.7
Fe	12.1	Fe	7.4

The EDS-mapping (Figure 3a) results show that Co, Fe, C, and N elements are uniformly distributed across the sample surface, indicating the successful integration and homogeneous dispersion of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ within the $\text{g-C}_3\text{N}_4$ matrix. No significant aggregation or phase separation was observed, suggesting strong interfacial compatibility between the two components. This uniform distribution supports the structural integrity of the composite and correlates well with the results obtained from XRD, FTIR, and SEM, reinforcing the successful synthesis of a well-dispersed hybrid photocatalyst.

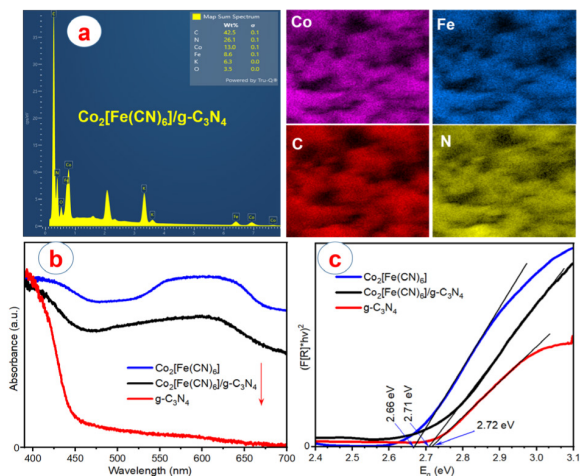


Figure 3. (a) Elemental mapping images of Co, Fe, C, and N for the Co₂[Fe(CN)₆]/g-C₃N₄ composite, (b) UV-Vis DRS spectra and (c) band gap energy of the materials.

The UV-Vis DRS (Figures 3b,c) reveal that all the materials exhibit absorption edges within the visible light region. Notably, the Co₂[Fe(CN)₆] and Co₂[Fe(CN)₆]/g-C₃N₄ samples show extended absorption edges reaching up to approximately 700 nm, which is consistent with the characteristic charge transfer transitions between Fe(II) and Fe(III):¹⁷



The band gap energy (E_g) of the materials was also estimated using this method. Accordingly, the band gap values of Co₂[Fe(CN)₆], g-C₃N₄, and the Co₂[Fe(CN)₆]/g-C₃N₄ composite were determined to be 2.66 eV, 2.72 eV, and 2.71 eV, respectively.

3.2. Photocatalytic activity

The photocatalytic performance of the materials was evaluated through the degradation of MB under sunlight irradiation, with the results illustrated in Figure 4a. After 210 minutes of exposure, the Co₂[Fe(CN)₆]/g-C₃N₄ composite exhibited a degradation efficiency of 93.38%, outperforming both pristine g-C₃N₄ and Co₂[Fe(CN)₆] (Figure 4b). In addition, to compare the MB degradation rates among the materials, the photodegradation kinetics were analyzed (Figure 4c and Table 2). Under identical

illumination conditions, the degradation rate of MB using the Co₂[Fe(CN)₆]/g-C₃N₄ composite was approximately five times higher than that of Co₂[Fe(CN)₆] and more than 19 times higher than that of pristine g-C₃N₄. This significant enhancement is attributed to the effective suppression of the rapid recombination of photogenerated electron-hole pairs, a common limitation in single-component g-C₃N₄ photocatalysts, as confirmed by the photoluminescence (PL) spectrum shown in Figure 4d.

Table 2. Results of MB degradation by the materials.

Materials	Photodegradation (%)	Rate constant, k (min ⁻¹)	Regression coefficient (R ²)
g-C ₃ N ₄	13.91	0.06.10 ⁻²	0.95
Co ₂ [Fe(CN) ₆]	38.74	0.24.10 ⁻²	0.99
Co ₂ [Fe(CN) ₆]/g-C ₃ N ₄	93.38	1.16.10 ⁻²	0.98

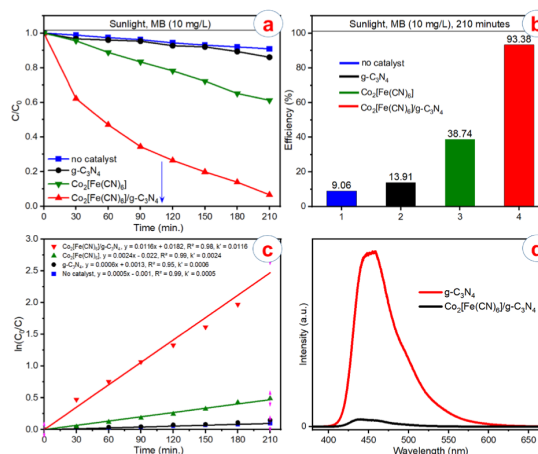


Figure 4. (a-c) Photocatalytic degradation of MB over Co₂[Fe(CN)₆], g-C₃N₄, and Co₂[Fe(CN)₆]/g-C₃N₄; (d) PL spectra of the corresponding materials.

The photoluminescence (PL) spectra of g-C₃N₄ and the Co₂[Fe(CN)₆]/g-C₃N₄ composite were recorded under 365 nm excitation to evaluate the separation and recombination behavior of photoinduced electron-hole pairs (e⁻/h⁺). In the spectrum, pristine g-C₃N₄ exhibits a strong emission peak around 400–550 nm,

which is indicative of the rapid recombination of photogenerated charge carriers. Notably, the PL intensity of the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite is significantly quenched compared to pure $\text{g-C}_3\text{N}_4$. This pronounced reduction in emission intensity suggests that the incorporation of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ effectively suppresses the recombination of charge carriers. As an efficient electron acceptor, $\text{Co}_2[\text{Fe}(\text{CN})_6]$ facilitates charge transfer and enhances charge separation at the heterojunction interface with $\text{g-C}_3\text{N}_4$. In summary, the PL analysis confirms that the formation of the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite improves electron-hole separation and reduces charge recombination, thereby enhancing the photocatalytic performance by making more charge carriers available for surface reactions. This property broadens the potential applications of the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite in the field of photocatalysis.

3.3. Photocatalytic reaction mechanism

To investigate the photocatalytic reaction mechanism, various scavengers were employed to identify the main reactive species involved. Tert-butyl alcohol (TBA) was used as a scavenger for hydroxyl radicals ($\cdot\text{OH}$), 1,4-benzoquinone (BQ) for superoxide radical anions ($\cdot\text{O}_2^-$),

ammonium oxalate (AO) for photogenerated holes (h^+), and dimethyl sulfoxide (DMSO) for photogenerated electrons (e^-).¹⁸ A quenching agent solution with an initial concentration of 10 mmol/L and a volume of 2 mL was added at the onset of light irradiation. As shown in Figure 5a, the presence of TBA and AO led to a noticeable decrease in the photocatalytic degradation of MB by the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite, compared to the control sample without any scavenger. This can be attributed to the quenching effects of ammonium oxalate (AO) on photogenerated holes (h^+) and of 1,4-benzoquinone (BQ) on superoxide radical anions ($\cdot\text{O}_2^-$), which significantly suppressed the activity of these reactive species in solution and thus reduced photocatalytic efficiency. These findings suggest that h^+ and $\cdot\text{O}_2^-$ are the primary active species responsible for the MB degradation process. Thus, the integration of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ and $\text{g-C}_3\text{N}_4$ into a composite structure resulted in $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$, which possesses critical properties for facilitating the generation of h^+ and $\cdot\text{O}_2^-$ radicals, while simultaneously suppressing the recombination of photogenerated electron-hole pairs during the photocatalytic degradation of MB.

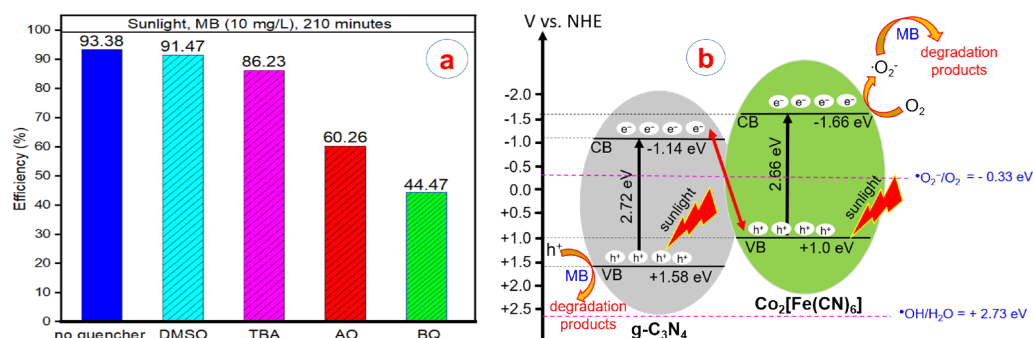


Figure 5. (a) Photocatalytic degradation of MB on $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ in the presence of various scavengers, and (b) Proposed Z-scheme mechanism for the photocatalytic activity of the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{g-C}_3\text{N}_4$ composite.

The valence band (VB) and conduction band (CB) positions of $\text{g-C}_3\text{N}_4$ and $\text{Co}_2[\text{Fe}(\text{CN})_6]$ can be estimated using the following equations:

$$E_{\text{VB}} = \chi - E^{\text{e}} + 0.5E_{\text{g}}$$

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}}$$

where χ is the absolute electronegativity of the semiconductor (defined as the arithmetic mean of the electron affinity and the first ionization energy of the constituent atoms), E^{e} is the energy of free electrons on the hydrogen scale (4.5 eV), and E_{g} is the band gap energy of the semiconductor.

According to Wu et al.,¹⁹ the absolute electronegativity (χ) of g-C₃N₄ is 4.72 eV. Based on Mulliken's theory, the electronegativity χ of a semiconductor can be accurately calculated using the following formula:

$$\chi = E_{\text{vacuum}} - \frac{E_g}{2}$$

Applied to Co₂[Fe(CN)₆]:

+ $E_g \approx 2.66$ eV (as determined from the UV-Vis DRS spectra);

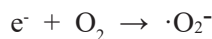
$$+ E_{\text{vacuum}} \approx 5.5 \text{ eV}.^{20}$$

The calculated absolute electronegativity (χ) is 4.17 eV.

Based on the calculations, the conduction band (CB) and valence band (VB) edge potentials of g-C₃N₄ are estimated to be -1.14 eV and +1.58 eV, respectively. Similarly, the CB and VB edge potentials of Co₂[Fe(CN)₆] are calculated to be -1.66 eV and +1.00 eV, respectively.

On this basis, the separation of photogenerated electron-hole pairs and the formation of reactive radicals in the Co₂[Fe(CN)₆]/g-C₃N₄ composite under illumination are illustrated in Figure 5b (Z-scheme). Under light irradiation, both semiconductor materials are photoexcited and generate electron-hole pairs. The photogenerated electrons in the conduction band (CB) of g-C₃N₄ tend to recombine with the holes in the valence band (VB) of Co₂[Fe(CN)₆]. This recombination occurs at the contact interface, leading to the accumulation of electrons in the conduction band (CB) of Co₂[Fe(CN)₆] and holes in the valence band (VB) of g-C₃N₄. Consequently, the photogenerated charge carriers are spatially separated across the two semiconductors, while maintaining strong redox potentials. The electrons in the conduction band (CB) of Co₂[Fe(CN)₆] reduce O₂ to superoxide radicals ($\cdot\text{O}_2^-$), which subsequently contribute to the degradation of MB. In contrast, the holes in the valence band (VB) of g-C₃N₄, due to

their insufficient oxidation potential, are unable to oxidize H₂O to generate hydroxyl radicals ($\cdot\text{OH}$), but can directly oxidize MB molecules. Accordingly, the photocatalytic degradation of MB may involve the following processes:



This mechanism satisfactorily explains the reduced recombination of photogenerated electron-hole pairs on the g-C₃N₄ component of the Co₂[Fe(CN)₆]/g-C₃N₄ composite, as confirmed by the photoluminescence (PL) analysis (Figure 4d) and the photocatalytic performance results (Figure 5a). This suppression of charge carrier recombination subsequently enhances the photocatalytic degradation efficiency of MB by the composite under light irradiation.

4. CONCLUSIONS

Nano-sized Co₂[Fe(CN)₆] and the Co₂[Fe(CN)₆]/g-C₃N₄ composite were successfully synthesized. The corresponding band gap energies were determined to be 2.66 eV for Co₂[Fe(CN)₆], 2.72 eV for g-C₃N₄, and 2.71 eV for the composite. Under natural sunlight irradiation for 210 minutes, the Co₂[Fe(CN)₆]/g-C₃N₄ composite exhibited a photocatalytic degradation efficiency of 93.38% for methylene blue in aqueous solution, significantly outperforming the individual components Co₂[Fe(CN)₆] and g-C₃N₄. The enhanced photocatalytic activity of the composite is mainly attributed to the effective suppression of photogenerated electron-hole recombination. A Z-scheme mechanism for the photocatalytic degradation of methylene blue over the Co₂[Fe(CN)₆]/g-C₃N₄ composite was proposed and discussed in detail by the authors.

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Thu hồi vật liệu từ pin sơ cấp thải để tổng hợp chất xúc tác quang composite trên cơ sở ZnO: vai trò của graphene

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TÓM TẮT

Pin sơ cấp đặc biệt là pin alkaline và Zn-C được sử dụng phổ biến trong các thiết bị điện tử gia dụng nhưng có vòng đời ngắn, chỉ dùng một lần và đang trở thành nguồn rác thải điện tử nguy hại nếu không được xử lý đúng cách. Trong nghiên cứu này, ba composite ZnO/X với chất nền X = graphene, graphitic carbon (g-C₃N₄), và graphene-graphitic carbon (graphene/g-C₃N₄) đã được tổng hợp bằng phương pháp thủy nhiệt với nguồn nguyên liệu ban đầu Zn, và C được thu hồi từ pin sơ cấp thải. Kết quả của phương pháp kính hiển vi điện tử quét (SEM), nhiễu xạ tia X (XRD), hồng ngoại biến đổi Fourier (FT-IR), quang phổ điện tử tia X (XPS), phổ tán xạ năng lượng tia X (EDS) và phổ phản xạ khuếch tán UV-Vis DRS đã làm rõ vai trò của graphene ảnh hưởng lớn đến: (i) khả năng hình thành tinh thể ZnO trên các vật liệu nền, (ii) cấu trúc bề mặt vật liệu đã làm giảm khả năng kết tụ các hạt ZnO, (iii) cải thiện khả năng hấp thụ ánh sáng khả kiến của vật liệu. Ảnh hưởng của graphene đến vật liệu composite được khẳng định thông qua phản ứng phân hủy kháng sinh rifampicin trong vùng ánh sáng khả kiến. Kết quả cho thấy ZnO/graphene có khả năng phân hủy rifampicin gấp 1,5 và 1,7 lần ZnO/graphene/g-C₃N₄ và ZnO/g-C₃N₄ trong cùng điều kiện khảo sát.

Từ khóa: Thu hồi pin sơ cấp thải, composite ZnO, ảnh hưởng graphene.

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Recycling of spent primary batteries for the synthesis of ZnO-based photocatalysts: the role of graphene

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ABSTRACT

Primary batteries, particularly alkaline and zinc-carbon (Zn-C) types, have a relatively short service life and are frequently discarded in landfills, leading to potential environmental risks and health concerns. To address this issue, we synthesized ZnO-based photocatalysts coupled with graphene, graphitic carbon (g-C₃N₄), and a graphene/g-C₃N₄ hybrid via a hydrothermal method, using ZnO, and graphene recovered from spent primary batteries. Techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier Transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance ultraviolet-visible spectroscopy (UV-vis DRS) have been employed to elucidate the strong influence of graphene on the crystal structure, surface morphology, optical characteristics, and photocatalytic performance of the synthesized composites. The results demonstrate that the ZnO/graphene catalyst exhibits 1.5- and 1.7-fold higher rifampicin degradation efficiency than ZnO/graphene/g-C₃N₄ and ZnO/g-C₃N₄ under the same conditions.

Keywords: Recovery spent primary batteries, composite ZnO-based, influence of graphene.

1. INTRODUCTION

The increasing amount of spent batteries, including non-rechargeable and lithium-ion batteries, is a key factor contributing to environmental pollution and health issues. Recently, considerable attention has been given to the recycling of spent primary batteries to recover valuable secondary resources such as Zn, Mn, and graphite, which serves as an effective approach to minimizing risks and mitigating environmental impacts at the end of life.¹⁻³

As a metal oxide semiconductor, ZnO possesses properties such as excellent chemical stability, strong oxidizing capability, and cost-effective production, offering broad

application prospects. However, ZnO absorbs only ultraviolet light due to its large band gap, while its photoexcited electrons and holes undergo rapid recombination, an intrinsic limitation that reduces photocatalytic efficiency.⁴ Consequently, considerable efforts have been made to enhance its optical absorption and photocatalytic activity under illumination with visible light, for example by combining ZnO with graphene or g-C₃N₄.⁵⁻⁷ Nevertheless, the effect of substrate on the structural and optical properties of ZnO-based composites remains unclear. Additionally, comparing the degradation efficiency of rifampicin antibiotic (Rif) under LED light is a practical approach to exploring the role of graphene in boosting the photocatalytic

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efficiency of ZnO/graphene, ZnO/g- C_3N_4 , and ZnO/graphene/g- C_3N_4 .

This work aims to develop a sustainable approach for synthesizing ZnO-based materials from alkaline battery waste, with subsequent applications in photocatalytic reactions. Notably, in this work, graphene was also synthesized from the graphite foil recovered from the spent batteries, further enhancing the sustainability of the process. In particular, the influence of graphene is clarified through various characterization techniques, which reveal its effects on the crystallinity of ZnO on the supporting substrate, the surface morphology, and the visible-light absorption properties.

2. EXPERIMENT

2.1. Material synthesis process

Chemicals

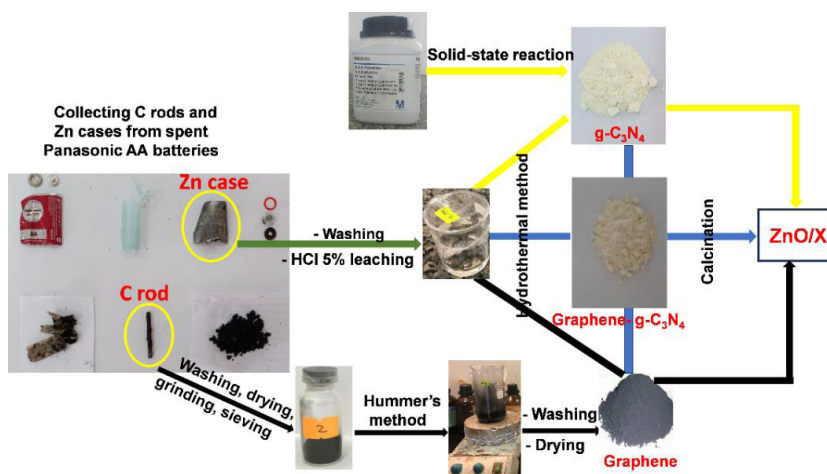
Spent primary Zn-C batteries (Panasonic AA 1.5 V). Sulfuric acid (H_2SO_4 , 98%), sodium nitrate ($NaNO_3$), hydrochloric acid (HCl, 36.5%), hydrogen peroxide (H_2O_2 , 30%), potassium permanganate ($KMnO_4$, 99%) were received from Xilong, China. Melamine ($C_3H_6N_6$, 99%), and rifampicin (95%) were Sigma-Aldrich, German.

Synthesis of composites ZnO/X ($X = \text{graphene}; g-C_3N_4; \text{graphene-}g-C_3N_4$)

- *The substrate X:* graphene was synthesized from the graphite foil of the spent batteries through a modified Hummer's method. In brief, the cell case was carefully dismantled, and the

carbon rod was collected and subsequently washed with distilled water to eliminate residual electrolytes. The graphite foils were initially washed with distilled water, dried, ground, and sieved to obtain graphite powder, which served as the precursor for graphene synthesis. Graphene powder was then produced using the modified Hummer's method, while g- C_3N_4 was prepared through the solid-state reaction of melamine.⁸ Finally, g- C_3N_4 /graphene composite was fabricated via a hydrothermal process, following the procedure reported in our earlier works.⁹

- *The composite ZnO/X* ($X = \text{graphene}; g-C_3N_4; \text{graphene-}g-C_3N_4$) were hydrothermally synthesized in ethanol from a dispersed mixture of as-synthesized *substrate X* and $ZnCl_2$ solution, which was leached from the Zn case of spent primary batteries with HCl 5% acid (Scheme 1). Specifically, 0.5 g of substrate X powder was dispersed to 100 mL of ethanol and stirred for 1 h with a magnetic stirrer to form a homogeneous suspension. Subsequently, 2 mL of $ZnCl_2$ solution was slowly introduced and stirred for an additional 2 h. The mixture was then transferred into a Teflon-lined autoclave and heated at 180 °C for 8 h. The resulting product was centrifuged, thoroughly washed with distilled water and ethanol until neutral pH was reached, dried in air at 80 °C for 12 h, and finally calcined at 300 °C for 2 h. The obtained samples were denoted as ZG, ZN, and ZGN, respectively.



Scheme 1. Illustration of the synthesis reaction for ZnO/X preparation.

2.2. Materials characterization

The crystalline structure was determined by powder X-ray diffraction (Bruker D2 Advance) with Cu-K α radiation ($\lambda = 0.154$ nm), and diffraction data were collected within a 2θ range of $10 - 70^\circ$. Elemental compositions and chemical states were examined by X-ray photoelectron spectroscopy (XPS), with binding energy values referenced to the adventitious carbon C 1s peak at 284.8 eV. Fourier-transform infrared (FT-IR) spectra were recorded on a Shimadzu FTIR-Iffrinity-1S spectrometer (S/N ratio 30000:1) using KBr pellets containing 1 wt% of sample. The morphology and elemental compositions of the obtained materials were analyzed using scanning electron microscopy combined with EDS (SEM, HITACHI S-4800). Optical properties were investigated by UV-Vis diffuse reflectance spectra (DRS) were measured with a Scinco S-4100 spectrophotometer, and absorption spectra were obtained using a Shimadzu UV-1800 instrument.

2.3. Photocatalytic study

The photocatalytic activity of the synthesized materials was evaluated by the degradation of Rifampicin antibiotic. Rif was prepared in a fixed concentration (20 mg/L), and the prepared solution was allowed to settle in the dark for 10 hours. To evaluate the photocatalytic activity, 20 mg of catalyst was dispersed in 80 mL of Rif solution contained in a 250 mL flask and kept in the dark box. The suspension was magnetically stirred for 1 hour to establish adsorption–

desorption equilibrium. Afterwards, the solution was exposed to visible light irradiation from an LED lamp (30 W). At every 10-minute interval, 5 mL of the suspension was collected and centrifuged to separate the catalyst. The remaining Rif concentration in the supernatant was analyzed by a photometric colorimetric method using a Shimadzu 1800 spectrometer.

3. RESULTS AND DISCUSSION

As shown in Figure 1a, the diffraction peaks of the ZG composite appearing at $2\theta = 31.7, 34.4, 36.2, 47.5, 56.6, 62.9,$ and 66.3° are indexed to the (100), (200), (101), (102), (110), (103), and (113) lattice planes of ZnO, which are consistent with the standard JCPDS card No. 36-1451. Moreover, the XRD pattern of the ZG sample shows an additional broadened diffraction peak at $2\theta = 25.9^\circ$ besides the peaks assigned to ZnO, which is the characteristic peak of the (002) plane of graphene.¹⁰ However, comparing the XRD curves of the ZN and ZGN composites with those of ZG, it can be observed that the major peaks are identical to those of g-C₃N₄ at 12.7 and 27.1° . And the weak ZnO-related peaks could be clarified due to the low content of this component. The XRD pattern analysis indicates that the graphene substrate can provides a substrate that facilitates or promotes the growth of well-crystallized ZnO, while g-C₃N₄ likely interacts more strongly with Zn²⁺, suppressing crystallization, resulting in poorly crystalline ZnO nanoparticles that are similar to our observed previous findings on TiO₂-based composites.^{8,11}

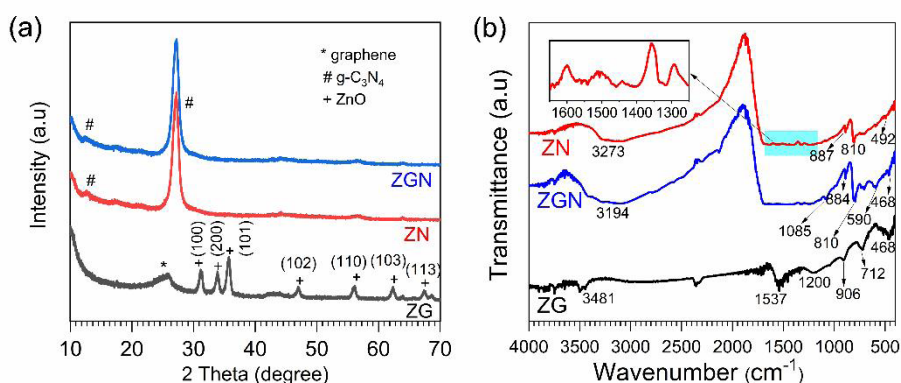


Figure 1. XRD patterns (a) and FTIR spectra (b) of the as-prepared ZG, ZN, and ZGN samples.

FTIR analysis was performed to identify the vibrational bands and displayed in Figure 1b. For ZG, the characteristic bands at 468 cm^{-1} are attributed to Zn–O vibrations, while the broad band around 3481 cm^{-1} is associated with O–H stretching of surface hydroxyl groups. The absorption peaks located at 1537 cm^{-1} and $1200\text{--}906\text{ cm}^{-1}$ can be assigned to C=C and C–O stretching of graphene, respectively. In the cases of ZN and ZGN, the broad band in the region of $3194\text{--}3273\text{ cm}^{-1}$ originates from N–H vibrations and O–H of adsorbed H_2O molecules. The intense peak at 810 cm^{-1} corresponds to the out-of-plane bending of the s-triazine ring in $\text{g-C}_3\text{N}_4$. Moreover, the characteristic bands of CN heterocycles and C–N–C groups between 1250 and 1630 cm^{-1} overlap into a broad band, which becomes more pronounced upon ZnO crystallization, as also observed by Anshu Sharma et al.¹² Additionally, the Zn–O stretching

vibrations appear weak at 468 cm^{-1} (ZGN) and 492 cm^{-1} (ZN), suggesting that ZnO is either poorly crystallized or present in a low amount. This observation is in good agreement with the XRD results.

The UV–vis diffuse reflectance spectra were recorded to investigate the optical characteristics of the composite and their corresponding Tauc plots¹³ were used, and the obtained results are shown in Figure 2. As expected, the ZG sample (Figure 2a) exhibits absorption in the visible region, which can be attributed to the incorporation of graphene into ZnO. For ZN, a bandgap of 2.77 eV is obtained, which is shown in Figure 2b, while the bandgap is 2.62 eV for ZGN (Figure 2c). These results indicate that graphene enhances visible-light absorption and promotes electron–hole separation, thereby improving photocatalytic activity.

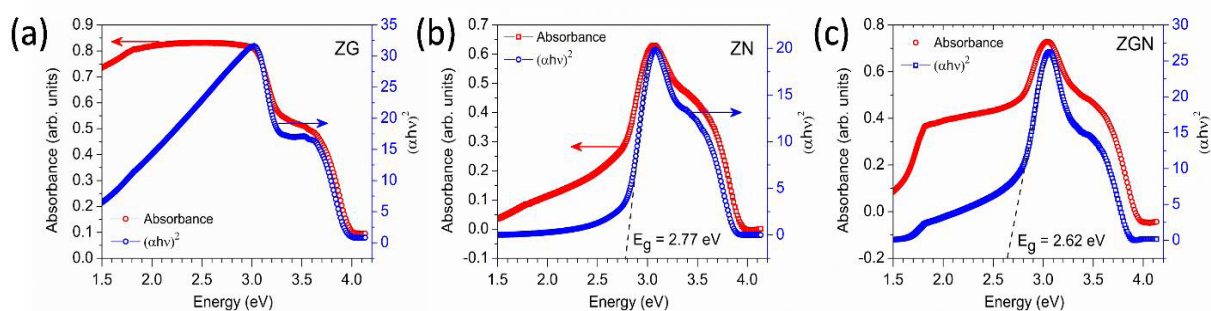


Figure 2. UV-Vis DRS and the associated Tauc plots of ZN (a), ZN (b) and ZGN (c).

The SEM-EDS analysis investigated the morphology and surface elements of the as-synthesized composites, as shown in Figure 3. Distinct morphologies of the ZG, ZN, and ZGN composites were observed, highlighting the influence of graphene incorporation on particle dispersion and surface structure. Figure 3a shows ZnO/graphene with a wrinkled appearance with multiple folds. These highly crumpled structures offer a large surface area and facilitate the uniform anchoring of ZnO nanoparticles. The intimate contact between ZnO and graphene

may promote effective interfacial charge transfer and suppress particle agglomeration, which are essential for enhancing photocatalytic activity. Additionally, the EDS analysis of the ZG sample (Figure 3b) reveals that the major elements are C, O, and Zn, while minor and trace elements such as Ca, Cl, Si, Na, Al, and S are also detected. The presence of these elements is attributed to the use of precursors derived from spent Panasonic AA primary batteries.

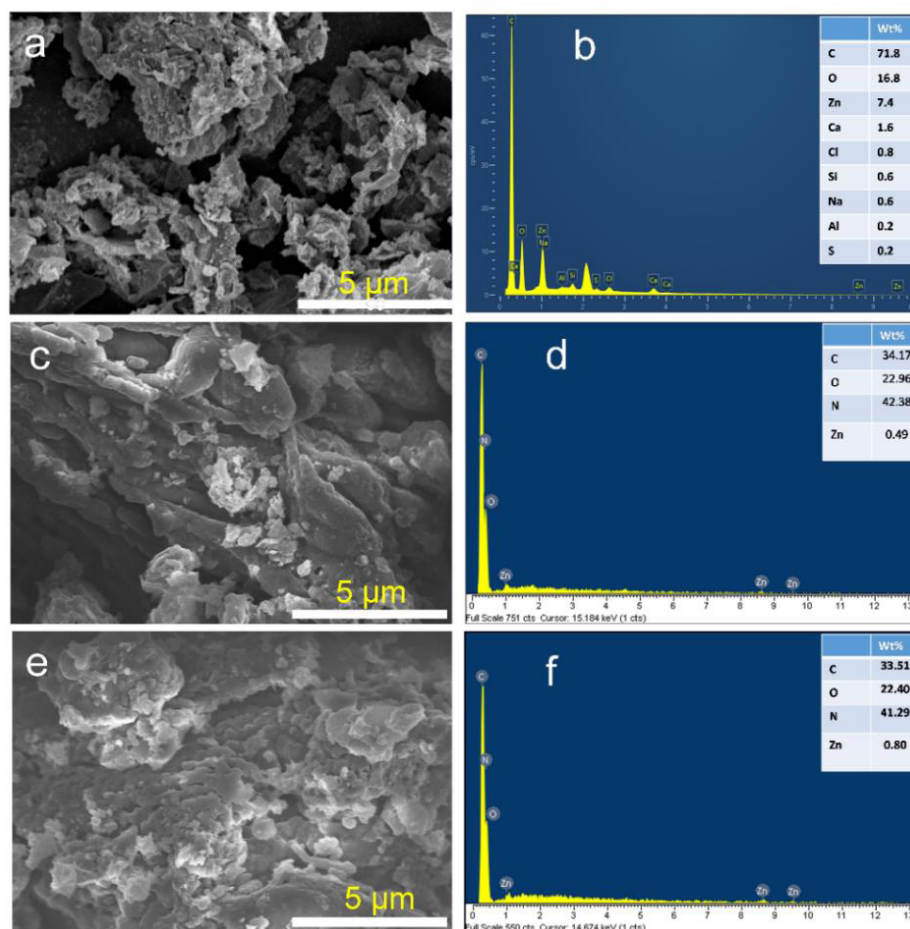


Figure 3. SEM image and EDS of ZG(a, b); ZN (c, d), and ZGN (e, f).

In contrast, the ZN sample (Figure 3c) exhibits a densely aggregated morphology, with irregularly shaped ZnO particles forming compact clusters, resulting in significant particle agglomeration and reduced dispersion. Although a two-dimensional lamella structure with wrinkles and irregular folding structure for ZGN (Figure 3e) is still observed, which suggests partial retention of the graphene structure, the ZnO particles are less uniformly distributed in comparison with ZG. This indicates that the observed morphology suggests less effective suppression of aggregation compared to the ZG sample. Nevertheless, the morphology is improved relative to the ZN composite, implying a moderate enhancement in interfacial interactions. Notably, the Zn content in ZN (0.49 wt%) (Figure 3d) and ZGN (0.80 wt%)

(Figure 3f) is significantly lower than that in ZG (7.4 wt%) (Figure 3b), suggesting that the incorporation of graphene components facilitates higher Zn loading in the ZG composite.

The surface chemical state of ZGN was investigated using the XPS technique. As shown in Figure 4a, the XPS survey spectra include signals of Zn 2p, F 1s, O 1s, N 1s, and C 1s corresponding to the composition of ZnO, graphene, and g-C₃N₄. The presence of fluorine in the composite, as indicated in the XPS survey spectrum, can be attributed to residual fluoride compounds derived from spent primary Panasonic AA batteries. According to Figure 4b, the Zn 2p core-level of the ZnO spectrum has two peaks located at approximately 1044.1 and 1021.1 eV, corresponding to the binding energies

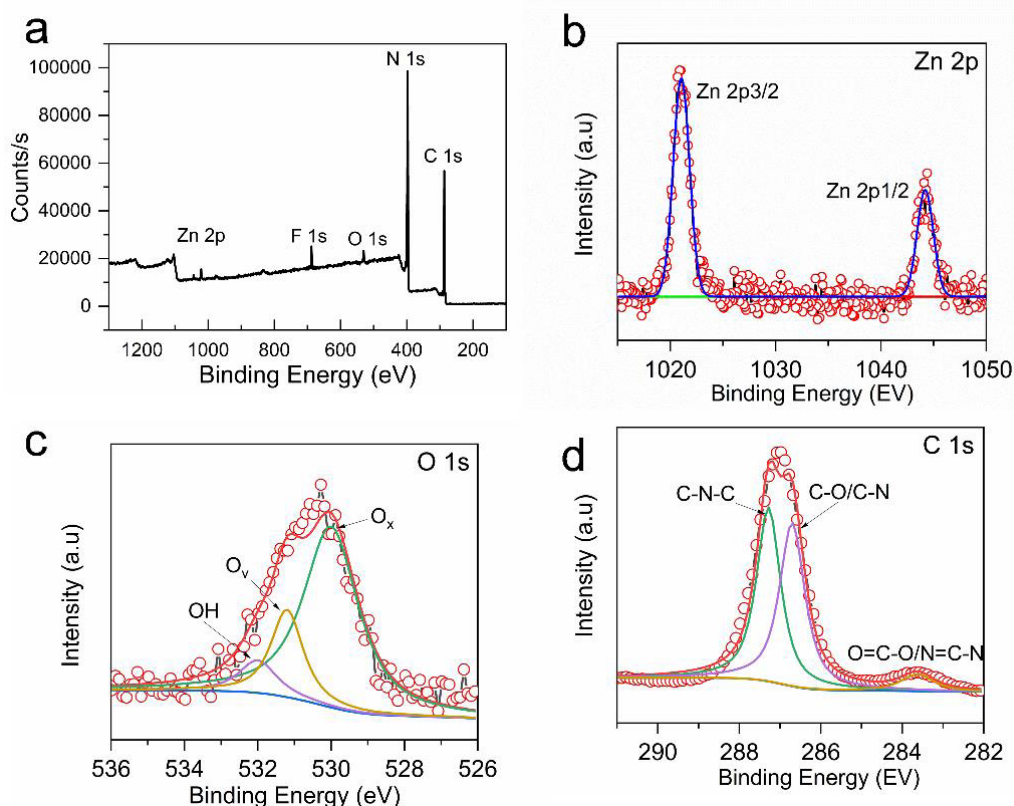


Figure 4. (a) XPS survey of ZGN composite (b) Zn 2p, (c) O 1s, and (d) C 1s spectral regions.

of Zn 2p_{3/2} and Zn 2p_{1/2}, indicating that the chemical valence of Zn at the surface of ZnO is a +2 oxidation state. In the O 1s spectrum (Figure 4c), three peaks are observed at 529.9, 531.2 and 532.0 eV, which can be assigned to oxygen in ZnO lattice (O_x), oxygen vacancies in the ZnO lattice (O_v), and surface hydroxyl groups attached to Zn^{2+} ions (O–OH), respectively. The C 1s spectrum of ZGN (Figure 4d.) indicates C–N–C at 287.3 eV, C=N/C=O at 286.7 eV, and N–C=N/O–C=O at 283.6 eV, respectively.

Figure 5a shows the decrease of Rif concentration as a function of irradiation time by the photocatalysts, including ZN, ZGN, and ZG. In comparison, the concentration of Rif as a function of exposure time in the absence of a catalyst shows virtually no self-degradation. The results demonstrate that, after

60 minutes of light irradiation generated by the LED lamp, the ZN, ZGN, and ZG cause Rif degradation of approximately 25.5%, 27.5%, and 41%, respectively. Additionally, the rate degradation of Rif (Figure 5c) by the highest photocatalytic activity is linked to its enhanced kinetic characteristics for ZG (Figure 5b), which exhibits 1.5 - 1.7 times higher activity than ZGN and ZN individually. Figure 5d shows the absorption spectra for the degradation process of Rif solution of the best with extended time under visible light irradiation. The enhanced photocatalytic performance of the ZG can be attributed to improved kinetic properties resulting from the ZnO content control, the well-distributed and wrinkled graphene-based morphology, and enhanced visible light absorption achieved through the contribution of graphene.

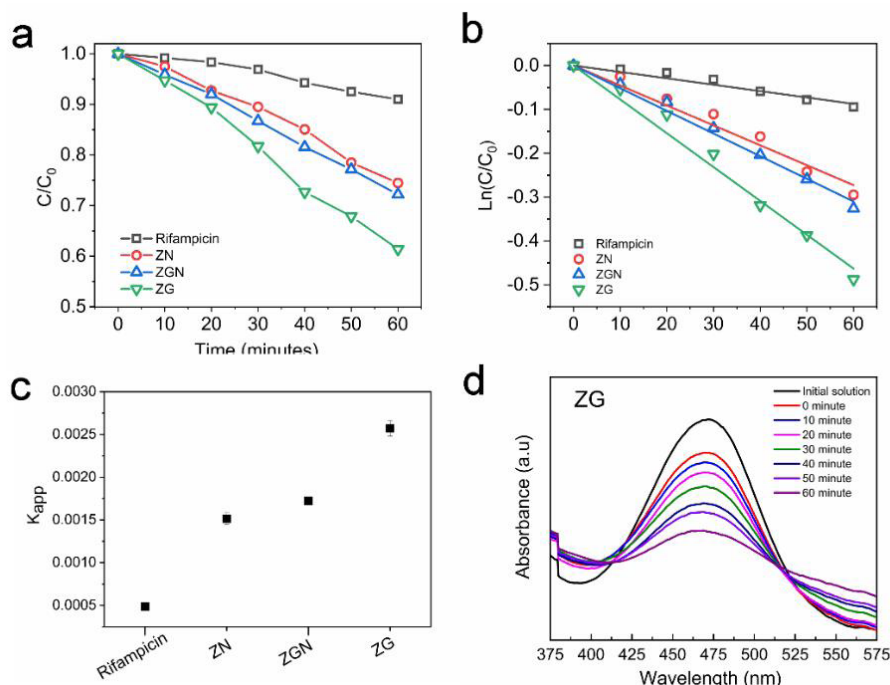


Figure 5. Photocatalytic degradation of Rif in the presence of ZG, ZN, and ZGN photocatalysts (a); the degradation kinetic plots (b); the degradation rate (k_{app}) of Rif obtained for materials (c); and UV-vis absorption spectra of ZG for different irradiation times (d).

4. CONCLUSION

In summary, three ZnO/X (X=graphene, g-C₃N₄, and graphene-g-C₃N₄) photocatalysts were prepared via a hydrothermal method using Zn, C recovered from spent primary batteries, and g-C₃N₄ from melamine. A comparative study has been conducted to demonstrate the role of graphene enhanced visible-light response and charge separation in the synthesis of ZnO-based photocatalysts. It is revealed that graphene provided a more favorable substrate for ZnO crystallization, improved particle dispersion, and enhanced visible light absorption, as confirmed by XRD, IR, SEM-EDS, and UV-Vis DRS. The photocatalytic efficiency of the synthesized materials under visible light exposure, evaluated by the degradation of the antibiotic rifampicin, was highest for the ZG composite, confirming the beneficial effect of graphene in the composite.

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Chế tạo màng cellulose acetate hoạt tính chứa tinh dầu oregano và sodium alginate dùng trong bao bì thực phẩm

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TÓM TẮT

Nghiên cứu này phát triển và đánh giá các màng cellulose acetate (CA) kết hợp với tinh dầu oregano (OEO) và sodium alginate (SA) nhằm ứng dụng làm bao bì thực phẩm hoạt tính. OEO là một chiết xuất thực vật tự nhiên có đặc tính kháng khuẩn và chống oxy hóa, được nhũ hóa bằng cách kết hợp pha dầu và pha nước để tạo thành hỗn hợp ổn định sau đó nhỏ từng giọt có kiểm soát vào gel CA trước khi tạo màng. Các màng được tạo ra bằng phương pháp đúc và được khảo sát hoạt tính chống oxy hóa, khả năng kháng khuẩn, đặc tính cản hơi nước, phổ IR, phân tích nhiệt và hình thái bề mặt. Hoạt tính chống oxy hóa được định lượng bằng phương pháp DPPH (2,2-diphenyl-1-picrylhydrazyl), cho thấy khả năng bắt gốc tự do tăng theo nồng độ, với màng CA/SA/OEO 4.5% đạt hiệu quả 84%. Thử nghiệm kháng khuẩn cho thấy vùng ức chế vi khuẩn là 35 mm đối với *Escherichia coli* và 44 mm đối với *Staphylococcus aureus*. Phân tích bằng kính hiển vi điện tử quét (SEM) cho thấy sự phân bố đồng đều của các giọt nhũ tương giúp cải thiện cấu trúc màng và tăng cường đặc tính cản hơi nước. Những kết quả này cho thấy màng CA chứa tinh dầu oregano là vật liệu phân hủy sinh học đầy hứa hẹn với nhiều chức năng cho ứng dụng bao bì thực phẩm hoạt tính.

Keywords: CA/SA/OEO, oregano, gel nhũ tương, bao bì hoạt tính.

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Preparation of cellulose acetate-based active films containing oregano essential oil and sodium alginate for food packaging

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ABSTRACT

This study developed and evaluated cellulose acetate (CA)-based films incorporating oregano essential oil (OEO) and sodium alginate (SA) for application as active food packaging. OEO, a natural plant extract with known antimicrobial and antioxidant properties, was emulsified by combining oil and water phases to form a stable mixture, which was then added dropwise into the CA gel before film formation. Films were produced using the casting method and investigated for antioxidant and antimicrobial activities, water vapor barrier properties, infrared spectra (IR), thermal behavior, and morphological characteristics. Antioxidant activity was quantified using the DPPH (2,2-diphenyl-1-picrylhydrazyl) assay, which demonstrated a concentration-dependent increase in radical scavenging, with the CA/SA/OEO 4.5% film achieving 84% activity. Antimicrobial assays, which test a material's ability to inhibit the growth of bacteria, indicated inhibition zones of 35 mm against *Escherichia coli* and 44 mm against *Staphylococcus aureus*. Scanning electron microscopy (SEM) analysis showed that uniform dispersion of emulsion droplets improved film structure and enhanced barrier properties. These findings indicate that CA-based films containing oregano essential oils are promising biodegradable and multifunctional materials for active food packaging.

Keywords: *CA/SA/OEO, oregano, emulsion gel, active packaging.*

1. INTRODUCTION

In recent years, food safety has gained significant attention, leading to an increased demand for “natural” antibacterial agents. Essential oils (EOs), derived from plant secondary metabolites, have gained attention as safe and effective natural preservatives due to their broad-spectrum antibacterial properties.¹⁻³ Currently, EOs are utilized in various fields, including food preservation, biomedicine, and cosmetics. Among them, oregano essential oil (*Origanum vulgare*) has been reported to possess strong antibacterial properties, effectively combating pathogens in fruits and food due to its high

concentration of phenolic compounds such as carvacrol and thymol.^{1,2,4}

The development of new, effective, biodegradable, and non-toxic materials for fruit and food preservation films has been attracting increasing attention from researchers.^{5,6} Cellulose acetate (CA) is one of the environmentally friendly polymers widely used in packaging materials, and thus, many studies have focused on creating active films based on this biopolymer.⁷⁻¹⁰ However, CA has some inherent drawbacks such as low flexibility and poor moisture barrier properties, limiting its application in food preservation packaging.

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Sodium alginate (SA) is an anionic polysaccharide with polyhydroxyl and carboxyl groups, typically extracted from brown algae, making it non-toxic and environmentally friendly. SA provides strong gel-forming, emulsifying, and film-forming properties.^{11,12} Its capacity to form hydrogel networks and prevent droplet aggregation makes it well-suited as an emulsifier for EO-based emulsions.¹³ Additionally, its ability to incorporate antioxidant and antibacterial compounds positions it as a valuable additive for enhancing the properties of food packaging films.^{14,15}

Despite the potential of essential oils in packaging, challenges remain in achieving uniform dispersion, maintaining mechanical integrity, and controlling the release of active compounds. The emulsification of OEO has proven to be an effective strategy for enhancing its stability and reducing volatility.^{16,17} Choosing the right emulsifier is crucial for making stable OEO emulsions. Previous studies have shown that using emulsification agents such as Tween 80 or SA not only improves the stability of essential oil emulsions but also increases their antimicrobial efficacy against pathogens like *Shewanella putrefaciens* and *Shigella sonnei*, while boosting antioxidant activity.^{13,18} However, there have been no studies combining OEO with cellulose acetate films using the emulsification method. This study aims to develop and characterize CA-based films with OEO, SA and Tween 80, focusing on their antioxidant and antimicrobial activities, water vapor barrier properties, and structural features. The findings are intended to advance biodegradable active packaging materials for food preservation.

2. MATERIALS AND METHODS

2.1. Materials

Cellulose acetate (CA, $M_w = 30,000$ g/mol, containing 39% acetyl groups) was purchased from Sigma-Aldrich (USA). Sodium alginate (analytical reagent grade) and Tween 80 were obtained from Shanghai Zhanyun Chemical Co., Ltd (China). Acetone (99%) was supplied

by Xilong (China), and pure oregano essential oil (OEO, 100%) was sourced from KeyPharm (Belgium).

2.2. Films preparation

The emulsion preparation method was carried out based on the report of Baranauskaite with modifications.¹⁷ A 2% sodium alginate (SA) solution was initially prepared by dissolving SA in distilled water, followed by continuous stirring at 60 °C for 3 hours to obtain a homogeneous gel. The stirring process was maintained while gradually cooling the gel to room temperature. Subsequently, Tween-80 and oregano essential oil (OEO) were incorporated into the SA solution under magnetic stirring at a ratio of 0.15:0.4:5 (Tween-80:OEO:SA) for 60 minutes at room temperature, resulting in the formation of the SA/OEO emulsion.

CA/SA/OEO films were prepared using the solvent evaporation casting method. CA (8% w/w) was dissolved in acetone and stirred at 50 °C for 3 hours to form a gel. The emulsion was added dropwise to the CA solution under continuous stirring at room temperature at concentrations of 0%, 3%, 4.5%, and 6% v/v, corresponding to CA/SA/OEO 0%, 3%, 4.5%, and 6%. After 2 hours, a homogeneous emulsion-gel mixture formed. The mixture was left undisturbed for 2 hours to remove air bubbles, then poured onto a glass plate and spread with a casting knife at 250 μm thickness and 1 mm/s speed. Films were left at room temperature for 40 minutes to complete phase inversion, then removed with tweezers and stored in zip-lock bags for analysis.

2.3. Film characterization

2.3.1. Moisture content (MC), total soluble matter (TSM) and water vapor transmission rate (WVTR)

Moisture content (MC) determined by the method of Erceg et al.¹⁰ The films were initially weighed at room temperature as m_1 (g), then dried at 105°C until their mass stabilized, at which point

it was recorded as m_2 (g). The calculation was performed using the following equation.

$$MC\% = \frac{m_1 - m_2}{m_1} \cdot 100 \quad (1)$$

The solubility of active films was assessed using a modified method based on Meerasri et al.¹⁹ Samples (1×2 cm²) were dried at 105 °C for 24 hours to a constant weight, cooled, weighed (m'), and then immersed in 20 mL of distilled water for 24 hours. The remaining insoluble material was then dried at 105 °C for 24 hours, cooled, and reweighed (m'') to determine solubility.

$$TSM(\%) = \frac{m' - m''}{m'} \cdot 100 \quad (2)$$

Water vapor transmission rate (WVTR) was determined according to ASTM E-996-00 (ASTM, 2000) with some modifications. The procedure involved the following steps: (1) 8 ml of distilled water was poured into each glass jar (mouth diameter: 3 cm, height: 5.3 cm) to create a relative humidity of 100%. (2) The mouth of each jar was then covered with a film (test sample). (3) The sealed jars were placed in a drying oven set at 40 °C. (4) The jars were weighed every 24 hours (accuracy 0.0001 g, measured at least 3 times) for a 24-hour period. (5) Linear regression was used to monitor the change in mass over time. The formula for water vapor transmission rate (WVTR (g.h⁻¹.m⁻²)) was calculated as follows:

$$WVTR = \frac{\Delta m}{A \times \Delta t} \quad (3)$$

In which: Δm is mass loss of water in the glass jar (g); A is area of the film through which water vapor permeates ($= 7.06 \times 10^{-4}$ m²); Δt : time (hour).

2.3.2. Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), and evaluation of their thermal stability

FTIR spectroscopy was used to analyze the infrared spectra of the fabricated films. Measurements were taken from 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹, averaging 32 scans

(Iffrany1s, Shimadzu, Japan). The surface and cross-sectional structures of the packaging films were examined using a scanning electron microscope (Hitachi S-4800, Japan) at an accelerating voltage of 5 kV. Before imaging, samples were coated with gold for 200 seconds using a sputter coater and mounted on aluminum stubs with conductive adhesive to improve conductivity. The thermal properties of the polymer films were studied using a Labsys Evo differential scanning calorimeter (France). Thermogravimetric analysis was performed under air flow (50 mL/min) at a temperature range from 25 to 600 °C at a heating rate of 10 °C/min.

2.3.3. Thickness and mechanical properties

Film thickness was measured with a digital micrometer (Mitutoyo Co., Tokyo, Japan) with a precision of ± 0.001 mm. Each film sample underwent five measurements at randomly selected points. The mean thickness was calculated and used to determine additional parameters, such as mechanical properties and water vapor permeability. Tensile strength (TS) and elongation at break (EB) were evaluated according to the ASTM D882 standard (ASTM, 2002) using a Mark-10 testing machine (USA). Rectangular film specimens measuring 8×2 cm were prepared. The initial gap between clamps was set at 60 mm, and a 100 N load cell was used. TS was calculated as follows:

$$TS(MPa) = \frac{F_{max}}{\Phi} \quad (4)$$

In which: F_{max} : maximum measured force (N); Φ : cross-sectional area of the membrane (mm²).

The elongation at break is calculated by the following formula:

$$EB(\%) = \frac{\Delta l}{l_0} \times 100 \quad (5)$$

Where: Δl is the measured elongation of the film sample during testing, expressed in millimeters (mm). l_0 is the initial length

of the sample prior to testing, expressed in millimeters (mm).

2.4. Antibacterial testing

To assess antibacterial properties, *Staphylococcus aureus* (PTCC 1112) and *Escherichia coli* (PTCC 1270) were chosen as representatives of Gram-positive and Gram-negative bacteria, respectively. The antibacterial performance was tested using the agar well diffusion method. Bacterial suspensions (0.1 mL, 10^7 CFU/mL) were evenly spread onto agar plates. Film samples were cut into 18 mm discs, consistent with commercial standards, and placed on the inoculated agar surfaces. The plates were then incubated at 37 °C for 24 hours. The effectiveness of the films was determined by measuring the diameter of the inhibition zones formed around each sample. The zone of inhibition (ZOI) was calculated using the formula:

$$\text{ZOI (mm)} = D - d \quad (6)$$

In this equation, D refers to the diameter of the inhibition zone (in mm), while d represents the diameter of the agar well (in mm).

2.5. Antioxidant activity

A 2 mmol/L DPPH solution in 70% ethanol was prepared. 2 mL of this solution was added to stoppered vials containing 2 mg film samples. The vials were wrapped in aluminum foil and incubated for 30 minutes before measuring absorbance at 517 nm using a spectrophotometer (Shimadzu UV1800). All measurements were performed in triplicate. The percentage of DPPH free radical scavenging activity was then calculated.

$$\%DPPH = \frac{Abs_{DPPH} - Abs_{sample}}{Abs_{DPPH}} \times 100 \quad (7)$$

Where: Abs_{DPPH} is the absorbance of the blank DPPH solution at 517 nm; Abs_{sample} is the absorbance of the film-treated sample at the same wavelength.

3. RESULTS AND DISCUSSION

3.1. Characterization of CA/SA/OEO active films

3.1.1. Chemical structures analysis

Figure 1 shows the FT-IR spectra of the prepared films. The spectra exhibited characteristic peaks of cellulose acetate (~ 1735 cm^{-1} for C=O ester, ~ 1215 cm^{-1} for C–O ester, and ~ 1029 cm^{-1} for C–O–C).⁷ The band at 3498 cm^{-1} , representing free OH groups in the CA polymer, was significantly reduced in the films incorporating OEO emulsion. This reduction indicates that embedding OEOs into the CA matrix limits the presence of free OH groups, thereby improving the water barrier properties of the film. The peaks at approximately 1637 and 1410 cm^{-1} correspond to the COO^- vibration of COO^- symmetric stretch of alginate. The increased intensity at 2949 cm^{-1} (C–H stretching)¹⁴ indicated the presence of OEO in the film matrix. The absorption peak at around 1561 cm^{-1} transformed into a series of small peaks in the range of 1500–1600 cm^{-1} , and peaks at 1508 cm^{-1} (conjugated groups) and 1457 cm^{-1} ($-\text{CH}_2$ bending vibration) confirmed the effective incorporation of OEO into the films.²⁰ The peaks at 810 cm^{-1} (C–H bending), 939 cm^{-1} (C–C bending vibration), and 1178 cm^{-1} (C–O–C stretching) were either very weak or not observed. The observed peak shifts imply molecular interactions among CA, SA, and OEO components during their dispersion within the film matrix.²¹

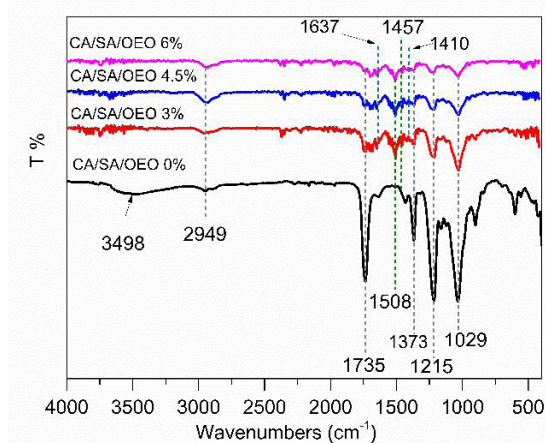


Figure 1. FTIR spectra of CA/SA/OEO films.

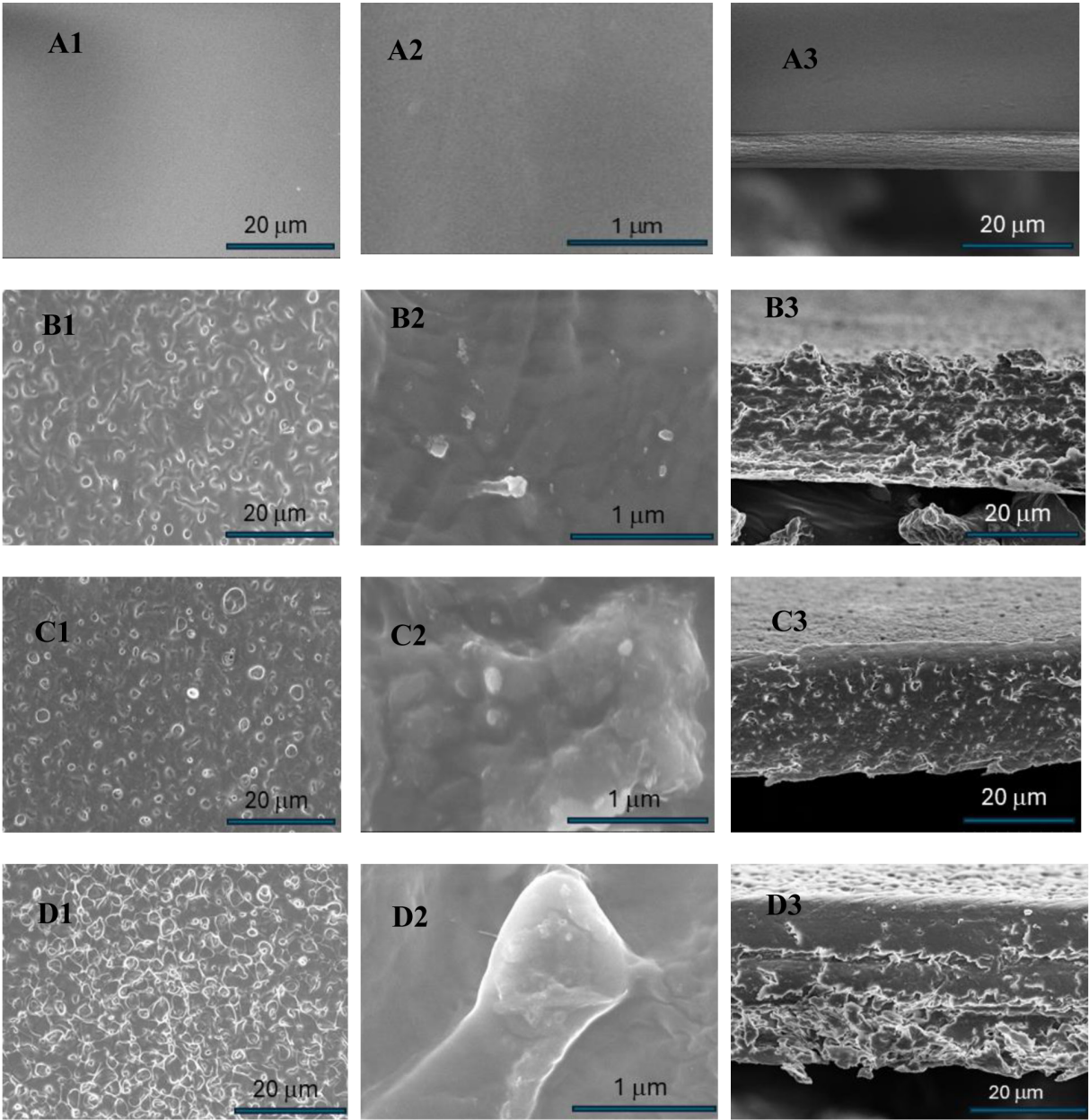


Figure 2. SEM images of surface (1, 2) and cross-section (3) of active films: (A1, A2, A3) CA/SA/OEO 0%; (B1, B2, B3) CA/SA/OEO 3%; (C1, C2, C3) CA/SA/OEO 4.5%; (D1, D2, D3) CA/SA/OEO 6%.

Table 1. Moisture content (MC), total soluble matter (TSM), water vapor transmission rate (WVTR), thickness, tensile strength (TS) and elongation at break (EB) of the CA/SA/OEO films.

Films	MC (%)	TSM (%)	WVTR (g.h ⁻¹ .m ⁻²)	Thickness (mm)	TS (MPa)	EB (%)
CA/SA/OEO 0%	8.32 ± 0.21	0.01 ± 0.01	46.86 ± 0.33	0.007 ± 0.003	33.32 ± 0.12	4.60 ± 0.92
CA/SA/OEO 3%	4.92 ± 0.06	2.50 ± 0.12	15.13 ± 0.14	0.021 ± 0.001	31.42 ± 1.59	4.88 ± 0.94
CA/SA/OEO 4.5%	1.35 ± 0.14	1.51 ± 0.05	8.58 ± 0.29	0.023 ± 0.005	16.76 ± 0.30	18.03 ± 3.28
CA/SA/OEO 6%	1.26 ± 0.02	2.36 ± 0.23	10.26 ± 0.52	0.032 ± 0.002	15.52 ± 1.22	4.82 ± 0.372

3.2.2. Morphologies analysis

Figure 2 presents SEM images illustrating the surface and cross-sectional morphology of CA and OEO emulsion incorporated films. SEM analysis revealed that the surface and cross-sectional views of the CA/SA/OEO 0% film were smooth and intact, with no visible holes or cracks, which was uniformly distributed and well-dispersed, without significant agglomerations (Figure 2.A1, 2.A2, 2.A3). Films containing 3, 4.5, and 6% OEO emulsion exhibit increased surface roughness characterized by valley-like grooves and circular bumps (Figure 2.B1, 2.C1, 2.D1). This surface morphology suggests effective encapsulation of OEO within the film, as indicated by the presence of sodium alginate (SA), Tween 80, and OEO from the emulsion. Emulsion instability during the drying process results in surface irregularities.²² At higher magnifications (Figure 2.A2, 2.B2, 2.C2, 2.D2), SEM images illustrate the dispersion of OEO particles within the CA matrix. In the CA/SA/OEO 4.5% film, the microparticles appear well-distributed and stable. However, in the film containing 6% OEO, particle agglomeration becomes evident, contributing to a noticeably rougher surface compared to the other OEO-containing films. Analysis of cross-sectional SEM images (Figure 2.A3, 2.B3, 2.C3, 2.D3) demonstrates that film thickness increases as the concentration of OEO emulsion rises, consistent with the thickness measurements in Table 1. The observation of cross-sectional pores (Figure 2.B3, 2.C3, 2.D3) further confirms the embedding of OEO within the film matrix, which aligns with findings reported by Xu et al.²³ The incorporation of OEO particles expands the spacing between CA chains, leading to an increase in the thickness of films. The film containing 4.5% OEO exhibits uniformly distributed particles and pores within the CA matrix.

3.2.3. Thermal stability analysis

Figure 3 illustrates the thermal degradation of the films via TGA and dTG analyses. The thermal

degradation of pure CA (CA/SA/OEO 0%, Figure 3.A) occurs in three distinct stages. The first stage, observed up to 120 °C, corresponds to a mass loss of 9.7%, primarily due to the evaporation of moisture and residual solvents.²⁴

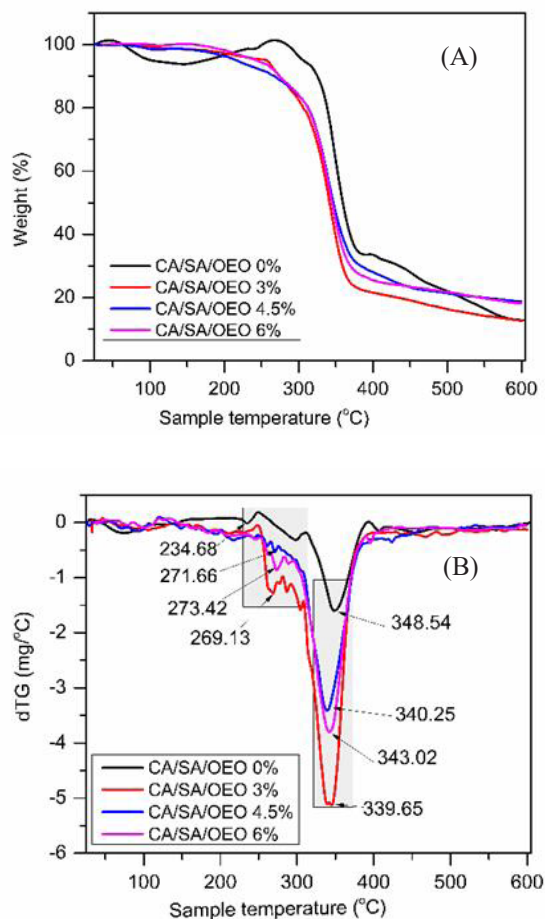


Figure 3. TG curves (A) and DTG curves (B) of fabricated films.

This mass loss was greater than that observed in the films containing OEO, indicating a higher moisture content, which aligns with the moisture values presented in Table 1. The second stage, occurring between 250 °C and 400 °C, is identified as the main thermal decomposition phase, with a significant mass loss of 90.04%. This stage is attributed to the breakdown of the CA polymer backbone, cleavage of glycosidic linkages, and the formation of furanic compounds.¹⁰ The third stage, above 500 °C, represents the final degradation phase, associated with complete decomposition and

carbonization of the sample. Similar to pure CA, the OEO-containing films also exhibited three distinct degradation stages. However, during the main decomposition stage, two separate mass loss events were observed, corresponding to the thermal degradation of sodium alginate (SA) between 250 °C and 280 °C.^{24,18} Notably, the mass loss for the CA/SA/OEO 4.5% film in this stage was 5.98% lower than that of the CA/SA/OEO 6% (12.39%) and CA/SA/OEO 3% (20.49%) films. The third stage occurs between 300 °C and 400 °C. At this stage, the mass loss for the CA/SA/OEO 4.5% film was approximately 75.26% higher than that of the CA/SA/OEO 3% film, which had a mass loss of about 66.93%, and the CA/SA/OEO 6% film, which had a mass loss of 69.54%. The primary cause of quality deterioration in this stage is the breakdown of the deacetylation of CA. The total mass loss in stage 2 of the CA/SA/OEO 4.5% film is 81.24%, exhibiting significantly lower mass loss compared to the films containing 3% and 6% OEO. The CA/SA/OEO 4.5% film demonstrated higher residual mass and improved thermodynamic stability when exposed to temperatures exceeding 550 °C. The dTG, which represents the first-order derivative of TGA, is shown in Figure 3B. The peak temperature in the dTG curve, indicating the highest degradation rate, is defined as the maximum degradation temperature (T_m). A slight decrease in T_m was observed with increasing OEO content, suggesting a minor reduction in thermal stability. This behavior may result from interactions among CA, OEO, and SA, which also influence the overall mass loss of the films.

3.2. Analysis of moisture content, total soluble matter and water vapor transmission rate

As shown in Table 1, the moisture content decreased with increasing OEO emulsion amount in the films. The moisture content ranges from 8.32% for CA/SA/OEO 0% film to 1.26% for CA/SA/OEO 6% film. The incorporation of OEO contributes to the hydrophobic nature of the film surface.¹⁹ Additionally, cross-linking between the CA polymer and OEO may further

reduce moisture content.²⁵ A study by Jiang et al. found that adding essential oil to multilayer gelatin/myofibrillar films decreased their wettability.²⁶

Film solubility, expressed as total soluble matter (TSM), is a critical parameter for packaging moisture-rich foods such as fruits. Lower solubility enhances structural integrity in humid environments, contributing to extended shelf life and reduced nutrient, water, and flavor loss.²⁷ Among the tested films, CA/SA/OEO 4.5% exhibited the lowest solubility (1.51%), making it the most suitable for humid conditions. In contrast, the higher solubility of CA/SA/OEO 3% may compromise its preservation performance. The interaction between OEO emulsion and the film matrix disrupted intermolecular forces and formed bonds with hydroxyl groups.¹⁰ This interaction reduced the film's solubility in water.

Water Vapor Transmission Rate (WVTR) is a critical parameter in food packaging, as moisture plays a key role in maintaining product stability and controlling microbial growth—both essential for preserving food quality. Films with high WVTR allow moisture to escape, potentially leading to dehydration and quality degradation. Conversely, low WVTR may cause moisture accumulation, promoting bacterial and mold growth. For specific packaging applications, increasing film thickness or using high-barrier materials typically achieves the required gas transmission rates. Incorporating hydrophobic OEO emulsion droplets into the CA matrix increased both hydrophobicity and the complexity of the water vapor diffusion pathway. Intermolecular interactions between the OEO emulsion and CA chains resulted in a denser surface structure. Of the samples tested, the CA/SA/OEO 4.5% film demonstrated the best water vapor barrier properties, likely due to its uniform structure as shown in SEM images (Figure 2). In comparison, 3% and 6% films showed uneven emulsion droplet distribution, which disrupted the compact CA structure and created pores and internal cavities that increased water vapor diffusion. While the pristine CA film was tightly

packed, its thinner and more hydrophilic nature led to a higher WVTR value.

3.3. Mechanical properties of CA/SA/OEO active films

3.3.1. The thickness

Table 1 shows that the addition of OEO emulsion significantly increased film thickness compared to the CA film. This finding is consistent with previous research indicating that plasticizers and lipid-based substances increase film thickness. Employing an optimal surfactant-to-oil ratio and sufficient acoustic energy during emulsification improved the stability of the film-forming solution during drying. This approach reduced OEO emulsion loss and increased film thickness.²⁷ The generation of microdroplets from hydrophobic OEO during homogenization also contributed to this outcome. Furthermore, higher concentrations of OEO emulsion increased the total solid content in the solution, further enhancing the final film thickness.

3.3.2. Tensile strength and elongation at break

Tensile strength (TS) and elongation are crucial factors for food packaging films. Films with high tensile strength are less likely to tear under stress, making them suitable for applications that require significant mechanical strength. In contrast, films with high elongation can stretch well and are less likely to break when bent or stretched, which is particularly important in stretch packaging or in applications that demand flexibility.²⁸ Table 1 demonstrates that incorporating OEO produced a typical plasticizing effect, marked by a decline in TS and an increase in elongation at break (EB).⁷ Pure CA film's rigidity and brittleness are reflected in its high TS (33.32 MPa) and EB of 4.60%. The incorporation of OEO emulsion into CA films resulted in a decrease in TS and a notable increase in EB. This mechanical behavior is attributed to molecular-level interactions between OEO emulsion and CA chains. Specifically, the well-dispersed OEO emulsion disrupts the intermolecular hydrogen bonding among CA chains,¹⁰ leading to an increase in free volume and enhanced polymer

chain flexibility.²⁹ The hydrophobic constituents of OEO, such as carvacrol and thymol, interact with the CA matrix primarily through van der Waals forces, which are weaker than hydrogen bonds. These interactions are evidenced by the reduced intensity of the O–H stretching band in the FTIR spectrum (Figure 1), indicating a weakening of hydrogen bonding. Additionally, shifts or decreases in the C=O and C–O stretching bands (Figure 1) suggest increased free volume and reduced intermolecular cohesion, consistent with the plasticizing effect of OEO.² However, when OEO is added in excess, it can form dispersed droplets within the film matrix (Figure 2.D2), which act as localized stress points. These microstructural discontinuities can slightly reduce EB due to uneven stress distribution during deformation. Consequently, the optimal CA/SA/OEO and Tween 80 ratios in the CA/SA/OEO 4.5% film demonstrate good compatibility, significantly improving elongation. According to Alqahtani et al., biodegradable films with tensile strengths ranging from 1 to 10 MPa are deemed acceptable for practical use.²⁸ Since all the prepared films have tensile strengths above 10 MPa, they are suitable for practical applications in active packaging.

3.4. Antibacterial and antioxidant properties

Figure 4 presents the antibacterial activity test results for as-prepared active films. Initially, the CA film without OEO did not show antibacterial inhibition zones, but no bacteria appeared on the film surface. In contrast, the OEO films demonstrated a distinct antibacterial zone. The determined by the concentration of carvacrol, its most active compound, as well as other phenolic constituents such as thymol and p-cymene, which act synergistically. These compounds disrupt bacterial outer membranes, increase permeability, and result in the loss of ions, adenosine triphosphate (ATP), and other cytoplasmic components, thereby inhibiting bacterial growth.³⁰ Subsequently, Table 2 displays the inhibition zone (ZOI) values for films tested against *E.Coli* and *S.aureus*. Analysis of these results shows that membrane CA/SA/OEO

4.5% exhibits the highest antibacterial activity, followed by CA/SA/OEO 6%. Overall, these findings suggest that the OEO emulsion with sodium alginate (SA) and Tween 80 effectively stabilizes OEO in microparticle form within the film matrix, which minimizes loss during film formation.

The antioxidant activity of the films was evaluated using various concentrations of film extract solutions (Table 3). According to the DPPH assay, the CA/SA/OEO 6% film exhibited the highest radical scavenging activity, reaching 84.2% after 12 hours. As expected, the pristine CA film showed no antioxidant activity due to

the absence of active compounds. The observed increase in antioxidant performance results from bioactive compounds present in oregano essential oil, including thymol and carvacrol. These compounds donate electrons or hydrogen atoms to neutralize free radicals. The DPPH% values presented in Table 3 demonstrate a consistent increase in antioxidant activity over time, suggesting a gradual and sustained release of essential oil from the film matrix. However, at higher concentrations, the essential oil may aggregate or distribute unevenly, potentially compromising the mechanical integrity and altering the surface morphology of the films.

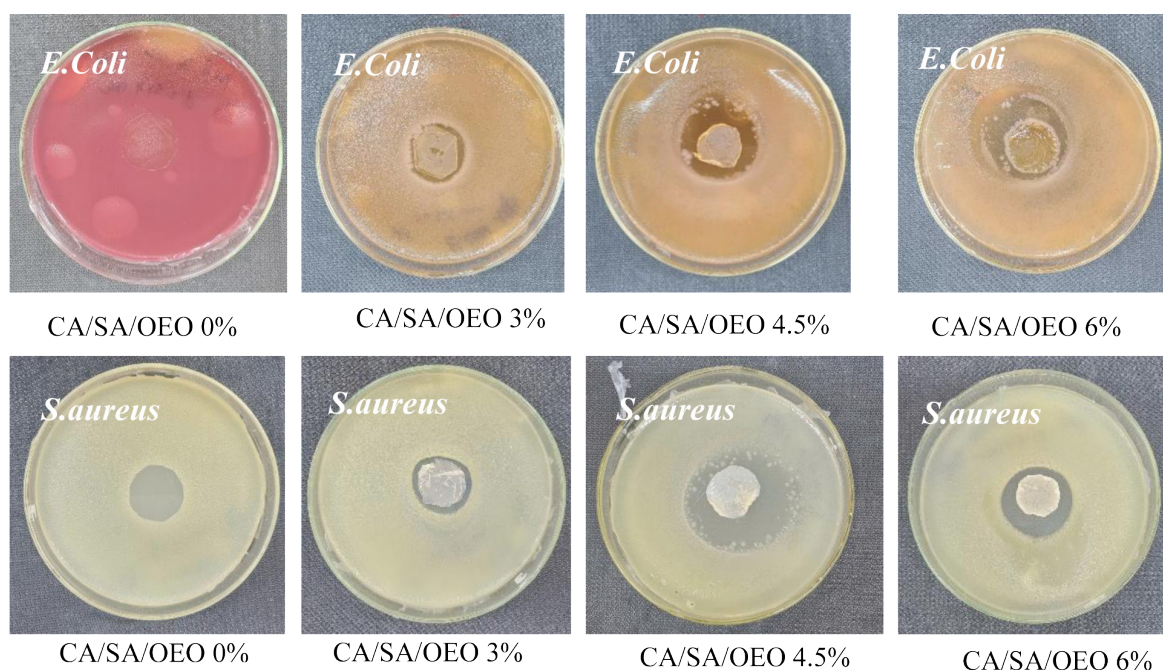


Figure 4. Photographs of inhibition zones formed by active films against *E. Coli* and *S. aureus*.

Table 2. Zone of inhibition (ZOI) values of the films against *E. Coli* and *S. aureus*.

Films	ZOI (<i>E. Coli</i>) (mm)	ZOI (<i>S. aureus</i>) (mm)
CA/SA/OEO 0%	nd	nd
CA/SA/OEO 3%	25 ± 0.3	25 ± 0.2
CA/SA/OEO 4.5%	35 ± 0.1	44 ± 0.1
CA/SA/OEO 6%	34 ± 0.1	33 ± 0.3

Table 3. DPPH Radical Scavenging Activity of CA/SA/OEO films.

Films	DPPH (%) 30 min	DPPH (%) 60 min	DPPH (%) 12 hour
CA/SA/OEO 0%	0	0	0
CA/SA/OEO 3%	36.3 ± 0.2	69.3 ± 0.1	83.2 ± 0.3
CA/SA/OEO 4.5%	39.9 ± 0.2	75.5 ± 0.3	84.0 ± 0.1
CA/SA/OEO 6%	45.8 ± 0.1	79.6 ± 0.5	84.2 ± 0.4

4. CONCLUSION

This study highlights the potential of cellulose acetate films with oregano essential oil emulsion, prepared using sodium alginate and Tween 80, as active packaging materials with improved antibacterial, antioxidant, and water barrier properties. The CA/SA/OEO 4.5% formulation achieved 84% DPPH radical scavenging activity, indicating sustained essential oil release. Antimicrobial tests showed inhibition zones of 35 mm for *E. Coli* and 44 mm for *S. aureus*, confirming strong antibacterial effects. SEM analysis showed that uniform emulsion droplet dispersion enhanced film morphology and barrier performance, while higher OEO concentrations led to aggregation and structural irregularities. These findings support the use of ternary CA composites as active packaging to extend the shelf life of various food products.

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Thích ứng khung nhìn theo QoE cho việc truyền phát video 360 độ với đa hướng và đơn hướng

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TÓM TẮT

Nhờ vào khả năng cung cấp trải nghiệm nhập vai cho người dùng, video 360 độ đã trở thành một trong những công cụ hỗ trợ chính của thực tế ảo (VR). Truyền phát trực tiếp video 360° nâng cao chất lượng trải nghiệm (QoE) bằng cách hỗ trợ người dùng điều chỉnh trường nhìn (FoV) theo thời gian thực. Các nghiên cứu gần đây đã đề xuất một mô hình truyền phát video 360 độ thích ứng khung nhìn sử dụng khả năng thích nghi tốc độ bit trong miền không gian và thời gian để sử dụng hiệu quả băng thông hạn chế. Trong bài báo này, chúng tôi giới thiệu một phương pháp ước tính cho việc truyền phát trực tiếp video 360 độ bằng cách sử dụng kỹ thuật đa hướng và đơn hướng qua mạng di động, nhằm mục đích tối ưu hóa việc phân bổ băng thông giữa các nhóm người dùng để cải thiện trải nghiệm bằng cách tận dụng sự khác biệt tự nhiên về điều kiện mạng và trường nhìn của người dùng. Kết quả thí nghiệm của chúng tôi cho thấy giải pháp đề xuất nâng cao ít nhất từ 11,04% đến 24,05% về tốc độ bit FoV khi so sánh với một số giải pháp đang tồn tại.

Từ khóa: Truyền tải thích ứng, chất lượng trải nghiệm, thực tế ảo, video 360 độ.

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QoE-driven viewport adaptation for live 360° video streaming with multicast and unicast

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ABSTRACT

Due to its capacity to deliver an immersive experience to users, 360° video has emerged as a crucial component of Virtual Reality (VR). Live 360-degree video streaming enhances the Quality of Experience (QoE) by allowing users to instantly adjust their Field of View (FoV). Recent studies have proposed a viewport-adaptive 360-degree video streaming model that uses bitrate adaptation in spatial and temporal domains to utilize limited bandwidth resources efficiently. In this paper, we introduce an estimation approach for Live 360° video streaming using multicast and unicast over mobile networks, aiming to optimize bandwidth allocation across user groups to improve user experience by leveraging the natural diversity in network conditions and users' fields of view. Our experimental results show that the proposed solution enhances at least 11.04% up to 24.05% in term of FoV bitrate in comparison with some existing solutions.

Keywords: *Adaptive streaming, quality of experience, virtual reality, 360-degree video.*

1. INTRODUCTION

Virtual reality¹⁻⁴ is a simulated environment generated by computer technology that users can explore in 360 degrees. It enables users to view, navigate, and engage with three-dimensional (3D) worlds. Virtual Reality provides an interactive and immersive experience that brings virtual environments to life through the use of VR headsets or other display technologies. As technology continues to advance, VR applications have been adopted across multiple fields, including entertainment, manufacturing, healthcare and education.

Viewed from a different angle, High-Efficiency Video Coding (HEVC) is a video

compression standard designed to greatly enhance compression efficiency without compromising video quality.⁵ Compared to H.265/AVC, HEVC can reduce the bitrate by as much as 50%, while still supporting multiple high and ultra high resolution videos.

In addition, the study in paper⁶ demonstrates that EMBMS (Evolved Multimedia Broadcast Multicast Services), supported by a 4G mobile network, enables multicast transmission to multiple terminals. This allows a group of users to stream and watch 360° video live via mobile network using virtual reality device. As shown in Figure 1, EMBMS provides an effective solution for distributing video content of high

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quality via mobile networks by employing video standardization through HEVC/H.265 to the encoder.⁷ EMBMS technology enhances network resource utilization and decreases the total bandwidth needed to deliver video content to multiple users by employing multicast and multimedia streaming.⁸

Through mobile networks, to design for multiple users of VR services, in this study we introduce a new approach for predicting the viewport of 360° videos. Based on client-side approach, referred to as QoE-ViLA (Viewport-

based Live-streaming Adaptation in multicast and unicast), allows for the assessment of data rate per bandwidth to enhance video signal quality for users in the context of QoE-Driven Viewport Adaptation for Live 360° Video Streaming in both multicast and unicast modes. Within QoE-ViLA, each video tile is encoded in different quality levels (called versions) using High-Efficiency Video Coding (HEVC). The main contributions of the proposed method are outlined as follows:

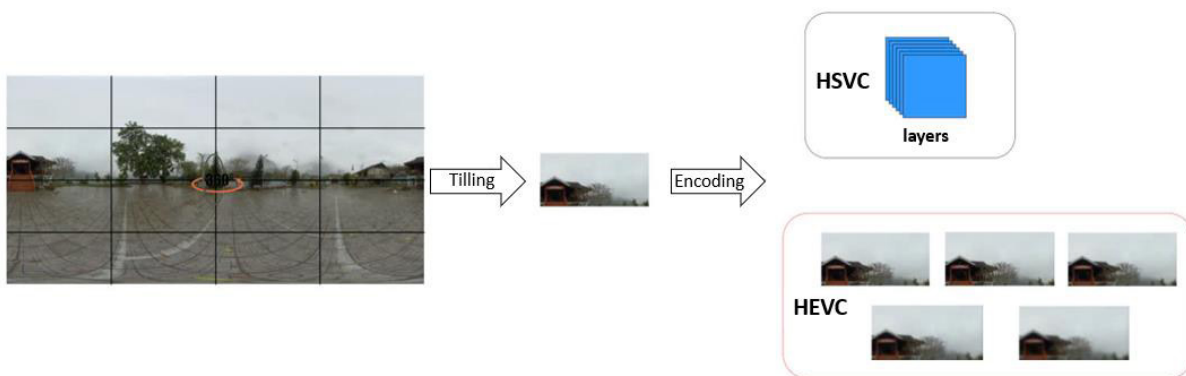


Figure 1. Video encoding standardized using H.265/HEVC.

- Throughout a video streaming session, tiles beyond the user's viewing area are assigned only basic representations to maintain a minimal quality level, while tiles within the viewport are transmitted in several enhanced versions. As a result, QoE-ViLA achieves more efficient use of available network resources compared to traditional methods.

- The paper evaluates the influence of spectrum efficiency on different multicast transport mode configurations to achieve reduced network bandwidth usage.

The structure of this paper is outlined as follows: Section 2 discusses about the state of the art. The resource allocation problem is shown in Section 3. The proposed method - QoE-ViLA - is described in Section 4 followed by an evaluation in Section 5. Finally, the conclusion is discussed in Section 6.

2. RELATED WORKS

Currently, researchers are making significant efforts to provide smooth omnidirectional video streaming with low latency, ensuring a satisfying viewing experience for users even under constrained network bandwidth. In the referenced study,⁹ the content introduced a 360° video streaming framework that adjusts bitrate according to the user's viewport. This approach incorporates the spatiotemporal rate-distortion properties of 360° videos along with user navigation patterns. By analyzing user behavior to predict viewport transitions, the system adapts video quality accordingly, resulting in an enhanced quality of experience.¹⁰ Another study¹¹ proposes an optimized video streaming approach using a chunk download scheduling framework, which enables the adjustment of each parallel stream's quality based on current bandwidth availability and the probability of stream switching.

Several recent studies¹²⁻¹⁴ have addressed the challenges associated with multicasting/unicasting 360° video to multiple mobile users, including large video data volumes, varying network conditions, limited bandwidth resources, and levels of user interaction. Paper¹⁴ presents a multi-quality multicast streaming approach for 360° videos targeting multiple users via Time Division Multiple Access (TDMA). To enhance transmission efficiency, the authors propose dividing encoded tiles into several representations at varying quality levels, enabling optimized decisions on quality selection, time allocation, and power distribution. Meanwhile, in paper,¹³ users are grouped into multiple multicast clusters, each assigned a specific quality representation to maximize perceived video quality. This approach ensures smooth playback quality of 360° content while conserving energy without compromising visual fidelity. In paper,¹² the authors introduced an innovative cross-layer framework designed for streaming 360° video to multiple users over cellular networks. At the content level, tiles are encoded into several layers using Scalable Video

Coding. Meanwhile, at the transport level, these tile layers are transmitted to users through a combination of unicast and multicast modes (For reference, we refer to this method as Multi-Hyb). Paper¹⁵ introduced a scalable framework for live 360-degree video streaming via multicast. It includes a rate-distortion analysis to model the trade-off between video quality and bitrate, an optimization approach for allocating data rates to different spatial regions of the video, and a scalable representation of 360° video data. In which, users are categorized into different classes based on their network bandwidth, with each layer corresponding to a multicast group receiving an identical set of tiles. In paper,¹⁶ a multicast fusion approach is introduced for adaptive multi-user 360° video streaming, aiming to maintain high quality of experience (QoE) in bandwidth-constrained scenarios. This solution allows for dynamic selection between multicast and unicast modes, as well as bitrate adaptation for each cell based on the user's available bandwidth and field of view (FoV).

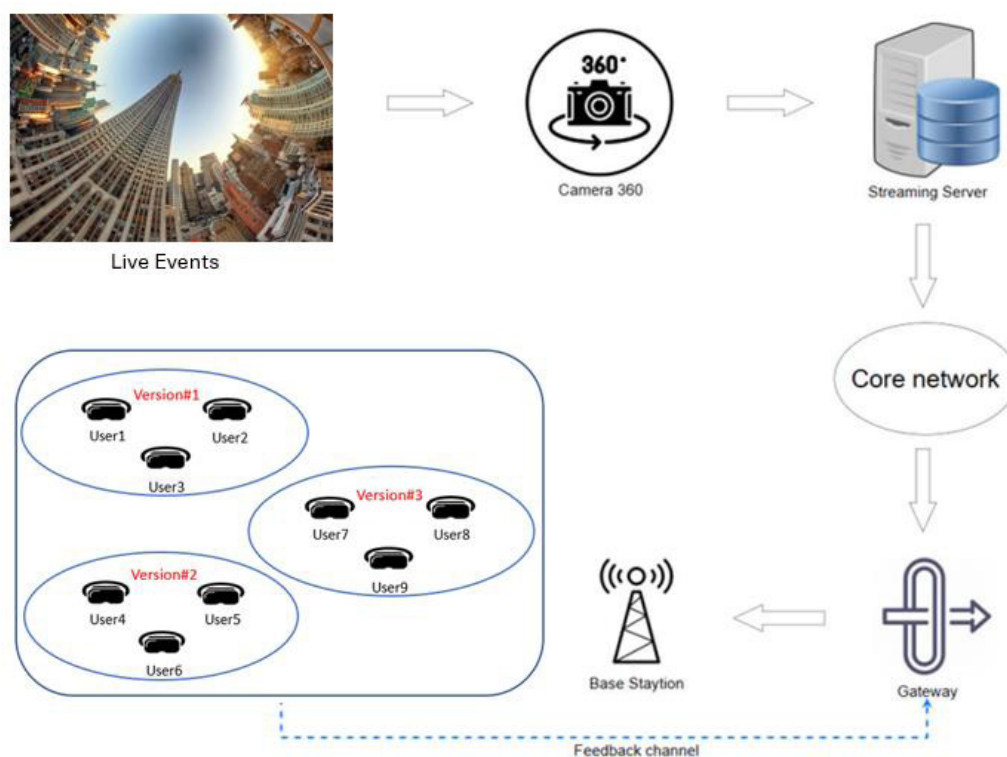


Figure 2. System architecture overview.

Alternatively, Viewport Adaptive Streaming (VAS) enhances user experience under fluctuating network throughput and dynamic head movements. Besides, VAS approaches also rely on accurate head movement data and highly reliable viewport motion prediction.¹⁷ By leveraging users' past viewport data, cross-user behavior patterns,¹⁸ and video content characteristics,^{19,20} it is possible to forecast users' future viewport positions. To address this challenge, another solution involves using Scalable Video Coding (SVC). Its goal is to ensure smooth video playback at the best achievable quality, even under difficult network conditions. This is achieved through the use of SVC's base and enhancement layers.²¹ Initially, all tiles of the base layer are preloaded, while the enhancement layers of visible tiles are subsequently retrieved to enhance frame quality and video playback will be smoother under varying frame and network conditions. This approach also allows users the flexibility to select which part of the video they wish to view at the highest Quality of Experience (QoE), limited to the visible portion within the video's viewport. In paper,¹ the authors propose a method that maintains a high buffer level and ensures consistent quality in subsequent segments, even when the average bitrate drops, thereby improving overall QoE. Since users seldom view areas outside their current viewports, more than 80% of bandwidth is wasted during 360° video streaming.²² Viewport Adaptive Streaming addresses this inefficiency by delivering the viewport region in high version and encoding the other areas with lower version, thereby optimizing bandwidth usage and reducing data waste.²³

To enhance the quality of 360-degree video delivery, the proposed solution employs multicast and unicast transmission over mobile networks to optimize bandwidth allocation across user groups. Specifically, the approach

leverages High-Efficiency Video Coding (HEVC) in conjunction with improved spectrum efficiency to maximize bandwidth utilization among users.

3. PROBLEM FORMULATION

Based on the aforementioned related works, our proposed architecture—illustrated in Figure 2—enables the flexible distribution of multimedia content in multiple versions for live 360° video streaming over a network system. This system leverages HEVC technology to efficiently allocate network bandwidth.

Let β_{tl} denote the bitrate, and Δ_{tl} denote the quality of tile t in layer l . Respectively, the parameters T , L , and U indicate the number of tiles, layers, and users. In telecommunication networks, an RB (resource block) is the basic resource unit in the frequency and time domains. Here we let B be a resource block. In addition, the group traffic is allocated B resource blocks and let η be the lowest efficiency of the group's spectrum usage.

Suppose that B blocks of network resources have been allocated to a specific group of users. The efficiency of spectrum usage for user u (where $1 \leq u \leq U$) characterizes the quality of the wireless link between the base station and the user's terminal device. A live 360° video stream is divided into T tiles, each of which is encoded into $(L + 1)$ layers of different quality levels, with each layer representing a distinct version. For each tile t ($1 \leq t \leq T$), layer l ($0 \leq l \leq L$) is associated with a bitrate β_{tl} and quality Δ_{tl} , corresponding to version h . In addition, each video quality level (version) is divided into segments, and each segment has a duration of τ seconds. The following formula specifies the amount of network resource blocks, denoted as B_{utl} , necessary to transmit version l of each tile t to user u :

$$B_{utl} = \frac{\beta_{tl} \times \tau}{\eta^u} \quad (1)$$

Where β_{il} denotes the bitrate of tile t in layer l , η^u denotes the spectrum utilization efficiency of the wireless communication link between the base station and the user's terminal device.

In the proposed architecture, multicast and unicast transmission techniques can be employed to deliver different video versions. In multicast mode, the versions are distributed to a group of users, whereas in unicast mode, each version is transmitted to an individual user. Furthermore, the spectral efficiency of multicast transmissions is constrained by the user with the lowest spectral efficiency in the group, which limits the overall multicast capacity.

4. PROPOSED SOLUTIONS (QoE-ViLA)

When viewing 360-degree videos under fluctuating mobile network bandwidth conditions that may cause buffering or playback interruptions, it becomes essential to adapt in real-time by dynamically modifying parameters like tile quality and transmission rate. By constantly tracking network performance and factoring in

available resources, device capabilities, latency, and the viewer’s current viewport, the proposed architecture is able to maintain high visual quality and smooth playback, providing viewers with an immersive real-world experience.

In the proposed solution, we present two transmission models for each layer of each tile using two binary variables, $\gamma_{tl}, \varphi_{utl} \in \{0, 1\}$, $\forall l \in L, t \in T, u \in U$. If a tile layer is transmitted via the multicast model to all users, then $\gamma_{tl} = 1$. If it is delivered through the unicast model to a particular user u , then $\varphi_{utl} = 1$; otherwise, $\gamma_{tl} = 0$ or $\varphi_{utl} = 0$.

The following expression defines the goal function for allocating network resources in multi-user streaming scenarios.

$$maxx \sum_{u \in U} \sum_{t \in T} \sum_{l \in L} \Omega_{ut} \Delta_{tl} (\gamma_{tl} + \varphi_{utl})$$

(2)

Where: Ω_{ut} represents the weighting of tile t corresponding to user u ; Δ_{tl} represents the quality level of the t^{th} tile and the l^{th} layer.

With constraints:

Table 1. The quality (dB) and average bitrate (kbps) of the four 360° videos used in the experiment for the Multi-Hyb and Multi-SVC approaches.

Version	RollerCoaster		Venice		Paris		Diving	
	Quality	Bitrate	Quality	Bitrate	Quality	Bitrate	Quality	Bitrate
# 1	39.45	55.33	32.73	50.34	38.20	61.44	34.50	158.72
# 2	42.72	106.74	35.92	114.24	41.94	88.75	38.25	313.76
# 3	44.75	179.11	38.50	216.24	44.63	114.02	40.85	504.54
# 4	27.14	389.12	41.57	483.58	47.55	191.33	43.89	1036.97
# 5	49.24	632.94	44.53	824.70	50.42	293.75	46.23	1418.46

Table 2. The quality (dB) and average bitrate (kbps) of the four 360° videos used in the experiment for the JUMP and QoE-ViLA approaches.

Version	RollerCoaster		Venice		Paris		Diving	
	Quality	Bitrate	Quality	Bitrate	Quality	Bitrate	Quality	Bitrate
# 1	39.44	54.85	32.72	60.06	38.20	60.79	34.48	158.14
# 2	42.87	131.72	36.08	183.03	42.20	130.40	38.23	393.64
# 3	44.98	250.54	38.70	384.88	44.98	209.69	40.98	752.27
# 4	47.27	515.86	41.77	826.39	47.87	340.26	44.02	1481.53
# 5	49.43	933.85	44.77	1520.16	50.73	532.45	46.58	2499.03

$$\sum_{t \in T} \sum_{l \in L} \frac{\beta_{tl} \times \tau}{\min_{u \in \beta_{tl} = 1} \eta^u} \leq B \quad (3)$$

Where: B is a resource block;

$$\beta_{tl} = \{ u \in \{1, \dots, U\} \mid \gamma_{tl} + \varphi_{utl} = 1 \}$$
$$\sum_u \sum_t \varphi_{utl} \leq 1, \forall u \in U, t \in T, l \geq 1 \quad (4)$$

$$\sum_t \gamma_{t0} + \varphi_{ut0} = 1, \forall u \in U, \forall t \in T \quad (5)$$

$$\eta^u = \frac{B_t(1 - \gamma)}{BW} \quad (6)$$

Where: BW denotes the user's bandwidth, while BW also refers to the channel bandwidth at the core; B_u indicates how many network resource blocks are available to user u ; and η^u has been presented above in Equation 1.

Accurate prediction of the future viewport direction is essential for effective network resource allocation, as it guides the selection of γ_{tl} and φ_{utl} values (as defined in Equation 2). The predicted direction affects γ_{tl} , which assigns weights to the views or tiles in the 360° video. By anticipating which areas the viewer is likely to focus on, those regions' tiles can receive higher γ_{tl} values, ensuring attention is directed toward the most relevant content. Likewise, φ - which represents the video quality or amount of visual detail for each tile - is also influenced by the predicted viewing direction, enabling optimized visual fidelity where it is most needed. To enhance visual fidelity and vividness in the expected viewing areas, it is necessary to estimate

the viewing direction in advance. Based on this prediction, higher bitrate tiles or higher-quality versions can then be allocated to those areas.

On the other hand, to optimize view-based streaming adaptation in both multicast and unicast scenarios, the proposed solution imposes the following conditions:

- The overall resources assigned for multicast and unicast must not exceed the value of B as defined in Equation 3.
- The constraints in Equations 4 and 5 guarantee that each user receives every FoV tile only once.
- The base layer of every tile is delivered to all users.

5. PERFORMANCE EVALUATION

5.1. Experimental settings

This section introduces four 360° videos - *Diving*, *Paris*, *Venice*, and *RollerCoaster* - prepared for the experimental setup and evaluation. All videos have a resolution of 3840×2048 and a fixed duration of 60 seconds. The videos were converted into the CubeMap format at a resolution of 2890×1920 using the 360Lib tool. Subsequently, each video was partitioned into 24 tiles, each sized 480×480 pixels. Each tile undergoes sequential encoding into five layers, including four booster layers and one fundamental layer. The quantization parameters for the respective layers are fixed as specified in Table 1 and Table 2. Here, the symbols #1÷#5

denote five quality levels corresponding to the video bitrates used in the experiment.

Following the setup in paper²⁴ we set the number of users U to 15, 30, 45 and 60. The η^u values are applied as defined in Equation 6. The experimental evaluation was conducted on a system running a Windows 10 (64-bit version) operating system with 16 GB of RAM and a 4.5 GHz HP EliteBook Core i7 processor. We compared the proposed solution (QoE-ViLA) with reference methods, including the approach from paper²⁴ (referred to as Multi-SVC), Multi-Hyb,¹² and JUMP.²⁵ The Multi-svc method streams multi-user VR video over a cellular network by combining Scalable Video Coding (SVC) and multicast to deliver popular tiles to users. In this method, tiles are encoded into multiple layers using SVC and then delivered to users via multicast. The JUMP approach enables a tile to be transmitted via either unicast or multicast. The tile versions and transmission modes are determined to optimize the weighted sum of FoV bitrates across all users. Additionally, we employ the average view PSNR (Peak Signal-to-Noise Ratio) parameter to recompute the performance scores of both the proposed approach and the baseline methods, as follows:

$$UVPR = \frac{1}{U} \sum_{u=1}^U UVPR_u \quad (7)$$

$$UVPR_u = \sum_{u=1}^U \Omega_{ut}^s \times \Delta_{tl_u}^s \quad (8)$$

Where: $UVPR_u$ denotes the viewport PSNR for user u ; Ω_{ut}^s represents the weighted sum of the quality of visible tiles; and l_u^s indicates the highest layer of tile t streamed to user u .

5.2. Experimental results and discussion

In this section, we evaluate the performance of the proposed framework in comparison with reference methods. A bitrate analysis is conducted using U multicast transmissions for user groups of 15, 30, 45, and 60 users, with B varying from 20.000 RBs to 700.000 RBs.

As shown in Figure 3, the QoE-ViLA method consistently outperforms all other referenced approaches across all four videos. For 15 users (or 60 users), the QoE-ViLA solution achieves an average bitrate ranging from 730 Kbps to 863 Kbps (2832 Kbps to 3412 Kbps), whereas the other methods achieve only 597 Kbps to 733 Kbps (2326 Kbps to 2906 Kbps). Specifically, the proposed method improves the average bitrate by more than 14.11% and 17.90% compared to the Multi-SVC and JUMP methods, respectively. In comparison with Multi-Hyb, the performance gain ranges from 16.86% with 15 users to 18.84% with 60 users.

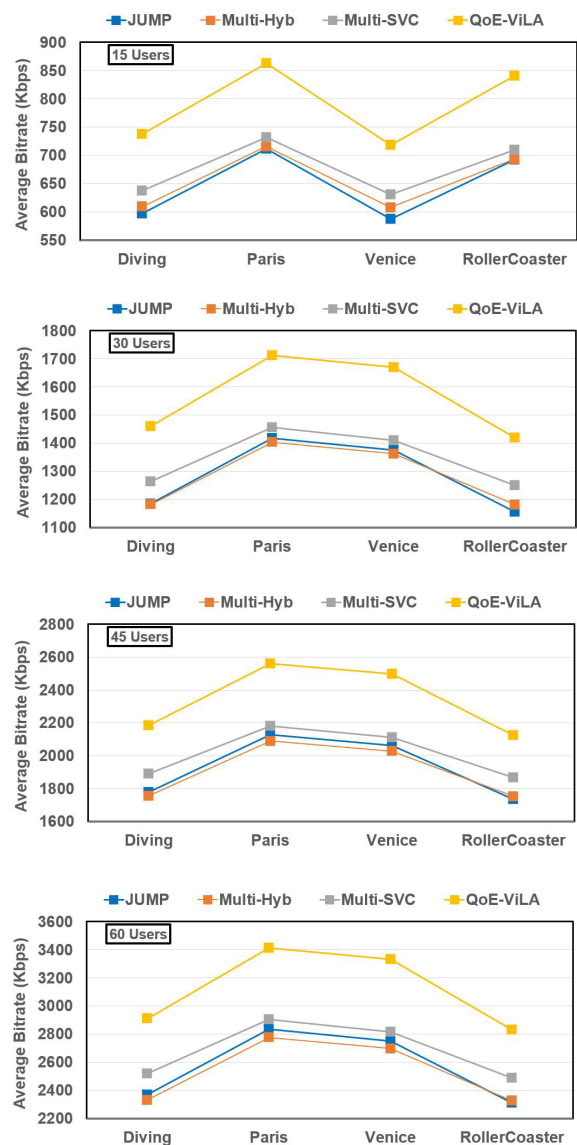
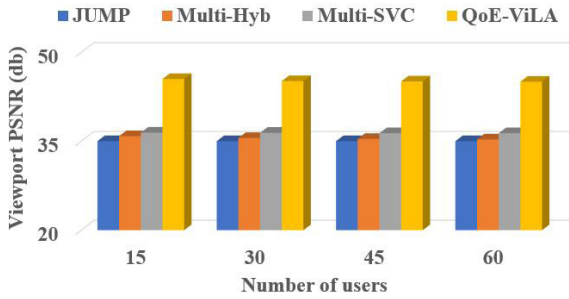
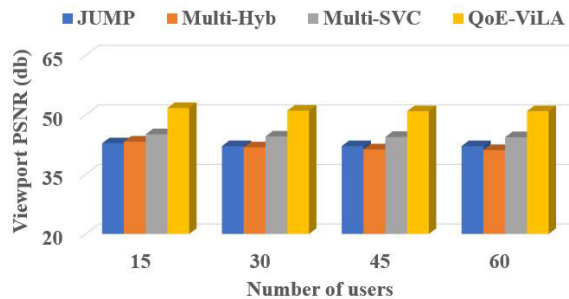


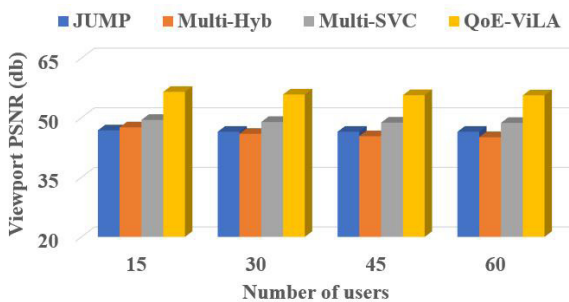
Figure 3. Average bit rate (Kbps) for 15, 30, 45, and 60 users.



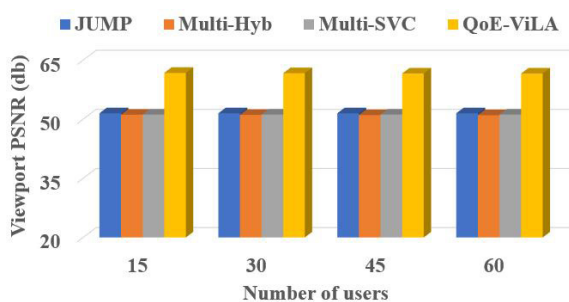
(a) Diving Video



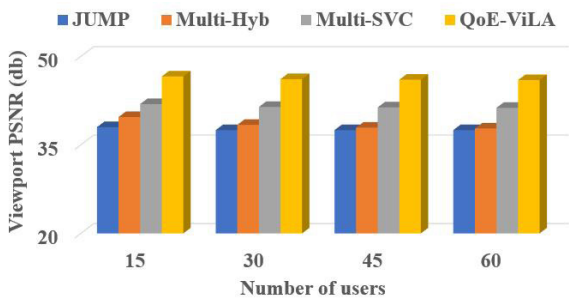
(a) Diving Video



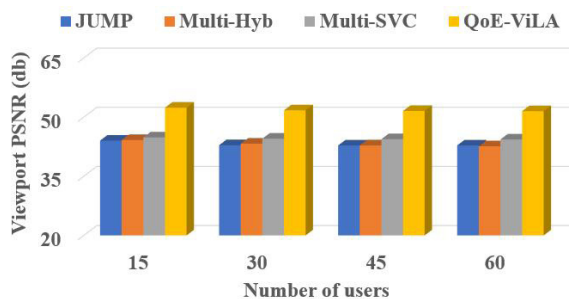
(b) Paris Video



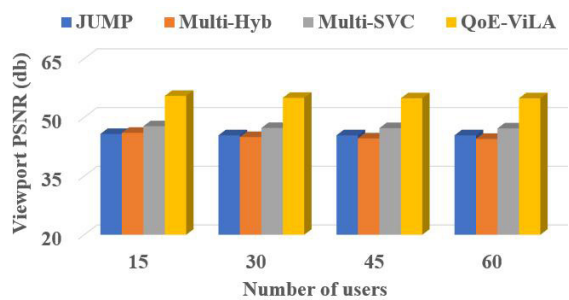
(b) Paris Video



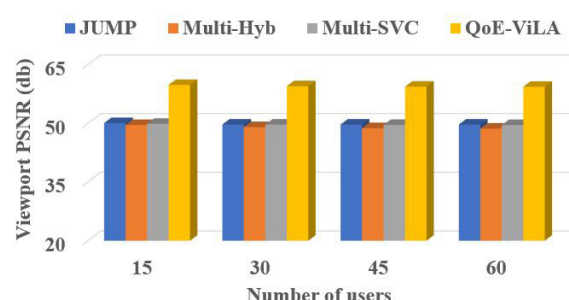
(c) Venice Video



(c) Venice Video



(d) Roller. Video



(d) Roller. Video

Figure 4. The performance across different numbers of users (with $B = 200.000$ RBs) varies between the proposed method and the reference methods.

Figure 5. The performance across different numbers of users (with $B = 700.000$ RBs) varies between the proposed method and the reference methods.

In addition, the performance based on the viewport PSNR metric will have been evaluated across all methods. In the experimental setup of this paper, four values of U —15, 30, 45, and 60—are specifically analyzed. Figures 4 and 5 illustrate the viewport PSNR results for both the proposed and reference methods at $B=200.000$ RBs and $B=700.000$ RBs, respectively. For $B = 200.000$ RBs, the viewport PSNR of the QoE-ViLA method ranges from 45.09 dB to 56.49 dB, whereas the other methods achieve only 35.02 dB to 49.43 dB (Figure 4). For $B = 700.000$ RBs, the proposed method ranges from 50.89 dB to 61.74 dB, while the other methods achieve only 41.10 dB to 51.50 dB (Figure 5). The results clearly show that our approach consistently outperforms all reference methods across all U values. The QoE-ViLA method achieves a viewport PSNR that is at least 6 dB and up to 12 dB higher than the reference methods (JUMP, Multi-Hyb, Multi-SVC) in all scenarios. Moreover, although the viewport PSNR of the proposed method slightly decreases when the number of users increases, the reduction remains minimal.

6. CONCLUSION

In this study, we introduce an innovative viewport prediction approach for multiple-user multicast video transmission over mobile networks. The proposed method utilizes the HEVC (High-Efficiency Video Coding) technique in combination with improved spectrum efficiency to optimize bandwidth usage among users. With the experimental results, it is demonstrated that the proposed method can achieve significant performance improvements, ranging from 11.04% to 24.05% across four test videos. In future studies, we aim to extend the capabilities of the proposed framework to support scenarios involving multiple users concurrently accessing various video assets, including live 360° video streams.

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Hệ thống giám sát và cảnh báo lũ lụt thời gian thực dựa trên nền tảng IoT và cảm biến mực nước kép

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TÓM TẮT

Lũ lụt là một trong những thảm họa thiên nhiên gây thiệt hại nặng nề về người và kinh tế. Việc phát hiện sớm và đưa ra cảnh báo kịp thời đóng vai trò then chốt trong công tác quản lý lũ, đặc biệt tại các khu vực có điều kiện địa hình phức tạp. Bài báo này đề xuất một hệ thống giám sát lũ lụt dựa trên công nghệ IoT, tận dụng dữ liệu mực nước từ hai cảm biến đặt cách xa nhau để nâng cao độ chính xác trong dự báo rủi ro và phát cảnh báo kịp thời. Một thuật toán phân tích mực nước mới dựa trên cảm biến kép được giới thiệu, nhằm đánh giá nguy cơ lũ thông qua việc phân tích tốc độ dâng mực nước và chênh lệch mực nước giữa hai vị trí cảm biến. Hệ thống tích hợp Node.js cho xử lý phía máy chủ và Google Maps API cho trực quan hóa không gian, giúp giám sát và phân phối cảnh báo theo thời gian thực. Kết quả thực nghiệm cho thấy hệ thống đạt độ chính xác cao, 94.66% trong việc phát hiện rủi ro lũ, và độ trễ thấp, chỉ 10 giây trong quá trình phát cảnh báo, khẳng định tính khả thi của hệ thống trong các khu vực thường xuyên xảy ra lũ lụt, điển hình như lưu vực sông Côn, tỉnh Bình Định.

Từ khóa: IoT, hệ thống cảnh báo lũ sớm, cảm biến kép, Node.js, Google Maps API.

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IoT-enabled flood risk detection via dual-sensor water level monitoring and real-time alerting

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ABSTRACT

Flooding is a devastating natural disaster that causes significant loss of life and economic damage. Early detection and real-time alerts are essential for effective flood management, particularly in regions with challenging geographical conditions. This paper proposes an IoT-based flood monitoring system that leverages dual-sensor water level data for accurate risk prediction and timely alerts. A novel dual-sensor water level analysis algorithm is introduced to evaluate flood risks by analyzing the rate of water level increase and the differential between two sensor locations. The system integrates Node.js for backend processing and Google Maps API for spatial visualization, enabling real-time monitoring and alert dissemination. Experimental results demonstrate high accuracy of 94.66% in detecting flood risks and low latency of 10 seconds in generating alerts, proving the system's suitability for flood-prone areas like the Con River basin, Binh Dinh province.

Keywords: *IoT, early warning system, dual-sensor water level prediction, Node.js, Google Maps API.*

1. INTRODUCTION

Flooding is one of the most catastrophic natural disasters, causing widespread destruction, loss of life, and economic damage globally. According to the report from the World Meteorological Organization (WMO), floods account for approximately 44% of all natural disasters, affecting millions of people annually (<https://wmo.int/media/news/weather-related-disasters-increase-over-past-50-years-causing-more-damage-fewer-deaths>). In developing countries, where infrastructure and disaster management systems are often underdeveloped, the impact of floods is particularly severe. Early detection and real-time alerts are critical for mitigating the adverse effects of floods, enabling communities

and authorities to take proactive measures such as evacuations, resource allocation, and emergency response planning.¹

Traditional flood monitoring systems often rely on manual measurements or single-point sensors, which may lack spatial coverage, accuracy, and timeliness. Water level data collected manually at specific locations may not reflect the dynamic changes occurring across a river basin. Similarly, single-point sensor systems fail to capture spatial variations in water levels, leading to delayed or inaccurate flood predictions.² These limitations highlight the need for advanced, scalable, and cost-effective solutions that can provide real-time insights into flood risks.

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Recent advancements in Internet of Things (IoT) technologies have enabled the development of smart flood monitoring systems capable of collecting and processing environmental data in real time. IoT-based systems offer several advantages, including continuous data collection, wireless communication, and integration with cloud platforms for analysis and visualization.³⁻⁴ However, most existing IoT-based flood monitoring systems focus on single-sensor data, which may not fully capture the complex dynamics of river systems. To address this gap, this paper proposes an IoT-based flood monitoring system that leverages dual-sensor water level data for enhanced flood risk prediction and timely alerts.

The proposed system integrates advanced technologies such as Node.js for backend processing and Google Maps API for spatial visualization, enabling real-time monitoring and alert dissemination. A novel dual-sensor water level analysis algorithm is introduced to predict flood risks by analyzing two key parameters: (i) the rate of water level increase at each sensor location and (ii) the differential between water levels measured by two sensors placed at different points along a river. This approach not only captures temporal changes in water levels but also accounts for spatial variations, providing a more comprehensive assessment of flood risks.

The remainder of this paper is organized as follows: Section II provides an overview of related work. Section III describes the system architecture and design. Section IV details the dual-sensor water level prediction algorithm. Section V presents the experimental results, including the field experiment conducted along the Con River. Finally, Section VI concludes the paper and discusses future work.

2. RELATED WORK

Flood monitoring and early warning systems have been extensively studied in recent years, driven by the increasing frequency and severity of floods due to climate change and urbanization.

Existing research can be broadly categorized into three main areas: (i) IoT-based flood monitoring systems, (ii) data analysis and prediction algorithms, and (iii) visualization and alert dissemination platforms. This section reviews key contributions in these areas and highlights the gaps addressed by the proposed system.

2.1. IoT-Based flood monitoring systems

The advent of IoT technologies has revolutionized flood monitoring by enabling real-time data collection and remote sensing. Masoudimoghaddam et al. proposed an IoT-based flood monitoring system using ultrasonic sensors to measure water levels in rivers.⁵ The system transmitted sensor data to a cloud platform for analysis and visualization. While effective, this approach relied on single-point sensors, which may not capture spatial variations in water levels across a river basin. Similarly, a wireless sensor network for flood detection, focusing on energy-efficient communication protocols was developed.⁶ However, the study did not incorporate advanced algorithms for flood risk prediction, limiting its ability to provide actionable insights.

More recently, the researchers introduced a multi-sensor IoT system for flood monitoring, integrating rainfall, soil moisture, and water level data.⁷ The system demonstrated improved accuracy in detecting flood risks compared to single-parameter approaches. Despite these advancements, most existing IoT-based systems lack the capability to analyze spatial relationships between multiple sensor locations, which is critical for understanding the dynamics of river systems.

2.2. Data analysis and prediction algorithms

Data analysis and prediction algorithms play a crucial role in flood risk assessment. Traditional approaches often rely on statistical models or hydrological simulations to predict flood events. A rainfall-runoff system was developed to estimate flood risks based on historical rainfall

data.⁸ While these systems are effective for long-term predictions, they may not be suitable for real-time monitoring due to their computational complexity.

Machine learning (ML) techniques have gained popularity in recent years for flood prediction. A deep learning model was deployed to predict flood risks using satellite imagery and environmental data.⁹ The model achieved high accuracy in detecting flood-prone areas but required extensive training data and computational resources. Similarly, a support vector machine (SVM) algorithm was employed to classify flood risks based on water level data.¹⁰ However, these ML-based approaches are often resource-intensive and may not be feasible for deployment in resource-constrained environments.

In contrast, rule-based algorithms have been explored as a lightweight alternative for real-time flood prediction. A threshold-based algorithm was introduced to detect rapid increases in water levels using single-sensor data.¹¹ While simple and efficient, this approach did not account for spatial variations in water levels, which are essential for accurate flood risk assessment.

2.3. Visualization and alert dissemination platforms

Visualization and alert dissemination platforms are critical components of flood monitoring systems, enabling users to interpret sensor data and respond to flood risks effectively. Recent studies have highlighted the importance of integrating geographic information systems (GIS) for spatial visualization. The researchers developed a flood monitoring system that used Google Maps API to display sensor locations and flood risk zones on an interactive map.¹² The system provided intuitive visualization and real-time alerts, enhancing situational awareness for users.

Other studies have explored mobile applications and web-based dashboards for alert

dissemination. A smartphone app that delivered flood alerts via push notifications, SMS, and email was proposed.¹³ While effective, the study did not address the integration of advanced data analysis algorithms for flood risk prediction. Similarly, a web-based platform for flood monitoring was introduced¹⁴ but the platform's effectiveness is limited by the absence of real-world validation during actual flood events, reducing its reliability in emergency scenarios.

2.4. Gaps addressed by the proposed system

Despite significant advancements in flood monitoring technologies, several gaps remain unaddressed in existing research. First, most IoT-based systems rely on single-point sensors or fail to analyze spatial relationships between multiple sensor locations. Second, many data analysis algorithms are either computationally intensive or lack the ability to capture both temporal and spatial variations in water levels. Third, while visualization platforms have improved user experience, they are often decoupled from robust prediction algorithms, limiting their effectiveness in providing actionable insights.

The proposed system addresses these gaps by leveraging dual-sensor water level data for enhanced flood risk prediction. A novel dual-sensor water level analysis algorithm is introduced to evaluate flood risks based on both the rate of water level increase and the differential between two sensor locations. The system integrates Node.js for efficient backend processing and Google Maps API for spatial visualization, enabling real-time monitoring and alert dissemination. Furthermore, the system is validated through a field experiment conducted along the Con River in Binh Dinh Province, demonstrating its suitability for real-world deployment in flood-prone areas.

3. SYSTEM ARCHITECTURE AND DESIGN

The architecture of the proposed IoT-based flood monitoring system is designed to provide real-time flood risk prediction and alert dissemination by leveraging dual-sensor water level data,

Node.js for backend processing, and Google Maps API for spatial visualization. The system architecture is shown in Figure 1. The system follows a modular design that integrates hardware components for data collection, software components for processing and analysis, and a robust data flow mechanism to ensure seamless operation.

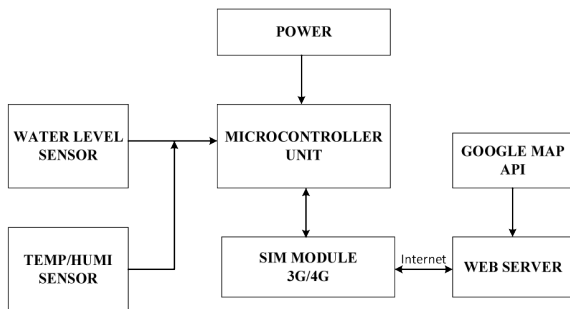


Figure 1. System architecture overview.

At the core of the system are the hardware components responsible for collecting water level data from the field. Two ultrasonic sensors are strategically deployed at different locations along the river, one upstream and the other downstream, to capture spatial variations in water levels. The distance between the two measuring points is 24 km along the length of the river, as shown in Figure 2. The 24 km separation between the upstream and downstream sensors was selected to cover the main floodplain area of the Con River basin, based on hydrological survey. These sensors are chosen for their accuracy and ability to withstand harsh environmental conditions. An ESP32 microcontroller with SIM module is used to collect data from the sensors and transmit it to the cloud via cellular network. The ESP32's low power consumption and wireless connectivity make it an ideal choice for remote deployments. To ensure reliable data transmission, a localhost acts as a gateway, aggregating sensor data from multiple locations and forwarding it to the Node.js server.

On the software side, the system relies on Node.js for backend processing and Google Maps API for visualization. The Node.js

backend is responsible for handling sensor data, executing the dual-sensor water level prediction algorithm, and generating real-time alerts. The dual-sensor algorithm calculates the rate of water level increase and the differential between the two sensor locations to assess flood risks. In case a high or medium risk is detected, the system generates alerts and sends them to users via SMS. Meanwhile, Google Maps API provides an intuitive interface for visualizing sensor locations, water level data at each measuring point in map. Additionally, The measured data is updated on the map in real time as new data becomes available, ensuring that users always have access to the latest information. The system also incorporates a MongoDB database to store historical sensor data for analysis and visualization. By storing data such as timestamps, sensor IDs, water levels, and flood risk levels, the system can generate insights into past flood events and help predict future risks.

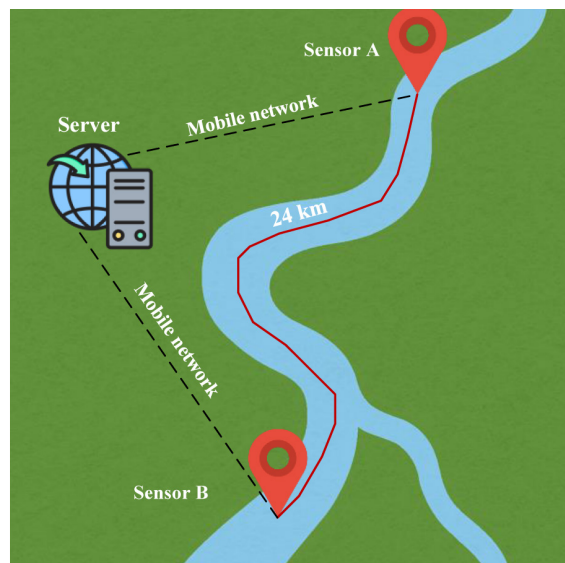


Figure 2. Two sensors are installed at two different locations on the river.

One of the key strengths of the proposed system is its ability to provide real-time monitoring while capturing spatial variations in water levels. By leveraging dual-sensor data, the system offers a more comprehensive assessment of flood risks compared to single-sensor approaches. Its scalability allows it

to support multiple sensor pairs, making it suitable for deployment across larger river basins. Furthermore, the user-friendly interface powered by Google Maps API ensures that even non-technical users can easily interpret the data and take appropriate actions. These features collectively enhance the system's effectiveness in mitigating the impact of floods, particularly in regions like the Con River basin in Binh Dinh Province, where rapid water flow and wide floodplains pose significant challenges.

4. DUAL-SENSOR WATER LEVEL PREDICTION ALGORITHM

The proposed dual-sensor water level prediction algorithm is a key component of the flood monitoring system, enabling accurate and timely flood risk assessment. This section provides a detailed description of the algorithm, including its operational principles, risk classification mechanism, and alert generation process.

4.1. Algorithm

The dual-sensor water level prediction algorithm analyzes two critical parameters to evaluate flood risks: (i) the rate of water level increase at each sensor location and (ii) the differential between water levels measured by the two sensors. These parameters are derived from real-time data collected by ultrasonic sensors deployed upstream and downstream along the river. To calculate the rate of water level increase, the algorithm computes the difference between the current water level and the previous water level for each sensor, divided by the time interval between measurements. Mathematically, this is expressed as:

$$Rate_A = \frac{WA_{current} - WA_{previous}}{\Delta t} \quad (1)$$

$$Rate_B = \frac{WB_{current} - WB_{previous}}{\Delta t} \quad (2)$$

where $WA_{current}$ and $WB_{current}$ represent the current water levels at Sensor A and Sensor B,

respectively, $WA_{previous}$ and $WB_{previous}$ represent the previous water levels, and Δt is the time interval between consecutive measurements. The water level differential is calculated as the absolute difference between the water levels at the two sensor locations:

$$\Delta = |WA_{current} - WB_{current}| \quad (3)$$

This parameter captures spatial variations in water levels, which are essential for understanding the dynamics of river systems. For instance, a significant differential may indicate uneven water flow or potential blockages between the two sensor locations. By combining these two parameters, the algorithm provides a comprehensive assessment of flood risks, accounting for both temporal changes and spatial relationships in water levels. Furthermore, sensor data are transmitted continuously every 5 seconds. To ensure that alerts are not triggered by transient anomalies or single noisy samples, the system aggregates and analyzes data over a sliding time window before making a decision. This design ensures that flood risk detection is based on stable patterns rather than instantaneous fluctuations, thereby enhancing reliability even under occasional transmission noise or packet loss.

4.2. Risk classification

Based on the calculated parameters, the algorithm classifies flood risks into three levels: low, medium, and high. The classification is determined by comparing the computed values with predefined thresholds, denoted as $Threshold_R$ for the rate of water level increase and $Threshold_D$ for the water level differential. These thresholds are established based on historical data and expert knowledge specific to the monitored river basin. The use of dual thresholds ensures that the algorithm can adapt to varying environmental conditions and provide reliable flood risk predictions. The algorithm of alert generation is shown in Algorithm 1.

Algorithm 1: Alert Generation Process

Initialize: RiskLevel=Low

1. Retrieve the computed values of $Rate_A$, $Rate_B$, and Delta from the dual-sensor algorithm.
2. Compare $Rate_A$ and $Rate_B$ with $Threshold_R$:
 - If $Rate_A > Threshold_R$ and $Rate_B > Threshold_R$, set RiskLevel=High.
3. Check the water level differential (Delta) against $Threshold_D$:
 - If Delta $> Threshold_D$, set RiskLevel=High.
4. Evaluate medium-risk conditions:
 - If $Rate_A > Threshold_R$, or $Rate_B > Threshold_R$, and Delta $< Threshold_D$, set RiskLevel=Medium.
5. Confirm low-risk conditions:
 - If $Rate_A \leq Threshold_R$, $Rate_B \leq Threshold_R$, and Delta $< Threshold_D$, set RiskLevel=Low.
6. Generate alerts based on RiskLevel:
 - If RiskLevel=High:
 - Send SMS and push notifications to emergency teams and authorities.
 - Highlight affected areas on Google Maps API with color-coded overlays.
 - If RiskLevel=Medium:
 - Send SMS and push notifications to users with precautionary messages.
 - If RiskLevel=Low:
 - No alerts generated; continue monitoring.

4.3. Alert generation

Once the flood risk level is determined, the system generates real-time alerts to inform stakeholders of potential flood threats. The alert generation process is triggered automatically when a medium or high-risk condition is detected. Moreover, thresholds for the rate-of-rise and water-level differential were initially derived from historical water-level records of the Con River basin and expert consultation with local hydrology specialists. A preliminary calibration process was performed on historical high-flow events to define operational values.

For high-risk conditions, the system prioritizes immediate alerts to emergency response teams and local authorities. The alerts include detailed information such as the sensor locations, current water levels, and predicted flood zones. Additionally, the Google Maps API interface highlights the affected areas on an interactive map, providing users with a visual representation of the flood risk zones.

For medium-risk conditions, the system sends precautionary alerts to users, advising them to monitor the situation closely and prepare for potential evacuations. These alerts are less urgent but still emphasize the importance of proactive measures to mitigate flood impacts.

The integration of automated alert generation with real-time visualization ensures that the system not only detects flood risks but also facilitates effective communication and decision-making. By leveraging Node.js for backend processing, the system achieves low-latency alert generation, with alerts typically delivered within 10 seconds of detecting a potential flood threat.

5. EXPERIMENTAL RESULTS

To evaluate the performance of the proposed flood monitoring system, a series of experiments were conducted using simulated data and limited field testing along the Con River in Binh Dinh Province. Two ultrasonic sensors were deployed at upstream (Tay Son district) and downstream (An Nhon district) locations, with a distance of approximately 24 km between them. Data was collected at 5 seconds intervals over a period of 48 hours, during which both normal and simulated high water level conditions were tested. The measurement results are displayed in real time, as shown in Figure 3.

The ultrasonic sensors successfully captured real-time water level data at regular intervals. The sensor monitoring interface effectively integrates Google Maps API and real-time data visualization to provide a comprehensive overview of environmental conditions across the

region. The interface is divided into two main sections: (i) a map displaying sensor locations and their corresponding data, and (ii) a sidebar showing detailed sensor readings and historical data trends. The map clearly highlights the spatial distribution of sensors at Tay Son and An Nhon, marked with red pins. Each pin provides a pop-up window with real-time environmental data. This visual representation allows users to quickly identify critical environmental data. This visual representation allows users to quickly identify critical environmental parameters at each location, providing valuable spatial context for decision-making.

The dual-sensor water level prediction algorithm was tested using simulated data to evaluate its ability to classify flood risks. The algorithm demonstrated high sensitivity to rapid increases in water levels ($Rate_A$ and $Rate_B$) and significant water level differentials Δ . However, determining accurate thresholds for parameters such as the rate of water level increase $Rate_A$, $Rate_B$ and the water level differential (Δ) remains a challenge that requires further investigation. To establish appropriate thresholds, the system needs to be supplied with more real-world data collected under various environmental conditions, particularly during actual flood events or abnormal flow situations. Additionally, the Δ threshold must also consider the distance between the two sensors

and the proximity of the sensors to the areas being forecasted. A larger distance between sensors may naturally result in water level differences due to terrain and flow dynamics, while the distance from the sensors to the forecasted areas will influence the accuracy and timeliness of the warnings. Therefore, optimizing these thresholds requires a combination of empirical data and spatial analysis to ensure the system performs effectively under all real-world conditions.

To evaluate the performance of the proposed flood monitoring system, we conducted a series of tests using both real-time field data and simulated flood conditions. The performance of the system was measured in terms of its accuracy, calculated using standard metrics derived from the confusion matrix (True Positives - TP, False Positives - FP, False Negatives - FN, and True Negatives - TN).

The accuracy of the system is defined as the proportion of correct predictions (both TP and TN) to the total number of predictions (TP, TN, FP, and FN). Specifically, the accuracy was calculated using the following formula:

$$Accuracy = \frac{TP + TN}{TP + FP + FN + TN} \quad (4)$$

From the Table 1, the accuracy of 94.66% is derived from the system's ability to correctly predict flood risks in 94.66% of the cases tested,

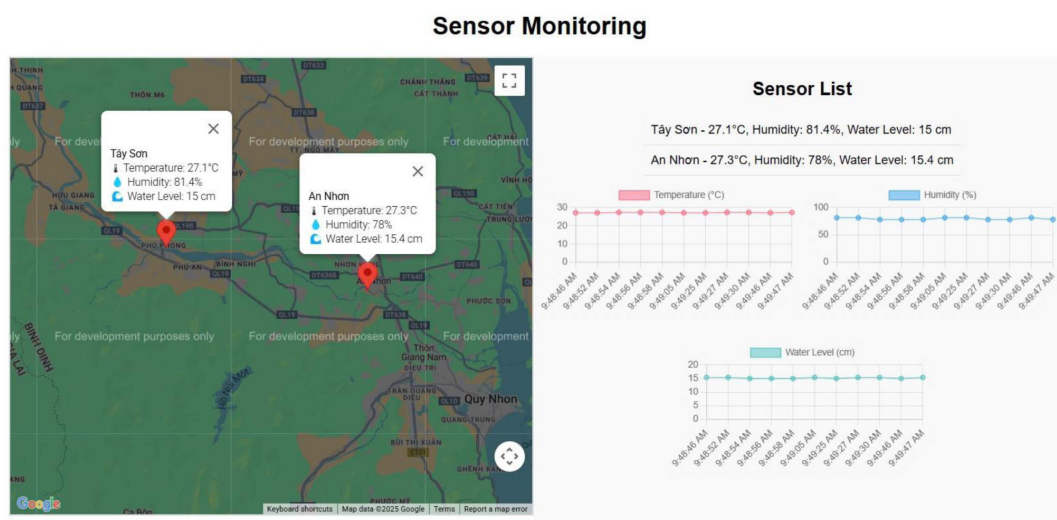


Figure 3. Experimental results displayed on web server.

Table 1. Simulation results and accuracy calculation.

Category	Number of Instances	Percentage (%)
True Positives (TP)	71	47.33%
False Positives (FP)	4	2.67%
False Negatives (FN)	4	2.67%
True Negatives (TN)	71	47.33%
Accuracy	—	94.66%

which indicates that the system's predictions matched the actual flood conditions observed during the test. Beyond accuracy, we also report precision (94.67%), recall (94.67%), F1-score (94.67%), and false alarm rate (2.67%) to provide a more comprehensive evaluation. These results confirm the reliability of the proposed method. This high accuracy was achieved by leveraging dual-sensor water level data, which enhanced the system's ability to detect rapid changes in water levels and spatial variations along the river.

The table clearly shows that the system was highly effective in identifying flood risks, with a minimal number of false positives (2.67%) and false negatives (2.67%). The 94.66% accuracy rate demonstrates the robustness and reliability of the system, particularly in rapidly changing water conditions.

Latency is a critical factor influencing the overall performance of the flood monitoring system. In the current implementation, the ESP32-based system achieves a low-latency data transmission and processing pipeline, with alerts typically generated within approximately 10 seconds after detecting a potential flood risk, as illustrated in Figure 4. In comparison, the Raspberry Pi 4 configuration demonstrated slightly faster response times, averaging around 7 seconds due to its higher processing capability. However, the ESP32 offers a significantly lower power consumption profile, making it a more suitable choice for long-term and energy-constrained IoT deployments.

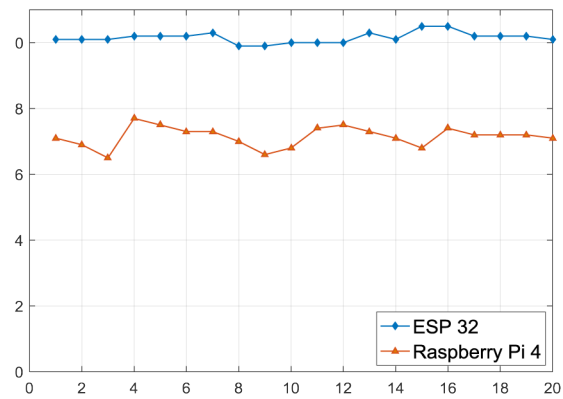


Figure 4. The latency when sending data from the sensor node to the webserver.

This experimental result is completely suitable for applying this system in practice. This rapid response is achieved through the integration of IoT sensors, efficient Node.js backend processing, and real-time communication protocols MQTT. However, certain factors can introduce delays in the system. Since signal transmission over long distances or through areas with poor network coverage may result in increased latency, particularly when using wireless communication methods like 4G. Additionally, the time required for data preprocessing and algorithm execution, though minimal, can also contribute to slight delays in generating predictions.

6. CONCLUSIONS

This paper presents an IoT-based flood monitoring system that leverages dual-sensor water level data, Node.js backend processing, and Google Maps API visualization to provide real-time flood risk prediction and alert dissemination. The proposed dual-sensor water level prediction algorithm effectively analyzes both temporal changes (rate of water level increase) and spatial variations (water level differential) to classify flood risks into low, medium, and high categories. Initial testing demonstrates the system's ability to achieve high accuracy of 94.66% in flood risk classification and generate alerts with minimal latency (around 10 seconds), outperforming traditional single-

sensor approaches. Furthermore, the integration of Google Maps API enhances situational awareness by providing intuitive spatial visualization of sensor locations and flood-prone areas.

Overall, the proposed system has several advantages: (i) a lightweight rule-based algorithm that is efficient for real-time operation, (ii) the dual-sensor approach that improves detection accuracy compared to single-sensor methods, and (iii) a user-friendly web interface integrated with Google Maps that supports practical usability by local authorities and communities.

Future work will include extended deployments covering the entire flood season to capture real high-flow events, validated against ground-truth gauge data and government flood warnings. Furthermore, we will focus on expanding the sensor network, incorporating additional environmental parameters such as rainfall and flow rate, and conducting long-term field testing during flood events. By addressing these limitations, the system has the potential to serve as a scalable and cost-effective solution for mitigating flood risks in vulnerable regions like the Con River basin in Binh Dinh Province, Vietnam and beyond.

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Mô hình dự báo và phát hiện các yếu tố gây ra mưa sử dụng thuật toán học sâu

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TÓM TẮT

Nghiên cứu này sử dụng các thuật toán học sâu để xây dựng mô hình dự báo trên các tập dữ liệu thực tế có dấu hiệu mưa, nhằm dự đoán có mưa hay không tại một thời điểm cụ thể cũng như phân tích cách mưa xuất hiện dựa trên các yếu tố liên quan. Nghiên cứu cũng hướng đến hỗ trợ dự báo chính xác lượng mưa rơi xuống tại một địa điểm vào một thời điểm xác định. Trong nghiên cứu, chúng tôi xây dựng mô hình học sâu nhằm hỗ trợ dự báo thời tiết, đặc biệt là dự đoán chính xác lượng mưa - một bài toán luôn thách thức không chỉ đối với các cơ quan dự báo tại Việt Nam mà còn đối với các hệ thống dự báo tiên tiến trên thế giới. Sử dụng tập dữ liệu thu thập được, chúng tôi tiến hành mô tả các thuộc tính của các trường dữ liệu, cũng như phân tích các tham số có tương quan đến hiện tượng mưa. Sau đó, chúng tôi áp dụng thuật toán học sâu để xây dựng mô hình dự đoán khả năng có mưa có thể xảy ra hay không và xảy ra như thế nào? Các kết quả thu được có thể được ứng dụng trong thực tế để dự đoán lượng mưa tại một địa điểm và thời điểm cụ thể từ dữ liệu đầu vào là dữ liệu dấu hiệu mưa được trích xuất từ cơ sở dữ liệu dự báo thời tiết. Từ đó, nghiên cứu mở ra tiềm năng ứng dụng trí tuệ nhân tạo trong lĩnh vực dự báo khí tượng nhằm nâng cao độ chính xác và giảm thiểu rủi ro do thời tiết cực đoan gây ra.

Từ khóa: Mô hình dự báo mưa, thuật toán LSTM, thuật toán RNN, thuật toán GRU, thuật toán học sâu.

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Predicting model and detecting factors causing rainfall using deep learning

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ABSTRACT

This study aims to employ deep learning algorithms to construct predictive models using real-world datasets containing indicators of rainfall. The objective is to determine the occurrence of rainfall at a specific point in time and to analyze the underlying factors contributing to its onset. Furthermore, the research is directed toward improving the accuracy of quantitative rainfall prediction for a given location and time. This study has developed a deep learning-based framework for weather forecasting with a particular focus on accurate rainfall prediction - a task that remains highly challenging not only for meteorological agencies in Vietnam but also for state-of-the-art forecasting systems worldwide. Using the collected dataset, we conducted descriptive statistical analyses to characterize its properties and investigated the parameters exhibiting correlations with rainfall events. Based on these findings, deep learning algorithms were applied to develop a classification model capable of predicting the probability of rainfall occurrence. The experimental results demonstrate that the proposed model can be applied to operational scenarios for forecasting rainfall at specific locations and times, utilizing rainfall indicators extracted from meteorological forecast databases. The outcomes of this research highlight the potential of artificial intelligence techniques in meteorological applications, offering the prospect of enhanced prediction accuracy and reduced risks associated with extreme weather phenomena.

Keywords: *Rainfall prediction model, LSTM algorithm, RNN algorithm, GRU algorithm, deep learning algorithm.*

1. INTRODUCTION

One of the critical inputs for hydrological computation models is rainfall forecasting. Rainfall prediction is an inherently complex task, especially when forecasting for specific locations across different months and seasons. To develop a low-cost yet effective method that delivers acceptable forecasting accuracy, we employed machine learning techniques to build a daily rainfall forecasting model. Unlike traditional approaches, this study utilized datasets collected from monitoring stations, combining observed

attributes with ERA5 reanalysis data, and applied suitable deep learning algorithms to construct models for rainfall prediction and related influencing factors. In this paper, we present a rainfall forecasting model developed using 16 years of data collected from monitoring stations and ERA5 reanalysis datasets. The forecast outputs from this model can support decision-making in operational forecasting and other related tasks at monitoring station locations.

Artificial Intelligence (AI) is playing an increasingly important role in meteorology and

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hydrology due to its capability to process large volumes of data from observation stations, forecasts, and historical weather records. Deep Learning, a subset of AI, employs multi-layer neural networks to learn complex patterns from data and construct predictive models.

In this study, we developed deep learning models based on the Long Short-Term Memory (LSTM) architecture to predict the occurrence and probability of rainfall. Model optimization was performed through the analysis of evaluation metrics such as the confusion matrix, ROC-AUC curve, and Precision-Recall curve, alongside the identification of key variables influencing predictive performance.

We also integrated meteorological data from observation stations with deep learning algorithms to construct a rainfall forecasting model that can assist meteorologists in their forecasting tasks and be transferable to other stations when necessary. By combining meteorological expertise with observational datasets, the model can analyze factors influencing rainfall based on meteorological parameters, thereby providing predictions on rainfall occurrence and the expected rainfall intensity.

2. RAIN FORECASTING PROBLEMS

2.1. Rain forecasting problem

Currently, accurately predicting rainfall at a specific location and time remains a significant challenge for meteorological agencies worldwide.

Rainfall is essentially the result of atmospheric processes in which water vapor in the atmosphere undergoes a phase change (condensation) into solid or liquid forms such as water, ice, or snow and falls to the ground under the influence of gravity. During the process of condensation and descent to the ground, raindrops are affected by horizontal air currents. Due to differences in environmental conditions, the raindrops themselves may partially evaporate during their fall.¹

In recent years, meteorology and hydrology have made significant progress in forecasting large-scale heavy rainfall events.

Such phenomena can be predicted 2–3 days in advance with an accuracy of about 70%, and in some cases, early warnings can be issued 5–7 days ahead. Forecast information for large-scale heavy rainfall events is generally reliable regarding the timing of rainfall onset, the affected areas, and the ending time of the event.

Early forecasting of large-scale heavy rainfall plays a crucial role in supporting flood, flash flood, landslide, and inundation warnings. These alerts are communicated to authorities and the public to enable proactive response planning and minimize damage.

However, when it comes to quantitative rainfall forecasts (for specific locations and times), current numerical weather prediction technology still faces many limitations. Notably, there are constraints in spatial resolution due to the use of numerous empirical parameters in physical models, as well as a shortage of observational input data particularly over oceans and at higher atmospheric layers.

Estimates indicate that the reliability of point-based quantitative forecasts within a 1–3 day range is only about 40–60% for light and moderate rainfall events (less than 16 mm/day).

In addition to improving the physical modeling capabilities of forecasting systems, the meteorological sector also focuses on enhancing the training and expertise of forecasters especially in utilizing intelligent decision-support systems. This allows for the integration of various types of observations and forecast products, enabling fine-tuning of rainfall and temperature predictions, as well as leveraging ensemble forecasting and other decision-support tools.^{2,3}

2.2. Rainfall database

In this study, we use data from the Quy Nhon Meteorological Station a Class I meteorological station with the international code “48870”. This station is internationally recognized as a high-accuracy data source and is frequently used in weather forecasting models.

The dataset spans from 2009 to 2024 and includes hourly observational variables such

as temperature, humidity, station pressure, and total rainfall. In addition, reanalysis data from ERA5 is incorporated, comprising 54 variables, primarily related to temperature, humidity, and wind vectors in the u and v directions at atmospheric pressure levels ranging from 950 hPa to 300 hPa. All data are organized as time series by hour, day, and month.

The objective of using these datasets is to explore and analyze the relationship between rainfall and other meteorological factors in the Quy Nhon area. Rainfall classification in the dataset follows the standards of the Vietnam Meteorology and Hydrology sector as follows:

- No rain = 0mm/day
- Rain < 16mm/day
- $16\text{mm/day} \leq \text{Moderate rain} < 50\text{mm/day}$
- $50\text{mm/day} \leq \text{Heavy rain} < 100\text{mm/day}$
- Very heavy rain $\geq 100\text{mm/day}$

Statistics show that “No rain” has the highest occurrence with 86601 cases, followed by “Rain” with 40752 cases, and then “Moderate rain” with 9157 cases. “Heavy rain” is significantly less frequent with 2476 cases, and finally, “Very heavy rain” has the fewest occurrences with 1192 cases.

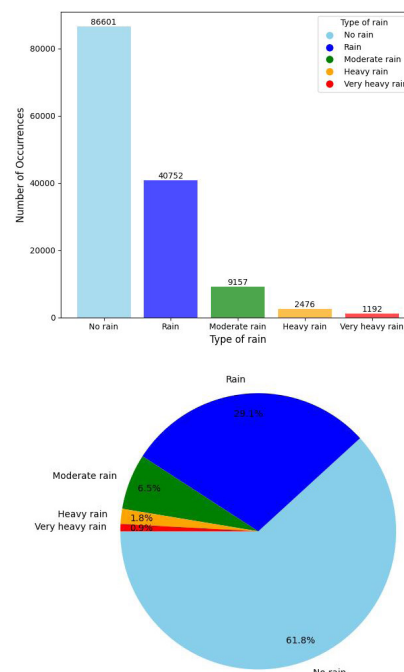


Figure 1. The distribution of rainfall categories in the dataset.

From Figure 1, it is evident that among 100 sampled values, there are 62 “No rain” cases, 29 “Rain” cases, 6 “Moderate rain” cases, 2 “Heavy rain” cases, and only 1 “Very heavy rain” case. This indicates an uneven distribution of data among rainfall categories, with heavier rainfall events occurring less frequently.

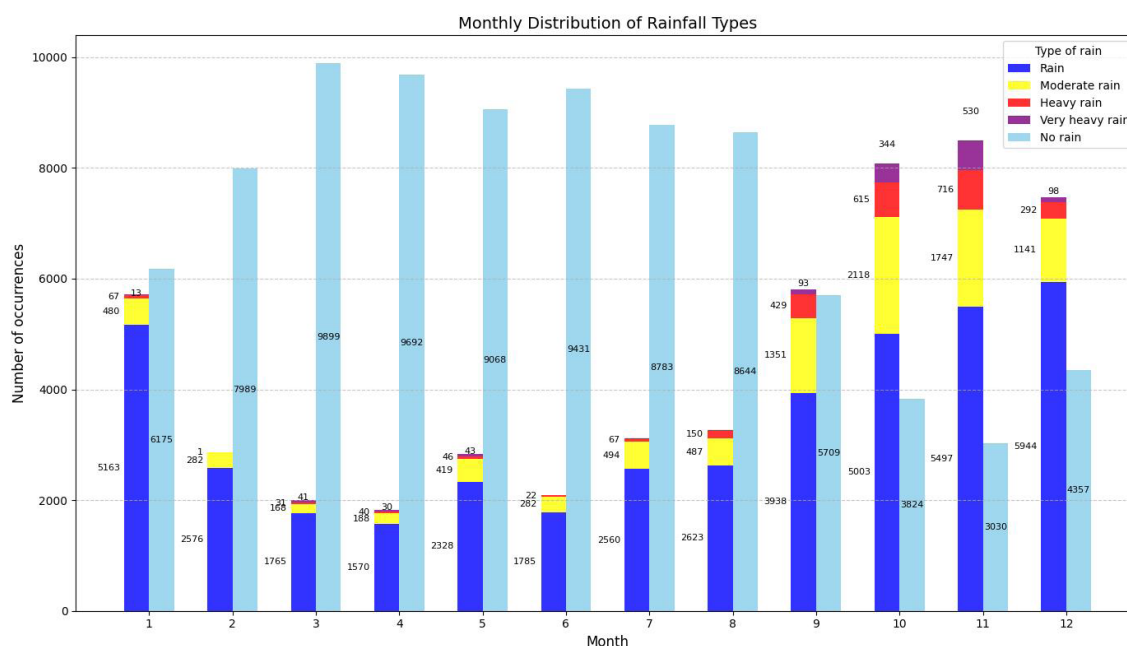


Figure 2. The distribution of rainfall categories by month.

Based on Figure 2, heavy and very heavy rainfall events are primarily concentrated between September and December, with a pronounced increase in their occurrence during September, October, and November. This period corresponds to the region's main rainy season, when active weather systems deliver abundant precipitation. In these months, not only does the number of rainfall events rise significantly, but rainfall intensity also increases, contributing substantially to the region's annual total precipitation.

Specifically, the number of moderate, heavy, and very heavy rainfall events increases sharply from September to December, whereas the rest of the year is dominated by no rain or rain events. This highlights a clear seasonal pattern in rainfall distribution within the study area.

As shown in Figure 3, rainfall events occur most frequently in the temperature

range of 24°C to 30°C, with particularly high concentrations in the 24–26°C and 26–28°C intervals. In these temperature ranges, the total number of rainfall samples (from light to very heavy) accounts for the majority compared to other temperature groups. Notably, very heavy rainfall events almost exclusively occur within the 24–26°C and 26–28°C intervals, indicating that this temperature range is the most favorable for extreme rainfall. Conversely, at lower temperatures (< 22°C) or higher temperatures (> 30°C), the frequency of rainfall events especially heavy and very heavy declines sharply, with almost no extreme rainfall observed above 30°C. This suggests that samples with excessively low or high temperatures are less likely to be associated with rainfall, particularly intense rainfall events.

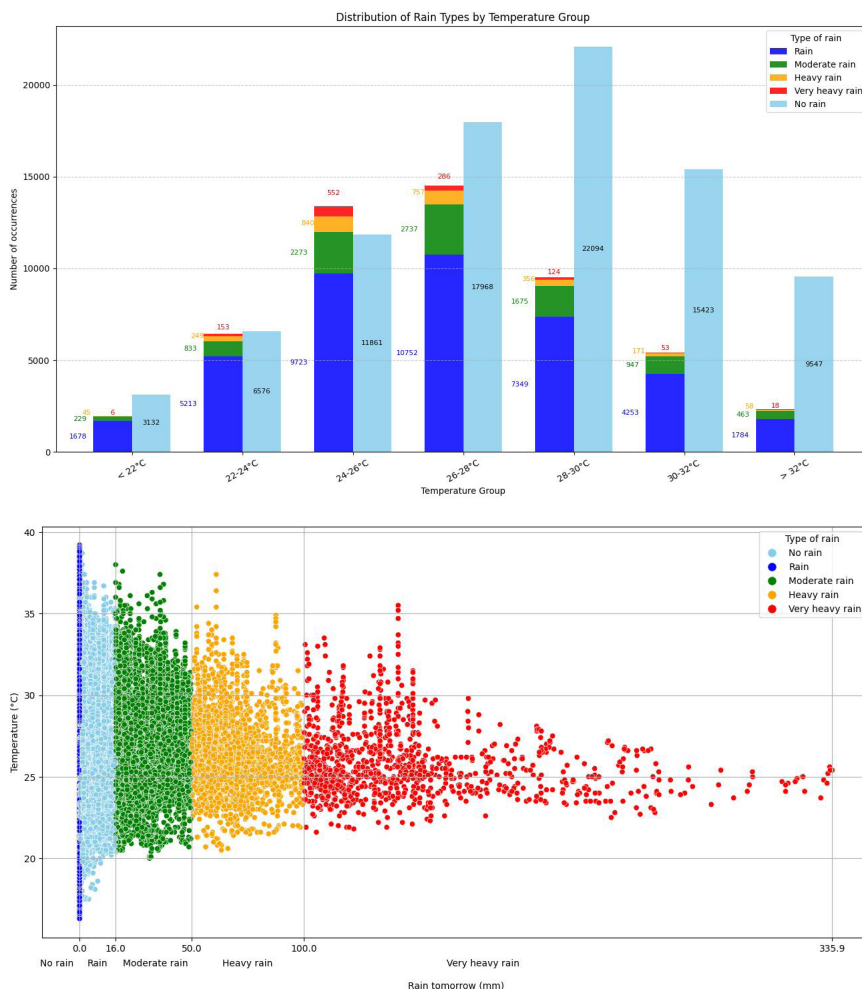


Figure 3. The distribution of rainfall types across temperature groups.

Figure 4 shows that the frequency of rainfall events (from light rain to very heavy rain) increases with higher humidity levels. In the 80-90% humidity range, the total number of rainy samples is the highest, with light rain and moderate rain dominating. This indicates that this humidity band is ideal for rain formation. The 70-80% range comes next, also showing a relatively large number of rainy samples, reflecting the clear trend that higher humidity is associated with a higher likelihood of rain.

Notably, heavy and very heavy rainfall events occur mainly in the two highest humidity groups 80–90% and >90% and are almost absent

in lower humidity groups. This suggests that extreme rainfall events often happen when the air holds a very high moisture content, providing favorable conditions for intense atmospheric condensation. In contrast, humidity groups below 60% and 60-70% record relatively few rainy samples, with heavy and very heavy rain almost non-existent, indicating that drier environments have little potential to produce rainfall, especially extreme events. Moreover, the >90% humidity group is the only one with the highest number of very heavy rain samples in the entire chart, emphasizing the role of extreme humidity in triggering severe weather phenomena.

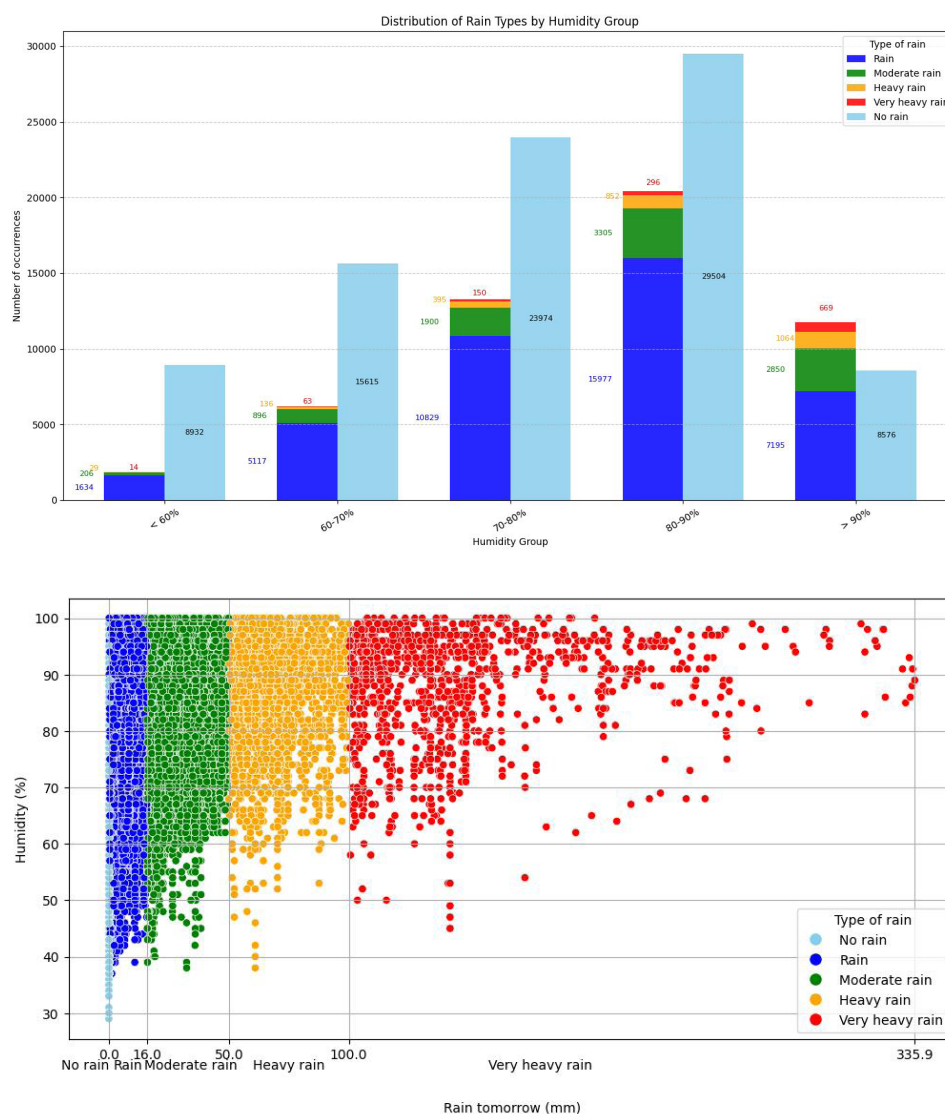


Figure 4. Distribution of rainfall types by humidity group.

In Figure 5, rainfall samples are concentrated mainly in the pressure range of 1005-1015 mb, with the 1005-1010 mb and 1010-1015 mb groups clearly dominating. This range not only shows a high number of rainy samples but also a noticeable increase in strong rainfall events, reflected in the frequent appearance of orange and red bars representing heavy and very heavy rain. This suggests that this pressure range is favorable for atmospheric conditions that lead to the formation and growth of convective rain clouds.

On the other hand, at the extremes of pressure specifically <1000 mb and >1025 mb the

number of rainy samples is very low, and heavy rainfall events are almost absent, indicating that both very low and very high pressure are not ideal environments for rain. The 1015-1020 mb group still maintains a considerable number of rainy samples but shows a slight decrease compared to the preceding range, suggesting that when pressure exceeds 1015 mb, the likelihood of rain begins to decline. Similarly, the 1020-1025 mb and >1025 mb groups are dominated by non-rain samples, reflecting a more stable atmosphere with fewer conditions supporting rainfall development.

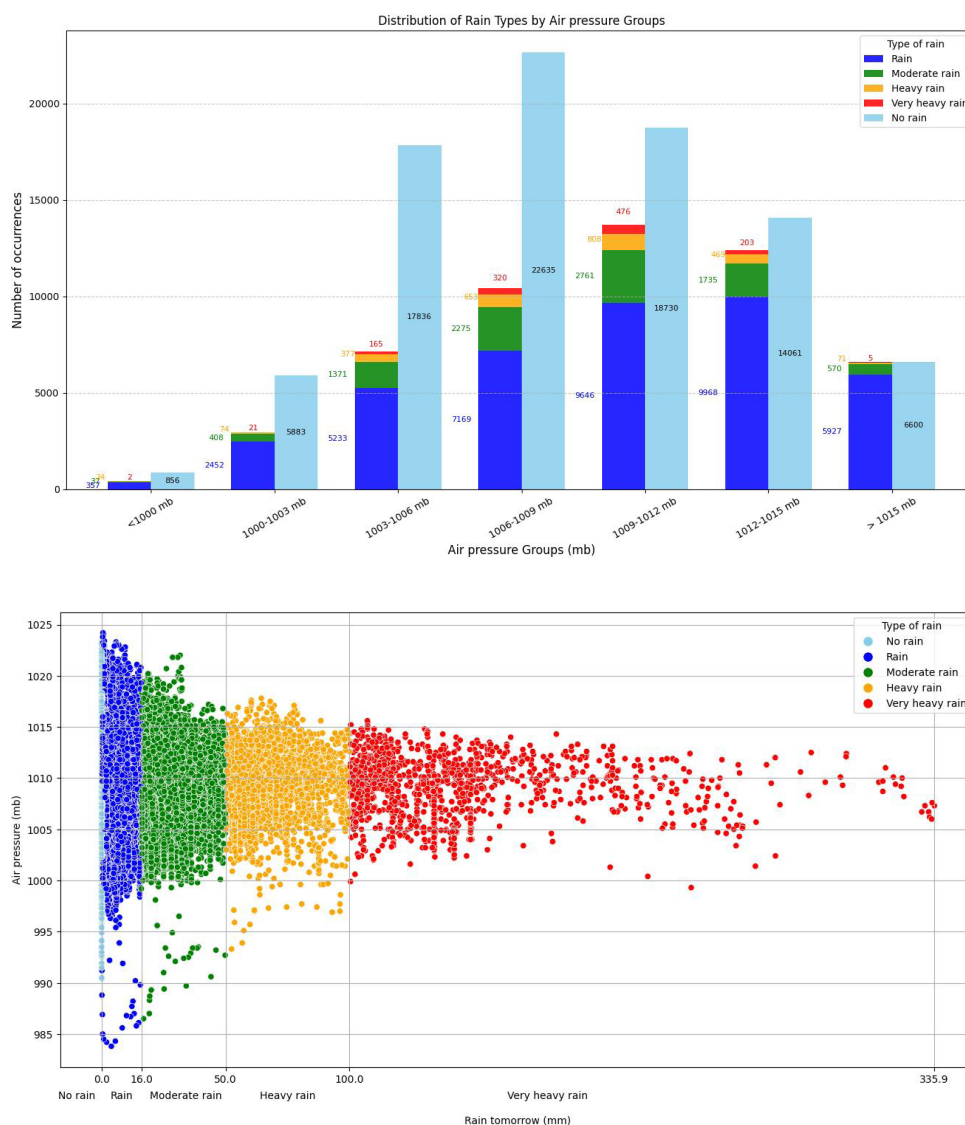


Figure 5. Distribution of rainfall types by pressure group.

Because the features in the dataset are independent, analyzing their correlations is essential to assess both their interrelationships and their relationship with the target variable in this case, the likelihood of rain the next day (rain_tomorrow).



Figure 6. Correlation matrix between factors.

From Figure 6, we observe that humidity, month, and rainfall all show positive correlations with the probability of rain on the following day, with previous-day rainfall exhibiting the strongest positive correlation with next-day rain. In contrast, factors such as temperature have a negative correlation with the likelihood of rain. Notably, atmospheric pressure shows a very weak correlation with next-day rain, with a coefficient of only 0.09.

3. ALGORITHMS AND PREDICTION MODELS

3.1. Deep learning algorithms

Deep learning is an important branch of artificial intelligence that focuses on building and training multi-layer neural networks to automatically learn complex features from data.

Unlike traditional machine learning methods, deep learning can extract features directly from raw data, reducing dependence on manual preprocessing steps while effectively capturing complex nonlinear relationships between input variables.

Thanks to these capabilities, deep learning has become a powerful tool in fields that require processing large and complex datasets, such as computer vision, natural language processing, and especially time series forecasting in meteorology and hydrology.⁵

In the context of weather forecasting and hydrometeorological phenomena, deep learning algorithms are widely applied to predict variables related to rainfall, temperature, humidity, pressure, and other meteorological parameters.

Sequential neural networks such as RNNs (Recurrent Neural Networks) allow the model to retain information from previous time steps, while more advanced variants such as LSTM (Long Short-Term Memory) and GRU (Gated Recurrent Unit) are specifically designed to address the vanishing gradient problem, enabling the learning of long-term dependencies in time series data.⁶

The choice of an appropriate deep learning algorithm depends on the specific characteristics of the problem and the data.

For example, with datasets containing long time series and requiring the capture of complex relationships among meteorological variables, LSTM is often preferred for its long-term memory capabilities, while GRU can be used when reducing the number of parameters and speeding up training is a priority. Thus, deep learning not only offers more accurate forecasting but also provides flexibility in uncovering hidden features in hydrometeorological data.

RNN Algorithm

RNN (Recurrent Neural Network) is a neural network architecture specifically designed to process time series data, where the current value depends on previous values. Unlike traditional neural networks, RNNs have the ability to retain information from previous time steps through a hidden state, enabling the model to predict future values based on historical data.⁵

RNN Training Algorithm: RNNs are trained using Backpropagation Through Time (BPTT), an extension of backpropagation, to update weights based on the gradient of the loss function with respect to the entire time sequence.⁴

Step 1: Weight Initialization - Randomly initialize the weights W_h (hidden state weights), W_x (input weights), W_y (output weights) along with biases b (hidden state bias) and c (output bias).

Step 2: Forward pass - Iterate through the entire time sequence. At each time step t , compute the hidden state h_t based on the current input x_t and the previous hidden state h_{t-1} according to the formula:

$$h_t = \tanh(W_x x_t + W_h h_{t-1} + b) \quad (1)$$

Then, compute the predicted output y_t from the hidden state h_t :

$$y_t = \text{softmax}(W_y h_t + c) \quad (2)$$

Step 3: Compute the loss function - Use an appropriate loss function based on the predicted output y_t and the actual label y^t

Step 4: Backward pass - Backpropagation of the error from the final time steps to the initial ones, computing the gradient of the loss function with respect to the weights W_x , W_h , W_y , b , c .

Step 5: Update weights - Use an optimization algorithm to update the weights based on the computed gradients, minimizing the loss function.

Step 6: Repeat - The process of forward pass, loss calculation, backward pass, and weight updates is repeated over many epochs until the model converges or meets the early stopping criterion.

Step 7: Prediction - Once the model is trained, the RNN can take a new input sequence and continuously compute the hidden states to predict the corresponding output sequence.

LSTM Algorithm

LSTM (Long Short-Term Memory) is an improved recurrent neural network (RNN) architecture designed to handle long time-series data and overcome the vanishing gradient problem often found in traditional RNNs. LSTM can retain long-term information thanks to its gating mechanism, which controls which information is kept, updated, or discarded in the cell state.^{5,7}

LSTM training algorithm: LSTM is also trained using Backpropagation Through Time, an extension of backpropagation, to update weights based on the gradient of the loss function over the entire time series.

Step 1: Initialize weights and states - Randomly initialize the weights for the forget gate W_f , input gate W_i , output gate W_o , cell input W_c along with the biases b_f , b_i , b_o , b_c . The hidden state h_0 and the cell state C_0 are usually initialized as zero vectors.

Step 2: Forward pass - Iterate through the entire time series. At each time step t :

Forget gate:

$$f_t = \sigma(W_f \cdot [h_{t-1}, x_t] + b_f) \quad (3)$$

Input gate:

$$i_t = \sigma(W_i \cdot [h_{t-1}, x_t] + b_i) \quad (4)$$

Cell input:

$$\tilde{i}_t = \sigma(W_i \cdot [h_{t-1}, x_t] + b_i) \quad (5)$$

Update cell state:

$$C_t = f_t * C_{t-1} + i_t * \tilde{C}_t \quad (6)$$

Output gate:

$$o_t = \sigma(W_o \cdot [h_{t-1}, x_t] + b_o) \quad (7)$$

Hidden state:

$$h_t = o_t * \tanh(C_t) \quad (8)$$

Output prediction (if needed):

$$y_t = \text{output_layer}(h_t) \quad (9)$$

Step 3: Compute the loss function - Use an appropriate loss function based on the predicted output y_t and the actual label.

Step 4: Backward pass—Backpropagation of errors from the last time step to the first (Backpropagation Through Time), computing the gradients of the loss with respect to all weights $W_f, W_i, W_o, W_c, b_f, b_i, b_o, b_c$.

Step 5: Update weights - Use an optimization algorithm to update weights based on computed gradients, minimizing the loss function.

Step 6: Repeat - Perform forward pass, loss computation, backward pass, and weight updates over many epochs until the model converges or meets early stopping criteria.

Step 7: Prediction - Once trained, the LSTM can take a new input sequence and compute hidden states sequentially to predict the corresponding output sequence.

GRU Algorithm

GRU (Gated Recurrent Unit) is an improved recurrent neural network architecture, similar to LSTM but with a simpler structure. It combines certain gates to reduce the number of parameters while still maintaining the ability to remember long-term information. GRU has two main gates: the update gate and the reset gate, which control which information should be retained or discarded in the hidden state.

The GRU training algorithm also uses Backpropagation Through Time to update weights based on the gradients of the loss function across the entire time sequence.

Step 1: Initialize weights and states - Randomly initialize the weights for the update gate W_z , reset gate W_r , candidate state W_h along with the biases b_z, b_r, b_h . The initial hidden state h_0 is usually set as a zero vector.

Step 2: Forward pass - Iterate through the entire time sequence. At each time step t :

- Update gate:

$$z_t = \sigma(W_z \cdot [h_{t-1}, x_t] + b_z) \quad (10)$$

- Reset gate:

$$r_t = \sigma(W_r \cdot [h_{t-1}, x_t] + b_r) \quad (11)$$

- Candidate hidden state:

$$\tilde{h}_t = \tanh(W_h \cdot [r_t * h_{t-1}, x_t] + b_h) \quad (12)$$

- New hidden state:

$$h_t = (1 - z_t) * h_{t-1} + z_t * \tilde{h}_t \quad (13)$$

- Output prediction (if needed):

$$y_t = \text{output_layer}(h_t) \quad (14)$$

Step 3: Compute the loss function - Use an appropriate loss function based on the predicted output y_t and the actual labels.

Step 4: Backward pass—Backpropagation of the error from the last time steps to the first, computing the gradients of the loss function with respect to all weights $W_z, W_r, W_h, b_z, b_r, b_h$.

Step 5: Update weights - Use an optimization algorithm to update the weights based on the computed gradients, minimizing the loss function.

Step 6: Repeat - The process of forward pass, loss computation, backward pass, and weight update is repeated for many epochs until the model converges or meets an early stopping criterion.

Step 7: Prediction - Once trained, the GRU can take a new input sequence and compute the hidden state continuously to predict the corresponding output sequence.

3.2. Prediction models using deep learning

The dataset from the Quy Nhon Meteorological Station, after being cleaned and encoded to convert categorical features into numerical values, can be used as input for deep learning models. The objective is to train and compare the performance of three deep learning algorithms: LSTM, RNN, and GRU. These models are highly suitable for time series data and have proven effective in weather forecasting tasks thanks to their ability to capture temporal dependencies, automatically extract features from raw data, and model complex nonlinear relationships between variables.^{4,9}

The processed dataset was divided into two subsets, with 80% allocated for training

and 20% reserved for testing. This partitioning strategy ensures that the models have sufficient data for effective learning while maintaining an independent subset for objective evaluation of generalization capability on unseen samples.

The input dataset consists of 54 meteorological variables derived from ERA5 reanalysis data including temperature, humidity, wind, and pressure at various atmospheric levels combined with surface observational time series from the Quy Nhon meteorological station. This integration captures both local-scale conditions and large-scale atmospheric circulation patterns, providing a comprehensive representation of the meteorological environment. The prediction target is the 24-hour accumulated rainfall, categorized into discrete rainfall intensity levels.

For efficient model training, rainfall observations were discretized into five distinct categories: (0) no rain, (1) rain, (2) moderate rain, (3) heavy rain, and (4) very heavy rain. These categorical labels were subsequently encoded using one-hot encoding to form five-dimensional binary vectors, each representing a specific rainfall class.

Following model architecture design, parameter optimization was conducted through systematic tuning of the training algorithm, loss function, and key hyperparameters. Specifically, all models employed the Adam optimizer with an initial learning rate of $\alpha = 0.001$. Adam, which combines the advantages of Momentum and RMSProp, dynamically adapts the learning rate during training, making it particularly effective for nonlinear and noisy meteorological datasets.⁸

The Categorical Cross-Entropy loss function was adopted as it is well-suited for multi-class classification tasks, enabling the models to learn class probability distributions rather than rigid decision boundaries.⁸ The training process was executed over 70 epochs with a batch size of 64, a configuration that balances learning efficiency and overfitting prevention. This setup ensures stable gradient updates,

effective utilization of computational resources, and robust model convergence, ultimately leading to improved predictive performance on independent test data.

Table 1. Comparison among the machine learning model.

Model	Accuracy	Kappa	AUC-ROC
LSTM	0.8211	0.6462	0.9544
RNN	0.7675	0.5254	0.9196
GRU	0.8115	0.6290	0.9514

Table 1 presents the performance comparison of the three deep learning models—LSTM, RNN, and GRU—in a multi-class classification problem. The results show that LSTM achieved the highest performance across all three evaluation metrics, with an Accuracy of 0.8211, a Kappa of 0.6462, and an impressive AUC-ROC of 0.9544. This indicates that LSTM not only delivers high predictive accuracy but also effectively distinguishes between classes, especially in the context of complex data.

GRU also demonstrated competitive performance, with an Accuracy of 0.8115, a Kappa of 0.6290, and an AUC-ROC of 0.9514 only slightly lower than LSTM. This suggests that GRU is an efficient choice when balancing accuracy and computational complexity is important.

In contrast, RNN achieved significantly lower results, with an Accuracy of only 0.7675, a Kappa of 0.5254, and an AUC-ROC of 0.9196. This gap is particularly evident in the Kappa score, indicating that RNN struggles to accurately classify classes when dealing with imbalanced data. Notably, while the AUC-ROC scores of all three models exceed 0.9, the differences in Accuracy and Kappa indicate that LSTM and GRU handle the task more effectively than the traditional RNN.

These results suggest that modern neural network architectures such as LSTM and GRU are better suited for multi-class classification

problems than basic RNNs, due to their ability to capture long-term dependencies in time series data.

Table 2. Regression error comparison of neural network models.

Model	RMSE	MAE
LSTM	0.5024	0.2012
RNN	0.5766	0.2617
GRU	0.5106	0.2096

Table 2 presents the RMSE and MAE for three neural network models: LSTM, RNN, and GRU. The LSTM achieved the lowest errors (RMSE = 0.5024, MAE = 0.2012), followed by the GRU (RMSE = 0.5106, MAE = 0.2096),

while the RNN exhibited the highest errors (RMSE = 0.5766, MAE = 0.2617). The average deviation between predicted and true labels is approximately 0.2–0.5 units on the 0–4 scale, indicating that all models reliably forecast rainfall categories. Overall, models with gating mechanisms (LSTM and GRU) outperform the standard RNN in capturing temporal dependencies and reducing prediction errors.

Confusion Matrix

Analysis of the confusion matrix in Figure 7 for the three deep learning models (LSTM, RNN, GRU) in the rainfall classification task (0: no rain, 1: rain, 2: moderate rain, 3: heavy rain, 4: very heavy rain) reveals distinct patterns.

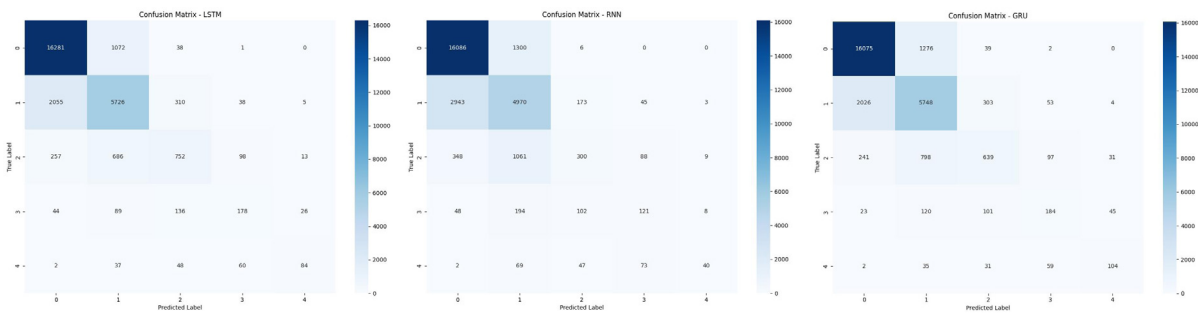


Figure 7. Confusion Matrices for LSTM, RNN and GRU Models.

For the LSTM model, classification performance decreases as rainfall intensity increases: it achieves the highest accuracy with 16281 correctly classified cases for the no-rain class (0), drops to 5726 for the light rain class (1), and only 84 correct predictions for the very heavy rain class (4). Notably, the model tends to confuse rainfall classes, as evidenced by 37 very heavy rain cases (4) being misclassified as light rain (1) and 2 cases as no rain (0). This outcome reflects a common challenge for models when dealing with minority classes that occur infrequently in the dataset, especially extreme rainfall events. The large disparity in the number of correct predictions between the majority class (no rain) and the minority classes (various rainfall types) highlights the need to apply data imbalance handling techniques to improve the model’s overall performance.

The RNN model demonstrates the most unstable performance among the three, with gaps in its confusion matrix. Although it achieves 16086 correct predictions for the no-rain class (0), it misclassifies up to 4900 cases. Its performance drops sharply for rainfall classes, with only 4970 correct predictions for light rain (1) and 102 for very heavy rain (4).

The GRU model shows inconsistent classification performance across classes. For the no-rain class (0), it performs well with 16075 correct predictions, but a wide range of abnormal values (1276–5748) suggests potential overfitting or issues in the data normalization process. Performance declines significantly for rainfall classes: the moderate rain class (2) achieves only 1216 correct predictions, heavy rain (3) drops to 398, and the very heavy rain

class (4) is almost entirely unrecognized, with correct predictions ranging from 0–4. This steep decline in accuracy with increasing rainfall intensity, along with extremely low values at the bottom of the matrix, points to limitations in input data quality or a suboptimal preprocessing pipeline, especially for extreme rainfall cases.

Overall, all three models struggled to accurately classify minority classes, with LSTM producing the most stable results despite being imperfect, while RNN and GRU exhibited

several anomalies that require further inspection of data quality and training processes. The large disparity in the number of predictions across classes highlights the issue of data imbalance.

Training progress - Loss log

Analysis of the learning curves (Figure 8) shows a clear difference in the training processes of the three models: LSTM, RNN, and GRU. All three display a general downward trend in loss as the number of epochs increases, but with distinct characteristics.

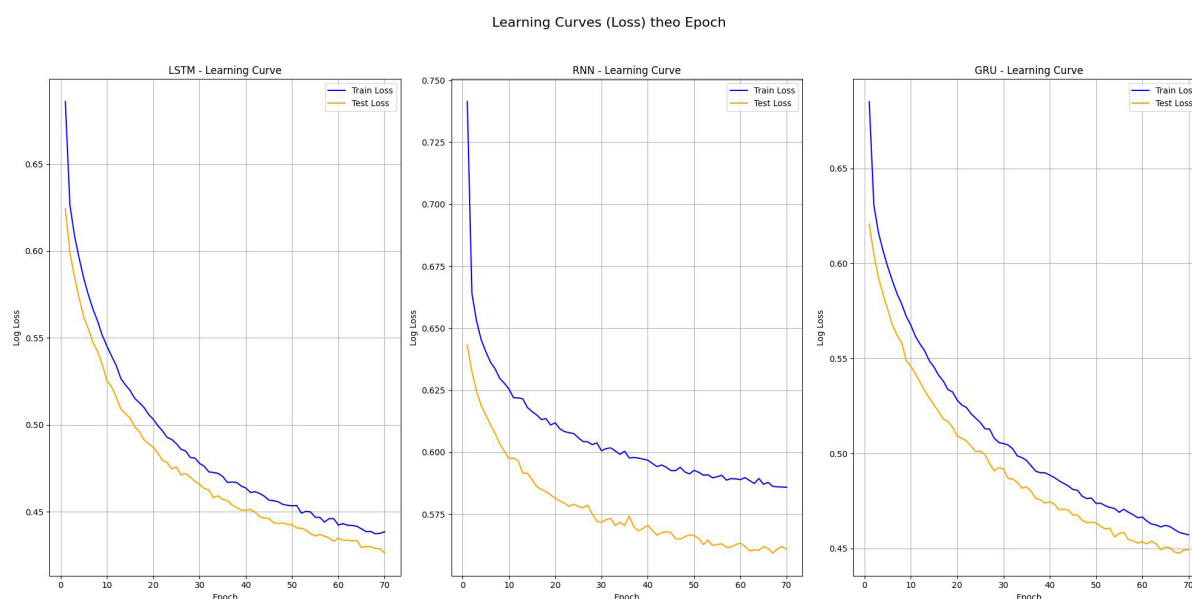


Figure 8. Training progress and loss log for LSTM, RNN, and GRU.

The LSTM model shows the most stable learning curve, with test loss decreasing gradually from 0.75 to 0.575 after 70 epochs, indicating a slow yet steady learning process. Notably, the gap between train loss and test loss is relatively small, suggesting that the model suffers little from overfitting.

RNN improves more quickly in the early stages, with test loss dropping from 0.65 to 0.45 in the first 30 epochs. However, it later exhibits strong fluctuations (especially between epochs 40–50), reflecting the inherent instability of the traditional RNN architecture.

GRU demonstrates a balance between the two above learning faster than LSTM but with more stability than RNN. Its test loss decreases steadily from 0.65 to 0.30. However, the sudden

drop in test loss at epoch 20 (from 0.60 to 0.35) followed by subsequent oscillations may point to optimization issues or an unsuitable learning rate.

In summary, LSTM shows an advantage in stability, GRU learns faster but is less stable, and RNN struggles to maintain consistent performance across epochs. These results align with theory: LSTM is designed to address the vanishing gradient problem faced by traditional RNNs, while GRU is a simplified version of LSTM with fewer parameters.

Feature Importance

Analysis of Figure 9 shows the contribution levels of input features for three deep learning models: LSTM, RNN, and GRU, highlighting

the 15 most important features for each model. The importance scores were determined using the permutation importance method, which measures the decrease in model accuracy when the values of a particular feature are randomly shuffled. A greater drop in accuracy indicates higher importance, reflecting the extent to which each meteorological variable influences the model's predictive performance.

For LSTM, temperature-related factors at various pressure levels, such as t_750hPa, t_950hPa, t_300hPa, and the Month variable, rank at the top, indicating that this model focuses on temperature variations across both time and atmospheric height. Additionally, humidity features like e_700hPa and wind components such as v_600hPa also play significant roles.

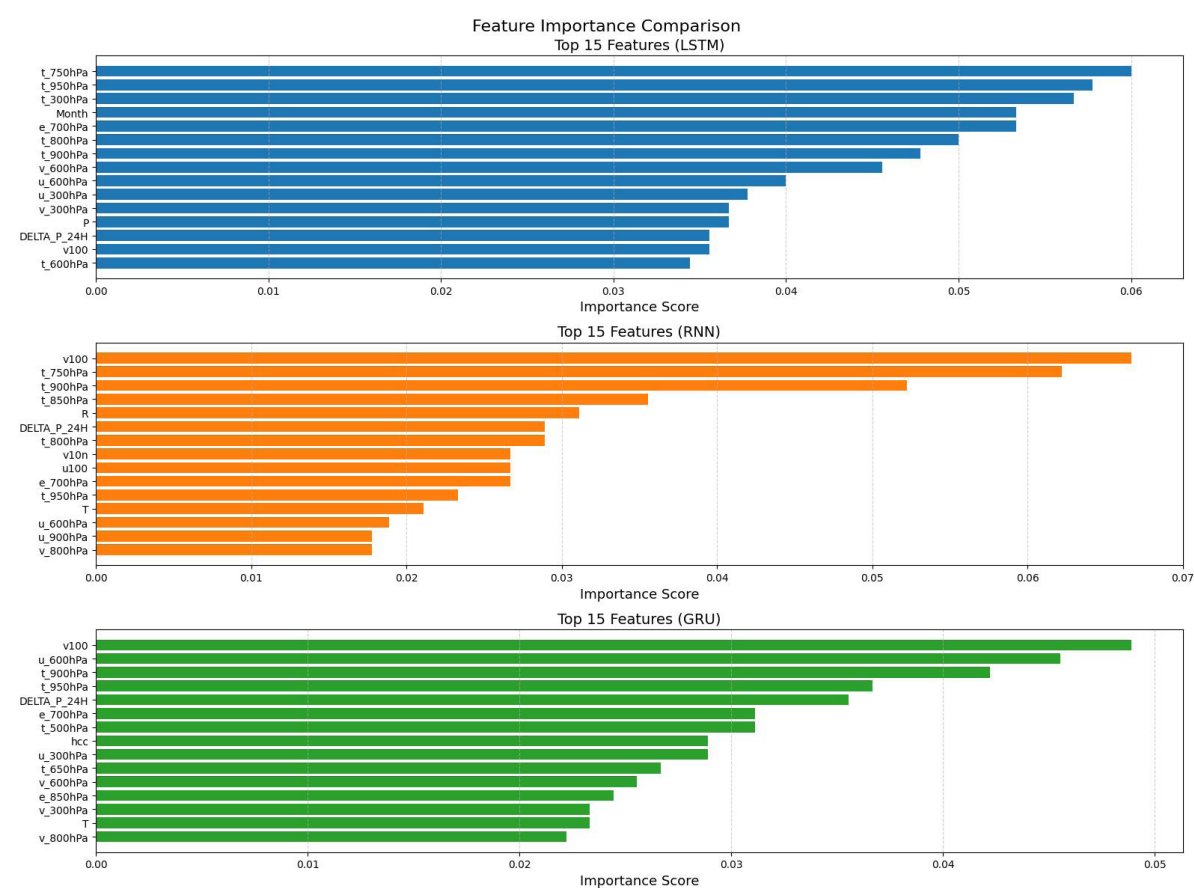


Figure 9. Importance of features.

For RNN, features related to surface and lower-level wind, such as v100 and v10n, along with mid and low-level temperatures (t_750hPa, t_900hPa) dominate. Notably, actual rainfall (R) and 24-hour pressure variation (DELTA_P_24H) are among the top features, reflecting the RNN's ability to strongly leverage local and direct weather signals.

Meanwhile, GRU prioritizes v100 and u_600hPa (zonal wind at 600hPa), combined with temperatures at multiple levels (t_900hPa, t_750hPa, t_650hPa) and mid-level humidity

(e_700hPa). The 24-hour pressure variation (DELTA_P_24H) is also among the important features, highlighting the role of large-scale dynamic factors.

Overall, all three models utilize a combination of temperature, wind, and pressure information, but LSTM emphasizes multi-level temperature analysis, RNN is more sensitive to surface wind and rainfall signals, while GRU balances wind, temperature, and pressure. These differences reflect the distinct strategies each architecture employs in rainfall prediction.

4. CONCLUSION

The study applied three deep neural network architectures LSTM, RNN, and GRU to classify rainfall by intensity, using observational data from the Quy Nhon meteorological station combined with ERA5 reanalysis data. The results indicate that all three models achieved good forecasting performance, with LSTM demonstrating superior accuracy, class discrimination ability, and training stability. GRU performed closely to LSTM, offering a balanced choice between accuracy and computational cost, while the traditional RNN was less stable and faced limitations in classifying minority classes.

Feature importance analysis revealed that the temporal factor (Month) plays a prominent role, clearly reflecting the seasonal nature of rainfall in the study area. In addition, meteorological features such as wind, temperature, humidity, and pressure variations at multiple atmospheric levels also contributed significantly, with each model tending to exploit information differently: LSTM focused on multi-level temperature variations, RNN was more sensitive to surface wind and rainfall signals, and GRU maintained a balance between wind, temperature, and pressure factors.

However, there exist a number of practical limitations in this study. Although ERA5 reanalysis data supplement large-scale information, they exhibit a time lag in updates, causing the model to rely primarily on surface observations and limiting its ability to respond rapidly to short-term atmospheric fluctuations. Moreover, model performance may decline over time if not periodically updated, due to climate change and evolving structures of meteorological variables. Therefore, regularly incorporating new data, retraining the model, and integrating real-time observations with multi-layer forecasting models and advanced

deep learning techniques will be crucial for improving accuracy, adaptability, and resilience to extreme weather event.

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Nghiên cứu cơ chế và động học phản ứng giữa methylene blue với gốc tự do OH trong pha khí bằng phương pháp tính toán DFT

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TÓM TẮT

Methylene blue (**MB**) là một loại thuốc nhuộm dị vòng thơm phổ biến, được sử dụng rộng rãi trong công nghiệp, đặc biệt là trong nhuộm giấy, bông, len, lụa và các loại sợi dệt khác. Cơ chế và động học liên quan đến quá trình phân hủy **MB** bởi gốc tự do HO[•] trong pha khí đã được tính toán trong nghiên cứu này bằng phương pháp hóa học lượng tử. Trong pha khí, **MB** chủ yếu bị phân hủy thông qua cơ chế cộng gốc tự do vào nối đôi, trong đó gốc HO[•] tấn công tại vị trí C4 ở nhiệt độ 298,15 K. Hằng số tốc độ tổng thể của bước 1 và bước 2 lần lượt là $3,24 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ và $1,48 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$; quá trình này tạo ra ba sản phẩm chính gồm . Hằng số tốc độ tổng thể của phản ứng phân hủy **MB** có xu hướng giảm nhẹ ($k_{\text{overall}} = 6.63 \times 10^{10} - 1.81 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) trong khoảng nhiệt độ từ 253 đến 323 K.

Từ khóa: Methylene blue, tính toán DFT, oxidation, cơ chế, phân hủy.

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DFT Study on the mechanism and kinetics of the gas-phase reaction between methylene blue and OH radicals

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ABSTRACT

Methylene blue (**MB**) is a representative aromatic heterocyclic dye extensively employed in industrial applications, particularly in the dyeing of paper, cotton, wool, silk, and related textiles. In this work, the mechanisms and kinetics governing the gas-phase degradation of MB by hydroxyl radicals (HO[•]) were elucidated through quantum chemical calculations. The results demonstrated that, at 298.15 K, **MB** predominantly underwent degradation *via* a radical adduct formation mechanism involving HO[•] addition at the C4 position. The overall rate constants for the first and second steps were calculated to be 3.24×10^{10} and $1.48 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$, respectively, leading to three major products. The overall degradation rate exhibited only a slight variation with increasing temperature from 253 to 323 K, suggesting that temperature exerts a limited effect on the oxidative removal efficiency of MB under environmentally relevant conditions.

Keywords: Methylene blue, DFT study, oxidation, mechanism, chemical fate.

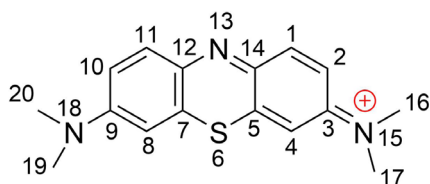
1. INTRODUCTION

Methylene blue (**MB**, Figure 1) is an aromatic heterocyclic dye widely utilized in industry, particularly for dyeing silk, cotton, wool, paper, and other materials.¹⁻³ **MB** is a cationic dye that is resistant to natural degradation, posing a risk to ecological systems and potentially leading to different health problems for humans in the event of uncontrolled release, despite its recognized clinical use.²⁻⁶ **MB** degradation can be significantly promoted by various oxidation technologies, such as electrochemical,⁷ photocatalytic⁸⁻¹⁰ and ozone¹¹ process. Among

advanced oxidation processes (AOPs), the introduction of reactive oxygen species - ROS (including HO[•], SO₄^{•-}, Cl[•], ClO[•], HOO[•], and O₂^{•-}), represents a simple yet highly effective approach. Notably, the HO[•] was regarded as the primary oxidizing species responsible for **MB** degradation due to its high redox potential and non-selective reactivity.^{12,13} Our recent analysis revealed that, in water, **MB** exhibited a quick reaction with the HO[•] radical, characterized by an overall rate constant ranging from 5.51×10^9 to $2.38 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, and a lifetime of 11.66 hours to 5.76 years at temperatures between 273 and 383 K.¹⁴

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Methylene blue (MB)

Figure 1. Structure of MB.

Given that **MB** can persist in aerosol drying layers, dye particulates, and spray processes,^{15,16} where solvent influences are substantially reduced, elucidating its gas-phase degradation mechanism offers valuable complementary insights into its atmospheric transformation behavior. Nonetheless, the atmospheric degradation of **MB** has yet to be investigated. This study examines the thermodynamic and kinetic aspects of the reaction between **MB** and hydroxyl radicals in the gas phase through computational methods.

2. COMPUTATIONAL METHODS

Computational calculations for this investigation were performed using the Gaussian 16 software suite at the M06-2X/6-311++G(d,p) level of theory.¹⁷ This methodology is widely recognized for its precision in determining thermodynamic and kinetic properties in modern computational chemistry studies.¹⁸⁻²⁰ Kinetic evaluations were conducted using the Quantum Mechanics-based Overall Free Radical Scavenging Activity (QM-ORSA) approach.²¹ This method has proven to yield reliable results, showing minimal errors from experimental observations ($k_{\text{calc}}/k_{\text{exp}} = 1-2.9$),²¹⁻²³ and has been extensively applied in kinetic investigations of radical reactions.^{14,24,25} Under standard conditions of 1 M concentration

and temperatures ranging from 253 to 323 K in the gas phase,²⁶ the reaction rate constant (k) was computed employing equation (1) and transition state theory (TST).²⁷⁻³³

$$k = \sigma \kappa \frac{k_B T}{h} e^{-(\Delta G^\ddagger)/RT} \quad (1)$$

The Gibbs free energy of activation, denoted as $\Delta G^\ddagger$, is used in conjunction with the Boltzmann constant (k_B) and the Planck constant (h). Tunneling corrections (κ) were calculated based on the Eckart barrier model.³⁴ The reaction symmetry number is represented by σ .^{35,36}

The radical adduct formation (RAF), or formal hydrogen transfer (FHT) pathways of the **MB** + HO $\cdot$ reaction were detailed in processes (2-3).^{20,32,37}



3. RESULTS AND DISCUSSION

3.1. Topology optimization of MB

MB can exist in multiple conformers; therefore, all possible conformations were systematically screened,³⁸ and the conformer exhibiting the lowest electronic energy was selected for subsequent analysis. The topology optimization was conducted to elucidate the molecular geometry and identify the most stable conformer. The M06-2X/6-311++G(d,p) level of theory was employed to optimize the molecular structure and to investigate the thermodynamic and kinetic characteristics of the degradation of **MB** by HO $\cdot$ radicals. The optimized structural parameters of **MB** are summarized in Table 1, and the corresponding optimized geometry is illustrated in Figure S1 (Supporting Information).

Table 1. Bond lengths (Å) and bond angles (°) in **MB**.

Bond	Length	Bond	Length	Bond	Angle
C5-S	1.735	C7-S	1.735	C5-S-C7	103.4
C12-N13	1.328	C14-N13	1.328	C12-N13-C14	123.8
C3-N15	1.342	C2-C3	1.439	C2-C3-N15	120.6
C16-N15	1.462	C17-N15	1.460	C16-N15-C17	119.0
C9-N18	1.342	C9-C10	1.439	C10-C9-N18	120.6

Bond	Length	Bond	Length	Bond	Angle
C1–C2	1.356	C2–C3	1.439	C1–C2–C3	120.6
C3–C4	1.417	C4–C5	1.379	C3–C4–C5	120.6
C5–C14	1.434	C4–C5	1.379	C4–C5–C14	121.4
C5–C14	1.434	C1–C14	1.429	C1–C14–C5	117.0
C10–C11	1.356	C11–C12	1.430	C10–C11–C12	122.1
C11–C12	1.430	C12–C7	1.434	C11–C12–C7	121.4
C7–C8	1.379	C8–C9	1.417	C7–C8–C9	120.6

Table 1 illustrates that the C5–S bond length is equal to the C7–S bond length (1.735 Å), and these atoms form a bond angle of 103.4°. The C12–N13 bond length and C14–N13 are also equal, measured at 1.328 Å, with a corresponding bond angle of 123.8°. The bond lengths of C1–C2 (1.356 Å) and C4–C5 (1.379 Å) are shorter than those of C2–C3 (1.439 Å), C3–C4 (1.417 Å), and C5–C14 (1.434 Å). The bond angles C1–C2–C3 and C3–C4–C5 show only negligible differences (120.6°). Compared with the experimental crystal structure of **MB**,³⁹ the calculated bond lengths and bond angles exhibit no significant deviations. Therefore, the optimized structure of **MB** is in good agreement with the experimental structure and is thus suitable for subsequent computational analyses.

3.2. The reaction of MB with HO• in the atmospheric environment

3.2.1. Thermodynamic evaluation

Table 2. Gibbs free energy change (ΔG° , kcal/mol) of the reaction between **MB** and HO• via different mechanisms in the gas phase at 298.15 K.

Mechanism	Position	ΔG°
FHT	C16–H	–30.0
	C17–H	–30.1
RAF	N13	–11.1
	C1	–15.4
	C2	–17.9
	C3	–4.4
	C4	–16.1
	C5	–11.7
	C14	–11.6

To assess the reactivity of **MB** at various carbon and nitrogen atomic sites via different reaction mechanisms, the Gibbs free energy change (ΔG° , kcal/mol) was evaluated. The results are summarized in Table 2.

A positive ΔG° value indicates that a reaction is thermodynamically unfavorable and non-spontaneous, whereas a negative ΔG° value corresponds to a thermodynamically favorable and spontaneous process. As presented in Table 2, the calculated ΔG° values reveal that both the FHT and RAF mechanisms proceed spontaneously. In particular, the RAF mechanism exhibits negative ΔG° values at the C1, C2, C3, C4, C5, N13, and C14 positions, while the FHT mechanism shows negative ΔG° values at the C16 and C17 positions. The ΔG° values for these reactive sites range from –4.4 to 30.1 kcal/mol, suggesting thermodynamically favorable pathways for these reactions. Consequently, the subsequent kinetic investigation focuses on the thermodynamically favorable reactions ($\Delta G^\circ < 0$) proceeding through the FHT and RAF mechanisms.

3.2.2. Kinetic evaluation

The kinetics of the **MB** + HO• reaction were computed following the QM-ORSA protocol.²¹ The results are summarized in Table 3 and the representative transition state structures are illustrated in Figure 2. As shown in Table 3, the reaction between **MB** and HO• radicals in the gas phase proceeds rapidly, with an overall rate constant of $3.24 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the first step. The degradation of MB was defined by the FHT mechanism at the C16 and C17 positions and by the RAF mechanism at the C2 and C4 positions.

The calculated rate constants at these reactive sites decrease in the following order: C4 ($2.65 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) > C17 ($3.01 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) > C16 ($1.51 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) > C2 ($1.39 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Accordingly, the relative abundances of the corresponding intermediates follow the order: **GI4** (81.7%) > **GI17** (9.3%) > **GI16** (4.6%) > **GI2** (4.3%).

These computational results suggest that the first step reaction preferentially proceeds via the RAF mechanism, rather than through the FHT mechanism. The intermediate originating from C4 contributes most significantly (81.7%) compared to the other three positions. This dominance can be attributed to the higher electron density at C4 relative to C2, making C4 more favorable for HO• radical addition. Within

the FHT pathway, the reaction is more favorable at C17 (9.3%) than at C16 (4.6%), likely due to the lower bond dissociation energy of the C17–H bond compared with C16–H.

In the second step, reactions involving transition states **GI2**, **GI4**, **GI16** and **GI17**, indicate that degradation predominantly proceeds through the **GI4** intermediate. The **GI4** predominantly undergoes degradation via the **RAF** mechanism. The most favorable site is C14, exhibiting a rate constant of $9.84 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ and leading to the formation of product **GP3**, which accounts for 66.5% of the total product yield. This is followed by C2, with a rate constant of $3.89 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, resulting in product **GP1** at 26.3%.

Table 3. Gibbs free energy of activation $\Delta G^\ddagger$ (kcal/mol), tunneling corrections κ , rate constants (k_{Eck} , k_r , k_{overall} $\text{M}^{-1} \text{ s}^{-1}$), and branching ratio Γ (%) of the HO• + **MB** reaction.

Comp.	Mechanisms	Positions	$\Delta G^\ddagger$	κ	k_{Eck}	r	k_r	Γ	Products
MB	FHT	C16–H	6.0	2.0	1.51×10^9			4.6	GI16
		C17–H	5.5	1.9	3.01×10^9			9.3	GI17
	RAF	C1	10.1	1.4	7.23×10^9			0.0	
		C2	5.5	1.2	1.39×10^9			4.3	GI2
		C3	10.9	1.2	1.45×10^5			0.0	
		C4	3.7	1.1	2.65×10^{10}			81.7	GI4
		C5	12.7	1.3	7.83×10^3			0.0	
		N13	13.1	1.6	4.94×10^3			0.0	
		C14	8.2	1.3	1.51×10^7			0.0	
		k_{overall} (MB + HO•, step 1)			3.24×10^{10}				
GI4	FHT	C16–H	7.1	6.8	8.43×10^8	0.817	6.89×10^8	0.0	
		C17–H	9.5	2.5	5.24×10^6	0.817	4.28×10^6	0.0	
		C19–H	6.0	1.7	1.26×10^9	0.817	1.03×10^9	0.1	
		C20–H	6.2	1.8	9.64×10^8	0.817	7.87×10^8	0.1	
	RAF	C1	8.2	1.3	7.83×10^6	0.817	6.40×10^6	0.0	
		C2	1.6	1.1	4.76×10^{11}	0.817	3.89×10^{11}	26.3	GP1
		C3	3.8	1.2	1.26×10^{10}	0.817	1.03×10^{10}	0.7	
		C5	6.9	1.5	8.43×10^7	0.817	6.89×10^7	0.0	
		C7	11.9	1.3	1.63×10^4	0.817	1.33×10^4	0.0	
		C8	2.6	1.1	8.43×10^{10}	0.817	6.89×10^{10}	4.7	GP2
		C9	13.5	1.2	1.02×10^3	0.817	8.37×10^2	0.0	

Comp.	Mechanisms	Positions	$\Delta G^\ddagger$	κ	k_{Eck}	r	k_r	Γ	Products
		C10	7.7	1.3	1.69×10^7	0.817	1.38×10^7	0.0	
		C11	10.9	1.3	7.83×10^4	0.817	6.40×10^4	0.0	
		C12	11.8	1.4	1.93×10^4	0.817	1.57×10^4	0.0	
		C14	1.0	1.0	1.20×10^{12}	0.817	9.84×10^{11}	66.5	GP3
		N13	15.0	1.7	1.08×10^2	0.817	88.60	0.0	
	$k_{\text{overall}}(r)$ (GI4 + HO $\cdot$)						1.45×10^{12}	98.3	
$k_{\text{overall}}(r)$ (MB + HO $\cdot$, step 2)						1.48×10^{12}			

At the C8 position, the reaction proceeds with a rate constant of $6.89 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, yielding product **GP2** with a contribution of 4.7%. C3 position has a rate constant of $1.03 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, generating only 0.7% of the product. Reactions via the **FHT** mechanism also occur at **C19** and **C20** positions, but their contributions are minimal (0.1% each). Therefore, the main products of the second step are **GP1**, **GP2**, and **GP3**, corresponding to the **C2**, **C8**, and **C14** positions of the **GI4** transition state.

Based on the above analysis, it can be concluded that in the gas phase at 298.15 K, **MB** is primarily degraded by the HO $\cdot$ radical via the **RAF** mechanism at the C4 position, leading to the formation of three major products (**GP1**, **GP2**, and **GP3**). The overall rate constants for steps 1 and 2 are $3.24 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $1.48 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$, respectively.

Compared with the reaction of **MB** with HO $\cdot$ radicals in the aqueous phase,¹⁴ the results indicate that the first-step reaction proceeds rapidly in both the gas phase and water, with overall rate constants of 3.24×10^{10} and $1.02 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, respectively. However, the second-step reaction in the gas phase ($k_{\text{overall}} = 1.48 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$) is faster than that in water, with ($k_{\text{overall}} = 9.39 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Furthermore, distinct mechanistic pathways and product distributions were observed in the two environments, highlighting the significant role of the surrounding medium in modulating the reaction energetics and kinetics of HO $\cdot$ -induced **MB** degradation.

3.2.3. Effect of temperature on the degradation of MB in the gas phase

To investigate the effect of temperature on the degradation of **MB**, the rate constants for reactions at various positions of **MB** were calculated within the typical environmental temperature range (253–323 K, equivalent to -20°C to 50°C). The results are presented in Figure 3. As the gas-phase temperature increases, all rate constants associated with the **FHT** mechanism (k_{16} , k_{17}) decrease. In contrast, the rate constants corresponding to the **RAF** mechanism exhibit inconsistent trends: k_1 , k_5 , and k_{14} increase with temperature, while k_2 and k_4 decrease. Notably, k_3 and k_{13} fluctuate irregularly. In the temperature range of 253 - 323 K, the overall rate constant for **MB** degradation tends to decrease slightly, primarily due to the decline in k_{16} , k_{17} , k_2 , and k_4 , which correspond to the four reactive positions previously discussed in Table 3. The study revealed that the decrease in rate constants at the C2, C4, C16, and C17 positions was attributed to the rapid decline of the tunneling corrections (κ) with increasing temperature, from 2.7 to 1.1 in the corresponding reactions. According to the Eyring analysis, this non-Arrhenius behavior arises from a combination of negative activation entropy ($\Delta S^\ddagger < 0$), reflecting a highly ordered transition state and the diminished contribution of quantum tunneling at higher temperatures. Similar entropic and tunneling effects have been extensively reported in radical–molecule association reactions, supporting the physical

plausibility of the observed trend.^{40,41} Among all, k_4 is the highest at every temperature (ranging from $6.63 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ to $1.81 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), indicating that the **RAF** mechanism at the C4

position is the most favorable. Therefore, the primary degradation products of **MB** are those formed via radical addition of $\text{HO}^\bullet$ to **MB**, specifically **GP1**, **GP2**, and **GP3**.

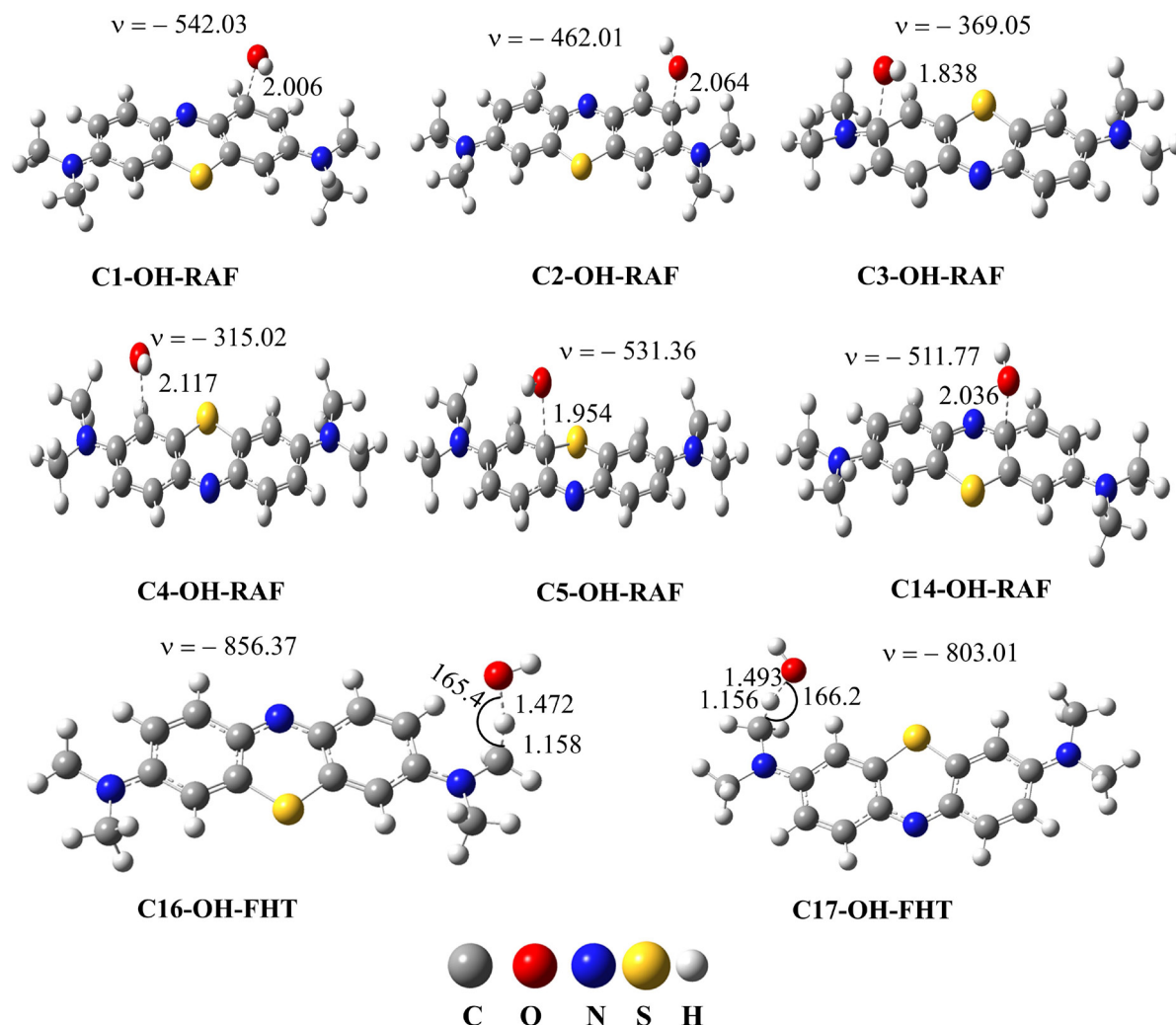


Figure 2. Structures of representative transition states *via* FHT and RAF mechanisms in the gas phase. Bond lengths (Å) and bond angles (°).

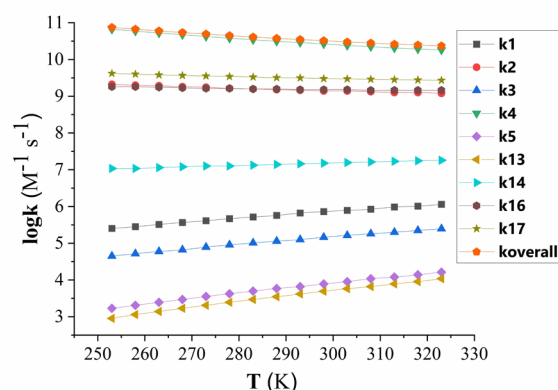


Figure 3. Temperature dependence of rate constants ($\log k$) in the gas phase in the range of 253 - 323 K.

4. CONCLUSION

This study elucidated the mechanism and kinetics of **MB** degradation $\text{HO}^\bullet$ radicals in the gas phase using quantum chemical calculations. At 298.15 K, MB degradation primarily proceeded via the **RAF** reaction occurring at the C4 position. This pathway led to the formation of three major products (**GP1**, **GP2**, and **GP3**), with the overall rate constants for the first and second reaction steps determined to be $3.24 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $1.48 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$, respectively. Within the temperature range of 253–323 K, variations

in the rate constants of individual reactive sites were observed; however, the **RAF** at the **C4** position consistently dominated the **MB** + **HO**[•] degradation process. Consequently, the overall degradation rate exhibited a minor decrease ($k_{\text{overall}} = 6.63 \times 10^{10} - 1.81 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

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Tổng hợp và đánh giá độc tính tế bào của các dẫn xuất benzimidazole kết hợp amino acid

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TÓM TẮT

Benzimidazole và các dẫn xuất của nó thể hiện hoạt tính sinh học đa dạng, gồm đặc tính kháng khuẩn, kháng viêm, kháng virus và đặc biệt là kháng ung thư. Các nghiên cứu gần đây cũng chỉ ra tiềm năng của các cấu trúc kết hợp giữa benzimidazole và amino acid/peptide trong nghiên cứu thiết kế các tác nhân kháng khuẩn và kháng ung thư mới. Trong báo cáo này, một quy trình tổng hợp hiệu quả gồm ba bước đã được phát triển thành công hướng đến các cấu trúc lai hóa bằng cách kết hợp các amino acid vào khung benzimidazole. Dựa trên quy trình này, sáu dẫn xuất benzimidazole kết hợp amino acid mới đã được tổng hợp thành công với hiệu suất 45–80%. Cấu trúc của các dẫn xuất này đã được xác định dựa trên các dữ liệu phổ nghiệm gồm 1D, 2D-NMR và HR-ESI-MS. Đánh giá độc tính tế bào chỉ ra rằng các dẫn xuất **7a** và **7c** có độc tính tế bào từ trung bình đến khá tốt đối với ba dòng tế bào ung thư bao gồm ung thư phổi, ung thư cổ tử cung và ung thư vú. Đáng chú ý, hợp chất **7c** ($IC_{50} = 18,88 \mu M$) mang nhóm L-phenylalanine ethyl ester thể hiện độc tính tốt trên dòng tế bào ung thư vú.

Từ khóa: Amino acid, benzimidazole, độc tính tế bào, hợp chất dị vòng, lai hóa phân tử.

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Synthesis and cytotoxicity evaluation of benzimidazole conjugated amino acid derivatives

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ABSTRACT

Benzimidazole and its derivatives displayed diverse biological activities, including antibacterial, anti-inflammatory, antiviral, and particularly anticancer properties. Recent studies also showed that the benzimidazole and amino acid/peptide conjugates displayed potential in designing novel antimicrobial and anticancer agents. In this report, an efficient three-step synthetic method has been successfully developed towards hybrid structures *via* conjugating amino acids to the benzimidazole framework. Based on this procedure, six novel benzimidazole-amino acid hybrid derivatives have been successfully synthesized in 45-80% yields. The structures of these derivatives were fully determined based on spectroscopic data including 1D, 2D-NMR, and HR-ESI-MS. Cytotoxicity assays indicated that compounds **7a** and **7c** possessed moderate to rather good cytotoxicities towards three cancer cell lines including lung cancer, cervical cancer, and breast cancer. Notedly, compound **7c** (IC₅₀ = 18.88 μ M) with the L-phenylalanine ethyl ester moiety displayed good cytotoxicity on the breast cancer cell line.

Keywords: Amino acids, benzimidazole, cytotoxicity, heterocyclic compounds, molecular hybridization.

1. INTRODUCTION

Nitrogen-containing heterocyclic compounds have exhibited diverse pharmacological activities, due to the ability of the nitrogen atom to easily form hydrogen bonding with biological receptors.¹ Among those, benzimidazole, an integral part of the structure of vitamin B₁₂, has exhibited a broad spectrum of biological activities including antimicrobial,^{2,3} antiviral,^{4,5} anti-inflammatory,⁶ antiulcer,⁷ and especially anticancer.⁸⁻¹⁴ Several anticancer drugs bearing the benzimidazole moiety's core structure have been approved by the FDA such as bendamustine for treating chronic

lymphocytic leukemia, selumetinib for treating neurofibromatosis type 1, binimetinib for treating certain types of melanoma.

Besides, α -amino acids are essential for the human body's production of proteins and participation in vital metabolic processes. Both structural modification and drug synthesis have frequently used these structural characteristics. It has been observed that the conjugation of amino acids and pharmacophores results in novel hybrid compounds with enhanced pharmacological activity,^{15,16} improved water solubility,¹⁷ and reduced cytotoxicity.¹⁸

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Several benzimidazole-conjugated amino acid derivatives have been known to demonstrate as lead anticancer agents. As shown in Figure 1, the poly (ADP-ribose) polymerase (PARP) inhibitor, veliparib¹⁹ (an anticancer drug) and the strong cytotoxic agent, compound **1**²⁰ share the common structural features of a benzimidazole core conjugated to an amino acid moiety at the C-2 position. Additionally, compound **2**²¹ bearing the tryptophan moiety at the C-5 position of the heterocyclic ring, acted as a potent sirtuin (Sirt) inhibitor. However, there have not been

many reports on the synthesis and assessment of anticancer activity for benzimidazole derivatives that contain amino acids at the *N*-1 position, despite the fact that this was also a crucial position that frequently results in anticancer activity.^{13,22,23} In light of these facts, this paper reports the synthesis of novel benzimidazole-conjugated amino acid derivatives *via N*-1 position of the benzimidazole core and their *in vitro* cytotoxicity towards the three cancer cell lines, including HeLa (cervical cancer), MCF-7 (breast cancer), and A549 (lung cancer) cell lines.

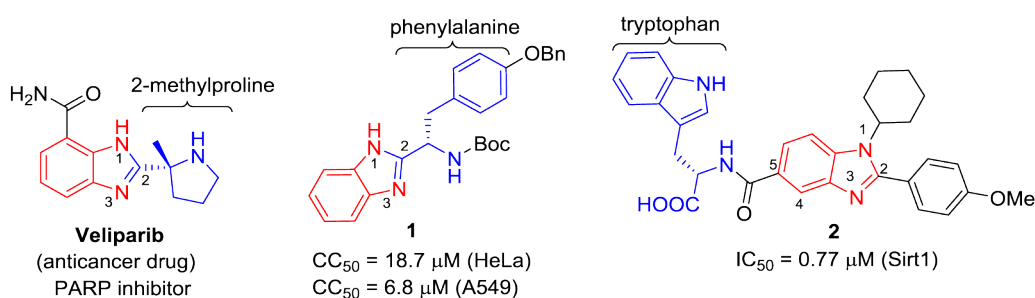


Figure 1. Several benzimidazole-amino acid hybrid derivatives as potent cytotoxic agents.

2. MATERIALS AND METHODS

2.1. Chemistry

2.1.1. General information

Reactions were monitored by thin layer chromatography (TLC) on 0.2 mm pre-coated silica gel 60 F254 plates (Merck). 1D and 2D-NMR spectra were measured with a JEOL 400 MHz spectrometer using DMSO- d_6 as solvent. HR-ESI-MS (high resolution electrospray ionization) data were performed on a X500R qTOF spectrometer. Chemical shifts are displayed in ppm (parts per million) compared to Me_4Si ($\delta = 0$). For column chromatography, silica gel 60 (0.063-0.200 mm, Prolabo) was utilized. Melting points (Mp, °C) were determined on an INE-X-4 melting point apparatus with microscope. Chemicals and solvents used are sourced from Macklin (1-fluoro-4-methyl-2-nitrobenzene, 4-chloro-1-fluoro-2-nitrobenzene, H-L-Tle-OMe·HCl, H-L-Phe-OEt·HCl, H-L-Val-OEt·HCl), Merck (4-methoxybenzaldehyde, DMSO, MeOH), China ($LiOH \cdot H_2O$, NH_4Cl ,

NaOAc, $NaHCO_3$, Na_2SO_4 , $Na_2S_2O_4$, ethyl acetate), Singapore (*n*-hexane) and Vietnam ($NaCl$, HCl , H_2O).

2.1.2. General procedure for the synthesis of benzimidazole-amino acid derivatives

Synthesis of derivatives 5a-c

To a solution of compound **3a-b** (1 mmol), L-amino acid ethyl/methyl ester hydrochlorides **4a-c** (1.5 mmol), $NaHCO_3$ (1.5 mmol), and NaOAc (10 mmol) in water (4 mL) was refluxed and stirred at 100°C for 8 hours. After completion, the temperature of reaction mixture was cooled down. The saturated aqueous solution of NH_4Cl was used to bring the mixture's pH to 7. Ethyl acetate (3×20 mL) was used to extract the combination, and washed with brine solution, dried on Na_2SO_4 , and then solvent was then evaporated under reduced pressure to give compounds **5a-c**, which was utilized without any additional purification for the following phase.

Ethyl (4-chloro-2-nitrophenyl)-L-valinate (5a): Yield 88%. Orange gel-like.

Methyl (S)-3,3-dimethyl-2-((4-methyl-2-nitrophenyl)amino)butanoate (5b): Yield 76%. Orange gel-like.

Ethyl (4-chloro-2-nitrophenyl)-L-phenylalaninate (5c): Yield 95%. Orange gel-like.

Synthesis of derivatives 7a-c

A mixture of compound **5a-c** (1 mmol), aldehyde **6** (1.1 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (4 mmol) in dimethylsulfoxide (DMSO, 4 mL) was stirred at 90°C for 2-4 hours. After completion, the temperature of reaction mixture was cooled down. The saturated aqueous solution of NaHCO_3 was used to bring the mixture's pH to 7. Ethyl acetate (3×20 mL) was used to extract the combination, then washed with brine solution, dried on Na_2SO_4 , and solvent was evaporated under reduced pressure. Purification of the crude products using silica gel column chromatography (*n*-hexane/ethyl acetate as eluent) afforded derivatives **7a-c**.

Ethyl (S)-2-(5-chloro-2-(4-methoxyphenyl)-1H-benzo[d]imidazol-1-yl)-3-methylbutanoate (7a): Orange-yellow gel-like. Yield 48%. $R_f = 0.61$ (*n*-hexane:ethyl acetate=3:1). $^1\text{H-NMR}$ (400 MHz, δ ppm) (J in Hertz): 7.77 – 7.74 (m, 2H), 7.68 – 7.64 (m, 2H), 7.32 (dd, $J = 2.2, 8.7$ Hz, 1H), 7.19 – 7.15 (m, 2H), 4.66 (d, $J = 11.0$ Hz, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 3.87 (s, 3H), 2.84 – 2.75 (m, 1H), 1.2 (t, $J = 7.1$ Hz, 3H), 0.96 (d, $J = 6.5$ Hz, 3H), 0.29 (d, $J = 6.7$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, δ ppm): 168.5, 160.6, 155.9, 143.8, 132.5, 131.1, 126.8, 122.6, 121.3, 118.7, 114.3, 114.1, 65.1, 61.7, 55.3, 28.0, 19.5, 18.0, 13.8. HRMS (m/z): $[\text{M}+\text{H}]^+$ found 387.1474 (calcd. for $\text{C}_{21}\text{H}_{24}\text{ClN}_2\text{O}_3^+$, 387.1470).

Methyl (S)-2-(2-(4-methoxyphenyl)-5-methyl-1H-benzo[d]imidazol-1-yl)-3,3-dimethylbutanoate (7b): White solid. Mp 128–130°C. Yield 45%. $R_f = 0.40$ (*n*-hexane:ethyl acetate=3:1). $^1\text{H-NMR}$ (400 MHz, δ ppm) (J in Hertz): 7.58 (d, $J = 8.7$ Hz, 2H), 7.45 (s, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.15 (d, $J = 8.7$ Hz,

2H), 7.06 (dd, $J = 1.2, 8.5$ Hz, 1H), 5.13 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 2.41 (s, 3H), 0.82 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, δ ppm): 168.5, 160.1, 154.6, 143.0, 132.3, 131.0, 123.6, 122.7, 118.9, 114.3, 113.2, 65.4, 55.2, 52.5, 37.2, 27.6, 20.9. HRMS (m/z): $[\text{M}+\text{H}]^+$ found 367.2017 (calcd. for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_3^+$, 367.2016).

Ethyl (S)-2-(5-chloro-2-(4-methoxyphenyl)-1H-benzo[d]imidazol-1-yl)-3-phenylpropanoate (7c): Orange-yellow gel-like. Yield 53%. $R_f = 0.49$ (*n*-hexane:ethyl acetate=3:1). $^1\text{H-NMR}$ (400 MHz, δ ppm) (J in Hertz): 7.71 (d, $J = 2.0$ Hz, 1H), 7.62 (d, $J = 8.7$ Hz, 1H), 7.35 (dd, $J = 2.1, 8.7$ Hz, 1H), 7.10 (t, $J = 7.4$ Hz, 1H), 7.03 – 6.96 (m, 6H), 6.54 (d, $J = 7.1$ Hz, 2H), 5.43 (t, $J = 8.0$ Hz, 1H), 4.26 – 4.20 (m, 2H), 3.82 (s, 3H), 3.44 (d, $J = 8.1$ Hz, 2H), 1.17 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, δ ppm): 168.6, 160.3, 155.6, 143.7, 135.8, 132.4, 130.5, 128.4, 128.1, 126.7, 126.6, 122.6, 121.1, 118.8, 113.8, 113.2, 61.8, 59.6, 55.2, 34.3, 13.8. HRMS (m/z): $[\text{M}+\text{H}]^+$ found 435.1473 (calcd. for $\text{C}_{25}\text{H}_{24}\text{ClN}_2\text{O}_3^+$, 435.1470).

Synthesis of derivatives 8a-c

To a round-bottom flask containing 0.5 mmol of ester **7a-c** and $\text{LiOH}\cdot\text{H}_2\text{O}$ (1.5 mmol) was added 4 mL of the solvent system ($\text{MeOH}:\text{H}_2\text{O}=8:1$), and stirred at room temperature for 24 hours. After completion, the mixture's pH was adjusted to 3 using 1N HCl solution. Ethyl acetate (3×10 mL) was used to extract the combination, then washed with brine solution, dried on Na_2SO_4 , and solvent was evaporated under reduced pressure. Purification of the crude products using silica gel column chromatography (*n*-hexane/ethyl acetate as eluent) afforded derivatives **8a-c**.

(S)-2-(5-Chloro-2-(4-methoxyphenyl)-1H-benzo[d]imidazol-1-yl)-3-methylbutanoic acid (8a): White solid. Mp 201–204°C. Yield 80%. $R_f = 0.20$ (*n*-hexane:ethyl acetate=1:3). $^1\text{H-NMR}$ (400 MHz, δ ppm) (J in Hertz): 7.76 (d, $J = 2.0$ Hz, 1H), 7.74 (d, $J = 8.8$ Hz, 1H), 7.70 – 7.67 (m, 2H), 7.31 (dd, $J = 2.1, 8.7$ Hz,

1H), 7.19 – 7.16 (m, 2H), 4.61 (d, $J = 11.0$ Hz, 1H), 3.87 (s, 3H), 2.80 – 2.70 (m, 1H), 0.97 (d, $J = 6.5$ Hz, 3H), 0.26 (d, $J = 6.7$ Hz, 3H). ^{13}C -NMR (100 MHz, δ ppm): 170.1, 160.5, 155.9, 143.8, 132.5, 131.0, 126.7, 122.5, 121.5, 118.7, 114.3, 114.1, 65.2, 55.3, 27.7, 19.7, 17.9. HRMS (m/z): $[\text{M}+\text{H}]^+$ found 359.1159 (calcd. for $\text{C}_{19}\text{H}_{20}\text{ClN}_2\text{O}_3^+$, 359.1157).

(S)-2-(2-(4-Methoxyphenyl)-5-methyl-1H-benzo[d]imidazol-1-yl)-3,3-dimethylbutanoic acid (8b): White solid. Mp 265–268°C. Yield 66%. $R_f = 0.25$ (*n*-hexane:ethyl acetate=1:3). ^1H -NMR (400 MHz, δ ppm) (J in Hertz): 7.56 (d, $J = 8.7$ Hz, 2H), 7.47 – 7.44 (m, 2H), 7.15 (d, $J = 8.7$ Hz, 2H), 7.05 (dd, $J = 1.4$, 8.5 Hz, 1H), 5.00 (s, 1H), 3.85 (s, 3H), 2.41 (s, 3H), 0.83 (s, 9H). ^{13}C -NMR (100 MHz, δ ppm): 169.6, 160.0, 154.7, 143.0, 132.3, 130.9, 130.8, 123.3, 122.9, 118.8, 114.2, 113.5, 65.6, 55.2, 36.8, 27.7, 20.9. HRMS (m/z): $[\text{M}+\text{H}]^+$ found 353.1860 (calcd. for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_3^+$, 353.1860).

(S)-2-(5-Chloro-2-(4-methoxyphenyl)-1H-benzo[d]imidazol-1-yl)-3-phenylpropanoic acid (8c): White solid. Mp 122–124°C. Yield 68%. $R_f = 0.13$ (*n*-hexane:ethyl acetate=1:3). ^1H -NMR (400 MHz, δ ppm) (J in Hertz): 7.70 (d, $J = 2.0$ Hz, 1H), 7.64 (d, $J = 8.7$ Hz, 1H), 7.35 (dd, $J = 2.0$, 8.6 Hz, 1H), 7.09 (t, $J = 7.3$ Hz, 1H), 7.03 – 6.96 (m, 6H), 6.53 (d, $J = 7.2$ Hz, 2H), 5.36 – 5.32 (m, 1H), 3.81 (s, 3H), 3.43 – 3.41 (m, 2H). ^{13}C -NMR (100 MHz, δ ppm): 170.2, 160.2, 155.6, 143.7, 136.2, 132.5, 130.4, 128.3, 128.0, 126.6, 126.4, 122.5, 121.3, 118.7, 113.8, 113.3, 59.8, 55.2, 34.4. HRMS (m/z): $[\text{M}+\text{H}]^+$ found 407.1164 (calcd. for $\text{C}_{23}\text{H}_{20}\text{ClN}_2\text{O}_3^+$, 407.1157).

2.2. Cytotoxicity evaluation

Cytotoxicity of the synthesized derivatives against three cancer cell lines (MCF-7, HeLa, and A549) were evaluated base on the MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] assay.²⁴ To create stock solutions (10 mM), the synthesized compounds were dissolved in DMSO and

dilutions were prepared in the culture medium. 5-fluorouracil (5-FU), the positive control, was mixed in DMSO to create a 10 mM stock solution, which was then kept at -20°C until it was needed.

The human cancer cell lines were cultivated at 37°C with 5% CO_2 atmosphere in α -MEM (α -minimum essential medium), supplemented with 10% fetal bovine serum and 1% antibiotic antimycotic solution. Following their collection, cells at 80–90% confluency were centrifuged for three minutes at 3,000 rpm. In order to resuspend the cell pellet in new media, the supernatant was disposed of. The cells were seeded in 96-well plates (1×10^4 cells/well) in aliquots (100 μL) and incubated for 24 hours. Five concentrations of the tested compounds (6.25, 12.5, 50, and 100 μM), together with the 5-FU, were then introduced to the wells after the cells had been cleaned with (PBS) phosphate-buffered saline. Following a 72-hour incubation period, the cells were rinsed with PBS, and each well was filled with 100 μL aliquots of media containing MTT solution (5 mg/mL) and incubated for three hours. A microplate reader was used to measure the absorbance at 570 nm. Percent proliferation inhibition was calculated using the following formula:

$$\% \text{ Proliferation cell inhibition} = [(A_t - A_b)/(A_c - A_b)] \times 100$$

A_t : Absorbance of test compound, A_b : Absorbance of blank, A_c : Absorbance of control.

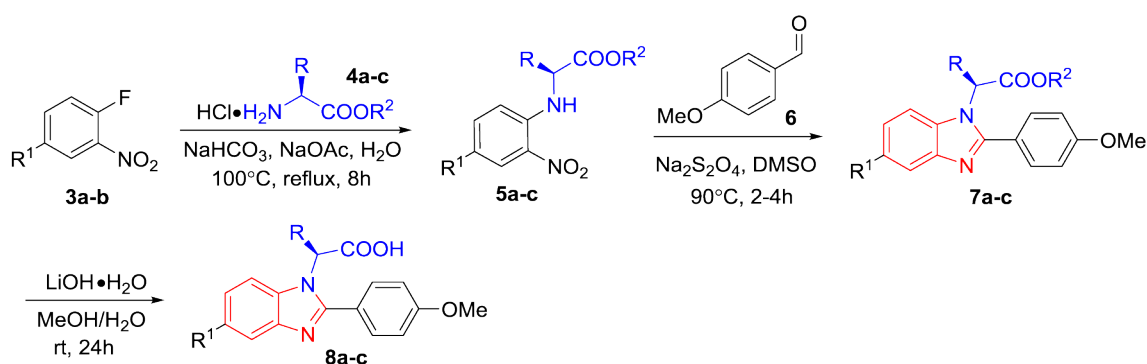
The IC_{50} values were determined by analyzing the correlation between the concentrations and the percentage of inhibition, using the GraphPad Prism 5.0 software. All data are shown as mean $\pm$ standard deviation (S.D.), and each experiment was run three times.

3. RESULTS AND DISCUSSION

The three-step synthetic procedure towards the benzimidazole-amino acid hybrid derivatives was described in Scheme 1. The precursors *N*-substituted *o*-nitroanilines **5a-c**, were prepared

via the nucleophilic aromatic substitution reaction of *o*-fluoro-nitrobenzenes **3a-b** and the free amino moiety of **4a-c**.¹³ The aqueous solution of NaHCO₃ was used as the base to deliver the free amino group of **4a-c** and the excess of NaOAc to maintain the alkaline medium. The use of other base such as K₂CO₃ just led to lower yield, probably due to saponification of the ester moiety. Next, the condensation reaction between **5a-c** and aldehyde **6** using sodium dithionite (Na₂S₂O₄) in DMSO through a one-pot reductive cyclization route²⁵ afforded derivatives **7a-c** in moderate yields (Table 1). The reagent Na₂S₂O₄ allowed the synthesis of benzimidazoles in just

one step from *N*-substituted *o*-nitroanilines, more efficiently than using the reagents Na₂S₂O₅²⁶ or NaHSO₃²⁷ (which required prior reduction of the nitro group). It seemed that the electron characteristic of the substituent at the C-4 position of the benzene ring of compounds **5a-c** did not affect the cyclization step although slightly higher yields were observed in the case of compound **5a** and **5c** with an electron withdrawing group Cl. Finally, the saponification reaction of **7a-c** took place readily using lithium hydroxide²¹ under mild conditions to afford the corresponding derivatives **8a-c** in reasonable to good yields (Table 1).



Scheme 1. Synthetic procedure towards the benzimidazole-conjugated amino acid derivatives.

Table 1. Synthetic yield and cytotoxicity of the synthesized derivatives.

Code	Structure	Yield ^a (%)	IC ₅₀ ^b (μM)		
			HeLa	MCF-7	A549
7a		48	25.54 ± 0.84	25.86 ± 1.25	35.85 ± 0.69
7b		45	>100	>100	>100
7c		53	21.57 ± 0.45	18.88 ± 0.13	25.97 ± 0.20
8a		80	>100	>100	>100

Code	Structure	Yield ^a (%)	IC ₅₀ ^b (μM)		
			HeLa	MCF-7	A549
8b		66	>100	>100	>100
8c		68	>100	>100	>100
5-FU			6.36 ± 0.39	8.59 ± 0.72	3.92 ± 0.22

^aIsolated yields; ^bIC₅₀: 50% inhibitory concentration. Data are presented as mean ± standard deviation (S.D.) (*n* = 3).

The synthesized compounds **7a–c** and **8a–c** were tested for their cytotoxicities against the cancer cell lines. The results, summarized in Table 1, indicated that compounds **7b** and **8a–c** with the free carboxylic moiety showed no cytotoxicity towards the tested cancer cell lines at the tested concentration. In contrast, two compounds **7a** and **7c** (IC₅₀ = 18.88–35.85 μM) with the ester moiety being maintained exhibited rather good cytotoxicities compared with the positive control 5-FU (IC₅₀ = 3.92–8.59 μM). These results likely emphasized the role of the ester moiety compared with the corresponding free carboxylic moiety (compared the activity of **7a** and **7c** against **8a** and **8c**). The higher activity was probably due to the better penetration ability through the plasma membrane of the ester moiety than the carboxylic acid functionality as indicated in previous reports.^{28,29} Notedly, compound **7c** (IC₅₀ = 18.88 μM) with the L-phenylalanine ethyl ester moiety displayed the best cytotoxicity towards the MCF-7 cancer cell line as compared with 5-FU (IC₅₀ = 8.59 μM). The observed activity of **7c** could be related to the aromaticity and hydrophobicity of the phenylalanine moiety as indicated in the previous reports.^{16,20,30–32} The two structures **7a** and **7c** could be served as the starting point for further optimization towards the potent cytotoxicity agents. Studies have been actively continuing in our lab with two goals. The first is to validate the developed synthetic procedure

to access the library of the benzimidazole and amino acid/peptide conjugates. The second is to clarify the structure-activity relationship (SAR) of the synthesized compounds for discovery of *hit* structures targeting anticancer activity. These results will be reported in due course.

4. CONCLUSION

Six novel benzimidazole-conjugated amino acid derivatives were successfully designed and synthesized in reasonable to good yields based on a three-step synthetic procedure starting from commercially available *o*-fluoro-nitrobenzenes. Among those, compound **7c** displayed rather good cytotoxicity against the breast cancer cell line. This structure may be regarded as a lead molecule that merits more refinement and the creation of new anticancer drugs.

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Hấp phụ Asen hiệu quả bằng vật liệu vỏ sò biến tính phosphate thân thiện môi trường

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TÓM TẮT

Ô nhiễm asen trong các hệ thống nước, đặc biệt là từ nguồn nước thải mỏ axit (acid mine drainage), gây ra những rủi ro nghiêm trọng đối với môi trường và sức khỏe con người do độc tính và khả năng di động cao của arsenat (As(V)). Trong nghiên cứu này, vỏ sò được tái sử dụng và chuyển hóa thành vật liệu vỏ sò biến tính phosphate (PMOS) như một chất hấp phụ thân thiện với môi trường và có chi phí thấp để loại bỏ As(V) . PMOS được chế tạo thông qua quá trình xử lý nhiệt - hóa học kết hợp với giai đoạn biến tính phosphate, và đặc tính hấp phụ của vật liệu được khảo sát có hệ thống dưới các điều kiện khác nhau. Kết quả cho thấy hiệu suất loại bỏ As(V) phụ thuộc mạnh vào pH, thời gian tiếp xúc, nồng độ ban đầu và liều lượng chất hấp phụ; hiệu suất tối ưu (~95%) đạt được trong khoảng pH từ 3 đến 7, với liều lượng 1,0 ÷ 1,5 g/L và đạt trạng thái cân bằng sau 100 phút. Phân tích động học xác nhận rằng quá trình hấp phụ tuân theo mô hình giả bậc hai (pseudo-second-order), cho thấy cơ chế hấp phụ hóa học chiếm ưu thế, trong khi các nghiên cứu đẳng nhiệt cho thấy mô hình Freundlich phù hợp nhất, với dung lượng hấp phụ cực đại đạt 46,34 mg/g. Kết quả đặc trưng cấu trúc xác nhận sự gắn kết thành công của các nhóm phosphate, giúp tăng cường ái lực đối với arsenat thông qua tương tác tĩnh điện, trao đổi ion và tạo phức bề mặt. Đáng chú ý, các thử nghiệm tái sử dụng cho thấy PMOS vẫn duy trì hơn 80% hiệu suất loại bỏ sau năm chu kỳ hấp phụ - giải hấp, chứng minh độ bền tái sinh tốt của vật liệu. Những phát hiện này cho thấy PMOS là vật liệu tiềm năng, bền vững và kinh tế cho quá trình xử lý asen trong nước bị ảnh hưởng bởi nước thải mỏ axit, đồng thời góp phần thúc đẩy chiến lược kinh tế tuần hoàn thông qua việc tái giá trị hóa chất thải nuôi trồng thủy sản.

Từ khóa: Arsenat, vỏ sò biến tính photphat, hấp phụ, động học và đẳng nhiệt hấp phụ, khả năng tái sử dụng.

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Eco-friendly utilization of phosphate-modified oyster shell for efficient arsenic adsorption

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ABSTRACT

Arsenic contamination in aquatic systems, especially from acid mine drainage, poses severe environmental and health risks due to the toxicity and mobility of arsenate (As(V)). In this study, oyster shell waste was valorized into phosphate-modified oyster shells (PMOS) as an eco-friendly and low-cost adsorbent for As(V) removal. PMOS was prepared through thermochemical treatment followed by phosphate functionalization, and its adsorption behavior was systematically investigated under different conditions. The results showed that As(V) removal efficiency strongly depended on pH, contact time, initial concentration, and adsorbent dosage, with optimal performance (~95% removal) achieved at pH 3 ÷ 7, a dosage of 1.0 ÷ 1.5 g/L, and equilibrium reached within 100 min. Kinetic analysis confirmed that the process followed a pseudo-second-order model, indicating chemisorption as the dominant mechanism, while isotherm studies revealed the Freundlich model provided the best fit, with a maximum adsorption capacity (q_{max}) of 46.34 mg/g. Structural characterization confirmed the successful incorporation of phosphate groups, enhancing affinity for arsenate through electrostatic attraction, ion exchange, and surface complexation. Importantly, reusability tests demonstrated that PMOS maintained more than 80% of its removal efficiency even after five adsorption-desorption cycles, confirming its regeneration stability. These findings highlight PMOS as a promising, sustainable, and cost-effective material for arsenic remediation in acid mine drainage-impacted waters while simultaneously contributing to circular economy strategies through aquaculture waste valorization.

Keywords: *Arsenate, phosphate-modified oyster shell, adsorption, kinetic and isotherm, reusability.*

1. INTRODUCTION

Arsenic contamination in aquatic systems has emerged as a critical global issue due to its extreme toxicity, persistence, and bioaccumulative character, with chronic exposure associated with severe health risks such as cancers, cardiovascular disorders, and dermatological

lesions. Among arsenic species, arsenate (As(V)) predominates under oxic conditions and is of particular concern because of its high solubility and mobility in water. In mining regions, the oxidative dissolution of sulfide minerals produces acid mine drainage, an effluent characterized by low pH and high concentrations of Fe and Mn,

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while simultaneously releasing considerable amounts of As(V), thereby intensifying ecological hazards and human health risks.¹⁻³ Although strict regulations have been established - such as the World Health Organization (WHO) provisional guideline of 0.01 mg/L and the Vietnamese national standard QCVN 01-1:2024/BYT -arsenic concentrations in acid mine drainage -impacted waters often exceed these limits by several orders of magnitude, highlighting the urgent need for efficient, robust, and affordable treatment technologies.^{3,4} Conventional remediation approaches, including precipitation, ion exchange, and membrane filtration, have been widely studied and applied but are often constrained by high chemical and energy demands, secondary waste generation, and limited stability under the harsh and complex chemical conditions of acid mine drainage.⁵

In recent years, the development of eco-friendly, low-cost, and sustainable adsorbents has become an essential research direction. Biomass wastes, particularly shellfish residues such as oyster shells, have attracted attention owing to their abundance, low cost, and high calcium carbonate content.⁶⁻⁹ Transforming such residues into water treatment materials offers a dual environmental benefit: reducing aquaculture-derived waste and providing a renewable adsorbent for pollutant removal, in line with circular economy principles. Previous studies have demonstrated the potential of oyster shells and related derivatives for capturing heavy metals such as Pb(II), Cd(II), and Hg(II).^{8,9} However, their direct application to As(V) removal remains limited due to the scarcity of active binding sites and insufficient surface reactivity. To overcome these drawbacks, surface modification has been explored, with phosphate functionalization emerging as a highly effective strategy as recently demonstrated in several biosorbent studies published.^{6,10} By introducing phosphate groups onto calcium-rich matrices, active functional sites are created that enhance

electrostatic interactions, ion exchange, surface complexation, and even co-precipitation with arsenate ions.^{11,12} This approach significantly improves the removal efficiency of arsenic compared to unmodified shells and provides a sustainable pathway for waste valorization in water treatment.

Despite these advances, the application of phosphate-modified oyster shells (PMOS) to arsenic remediation in acid mine drainage -related contexts remains underexplored. This knowledge gap is crucial, since acid mine drainage presents one of the most demanding scenarios for treatment technologies due to its extreme acidity and the presence of competing metal ions. Addressing this challenge, the present study aims to transform oyster shell waste into a phosphate-modified adsorbent and evaluate its potential for efficient As(V) removal. Specifically, the work pursues three objectives: (i) to investigate the adsorption behavior of As(V) under varying conditions and optimize operational parameters, (ii) to elucidate the adsorption mechanisms through kinetic and isotherm modeling, and (iii) to assess the regeneration and reusability of PMOS across multiple cycles to determine its long-term stability. By simultaneously addressing the urgent environmental challenge of arsenic pollution in acid mine drainage -impacted waters and the sustainable valorization of aquaculture waste, this research provides both a practical solution for water treatment and a contribution to eco-friendly resource utilization.

2. EXPERIMENT

2.1. Material

Raw oyster shells were collected from seafood processing waste in Quang Ninh. Analytical-grade Sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) was purchased. Other reagents, including hydrochloric acid (HCl), sodium hydroxide (NaOH), and phosphoric acid (H_3PO_4), were of analytical grade.

2.2. Preparation of Phosphate-modified oyster shells

The thermochemical modification of oyster shells followed the method outlined by Huong et al.¹³ The collected oyster shells were thoroughly washed, dried at 105°C for 24 hours, and crushed into particles < 0.25 mm. The pretreated shells were then subjected to thermal activation in a muffle furnace at 500°C for 2 hours. Phosphate modification was performed by immersing the calcined shells in 0.5 M phosphoric acid solution at 65°C for 2 hours under agitation to induce partial phosphatization, forming a calcium phosphate-carbonate hybrid structure. The modified material was then filtered, rinsed with DI water until reaching neutral pH, dried at 90 °C for 4 hours, and stored in airtight containers. The resulting material was labeled as PMOS.

2.3. Study on As(V) adsorption

As(V) adsorption was investigated at contact times of 15, 30, 45, 60, 90 and 120 minutes, at different initial concentrations from 5 ÷ 30 mg/L, with PMOS dosage varying from 0.25 ÷ 1.5 g/L, and environmental pH adjusted to 3, 5, 7, 9 and 11. All experiments were performed at room temperature (25 ± 2 °C) under continuous stirring at 150 rpm in 50 mL of solution. After adsorption, the suspensions were filtered, and the residual As(V) concentration was determined by ICP-MS. Adsorption kinetics and adsorption isotherm models were subsequently evaluated under the same experimental conditions. To investigate the regenerative properties of PMOS, desorption was carried out using 50 mL of 0.1 M HCl for 60 minutes. Then filter, wash, and dry at 90 degrees for 4 hours. The properties of purPMOS and desPMOS were examined by FT-IR.

2.4. Equations used

The removal efficiency (R, %) of As(V) and the adsorption capacity at equilibrium (q_e, mg/g) were calculated using the following equations:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where

C_0 (mg/L) is the initial As(V) concentration,

C_e (mg/L) is the equilibrium concentration,

V (L) is the solution volume, and

m (g) is the dry mass of the adsorbent (PMOS).

To evaluate the adsorption behavior of As(V) on PMOS, several commonly used kinetic and isotherm equations in linear form were employed. Only the mathematical expressions required for fitting are provided here.

Kinetic equations

Pseudo-first-order (PFO):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Pseudo-second-order (PSO):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Elovich:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (5)$$

Intraparticle diffusion (IPD):

$$q_t = k_i t^{1/2} + C \quad (6)$$

Bangham:

$$\log \left[\log \left(\frac{C_0}{C_0 - q_t m / V} \right) \right] = \log \left(\frac{k_0 m}{2.303 V} \right) + \alpha \log t \quad (7)$$

where:

k_1 (min⁻¹): pseudo-first-order rate constant,

k_2 (g/mg.min): pseudo-second-order rate constant,

α (mg/g.min): initial Elovich adsorption rate,

β (g/mg): Elovich desorption coefficient,

k_0 : Bangham kinetic constant,

α (dimensionless in Bangham eq.): diffusion exponent,

k_i (mg/g.min^{0.5}): intraparticle diffusion constant,

C : boundary layer thickness parameter.

Isotherm equations

Freundlich isotherm (multilayer, heterogeneous surface):

$$\log q_e = \log K_F - \frac{1}{n} \log C_e \quad (8)$$

Langmuir isotherm (monolayer):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (9)$$

Temkin isotherm:

$$q_e = B \ln K_T + B \ln C_e \quad (10)$$

K_T (L.mg⁻¹): Temkin equilibrium binding constant,

B (mg.g⁻¹): Temkin constant related to adsorption heat .

Dubinin–Radushkevich (D–R) isotherm:

$$\ln q_e = \ln q_{max} - \beta \varepsilon^2 \quad (11)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

Adsorption energy:

$$E = \frac{1}{\sqrt{2\beta}} \quad (13)$$

Henry isotherm:

$$q_e = K_H C_e \quad (14)$$

where:

K_L (L/mg): Langmuir constant,

q_{max} (mg/g): maximum adsorption capacity,

K_F ((mg/g)(L/mg)^{1/n}): Freundlich constant,

$1/n$: Freundlich heterogeneity factor,

K_T (L/mg): Temkin binding constant,

B (mg/g): Temkin constant proportional to adsorption heat,

β (mol²/kJ²): D–R constant related to adsorption energy,

ε : Polanyi potential,

K_H (L/mg): Henry constant.

3. RESULTS AND DISCUSSION

3.1. Study on the adsorption conditions of As(V) in water by PMOS

Figure 1 shows that the As(V) ion removal efficiency strongly depends on the environmental conditions and the dosage of PMOS adsorbent. In graph (a), the adsorption efficiency reaches the highest value (~97.5%) at pH = 2 ÷ 4 and gradually decreases as the pH increases, especially at alkaline pH (>10). This phenomenon can be explained through two key factors: (i) the chemical transformation of As(V) with pH and (ii) the surface charge state of PMOS (pHpzc = 8.054). The pHpzc value of PMOS was determined using the pH drift method, in which the adsorbent was added to a series of 0.01 M NaCl electrolyte solutions with initial pH values adjusted from 2 to 12 and allowed to equilibrate for 24 hours.

At low pH, the main form is $H_2AsO_4^-$; when pH increases to neutral and slightly alkaline, $HAsO_4^{2-}$ predominates; and in strong alkaline environments, AsO_4^{3-} becomes the main form. On the material side, pHpzc = 8.054. When pH < pHpzc, the PMOS surface carries a positive charge, which is favorable for electrostatic attraction of arsenate anions. On the contrary, at pH > pHpzc, the surface turns negatively charged, causing electrostatic repulsion of anions and simultaneously competes with OH⁻ in the solution. Therefore, in acidic environments (3 < pH < 7), when As(V) mainly exists in the form of $HAsO_4^{2-}$ and the material surface is positively charged, the adsorption mechanism occurs strongly thanks to the combination of electrostatic interactions and ion exchange at the active phosphate groups on the brushite structure (CaHPO₄·2H₂O). Graph (b) shows that the adsorption rate of As(V) is fast, with an efficiency of over 80% after only 45 min and almost saturated (~95%) after 100 ÷ 120 min. This reflects the adsorption mechanism that combines surface interaction and intraparticle diffusion, and demonstrates that PMOS has the ability to process quickly and efficiently.

In graph (c), the efficiency decreases as the initial As(V) concentration increases. At low concentrations ($5 \div 10$ mg/L), the efficiency reaches over $94 \div 95\%$, but drops to about 90% when the concentration increases to 30 mg/L.

The reason is that the number of adsorption sites is limited, when the pollutant concentration is too high, the material is saturated and the efficiency decreases.

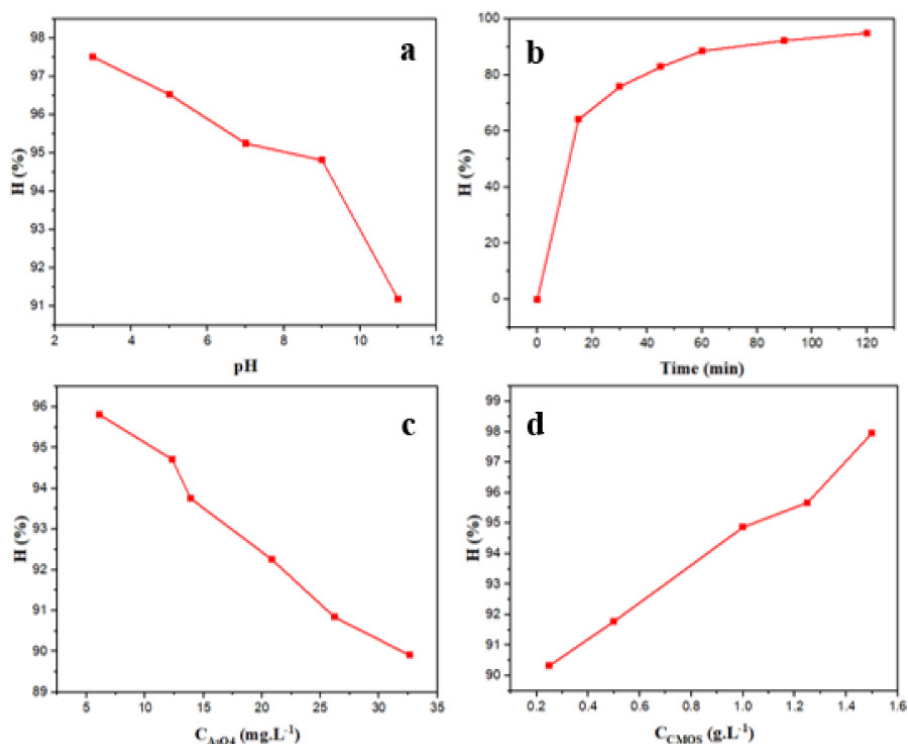


Figure 1. Graph of As(V) treatment efficiency at different environmental pH (a), contact time (b), initial As(V) concentration (c), and PMOS dosage (d). Unless otherwise stated, the experiments were conducted at pH = 5, an initial As(V) concentration of 5 mg/L, a PMOS dosage of 1.0 g/L, and a contact time of 100 min.

3.2. Kinetic model and As(V) adsorption isotherm

Based on Figure 2 and the data in Table 1, it can be seen that the adsorption process of As(V) on PMOS materials is best described by the pseudo-second-order kinetic model, with a correlation coefficient R^2 of 0.9997 and a q_e value (11.78 mg/g) that closely matches the experiment. This shows that the main mechanism of the process is chemisorption, in which the active hydroxyl and phosphate groups on the material surface play a central role, creating a strong interaction with arsenate ions. Meanwhile, the pseudo-first-order model also shows a certain level of agreement ($R^2 = 0.9742$) but the q_e value is significantly different, indicating that it does not accurately

reflect the actual kinetics. The Elovich model ($R^2 = 0.9839$) adds further evidence of the energy heterogeneity at the adsorption sites, indicating that the PMOS surface contains many active sites with different properties. In particular, the bangham model has a very high R^2 (0.9968), confirming the significant role of capillary diffusion in controlling the adsorption rate. In contrast, the intraparticle diffusion model with R^2 of only 0.7710 shows that intraparticle diffusion is not the decisive step but only contributes to support. Observation of the time survey curve (Figure 2f) shows that the adsorption rate is fast in the initial stage, the efficiency reaches more than 80% after only 45 minutes and approaches equilibrium at about 100 minutes with an efficiency of nearly 95%. This evolution reflects

a multi-stage adsorption mechanism: initially, the rapid capture of As(V) ions on the surface, followed by a slow diffusion process into the pores inside the material.

Thus, combining the data in Figure 2 and Table 1, it can be confirmed that the adsorption kinetics of As(V) on PMOS follows

a pseudo-second-order model, which is typical for chemical adsorption, and is supported by the diffusion mechanism in the capillary. This is an important factor that helps the material achieve fast processing speed, high efficiency and potential for practical application in the treatment of arsenic in water.

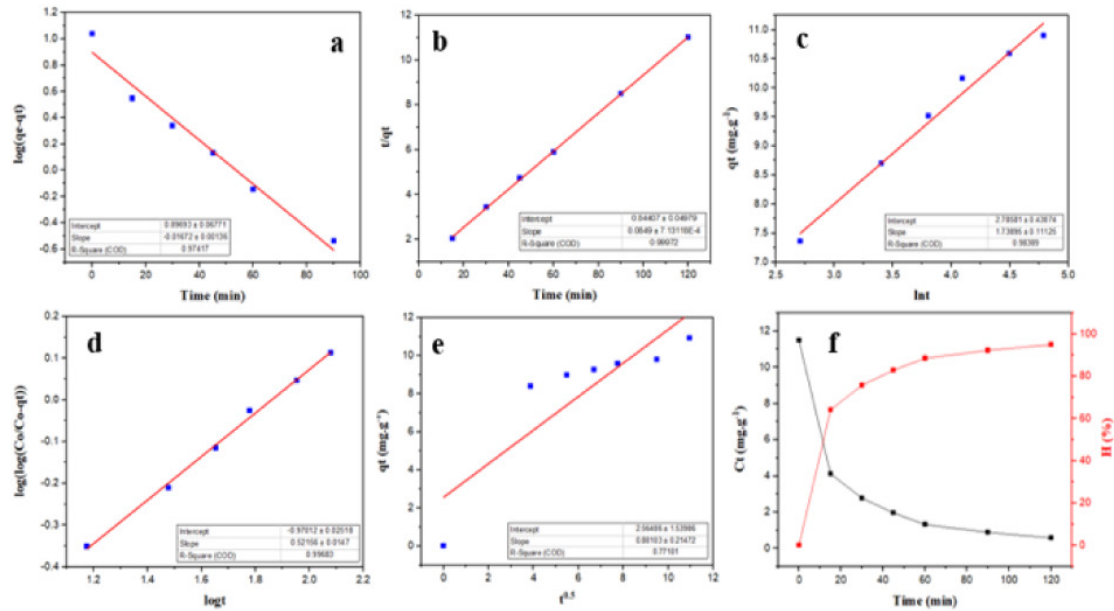


Figure 2. Kinetic model of As(V) adsorption by PMOS according to first-order kinetics (a), second-order kinetics (b), Elovich (c), Bangham (d), intraparticle diffusion (e), and time study (f) of the process.

Table 1. Parameters of As(V) adsorption kinetic models on phosphate-modified oyster shells (PMOS).

Kinetic model	Parameter	Value
Pseudo-first order	k_1 (min ⁻¹)	0.0385
	q_e (mg/g)	7.8873
	R^2	0.9742
Pseudo-second order	k_2 (g/mg.min)	0.0085
	q_e (mg/g)	11.7786
	R^2	0.9997
Elovich	a (mg/g)	2.7858
	b (g/mg)	1.7390
	R^2	0.9839
Bangham	α	0.157
	$\log(k_o m / 2.303V)$	-0.9701
	R^2	0.9968
Intraparticle diffusion	k_i (mg/g.min ^{0.5})	0.8810
	C (mg/g)	2.5649
	R^2	0.7710

Based on Figure 3 and the isotherm parameters summarized in Table 2, the adsorption behavior of As(V) on PMOS was systematically evaluated using different isotherm models. Models exhibiting relatively low coefficients of determination, including the Dubinin–Radushkevich model ($R^2 = 0.8832$), show limited agreement with the experimental data and are therefore less suitable for describing the adsorption process, requiring no further detailed interpretation. Nevertheless, the low adsorption energy value ($E = 2.22$ kJ/mol) derived from this model suggests that physical adsorption contributes to the overall adsorption mechanism.

In contrast, both the Freundlich ($R^2 = 0.9868$) and Langmuir ($R^2 = 0.9803$) models exhibit high and comparable correlation coefficients, indicating that the adsorption of As(V) on PMOS cannot be exclusively described by a single idealized mechanism. The

good fit of the Freundlich model implies that the PMOS surface is energetically heterogeneous, providing multiple adsorption sites with different affinities for As(V), and that adsorption proceeds

via a multilayer mechanism. This interpretation is further supported by the Freundlich constant n value of 1.56 (> 1), confirming favorable adsorption behavior.

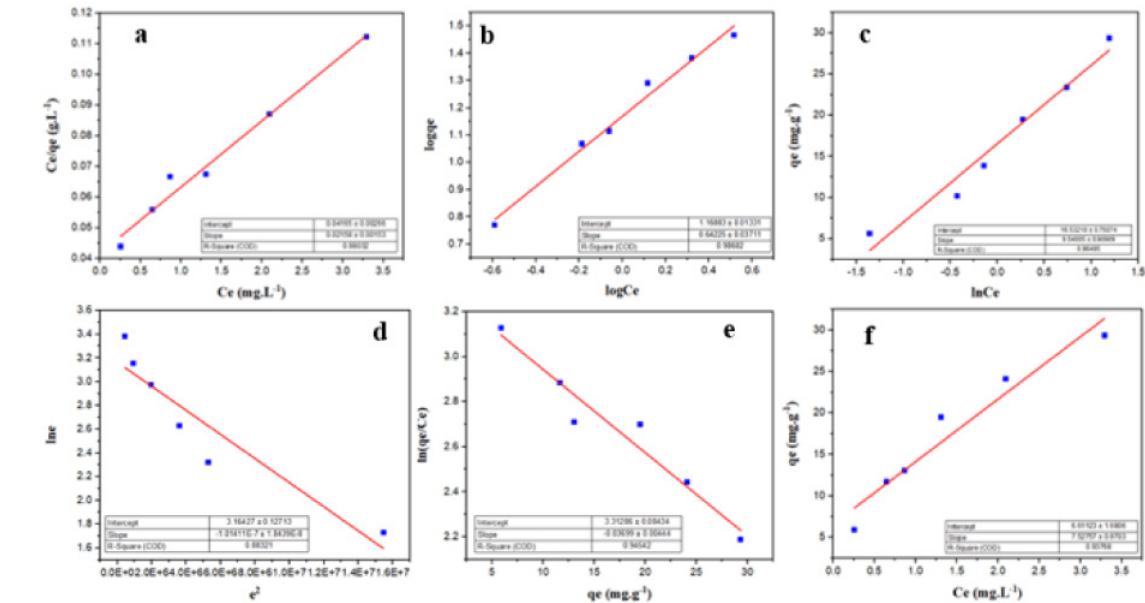


Figure 3. PMOS adsorption isotherm models of As(V) according to Langmuir (a), Freundlich (b), Temkin (c), Dubinin–Radushkevich (d), Elovich (e), Henry (f).

Table 2. Parameters of isotherm models for As(V) adsorption on phosphate-modified oyster shell (PMOS).

Isothermal model	Parameter	Value
Langmuir	K_L (L/mg)	0.518
	q_{max} (mg/g)	46.34
	R^2	0.9803
Freundlich	K_F (mg/g).(L/mg) ^{1/n}	14.75
	n	1.56
	R^2	0.9868
Temkin	K_T	5.657
	b_T (J/mol)	9.540
	R^2	0.9650
Dubinin-Radushkevich	q_{max} (mg/g)	23.67
	β (mol ² /kJ ²)	$1.0141 \cdot 10^{-7}$
	E (kJ/mol)	2220.46
	R^2	0.8832
Elovich	α (mg/g)	27.463
	β (g/mg)	0.0370
	R^2	0.9454
Henry	K_H	7.5276
	R^2	0.9377

Meanwhile, the satisfactory agreement with the Langmuir model indicates that monolayer adsorption also plays a significant role, particularly at higher-affinity sites. The relatively high maximum adsorption capacity ($q_{max} = 46.34$ mg/g) reflects the strong interaction between As(V) species and active functional groups on the PMOS surface, and demonstrates the superior adsorption performance of PMOS compared with many reported bio-based adsorbents.

The Temkin model ($R^2 = 0.9650$) further suggests that the adsorption energy gradually decreases with increasing surface coverage, which is consistent with the progressive occupation of high-energy sites followed by lower-energy sites, especially in materials rich in phosphate functional groups. Although the Elovich ($R^2 = 0.9454$) and Henry ($R^2 = 0.9377$) models show relatively good correlations, they provide limited mechanistic insight into the adsorption behavior and therefore were not considered dominant descriptors of the adsorption process.

Overall, these results indicate that the adsorption of As(V) on PMOS is governed by a mixed mechanism involving monolayer adsorption on relatively homogeneous high-energy sites and multilayer adsorption on heterogeneous surfaces. Consequently, while the Freundlich model better captures the surface heterogeneity and multilayer nature of the adsorption process, the Langmuir model remains essential for quantifying the maximum adsorption capacity. This combined interpretation confirms the high efficiency and strong application potential of PMOS for the treatment of arsenic-contaminated water.

The results in Table 3 show that the phosphate-modified oyster shell material (PMOS) achieved a maximum adsorption capacity of $q_{\max} = 46.34 \text{ mg/g}$ for As(V), confirming its remarkable arsenate removal efficiency. Compared with natural and simply modified mineral materials, PMOS showed outstanding advantages. Specifically, the $q_{\max}$ value of PMOS was several times higher than that of the kaolin mixture system ($0.695 \div 4.17 \text{ mg/g}$),¹⁴ and nearly three times higher than that of ascorbic acid-coated Fe_3O_4 magnetic nanoparticles (16.56 mg/g).⁴ At the same time, PMOS also surpasses other As(V) removal materials such as NaOH-modified electrolytic manganese sludge (23.96 mg/g),¹⁵ iron-modified concrete sludge ($27.8 \div 41.7 \text{ mg/g}$),¹⁶ or GUT-3 metal-organic framework (33.91 mg/g). This demonstrates that the phosphate modification process significantly optimized the surface activity of oyster shells, helping to increase the density of phosphate and hydroxyl functional groups, thereby enhancing the ability to capture arsenate anions. In addition, when compared with more advanced material systems, PMOS continues to maintain its competitive position. The adsorption capacity of PMOS is higher than that of the metal-organic framework – chitosan – nanocellulose (CS-NC-MIL-53(Fe)) (36.76 mg/g),¹⁷ and only lower than some materials with more complex structures such as the polymer-Fe-Al hydroxide hybrid (49.6

mg/g)¹⁸ or amine-modified lignin (64.08 mg/g).¹⁹ This shows that PMOS, although developed from simple biological waste sources, can still achieve adsorption efficiency approaching or even surpassing some modern nano-composite materials which have complex manufacturing processes, high costs and are difficult to apply on a large scale.

Table 3. Comparison of maximum adsorption capacity ($q_{\max}$) of PMOS and As(V) adsorbent tracks.

Adsorbent material	$q_{\max}$ (mg/g)	References
Kaolin mixed system	$0.695 \div 4.17$	14
Ascorbic Acid Coated Superparamagnetic Fe_3O_4 Magnetic Nanoparticles	16.56	4
NaOH modified electrolytic manganese residues (M-EMRs)	23.96	15
Waste sludge from the production of iron-modified concrete (CWSFe)	$27.8 \div 41.7$	16
Metal-organic framework – chitosan -nanocellulose (CS-NC-MIL-53(Fe))	36.76	17
GUT-3 metal organic framework	33.91	12
Phosphate - modified oyster shell	46.34	This study
Polymer-Fe-Al hydroxide hybrid material	49.6	18
Amine-modified lignin (Lignin@N-X)	64.08	19

3.3. Reuse of PMOS in As(V) adsorption

Figure 4 shows the FT-IR graphs of PMOS before adsorption (purPMOS) and after desorption (desPMOS). The PMOS sample before adsorption (purPMOS) exhibits the inherent absorption bands of CaCO_3 , and the PMOS FT-IR spectrum shows many important new signals. The broad peaks at 3479 and 3160 cm^{-1} reflect the O–H stretching vibrations, indicating the presence of hydroxyl groups

or adsorbed water. The peak at 1646 cm^{-1} is assigned to the bending vibration of H–O–H, further confirming the existence of water molecules in the newly formed structure. In particular, a series of bands at 1416, 1123, 1056 and 984 cm^{-1} are characteristic of the valence and deformation vibrations of the phosphate group ($\text{PO}_4^{3-}/\text{HPO}_4^{2-}$).²⁰ In addition, the peak at 522 cm^{-1} is attributed to the Ca–O and P–O bond vibrations in the calcium phosphate salt structure. The appearance of these peaks shows that the denaturation process was successful in introducing phosphate groups into the CaCO_3 matrix, while forming the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Brushite) phase.²¹

It can be seen that after desorption with 0,1 M HCl (desPMOS), most of the main peaks were restored to almost the original spectrum, especially –OH and CO_3^{2-} , indicating that the $\text{Ca}^{2+} - \text{PO}_4^{3-} - \text{CO}_3^{2-}$ framework structure of the material is still stable. However, the intensity of the clusters at $1123.09 \div 1056.19\text{ cm}^{-1}$ and 522.64 cm^{-1} remain lower than the original spectrum, indicating that part of the metal ions are still firmly bound in the form of stable phosphate or carbonate species, which are difficult to remove completely. This confirms that the adsorption mechanism of PMOS is based on the coordination between ion exchange, surface precipitation and strong chemical bonding, and the material has good regeneration ability after desorption.

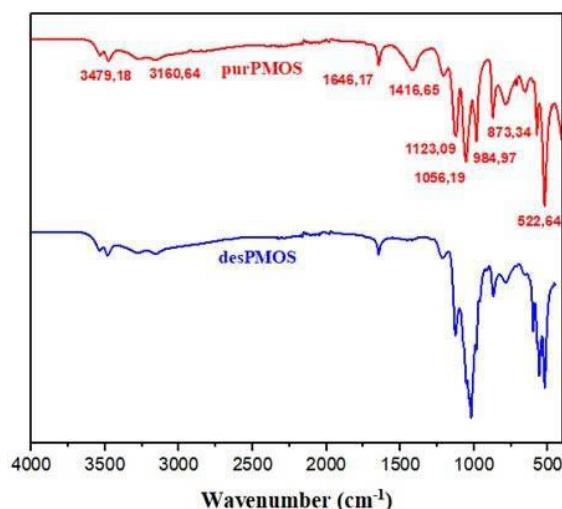


Figure 4. FT-IR graphs of the material before adsorption (purPMOS), and after desorption (desPMOS).

The results of the reusability evaluation (Figure 5) showed that PMOS exhibited stable and sustainable regeneration in the process of As(V) removal. In the first cycle, the adsorption efficiency reached 94.96%, reflecting the very high ability of the material to capture As(V) ions. During desorption and reuse, the efficiency slightly decreased but remained high through the following cycles, with a value of over 90% in the second cycle, about 88 ÷ 89% in the third cycle, and still reaching about 84% and 81% after the fourth and fifth cycles. This decrease is inevitable because a part of As(V) ions are tightly held at adsorption sites with high binding energy or due to local changes on the material surface after many treatments, however, the level of decrease is quite small compared to the total initial efficiency. It is noteworthy that the decreasing trend occurred gradually rather than abruptly, clearly reflecting the structural stability and the ability to preserve the active functional groups of PMOS during the repeated adsorption-desorption process. This shows that most of the active sites can still be effectively reactivated after the desorption process, and proves that the material is not destroyed or deactivated as quickly as many traditional adsorbents. Maintaining the As(V) removal efficiency above 80% even after 5 consecutive reuse cycles confirms that PMOS is a material with good regenerability, high durability and promise for practical implementation. With this characteristic, PMOS not only meets the requirements for treatment efficiency but also brings great economic and sustainability advantages, because the ability to regenerate many times will reduce operating costs, limit the need to replace new materials, and reduce the amount of solid waste generated during the water treatment process. Thus, the adsorption capacity combined with sustainable regeneration makes PMOS a promising adsorption candidate for As(V) removal in aquatic environments, serving long-term, safe and effective treatment solutions.

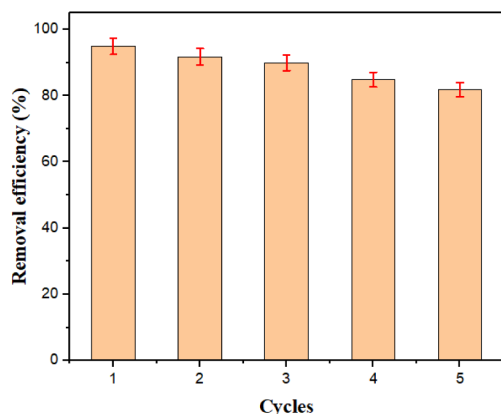


Figure 5. Reusability of PMOS for As(V) adsorption.

4. CONCLUSION

In this study, a phosphate-modified oyster shell (PMOS) adsorbent was successfully developed and systematically evaluated for As(V) removal from aqueous environments. The novelty of this work lies in: (i) introducing phosphate groups onto a naturally calcium-rich biomaterial to create new, highly reactive As(V) binding sites; (ii) converting low-value aquaculture waste into an efficient functional adsorbent; and (iii) demonstrating high adsorption performance under acidic conditions that are characteristic of acid mine drainage - an application scenario rarely addressed for biosorbent-based materials.

PMOS exhibited outstanding removal efficiency (~95%) under optimal conditions (pH 3 ÷ 7, dosage 1.0 ÷ 1.5 g/L, equilibrium time ~100 min). The adsorption followed a pseudo-second-order kinetic model, suggesting chemisorption dominated by surface interaction with phosphate-calcium active centers, while Freundlich isotherm fitting confirmed multilayer adsorption on heterogeneous surfaces. The material achieved a high maximum adsorption capacity ($q_{\max} = 46.34$ mg/g), which surpasses many previously reported biosorbents and highlights the enhanced reactivity generated by phosphate modification.

Structural analysis verified the successful incorporation of phosphate functionalities, which played a decisive role in strengthening the affinity toward arsenate oxyanions. Furthermore, regeneration experiments demonstrated that

PMOS maintained over 80% of its adsorption efficiency after five reuse cycles, confirming the stability of its modified framework and its practical suitability for long-term operation.

Overall, the present study not only clarifies the adsorption mechanisms of As(V) on phosphate-modified calcium biomaterials but also provides a sustainable, low-cost, and scalable solution for arsenic removal in acidic mining-impacted waters. By integrating waste valorization with high-performance water treatment, this work contributes a new material concept and practical pathway aligned with circular-economy strategies and environmentally responsible remediation technologies.

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