Removal of Pb(II) using Polyethylenimine-Crosslinked Polyvinyl Chloride Fiber

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Heavy metals such as Pb(II) are toxic to ecosystems and humans, and removing heavy metals from water has always been a hot issue. Polyvinyl chloride (PVC) is a widely used synthetic polymer, however, the disposal of waste PVC is still challenging. In this study, polyethylenimine-crosslinked PVC fiber (PEI-PVCF) was developed to remove Pb(II) from aqueous solutions, which not only helps to remove heavy metals, but also provides a possible method for the recycling of waste PVC. The FTIR analysis verified that the PEI was successfully crosslinked with PVC. The effect of pH, contact time, and initial concentration on the adsorption of Pb(II) by PEI-PVCF were evaluated. Through the pH effect experiment, pH 6 was determined as the most suitable pH for Pb(II) removal from aqueous solutions. The isotherm experimental data was well explained by Langmuir model and the maximum Pb(II) uptake was evaluated to be 233.3 mg/g. Pseudo-second-order kinetic model well described the adsorption kinetic data of Pb(II) on PEI-PVCF. The adsorption equilibrium was reached within 120 min at all initial concentrations evaluated. Besides, intraparticle diffusion model proved multiple rate-limiting steps involved in Pb(II) adsorption process. As a result, PEI-PVCF can be considered as a promising adsorbent for Pb(II) removal due to its low cost, high adsorption capacity, and short adsorption equilibrium time.

1. Introduction

Lead (Pb) is a highly toxic heavy metal that exist in wastewater released during various industrial processes (Chen et al., 2020). The discharge of Pb(II)-containing wastewater into aquatic systems will not only harm the aquatic organisms but also pose a significant risk to human health (Lyu et al., 2021). It has been proved that prolonged exposure to Pb not only causes reproductive problems, affects embryonic development, but also has teratogenic, carcinogenic, and mutagenic effects (Zhang et al., 2021). Therefore, there is an urgent need to remove Pb(II) from wastewater/aqueous solution before it is discharged into water bodies.

Various technologies have been adopted to remove heavy metals from wastewater, of which, adsorption has the advantages of cost-effectiveness, simple operation, and high efficiency, and is considered as one of the most promising methods (Deng et al., 2017). Traditional adsorbents such as activated carbon have been applied for heavy metals removal, however, they are relatively expensive (Zhang et al., 2020). Many researchers have focused on the development of novel adsorbents based on low-cost materials such as industrial wastes (Lyu et al., 2021) and natural wastes (Li et al., 2018).

Polyvinyl chloride (PVC) is an inexpensive and widely used synthetic polymer, but waste PVC is difficult to recycle, it is usually landfilled or incinerated (Liu et al., 2020). Since landfills occupy a large number of land resources and incineration may release highly toxic by-products such as dioxins (Liu et al., 2020). The development of a suitable method for recycling waste PVC is extremely important. It has been reported that PVC can be crosslinked with various amine-rich reagents (Singh et al., 2010). Sneddon et al. (2017) have reported several aminated PVC adsorbents for CO_2 capture. Even in our previous studies, polyethylenimine (PEI) crosslinked PVC has been successfully prepared for Pd(II) recovery (Choi et al., 2017) and reactive dye removal (Wang et al., 2021). However, studies on the removal of heavy metals have seldom been reported.

Therefore, in this work, we prepared PEI crosslinked PVC fiber (PEI-PVCF) and introduced it as an adsorbent for Pb(II) removal. The surface morphology of PEI-PVCF was recorded using a field emission scanning electron microscope (FE-SEM). The adsorption properties of the developed adsorbent for Pb(II) were evaluated through pH edge, isotherm, and kinetic experiments.

2. Materials and method

2.1 Materials

PVC (Mw = 80,000) was supplied by Sigma-Aldrich US Ltd. (St. Louis, US). PEI (Mw = 70,000, 50 % solution) was obtained from Habjung Moolsan Co., Ltd. (Seoul, Korea), and a certain amount of PEI was freeze-dried to remove the water content before use. N, N-Dimethylformamide (DMF, 99.5 %) and $Pb(NO_3)_2$ (331.21 g/mol, > 99.5 %) were supplied by Daejung Chemicals & Metals Co., Ltd. (Siheung, Korea). Other reagents such as HCl and NaOH used in this study were of analytical grade.

2.2 Preparation of PEI-PVCF

The method for preparing PEI-PVCF was modified based on our previous report (Wang et al., 2021). First of all, 10 wt% PVC and 20 wt% PEI solutions were prepared by dissolving a certain amount of PVC and PEI into 100 mL of DMF. Next, 10 mL of 10 wt% PVC and 10 mL of 20 wt% PEI were added to a 50 mL-flat bottom flask. The flask equipped with a reflux condenser was put in a water bath at 80 °C and magnetically stirred for 4 h to produce PEI-crosslinked PVC solution. Then, the synthesized polymer solution was cooled to 25 ± 1 ° C. Hereafter, the synthesized polymer solution was wet-spun into deionized water through a 30 G nozzle at 0.5 MPa to form PEI-PVCF. To remove any residuals, the prepared PEI-PVCF was washed for 24 h in deionized water. For comparison analysis, the PVC fiber (PVCF) was prepared by directly wet spinning 10 wt% PVC solution into water. Finally, the PVCF and PEI-PVCF were dried using a vacuum freeze-dryer (HC-4100, GYROZEN Co., Ltd., Korea) for 36 h, and then stored in a desiccator for further use.

2.3 FE-SEM analysis

The surface morphologies of PVCF and PEI-PVCF were observed on FE-SEM (JSM-7610F, Jeol, Japan). The FTIR spectra of PVCF and PEI-PVCF were recorded by FTIR spectrometer (Nicolet IS50, Thermo Fisher, USA).

2.4 Batch adsorption experiments

Batch adsorption experiments were performed to assess the adsorption performance of Pb(II) on PEI-PVCF. In all batch experiments, 30 mL of Pb(II) solution was mixed with 10 mg of PEI-PVCF and agitated at 160 rpm and 25 °C. pH edge experiments were carried out at pH 2–6 under 100 mg/L of initial Pb(II) solution for 24 h. The pH of Pb(II) solution was adjusted using 1 mol/L HCl and NaOH solutions. Isotherm experiment was performed in the range of 30 to 300 mg/L of initial Pb(II) concentration at pH 6 for 24 h. Adsorption kinetic experiments were performed for 420 min in 50, 100, and 200 mg/L of Pb(II) solutions at pH 6, and samples were collected at regular time intervals. The Pb(II) concentrations were analyzed using ICP-OES (Avio 200, PerkinElmer, USA). The Pb(II) uptake q (mg/g) was calculated using Eq(1).

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

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

3. Results and discussion

3.1 The surface morphology and FTIR spectra of PVCF and PEI-PVCF

The morphologies of PVCF and PEI-PVCF are demonstrated in Figure 1a-c. It can be observed that the surface of PVCF was smooth (Figure 1a), but the surface of PEI-PVCF was relatively rough and exists many large pores (Figure 1b). The cross-section image of PEI-PVCF (Figure 1c) demonstrated that the inner structure of the PEI-PVCF was highly porous. The high porosity provides a fast path for Pb(II) ions to meet the internal binding sites, which can achieve a rapid adsorption rate and high adsorption capacity. Figure 1d displays the difference between the FTIR spectra of PVCF and PEI-PVCF. The peak at 613 cm^{-1}, assigned to C-Cl stretching vibration, was the characteristic peak of PVC (Choi et al., 2017). The peak at 2910 cm^{-1} was attributed to C-H stretching vibration of -CH$_2$ (Choi et al., 2017). After crosslinking with PEI, the peak at 2910 cm^{-1} was shifted to 2821 cm^{-1},which was due to the introduce of extra -CH$_2$ into PVC from PEI. In addition, new peaks at 3258 and 1659 cm^{-1}, corresponding to N-H stretching and bending vibrations of N-H, appeared

in the FTIR spectrum of PEI-PVCF (Wang et al., 2021). These findings confirmed that PEI has successfully crosslinked with PVC.
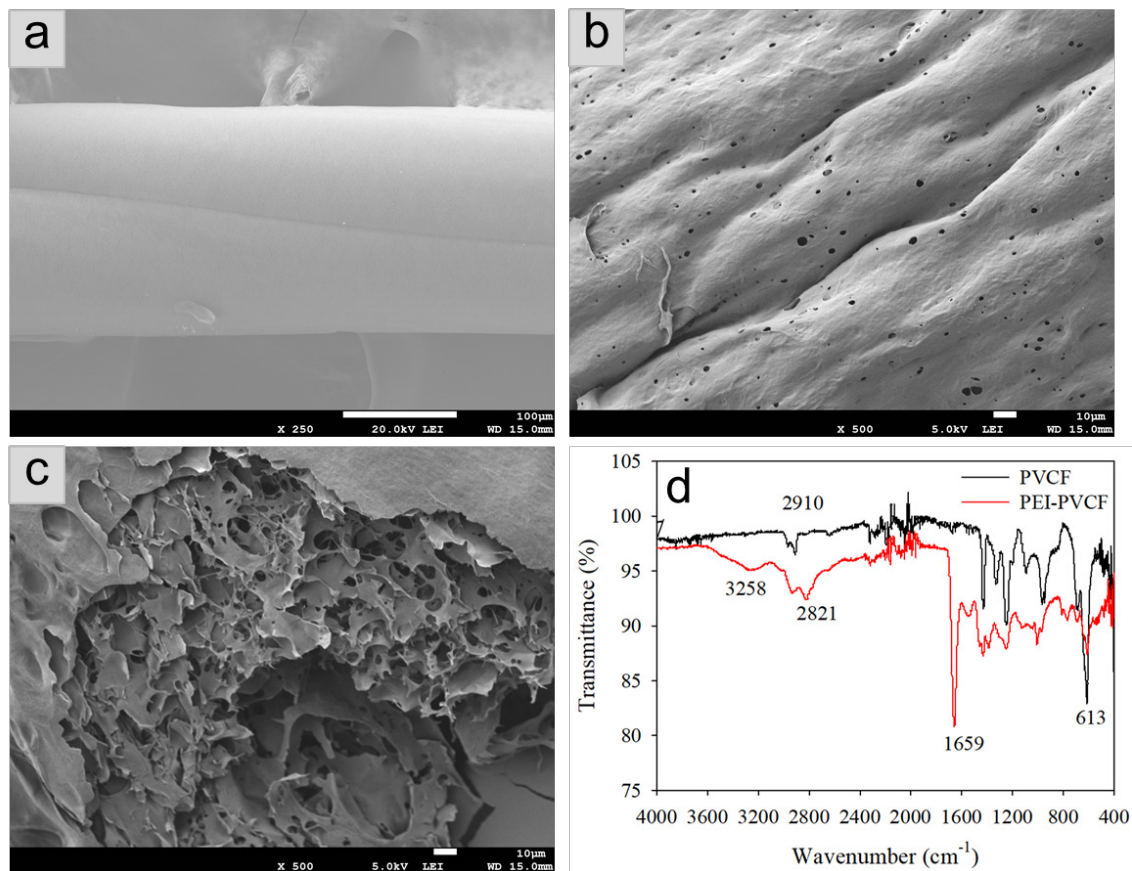

Figure 1: (a) Surface image of PVCF, (b) surface and (c) cross-section images of PEI-PVCF (× 500 magnification), and (d) FTIR spectra of PVCF and PEI-PVCF
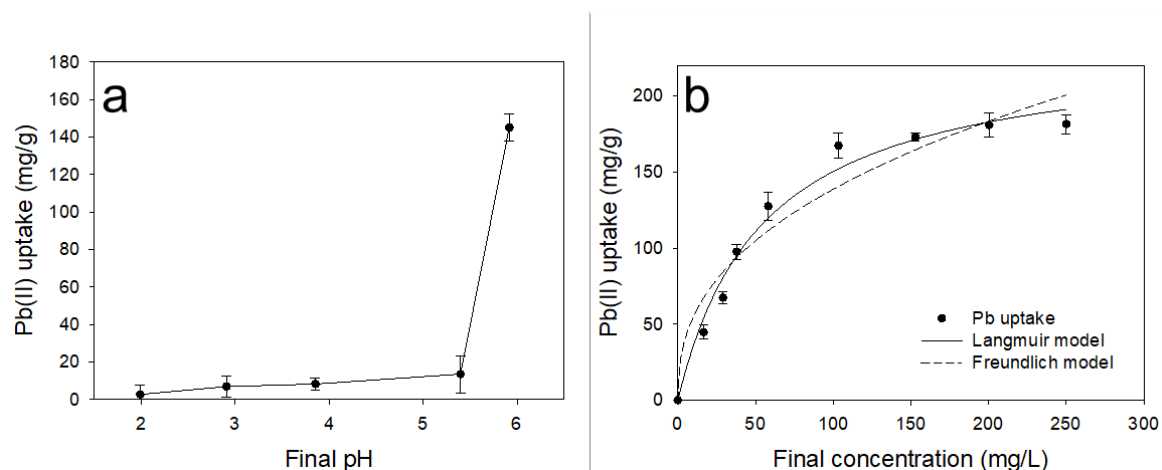
3.2 Effect of pH

Figure 2: (a) Effect of pH on the adsorption of Pb(II) by PEI-PVCF, (b) Adsorption isotherm of Pb(II) by PEI-PVCF

pH is a vital factor that affects the adsorption performance of adsorbents to adsorbates. The effect of pH on Pb(II) adsorption by PEI-PVCF was investigated over a pH range of 2 to 6 using 100 mg/L Pb(II) solution. As

displayed in Figure 2a, the Pb(II) uptake was very low in the pH range of 2 to 5.5, and the Pb(II) uptake increased slightly from 2.7 to 13.5 mg/g. However, when the pH was reached 6, the Pb(II) uptake dramatically increased to 145.1 ± 7.3 mg/g. At low pH, most of the amine groups are protonated, causing electrostatic repulsion with Pb(II) cations, resulting in low adsorption capacity (Li et al., 2018). As the pH rises, the protonated amine groups became deprotonated, which is favourable for them to co-ordinate with Pb(II) ion, leading to higher Pb(II) uptake (Deng et al., 2017). The sharply increased Pb(II) uptake was due to an increase in adsorption sites and a decrease in electrostatic repulsion, which agreed with the findings of Lyu et al. (2021). According to these facts, pH 6 was determined as the most suitable pH for the following adsorption experiments.

3.3 Batch adsorption isotherm

Adsorption isotherm was conducted to understand the adsorption performance of the adsorption process. The isotherm experimental results are presented in Figure 2b. The Langmuir and Freundlich models were applied to fit the isotherm experimental data. The Langmuir and Freundlich models are presented as Eq(2) and Eq(3).

Langmuir model: $q_e = \frac{q_{max}K_LC_e}{1+K_LC_e}$ (2)

Freundlich model: $q_e = K_F C_e^{1/n}$ (3)

where q_e and q_{max} are the equilibrium and maximum Pb(II) uptake (mg/g), C_e represents the Pb(II) concentration at equilibrium (mg/L), K_L (L/mg) and K_F (L/g) are the Langmuir and Freundlich constant, and n indicates the Freundlich exponent.

The data were analyzed by non-linear regression fitting and the corresponding parameters are listed in Table 1. According to Table 1, the R^2 value of the Langmuir model was larger than that of the Freundlich model, suggesting that the Langmuir model was more appropriate for explaining the adsorption of Pb(II) by PEI-PVCF. Besides, the adsorption of PEI-PVCF towards Pb(II) was monolayer adsorption (Zhou et al., 2018). The Langmuir constant K_L (0.018) is between 0 and 1, indicating the adsorption of Pb(II) on PEI-PVCF was favourable (Lyu et al., 2021). In addition, the 1/n value was 0.403 in the range of 0–1, suggesting chemisorption was the main controlling step in the adsorption process (Wang et al., 2020)

The separation factor R_L, which was used to depict the adsorption characteristics of the Langmuir model, was also calculated based on Eq(4).

Separation factor: $R_L = \frac{1}{1+K_LC_i}$ (4)

where C_i (mg/L) denotes the initial Pb(II) concentration. The R_L value represents the affinity between adsorbent and adsorbate, either irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), liner ($R_L = 1$) or unfavourable ($R_L > 1$). The calculated R_L values (0.152–0.639) were between 0 and 1, which further revealed that the adsorption of Pb(II) by PEI-PVCF was favourable at all studied initial concentrations (Deng et al., 2017).

Table 1: Model parameters for isotherms.

	Langmuir model				Freundlich model	
q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	1/n	K_F (mg/g)	R^2
233.3	0.018	0.152–0.639	0.982	0.403	21.7	0.938

3.4 Batch adsorption kinetics

The adsorption rate is a critical consideration when using adsorbents in practical applications (Zhou et al., 2018). To estimate the adsorption rate of Pb(II) by PEI-PVCF at different initial concentrations, kinetic experiments were carried out under 50, 100, and 200 mg/L of Pb(II) solutions, and the results are demonstrated in Figure 3. As illustrated in Figure 3a, the Pb(II) adsorption capacity and equilibrium time increased with the increase of the initial Pb(II) concentration. As the initial concentration rose from 50 to 200 mg/L, the adsorption equilibrium time increased from 100 to 120 min. For further understanding the adsorption performance, the kinetic experimental data were explained by pseudo-first-order (PFO) model (Eq(5)), pseudo-second-order (PSO) model (Eq(6)), and intraparticle diffusion model (Eq(7)) The equations are given below:

Pseudo-first-order kinetic model: $q_t = q_1\big(1 - exp(-k_1t)\big)$ (5)

Pseudo-second-order kinetic model: $q_t = \frac{q_2^2 k_2 t}{1+q_2 k_2 t}$ (6)

Intraparticle diffusion model: $q_t = k_3 t^{0.5} + C$ (7)

where q_t, q_1, and q_2 are the Pb(II) uptake (mg/g) at time t and adsorption equilibrium, k_1 (L/min), k_2 (g/(mg min)), and k_3 (mg/g/min$^{0.5}$) are the rate constant of PFO, PSO, and intraparticle diffusion models, and C (mg/g) is the intercept.

Table 2: Model parameters for kinetics.

Pb(II) (mg/L)	q_{exp} (mg/g)	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
		q_1 (mg/g)	k_1 (L/min)	R^2	q_2 (mg/g)	k_2 (g/mg min)	R^2	k_3 (mg/g/min$^{0.5}$)	C (mg/g)	R^2
50	70.1	65.0	0.0591	0.966	71.3	0.0011	0.990	10.005	-1.8	0.993
100	122.5	112.5	0.0592	0.985	123.3	0.0006	0.993	18.891	-9.5	0.989
200	203.7	183.3	0.0707	0.970	198.5	0.0005	0.987	28.447	2.7	0.993

Table 2 lists the corresponding parameters of the PFO and PSO models. The R^2 values of the PSO model were higher than that of the PFO model at 50–200 mg/L of initial Pb(II) concentrations. Furthermore, compared with that of the PFO model, the q_2 values calculated from the PSO model were closer to the experimental results (q_{exp}). These findings indicated that the PFO model was better for describing the adsorption kinetic of PEI-PVCF for Pb(II), and chemisorption was dominant during the adsorption process (Chen et al., 2020). The k_2 value was decreased from 0.0011 to 0.0005 as the initial concentration of Pb(II) increased from 50 to 200 mg/L. The smaller the k_2 value, the longer it takes to reach the adsorption equilibrium (Deng et al., 2017). Therefore, the reason why the time required to reach adsorption equilibrium increases with the increase of the initial Pb(II) concentration is due to the decrease of the k_2 value.

Generally, the adsorption process is mainly divided into three steps: (1) film diffusion; (2) intraparticle diffusion; (3) the adsorption of adsorbates on adsorbents (Wang et al., 2018). Considering that the PSO kinetic model cannot provide a comprehensive view of a series of different rate-controlling steps (Zhou et al., 2018). The intraparticle diffusion model was used to illustrate the possible rate-limiting step in the adsorption of Pb(II) by PEI-PVCF. As depicted in Figure 3b, the plots were divided into two distinct linear zones over the entire time range, revealing that the intraparticle diffusion process was negligible, which could be attributed to the large pores in PEI-PVCF as demonstrated in Figure 1b. Besides, the intercept C was not equal to 0 (Table 1), which means the plots were not passing through the origin, implying a fast intraparticle diffusion process (Li et al., 2019) and the rate controlling step was more than just intraparticle diffusion (Wang et al., 2018). Therefore, the intraparticle diffusion process was very fast that can be ignored, and other rate-controlling steps were participated in the adsorption process.
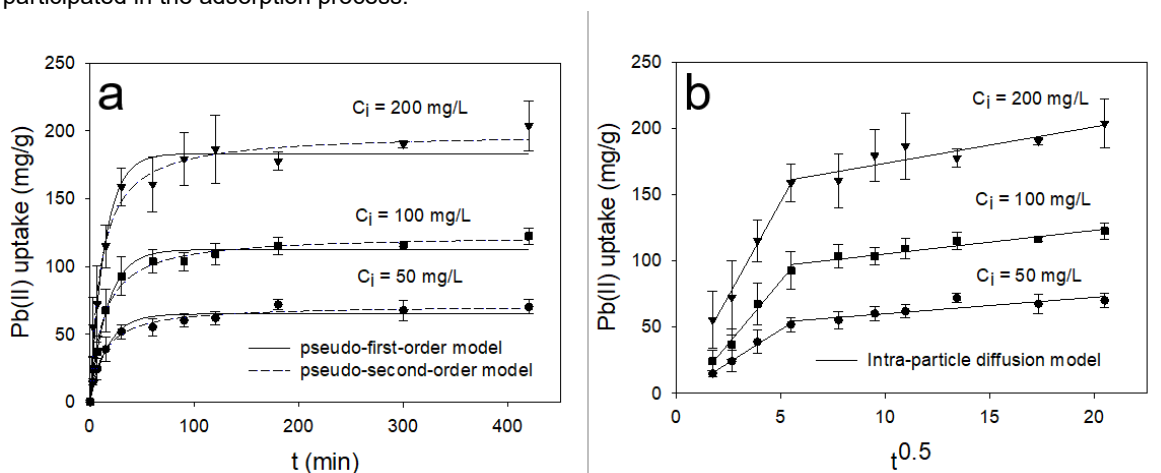

Figure 3: Plots of (a) adsorption kinetics and (b) intraparticle diffusion of Pb(II) onto PEI-PVCF at 50-200 mg/L of initial Pb(II) concentrations.

4. Conclusions

In this study, PEI-PVCF as a promising adsorbent for Pb(II) was successfully prepared via crosslinking, wet spinning, and freeze-drying processes. FE-SEM analysis revealed that the prepared fiber was highly porous, which contributed to the rapid adsorption rate and high adsorption capacity. FTIR spectra confirmed that the PEI-PVCF was successfully prepared. The pH edge experiment revealed that pH 6 was optimal for Pb(II) removal by PEI-PVCF. The adsorption isotherm was well explained by the Langmuir model, while the

adsorption kinetic was well described by pseudo-second-order model. In addition, the intraparticle diffusion model indicated that the Pb(II) adsorption process involved multiple rate-limiting steps. The maximum adsorption capacity of PEI-PVCF for Pb(II) measured by the Langmuir model was 233.3 mg/g. The adsorption equilibrium was reached within 120 min at 50 to 200 mg/L of initial Pb(II) solution. Overall, PEI-PVCF can serve as a promising adsorbent for Pb(II) removal.

Acknowledgments

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