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Evaluation of Adsorption and Desorption Properties of PAA-PSBF for Cd(II) from Aqueous Solution

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In this study, a poly(acrylic acid)-modified polysulfone-*Escherichia coli* biomass composite fiber (PAA-PSBF) was used for the removal of Cd(II) from aqueous solution. FT-IR analysis confirmed that PAA was successfully modified on the PSBF surface. The adsorption and desorption properties of PAA-PSBF for Cd(II) were evaluated through pH edge, adsorption kinetic, adsorption isotherm, and desorption experiments. The pH edge experiments were carried out at initial Cd(II) concentrations of 50 and 100 mg/L, in the pH range of 2-7. The results showed that the optimal pH for Cd(II) removal was 7. The adsorption kinetic experiments confirmed that the adsorption equilibrium at pH 7 requires at least 240 min. The isotherm experimental data were well fitted by the Langmuir model, and the maximum Cd(II) uptake on PAA-PSBF was calculated as 47.39 mg/g. In addition, the reusability study revealed that the adsorption capacity of PAA-PSBF for Cd(II) was only slightly decreased while its desorption efficiency remained at above 93.88 %.

1. Introduction

Due to the rapid development of modern industries, heavy metal pollution goes beyond common environmental problems and causes fatal damage to human health and ecosystems (Cimá-Mukul et al., 2019). Among heavy metals, cadmium (Cd(II)) is a major public health concern when distributed in the atmosphere, water, and soil due to its high mobility and potential toxicity (Zhang et al., 2019). Humans have large quantities of Cd(II) into the biosphere through industrial emissions such as paint-making, batteries, manufacture of plastic, and electroplating, which have greatly altered the biogeochemical cycle of Cd(II). In addition, exposure to Cd(II) can cause many diseases and cancers in human organs such as the lungs, liver, immune, and cardiovascular (Matés et al., 2010). Therefore, it is important to remove or reduce the concentration of Cd(II) in ecosystem.
Adsorption, known as a low-cost, efficient, and simple method, has been widely applied to remove heavy metals (Kong et al., 2019). Recently, biomass has attracted a lot of attention due to its environment-friendly, biodegradable, and renewable properties. Various biomasses have been used as adsorbents to remove pollutants such as dyes and heavy metals from aqueous solution/wastewater. *Escherichia coli* biomass, one of the industrial wastes, is an attractive bio-adsorbent due to the existence of various functional groups such as amine, phosphate, hydroxyl, and carboxyl (Kang et al., 2021). However, since raw *E. coli* biomass has a low adsorption capacity and difficulty in solid-liquid separation, researchers have tried surface modification methods such as crosslinking to increase the adsorption capacity of raw biomass. Besides, methods for immobilizing biomass have been developed to improve the efficiency of solid-liquid separation.
In this work, two strategies were applied to overcome the shortcomings of raw *E. coli* biomass. Firstly, polysulfone immobilized *E. coli* biomass fiber (PSBF) was prepared by wet spinning according to our previous method (Kang et al., 2020). This made it easy to separate biomass from water. Secondly, poly(acrylic acid) (PAA) was crosslinked to the surface of the immobilized *E. coli* biomass to improve its adsorption performance. Fourier-transform infrared spectroscopy (FT-IR) analysis was applied to prove the successful preparation of PAA-PSBF. To verify the advantage of PAA-PSBF, the adsorption performance of PAA-PSBF for Cd(II) was

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compared with two commercial adsorbents (Lewatit® VP OC 1026 and SPS-100) by batch adsorption experiments. The reusability of PAA-PSBF was also evaluated through repeated adsorption-desorption cycles.

2. Materials and methods

2.1 Materials

E. coli biomass powder was obtained from L-phenylalanine fermentation industry (Daesang, Gunsan, Korea). Polysulfone (PS, molecular weight (M_w) ~35,000), PAA(M_w = 1800) were purchased from Sigma-Aldrich Korea Ltd. (Yongin, Korea). $Cd(NO_3)_2 \cdot 4H_2O$ was provided from Kanto chemical Co., Inc. (Tokyo, Japan). Activated carbon SPS-100 and ion-exchange resin Lewatit® VP OC 1026 were provided from Samchully Carbotech co., Ltd. (Gimcheon, Korea) and Lanxess energizing chemistry Co., Ltd. (Seoul, Korea). N,N-Dimethylformamide (DMF, 99.5 %) was obtained from Daejung chemicals & metals Co., Ltd. (Siheung, Korea). All the other reagents were of analytical grade.

2.2 Preparation of PSBF and PAA-PSBF

To fabricate PSBF, 10 % (w/v) PS solution was prepared by dissolving 10 g of PS 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 suspension was then wet spun into deionized water using a nozzle having an inner diameter of 0.57 mm to form 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 then freeze-dried for 24 h.

2.3 FT-IR analysis

PSBF and PAA-PSBF were analyzed using an FTIR spectrometer (FT/IR-300E, Jasco, Japan) to confirm successful crosslinking of PAA on the surface of PSBF. The IR spectra were investigated in the range of 4,000 - 400 cm^{-1}. The specimens for FTIR analysis were formed into pellets by uniformly mixing the adsorbent and KBr reagent and compressing the mixture.

2.4 Adsorption experiments

100 mg/L of Cd(II) stock solution was prepared by dissolving a certain amount of $Cd(NO_3)_2 \cdot 4H_2O$ in distilled water. The working solutions were diluted from the stock solution if necessary. Batch adsorption experiments were carried out by adding 0.02 g of PAA-PSBF and 30 mL Cd(II) solution into a 50 mL conical tube and shaking at 160 rpm under 25 °C. The effects of pH (2-7) contact time (0-720 min) and initial Cd(II) concentration (0 - 100 mg/L) on the adsorption of Cd(II) by PAA-PSBF were investigated. The collected samples were centrifuged for 10 min at 10,000 rpm and diluted appropriately with distilled water. Residual Cd (II) concentration was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Avio200, PerkinElmer, America), and the Cd(II) 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 Cd(II) concentrations. V_i and V_f (L) are the initial and final volume of the solution. m (g) is the dry weight of adsorbent.

2.5 Desorption and reuse experiments

In the adsorption cycle, 0.02 g of PAA-PSBF was mixed with 30 mL of 100 mg/L of Cd(II) solution for 24 h at room temperature. After adsorption, Cd(II)-loaded adsorbent was washed with distilled water. Then, the desorption cycle was carried by using 0.1 M HNO_3 solution as an eluent to desorb Cd(II) from Cd(II)-loaded PAA-PSBF. The adsorption-desorption experiments were conducted in three consecutives cycles to evaluate the reusability of PAA-PSBF. The samples were appropriately diluted, and the remaining Cd(II) concentration was analyzed using ICP-OES. The desorption efficiency was calculated using Eq(2).

$$Desorption\ efficiency\ (\%) = \frac{Desorbed\ Cd(II)\ amount\ (mg)}{Initailly\ adsorbed\ Cd(II)\ uptake\ (mg)} \times 100 \quad (2)$$

3. Results and discussion

3.1 FT-IR analysis of PAA-PSBF

To confirm the change of functional groups on the PSBF surface after PAA coating, FT-IR spectra of PSBF and PAA-PSBF were recorded as showed in Figure 1. In the case of PSBF (Figure 1a), the broad bands at 3,700 - 3,200 cm^{-1} were due to the overlapping of O–H in the carboxyl group (Mao et al., 2013). The peak at 2,923 cm^{-1} was attributed to CH_2 stretching vibration (Padmavathy et al., 2003). The absorption peaks at 1,729 cm^{-1} and 1,400 cm^{-1} assigned to the stretching vibration of C═O (Yee et al., 2004). After PAA was coated onto the PSBF surface (Figure 1b), the peaks at 3,444 and 2,923 cm^{-1} were shift to 3,427 and 2,925 cm^{-1}. Moreover, the peaks associated with C═O stretching vibration were moved to 1,724 and 1,404 cm^{-1}. These results reflect an increase in carboxyl groups on the adsorbent surface after PAA modification.

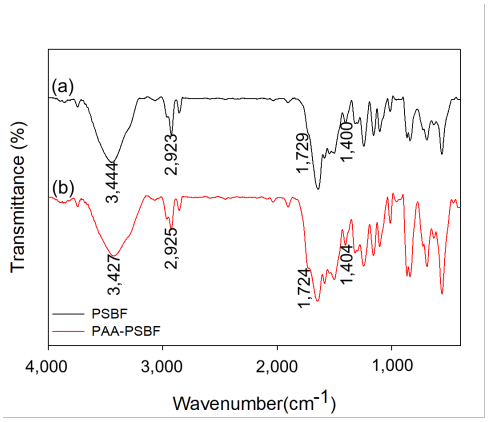

Figure 1: FT-IR spectrums of the PSBF and PAA-PSBF

3.2 Effect of pH

The pH of Cd(II) solution is known as one of the main factors affecting adsorption performance. This is because the pH of Cd(II) solution affects the competitive adsorption between Cd(II) and hydrogen ions, protonation and deprotonation of functional groups, and the form of Cd(II). Therefore, the pH edge experiment was performed to confirm the optimal pH value for Cd(II) removal. The pH range was selected as 2-7 because it is well known that Cd^{2+} precipitates as calcium hydroxide when the pH exceeds 8.0 (100 mg/L of Cd(II) solution at 25°C). The PAA-PSBF has a large quantity of carboxyl groups provided by PAA, and the pK_a value of the carboxyl group is approximately 4.5 (Mao et al., 2013). The carboxyl groups are present in the form of –COOH at pH 4.5 or below, which is not involved in the adsorption of Cd(II) cations. On the other hand, as the pH increases, carboxyl groups become carboxylate anions ($–COO^-$) from –COOH forms. Since these carboxylate anions existed in the adsorbent can be combined with Cd^{2+} ions by electrostatic attraction, the Cd(II) uptake increased significantly as the pH increased above 4 as shown in Figure 2. The Cd(II) adsorption within in the examined pH range was the best at pH 7, and pH 7 was selected as the optimal pH for the following adsorption experiments.

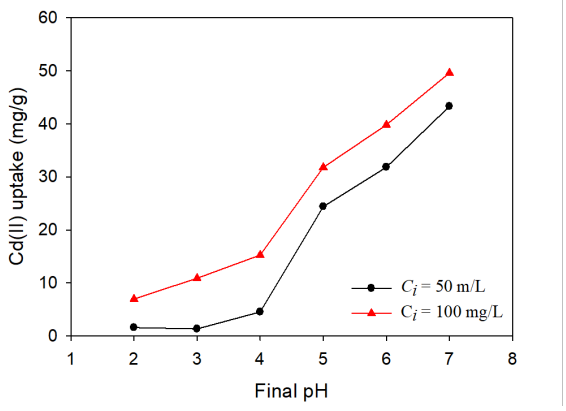

Figure 2: Effect of pH on Cd(II) uptake by PAA-PSBF

3.3 Isotherm studies

To evaluate the maximum adsorption capacity of PAA-PSBF for Cd(II), isotherm experiments were conducted at pH 7 in the Cd(II) concentration range of 0-100 mg/L. Besides, its adsorption performance was compared with ion-exchange resin (Lewatit® VP OC 1026) and activated carbon (SPS-100), and the result is presented in Figure 3. The Cd(II) uptake increased with the increase of initial Cd(II) concentration at low concentration and then reached equilibrium at high concentration. For better understanding the adsorption performance, isotherm experimental data were 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 Cd(II) at equilibrium, C_e (mg/L) represents the Cd(II) concentration at equilibrium, q_{max} (mg/g) is the maximum Cd(II) adsorption capacity, b_L (L/mg) is the Langmuir binding constant, K_F (mg/g) is the Freundlich constant, and 1/*n* is related to the adsorption intensity either effective (0 < 1/n < 1) or cooperative (1/n > 1).

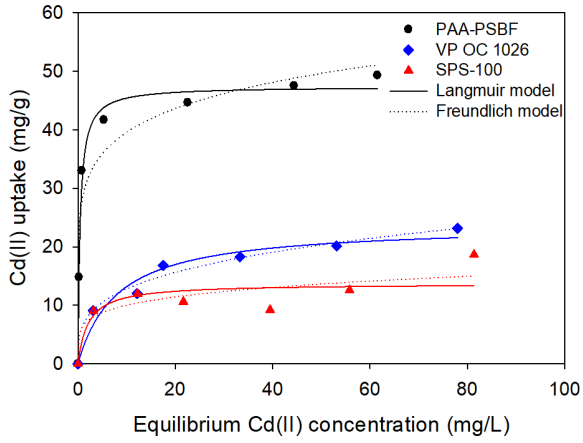

Figure 3: Adsorption isotherm of Cd(II) on PAA-PSBF, Lewatit® VP OC 1026, and SPS-100 at pH 7.

The isotherm parameters are listed in Table 1, and the adsorption isotherms of Cd(II) on PAA-PSBF, Lewatit® VP OC 1026, and SPS-100 were fitted by Langmuir and Freundlich models (Figure 3). For PAA-PSBF and Lewatit® VP OC 1026, the R^2 values of Langmuir model were higher than those of Freundlich models, suggesting the monolayer adsorption of Cd(II) on PAA-PSBF and VP OC 1026. Conversely, the Freundlich model is well-matched with experimental data of SPS-100, indicating that the adsorption of SPS-100 for Cd(II) can be multilayer adsorption (Wang et al., 2021). According to the Langmuir model, the q_{max} value of PAA-PSBF was estimated to be 47.40 mg/g, which is superior to Lewatit® VP OC 1026 and SPS-100. For the Freundlich model, the values of 1/*n* were 0.14, 0.29, and 0.19, indicating that the Cd(II) sorption by PAA-PSBF, VP OC 1026, and SPS-100 are favourable.

Table 1: Isotherm parameters for the adsorption of Cd(II) onto PAA-PSBF, VP OC 1026, and SPS-100

	Langmuir model			Freundlich model		
Sorbent	q_{max} (mg/g)	b_L (L/mg)	R^2	1/*n*	K_F (L/g)	R^2
PAA-PSBF	47.40	2.29	0.989	0.14	28.64	0.935
Lewatit® VP OC 1026	23.76	0.12	0.958	0.29	6.59	0.938
SPS-100	13.69	0.48	0.748	0.19	6.40	0.816

3.4 Kinetic studies

Adsorption kinetic experiments were performed at pH 7 and initial Cd(II) concentration of 100 mg/L to evaluate the time required for adsorption equilibrium. The experimental data were fitted by pseudo-first-order and pseudo-second-order models (Figure 4), and the kinetic parameters are listed in Table 2.

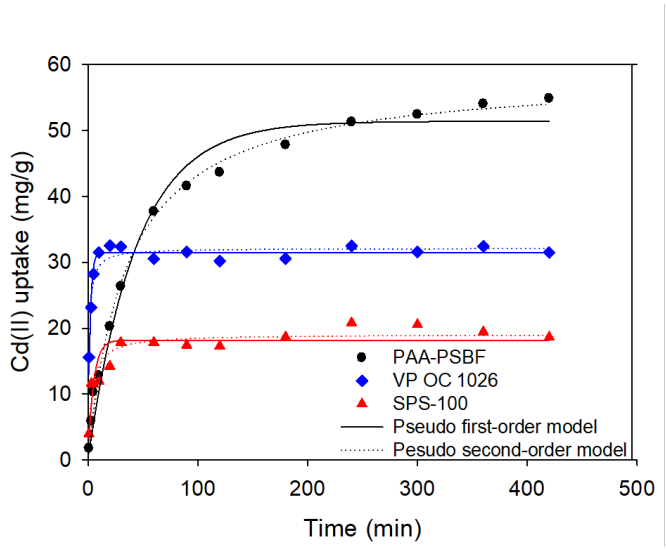

Figure 4: Adsorption kinetics of Cd(II) on PAA-PSBF, Lewatit® VP OC 1026, and SPS-100 at pH 7

Table 2: Kinetic parameters for the adsorption of Cd(II) onto PAA-PSBF, Lewatit® VP OC 1026, and SPS-100

	Pseudo-first-order model			Pseudo-second-order model		
Sorbent	q_1 (mg/g)	k_1 (L/min)	R^2	q_2 (mg/g)	k_2 (g/mg min)	R^2
PAA-PSBF	51.38	0.226	0.981	58.53	0.0005	0.996
Lewatit® VP OC 1026	31.45	0.533	0.935	32.15	0.0324	0.930
SPS-100	18.18	0.199	0.806	19.08	0.0154	0.906

The equations of pseudo-first-order and pseudo-second-order kinetic models are described in Eq(5) and (6):

$$q_t = q_1\left(1 - exp(-k_1 t)\right) \quad (5)$$

$$q_t = \frac{q_2^2 k_2 t}{1 + q_2 k_2 t} \quad (6)$$

where q_1 and q_2 (mg/g) are the amounts of Cd(II) adsorbed at equilibrium, q_t (mg/g) is the amount of Cd(II) adsorbed at time, t, and k_1 (L/min) and k_2 (g/ (mg min)) are the pseudo-first-order and pseudo-second-order rate constant.

The adsorption equilibrium of PAA-PSBF, Lewatit® VP OC 1026, and SPS-100 for Cd(II) was reached within 240, 30, and 60 min. For PAA-PSBF and SPS-100, the R^2 values of the pseudo-second order model were greater than those of the pseudo-first order model. This indicated that the adsorption of Cd(II) on PAA-PSBF and SPS-100 was dominated by chemisorption (Wang et al., 2021). On the contrary, for Lewatit® VP OC 1026, the R^2 value of pseudo-first order model was larger than that of the pseudo-second order model. In addition, the q_1 value of PAA-PSBF and SPS-100, and the q_2 value of Lewatit® VP OC 1026 were closer to the experimental values (52.42, 17.83, and 32.54 mg/g for PAA-PSBF, SPS-100, and VP OC 1026). Therefore, the pseudo-first-order model was better for depicting the adsorption kinetics of Cd(II) by Lewatit®, while the pseudo-second-order model was fit for explaining the adsorption of Cd(II) onto PAA-PSBF and SPS-100.

3.5 Desorption and reusability studies

Adsorbents with good reusability will help reduce operating costs as well as the burden of disposal of depleted adsorbents. Thus, reusability studies were carried out using 0.1 M HNO_3 to evaluate the reusability of PAA-PSBF for Cd(II) removal. The adsorption-desorption cycle was repeated 3 times and the results are displayed in Figure 5. After 3rd cycle, the adsorption capacity of PAA-PSBF decreased from 53.51 mg/g to 48.62 mg/g by 9.1 %. In the 3 cycles, the desorption efficiencies were 93.88 %, 97.84 %, and 102.16 %. This indicates that PAA-PSBF has good reusability even after 3 cycles.

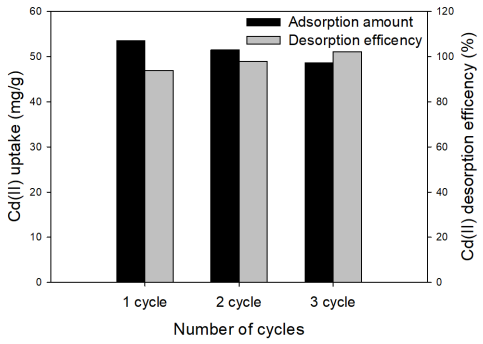

Figure 5: Repeated adsorption and desorption cycles

4. Conclusions

In this study, a reusable adsorbent PAA-PSBF was used for the removal of Cd(II) from aqueous solution. The Langmuir model and the pseudo-second-order model describe the PAA-PSBF adsorption isotherm and kinetic data well. The maximum Cd(II) uptake at pH 7 was predicted as 47.40 mg/g by the Langmuir model. Reusability studies showed that Cd(II)-loaded PAA-PSBF was easily regenerated by 0.1 M HNO_3 solution used as eluent and can be reused without significant performance degradation. In conclusion, PAA-PSBF has high potential as a promising adsorbent to remove cationic contaminants such as Cd(II) in aqueous solution.

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