Plant-mediated synthesis of sustainable nZVIs anchored on loofah fiber for the degradation of Rhodamine B dye

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Received 7 Aug. 2025; Revised 30 Sep. 2025; Accepted 16 Oct. 2025; Published 18 Nov. 2025.
DOI: https://doi.org/10.54939/1859-1043.j.mst.IMBE.2025.115-121

ABSTRACT

This study reports a sustainable method for synthesizing zero-valent iron nanoparticles (nZVI) immobilized on loofah sponge (LS) fibers using Cleistocalyx operculatus leaf extract as a green reducing and stabilizing agent. Comprehensive characterization through scanning electron microscopy (SEM), plant digital microscopy (PDM), Fourier-transform infrared spectroscopy (FTIR), confirmed successful nanoparticle formation, uniform dispersion, and effective stabilization. The synthesized composite demonstrated exceptional removal efficiency for Rhodamine B dye, exceeding 97% under optimized conditions. Importantly, the composite maintained robust performance (>65% removal efficiency) across multiple reuse cycles. The integration of biodegradable loofah sponge fibers with bioderived iron nanoparticles offers an innovative, cost-effective, and environmentally friendly approach for dye wastewater remediation, aligning closely with global sustainability and green chemistry objectives.

Keywords: Zero-valent iron nanoparticles; Loofah sponge; Green synthesis; Cleistocalyx operculatus; Rhodamine B removal; Sustainable materials.

1. INTRODUCTION

In recent decades, accelerating industrialization coupled with rapid urbanization has markedly intensified environmental challenges, particularly through the contamination of water resources by persistent organic pollutants such as synthetic dyes. Industries including textile, leather, paper, and printing continuously discharge substantial volumes of dye-laden wastewater, severely impacting ecosystems and human health due to the inherent toxicity, carcinogenicity, and recalcitrance of these compounds. Thus, addressing such intricate environmental problems necessitates innovative, sustainable approaches grounded in the principles of green chemistry [1].

In response to this pressing issue, zero-valent iron nanoparticles (nZVI) have emerged as a promising remediation technology, attributed to their exceptional chemical reactivity, extensive surface area, and potent reducing capabilities. These nanoparticles have demonstrated significant effectiveness in degrading diverse organic contaminants and immobilizing heavy metals, surpassing traditional wastewater treatment methods in terms of efficacy and adaptability [2]. However, despite their considerable advantages, the practical implementation of nZVI remains hindered by critical limitations, notably rapid aggregation, susceptibility to oxidation, and challenging recovery processes after application [3]. Such constraints substantially reduce their reuse potential and introduce risks of secondary environmental pollution.

To address these limitations, recent studies have increasingly focused on immobilizing nZVI onto stable and environmentally benign supports. Among the available options, natural fiber-based materials have attracted significant attention due to their biodegradability, structural integrity, and wide availability. *Loofah sponge (Spelled Luffa)*, characterized by its highly porous and interconnected fibrous matrix primarily composed of cellulose, hemicellulose, and lignin, has been identified as an ideal support for nanoparticle immobilization [4]. Its three-dimensional fibrous structure effectively mitigates nanoparticle aggregation, promotes homogeneous nanoparticle distribution, enhances pollutant accessibility, and facilitates easy recovery and reuse.

Consistent with the principles of green chemistry, nanoparticle synthesis using plant-based reducing agents has garnered considerable attention. Plant extracts, abundant in bioactive compounds such as polyphenols and flavonoids, offer sustainable alternatives to conventional chemical reductants. *Cleistocalyx operculatus*, a widely available tropical plant, is particularly advantageous due to its high polyphenolic content, which confers effective reducing and stabilizing properties beneficial to nanoparticle synthesis [5].

Motivated by these insights, this research aims to develop a sustainable composite material via a green synthesis of zero-valent iron nanoparticles directly immobilized onto *Loofah sponge (LS)* fibers using *Cleistocalyx operculatus* leaf extract as a reductant.

2. EXPERIMENTAL SECTION

2.1. Materials and chemicals

Loofah sponge (Moc Xo store (Da Nang, Vietnam)), dried *Cleistocalyx operculatus* leaf powder (Academy of Military Science and Technology, Vietnam), $FeCl_3$ 99.0% (China), Ethanol 99.7% (China), Aceton 99.5% (China), NaOH 96.0% (China), Rhodamine B 99.5% (China).

2.2. Synthesis of the composite

LS fibers were thoroughly cleaned with acetone, then ultrasonically treated for 7 minutes using a Cole-Parmer 8891 ultrasonic cleaner, extensively rinsed with distilled water, and dried at 60 °C. Then, LS fibers were treated with 0.1 M NaOH solution at 80 °C for 2 hours to remove impurities and enhance surface reactivity. Afterward, fibers were rinsed thoroughly with distilled water until a neutral pH was achieved. This NaOH treatment and rinsing procedure was repeated three times.

Cleistocalyx operculatus leaf extract was prepared by refluxing 5 g of dried leaf powder in 30 mL of ethanol at 50 - 60 °C for 2 hours. The resulting extract was filtered and diluted (1:20 v/v) with distilled water prior to use.

Pre-treated LS fibers (0.5 g) were immersed in a $FeCl_3$ solution (0.005 M, ethanol/water = 3:1 v/v) with volumes adjusted to achieve different Fe^0 loadings (3–7 mg), as shown in table 1. The suspension was ultrasonicated for 30 min to promote Fe^{3+} adsorption. Subsequently, *Cleistocalyx operculatus* leaf extract was added dropwise at a volume equal to three times that of the $FeCl_3$ solution, under continuous stirring at 250 rpm at room temperature. After complete addition, the mixture was stirred for an additional 15 min, rinsed with ethanol and diluted water, and dried under vacuum at 60 °C for 12 h.

Table 1. *Chemical components employed in the synthesis of nZVI.*

nZVI loading (mg)	**3**	**4**	**5**	**6**	**7**
Mass of $FeCl_3$ (mg)	8.7	11.6	14.6	17.6	20.4
Volume of C_2H_5OH (mL)	8.0	10.7	13.4	16.1	18.8
Volume of distilled water (mL)	2.7	3.6	4.5	5.4	6.3
Volume of 0.005 M $FeCl_3$ (mL)	10.7	14.3	17.9	21.5	25.1
Volume of leaf extract (mL)	40.5	43.2	54.0	65.1	75.0

2.3. Material characterization

The morphology and nanoparticle distribution on the composite were analyzed using scanning electron microscopy (SEM, Hitachi S-4600) and digital microscopy (PDM). Functional groups involved in nanoparticle synthesis and stabilization were identified by Fourier-transform infrared spectroscopy (FTIR, PerkinElmer Spectrum 100). Dye removal efficiency was evaluated using UV-visible spectroscopy (UV-Vis, Agilent 8453).

2.4. Evaluation of RhB removal performance

The dye removal capability of the synthesized composite was investigated using batch experiments. Briefly, 0.5 g composite was placed into 50 mL Rhodamine B (RhB) solutions at varying concentrations (2–8 mg/L). Influencing parameters such as initial dye concentration, solution pH (3–9), and contact time (10–60 min) were systematically examined. Post-treatment RhB concentration was measured using UV-Vis spectroscopy at the characteristic wavelength (λ_{max} = 554 nm). Removal efficiency (%) was calculated as follows:

$$\text{Removal efficiency (\%)} = \frac{A_0 - A_t}{A_0} \tag{1}$$

where A_0 and A_t represent the absorbance at the initial time and at time t, respectively.

In addition, the RhB removal capacity normalized per mass of nZVI was calculated by equation (2):

$$q = \frac{(C_0 - C_t).V}{m_{nZVI}} \tag{2}$$

where q is the RhB removal capacity (mg RhB per mg nZVI), C_0 and C_t are the initial and equilibrium concentrations of RhB (mg/L), V is the solution volume (L), and m_{nZVI} is the mass of nZVI in the composite (mg). This mass-normalized uptake facilitates comparison of performance with other nZVI-based materials.

The composite was repeatedly used under optimized conditions for several cycles. After each cycle, the composite was rinsed thoroughly with ethanol and distilled water, dried, and reused. Removal efficiency was monitored to assess the composite's stability and durability upon repeated usage.

3. RESULTS AND DISCUSSION

3.1. Characterization of the material

The morphology of the LS, LS after surface treatment, and nZVI/LS composite was observed using a portable digital microscope (PDM) and a scanning electron microscope (SEM).

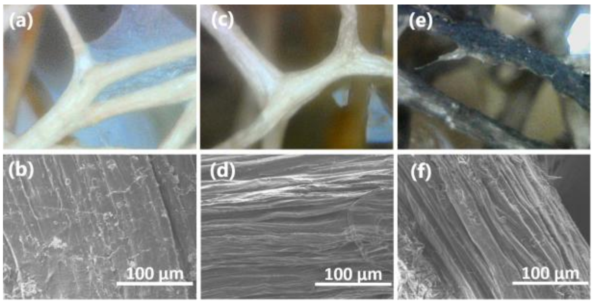


Figure 1. *Raw LS (a, b); Alkali-treated LS (c, d); nZVI/LS (e, f).*

The results shown in figure 1 indicate that the raw LS (figures 1a and 1b) exhibits a porous structure with tightly bound fibers. Its surface presents numerous adhering patches and an unevenly distributed thin organic film, which is likely residual lignin and hemicellulose [6]. Observations of the LS after alkali-treatment (figures 1c and 1d) reveal that the organic film was completely removed, resulting in a cleaner and more uniform surface that exposes the underlying cellulose structure. Fiber bundles tend to separate, forming microvoids that serve as favorable sites for the attachment of nanomaterials. After modification with nZVI (figures 1e and 1f), the surface of the LS displays the characteristic black color of zero-valent iron nanoparticles, along with the appearance of numerous small particles of irregular size distributed across the entire surface. These particles are more concentrated in heterogeneous areas or at sites with microcracks. These morphological changes suggest that the surface of the LS underwent significant transformation, possibly due to chemical interactions or the attachment of materials during the treatment process.

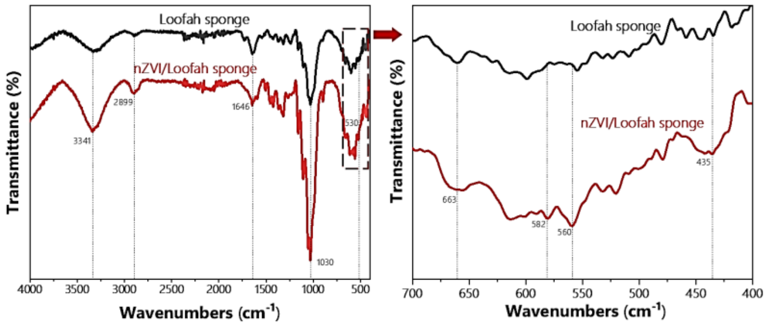
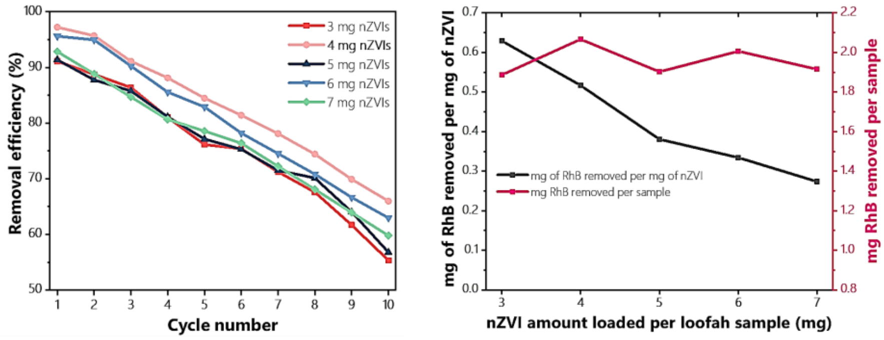


Figure 2. *FTIR spectrum of LS and nZVI/LS.*

FTIR spectroscopy was employed to investigate the bonding and chemical structure of the materials, as shown in figure 2. The spectra of raw LS fabric and nZVI/LS were compared to identify functional group changes. In raw LS, a distinct peak at 1030 cm^{-1} corresponds to C–O and C–C stretching vibrations in cellulose and hemicelluloses [7]. Upon loading with nZVI, a new absorption band appeared at 530 cm^{-1}, which is characteristic of Fe–O bonding [7]. This shift indicates successful deposition of nZVI on the LS surface and highlights the chemical interactions between the iron nanoparticles and the lignocellulosic matrix.

3.2. Investigation of RhB removal from aqueous solution

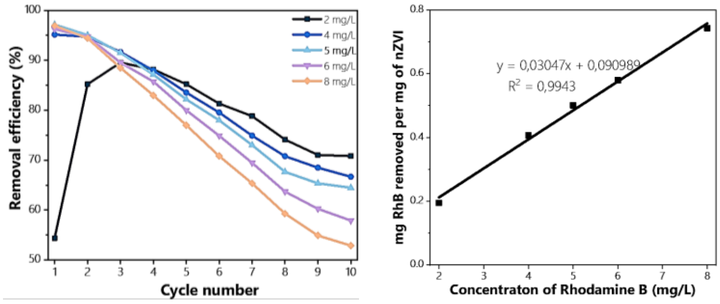
The amount of nZVI immobilized on each nZVI/LS sample was assessed by its ability to remove Rhodamine B (RhB) dye over multiple reuse cycles. The experimental conditions included a 5 mg/L RhB concentration, room temperature, and pH 5, with 30-minute treatment cycles at 550 rpm. Results showed that 4 mg of nZVI provided optimal performance, maintaining over 80% efficiency after five cycles and 60% after ten. Iron content above or below 4 mg led to reduced efficiency due to particle aggregation or insufficient active iron.



(a) *(b)*

Figure 3. *(a) RhB removal efficiency of nZVI/LS materials with different iron loadings (3–7 mg) over 10 reuse cycles. (b) Cumulative RhB removal expressed as mg per mg of nZVI and mg per sample as a function of iron loading.*

Under the initial experimental conditions – including a fixed nZVI material dosage of 4 mg, room temperature, pH 5, a treatment duration of 30 minutes per cycle, and stirring at 550 rpm – the Rhodamine B (RhB) removal efficiency of immobilized nZVI – supported LS material was evaluated at five different initial RhB concentrations (2, 4, 5, 6, and 8 mg/L) over 10 reuse cycles (figure 4). The results revealed pronounced fluctuations in removal efficiency depending on the concentration of RhB, reflecting the combined influence of solution properties and material activity. At 2 mg/L, the initial removal efficiency was low (only 54.36% in cycle 1) but increased over subsequent cycles. This may have been caused by interference from residual *Cleistocalyx operculatus* extract on the material, affecting color measurements in low-concentration dye solutions [5].

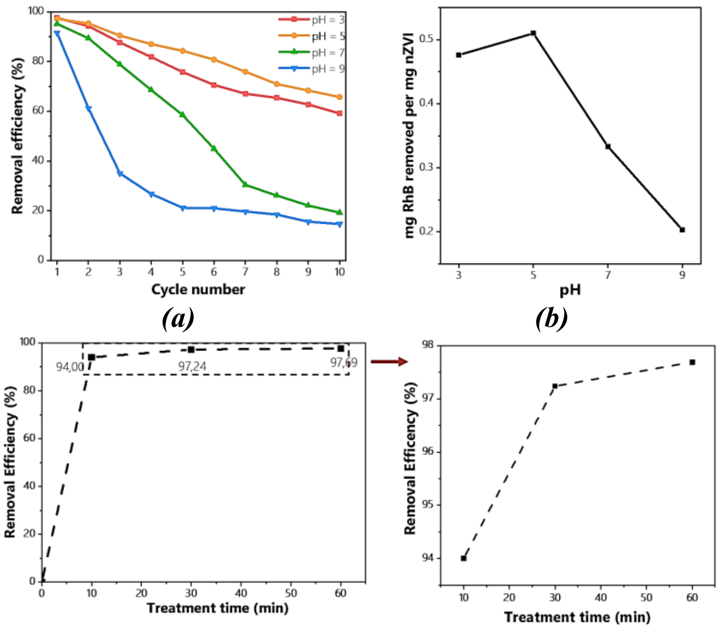


(a) ***(b)***

Figure 4. *Effect of RhB concentration on the removal efficiency of nZVI/LS material.*
(a) RhB removal efficiency over 10 reuse cycles at different initial concentrations (2–8 mg/L).
(b) Mass-normalized RhB removal as a function of initial RhB concentration.

Figure 5b shows the effect of initial Rhodamine B (RhB) concentration on dye removal per milligram of nZVI. At 2 mg/L, removal efficiency stayed above 70% after 10 cycles, but the dye removed was low (0.19 mg). The highest removal capacities were observed at 8 and 10 mg/L, reaching 0.57 mg and 0.74 mg, respectively, though efficiency dropped below 60% by the 10th cycle. At 5 mg/L, removal reached 0.51 mg with over 90% efficiency in the third cycle. Therefore, 5 mg/L was selected as the optimal RhB concentration for further experiments.

In addition to dye concentration, environmental factors such as pH and treatment time significantly impact RhB removal efficiency. Experiments with a 4 mg nZVI dosage, room temperature, 550 rpm stirring, and 5 mg/L RhB were conducted. Results show that pH strongly affects efficiency (figure 5). At pH 5, the highest and most stable removal efficiency is achieved. In acidic conditions (pH 3), efficiency decreases over time, while in alkaline conditions (pH 7 and 9), efficiency drops, particularly at pH 9. RhB removal increases rapidly in the first 10 minutes, reaching 97.24% at 30 minutes, which was selected as the optimal treatment time.



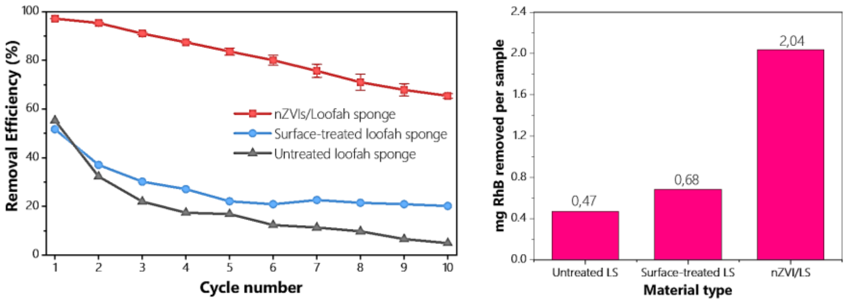
(c)

Figure 5. *Effect of pH and contact time on RhB removal efficiency of nZVI/LS material.*
(a) RhB removal efficiency over 10 reuse cycles at different pH values (3 - 9).
(b) Mass-normalized RhB removal (mg RhB per mg nZVI) as a function of solution pH.
(c) RhB removal efficiency as a function of treatment time (0 - 60 min).

After establishing the optimal conditions including a fixed nZVI dosage of 4 mg, room temperature, stirring at 550 rpm, an initial Rhodamine B (RhB) concentration of 5 mg/L, pH 5, and a treatment time of 30 minutes, a comparative evaluation was conducted to assess the RhB removal efficiency and reusability of three materials: raw loofah sponge (LS), alkali-treated LS, and nZVI/LS. The results, presented in figure 6, indicate that the nZVI/LS material exhibited superior removal performance compared to the other two, particularly in terms of stability over multiple reuse cycles. In the first cycle, nZVI/LS removed over 97% of RhB, while raw LS and surface–treated LS achieved approximately 55% and 52%, respectively. After 10 cycles, the iron-loaded material maintained removal efficiency above 65%, whereas the other two dropped below 10%, indicating a significant loss of activity in the absence of nZVI. This performance enhancement results from the dual mechanism of the composite: primary adsorption by the LS and strong redox reactions from the nZVI particles. The three–dimensional porous structure and functional groups such as –OH and –COOH on the cellulose facilitate retention of RhB molecules near the reactive surface. Meanwhile, Fe^0 particles serve as central reductive agents, disrupting the RhB structure via direct or indirect electron transfer through Fenton–like reactions that generate highly oxidative •OH radicals [8]. This cooperation increases the interaction density between the reactive agent and the pollutant, thereby enhancing removal efficiency.

The bar chart illustrates RhB removal expressed as mg of RhB per material sample, showing that nZVI/LS achieved 2.04 mg – approximately four times higher than the untreated LS. This confirms that LS not only serves as a support for nZVI but also significantly contributes to treatment efficiency through its adsorption–concentrating mechanism and the uniform dispersion of iron nanoparticles. Furthermore, immobilizing nZVI limits particle aggregation, reduces unwanted oxidation, and extends the material's active lifespan, playing a key role in sustaining efficiency across multiple reuse cycles.

In the study by Le et al. (2022) [5], green-synthesized nZVI using Cleistocalyx operculatus leaf extract as the reducing agent was evaluated for Rhodamine B (RhB) removal under identical experimental conditions (initial RhB concentration of 5 mg/L, pH 5, room temperature, and 30-minute treatment time). The results showed that 1 mg of nZVI removed approximately 0.04 mg of RhB. However, the recovery and reuse of free nZVI particles remained challenging. In the present study, nZVI was immobilized on a loofah sponge, enabling easy recovery and reuse. The material achieved a cumulative removal of 2.04 mg RhB per 1 mg of nZVI over 10 treatment cycles. This demonstrates the enhanced performance of immobilized nZVI – supported LS material and further confirms its potential as a feasible and sustainable solution for dye-contaminated wastewater treatment.



(a) ***(b)***

Figure 6. *a) Reusability performance of the three tested materials over 10 reuse cycles. b) Cumulative RhB removed after 10 cycles for untreated LS, surface-treated LS, and nZVI/LS.*

4. CONCLUSIONS

This study successfully synthesized nano zero valent iron material on a loofah sponge substrate using a green method with Cleistocalyx operculatus leaf extract. SEM, PDM, and XRD analyses confirmed that the nZVI was uniformly distributed on the loofah surface. The synthesized material demonstrated excellent performance in the removal of Rhodamine B dye, achieving over 97% efficiency under optimal conditions (4 mg nZVI, RhB concentration of 5 mg/L, pH = 5, reaction time of 30 minutes). Notably, the material maintained high treatment efficiency over multiple reuse cycles, whereas the loofah sponge without nZVI showed a rapid decline in activity. These results reaffirm the key role of nZVI in the removal mechanism and highlight the effectiveness of the natural–nano hybrid material design. nZVI acts as the primary reactive agent, degrading RhB through efficient redox reactions. Additionally, the entire synthesis process adheres to green chemistry principles, employing bio–based, recoverable, and environmentally friendly materials. The obtained results demonstrate the practical application potential of nZVI/LS material in treating dye-containing wastewater and pave the way for the development of sustainable green materials in environmental technology.

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TÓM TẮT

Nghiên cứu tổng hợp xanh các hạt nano sắt hóa trị 0 (nZVI) trên sơ mướp ứng dụng phân hủy chất nhuộm Rhodamine B

Hóa học xanh ngày càng đóng vai trò quan trọng trong công nghệ xử lý môi trường. Nghiên cứu này giới thiệu hệ vật liệu xử lý nước thải sử dụng hai nguyên liệu tự nhiên đặc trưng của Việt Nam: xơ mướp và dịch chiết lá vối. Vật liệu được tạo thành bằng cách cố định hạt sắt nano hóa trị 0 (nZVI) lên nền xơ mướp, trong đó Fe^{3+} được khử về Fe^{0} nhờ các hợp chất polyphenol và flavonoid trong dịch chiết. Hình thái và cấu trúc vật liệu được phân tích bằng kính hiển vi kỹ thuật số cầm tay (PDM); kính hiển vi điện tử quét (SEM); phổ nhiễu xạ tia X (XRD); phổ hồng ngoại biến đổi Fourier (FTIR). Hiệu quả xử lý Rhodamine B (RhB), một thuốc nhuộm phổ biến trong nước thải dệt may, được đánh giá bằng phổ UV–Vis. Kết quả cho thấy vật liệu đạt hiệu suất xử lý RhB đến 97% ở chu kỳ đầu và duy trì trên 65% sau 10 chu kỳ tái sử dụng. Qua đó mở ra một hướng tiếp cận mới trong lĩnh vực xử lý chất ô nhiễm bằng vật liệu có nguồn gốc tự nhiên.

Từ khoá: Tổng hợp xanh; Hạt sắt nano hóa trị 0; Xơ mướp; Dịch chiết lá vối; Xử lý nước thải; Rhodamine B.