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Adsorption Characteristics of Methylene Blue on PAA-PSBF Adsorbent

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In this study, a polysulfone Escherichia coil biomass composite fiber (PSBF) was prepared by thoroughly mixing and extruding a mixture of polysulfone and *E. coil* biomass. poly(acrylic acid) (PAA) was then crosslinked on the PSBF surface to fabricate PAA-PSBF. The adsorption performance of PAA-PSBF on Methylene Blue (MB) was evaluated by several batch tests such as pH edge, adsorption kinetics and adsorption isotherm. Desorption experiments were also conducted to examine the desorption efficiency and reusability of PAA-PSBF. As a result, it was optimal at pH 7 to remove MB by PAA-PSBF. The result of the kinetic experiments showed that at least 300 min was required to reach the adsorption equilibrium at the initial dye concentration of 200 mg/L. The isotherm experiment data were well illustrated by the Langmuir model and the maximum dye uptake was 225.2 mg/g at pH 7. By using a HCl-acidified solution with pH 2 as an eluent, the MB adsorbed on the PAA-PSBF was easily desorbed and the depleted PAA-PSBF was successfully regenerated. In addition, PAA-PSBF can be reused at least 3 times with good reusability.

1. Introduction

Methylene Blue (MB), a cationic dye and a drug, is widely used in industries, such as textile, pharmaceutical, printing, food, paint and cosmetics, but the usage process generates large amounts of MB-containing wastewater (Cao et al., 2018). MB is very poisonous, and its molecule is difficult to break down under natural conditions, hence, its existence in water is harmful to the ecosystem (Rahmi et al., 2019) and human's health (Cao et al., 2018). Therefore, it is essential to remove MB molecules from the effluent before discharging into the water body.

Several methods including microbiological decomposition, photocatalytic degradation, filtration, oxidation and adsorption have been applied for dye wastewater treatment (Chen et al., 2014). But there are some drawbacks such as generation of sludge, high investment and low efficiency. On the other hand, the adsorption process is recognized as a cost effective and high efficiency method (Rafeek et al., 2019). In recent years, biomaterials have attracted much attention due to their biodegradability, non-toxicity and, renewability (Deniz et al., 2019). Adsorption by biomaterials is regarded as a promising way to remove pollutants such as heavy metals, precious metals and dyes from wastewater (Kim et al., 2015). One of the abundant industrial wastes, E. coli biomass is useful for wastewater treatment. However, E. coli biomass is available only for one-time use because it is difficult to separate from water (Mao et al., 2013). The immobilization of E. coli can be a good alternative to avoid this defect, and surface modification methods such as crosslinking may also help improve the sorption ability of adsorbents. The cell wall of E. coli has the most representative functional groups such as carboxyl, hydroxyl, amine and phosphate groups. Hence, these functional groups can be easily modified through a crosslinking method (Mao et al., 2013).

Considering the drawbacks and characteristics of E. coli biomass, the present study has attempted to develop a new biosorbent with high adsorption capacity and easy regeneration through immobilization and surface modification. For this study, polysulfone was used to immobilize E. coli biomass and poly(acrylic acid) (PAA) was crosslinked on the surface of immobilized E. coli biomass to enhance adsorption capacity. As a result,

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PAA-crosslinked PSBF (PAA-PSBF) was prepared and used in all experiments. The surface morphology of PAA-PSBF, MB-loaded and MB-desorbed PAA-PSBF was observed by Scanning Electron Microscope (SEM) analysis. The adsorption and desorption properties of PAA-PSBF on the cationic dye Methylene Blue (MB) were evaluated by various batch experiments.

2. Materials and methods

2.1 Materials

The powder type of E. coli biomass was obtained from L-phenylalanine fermentation industry (Daesang, Gunsan, Korea). Polysulfone (Molecular weight (M_w) = ~35,000), PAA (M_w = 1,800), and MB (dye content, ≥82%) were purchased from Sigma-Aldrich Korea Ltd. (Yongin, Korea). N,N-Dimethylformamide (DMF, 99.5 %) was obtained from Daejung chemicals & metals co., Ltd. (Siheung, Korea). All the other reagents such as HCl and NaOH were of analytical grade.

2.2 Preparation of PSBF and PAA-PSBF

To fabricate PSBF, 10 % w/v polysulfone solution was prepared by dissolving 10 g of polysulfone in 100 mL DMF solution at 40 °C for 6 h. Thereafter, E. coli biomass (10 g) was mixed into the PS solution for 6 h under room temperature. The well mixed solution was then extruded into deionized water using a nozzle having an inner diameter of 0.57 mm to form polysulfone-E. coli biomass composite fibers (PSBF) by the phase inversion process. PSBF was washed several times with distilled water and freeze-dried for 24 h.
The surface of PSBF was modified by coating with PAA using HCl as a catalyst. More specifically, 2 g of PSBF and 4 g of PAA were mixed at 25 °C for 1 h in 2 L of distilled water. 60 mL of concentrated HCl was added to the mixture and stirred for 2 h. The final product, PAA-PSBF was cleaned several times with distilled water to remove any remaining reagents and freeze-dried for 24 h.

2.3 SEM analysis

The surface morphology of PAA-PSBF was characterized at 160x and 2,000x magnifications using SEM (JSM-6400, Jeol, Japan). Two samples of MB-adsorbed and MB-desorbed adsorbents were also analysed at the same magnification to observe surface changes of PAA-PSBF after sorption and desorption.

2.4 Adsorption experiments

The MB stock solution of 1,000 mg/L was prepared and diluted for use in all experiments as necessary. Basically, batch adsorption experiments were carried out by adding 0.02 g of PAA-PSBF and 30 mL MB solution into a 50 mL conical tube and stirring at 160 rpm and 25 °C. The adsorption performance of PAA-PSBF on MB was evaluated for three different parameters such as pH (2-7), time (0-720 min) and initial concentration (0-300 mg/L). The MB concentration of the sample was measured at 660 nm using a spectrophotometer (X-ma 3000 pc, Human, Korea) after appropriate dilution. The amount of MB adsorbed on the adsorbent was calculated using the following mass balance in Eq(1):

$$q = \frac{V_i C_i - V_f C_f}{m} \tag{1}$$

where C_i and C_f (mg/L) are the initial and final MB concentrations, V_i and V_f (L) are the initial and final volume of the solution, and m (g) is the dry weight of adsorbent.

2.5 Desorption and reuse experiments

For the desorption experiment, 0.02 g of PAA-PSBF was mixed with 30 mL of MB solution having an initial concentration of 200 mg/L for 24 h at room temperature. After adsorption, MB-loaded adsorbent was washed with distilled water. The loaded PAA-PSBF was desorbed by acid solution (pH=2). The continuous adsorption-desorption experiments were conducted 3 cycles to evaluate the possible reusability of PAA-PSBF. The released dye concentration was determined at 660 nm by a UV-Vis spectrophotometer and desorption efficiency was calculated using Eq(2).

$$Desorption\ efficiency\ (\%) = \frac{Desorbed\ dye\ amount\ (mg)}{Initailly\ adsorbed\ dye\ amount\ (mg)} \times 100 \tag{2}$$

3. Results and discussion

3.1 SEM image of PAA-PSBF

Figure 1a - f show SEM images of free, MB-loaded, and MB-desorbed PAA-PSBF at 160x and 2,000x magnifications. As shown in Figure 1a, the surface of the PAA-PSBF was rough and partially porous, and its diameter was about 650 μm. Figure 1b shows the surface change of the PAA-PSBF after MB adsorption. The surface of the MB-loaded PAA-PSBF was much smoother than that of the free PAA-PSBF and the pores appeared to be filled with dye molecules. Another significant change was observed that the fiber diameter increased to 720 μm after MB adsorption, which was 10.8 % increase in diameter compared to the original form. This indicates that the adsorbent may swell during MB adsorption and dye sorption may occur mainly on the surface of the adsorbent. On the other hand, the diameter of PAA-PSBF returned to its original shape after desorption as shown in Figure 1c. This shows that PAA-PSBF was not damaged during the adsorption-desorption process of MB.

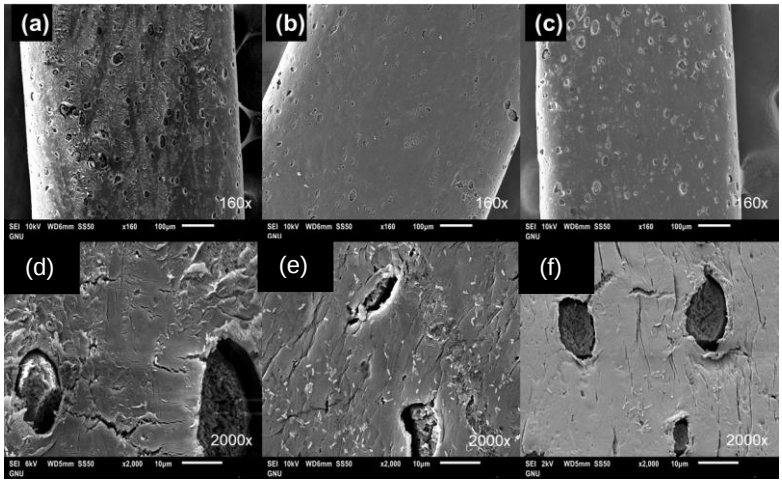

Figure 1: SEM images of (a) free PAA-PSBF, (b) MB-adsorbed PAA-PSBF, (c) MB-desorbed PAA-PSBF at 160x magnifications and (d) free PAA-PSBF, (e) MB-adsorbed PAA-PSBF, (f) MB-desorbed PAA-PSBF at 2,000x magnifications

3.2 Effect of pH

The pH of aqueous solution is known to be one of the main factors affecting the adsorption performance of the adsorbent. Due to the dye precipitation observed at pH above 7, the effect of pH on MB adsorption by PAA-PSBF was examined in the pH range of 2 - 7 and the results was given in Figure 2. As shown in Figure 2, MB adsorption by PAA-PSBF was very sensitive to pH change. The dye uptake increased with increasing pH and showed the highest dye uptake at pH 7. Therefore, pH 7 was selected as the optimal pH for the following adsorption experiments.

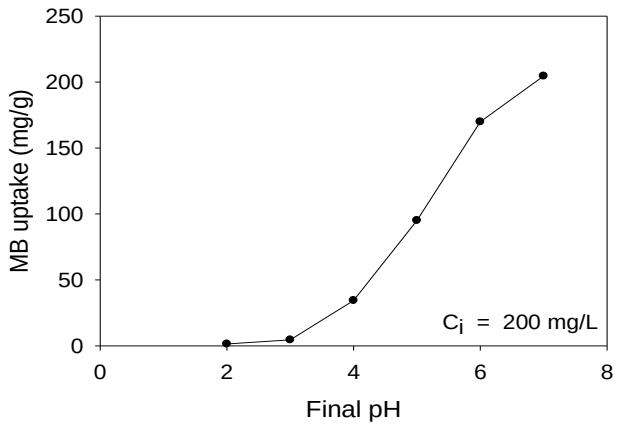

Figure 2: Effect of pH on MB uptake by PAA-PSBF

This pH dependency is deeply related to the specific functional groups of the adsorbent. Mao et al. (2013) reported that "The carboxyl groups in biological polymers have pK_a values ranging from 3.5 to 5.0". The carboxyl groups are then present in the protonated form of –COOH at pH 3 or below, which is not involved in the adsorption of cationic dye MB. On the other hand, as the pH increases, more carboxyl groups become carboxylate anions ($–COO^-$) rather than protonated forms. Since the carboxylate anions on the adsorbent can induce the binding with cationic MB, it can lead to more dye uptake with increasing pH.

3.3 Isotherm studies

To examine adsorption isotherms, isotherm experiments were conducted at pH 7 in the MB concentration range of 0-300 mg/L, and the result is presented in Figure 3. The MB uptake increased in proportion to the equilibrium concentration at a low dye concentration range. As the dye concentration further increased, the amount of adsorption gently increased and finally saturated at a certain point. Isotherm experimental data were also fitted by the Langmuir (Eq(3)) and Freundlich models (Eq(4)).

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q_e = K_F C_e^{1/n} \tag{4}$$

In these equations, q_e (mg/g) represents the adsorption capacity of MB at equilibrium, C_e (mg/L) represents the MB concentration at equilibrium, q_{max} (mg/g) is the maximum MB uptake, b_L (L/mg) is the Langmuir binding constant, K_F (mg/g) is Freundlich constant, and 1/n is related to the adsorption intensity either effective (0 < 1/n < 1) or cooperative (1/n > 1).

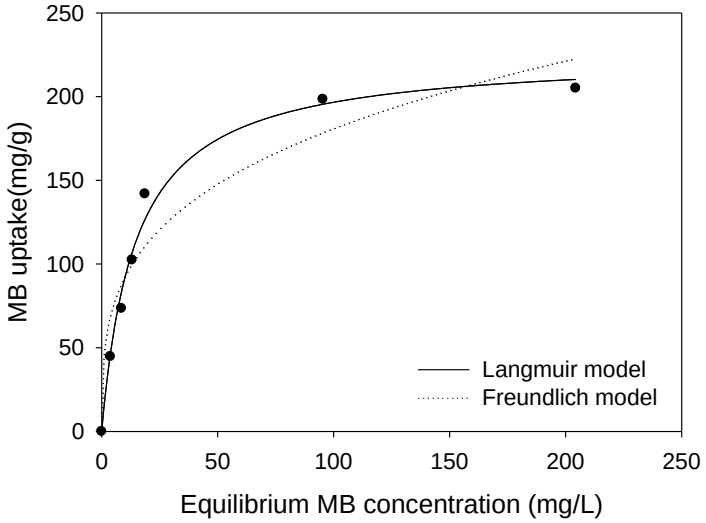

Figure 3: Adsorption isotherm of MB on PAA-PSBF at pH 7

The parameters obtained from two isotherm models were summarized in Table 1. The coefficient of determination (R^2) value of the Langmuir model was 0.982, which was higher than that of the Freundlich model (0.883), indicating that the Langmuir model is more suitable for describing the experimental data. According to the Langmuir model, the values of q_{max} and b_L were estimated to be 225.2 mg/g and 0.0688 L/mg. Compare to previous studies (Zou et al., 2019) in this work the adsorption capacity of PAA-PSBF is higher. That is, this result shows that PAA-PSBF has a high adsorption capacity and a high affinity for MB molecules. For the Freundlich model, the value of 1/n was 0.29, which indicated that the MB sorption by PAA-PSBF was favourable.

Table 1: Parameters of the Langmuir and Freundlich models

	Langmuir model			Freundlich model		
pH	q_{max} (mg/g)	b_L (L/mg)	R^2	1/n	K_F (L/g)	R^2
7	225.2	0.0688	0.982	0.29	47.54	0.883

3.4 Kinetic studies

Adsorption kinetic experiments were performed at pH 7 and the initial MB concentration of 200 mg/L to evaluate the time required for adsorption equilibrium. Figure 4 exhibits the plot of MB uptake versus contact time for MB adsorption by PAA-PSBF.

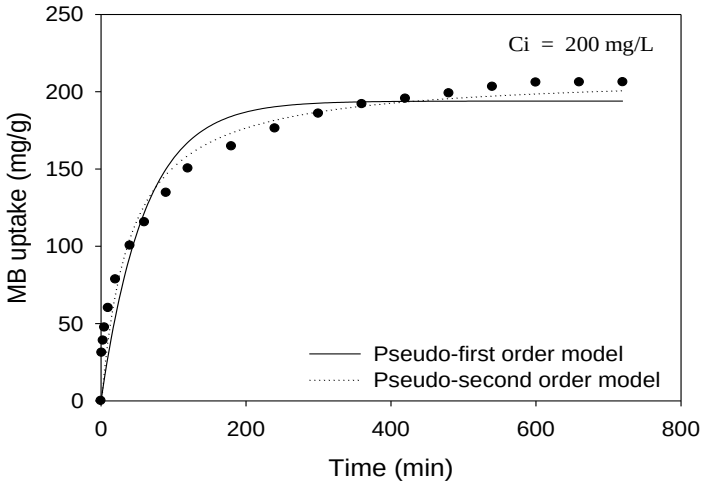

Figure 4: Adsorption kinetics of MB on PAA-PSBF at pH 7

The MB amount adsorbed on the adsorbent increased with the increase of the contact time, but after 600 min, the MB uptake showed a constant value without any significant change. Therefore, it was experimentally confirmed that the MB adsorption on PAA-PSBF needs at least 600 min to reach adsorption equilibrium under the experimental conditions of pH 7 and initial dye concentration of 200 mg/L.
The kinetic experimental data were analyzed by the pseudo-first-order and pseudo-second-order kinetic models as described in Eq(5) and (6):

$$q_t = q_1\left(1 - exp(-k_1 t)\right) \tag{5}$$

$$q_t = \frac{q_2^2 k_2 t}{1 + q_2 k_2 t} \tag{6}$$

where q_1 and q_2 (mg/g) are the amounts of MB adsorbed at equilibrium, q_t (mg/g) is the amount of MB adsorbed at regular intervals (t), k_1 (L/min) and k_2 (g/ (mg min)) are the pseudo-first-order and pseudo-second-order rate constant. The parameters of two kinetic models are shown in Table 2.

Table 2: Parameters of two kinetic models

Initial MB conc.	Pseudo-first-order model			Pseudo-second-order model		
(mg/L)	q_1 (mg/g)	k_1 (L/min)	R^2	q_2 (mg/g)	k_2 (g/mg min)	R^2
200	193.9	0.017	0.935	212.6	0.0001	0.968

The R^2 value of pseudo-second-order model was higher than that of pseudo-first-order model. The MB uptake at equilibrium, q_2 value predicted by the pseudo-second-order model MB uptake was close to the experimental result (205.0 mg/g). Therefore, the pseudo-second-order model is suitable for fitting kinetic experimental data on MB adsorption by PAA-PSBF. It also suggests that chemisorption dominates physisorption during the adsorption process (Chen et al., 2014).

3.5 Desorption and reusability studies

To be a promising adsorbent, the adsorbent has to have good reusability. Thus, desorption and reusability studies were performed and dye desorption from the adsorbent was carried out using distilled water acidified to pH 2 (Wang et al., 2011). Adsorption and desorption experiments were conducted continuously for up to 3 cycles and the results are displayed in Figure 5.

After 3rd cycle, the adsorption capacity of PAA-PSBF decreased from 218.3 mg/g to 207.0 mg/g by 5.2 %, while the desorbed dye amount per adsorbent dose was maintained at 197.5±1.0 mg/g. In the 3 cycles, the desorption efficiencies were 90.16 %, 95.77 %, and 95.70 %. This indicates that PAA-PSBF has good reusability even after 3 cycles.

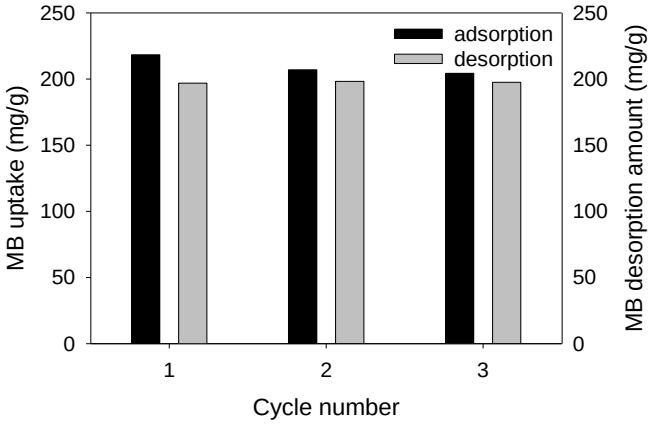

Figure 5: Repeated adsorption and desorption cycles

4. Conclusion

In this study, a reusable adsorbent, PAA-PSBF was successfully fabricated. Isotherm and kinetic data were well fitted by the Langmuir model and the pseudo-second-order model. The maximum MB uptake at pH 7 was predicted to be 225.2 mg/g by the Langmuir model. According to reusability studies, PAA-PSBF was easily regenerated using a HCl-acidified solution (pH 2) and can be reused without significant performance degradation. Therefore, PAA-PSBF has high potential as a promising adsorbent to remove cationic dyes such as MB in aqueous solution.

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