Sustainable application of silvered nickel foam for the highly efficient degradation of rhodamine B

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Abstract
The use of organic dyes has led to serious environmental problems resulting from contaminated wastewater; hence, the development of new dye-removal methods is an important objective. Herein, silvered nickel foam (nickel foam loaded with silver nanoparticles) is reported to significantly degrade an organic dye in aqueous solution. 20 mg l⁻¹ rhodamine B is completely reduced within 20 min with a rate constant of 0.26 min⁻¹ in the presence of nickel foam sparsely loaded with silver. A mechanism for the reduction of rhodamine B is proposed. Moreover, the silvered nickel foam can be recycled at least five times. This research demonstrates that silvered nickel foam is a promising pollution-control candidate material.

1. Introduction
Over the past few decades, large amounts of organic dye have led to serious environmental problems because many industries, such as the textiles, printing, and paint industries, release seriously contaminated dye-containing wastewater into the environment.

Among various dyes, rhodamine B (Rh B) is commonly regarded to be a representative water pollutant, being hazardous and toxic to humans and animals. Rh B is widely used as a coloring agent in the textiles industry. Therefore, the removal of Rh B from industrial wastewater has attracted significant interest, with many physical and chemical approaches explored to date for its removal from aqueous solutions. Among these methods, adsorption [1–3] and catalysis [4, 5] are the most widely used techniques for removing Rh B. For example, Saini et al reported the use of red mud to successfully remove Rh B from wastewater [6]. This removal method has the advantages of cost-effectiveness and high adsorption capacity; however, Rh B is not degraded by adsorption, it is simply moved from one phase to another. In order to degrade Rh B, Mittal et al reported the photocatalytic degradation of Rh B using anatase titanium dioxide [7]. Despite the dye being degraded into inorganic materials, the photocatalytic behavior of TiO₂, like most semiconductors, is pH-dependent owing to its amphoteric nature. In addition, UV or visible light is needed to initiate photocatalysis. Sharma et al reported the preparation of bimetallic Pt–Cu nanoparticles that degraded Rh B in the presence of NaBH₄ [8]. Although this catalytic process occurs in the absence of UV irradiation, this catalyst is disadvantageous because of its high cost, low stability, and poor reusability. Therefore, finding new highly catalytic, recyclable, and cost-effective routes for the degradation of Rh B remains challenging.

Due to its low cost and good mechanical and conductive properties, nickel foam is often used as a support [9–11] or current collector [12, 13]. Silvered Ni foams have been reportedly used as electrodes in fuel cells or for the reduction of benzyl bromide [14–16]. Despite having been synthesized, the performance of silvered Ni foams and the degradation mechanism for dyes, such as Rh B, are less investigated. In the present work, nickel foam was sparsely loaded with silver nanoparticles to form silvered nickel foam, with the resulting product used to degrade Rh B. The present study provides a promising wastewater-purification method.
2. Materials and methods

2.1. Materials
Analytical grade AgNO₃, Rh B, and NaBH₄ were purchased from the Aladdin Industrial Corporation (Shanghai, China) and used without further purification. Nickel foam (1.5 mm thick) was obtained from the Henan New Material Co. Ltd (China). The nickel foam was cut into square 2 cm × 2 cm panels, successively cleaned in acetone, 2 M HCl, and distilled water, and then dried at 100 °C for 1 h.

2.2. Synthesis of silvered nickel foam
Silvered Ni foam was synthesized using the following procedure. A treated Ni foam panel was placed in a beaker to which 25 ml of a 0.5 M aqueous solution of silver nitrate was added. The mixture was maintained at room temperature for 24 h, after which the sample was removed from the solution, washed thoroughly with distilled water, and dried at 100 °C for 1 h.

2.3. Characterization
Optical properties were characterized using a visible spectrophotometer (Model 721, Shanghai Optical Instrument Factory, Shanghai, China). The crystal structure of the silvered nickel foam was analyzed by x-ray powder diffractometry (XRD, Rigaku D/Max 2200PC, Rigaku Corporation, Tokyo, Japan) with a graphite monochromator and CuKα radiation (λ = 0.15418 nm). The morphologies of nickel foam and the silvered nickel foam were examined by field-emission scanning electron microscopy (FESEM, JEOL JSM–6700F, JEOL Electronics Co., Ltd, Tokyo, Japan) augmented with energy dispersive x-ray spectroscopy for determining the chemical composition of the silvered nickel foam. The surface state of the silvered nickel foam was examined by x-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo Scientific, USA).

2.4. Catalysis experiments
Catalysis experiments were performed in the presence of room light. The catalytic activity of the synthesized silvered nickel foam was evaluated at room temperature by the reduction of Rh B with NaBH₄ as the reducing agent. In a typical experiment, a piece of the prepared sample was immersed in 100 ml of a mixed solution containing 20 mg \cdot 1⁻¹ Rh B and 10 mM NaBH₄. About 3 ml of the mixture was withdrawn using a glass dropper every 5 min, and its absorbance measured using the abovementioned spectrophotometer at the Rh B absorption wavelength maximum (542 nm) at room temperature.

Recycling performance testing was carried out as follows. The used silvered Ni foam was removed from the reaction mixture, washed three times with distilled water, and then dried in an oven at 100 °C for 1 h for in use in a subsequent experimental run.

3. Results and discussion

XRD was used to investigate the crystal structure of the as-prepared silvered nickel foam. The XRD pattern shown in figure 1 reveals diffraction peaks at 44.5°, 51.8°, and 76.4°, which are indexed to the (111), (200), and (220) lattice planes of nickel (JCPDS card No. 65-2865). Apart from the three characteristic peaks derived from the nickel foam, no peaks corresponding to silver were observed in the XRD pattern, which is ascribable to the sparseness of the silver in the silvered nickel foam [17].

XPS was used to investigate interactions between silver and nickel. The Ni 2p XPS spectra of the nickel foam and silvered nickel foam are showed in figure 2, which show characteristic Ni 2p₃/₂ and Ni 2p₁/₂ peaks at 855.28 and 872.98 eV (with a spin-energy separation of 17.7 eV), respectively, for the nickel foam, while characteristic Ni 2p₃/₂ and Ni 2p₁/₂ peaks at 854.98 and 872.68 eV (with a spin-energy separation of 17.7 eV), respectively, were observed for the silvered nickel foam. Compared to the Ni 2p binding energies of the nickel foam, those of the silvered nickel foam were lower, suggestive of charger transfer from silver to nickel [18]. Because the Fermi level of nickel is lower in energy than that of silver, electrons will transfer from silver to nickel in order to lower their overall energy [19].

SEM and EDX were used to study the morphology and determine the composition of the generated product. The SEM image shown in figure 3(A) reveals that the nickel foam possesses an open three-dimensional multichannel structure of the order of hundreds of micrometers in size. The smooth surface of the nickel foam skeleton disappeared after wetting with an aqueous solution containing AgNO₃ (figure 3(B)). Small metallic silver particles 9–21 nm in size are present on the surface of the foam (figure 3(C)), as confirmed by EDX (figure 3(D)), which revealed a silver loading of 2.44 wt%. The low silver loading is consistent with the XRD data presented above. In addition, the low silver content is also beneficial for reducing the cost of the silvered nickel foam.
The formation of silver nanoparticles through galvanic replacement at room temperature ($2\text{Ag}^+ + \text{Ni} = 2\text{Ag} + \text{Ni}^{2+}$) is reasonable considering the difference between the $\text{Ag}^{+}/\text{Ag}^0$ (0.80 V) and $\text{Ni}^{2+}/\text{Ni}^0$ (−0.22 V) electrode potentials. Unlike previously reported [20], no other external reducing agent was introduced in the current process. Moreover, the generated silver nanoparticles were observed to be highly dispersed over the surface of the nickel foam without the addition of any organic ligands or inorganic capping materials, which is ascribable to the advantages of nickel foam that inhibits particle growth as well as reducing particle aggregation [20]. On the
basis of the abovementioned results, the nickel foam was clearly sparsely loaded with silver nanoparticles in a sustainable protocol.

Figure 4 shows degradation rates \( \frac{C}{C_0} \), where \( C \) and \( C_0 \) are the concentrations of Rh B at times \( t \) and 0, respectively) of Rh B as functions of time under various experimental conditions. According to the Beer–Lambert law, \( C \) is proportional to the absorbance \( A \) at 542 nm; consequently, \( \frac{C}{C_0} \) can be calculated from \( \frac{A}{A_0} \). Various control experiments were conducted to unravel the role of each experimental parameter. Degradation activities were first determined using \( \text{NaBH}_4 \), the nickel foam, and the silvered nickel foam as individual components; none of these conditions resulted in significant degradation of Rh B. In contrast, the nickel foam + \( \text{NaBH}_4 \) and the silvered nickel foam + \( \text{NaBH}_4 \) show excellent catalytic activities; a degradation rate of 100% within 20 min was observed for the system containing silvered nickel foam, while 70% was observed for the nickel foam system. These results indicate that, compared to nickel foam, the silvered nickel foam...
foam is a highly efficient catalyst for the degradation of organic dyes. Clearly, the silver loading has an effect on the degradation of Rh B.

To understand Rh B degradation, the degradation kinetics for the nickel foam and the silvered nickel foam were fitted to the first-order kinetic model, with the equation: \( \ln\left(\frac{C}{C_0}\right) = -kt \) used to evaluate \( k \), where \( k \) is the first-order rate constant and \( t \) is the reaction time. As shown in figure 5, the degradation of Rh B is well fitted by first-order kinetics, as evidenced by the linear relationships between \( \ln\left(\frac{C}{C_0}\right) \) and reaction time. The reaction rate constant for the silvered nickel foam was determined to be 0.26 min\(^{-1}\) while that for the Ni foam is 0.062 min\(^{-1}\); \( k \) for the silvered nickel foam is about four-times higher than that of the nickel foam. These results clearly show that the introduction of silver nanoparticles on the nickel foam significantly affects catalytic performance for Rh B degradation.

Catalyst stability is crucial for practical applications, and immobilizing silver nanoparticles on a nickel foam support transforms them into a practically recyclable catalyst; the nickel foam support is also beneficial for catalyst reusability. The catalyst was cycled five times under the same conditions to evaluate the reusability of the silvered nickel foam. As shown in figure 6, the silvered nickel foam was reusable at least five times without any obvious decline in Rh B degradation performance. In contrast to the TiO\(_2\) photocatalyst, which suffers from stability issues \([22]\), the silvered nickel foam exhibited good stability during repeated catalytic reactions.

Taken together, as a catalyst, the silvered nickel foam shows excellent catalytic activity, stability, and recyclability. On the basis of the Langmuir–Hinshelwood mechanism, catalytic reduction of Rh B needs the
adsorption of the BH$_4^-$ and Rh B onto the surface of the catalyst. As a reducing agent, the adsorbed BH$_4^-$ ions donate electrons to the surface of the catalyst for reduction of adsorbed Rh B [23]. When silver nanoparticles are loaded on the surface of the nickel foam, electron transfer occurs in the silver–nickel junctions because the Fermi level of silver is higher than that of nickel. This electron migration results in the formation of electron–enriched areas on the nickel foam. The accumulated electrons accelerate electron transfer between the nickel foam and the adsorbed Rh B. In addition, the highly dispersed silver nanoparticles have a high surface area and can boost this catalytic capability. Consequently, synergism between the silver nanoparticles and the nickel foam contributes to the highly efficient performance of the silvered nickel foam. The proposed electron-transfer process for the reduction of Rh B over silvered nickel foam is shown in scheme 1.

4. Conclusions

Nickel foam was sparsely loaded with silver nanoparticles in a sustainable manner. The size of the silver nanoparticles ranged from 9 nm to 21 nm. By combining nickel foam with silver nanoparticles, the prepared silvered nickel foam exhibited remarkable catalytic behavior, as demonstrated by the reduction of Rh B with NaBH$_4$. The investigation of catalytic reduction mechanism showed that excellent catalytic activity of the silvered nickel foam mainly resulted from synergistic effect between silver nanoparticles and nickel foam. This facile method offers a novel approach for the highly efficient degradation of Rh B.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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