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Removal of Dyes in Wastewater Using Pitch-based Carbon Waste Modified with Polyethylenimine

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In this study, pitch-based carbon (PC) was modified with polyethylenimine (PEI) to produce PEI-modified PC (PEI-PC) for wastewater treatment. PEI, containing amine groups, shows advantages in adsorbing ionic dyes. The adsorption and desorption properties of PEC-PC for dyes were evaluated through pH edge, experiments, adsorption kinetics, isotherm studies, and desorption tests. We selected Cibacron Brilliant Yellow 3G-P (Reactive Yellow 2: RY2) as the model dye for our study. pH edge experiments were conducted in a pH range of 2-12 with an initial dye concentration of 100 mg/L. The results showed that dye uptake on PEI-PC increased as the pH value decreased. Adsorption kinetic experiments confirmed that adsorption equilibrium at pHs 2 and 7 was achieved within 30 min. The adsorption isotherm experiments, conducted at initial dye concentrations ranging from 10 to 300 mg/L, revealed that the experimental data fit well with the Langmuir model. The dye-loaded PEI-PC was desorbed using a 0.05 M NaOH solution, and this adsorption-desorption process was repeated. It was observed that when the adsorption-desorption cycles were repeated from 1 to 5 times, the adsorption efficiency decreased by 29 %.

1. Introduction

Water scarcity is one of the most pressing issues today, bringing the availability and quality of water supply into sharp focus. Many national policies now encourage companies to reduce water consumption and promote water reuse to ensure sustainable water resources (Waghchaure et al., 2022). Industrial processes are major contributors to water pollution, particularly through the release of organic compounds, which significantly impact the aquatic environment (Zhang et al., 2019). Various synthetic substances such as pesticides, persistent organic pollutants (POPs), and synthetic dyes have become significant environmental concerns. Among these, synthetic dyes are particularly prominent in the textile industry, where they are produced in large volumes worldwide. These dyes consume vast amounts of water and are highly toxic, causing health issues such as dermatitis, keratitis, and central nervous system damage (Zhang et al., 2023). They also severely impact ecosystems by blocking sunlight for aquatic plants.

Despite regulations in many countries aimed at limiting dye wastewater discharge, more than 10,000 types of dyes are produced annually, totalling over 700,000 t, with more than 300 Mt of dye wastewater discharged each year (Waghmare et al., 2024). This highlights the inadequacy of current treatment methods and the urgent need for more effective solutions. Several techniques, including flocculation, biodegradation, filtration, oxidation, photolysis, and adsorption have been studied to remove dyes from water. Among these, adsorption is widely used due to its ease of use, low cost, and low energy requirements.

A key factor in adsorption is finding a suitable adsorbent. Carbon materials are effective adsorbents because of their wide availability and high adsorption capacity. Coal tar pitch, a by-product of petroleum, is a carbon compound with excellent thermal stability, chemical resistance, and low cost (Kim et al., 2021). It is a high value-added raw material and suitable as a carbon precursor for the adsorption of dye substances in water.

In this study, pitch-based carbon (PC) was impregnated with polyethylenimine (PEI) and functionalized by coating its surface. The PEI-modified PC (PEI-PC) was analysed using scanning electron microscopy (SEM)

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and energy dispersive X-ray spectroscopy (EDS). Cibacron Brilliant Yellow 3G-P (Reactive Yellow 2) was used as a representative dye to evaluate the adsorption capacity. This uptake was assessed through isotherm, kinetic experiment, and pH edge test. Additionally, reuse experiments were conducted to determine the recyclability of PEI-PC in the wastewater treatment process. This study aims to investigate the effectiveness and reusability of PEI-PC as a novel adsorbent for dye removal contributing to the development of sustainable water treatment technologies.

2. Materials and methods

2.1 Materials

The PC waste was obtained from Smart Korea Co., Ltd. (Daejeon, South Korea). PEI was purchased from Nippon Shokubai CO., Ltd. in Japan. Sigma-Aldrich provided the RY2. Other remaining chemicals used, such as isopropyl alcohol, methyl alcohol, HCl, and NaOH, were of analytical grade.

2.2 Preparation of PEI-PC

The PEI to use for PC modification was 1.25 g, filled with 50 mL of distilled water to make a 2.5 % PEI solution and dissolved for 1 h. To create PEI-PC, 2 g of PC was added to a 2.5 % PEI solution 50 mL and reacted in an incubator at 25 ℃ and 160 rpm for 3 days. Afterward, it was washed three times with distilled water and wet PEI-PC was freeze-dried at -110 °C for 24 h.

2.3 Analytical methods

The surface morphologies and elemental compositions were examined using Field Emission Scanning Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy (FE-SEM/EDS) on an Apreo S instrument (Thermo Fisher, USA).

2.4 Adsorption experiments

The UV-Vis spectroscopy (X-ma 3000pc, Human, Korea) was used to analyze the adsorption experiments. The wavelength of the dye was measured at 404 nm (for RY2). The calculation of dye adsorption q (mg/g) on PC and PEI-PC was performed using Eq(1).

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

The initial concentration (C_i) of dye solution was set at 100 mg/L, volume of 30 mL (V_i and V_f), and mass of the adsorbent (m) was 0.03 g. Each conical tube (50 mL) contained the dye and adsorbent and was shaken at 25 °C and 160 rpm for 24 h. The experiment for pH effects was evaluated in a range of 2 to 12, and the isotherm and kinetic experiments were evaluated at pH 2 with different contact times (ranging from 0 to 240 min) and initial concentrations of dye (ranging from 10 to 300 mg/L). Then, the relevant model equations were substituted for optimization and characterization.

2.5 Reusability experiments

The desorption process was performed by centrifuging the adsorbed mixture to remove the supernatant, adding 30 mL of 0.05 M NaOH solution and reacting 24 h (Kang et al., 2023). The re-adsorption process was similar to desorption, with the mixture centrifuged to remove the supernatant and reacted under the same conditions as the initial adsorption. The adsorption-desorption process was repeated five times in succession. The UV-Vis spectroscopy was used to analyze the dye concentration after dilution. The adsorption-desorption efficiencies were calculated using Eq(2) and Eq(3). The adsorbed dye amount (mg) was measured by multiplying the uptake (mg/g) of dye and amount of adsorbent (g). The desorbed dye amount (mg) was measured by multiplying the concentration (mg/L) of dye after desorption and the volume of NaOH solution (mL).

$$Adsorption\ efficiency\ (\%) = \frac{adsorbed\ dye\ amount\ (mg)}{Initailly\ adsorbed\ dye\ amount\ (mg)} \times 100 \quad (2)$$

$$Desorption\ efficiency\ (\%) = \frac{Desorbed\ dye\ amount\ (mg)}{adsorbed\ dye\ amount\ (mg)} \times 100 \quad (3)$$

3. Results and discussion

3.1 Comparative dye adsorption capacity to the influencing factor at pH 2

To identify the factors influencing the fabrication of PEI-PC, materials were produced using different molecular weights of PEI: low molecular weight PEI (L-PEI, m.w.=800) and high molecular weight PEI (H-PEI, m.w.=70,000). Additionally, the solvents used for impregnation—distilled water (DW), isopropyl alcohol (IPA), and methyl alcohol (MA)—were varied during the manufacturing and evaluation process (Figure 1).

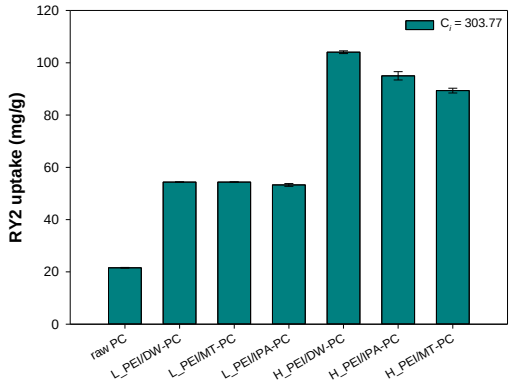

Figure 1: Comparison of dye uptakes in difference PEI molecular weight and solvents

H-PEI-PC increased in dye uptake, ranging from 89.38 to 104.05 mg/g, in comparison to L-PEI-PC (ranging from 53.27 to 54.27 mg/g). The difference in adsorption capacity between the H- and L-PEI was 1.65 to 1.93 times, indicating that molecular weight substantially affects RY2 adsorption capacity. The variations in solvent did not have a significant influence, with differences less than 1 mg/g for the L-PEI-PC and 15 mg/g for the H-PEI-PC. All subsequent experiments and analyses were performed using PEI-PC prepared with 2.5 % PEI with a molecular weight 70,000 and distilled water as solvent, which showed the highest uptake in Figure 1.

3.2 Characterization of PC, PEI-PC, and RY2 loaded PEI-PC

SEM images were used to investigate the surface morphology of the adsorbents, and EDS analysis provided information on their elemental composition.

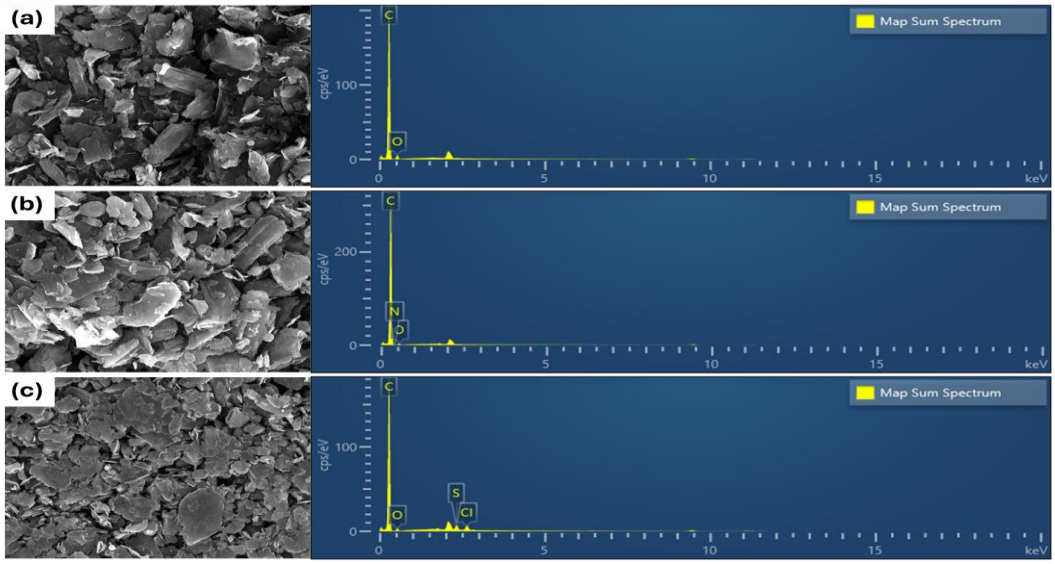

Figure 2: SEM/EDS of (a) the raw PC, (b) PEI-PC, and (c) RY2 loaded PEI-PC (magnification ×3000)

The surface of the PC appeared non-porous and smooth surface and the elemental properties are mostly made of carbon and contain some oxygen (Figure 2a). In the PEI-PC, nitrogen was detected, which can be attributed

to the amine groups presented in PEI (Figure 2b). After RY2 adsorption on PEI-PC, the surface was observed roughly due to the effect of RY2 molecule, and additional elements such as sulfur and chlorine were detected (Figure 2c). This confirms that PEI has been functionalized on the surface of the PC, facilitating the adsorption of RY2 onto the developed adsorbent surface.

3.3 Dye adsorption performance of PC and PEI-PC under different pHs

The surface charge of the dye molecules and the adsorbent changes according to the pH of the solution (Wamba et al., 2018). The adsorption performance depends on the pH, which is a crucial factor (Figure 3a). It can be seen that the adsorption capacity of PEI-PC increased under the low pH conditions. The adsorption capacity was 92.51 mg/g at pH 2, and the adsorption capacity in the neutral solution (over pH 6) decreased rapidly to 58.41 mg/g and 11.82 mg/g under alkaline conditions.

3.4 Isotherm experiment

The adsorption isotherm of RY2 onto PEI-PC is shown in Figure 3b. Isotherm is useful for investigating various aspects of adsorption, including maximum adsorption capacity, adsorbent properties, and adsorption mechanism. The Langmuir model and the Freundlich model were utilized to optimize the adsorption results and used each equation (Eq(4) and Eq(5)).

$$\text{Langmuir model: } q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (4)$$

$$\text{Freundlich model: } q_e = K_F C_e^{1/n} \quad (5)$$

The model equations were characterized by several parameters including b_L (L/mg), q_{max} (mg/g), q_e (mg/g), K_F (mg/g), C_e (mg/L), and $1/n$ of the adsorption strength. The isotherm models can sort the adsorption intensity as either cooperative ($1/n > 1$) or effective ($0 < 1/n < 1$). According to Table 1, the parameters of Langmuir model for PEI-PC at pH 2 indicate a q_{max} of 96.59 mg/g at pH 7, q_{max} is 60.76 mg/g. The Freundlich model parameters also reflect similar trends with K_F value of 50.26 L/g at pH 2 and 36.07 L/g at pH 7. Analysis of the coefficient of determination (R^2) suggests a better fit with the Langmuir model (R^2 = 0.969 at pH 2 and 0.968 at pH 7) compared to the Freundlich model (R^2 = 0.835 at pH 2 and 0.808 at pH 7). The higher Langmuir constant (b_L), 2.620 L/mg at pH 2 and 2.402 L/mg at pH 7, indicates a stronger affinity between the adsorbate (RY2) and the adsorbent (PEI-PC) under the experimental conditions (Wang et al., 2020). The notable difference in b_L values between PEI-PC and raw PC underscores the enhanced interaction between PEI-PC and RY2.

Table 1: Adsorption isotherm parameters onto PEI-PC and raw PC

		Langmuir model			Freundlich model		
		b_L (L/mg)	R^2	q_{max} (mg/g)	K_F (L/g)	R^2	1/n
PEI-PC	pH 2	2.620	0.969	96.59	50.26	0.835	0.141
	pH 7	2.402	0.968	60.76	36.07	0.808	0.111
raw PC	pH 2	4.792	0.919	46.95	10.43	0.992	0.112
	pH 7	0.366	0.991	13.38	7.415	0.980	0.119

3.5 Kinetic studies

The kinetics experiments were conducted with an initial dye concentration of 100 mg/L at pH 2 and pH 7. The pseudo-first and second models were used to analyze the kinetic results (Figure 3c, Eq(6), and Eq(7)).

$$\text{Pseudo-first-order model (PFO): } q_t = q_1\left(1 - exp(-k_1 t)\right) \quad (6)$$

$$\text{Pseudo-second-order model (PSO): } q_t = \frac{q_2^2 k_2 t}{1 + q_2 k_2 t} \quad (7)$$

The equations variables of the kinetic models signify the number of dyes at the equilibrium adsorption state (q_1 and q_2 (mg/g)), the number of dyes adsorbed at a given time (q_t (mg/g)), t, and k_1 (L/min) and k_2 (g/(mg·min)) are the rate constants.

The adsorption equilibrium of PEI-PC for RY2 was reached within 60 min. For PEI-PC at pH 2, the PFO model showed an R^2 of 0.974 with q_1 at 79.53 mg/g and k_1 at 2.082 L/min. The PSO model provided an R^2 of 0.988, with q_2 at 81.21 mg/g and k_2 at 0.058 g/(mg·min), indicating a closer fit to the experimental values of q_e at 84.08 mg/g for RY2. Similarly, at pH 7, the q_1 was 46.92 mg/g and k_1 was 1.608 L/min with an R^2 of 0.961 for the PFO model, while the PSO model yielded q_2 at 48.22 mg/g and k_2 at 0.064 g/(mg·min) with an R^2 of 0.981. Comparatively, raw PC showed lower kinetic adsorption performance. At pH 2, the q_1 value was 17.61 mg/g

and k_1 was 1.163 L/min (PFO: R^2 of 0.949), while q_2 was 18.22 mg/g with k_2 at 0.113 g/(mg·min) and R^2 of 0.979 for the PSO model. At pH 7, the respective values for q_1 and q_2 were 13.25 mg/g and 13.75 mg/g, with R^2 values of 0.967 and 0.970. These results confirm that the PSO model is more suitable for describing the adsorption kinetics of reactive dyes onto PEI-PC, reflecting higher compatibility with the experimental observations and a better understanding of the adsorption process (Kang et al, 2023).

Table 2: Adsorption kinetic parameters onto PEI-PC and raw PC

		Pseudo-first-order (PFO) model			Pseudo-second-order (PSO) model		
		q_1 (mg/g)	R^2	k_1 (L/min)	q_2 (mg/g)	R^2	k_2 (g/mg min)
PEI-PC	pH 2	79.53	0.974	2.082	81.21	0.988	0.058
	pH 7	46.92	0.961	1.608	48.22	0.981	0.064
raw PC	pH 2	17.61	0.949	1.163	18.22	0.979	0.113
	pH 7	13.25	0.967	0.619	13.75	0.970	0.080

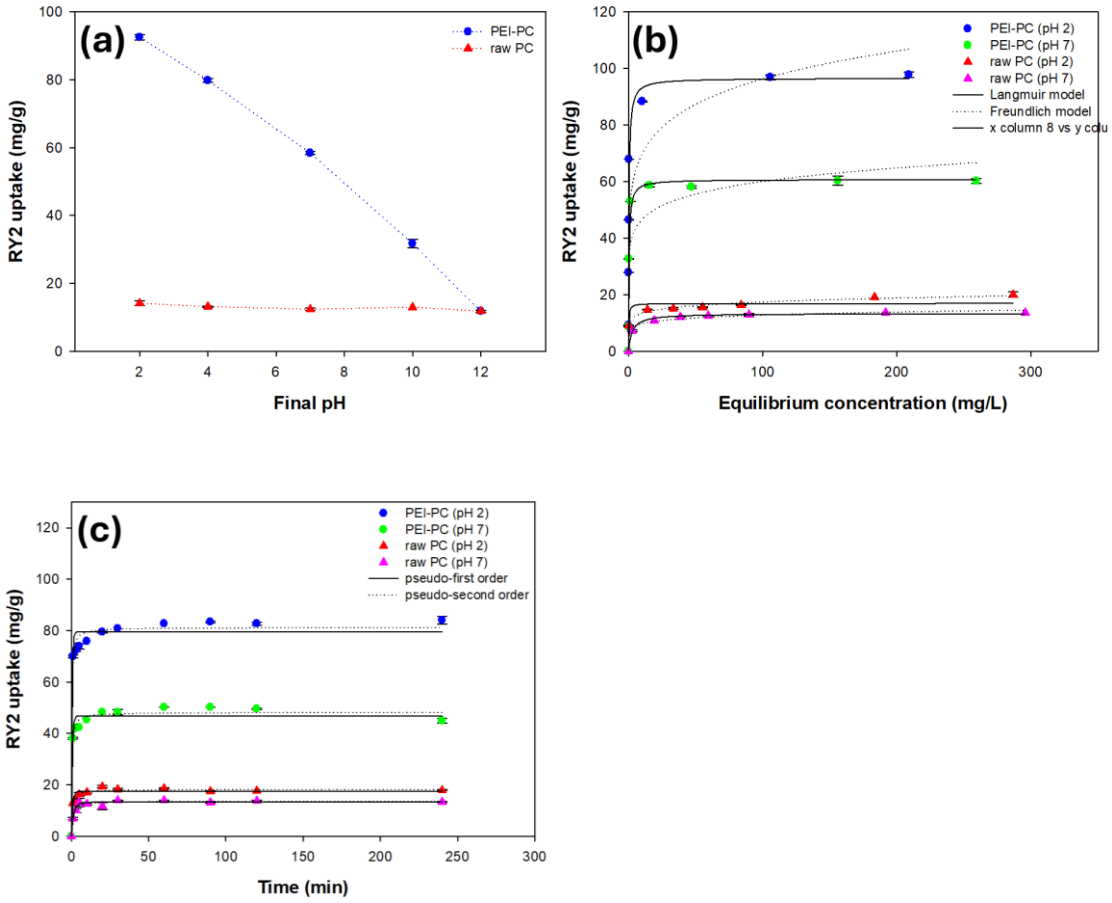

Figure 3. (a) The pH effects on dyes uptakes by raw PC and PEI-PC (b) Adsorption isotherm of dyes on raw PC and PEI-PC at pH 2 and pH 7 (c) Adsorption kinetics of dyes on raw PC and PEI-PC at pH 2 and pH 7

3.6 Reusability studies

One critical aspect of adsorbents is their reusability, which offers significant economic benefits. As depicted in Figure 4, the reuse efficiency of the PEI-PC adsorbent was evaluated over five cycles using 0.05 M NaOH as the desorbing agent.

The desorption efficiencies consistently exceeded 94 % throughout all cycles, demonstrating the adsorbent's capacity for effective regeneration. Subsequent re-adsorption tests showed that the PEI-PC retained between 72.54 % and 81.37 % of its initial adsorption capacity after each cycle. These results confirm the robust reusability of PEI-PC, underlining its potential for cost-effective application in dye removal processes.

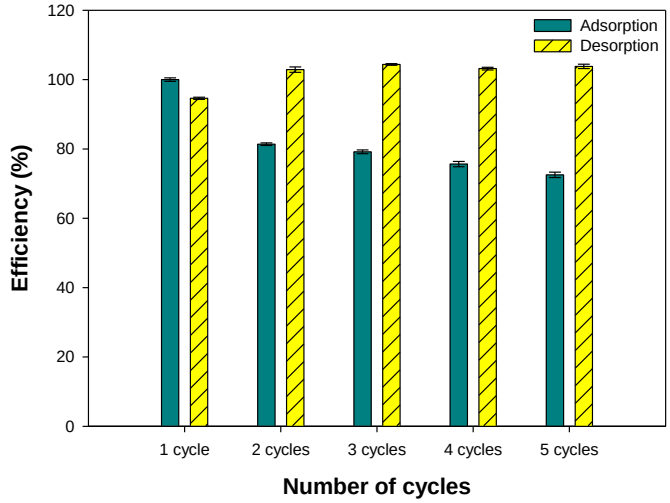

Figure 4: Efficiency of repeated adsorption and desorption cycles

4. Conclusions

PEI-PC was prepared through the impregnation of PEI onto the surface of the PC. The amine groups from the PEI coating impart a positive charge to the PEI-PC adsorbents, which exhibit outstanding adsorption capabilities for anionic reactive dyes, particularly under acidic conditions. At a pH of 2, the Langmuir model appeared an adsorption capacity of 94.32 mg/g. Furthermore, the adsorption efficiency remained above 70 % through five cycles of reuse evaluations, demonstrating the robust reusability of the adsorbent. The simplicity of the manufacturing process, coupled with the absence of a specific pretreatment requirement, underscores the commercial viability of PEI-PC for dye removal applications.

Acknowledgments

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