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Removal of Reactive Black 5 from Water by Polyethylenimine-Crosslinked Polyvinyl Chloride Electrospun Nanofiber Adsorbent

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In this study, an effective polyethylenimine-crosslinked PVC electrospinning nanofiber (PEI/PVC-NF) adsorbent was developed to remove Reactive Black 5 (RB5) from water. FT-IR and FE-SEM analysis showed that PEI/PVC-NF was prepared successfully, and the desorption process under strongly alkaline conditions had a negligible effect on the nanofiber structure. The adsorption performance of RB5 on PEI/PVC-NF was evaluated using pH edge, adsorption kinetics, and adsorption isotherm studies. The results were as follows: the pH edge experiment revealed that PEI/PVC-NF has a high adsorption capacity for RB5 from pH 2 to 8. Kinetic experimental results demonstrated that the pseudo-first-order and the pseudo-second-order kinetic models described the adsorption of PEI/PVC-NF to low and high concentrations of RB5. The adsorption process was exothermic in isotherm studies, and the Langmuir model suited the data better. At 25 °C, the Langmuir model indicated that RB5 had a maximum adsorption capacity of 1,017.06 mg/g. Five repeated regeneration experiments proved its good reusability. PEI/PVC-NF is a prospective adsorbent for reactive dye removal because of its high adsorption capacity, rapid adsorption kinetics, easy separation, and acid and base resistance.

1. Introduction

The global production of synthetic dyes, including acidic, direct, and azo, has exceeded $1x10^6$ t annually (Fadaei et al., 2021). Most of them are toxic and have carcinogenic, teratogenic, and mutagenic effects (Wang et al., 2020a). Reactive Black 5 (RB5) is an azo dye that has been widely used with the rapid development of the textile industry; a large amount of reactive dye wastewater is being generated along with the textile process (Erkurt, 2010). Reactive dyes have high solubility and low biodegradability due to the presence of azo (-N=N-) and sulfonic (-SO_3H) groups (Mengelizadeh et al., 2021). The discharge of inadequately treated dye wastewater into the environment can threaten aquatic ecosystems and human health. It is critical to adequately remove reactive dyes from dye wastewater before releasing them into natural water bodies.
Various methods have been developed to treat dye wastewater, among which adsorption is considered one of the most suitable methods due to its high efficiency, low cost, and ease of operation (Kiwaan et al., 2021). Current adsorbents of high interest, such as granular adsorbents and nanoparticle adsorbents, have a number of drawbacks. Granular adsorbents are easy to recover but have low adsorption capacity. In contrast, nanoparticle adsorbents have high adsorption capacity and fast adsorption rate but are challenging to recover and risk secondary contamination (Zhu et al., 2021). Electrospun nanofiber adsorbents have received much attention in recent years because of their easy recovery, high adsorption capacity, and fast adsorption rate (Pereao et al., 2019). Polyvinyl chloride (PVC) is a common polymer material because it is inexpensive, lightweight, and resilient, and it may also be used to make electrospun nanofibers (Wang et al., 2022b). Polyethylenimine (PEI) is an amine-rich reagent that converts PVC into an amine-functionalized adsorbent (Wang et al., 2022a).

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This study reports a PEI-crosslinked PVC electrospinning nanofiber (PEI/PVC-NF) as an adsorbent for reactive dye removal from aqueous systems. FT-IR and FE-SEM analyses were used to describe the surface functional group alterations and surface morphology of PEI/PVC-NF, RB5-loaded PEI/PVC-NF, and desorbed-PEI/PVC-NF. pH edge, adsorption kinetics, and adsorption isotherm studies were used to study the adsorption performance of PEI/PVC-NF for RB5. Five adsorption-desorption cycles were used to confirm the reusability of the adsorbent.

2. Materials and method

2.1 Materials

PVC (M_w = 80,000) and RB5 ($C_{26}H_{21}N_5Na_4O_{19}S_6$, 991.82 g/mol, dye content = 55 %, λ_{max} = 597 nm) were purchased Sigma-Aldrich US Ltd. (St. Louis, US). PEI (Mw = 70,000, 50 % solution) was obtained from Habjung Moolsan Co., Ltd. (Seoul, Korea) and was freeze-dried to remove the water content before use. Tetrahydrofuran (THF, 99 %) and N, N-dimethylformamide (DMF, 99.5 %) were supplied by Daejung Chemicals & Metals Co., Ltd. (Siheung, Korea). This study's other reagents such as HCl and NaOH were analytical grade.

2.2 Preparation of PEI/PVC-NF

The method for the preparation of PEI-PVC-NF was modified based on our previous report (Wang et al., 2022b). First, 1 g PVC and 2 g PEI were dissolved in 10 mL of DMF: THF (1:1) solution. Next, the solutions were added to 50 mL round bottom flask with a condensing reflux device and placed in a water bath at 80 °C for 4 h to produce a PEI-crosslinked PVC solution. Then, the solution was cooled to 25 °C and loaded in a plastic syringe to prepare PEI/PVC-NFs via electrospinning. At 25 kV voltage, the spinning solution was converted into nanofibers through a 25 G needle and was sprayed onto a flat plate collector at 15 cm from the needle tip. The prepared PEI/PVC-NFs were washed for 24 h in deionized water to remove unreacted residuals. Finally, the PEI/PVC-NFs were freeze-dried for 24 h and then stored in a desiccator for further analysis.

2.3 FT-IR and FE-SEM analysis

The FT-IR spectra of the samples were documented using an FT-IR spectrophotometer (Nicolet IS50, Thermo Fisher, USA). The surface morphologies of the samples were visualized on FE-SEM (JSM-7610F, Jeol, Japan).

2.4 Batch adsorption experiments

Batch adsorption experiments were carried out to evaluate the adsorption performance of PEI-PVC-NF for R.B. 5. In all batch experiments, if not otherwise specified, 30 mL of RB5 solution was mixed with 10 mg of PEI-PVC-NF and stirred at 160 rpm and 25 °C for 24 h. pH edge experiments were carried out at pH 2–12 at 500 mg/L of initial RB5 solution. The pH of the RB5 solution was adjusted using 1.0 M HCl and 1.0 M NaOH solutions. At pH 7, isotherm studies were carried out in 30 to 500 mg/L starting RB5 concentrations. Adsorption kinetic measurements were conducted at pH 7 in 100 and 500 mg/L RB5 solutions. A UV-Vis spectrophotometer was used to examine the RB5 concentrations (X-ma 3000 pc, Human, Korea). The RB5 uptake q (mg/g) was calculated using Eq(1).

$$q = \frac{V_i C_i - V_f C_f}{m} \quad (1)$$

where C_i and C_f (mg/L) are the initial and final concentrations of RB5. V_i and V_f (L) represent the initial and final volume of the RB5 solution. m stands for the weight of adsorbent (g).

2.5 Reusability experiments

In a 50-mL falcon tube, 0.01 g of PEI/PVC-NF and 30 mL of 100 mg/L dye solution were combined to make a dye-loaded adsorbent. Based on the results of adsorption kinetics, the adsorption process was performed at 25 °C and 160 rpm for 120 min to allow the adsorption to reach complete equilibrium. The remaining dye concentration was measured using a UV-Vis spectrophotometer once the adsorption equilibrium had been reached. The dye-loaded adsorbent was washed three times with distilled water and then immersed in a 0.02 M NaOH solution for 2 h under the same conditions to desorb the dye from the nanofiber surface completely. The desorbed adsorbent was then washed with water to neutralize and subjected to the next adsorption-desorption cycle 5 times. The amount of the desorbed dye was measured using a UV-Vis spectrophotometer, and the desorption efficiency was calculated using Eq(2).

$$Desorption\ efficiency\ (\%) = \frac{Desorbed\ RB5\ amount\ in\ each\ cycle\ (mg)}{Adsorbed\ RB5\ amount\ in\ each\ cycle\ (mg)} \times 100 \quad (2)$$

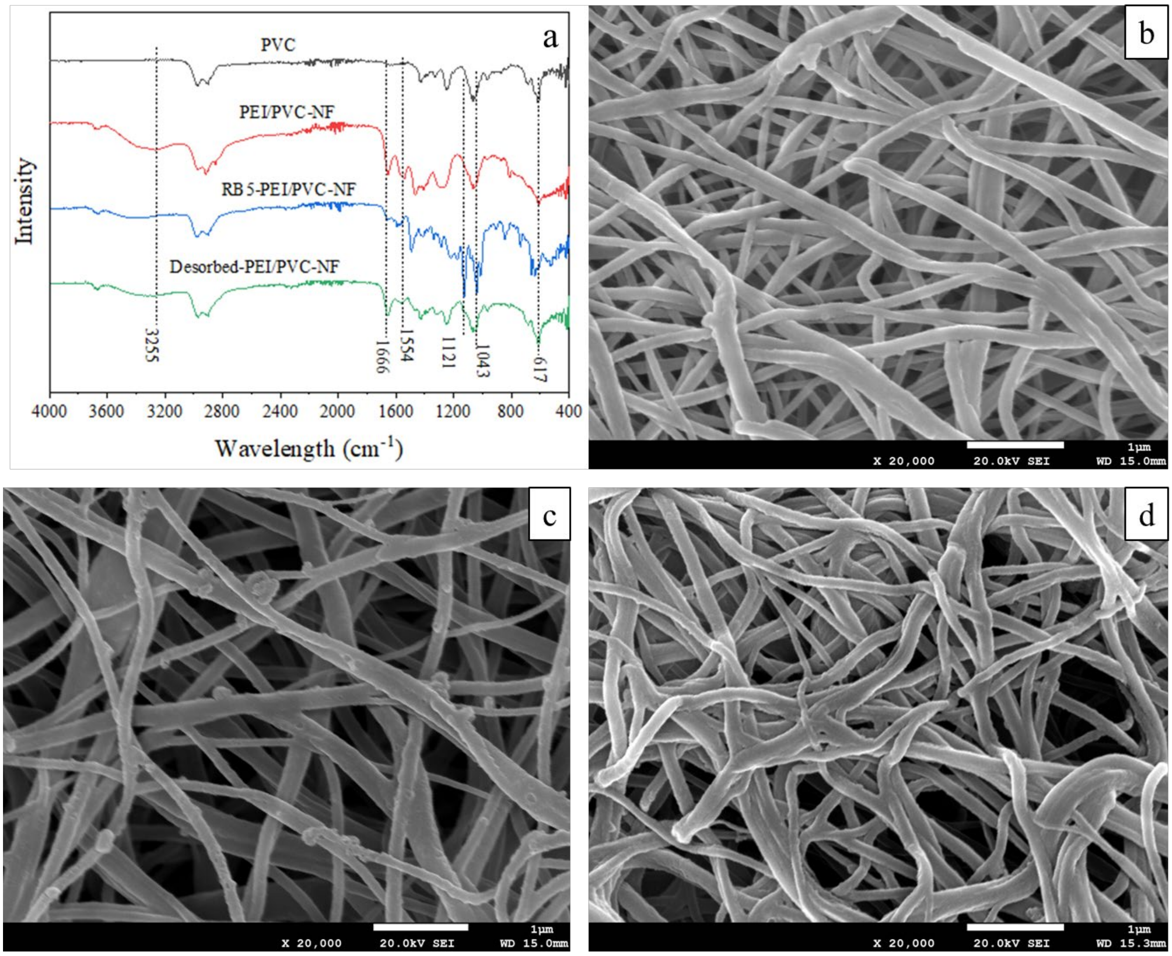

Figure 1: (a) FTIR spectra of the PVC and PEI/PVC-NFs under different states, and FE-SEM images of (b) PEI/PVC-NF, (c) RB5-loaded PEI/PVC-NF, and (d) desorbed PEI/PVC-NF (× 20,000 magnification)

3. Results and discussion

3.1 The surface morphology of PEI-PVCF

The FT-IR spectra of PVC, PEI/PVC-NF, RB5-PEI/PVC-NF, and desorbed-PEI/PVC-NF were displayed in Figure 1a. Compared with the FT-IR spectrum of PVC, that of PEI/PVC-NF showed new peaks corresponding to N-H stretching (3,255 cm^{-1}) and bending (1,666 and 1,554 cm^{-1}) vibrations as well as characteristic peaks of C-Cl, indicating the successful crosslinking of PEI with PVC (Sneddon et al., 2017). After adsorption of RB5, the peaks at 3,255, 1,666, and 1,554 cm^{-1} were shifted to higher positions, and their intensity was decreased. Two new peaks attributed to asymmetric and symmetric stretching of $-SO_3^-$ were observed at 1,121 and 1,043 cm^{-1}. These findings indicated that the RB5 molecules were adsorbed on PEI/PVC-NF through electrostatic attraction between amine and $-SO_3^-$ groups (Wang et al., 2022a). By comparing the FT-IR spectra before adsorption and after desorption, it can be concluded that the desorption conditions have little effect on the stability of the nanofibers. Figure 1b, 1c, and 1d are FE-SEM images of PEI/PVC-NF before and after adsorption and desorption of RB5. PEI/PVC-NF was highly porous and showed no significant damage in adsorption and desorption processes. PEI/PVC-NF was successfully prepared as intended and exhibited good structure stability under adsorption and desorption experimental conditions.

3.2 Effect of pH

The influence of pH on RB5 adsorption by PEI/PVC-NF was investigated at 500 mg/L RB5 solution in pH 2-12 (Figure 2a). It can be observed that the adsorption capacity of PEI/PVC-NF for RB5 decreased from 1,309.21 mg/g to 1,030.65 mg/g as the pH increased from 2 to 8. Hereafter, it dramatically decreased to zero as the pH increased to 12. Although the adsorption capacity of RB5 decreased from 1,309.21 to 1,030.65 mg/g in the pH range of 2 to 8, it was still higher than that of most adsorbents reported in the literature (Wang et al., 2022a). At low pH, the amine groups on the surface of PEI/PVC-NF become protonated and can readily bind to negatively charged RB5 molecules by electrostatic interaction. As the pH increased, the protonated amine groups gradually deprotonated, which may lead to a decrease in the uptake of RB5 by PEI/PVC-NF (Zhao et al., 2022). Considering that most textile wastewater has a pH value between 6 and 10 (Ben Dassi et al., 2020), and acid and alkaline conditions are more demanding for the equipment, which leads to higher investments (Wang et al., 2022a), pH = 7 was chosen for the rest of the adsorption experiments.

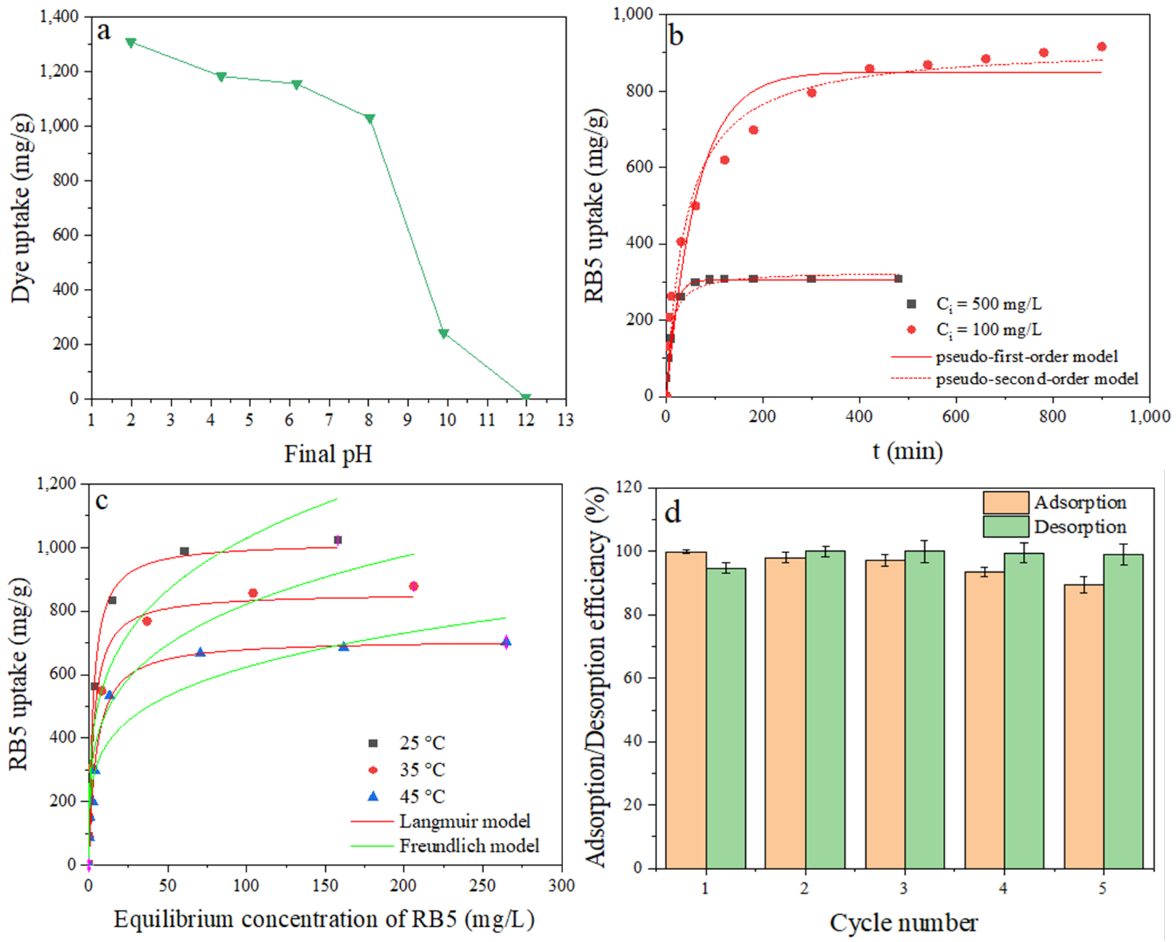

Figure 2: (a) Effect of pH on the adsorption of RB5 by PEI/PVC-NF, (b) adsorption kinetics for RB5 at 100 and 500 mg/L initial concentrations, (c) adsorption isotherm of PEI/PVC-NF for RB5 under 25, 35, and 45 °C, and (d) Efficiency of five adsorption-desorption cycles of PEI/PVC-NF for RB5.

3.3 Batch adsorption kinetics

The adsorption rate is an essential parameter for the practical application of adsorbents. The findings of kinetic studies of RB5 adsorption by PEI/PVC-NF at 100 and 500 mg/L of RB5 solution are presented in Figure 2b. The adsorption capacity and equilibrium time rose from 306.74 mg/g and 90 min to 916.12 mg/g and 400 min, when the starting RB5 concentration increased from 100 to 500 mg/L. The experimental kinetic data were described using pseudo-first-order and pseudo-second-order models to understand the adsorption performance better. The corresponding equations of the models are given by Eq(3) – Eq(4):

Pseudo-first-order kinetic model: $q_t = q_1\left(1 - exp(-k_1 t)\right)$ (3)

Pseudo-second-order kinetic model: $q_t = \frac{q_2^2 k_2 t}{1+q_2 k_2 t}$ (4)

where q_t (mg/g) is the RB5 uptake at time t, q_1, and q_2 (mg/g) are the RB5 uptake at adsorption equilibrium, k_1 (L/min) and k_2 (g/(mg min)) is the rate constant of pseudo-first-order and pseudo-second-order models.

Table 1 lists the corresponding parameters of the pseudo-first-order and pseudo-second-order models. At the initial RB5 concentration of 100 mg/L, the R^2 values of the pseudo-first-order model were higher than that of the pseudo-second-order model. The opposite result was observed at the initial dye concentration of 500 mg/L. The q_1 and q_2 values were closer to the experimental results (q_{exp}) obtained at 100 and 500 mg/L initial RB5 concentrations. These findings suggest that when describing RB5 adsorption kinetic performance on PEI/PVC-NF, the pseudo-first-order model is appropriate for low dye concentrations; in contrast the pseudo-second-order model is appropriate for high dye concentrations. The k_1 and k_2 values fell as the initial concentration of RB5 grew from 100 to 500 mg/L. A smaller K value means a longer time to reach adsorption equilibrium (Wang et al., 2021). As a result, the adsorption equilibrium period increased as the initial RB5 concentration rose.

Table 1: Parameters of adsorption kinetic models

		Pseudo-first-order model			Pseudo-second-order model		
RB5 (mg/L)	q_{exp} (mg/g)	q_1 (mg/g)	k_1 (L/min)	R^2	q_2 (mg/g)	k_2 (g/mg min)	R^2
100	305.74	304.95	0.0712	0.9941	327.27	3.1365×10^{-4}	0.9897
500	916.12	850.03	0.0158	0.9305	919.94	2.6940×10^{-5}	0.9678

3.4 Batch adsorption isotherm

Adsorption isotherms are intended to illustrate the adsorption capacity of the adsorbent at different concentrations of the adsorbate and to describe the liquid-solid interactions (Kiwaan et al., 2021). The adsorption isotherm was carried out under different temperatures (25, 35, and 45 °C), and the results are shown in Figure 2c. As shown in Figure 2c, the adsorption capacity of RB5 decreased with increasing temperature from 25 to 45 °C, which indicated that the adsorption process was exothermic (Wang et al., 2022a). The Langmuir and Freundlich models (Eq(5) and Eq(6)) were used to describe the isotherm experimental data .

Langmuir model: $q_e = \frac{q_{max}K_LC_e}{1+K_LC_e}$ (5)

Freundlich model: $q_e = K_FC_e^{1/n}$ (6)

where q_e and q_{max} (mg/g) are the theoretical and experimental maximum RB5 uptake, C_e (mg/L) is the RB5 concentration at equilibrium, $K_{L.}$ (L/mg), and $K_{F.}$ (L/g) represent the Langmuir and Freundlich constant, and n indicates the Freundlich exponent.
The data were fitted by non-linear regression models (Figure 2c), and the corresponding parameters are listed in Table 2. According to Table 2, the R^2 values of the Langmuir model were more significant than those of the Freundlich model. The experimental maximum adsorption capacities were closer to those calculated by the Langmuir model. These findings suggest that the Langmuir model is more suited to describe RB5 adsorption by PEI/PVC-NF. Furthermore, RB5 adsorption on PEI/PVC-NF was monolayer adsorption (Zhou et al., 2018). The Langmuir constant $K_{L.}$ values ranged from 0 to1, showing that RB5 adsorption on PEI/PVC-NF was favorable between 25 and 45 °C (Lyu et al., 2021). The theoretical maximum adsorption capacity of RB5 on PEI/PVC-NF was compared with other adsorbents summarized in our previous work (Wang et al., 2022a). The results showed that the adsorption capacity of PEI/PVC-NF on RB5 was better than most of the adsorbents.

Table 2: Parameters of adsorption isotherm models

		Langmuir model			Freundlich model		
T (°C)	q_{exp} (mg/g)	q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)	R^2
25	1022.08	1017.06	0.3684	0.9953	3.9990	325.43	0.9163
35	877.91	856.94	0.3291	0.9889	4.1052	267.53	0.9396
45	702.06	710.69	0.2075	0.9885	4.3832	217.95	0.9252

3.5 Reusability studies

The reusability is considered an essential property necessary for promising adsorbents. In this study, repeated adsorption-desorption experiments were conducted to confirm the reusability of PEI/PVC-NF. The RB5 adsorption-desorption cycles on PEI/PVC-NF were repeated five times. The efficiency of each adsorption and desorption was calculated, and the results are shown in Figure 2d. The adsorption efficiency of PEI/PVC-NF for RB5 remained at about 90 % even after five cycles. The desorption efficiency remained above 99.5 % except for the first cycle. These results indicate that PEI/PVC-NF is a reusable adsorbent that removes reactive dyes.

4. Conclusions

As evidenced by FT-IR and FE-SEM data, PEI/PVC-NF was effectively synthesized as a potential adsorbent for RB5 in this investigation. The PEI/PVC-NF adsorbent remained stable during the adsorption and desorption processes. The pH edge experiment revealed that PEI/PVC-NF exhibited a high adsorption capacity for RB5 in the pH range of 2 to 8. Kinetic experiments showed that the pseudo-first-order and pseudo-second-order models could better describe the kinetic performance of RB5 adsorption on PEI/PVC-NF at low and high initial concentrations. The Langmuir model illustrated the adsorption isotherm well, and the maximum RB5 uptake was 1017.06 mg/g. Five consecutive adsorption-desorption cycles demonstrated the good reusability of PEI/PVC-NF. Overall, the PEI/PVC-NF adsorbent can be a promising adsorbent for RB5 removal.

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