

Preparation of Calixarene-PI Nanofibers and Application as a Selective Adsorbent for Heavy Metal Ions

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ABSTRACT

In order to utilize the adsorption selectivity of calixarenes towards heavy metal ions, calixarene functionalized polyimide (Calix-PI) fibers were prepared by three main synthesis procedures including preparation of the calixarene polyamide acid (Calix-PAA) spinning solution via amidation, fabrication of the Calix-PAA fibers by electrospinning, and preparation of the Calix-PI fibers via thermal imidization on the Calix-PAA fibers. The Calix-PI fibers were characterized by Fourier transform infrared spectroscopy, scanning electronic microscopy and thermogravimetric analysis. The Calix-PI fibers display selective adsorption on Pb(II), which is fit with the pseudo-second-order adsorption kinetics model and the Freundlich adsorption isothermal model. The rate constant of the pseudo-second-order adsorption kinetics model and the maximum Pb(II) uptake have all been calculated. The practical adsorption of Pb(II) on the Calix-PI fibers is mainly attributed to the monolayer chemical adsorption and slightly depended on the physical adsorption.

Keywords: Calixarene, Polyimide, Nanofibers, Adsorption

INTRODUCTION

Heavy metals eg., Pb, Hg, have been used extensively in various fields including the chemical, battery and electronic industries. However, heavy metals are noxious substances which cause diseases when consumed by humans [1-2]. Therefore, attention to recovery of heavy metals, especially from waste water, is of increasing importance.

Many methods for separating metal ions have been reported, such as solvent extraction [3], ion-exchange [4], membrane filtration [5] and adsorption [6-7]. Due to advantages such as low cost, high efficiency and easy regeneration, adsorption is considered to be one of the most feasible recovery methods.

Research concerning various adsorption materials, including chelating resin [4,8], ion-imprinted polymer [6] and various electrospun fibers such as the PAN/crown ether nanofibers [9], poly(NPEMA-co-CMPMA) electrospun fibers [10] and the cellulose acetate electrospun fibers [11] has been reported. However, the electrospun fibers mentioned above have certain limitations such as lower adsorption selectivity as well as weaker chemical and mechanical stability.

Calixarenes are well known for their adsorption selectivity towards heavy metal ions [12,13]. They can be prepared by ring-closing condensation of p-tert-butylphenol and formaldehyde under alkaline conditions. They are cyclic oligomers composed of phenol units. Calixarenes can be modified chemically on either the upper or the lower rim to obtain a wide range of various calixarene derivatives containing selected functional groups at desirable locations on the calixarene skeleton [14]. Due to unlimited derivative possibilities induced by their unique three-dimensional structure and their ability to form complexes with metal ions and neutral molecules, calixarenes are widely utilized in host-guest chemistry.

The incorporation of calixarenes into polymers can result in the development of ion-sorption materials. Polyimides are well known for their excellent chemical and mechanical stability as well as strong corrosion resistance. Some work has focused on the design and fabrication of calixarene nanofibers with polyacrylonitrile [15-16]. However, best effort investigation suggests that the fabrication of calixarene nanofibers with polyimide has not been reported.

Nanofibers are ultrafine solid fibers noted for their outstanding properties, including very small diameters, large surface area per unit mass, flexibility

for chemical functionalization and strong adsorption [17-18]. A number of techniques have been reported for preparation of nanofibers, such as electrospinning, phase separation, self-assembly and template polymerization. Among these techniques, electrospinning is an excellent way to produce continuous fibers with diameters ranging from micrometers to nanometers [19-20]. Furthermore, consistent production of electrospun nanofibers allows their application in numerous fields, such as filter media, semi-conductive materials and tissue engineering scaffolds [21-23].

This work describes the preparation of calixarene functionalized polyimide nanofibers (Calix-PI fibers) as well as their ion-sorption selectivity and morphology. Based on a two-step process for preparing polyimide nanofibers [24], a three-step process for preparing the Calix-PI fibers is set forth, including preparation of calixarene polyamide acid (Calix-PAA) solution, fabrication of Calix-PAA fibers via electrospinning and transformation of the Calix-PAA fibers to the Calix-PI fibers via thermal imidization. Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and thermogravimetric analysis (TGA) are utilized to characterize the Calix-PI fibers. The adsorption selectivity, kinetics and isotherms of the Calix-PI fibers absorbing Pb(II) are investigated.

EXPERIMENTAL

Materials

5,17-Diamino-26,28-(1',11'-dioxo-4',8'-dithiaoctane)-calix[4]arene (calixarene1) was synthesized in advance according to the literature [25]. 4,4'-Oxydiphthalic anhydride (ODPA, Aldrich) was used after heating at 180°C for 12 h in vacuum. Dimethylformamide (DMF), mercuric nitrate, lead nitrate and nitrate were purchased from Guoyao Chemical Reagents Company in China.

The Calix-PI fibers preparation process is depicted in Figure 1.

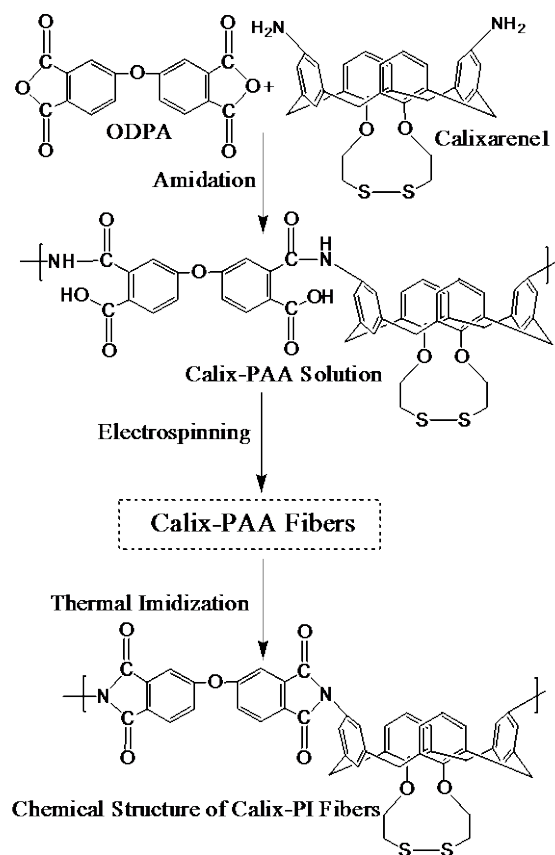


FIGURE 1. The Calix-PI fibers preparation process.

Preparation of Calix-PAA solution

The calixarene1 solution was prepared by dissolving the calixarene1 (2.7 g, 5 mmol) into 50 mL DMF under stirring. Then, ODPA (1.55 g, 5 mmol) was added so that an equimolar ratio of amino and anhydride groups was maintained in the amidation reaction system. The reaction was allowed to proceed at room temperature for 4 h.

Electrospinning

In the electrospinning process, the Calix-PAA solutions (15 wt%) were put into a plastic syringe fitted with a stainless steel needle of 0.7 mm inner diameter. Then, the syringe was placed into the electrospinning machine (NEC-10, Japan). The working distance between the needle tip and the aluminum-covered collector was 180 ± 10 mm. The electrospinning voltage was 20 ± 1 kV. The spinning solution flow rate was 0.6 ± 0.05 mL/h. After electrospinning for 4 h, the Calix-PAA random fibrous mats were pulled off and dried at room temperature in vacuum for 5 h.

Thermal Imidization

The Calix-PI fibers preparation was carried out through thermal imidization of the Calix-PAA fibers in a muffle furnace, where the thermal imidization temperature was raised to 330°C and held for 0.5 h.

Characterization

The morphologies of the Calix-PI and Calix-PAA fibers were observed using a SEM (Hitachi S-4800, Tokyo, Japan). All specimens were sprayed with gold prior to imaging and observed at a voltage of 5.0 kV. The infrared spectra of the Calix-PI and Calix-PAA fibers were obtained by FTIR (IR Prestige-21, Shimadzu, Japan). The thermal stability of the samples was analyzed by TGA (TG209F1, Netzsch, Germany). The thicknesses of 20 layers prepared fibrous mats were tested by Fabric Thickness Tester (YG141D, Fangyuan, China) according to American Society for Testing and Materials (ASTM D 1777-2007) standard, and then the thickness of monolayer fibrous mat could be calculated.

Adsorption Experiments

The adsorption experiments were performed by agitating 100 mL of metal ion solution with the Calix-PI and Calix-PAA fibers in glass bottles at 150 rpm under room temperature. In the selective adsorption experiment, multiple-ions solution (pH=1,3,5,7,9) contained 40 mg/L Pb(II) and 40 mg/L Hg(II). However, only Pb(II) as a single ion solution was used in the adsorption kinetics and isotherms experiments. For each sample, identical adsorption experiments were carried out for 9 h and repeated three times. The metal ions concentrations were measured by potentiometry with a Pb(II) or Hg(II) ion-selective electrode. The equilibrium uptake of metal ions, q_e (mg/g) was calculated by Eq. (1).

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where c_0 and c_e are the initial and equilibrium concentrations (mg/L) of metal ions, respectively, V is the volume of metal ions solution (L), and m is the mass of the Calix-PI or Calix-PAA fibers (0.02 g). The adsorption selectivity of the Calix-PI fibers was defined according to the literature [6] and calculated by Eq. (2) and Eq. (3).

$$K_d = \frac{q_e}{c_e} \quad (2)$$

$$\beta = \frac{K_{dPb(II)}}{K_{dHg(II)}} \quad (3)$$

where K_d is the distribution coefficient. q_e and c_e are the equilibrium uptake (mg/g) and equilibrium concentration (mg/L) of metal ions, respectively. β is the selectivity coefficient of Pb(II) in the presence of Hg(II). $K_{dPb(II)}$ and $K_{dHg(II)}$ are the distribution coefficients of Pb(II) and Hg(II), respectively.

RESULTS AND DISCUSSION

Morphology

The SEM images of the Calix-PAA and Calix-PI fibers are shown in *Figure 2*. The prepared fibers have smooth appearance and certain intensity. The thicknesses of monolayer Calix-PI fibrous mat and monolayer Calix-PAA fibrous mat are calculated as $40 \pm 7 \mu\text{m}$ and $42 \pm 8 \mu\text{m}$, respectively. Average diameters of the Calix-PI fibers ($440 \pm 105 \text{ nm}$) and the Calix-PAA fibers ($665 \pm 110 \text{ nm}$) are larger than the PAN/crown ether composite fibers (138 to 270 nm) [9] but thinner than the poly (NPMA-co-CMPMA) electrospun fibers (700 nm) [10].

The Calix-PAA fibers are crosslinked with each other, but the crosslink phenomenon is decreased for the Calix-PI fibers. Since the Calix-PAA solution absorbed water easily from the atmosphere, the volatilization of DMF was inhibited during electrospinning and the Calix-PAA fibers were accordingly crosslinked with each other. A similar phenomenon was reported previously [26]. However, due to the further volatilization of residual DMF in the Calix-PAA fibers and the release of water molecules during thermal imidization [24], the Calix-PAA fibers shrank gradually and were eventually converted into the Calix-PI fibers.

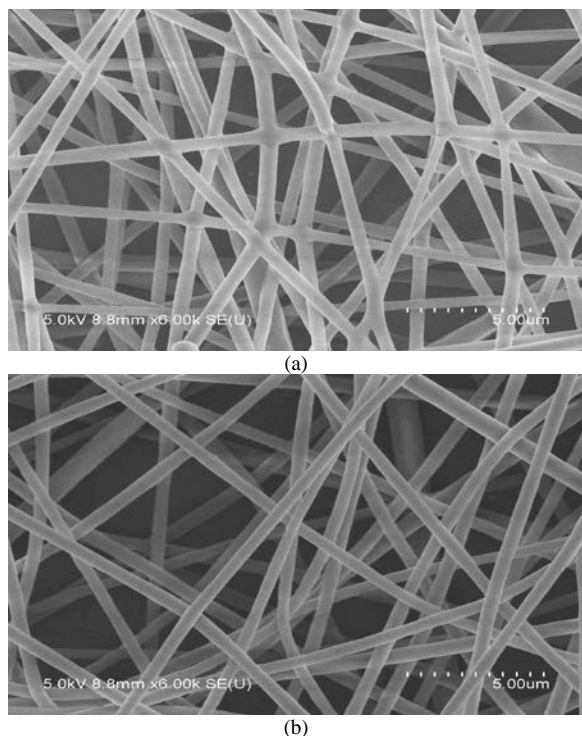


FIGURE 2. SEM images of the Calix-PAA fibers (a) and the Calix-PI fibers (b).

Structural Analysis

The FTIR spectra of the Calix-PAA and Calix-PI fibers are depicted in Figure 3. From Figure 3a, there is no symmetric carbonyl mode of a dianhydride at 1860 cm^{-1} , indicating that ODPAA has been consumed completely in amidation reaction. The stretching vibrations of the carbonyl at 1717 cm^{-1} and the hydroxyl in the range of $2500\text{--}3100\text{ cm}^{-1}$ correspond to the carboxyl. The stretching vibration of the carbonyl at 1641 cm^{-1} and the bending vibration of the secondary amino at 1536 cm^{-1} are the characteristic absorption bands of the amide [24]. The weak adsorption at 653 cm^{-1} is assigned to the C-S bond of the calixarene1 fragment in the Calix-PAA fibers [27].

From Figure 3b, two adsorption bands at 1779 cm^{-1} and 1722 cm^{-1} can be observed, which are assigned to the symmetric and the asymmetric carbonyl vibration modes of the imide [24]. The absorption at 1381 cm^{-1} is due to the stretching vibration of the C-N in imide. The C-S of the calixarene1 fragment in the Calix-PI fibers is found at 655 cm^{-1} . In addition, the absorption bands characterizing the amide disappear in Figure 3b.

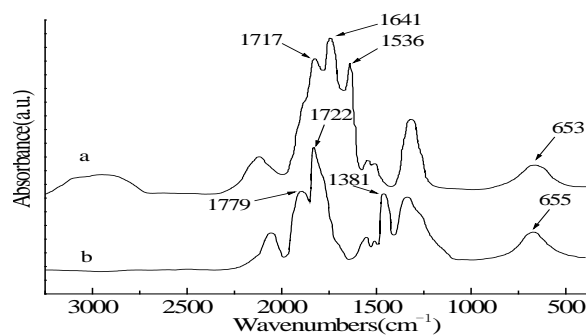


FIGURE 3. FTIR spectra of the Calix-PAA fibers (a) and the Calix-PI fibers (b).

Thermogravimetric Analysis

The thermal behaviors of the Calix-PAA and Calix-PI fibers are shown in Figure 4. From Figure 4a, the weight loss of the Calix-PAA fibers under the temperature ranging from 100 to 160°C is due to the evaporation of residual solvent. The weight loss from 300 to 500°C is caused by the side chain degradation of the Calix-PAA fibers. The rapid weight loss beginning at 500°C can be attributed to the main decomposition of the Calix-PAA fibers. From Figure 4b, the side chain degradation of the Calix-PI fibers is in the range $300\text{--}600^\circ\text{C}$. However, the major decomposition of the Calix-PI fibers begins at 600°C , suggesting that the Calix-PI fibers have better thermal stability than the Calix-PAA fibers. In addition, the Calix-PI fibers have the similar thermal stability as reported for neat PI nanofibers [24].

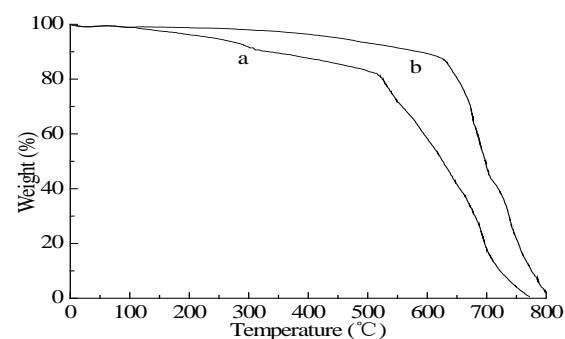


FIGURE 4. TGA curves of the Calix-PAA fibers (a) and the Calix-PI fibers (b).

Selective Adsorption

As shown in Figure 5, better adsorption is found in the neutral solution. At low pH, hydrogen ions may compete for adsorption with Pb(II) and Hg(II). However, Pb(II) and Hg(II) may precipitate under alkaline conditions, affecting the authenticity of data.

The Calix-PAA fibers can absorb Pb(II) and Hg(II), whereas only Pb(II) can be absorbed on the Calix-PI fibers. This phenomenon can be interpreted from two perspectives- the adsorption sites of the prepared fibers and the charge-radius ratio of the metal ions. There are two kinds of adsorption sites in the Calix-PAA fibers. The first type is the amide and its ortho position carboxyl; the second is 1,8-dioxo-4,5-dithia-octane attached in the calixarene fragment. However, due to the transformation of the amide and its ortho-position carboxyl to the imide in thermal imidization, the Calix-PI fibers only have the second kind of adsorption site and accordingly exhibit adsorption selectivity. The metal ion with higher charge-radius ratio is more stably coordinated with the same ligand. The values of charge-radius ratio for Pb(II) and Hg(II) are 1.96 and 1.82 respectively [28], thus the Calix-PI fibers adsorb more Pb(II).

The selectivity of the Calix-PI fibers for Pb(II) (pH=7) has been estimated using the selectivity coefficient β . The value of $\beta_{Pb(II)/Hg(II)}$ is 9.6, indicating that the Calix-PI fibers have high selective adsorption capacity on Pb(II) in the presence of Hg(II).

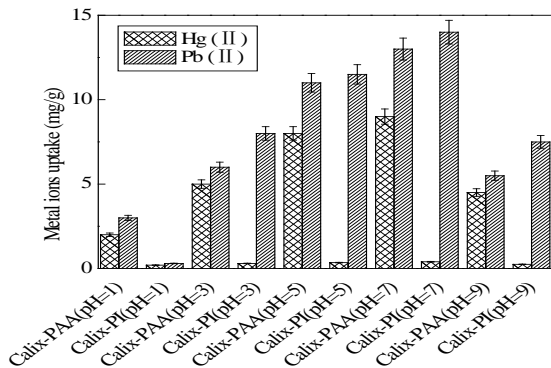


FIGURE 5. Adsorption performances of various metal ions uptakes on the Calix-PAA and Calix-PI fibers.

Adsorption Kinetics

The adsorption kinetics is critically important in understanding the adsorption reaction between the Calix-PI fibers and metal ions. In the Pb(II) solution (40 mg/L, pH=7), the adsorption kinetics experimental data at room temperature are described in Figure 6a and fitted using a pseudo-first-order model Eq. (4) and a pseudo-second-order model Eq. (5).

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_e and q_t (mg/g) are the adsorption capacities of Pb (II) adsorbed at equilibrium and at various time, respectively. k_1 (min^{-1}) and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are the adsorption rate constants of the pseudo-first-order and the pseudo-second-order equations, respectively.

According to the adsorption data from Figure 6a, the fitting validity of a pseudo-first-order model and a pseudo-second-order model are shown in Figure 6b and c, respectively. The value of correlation coefficient (0.9933) of the pseudo-second-order model is higher than the value (0.8122) of the pseudo-first-order model, suggesting that the adsorption of Pb(II) on the Calix-PI fibers fits a pseudo-second-order reaction. From the intercept and slope of the fitting straight line in Figure 6c, the pseudo-second-order rate constant is calculated as $1.11 \times 10^{-3} \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$.

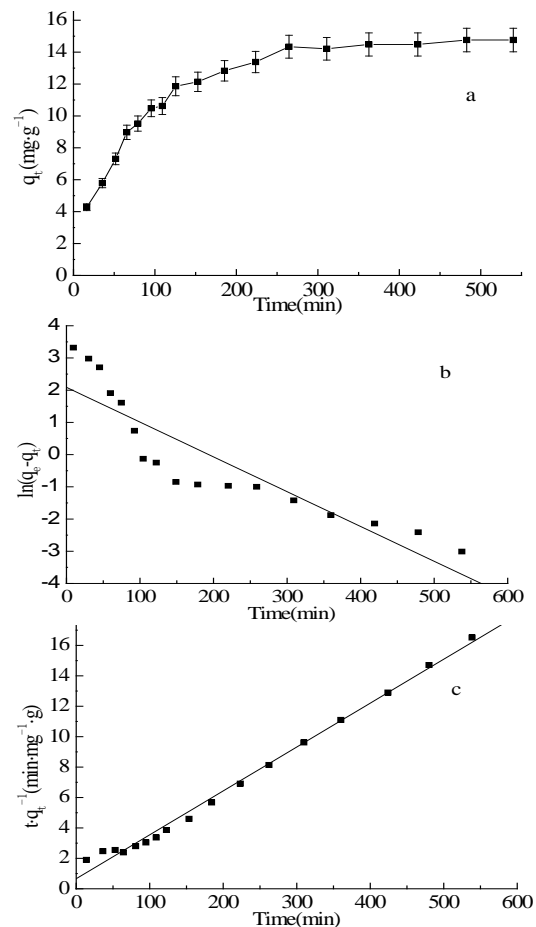


FIGURE 6. (a) Adsorption kinetics of Pb (II) on the Calix-PI fibers. (b) The pseudo-first-order model. (c) The pseudo-second-order model.

Adsorption Isotherms

In the Pb(II) solution with different initial concentrations (30, 35, 40, 45, 50 mg/L, pH=7), the equilibrium adsorption data at 25°C are fitted using Langmuir model Eq. (6) and Freundlich model (Eq. (7) and depicted in Figure 7.

$$\frac{1}{q_e} = \frac{1}{aq_m} \times \frac{1}{c_e} + \frac{1}{q_m} \quad (6)$$

$$\ln q_e = \ln K + \frac{1}{n} \ln c_e \quad (7)$$

where c_e (mg/L) is the equilibrium concentration of Pb(II) in solution. q_e (mg/g) and q_m (mg/g) are the equilibrium uptake and the maximum adsorption uptake of Pb(II), respectively. a (L/mg) is the Langmuir constant. K and n are the dimensionless Freundlich empirical constants.

From Figure 7, the value of correlation coefficient (0.9932) in the Freundlich model is higher than the value (0.9855) in the Langmuir model, indicating that the adsorption of Pb(II) on the Calix-PI fibers corresponds to the Freundlich model. In addition, from the slope of Figure 7a, the Freundlich constant (n) is calculated as 1.877, suggesting that the adsorption of Pb(II) on the Calix-PI fibers is fit for the favorable adsorption [29]. The maximum Pb(II) uptake calculated according to the intercept in Figure 7b is 28 mg/g, which is lower than the uptake (500mg/g) absorbed by the porous chelating fiber [30] but higher than the uptakes (18.6mg/g, 22.2 mg/g) absorbed by palm fibers [31] and PANI/MWCNTs [32], respectively. Further research will focus on enhancing the uptake by synthesizing new calixarene derivatives and optimizing the molecular chain structure of the Calix-PI fibers.

Based on the comprehensive analysis on the adsorption kinetics and isotherms, it can be concluded that the practical adsorption of Pb(II) on the Calix-PI fibers is mainly attributed to the monolayer chemical adsorption and slightly depended on the physical adsorption.

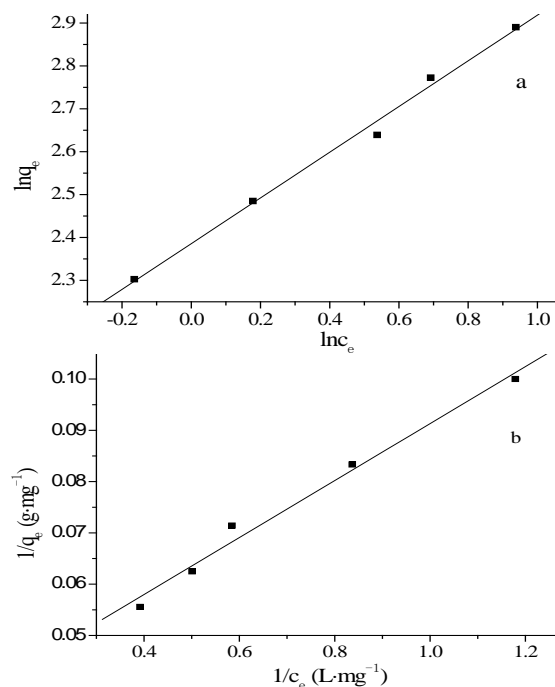


FIGURE 7. Adsorption isotherms of Pb(II) on the Calix-PI fibers.(a) The Freundlich model.(b) The Langmuir model.

CONCLUSION

Calix-PI fibers were successfully prepared by amidation, electrospinning and thermal imidization. The prepared fibers have uniform diameters and smooth appearance. Compared with the Calix-PAA fibers, the Calix-PI fibers having only one kind of adsorption site display selective adsorption on Pb(II). The adsorption kinetics and isotherm of Pb(II) adsorbed on the Calix-PI fibers are fit with the pseudo-second-order model and the Freundlich model, respectively. The pseudo-second-order rate constant is $1.11 \times 10^{-3} \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$, and the maximum Pb(II) uptake is 28 mg/g. The adsorption process is fit for the favorable adsorption in this work.

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