Korean J. Chem. Eng., 38(3), 523-530 (2021)
DOI: 10.1007/s11814-020-0716-x

pISSN: 0256-1115
eISSN: 1975-7220

Application of polyethylenimine multi-coated adsorbent for Pd(II) recovery from acidic aqueous solution: batch and fixed-bed column studies

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(*Received 2 September 2020 • Revised 11 November 2020 • Accepted 16 November 2020*)

Abstract−PEI multi-coated PSBF (PEI-M-PSBF) with high adsorption efficiency and good reusability for Pd(II) recovery was prepared by a PEI multi-coating method. The results of FT-IR and FE-SEM showed that the PEI-M-PSBF was successfully prepared. Batch experiments were conducted to study the adsorption/desorption performance of PEI-M-PSBF to Pd(II). The Langmuir and pseudo-second-order models were well suited for the batch experiment isotherm and kinetic data, respectively. The adsorption capacity of Pd(II) by Langmuir model was 327.14 mg/g, and the initial adsorption rate of 3-PEI-PSBF was 37.19 mg/g min. As a result, the increase in amine groups on the PEI-M-PSBF surface through the PEI multi-coating directly influenced the adsorption amount of the biosorbent. The effects of initial concentration, bed column depth, and flow rate were determined in a column system and the breakthrough curves were detected by Thomas model. In addition, the recycle of the adsorbent was examined by multiple time performing adsorption/desorption cycles up to ten times in a fixed-bed column.

Keywords: Palladium, Polyethylenimine, Multi-coating, Recovery, Column Process

INTRODUCTION

Platinum group metals (PGMs) are largely used in autocatalytic, electronics, chemical and pharmaceutical industries owing to their unique physico-chemical properties [1]. The demand for palladium (Pd), one of the PGMs, has recently increased, but the price of Pd has skyrocketed due to limited supply. The bulk of Pd is limited to countries like South Africa, Russia, the United States and Canada, and its natural abundance is also very low (~0.01 g/kg) [2]. However, wastes such as spent catalytic converters contain 2-10 g of Pd per kg of waste [3]. For these reasons, the recovery of Pd from wastes containing Pd is economically significant. Various techniques, such as membrane separation, ion exchange, liquid-liquid extraction, and adsorption, have been used to obtain Pd from aqueous liquids, but such processes are expensive, unreliable, difficult to perform and may create secondary contaminants [4]. Therefore, an eco-friendly, with low production cost and high efficiency method should be developed to recover Pd from aqueous solutions.

Biosorption is a substitute technique for removing or recovering contaminants from wastewater and aqueous solutions. This method is particularly eco-friendly because it utilizes biomasses such as algae, fungi, bacteria, and agricultural/fermentation wastes as biosorbent or sorbent material [5]. Inactive or dead biomass was used to bind and concentrate precious metals in wastewater [6]. Adsorption by this kind of biomass is independent of metabolism but occurs primarily in the cell wall through electrostatic interaction [6]. A number of functional groups, such as phosphonate, carboxyl, hydroxyl and amine, also exist on the biomass surface [7]. Thus, many researchers have tried various attempts to use raw biomass as an adsorbent. However, the biomass in powder form showed limitations, such as difficulty in solid-liquid separating, regenerating, and pressure drop in the fixed-bed column [8]. Therefore, there is a need for a technique capable of effectively immobilizing biomass while improving adsorption performance on target pollutants.

To address these problems in our previous study [9], a fiber-type adsorbent, polyethylenimine (PEI)-coated polysulfone/*Escherichia coli* biomass composite fiber (PEI-PSBF) was developed by crosslinking PEI to the PSBF surface using a crosslinker glutaraldehyde (GA). Polysulfone was used as an immobilization material for *E. coli* biomass due its high mechanical strength, chemical stability, and high acid resistance [10]. PEI is an amine-rich polymer that has been widely used to enhance the adsorption capacity of adsorbents for various metals [11-13]. Amine groups are easily protonated under acidic conditions and are known to have good affinity for anionic Pd(II) ($[PdCl_4]^{2-}$) [14]. To introduce a large number of amine groups on the adsorbent surface, PEI rich in amine groups was used for surface modification as an amine donor [15]. The adsorption performance of Pd(II) by PEI-PSBF was examined and the maximum adsorption amount of PEI-PSBF (216.9 mg/g) was similar to that of a commercial resin and higher than that of PSBF developed in previous study (30.8 mg/g). Eventually, implementation of PEI to the surface of the PSBF increased the adsorption capacity [9].

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In this research, we attempted a PEI multi-coating process to further enhance the adsorbent performance of PEI-PSBF. The PEI multi-coated PSBF (PEI-M-PSBF) was developed using a multi-coating method. Briefly, the PSBF was first treated with GA solution, the GA treated PSBF was washed with distilled water one time and mixed with PEI solution. This process was repeated three times. During the preparation process, the PEI crosslinked PSBF (X-PEI-PSBF, X=1, 2, 3) was set aside from each step for further analysis. The PEI-M-PSBF was evaluated for Pd(II) adsorption and desorption in batch and column system, respectively. These evaluations verified that the PEI multi-coating can effectively enhance the adsorption ability of the biosorbent. In addition, the characteristics of the adsorbent were analyzed using Fourier transform-infrared spectroscopy (FT-IR) and field emission scanning electron microscopy (FE-SEM).

MATERIALS AND METHODS

1. Materials

Branched PEI (MW: 70,000, content: 50%) was purchased from Habjung Moolsan Co., Ltd. (Seoul, Korea). E. coli biomass was obtained from Daesang Co., Ltd. (Gunsan, Korea). Polysulfone (MW: ~35,000) was supplied by Sigma-Aldrich Korea Ltd. (Yongin, Korea). N,N-dimethylformamide (purity: 99.5%) was provided by Daejung Chemical & Metals Co., Ltd. (Siheung, Korea). $PdCl_2$ (purity: 99.0%) was obtained from Kojima Chemicals Co., Ltd. (Saitama, Japan) and glutaraldehyde (25% solution, extra pure) was purchased by Junsei Chemical Co. Ltd. (Tokyo, Japan). Other reagents, such as Thiourea, NaOH, and HCl, used in this research were of analytical grade.

2. Manufacturing of PEI-M-PSBF

The PEI-PSBF was prepared using our previous method [9] with slight modification. In this study, the content of PS was increased to strengthen the physical property of the biosorbent and PEI coating was applied up to three times on the surface of PSBF to enhance the sorption performance for Pd(II). First, 10 g of PS was added to 100 mL of DMF at 40 °C and stirred for 10 h, then 10 g of *E. coli* biomass was diffused into the PS solution and mixed at room temperature for overnight. The well-mixed solution was squeezed into deionized water under 0.1 MPa pressure using a 0.52 mm inner diameter needle. To remove residual DMF, the PSBF was washed three times with distillated water. Thereafter, 60 g of wet material was stirred with 1.5 L of 10% (v/v) GA solution at 40 °C for 2 h. GA-treated PSBF was transferred to 1.5 L of 10% (v/v) PEI solution and its surface was coated with PEI molecules at 25 °C for 1 h. Through this process, primary PEI-PSBF (1-PEI-PSBF) was prepared. To fabricate secondary PEI-PSBF (2-PEI-PSBF), 1-PEI-PSBF was treated with 1.5 L of 0.033% GA solution at 40 °C for 10 min and coated with 1.5 L of 10% PEI at 25 °C for 30 min. The above procedure was repeated once again to obtain tertiary PEI-PSBF (3-PEI-PSBF). Each product, 1-, 2-, and 3-PEI-PSBF, was sufficiently washed with distilled water, freeze-dried overnight and deposited in a desiccator before it was included in the experiment.

3. Batch Experiments

The Pd(II) stock solution of 1,000 ppm was made by dissolving a suitable quantity of $PdCl_2$ in 0.1 M HCl solution, and the Pd(II) concentration used in this study was correctly formulated by watering down the Pd(II) stock solution with 0.1 M HCl solution. In all batch experiments, 0.02 g of biosorbent and 30 mL of Pd(II) solution were placed in a 50 mL conical tube and stirred in a shaking incubator at room temperature and 160 rpm. Isotherm tests were conducted at various Pd(II) concentration of 0-500 ppm at room temperature for overnight to assess the maximum capacity of the adsorbents. After reaching equilibrium, samples were collected from the supernatant to analyze the final concentration of Pd(II). Kinetic experiments with 100ppm Pd(II) solution were conducted to approximate the period to maintain adsorption control, and samples were obtained from the supernatant at fixed time intervals. The samples collected were centrifuged for 5 min at 9,000 rpm and diluted appropriately with tertiary distilled water. Residual Pd(II) concentration was measured by ICP-OES (Avio200, PerkinElmer, America), and the Pd(II) adsorption amount q (mg/g) was calculated using Eq. (1).

$$q=\frac{(C_i-C_f)V}{m} \tag{1}$$

In Eq. (1), the initial and final Pd(II) concentrations are expressed by C_i and C_f (mg/L), respectively, the working volume is indicated by V (L) and the weight of adsorbent is marked by m (g).

To confirm the reusability of the multi-coated biosorbent, Pd(II)-loaded 3-PEI-PSBF was prepared by adding 0.02 g of 3-PEI-PSBF and 30 mL of 100 ppm Pd(II) solution in 50 mL conical tube and placed in the shaking incubator at room temperature and 160 rpm for 24 h prior to the desorption experiment. This adsorbent was washed quickly with de-ionized water and re-suspended in the mixed solution of 0.01 M thiourea and 0.01 M HCl used as eluent. Kinetic experiment for desorption was conducted by mixing Pd(II)-loaded 3-PEI-PSBF with 30 mL of 0.1 M HCl solution, and other experimental conditions were the same as that of the adsorption kinetic experiment. The above adsorption/desorption cycles were repeatedly performed three times in total. The samples collected from adsorption and desorption kinetic experiments were appropriately diluted and the remaining concentration of the samples Pd(II) was analyzed using ICP-OES. Eq. (2) was used to calculate the desorption efficiency:

$$\text{Efficiency of desorption (\%)} =\frac{\text{Released Pd(II) weight (mg)}}{\text{Initially adsorbed Pd(II) weight (mg)}}\times 100 \tag{2}$$

4. Column Experiments

For adsorption studies in a bed column, 3-PEI-PSBF was packed into a glass column with an inner diameter of 7 mm and a height of 100 mm. To support the filler, the bottom and top of the column were filled with glass wool. After then, Pd(II) solution was continuously pumped by a tubing pump until it reached the breakthrough point. The effects of bed column height (2.5-4.5 cm), initial Pd(II) concentration (50-150 ppm), and flow rate (0.5-1.5 mL/min) on breakthrough curves were investigated. The Pd(II) solution was gathered at periodic times at the outlet of the column and the sample was confirmed by ICP-OES analysis.

Column adsorption capacity is commonly calculated as a breakthrough curve. Mass of Pd(II) (q_m, mg), adsorption capacity of 3-

PEI-PSBF (q_e, mg/g), and solution volume (V_s, mL) were calculated by the following Eqs. [16].

$$V_s = Qt_{total} \tag{3}$$

$$q_m = \frac{Q}{1{,}000}\int_0^{t_{total}} (C_i - C_t)dt \tag{4}$$

$$q_e = \frac{q_m}{m} \tag{5}$$

where Q (mL/min) is the flow rate of the solution, C_i and C_f are the concentration of Pd(II) solution sample in influent and effluent, respectively, t_{total} (min) is the total flow time, and m (g) is the mass of adsorbent. In addition, column experimental data were represented by the Thomas model as follows [17]:

$$\ln\left(\frac{C_i}{C_t} - 1\right) = \frac{K_{Th}q_0 m}{Q} - K_{Th}C_i t \tag{6}$$

In Eq. (6), q_0 (mg/g) is the maximum solid phase concentration, and K_{Th} (mL/min·mg) is the Thomas rate constant.

5. FT-IR and SEM Analyses

To observe the surface change of the adsorbent according to the number of PEI coatings, three adsorbents, such as 1-, 2-, and 3-PEI-PSBFs, were examined using an FTIR spectrometer (FT/IR-300E, Jasco, Japan) and FE-SEM (JSM-7610F, Jeol, Japan), respectively. The IR spectra were investigated in the range of 4,000-400 cm^{-1} and images of FE-SEM were taken at 500x magnification. The specimens for FTIR analysis were arranged in pellet form by uniformly mixing the adsorbent and KBr reagent and compressing the mixture.

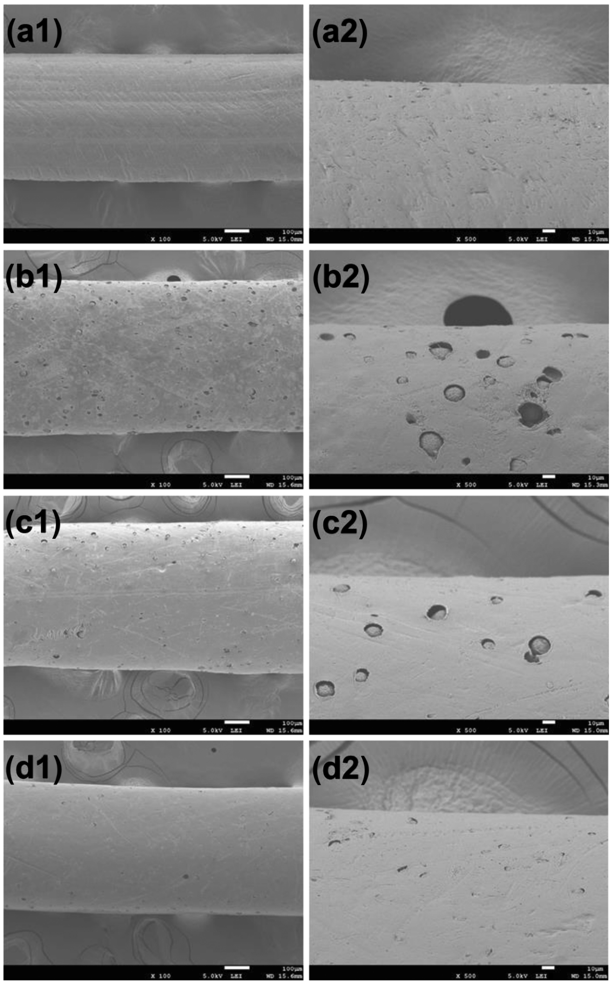

Fig. 1. SEM images of (a) PSBF, (b) 1-PEI-PSBF, (c) 2-PEI-PSBF, and (d) 3-PEI-PSBF at 100x and 500x magnification.

RESULTS AND DISCUSSION

1. Characterization of PEI Multi-coated PSBF

Fig. 1 shows the FE-SEM images of PSBF, 1-, 2-, and 3-PEI-PSBF observed at 100x and 500x magnification. Fig. 1(a) shows that *E. coli* biomass was well embedded in PS. On the other hand, 1-PEI-PSBF showed the entire surface covered by the PEI coating (Fig. 1(b)). Furthermore, due to the additional coating, the size and number of pores present on the surface of 2-PEI-PSBF were reduced (Fig. 1(c)). 3-PEI-PSBF displays a smooth surface that was different from 1-PEI-PSBF and 2-PEI-PSBF (Fig. 1(d)). As a result, significant surface changes of PSBF were observed as the number of PEI coatings increased.

FT-IR analysis was conducted to validate the differences of PSBF, 1-PEI-PSBF, 2-PEI-PSBF, and 3-PEI-PSBF, and the result is shown in Fig. 2. The peaks at 1,015 and 1,489 cm^{-1} (aromatic group), 1,244 cm^{-1} (S=O), and 1,151 cm^{-1} (C-SO_2-C and C-O-C) are the signature peaks of polysulfone matrix of the adsorbent [18]. The peak at 1,080 cm^{-1} denotes the extending vibration of P-OH in the *E. coli* biomass [18]. The broad peak at 3,435 cm^{-1} represents the O-H and N-H extending vibration of amine and hydroxyl groups [19]. In addition, the peak at 1,575 cm^{-1} was attributed to N-H extending vibration of N-H group [19]. The peak observed at 2,925 cm^{-1} was allocated to the displacement vibration of C-H and -CH_3 symmetric stretch of -CH_2 [20]. The peak at 1,655 cm^{-1} was attributed to extending vibrations of C=O/C-N groups [18]. The intensity of the peaks at 3,435, 2,925, and 1,655 cm^{-1} was enhanced

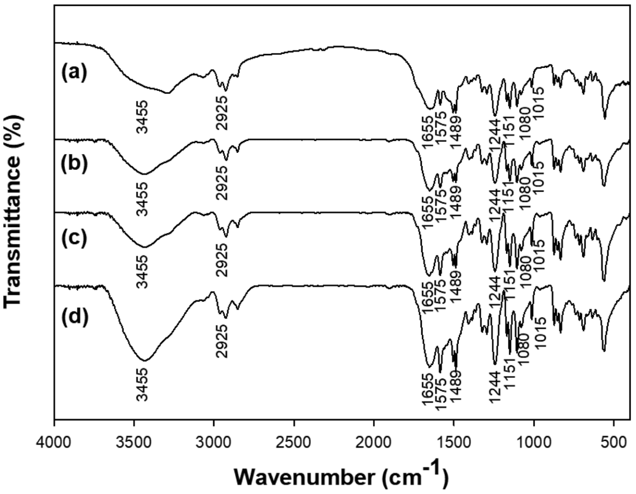

Fig. 2. FT-IR spectra of (a) PSBF, (b) 1-PEI-PSBF, (c) 2-PEI-PSBF, and (d) 3-PEI-PSBF.

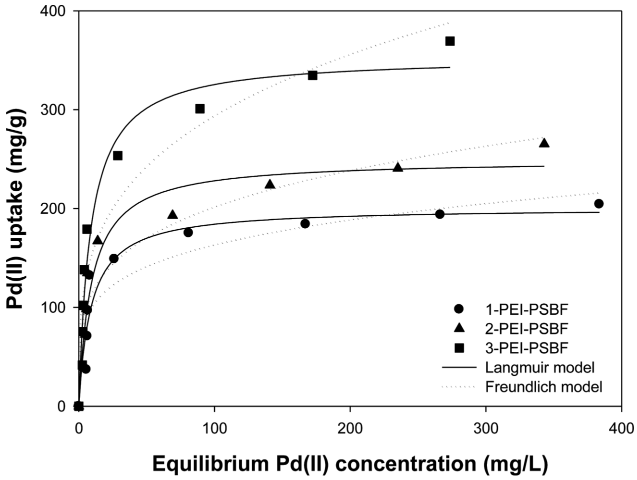

Fig. 3. Langmuir and Freundlich isotherm models for Pd(II) adsorption onto 1-, 2-, and 3-PEI-PSBFs (Experimental conditions: volume of solution, 30 mL; mass of adsorbent, 20 mg; initial Pd(II) concentration range, 30-500 mg/L).

Table 1. Isotherm parameters for Pd(II) adsorption by 1-, 2-, and 3-PEI-PSBFs

Isotherm model	Parameter	1-PEI-PSBF	2-PEI-PSBF	3-PEI-PSBF
Langmuir	q_{max} (mg/g)	193.56	241.10	324.17
	b_L (L/mg)	0.121	0.105	0.118
	R^2	0.907	0.902	0.918
Freundlich	K_F (L/g)	63.64	63.54	72.30
	1/n	0.199	0.243	0.287
	R^2	0.862	0.886	0.938

after each coating step, indicating that more PEI was introduced to PSBF surface along with the coating process [18,20]. The results of FT-IR analysis revealed that PEI was located to the surface of PSBF in each step.

2. Adsorption Isotherms and Modeling

To evaluate the adsorption process and the adsorption capacity of Pd(II) at the sites of 1-, 2-, and 3-PEI-PSBF, adsorption isothermal experiments were performed. The experimental results are indicated in the Fig. 3 and reported using the Langmuir and Freundlich models, respectively. In general, these two models are used to predict the maximum amount that is difficult to obtain experimentally. The Langmuir and Freundlich models can be expressed as:

$$\text{Langmuir model: } q_e=\frac{q_{max}b_LC_e}{1+b_LC_e} \tag{7}$$

$$\text{Freundlich model: } q_e=K_FC_e^{1/n} \tag{8}$$

where q_e (mg/g) represents the amount of Pd(II) adsorbed at equilibrium, C_e (mg/L) represents the concentration of Pd(II) remaining, and q_{max} (mg/g) is the maximum adsorption amount. b_L (L/g) is Langmuir constant which is related to the adsorption free energy. K_F (L/g) and n are Freundlich constant and Freundlich exponent, respectively. Coefficient of determination (R^2) values and each parameters of models are summarized in Table 1. Based on the higher R^2 values, the Langmuir model was better suited to fit the isotherm experimental data than the Freundlich model.

The maximum 1-, 2-, and 3-PEI-PSBF uptakes were estimated to be 193.56, 241.10, and 324.17 mg/g, respectively, according to the Langmuir model. The equilibrium constant (b_L) values of Langmuir model were 0.121, 0.150, and 0.118 L/mg for 1-, 2-, and 3-PEI-PSBF, respectively. Note that the Pd(II) ions adsorbed by 3-PEI-PSBF are 1.7-times higher than 1-PEI-PSBF in 0.1 M HCl solution. Moreover, in the case of the Freundlich constant (K_F) related to adsorption amount, 3-PEI-PSBF was 72 L/g, indicating a higher K_F value than that of the other 1- and 2-PEI-PSBF. These results show that the adsorption amount can be successfully improved by repeatedly coating PEI on the surface of the PSBF. The Freundlich constant (n), which represents the adsorption intensity, has been reported to be an effective adsorption operation in the range of $0<1/n<1$. When the 1/n value approaches 0, the adsorption intensity increases, but if it is higher than 1, cooperative adsorption appears [21]. As can be seen in Table 1, 1/n values of 1-, 2-, and 3-PEI-PSBF were 0.199, 0.243, and 0.287, respectively, and all values were in the range of $0<1/n<1$. However, as PEI coating increased from 1 to 3, the value of 1/n slightly increased from 0.199 to 0.287.

The maximum adsorption amount of 3-PEI-PSBF for Pd(II)

Table 2. Comparison of the adsorption capacity for Pd(II) in various sorbents

Sorbents	q_{max} (mg/g)	HCl-controlled solution	Ref.
p-Sulfonatothiacalix[6]arene-loaded IRA-400	303.0	pH 4.0	[22]
p-Sulfonatothiacalix[6]arene-loaded IRA-411	289.0	pH 4.0	[22]
p-Sulfonatothiacalix[6]arene-loaded XAD-7	134.7	pH 4.0	[22]
Cyphos IL-101-immobilized capsule	120.9-140.9	0.1-1 M HCl	[23]
PEI-modified *Corynebacterium glutamicum* biomass	176.8	0.1 M HCl	[19]
β-Cyclodextrin grafted chitosan cross-linked glutaraldehyde	202.02	pH 6.0	[24]
PSBF	30.8	0.1 M HCl	[9]
PEI-PSBF	216.9	0.1 M HCl	[9]
1-PEI-PSBF	193.56	0.1 M HCl	This work
2-PEI-PSBF	241.10	0.1 M HCl	This work
3-PEI-PSBF	324.14	0.1 M HCl	This work

adsorption was compared with several other sorbents published in the literature (Table 2). The PSBF and PEI-PSBF prepared in a slightly different method from this study had the maximum uptake, 30.8 and 216.9 mg/g for Pd(II), respectively [9]. On the other hand, 3-PEI-PSBF showed a 1.49-fold improvement in adsorption capacity compared to the previous reported PEI-PSBF, which means that the adsorption performance can be improved by repeated PEI coating. In addition, 3-PEI-PSBF showed significantly better Pd(II) adsorption amount than other biosorbents/resins such as PEI-modified *Corynebacterium glutamicum* biomass (176.8 mg/g) [19], *p*-Sulfonatothiacalix[6]arene (**1**)-impregnated resins (**1**IRA-400 (303.0 mg/g), **1**IRA-411 (289.0 mg/g), **1**XAD-7 (134.7 mg/g)) [22], Cyphos IL-101-immobilized capsule (120.9-140.9 mg/g) [23], and *β*-cyclodextrin grafted chitosan (202.02 mg/g) [24]. Therefore, 3-PEI-PSBF could be considered as an appropriate sorbent for Pd(II) adsorption in strongly acidic wastewater.

3. Adsorption Kinetics and Modeling

Adsorption rate is a key factor determining the efficacy of the whole adsorption process, gaining scientific insight into the adsorption mechanism. The effect of contact time was evaluated in order to find the equilibrium time of Pd(II) adsorption on 1-, 2-, and 3-PEI-PSBF. The experiment was performed for 9 h at 25 °C with an initial Pd(II) concentration of 100 ppm. As shown in Fig. 4, all three adsorbents reached more than 90% of the equilibrium within 100 min and eventually reached equilibrium by 300 min. Interestingly, adsorbents with a higher number of PEI coatings reached equilibrium faster. This suggests that repetitive PEI coating significantly increases the number of binding groups, such as amine, on the PSBF surface and thus improves the Pd(II) adsorption rate.

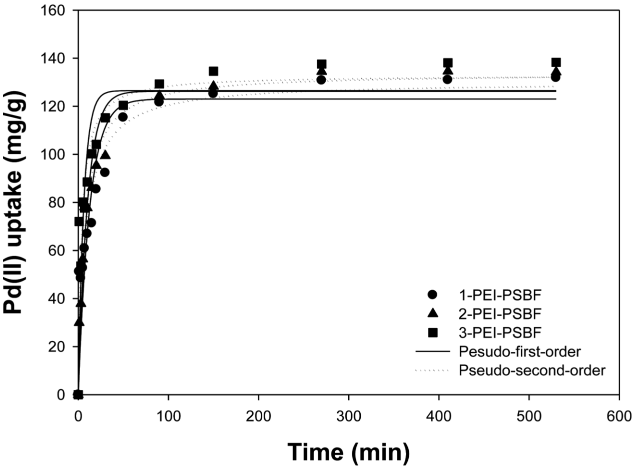

Fig. 4. Pseudo-first- and pseudo-second-order kinetic models for Pd(II) adsorption onto 1-, 2-, and 3-PEI-PSBFs (Experimental conditions: volume of solution, 30 mL; mass of adsorbent, 20 mg; initial Pd(II) concentration, 100 mg/L).

Equilibrium adsorption data is described by the pseudo-first-order and pseudo-second-order kinetic models. The non-linear forms of these models can well be expressed as follows:

$$\text{Pseudo-first-order kinetic model: } q_t = q_1(1 - \exp(-k_1 t)) \tag{9}$$

$$\text{Pseudo-second-order kinetic model: } q_t = \frac{q_2^2 k_2 t}{1 + q_2 k_2 t} \tag{10}$$

In the above formula, q_t (mg/g) is the Pd(II) uptake at time t, and q_1 and q_2 (mg/g) are the Pd(II) uptake at equilibrium. k_1 (L/min) and k_2 (g/mg·min) are the rate constants of pseudo-first- and pseudo-second-order kinetic models, respectively. The initial sorption rate, h (mg/g min), at t→0 is defined as Eq. (11):

$$h = k_2 q_2^2 \tag{11}$$

The kinetic model's parameters R^2 values and h are presented in Table 3. The R^2 values of 1-, 2-, and 3-PEI-PSBF by the pseudo-second-order model were 0.986, 0.987, and 0.886, respectively, which were higher than the R^2 values (0.946, 0.942, and 0.794) by the pseudo-first-order model. In addition, the q_2 values for 1-, 2-, and 3-PEI-PSBF were close to the experimental q_{exp} (131.8, 134.6, and 138.3 mg/g) when compared with q_1. The kinetic pseudo-second-order model can be predicted by the adsorption behavior throughout the whole research [25]. Furthermore, the h value of 3-PEI-PSBF was calculated to be 37.19 mg/g·min, which was 2.9 and 1.5-times higher than that of 1-PEI-PSBF (12.51 mg/g·min) and 2-PEI-PSBF (18.10 mg/g·min). It was also confirmed that PEI multi-coated adsorbent had a faster initial adsorption rate than PSBF (9.28 mg/g·min) [9], **1**IRA-400 (9.149 mg/g·min), **1**IRA-411 (7.634 mg/g·min), and **1**XAD-7 (2.695 mg/g·min) [23]. Therefore, the PEI multi-coating can highly enhance the adsorption rate by introducing more ligand-binding sites on the adsorbent surface.

4. Reusability of PEI Multi-coated PSBF

Adsorbent reusability is an important property required for promising adsorbents. If an exhausted adsorbent can be reused, the replacement cycle of an adsorbent becomes longer and economical profit can be also obtained. The adsorption/desorption cycle kinetic experiments were repeated at 100 ppm of the initial Pd(II) concentration for 3-PEI-PSBF, showing the best adsorption performance, up to three times. As shown in Fig. 5(a), the Pd(II) uptake

Table 3. The parameters of kinetic models for Pd(II) adsorption by 1-, 2-, and 3-PEI-PSBFs

Kinetic model	Parameter	1-PEI-PSBF	2-PEI-PSBF	3-PEI-PSBF
Pseudo-first-order	q_1 (mg/g)	124.94	126.73	126.52
	k_1 (L/min)	0.0670	0.0939	0.1597
	R^2	0.946	0.942	0.794
Pseudo-second-order	q_2 (mg/g)	133.67	134.55	133.08
	k_2 (g/mg·min)	0.0007	0.0010	0.0021
	R^2	0.986	0.987	0.886
	h (mg/g·min)	12.51	18.10	37.19

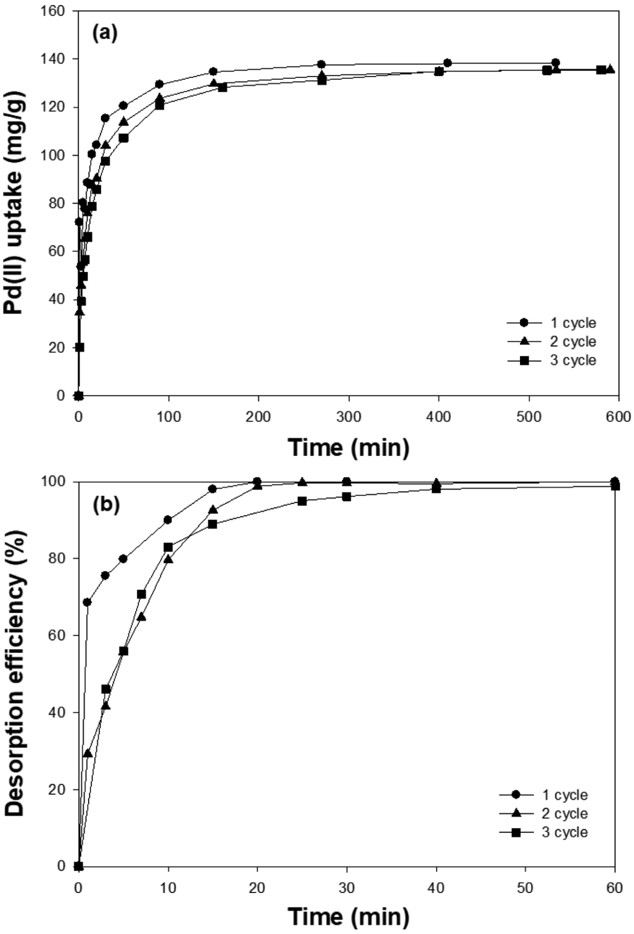

Fig. 5. Repeated adsorption (a) and desorption (b) kinetics of Pd(II) on 3-PEI-PSBF in a batch process (Experimental conditions: (a) volume of solution, 30 mL; mass of adsorbent, 20 mg; initial Pd(II) concentration, 100 mg/L, (b) volume of solution, 30 mL; mass of adsorbent, 20 mg; desorption eluent, 10 mM thiourea-0.1 M HCl).

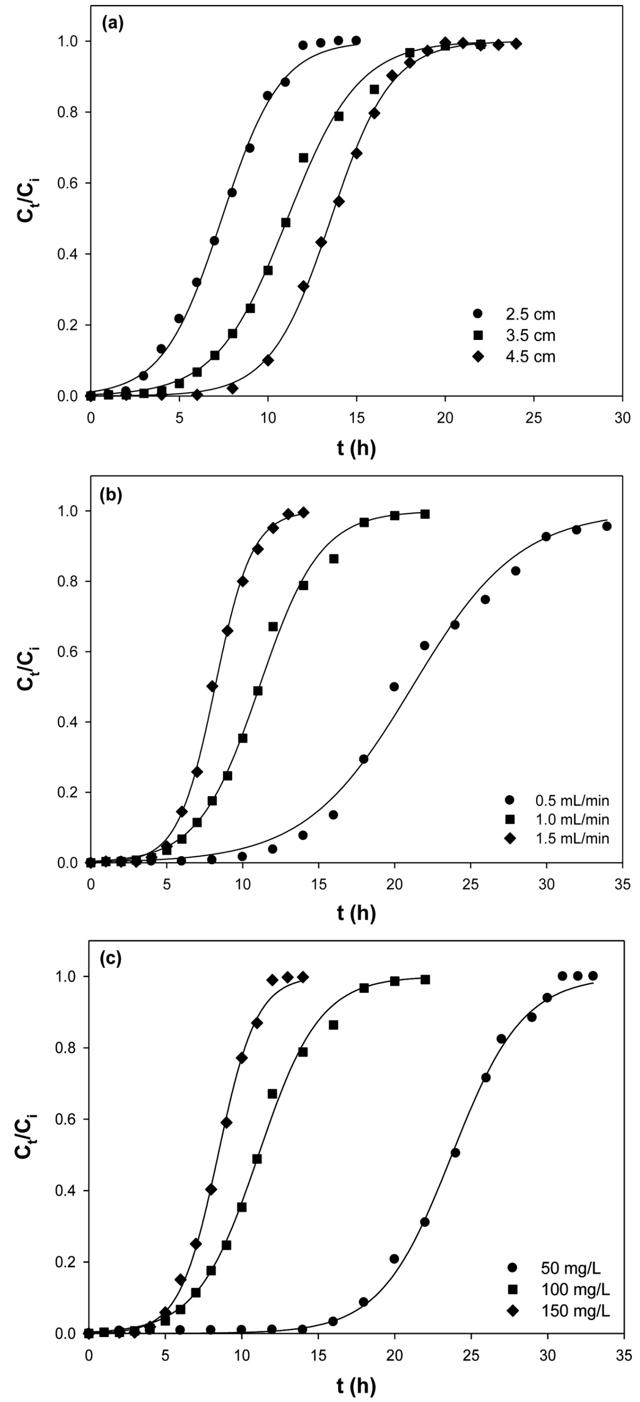

Fig. 6. Effects of fixed-bed column height (a), flow rate (b), and initial concentration (c) on Pd(II) adsorption by 3-PEI-PSBF in a column system. The solid lines are the breakthrough curves predicted by the Thomas model (Experimental condition: (a) bed height, 2.5-4.5 cm; flow rate, 1 mL/min; initial Pd(II) concentration, 100 mg/L, (b) bed height, 3.5 cm; flow rate, 0.5-1.5 mL/min; initial Pd(II) concentration, 100 mg/L, (c) bed height, 3.5 cm; flow rate, 1.0 mL/min; initial Pd(II) concentration, 50-150 mg/L).

was almost constant at 138.3, 135.5, and 135.3 mg/g during the three cycles. Adsorption equilibrium also was reached within 300 min. However, the slope of the initial adsorption rate became somewhat gentle as the number of adsorption cycles increased.

Acidified thiourea solution is effective in desorbing Pd from the loaded adsorbent. The desorption process involved in thiourea is pH dependent [26], and at neutral pH, thiourea forms coordination bonds with metal ions, but at acidic pH, it is known to desorb via anion exchange mechanism with $PdCl_4^{2-}$ [27]. Thus, a mixture of 0.1 M HCl and 10 mM thiourea was used as the eluant for desorption kinetic experiments. Fig. 5(b) shows the results of desorption kinetic experiments over three cycles. More than 85% of Pd from Pd-loaded 3-PEI-PSBF was desorbed within 20 min, and a desorption efficiency of nearly 100% was reached after 40 min. Desorption equilibrium took 20, 25, and 60 min for the first, second and third desorption experiments, respectively. Similar to the adsorption results, in the desorption experiments, the rate of desorption tended to be slightly slower as the desorption cycle was repeated. However, the adsorption/desorption rate of 3-PEI-PSBF was included in the very fast side, and the adsorbent maintained excellent results during the three repeated adsorption-desorption cycles.

5. Fixed-bed Column Studies

Bed column height, flow rate, and initial concentration are essential factors that affect the sorption performance (e.g., adsorption capacity, breakthrough time, and saturation time) of 3-PEI-PSBF for Pd(II) in continuous flow column systems. The dynamic adsorption behavior was investigated via modulating bed depth (2.5, 3.5, and 4.5 cm), flow rate (0.5, 1.0, and 1.5 mL/min), and initial concentration (50, 100, and 150 ppm), and the breakthrough curves are displayed in Fig. 6. The simulation of breakthrough curves was also applied to the Thomas model. Breakthrough curves at faster flow rate, smaller bed height, and higher initial concentration showed steeper slopes, implying earlier breakthrough and saturation of the fixed-bed columns. The breakthrough curves of Pd(II) adsorption onto 3-PEI-PSBF at different fixed-bed column height are expressed in Fig. 6(a). While the depth of bed increased 2.5-4.5 cm, the breakthrough curve and saturation time increased, the experimental Pd(II) uptake (153.2, 164.97 and 156.35 mg/g) was little different. Fig. 6(b) exhibits the breakthrough curves at the flow rate of 0.5, 1.0, and 1.5 mL/min. As the flow rate increased from 0.5-1.0 mL/min, both of breakthrough and saturation times were significantly reduced, but further increase in the flow rate had little effect on reducing the penetration and saturation time. The experimental Pd(II) adsorption amount at 0.5 and 1.0 mL/min of flow rates was similar to 154.52 and 164.97 mg/g. However, the Pd(II) uptake increased to 183.07 mg/g as the flow rate increased to 1.5 mL/min. The influence of initial Pd(II) concentration (50, 100, and 150 ppm) on the breakthrough curves is illustrated in Fig. 6(c). It is shown that the breakthrough period and saturation period decreased significantly as the initial concentration increased from 50-100 ppm, but only slightly decreased as the initial concentration continued to increase to 150 ppm. The experimental Pd(II) adsorption capacity was 197.15, 164.97, and 192.60 mg/g, respectively, for initial concentration of 50, 100, and 150 ppm. Using the Thomas model the experimental results were modeled and the measured parameters are shown in Table 4. The R^2 values of Thomas model were larger than 0.9915. The calculated Pd(II) uptakes were also close to the experimental results. These facts indicate that the Thomas model is suitable for a fixed-bed column system to describe the adsorption of Pd(II) on 3-PEI-PSBF.

Reusability is another important factor affecting the practical application of adsorbents and an important feature of a promising adsorbent. A regeneration study was performed in a fixed-bed column at 3.5 cm bed depth, 100 ppm Pd(II) solution, and 1.5 mL/min flow rate. After adsorption, the exhausted 3-PEI-PSBF was regenerated using an acidic thiourea solution (0.1 M HCl+10 mM thiourea) at the same flow rate. After each adsorption/desorption process, the column was washed with 0.1 M HCl until the Pd(II) concentration in effluent water reached 0 mg/L. The adsorption-desorption process was conducted for ten cycles and the results are displayed in Fig. 7. Fig. 7(a) depicts the results of 10 adsorption, showing that the adsorption amount of 3-PEI-PSBF for Pd(II) can

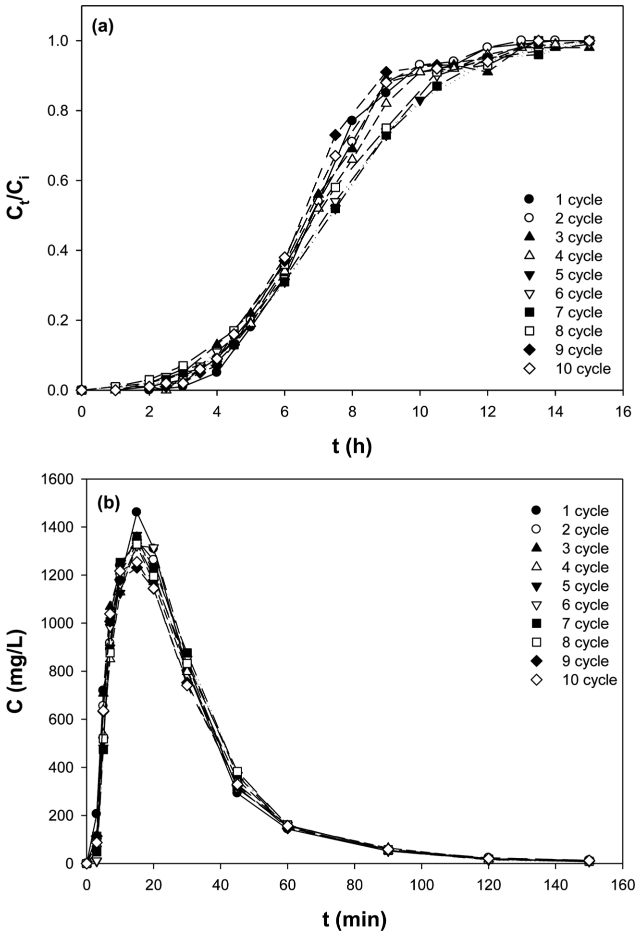

Fig. 7. Repeated adsorption (a) and desorption (b) curves of Pd(II) on 3-PEI-PSBF in a fixed-bed column (Experimental conditions: (a) bed height, 3.5 cm; flow rate, 1.5 mL/min; initial Pd(II) concentration, 100 mg/L, (b): bed height, 3.5 cm; flow rate, 1.5 mL/min, desorption eluent, 10 mM thiourea-0.1 M HCl).

Table 4. The parameters of Thomas model at different experimental conditions

Z (cm)	Q (mL/min)	C_i (mg/L)	M (g)	q_0 (mg/g)	K_{Th}	R^2
2.5	1	100	0.285	210.59	0.0022	0.9971
3.5	1	100	0.4	164.20	0.0051	0.9969
4.5	1	100	0.514	156.36	0.0060	0.9991
3.5	0.5	100	0.4	196.35	0.0038	0.9915
3.5	1.5	100	0.4	238.79	0.0032	0.9986
3.5	1	50	0.4	197.50	00077	0.9981
3.5	1	150	0.4	192.86	0.0052	0.9981

be maintained for more than ten cycles without significant decrease. The results of ten desorption process are demonstrated in Fig. 7(b). According to the results, desorption was almost complete in 60 min. In the initial 20 min, the effluent Pd(II) concentration was very high, a property which can be beneficial to Pd(II) recovery. The decrease in adsorption and desorption efficiencies during ten cycles was negligible below 3.5%. Therefore, 3-PEI-PSBF can be considered as a promising adsorbent that can be used for Pd(II) recovery in fixed-bed column processes.

CONCLUSION

PEI-M-PSBF was prepared by using the PEI multi-coating technique to further enhance the Pd(II) adsorption performance of the previously reported PEI-PSBF. The surface change of the adsorbents according to the number of PEI coatings was clearly proved through FE-SEM and FT-IR analysis. From batch experiments, the maximum Pd(II) adsorption amount of 1-, 2-, and 3-PEI-PSBF was evaluated to be 193.56, 241.10, and 324.17 mg/g, respectively, and 3-PEI-PSBF showed 1.7-fold higher adsorption capacity than 1-PEI-PSBF in 0.1 M HCl solution. In addition, the h value of 3-PEI-PSBF was 37.19 mg/g·min, which was 2.9 and 1.5 times higher than that of 1-PEI-PSBF (12.51 mg/g·min) and 2-PEI-PSBF (18.10 mg/g·min). The column breakthrough curves were explained using the Thomas model. Pd(II) adsorption process by developed biosorbent was impacted by initial concentration, flow rate, and column depth, increasing breakthrough time as initial concentration decreased, flow rate slowed, and column depth increased. The reusability study demonstrated that 3-PEI-PSBF can be reused at least ten times without reducing the adsorption capacity. In conclusion, applying the PEI multi-coating technique to the surface of the PSBF can provide more amine groups, which can also dramatically improve the adsorption ability of the Pd(II) adsorbent in acidic solutions.

ACKNOWLEDGEMENTS

This work supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (2020R1F1A1065937).

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