



Removal of Rhodamine B from Wastewater by Adsorption using Iron Oxide-Polymer Composite Material

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The discharge of dye-containing wastewater from textile, paper and plastic industries poses serious environmental pollution hazards. This study investigates the potential application of an ion exchange material-iron oxide composite to remove rhodamine B dye from aqueous solutions. The composite was synthesized by incorporating iron oxide nanoparticles into a cationic ion exchange matrix containing amine groups with high affinity for rhodamine B dye. Batch adsorption experiments were conducted under controlled pH, temperature and initial rhodamine B dye concentrations. The results demonstrate that the composite material can effectively remove rhodamine B dye, with adsorption capacities reaching 23570.4 mg/g and removal efficiencies over 90% under the optimal conditions at pH 7 and 30 °C. The adsorption followed pseudo-second order kinetics indicating chemisorption as the main mechanism. The findings suggested that this composite material can serve as an efficient and low-cost adsorbent for removing cationic dyes like rhodamine B dye from textile and other industrial wastewaters due to its high capacity, rapid adsorption rate and magnetic properties that enable easy separation.

Keywords: Rhodamine B, Wastewater treatment, Adsorption, Ion exchanger, Adsorption kinetics, Chemisorption.

INTRODUCTION

A growing global environmental concern is water contamination due to the release of industrial effluent containing synthetic colours. Among various industries, textile manufacturing generates extremely high volumes of contaminated effluents due to the use of many different dyes and chemicals in the production processes [1]. It is reported that over 7×10^5 tonnes and about 10,000 different types of dyes and pigments are produced annually across the globe [2]. Many of these dyes are difficult to degrade and can have toxic, carcinogenic and mutagenic effects on aquatic life [3].

Rhodamine B dye is a brightly coloured and water-soluble xanthene dye that is extensively used in textile dyeing, printing, coloured papers and pulp, plastics and other industries [4]. The release of rhodamine B dye in wastewater poses serious health risks as it is harmful if swallowed, inhaled or absorbed through the skin. It can cause irritation in the eyes, skin, gastrointestinal tract and respiratory tract in humans and animals [5]. Conven-

tional wastewater treatment methods like microbial degradation, coagulation, activated sludge processes and membrane filtration have shown limited efficiency for removing rhodamine B dye [6]. Among various technologies, adsorption has shown great potential as an effective, low-cost technique for removing dyes from effluents [7].

Several adsorbents derived from agricultural wastes, clay materials, nanomaterials and polymer composites have been explored for dye removal, but most suffer from low adsorption capacity, poor selectivity or difficulty in separation [8-10]. Magnetic polymer nanocomposites have recently emerged as promising adsorbent materials owing to their high capacity, rapid kinetics, ease of magnetic separation and potential for regeneration and reuse [11,12]. However, the development of such magnetic nanocomposite adsorbents for effective removal of rhodamine B dye remains a key research need. This study aims to synthesize an iron oxide-cationic ion exchange composite material as adsorbent and investigate its potential for removal of rhodamine B dye from wastewater by adsorption.

EXPERIMENTAL

Chemicals used in this research work include anion exchange materials synthesized on the basis of urea modification of poly(vinyl chloride) (PVC) and poly(ethylenimine) (PEI), iron salts ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), rhodamine B dye ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$) (Zibo Rongzhi Chemical Corporation, China), ethanol (Xilong Scientific), ethyl acetate, hydrochloric acid, sodium alkali and other chemicals used in this research work were analytically pure. Milli-Q (Haijulab Ware, China) and a magnetic stirrer AZ magnet Nyu-Delhi) were also procured.

Characterization: FT-IR spectroscopy was utilized to measure the infrared light absorbance of the ion exchange material and to generate a functional group-based spectrum. The Fourier-transform infrared (FT-IR) spectrometer used in this study was a Perkin-Elmer Spectrum 100 spectrometer equipped with an FT-IR microscopy accessory and was conducted at room temperature with a frequency range of $4000\text{--}400\text{ cm}^{-1}$ on an attenuated total reflection (ATR) diamond crystal. Raman spectroscopy was carried out using a Bruker BRAVO spectrometer (model R35), which recorded a broad spectral range from 3200 cm^{-1} to 300 cm^{-1} . The Fe_3O_4 and ion exchange material magnetic composite was synthesized using a magnetic stirrer.

Synthesis of ion exchange material: The anion-exchange sorbent was obtained by chemical modification of PVC with PEI according to the reported procedure [13]. Fe(III) and Fe(II) ions were sorbed on anion-exchanger containing an amino group and a Fe_3O_4 & ion-exchanger composite with magnetic properties was obtained by NaOH precipitation. On the basis of the kinetic model, the pseudo-first-order and pseudo-second-order of the reaction [14,15] of the resulting composite material with respect to the organic RhB dye in wastewater was studied.

Adsorption of rhodamine B (RhB) dye: To investigate the adsorption process of RhB dye onto Fe_3O_4 and ion-exchange composite, an experimental study was conducted under controlled conditions of pH 6-7 and temperature (303 K) with respect to the molecular characteristics of rhodamine B dye. A 100 mmol dye solution was prepared by dissolving the dye in 250 mL of distilled water and the concentration of remaining solution was adjusted by dilution. The adsorption process was carried out using 0.3 g of Fe_3O_4 and ion-exchange composite. After the adsorption process, the dye concentration was measured using a Shimadzu UV-1900i spectrophotometer, by measuring the absorbance at 554 nm [16]. The adsorption capacity of the adsorbent at equilibrium (q_e) and the removal efficiency (q_t) were calculated using the following equations:

$$q_e = \frac{C_o - C_e}{m} \times V \quad (1)$$

$$q_t = \frac{C_o - C_t}{m} \times V \quad (2)$$

where q_e is the adsorption capacity at equilibrium measured in mg/g; V is the volume of solution (L); C_o is the initial concentration of RhB (mg/L); C_e is the equilibrium concentration of RhB dye (mg/L) and m is the weight of dry composite (g).

RESULTS AND DISCUSSION

An anion-exchange sorbent has been synthesized based on the modification of polyvinyl chloride with polyethyleneimine. A 0.1 mol/L solution of Fe^{2+} and Fe^{3+} salts was poured into a flat-bottomed flask while being stirred by a magnetic stirrer. To do this, 20 g of dry sorbent with a static HCl exchange capacity of 6.5 mg-eq/g was weighed and NaOH solution was added dropwise until the colour of reaction solution changed [17].

FT-IR and Raman studies: The ion exchange nanometal composite based on modified PVC and PEI containing Fe_3O_4 exhibits several characteristic absorption peaks (Fig. 1), indicating the presence of different functional groups. It was found that the stretching vibrations of amino groups in the PVC-based PEI ion exchanger corresponded to the range of $3328.37\text{--}2827.13\text{ cm}^{-1}$ [18], while the deformation vibrations were in the range of $1633\text{--}1563\text{ cm}^{-1}$ [19]. The C=C groups in the ion exchange composite were detected in the vibration regions of $1680\text{--}1630\text{ cm}^{-1}$ [20], while the stretching vibrations of the C-Cl bond were found in the regions of $825\text{--}670\text{ cm}^{-1}$ [21]. The Fe_3O_4 and ion exchange composite showed a shift in the fields of stretching and deformation vibrations, indicating a decrease in the intensity of the primary and secondary amino groups in the anion exchanger due to the formation of a complex with iron ions [22,23]. Additionally, new vibration peak was also observed in the $645\text{--}501\text{ cm}^{-1}$ region, which belongs to the characteristic of the Fe-O stretching vibration of Fe_3O_4 [24,25].

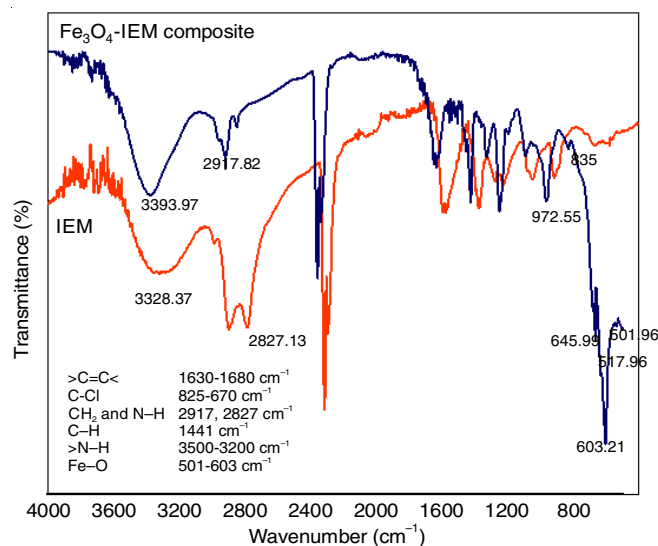
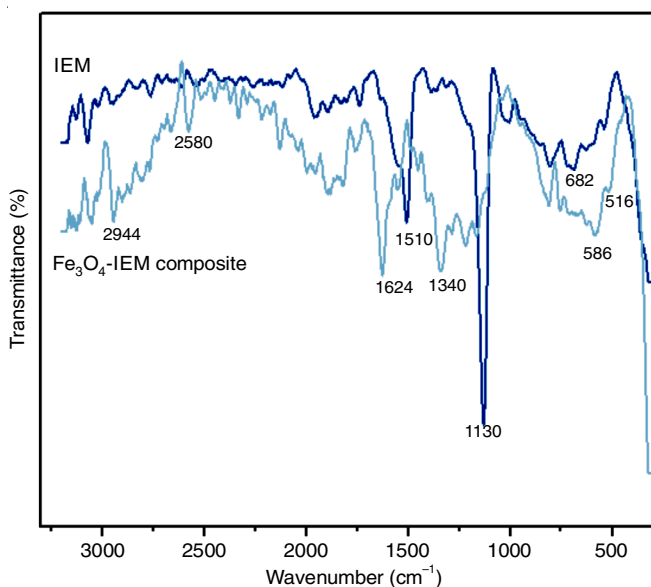


Fig. 1. FT-IR spectrum of Fe_3O_4 -IEM composite and ion exchange material (IEM)

Since FT-IR spectroscopy could not sufficiently show the fields of vibrations of the Me-O bond, we performed a spectral analysis of the Raman scattering of the Fe_3O_4 and ion exchange composite (Fig. 2). When analyzing the Raman spectrum, the vibrational fields at 586 and 516 cm^{-1} , which were not detected in the ion exchange material, indicating the presence of a characteristic Fe_3O_4 peak with magnetic properties in the composite [26]. The vibrational characteristic of the imine

Fig. 2. Raman spectrum of Fe₃O₄-IEM composite and IEM

groups in the ion exchange material indicates the formation of a composite, as shown by the decrease in intensity of the regions 2944-2580 cm⁻¹.

Moreover, the shift to the left of the peak at 1624 cm⁻¹ as observed indicates the formation of Me-O bonds, which is consistent with the literature [26]. This shift is attributed to the interaction between the polyethyleneimine and the Fe₃O₄ nanoparticles, resulting in the formation of metal-ion exchanger complex [27-29].

Adsorption kinetic study: Research have shown that pH has a significant impact when organic dyes are removed from solutions. The impact of pH on the processes involved in the adsorption of various dyes with nanoparticles is shown in Table-1 [30]. The adsorption of rhodamine B dye at different concentration of 0.1, 0.75 and 0.05 mol/L was studied at 303 K in the pH range of 6-7. More than 90% of dye was removed at pH 6-7, 0.3 g of adsorbent at a 0.1 M concentration of dye provides 98% removal in 150 min. Adsorption increased with increasing dye concentration ($q_e = 11739.2-23570.4$ mg/g).

Fig. 3 shows the adsorption kinetics of RhB molecules on the Fe₃O₄ and ion exchange composite at various concentrations (0.05 C_M, 0.075 C_M, 0.1 C_M). The adsorption process was carried out for 150 min and the equilibrium was reached. As a result, it was observed that the amount of sorbed RhB (mg/g) increases with increasing adsorption time.

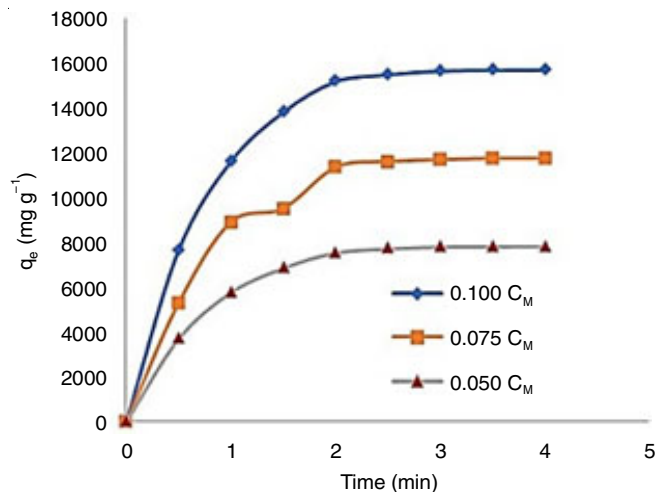


Fig. 3. Adsorption kinetics

Kinetic studies: The mechanism of the sorption process was determined using a variety of kinetic models [31,32]. The adsorption of RhB dye on the Fe₃O₄ and ion exchange was determined using the pseudo-first-order and pseudo-second-order (4) models and the kinetic parameters of the adsorption process are shown in Table-2.

Pseudo-first order kinetic model: Based on eqn. 3, it is evident that q_t and q_e correspond to the amount of sorbed dye (mg/g) on the Fe₃O₄ and ion exchange composite at a particular time and at equilibrium. Additionally, the slope of the linear plot's intercept, represented by angular value a , with respect to time is equivalent to $-k_1/2.303$, where k_1 is the rate constant of the adsorption process. This relationship between the slope of the intercept and the rate constant k_1 has been previously documented in the literature [33].

TABLE-1
COMPARISON OF DEGRADATION EFFICIENCY OF VARIOUS FeNPs AND REACTIVE DYES [Ref. 30]

Nanocomposites	pH	Dyes	Adsorption amount
Iron CNPs	298 K; pH 7.0	Congored paint (CR)	43.10 (µg/g)
FONPs (<i>P. pterocarpum</i>)	pH uncontrolled	Methylene blue (MB)	-
PLE@FeNPs (<i>P. lanceolata</i>)	298 K; pH 8.0	Congored paint (CR)	136.79 mg/g
Ironoxide (Fe ₂ O ₃)	pH uncontrolled	Congored paint (CR)	253 mg/g
FeNPs	308 K; pH 2.0	Methylene orange (MO)	81.967 mg/g
Fe ₃ O ₄ & IEM	303 K; pH 7.0	Rodamin B	23570.4 mg/g

TABLE-2
KINETIC PARAMETERS OF RhB ADSORPTION BY Fe₃O₄ & IEM COMPOSITE

IEM	Dyes	Initial conc. (ppm)	Pseudo-first-order			Pseudo-second-order		
			q_e (mg/g)	k_1 (min ⁻¹)	R ¹	q_e (mg/g)	k_2 (g/mg min)	R ²
Fe ₃ O ₄ & IEM	Rhodamine B	0.050	11739.19	0.056653	0.7466	11739.19	0.000196	0.9924
		0.075	17667.92	0.064253	0.8437	17667.92	0.000131	0.9899
		0.100	23570.39	0.052969	0.8277	23570.39	0.000133	0.9934

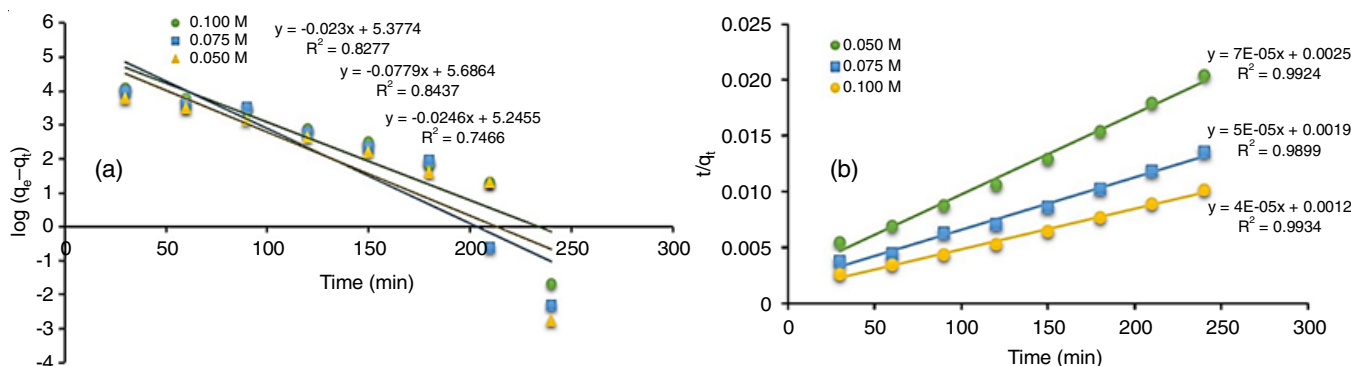


Fig. 4. Kinetic models: (a) determination of the pseudo-first order kinetic parameters from the plot of $\log(q_e - q_t)$ versus time t , (b) determination of the pseudo-second order kinetic parameters from the plot of t/q_t at time t

$$\log(q_e - q_t) = \log q_e \left(\frac{k_1}{2.303} \right) t \quad (3)$$

Pseudo-second order kinetic model: It is expressed by the following formula:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where $t = 0$ is found as follows: k_2 is the rate constant, q_e is the amount of dye adsorbed into the composite (mg/g), measured in a certain amount and time t (min).

Based on Fig. 4a-b, the rate constants (k_1 and k_2) and correlation coefficients (R^1 and R^2) for pseudo-first and pseudo-second order and the kinetics parameters of the sorption process of RhB dye by Fe_3O_4 and ion exchange composite were calculated. It was observed that the adsorption of RhB dye by the composite follows pseudo-second-order kinetics as evidenced by the higher correlation coefficient ($R^2 = 0.9934$) and higher k_2 value (0.000133 g/mg min). The pseudo-first-order kinetics also show a good correlation with the experimental data ($R^1 = 0.8277$, $k_1 = 0.052969 \text{ min}^{-1}$) indicating that both models can be used to describe the adsorption process, but these results indicate that the pseudo-second-order kinetic model provides a better fit to the experimental data than the pseudo-first-order kinetic model, which implies that RhB molecules chemically interact with the adsorbent (chemi-sorption) [34].

Conclusion

An ion exchange material-iron oxide composite as potential adsorbent for the removal of rhodamine B dye from aqueous solution has been established. The adsorbent was prepared by mixing cationic ion exchanger containing amine groups that have a strong affinity for rhodamine B dye with iron oxide nanoparticles. Incorporating the nanosized iron particles into the ion exchange matrix significantly improves the adsorption capacity of the material due to the high surface area and porosity of the nanoparticles. The present results showed that the functional groups in the composite and the porosity of nanoparticles further improve the adsorption performance by attracting ionic groups in the dye molecules. In addition, in some cases, heterogeneous composite can even degrade adsorbed functional groups, further increasing the efficiency of adsorption.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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