Effective Decolorization of Rhodamine B by a Ti Foam-Based Photocatalytic Membrane Reactor

Xiaoping Chen,* Yuansong Wei, Bohong Chen, and Jiaqi Fu

ABSTRACT: In this study, a Ti foam-based photocatalytic membrane reactor (PMR) was constructed for rhodamine B (RhB) wastewater decolorization. Ti foam was chosen as a membrane and visible-light-driven C₃N₄ was chosen as a photocatalyst. The results showed that the decolorization efficiency could be up to 100% with a flow rate of 6.93 mL/min when the PMR was applied in the treatment of a 30 mg/L RhB solution and the concentration of C₃N₄ was 1 g/L. pH played an important role in the decolorization performance of the PMR. Alkalinity was not conducive to the decolorization of RhB in the PMR, which was mainly due to the property that RhB was difficult to dissolve in an alkaline solution. Membrane fouling was mainly caused by a C₃N₄ photocatalyst, while the effect of RhB on membrane fouling was negligible. Membrane fouling could be retarded when the PMR was applied for RhB treatment under visible-light irradiation, which was because of photoinduced hydrophilicity of C₃N₄. The membrane flux could be restored to its initial values after simple ultrasonic cleaning and backwashing. This was due to the large difference between the pore size of Ti foam and the particle size of C₃N₄ and the super hydrophilicity of Ti foam and C₃N₄.

1. INTRODUCTION

Colourful dye wastewater is chemically stable, nonbiodegradable, toxic, and carcinogenic, which is threatening the environment, ecosystem, and health of all living beings.¹⁻⁴ The conventional methods such as physical methods,⁵⁻⁶ biological methods, and chemical oxidation⁷⁻⁸ have been employed for dye wastewater treatment. However, these technologies are usually not effective in color removal and the treatment cost is relatively high. Meanwhile, they are easy to cause secondary pollution.⁹ Therefore, developing an economical, effective, and ecofriendly technology is imperative for the decolorization of dye wastewater.

PMR is a system coupling photocatalysis and membrane separation in one unit, which shows great potential for use in wastewater treatment.¹⁰,¹¹ The performance of PMR mainly depends on the choice of a photocatalyst and a membrane. TiO₂ was most commonly chosen as a photocatalyst in slurry PMRs for dye wastewater treatment because of its high effectiveness and chemical stability.¹²,¹³ However, it can only respond to ultraviolet light because of its spacious band gap. Polymer membranes have been widely reported to be used in PMRs for wastewater treatment.¹⁴,¹⁵ Nevertheless, the light or active species produced during the photocatalytic process may damage polymer membranes. In addition, the antifouling performance of the membrane and the difficulty of cleaning strategies mainly depend on the properties of the membrane and the photocatalyst.¹⁶,¹⁷ Therefore, the choice of the membrane and the photocatalyst is crucial for PMR construction.¹⁸,¹⁹

Microporous Ti foam shows great potential in the field of wastewater treatment because of its significant mechanical strength and excellent stability.²⁰,²¹ However, the literature about microporous Ti foam applied in PMRs for wastewater treatment is, in general, very scarce. C₃N₄ was chosen as a promising photocatalyst because it could respond to visible light besides having excellent photocatalytic activity, low cost, and stability.²²,²³ Thus, in this study, a PMR constructed with Ti foam and C₃N₄ was developed for RhB decolorization. The performance of the PMR was investigated as well as the parameter flow rate, pH etc. were studied and optimized. Moreover, the influence of characteristics of Ti foam and C₃N₄ on membrane fouling as well as membrane cleaning was also investigated.

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2. RESULTS AND DISCUSSION

2.1. Characterization of C₃N₄ and Ti Foam. The X-ray diffraction (XRD) pattern of the photocatalyst prepared is shown in Figure 1A. The strongest XRD peak at 27.8° can be indexed as the (002) plane of C₃N₄ (JCPDS 087-1526), which represents the stacking of the conjugated aromatic systems in the layered structure.²⁴,²⁵ XRD results indicate that the photocatalyst prepared is C₃N₄. The BET surface area and pore volume of C₃N₄ are 80.1 m²/g and 0.58 cm³/g, respectively, which indicates that C₃N₄ obtained is a porous material. The average pore diameter is 28.9 nm. The shape of the hysteresis loops of C₃N₄ is type H₃ at a high relative pressure range (Figure S1), indicating the presence of slit-like pores.²⁶ Ultraviolet–visible (UV–vis) diffuse reflectance spectra of C₃N₄ are shown in Figure 1B. The absorption wavelength of the photocatalyst prepared is around 440 nm. According to the band gap (Eₕ) calculation equation \( Eₕ = \frac{1240}{\lambdaₖ} \) (λₖ represents the semiconductor optical absorption edge),²⁷ the band gap of C₃N₄ prepared is estimated to be 2.82 eV, which confirms that the photocatalyst prepared is C₃N₄ and it is a visible-light-response photocatalyst.

The morphologies of C₃N₄ and Ti foam are shown in Figure 2. Figure 2A,B shows the FESEM images of the as-prepared C₃N₄. The morphology of C₃N₄ is mainly nanosheets with the size in the region of 50–1000 nm, which gather together. Particles with different sizes can be seen clearly from the SEM images of Ti foam (Figure 2C). The pores exist in the form of
the slits of particle stacking. The shape of the pores in the skin layer is irregular. The diameter of large surface pores can be up to 20 μm (Figure 2D). Thus, the C₃N₄ photocatalyst can enter into the pores of Ti foam and cause membrane pollution because the size of C₃N₄ is much smaller than the pore size of Ti foam, which will be discussed in the following section.

The effect of C₃N₄ dosages on the photocatalytic decolorization of a 30 mg/L RhB solution was then studied. Experimental data (Figure 3A) demonstrated that the photocatalytic decolorization activity increased with the increase of C₃N₄ dosages. It should be noted that the photocatalytic decolorization activity increased slowly when the C₃N₄ dosage reached 1.0 g/L or above. This was because the light could be almost absorbed when the C₃N₄ dosage reached 1.0 g/L. The results also indicated that the photocatalytic decolorization of RhB was a zero-order reaction within 20 min of initial irradiation and was a first-order reaction after 20 min of irradiation, as shown in Figure 3B. This meant that the concentration of RhB was only related to the time of irradiation and not to its initial concentration within 20 min of irradiation during this decolorization experiment when RhB concentration was 30 mg/L and C₃N₄ dosage was 1.0 g/L. The constant k of photocatalytic decolorization after 20 min of irradiation was calculated to be 0.29 min⁻¹ by the following eq 1²⁸

\[
\frac{C_t}{C_0} = e^{-kt}
\]

where \(C_0\) (mg L⁻¹) is the initial concentration of RhB, \(C_t\) (mg L⁻¹) is the concentration at time of t (min), and k is the rate constant (min⁻¹).

2.2. Performance of PMR for RhB Decolorization. The liquid flow rates were adjusted by peristaltic pumps, which retained the same rotation rate. Figure 4 shows the results of the photocatalytic decolorization efficiency vs flow rates. The PMR showed effective decolorization efficiency for RhB. For instance, the decolorization efficiency was almost 100% when the flow rate was 6.93 mL/min (the corresponding residence time was 7.2 h) or below. When the flow rate increased to 7.80 mL/min or above, the color of the permeate solution began to appear. However, the decolorization efficiency was still as high as 99.6%. The decolorization efficiency of PMR could be controlled via adjusting flow rates. The total organic carbon (TOC) of the feed solution was 19.4 mg/L. As shown in Figure 5, the TOC of permeate was 4.75–6.78 mg/L when the decolorization of RhB was conducted in the PMR with different flow rates in a dark environment. This was because the RhB solution could be diluted when it was added into the PMR. In addition, C₃N₄ could adsorb some RhB. When the decolorization of RhB was conducted in the PMR with different flow rates under visible-light irradiation, the TOC of permeate was reduced to 0.5–1 mg/L, respectively, compared
with the ones in the dark environment. This meant that the main function of photocatalysis was decolorization, although it had a small effect on TOC removal.

The effect of pH values on the decolorization of RhB in the PMR is shown in Figure 6. It could be clearly seen that pH values played an important role in the decolorization in the PMR. When the pH was 10 and 13, the characteristic absorption peaks of RhB appeared. This was mainly because RhB was difficult to dissolve in an alkaline solution. Thus, it was difficult to adsorb on the surface of C3N4 for further photocatalytic decolorization. No Ti was detected (measured by an inductively coupled plasma analyzer) in the permeate when the PMR was operated under different pH values, which proved that Ti foam had excellent stability.

2.3. Membrane Fouling and Cleaning. Membrane fouling in PMRs is mainly caused by the photocatalysts or/and pollutants from the wastewater. To investigate membrane fouling, the PMR was operated with the flow rate of 6.93 mg/min under different conditions. As shown in Figure 7, the flux of a Ti foam membrane in the PMR decreased rapidly in the early operation stage, which was mainly due to the pore blocking and the cake layer by a C3N4 photocatalyst. An interesting phenomenon was observed that the flux of the Ti foam membrane in PMR under visible-light irradiation decreased slower than the one in PMR without visible-light irradiation. This was mainly because of photoinduced hydrophilicity of C3N4, which retarded membrane fouling. However, the fluxes of the Ti foam membrane under different conditions were almost the same after the PMR was operated for 6 h, which confirmed that membrane fouling was mainly caused by the C3N4 photocatalyst and RhB almost had no effect on membrane fouling. This was mainly due to the large difference between the molecular size of RhB and the pore size of Ti foam.

The C3N4 photocatalyst could be seen clearly on the surface of the Ti foam membrane after 6 h of operation in PMR, as shown in Figure S2A, which was the main reason for the decline of the Ti foam membrane flux during the photocatalytic decolorization of RhB in the PMR. The peak at 500–600 nm (Figure S2B) of UV–vis diffuse reflectance spectroscopy for C3N4 on the surface of the Ti foam membrane indicated that RhB could be easily adsorbed on C3N4. The flux of the Ti foam membrane could be restored to its initial value easily after ultrasonic cleaning and backwashing were carried out successively, as shown in Figure 8. This was mainly due to super hydrophilicity of C3N4 because there were lots of hydrophilic amino groups on the surface of C3N4, which could be verified from the Fourier-transform infrared (FTIR) results. As shown in Figure 9, the peak located at 810 cm⁻¹ was related to the out-of-plane bending mode of tri-s-triazine rings, which indicated the existence of basic melon units with NH/NH2 groups and the peak at 1637 cm⁻¹ was attributable to the C= N stretching vibration modes, while the peaks at 1251, 1325, and 1419 cm⁻¹ were due to the aromatic C–N stretching. In addition, the peaks among 3000–3300 cm⁻¹ were due to the N–H and the O–H vibrations, caused by the surface uncondensed amine groups or/and the absorbed water molecules. The interaction between C3N4 and Ti foam should be weak because Ti foam was also super hydrophilic. Thus, C3N4 in the pores of Ti foam could be easily dispersed or even partially dissolved in an aqueous solution after ultrasonic cleaning and then they could be removed from the pores of Ti foam along with backwashing. EDAX results in Figure S3 indicate that only carbon and titanium existed in the Ti foam membrane. Whereas, no nitrogen was found in the Ti foam membrane after cleaning (Figure S4), which was used in the PMR applied for RhB decolorization. This proved that C3N4 could be removed completely and the flux of the Ti foam membrane could be restored after ultrasonic cleaning and backwashing.

3. CONCLUSIONS

In this study, a Ti foam-based PMR was developed for effective RhB wastewater decolorization. The apparent decolorization kinetics of C3N4 was a zero-order reaction within 20 min of initial irradiation and was a first-order reaction after 20 min of irradiation when RhB concentration was 30 mg/L and C3N4 dosage was 1 g/L. The decolorization efficiency of the PMR could be 100% with a flow rate of 6.93 mL/L or below during the treatment of a 30 mg/L RhB solution. RhB was difficult to dissolve in an alkaline solution. Thus, alkalinity was not conducive for the decolorization of RhB in the PMR. Membrane fouling was mainly caused by a C3N4 photocatalyst and the effect of RhB on membrane fouling was negligible. Membrane fouling could be retarded under visible-light irrigation because of photoinduced hydrophilicity of C3N4. The membrane flux could be restored to its initial value easily after ultrasonic cleaning and backwashing. This was mainly due to the weak interaction between C3N4 and Ti foam because of their hydrophilicities. C3N4 in the pore of a Ti foam membrane could be easily dispersed in an aqueous solution after ultrasonic cleaning, and then be removed thoroughly from
the large pores of the Ti foam membrane along with backwashing. Through this study, we hope it can provide some new ideas for the construction of effective PMRs applied in wastewater treatment.

4. EXPERIMENTAL SECTION

4.1. Materials. Urea (CH_{2}N_{2}O, ≥99.0 wt %), sulfuric acid (H_{2}SO_{4}, 95.0−98.0 wt %), and sodium hydroxide (NaOH, ≥96.0 wt %) of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Rhodamine B (C_{28}H_{31}ClN_{2}O_{3}) of analytical grade was obtained from Aladdin−Holdings Group. Ti foam (the thickness 2.0 mm, 80−95 wt % Ti) was obtained from Shijiazhuang Yida Filter Equipment Company (Shijiazhuang, China). Ultrapure water was purified with a Milli-Q water system (Aquapro) and used in all of the experiments.

4.2. Synthesis and Photocatalytic Performance Characterization of C_{3}N_{4}. Urea was dried in an oven at 110 °C for 4 h. Then, the dried urea was heated to 550 °C with a heating rate 5 °C/min in an alumina crucible with an aluminum foil as a cover for 3 h. After cooling to room temperature naturally, C_{3}N_{4} was obtained without further treatment. To obtain the optimal catalyst dosage, some batch experiments were conducted at room temperature (25 °C) with a certain amount of C_{3}N_{4} added into 500 mL of a 30 mg/L RhB solution. Prior to irradiation, the suspension was stirred in a dark environment for 30 min after ultrasonic dispersion to attain adsorption and desorption equilibriums. Then, the suspension was irradiated by a Xe lamp (300 W, PLS-SXE300, Beijing) equipped with an optical cutoff filter (λ > 400 nm). The distance between the optical cutoff filter and the surface of suspension was 10 cm. At certain time intervals, 3 mL of the sample was taken from the suspension and then centrifuged to remove the photocatalyst particles. The RhB concentrations were determined at its maximum absorption wavelength of 554 nm by a UV−vis spectrophotometer (UV-1800, Shimadzu, Japan).

4.3. Characterization. The crystal structures of C_{3}N_{4} were confirmed by X-ray diffraction on a Shimadzu XRD-7000 diffractometer operated at 40 kV and 30 mA using Cu Kα irradiation. The scanning speed was 5°/min. UV−vis diffuse reflectance spectra (DRS) were observed at room temperature (25 °C) between 230 and 800 nm from a UV−vis spectrophotometer (UV-2450, Shimadzu, Japan) using BaSO_{4} as a reflectance standard. The surface area of C_{3}N_{4} was characterized by BET measurement (Micromeritics, ASAP 2460). The morphologies of the samples were investigated by field-emission scanning electron microscopy (FESEM, HITACHI S-4800). Energy-dispersive atomic X-ray analysis (EDAX) was done for elemental analysis. The RhB concentrations of the permeate were determined by a TOC analyzer (Multi. N/C. 3100, Analytikjena, Germany). An inductively coupled plasma analyzer (ICAP 6000 Radial, Thermo) was used to measure the leaching concentration of Ti in the permeate under different pH values.

4.4. PMR for RhB decolorization. The schematic illustration of the PMR for RhB decolorization under room temperature (25 °C) is given in Figure 10. RhB solution (30 mg/L) was fed into the reactor through a feed tank with 3000
mL of the C₃N₄ slurry (the concentration of C₃N₄ was 1 g/L). The light was from a Xe lamp (300 W, PLS-SXE300, Beijing) equipped with an optical cutoff filter (λ > 400 nm). The distance between the optical cutoff filter and the surface of suspension was 10 cm. The decolorization of RhB took place in the PMR. C₃N₄ was retained in the reactor through the interception of the Ti foam membrane. The working area of the Ti foam membrane was 7.1 cm². The liquid flow rates (input and output) were set to 4.33, 5.20, 6.06, 6.93, 7.80, and 8.66 mL/min, which were adjusted by controlling the rotation speed of peristaltic pumps, and the pH of the solution was 7. For comparison, the decolorization experiments of 30 mg/L RhB in the PMR with different flow rates were also conducted in a dark environment. To study the effects of pH on the decolorization performance of the PMR, NaOH and H₂SO₄ were used to adjust the pH of the solution to different values, and the flow rate of the PMR was kept at 6.93 mL/min.

To study the causes of membrane fouling formation, three experiments were conducted as follows:

**Experiment (1):** 1 g of C₃N₄ was added in the PMR. The PMR was conducted for 6 h under room temperature (25 °C) without visible-light irradiation. No RhB solution was added in the PMR, while pure water with a flow rate of 6.93 mL/L was added in the PMR.

**Experiment (2):** 1 g of C₃N₄ was added in the PMR. The PMR was conducted for 6 h under room temperature (25 °C) with visible-light irradiation. No RhB solution was added in the PMR, while pure water with a flow rate of 6.93 mL/L was added in the PMR.

**Experiment (3):** 1 g of C₃N₄ was added in the PMR. The PMR was conducted for 6 h under room temperature (25 °C) with visible-light irradiation. RhB solution with a flow rate of 6.93 mL/L was added in the PMR. After the experiment, C₃N₄ on the surface of the Ti foam membrane was dried in vacuum at 50 for 24 h, which was for further DRS characterization.

The membrane cleaning process was as following: first, the membrane was cleaned by ultrasonication for 30 min. The frequency and power of the ultrasonication used were 40 kHz and 240 W, respectively. Then, C₃N₄ was removed from the Ti foam membrane through backwashing.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04476.

The nitrogen adsorption–desorption isotherms of C₃N₄, the photograph of the polluted Ti foam membrane and the UV–vis diffuse reflectance spectra of C₃N₄ on the surface of the Ti foam membrane, the EDAX spectra of the Ti foam membrane, and the EDAX spectra of the Ti foam membrane after cleaning (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Xiaoping Chen — Institute of Energy Research, Jiangxi Academy of Sciences, Nanchang 330096, China; orcid.org/0000-0002-9391-4412; Phone: 86-0791-88337597; Email: cxpjxskxy@126.com

**Authors**

Yuansong Wei — Institute of Energy Research, Jiangxi Academy of Sciences, Nanchang 330096, China; State Key Joint Laboratory of Environmental Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Bohong Chen — Institute of Energy Research, Jiangxi Academy of Sciences, Nanchang 330096, China

Jiaqi Fu — Institute of Energy Research, Jiangxi Academy of Sciences, Nanchang 330096, China

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c04476

**Notes**

The authors declare no competing financial interest.

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