Preparation of Phytic Acid Modified Polyurethane Wet Spinning Fibers for Application in Pb^{2+} Adsorption

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ABSTRACT

Polyurethane (PU) possesses excellent mechanical properties which has been used as the matrix for heavy metal ions removal. However, it has poor adsorption capacity due to there doesn't exist chelating groups. In this study, phytic acid modified polyurethane (PU) fibers have been successfully prepared by wet spinning which was used for Pb^{2+} removal. The modified fibers achieved the highest adsorption capacity under the conditions of the mass ratio of phytic acid and PU was 5:7, the pH of Pb^{2+} solution was 6 and the adsorption temperature was 20 °C. The adsorption process of Pb^{2+} by phytic acid modified PU fibers belongs to monolayer adsorption. The saturated Pb^{2+} adsorption capacity of the modified PU fibers was over 7 times higher than the pure one's. Phytic acid modified PU fibers could greatly improve the adsorption capacity of Pb^{2+} which could be used as the potential adsorbent for heavy metal ions removal.

KEY WORDS : *Phytic acid, Polyurethane, Wet spinning, Pb^{2+}, Chelating adsorption*

1. INTRODUCTION

With the increasing awareness of environmental protection, environmental pollution has received more and more attention. Heavy metal ions pollution is as one of the most serious environmental pollution due to they are significantly harmful to human bodies which could inactivate the enzymes and proteins. They would accumulate in human body and can not be degraded or destroyed [1-3]. Lead is one of the five heavy metal pollutants, it brings about severe damage to the nervous system, reproductive system, liver, brain and causes sickness, sterility, abortion and neonatal deaths [4-7]. As China is one of the world's largest refine lead consumer countries, the removal of lead ions from the wastewater is urgent.

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Numerous technologies have been studied for the effective removal of lead, such as ion exchange [8], membrane separation [9], electrochemical treatment [10], chemical precipitation [11] electrolytic process and electrodialysis [12,13]. Due to the low cost, flexibility and simplicity of design, adsorption has received more and more attentions [14,15]. The adsorption efficiency was determined by the adsorbents which related to their surface area and surface chemical structure [16,17]. A lot of materials have been studied as adsorbents for the removal of Pb^{2+}, for example nanocomposite [18], amphiphilic hybrid material [19], mesoporous silica [20], polymer particles [21], carbon nanotubes [22] and nanofibers [23]. Therefore, developing novel efficient and stable materials for heavy metal removal is still keeping on the way. Polyurethane (PU) is the polymers containing many carbamate groups in their main chains possessing excellent mechanical properties, elasticity and toughness, good organic durability which are widely used in many fields [24,25]. PU has been explored as the matrix for removal of heavy metal ions [26,27]. However, pure PU fibers have poor adsorption capacity of heavy metal ions due to there doesn't exist chelating groups. Phytic acid is a biocompatible and degradable substance containing 6 phosphate groups which could offer the good chelating ability [28,29]. It has been studied as the chelating agent of the metal ions such as magnesium [30], copper [31] and calcium[32].

In this study, the phytic acid modified PU fiber was prepared by wet spinning which was used for adsorption of Pb^{2+}. To optimal spinning process, the concentration of PU in the spinning solution and the coagulation bath were investigated. The influences of the mass ratio of phytic acid and PU, the pH of adsorption solution and adsorption temperature on the adsorption capacity were investigated. The adsorption kinetics and saturated adsorption capacity of the modified PU fiber was also analyzed. The aim of the research was developed a low cost and high efficient adsorbent with high adsorption capacity of Pb^{2+}.

2. EXPERIMENTAL

2.1 Materials

Polyurethane (PU) was purchased from Shaoxing Keqiao Linaixi Fiber Co. Ltd, (Zhejiang, China). Phytic acid was purchased from Huainan Tianli Biological Engineering Development Co., Ltd (Anhui, China); N,N-Dimethylformaide (DMF), tetrahydrofuran (THF), ethylenediamine tetraacetic acid (EDTA), acetic acid, sodium acetate, xylenol orange (XO) and lead nitrate were purchased from Sinopharm Chemical Reagent Co.,Ltd (Shanghai, China).

2.2 Preparation of PU wet spinning fibers modified by phytic acid

Preparation of PU basic solution: A certain amount of PU fiber was added into the DMF/THF (W/W=1:1) mixed solvents, the PU basic solutions with different concentration were obtained by stirring at room temperature.

Preparation of phytic acid solution: Using DMF as solvent to prepare the 30% phytic acid solution (w/w), the chemical structure of phytic acid was as shown in Figure 1.

Preparation of PU wet spinning fibers modified by phytic acid: Different amount of 30% phytic acid solution was added into the PU basic solution which was stirred at room temperature to obtain the homogeneous spinning solution. Then phytic acid modified PU fiber was obtained by wet spinning in coagulating bath and heating at 50 °C for 12 h.

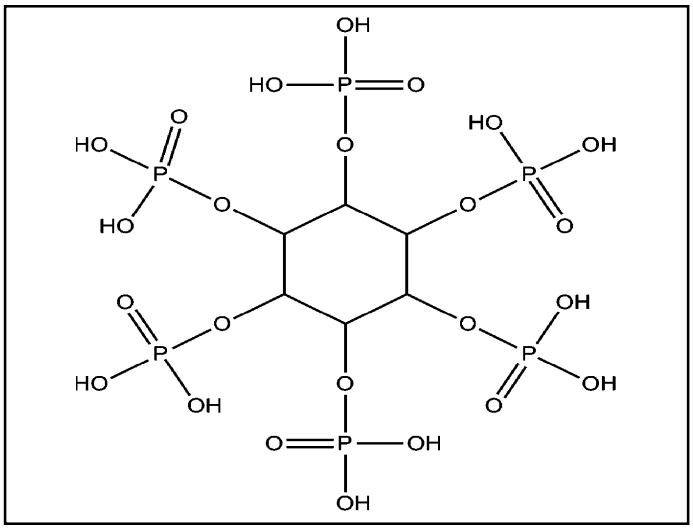

Fig. 1. The chemical structure of phytic acid

2.3 Determine the adsorption performance of modified PU fibers

50 mL Pb^{2+} solution with certain concentration and 0.1 g modified fibers were added into the flask for adsorption under the constant temperature oscillation. The method of EDTA titration was used to determine the adsorption capacity. The adsorption time, pH value, temperature and the content of phytic acid which influenced the adsorption performances were investigated.

Titration method and mechanism: 10 mL Pb^{2+} solution before or after adsorption was added into the Erlenmeyer flask, and then 10 mL acetate-sodium acetate buffer solution (pH about 5.0~6.0) was added to tune the pH to 5.0~6.0. 2 drops of xylenol orange was used as the color indicator, EDTA was used to titrate this solution when the color of the solution changed from red to yellow suddenly. The mechanism was as follow:

$$Pb^{2+}+H_3In=PbIn^{-}(red)+3H^{+}$$

$$PbIn^{-}+H_4Y=PbY^{2-}+H_4In^{+}(yellow)$$

H_3In is stand for XO, H_4Y is stand for EDTA.

Then the adsorption capacity was calculated from Equation (1)

$$Q=\frac{207.2(V_0-V_1)\times C}{M} \quad (1)$$

Where Q is the adsorption capacity (mg/g), V_0 is the EDTA volume which consumed by the Pb^{2+} solution before adsorption (mL), V_1 is the EDTA volume which consumed by the Pb^{2+} solution after adsorption (mL), C is the concentration of the EDTA solution (mol/L), M is the adsorbent mass (g).

3. RESULTS AND DISCUSSION

3.1 Optimization of spinning process parameters

The spinnability of the wet spinning was greatly influenced by the concentration of the spinning solution. In this study the mass concentration 4%, 6% and 8% of the PU solution was investigated. The fiber could hardly be formed when the concentration was 4% due to the low viscosity. While the concentration was 8%, PU could hardly dissolve and the viscosity was too high which influenced the spinning process.

The spinning solution was stable and uniform when the concentration of PU was 6%, the viscosity of this solution was moderate and easy spinning to obtain the good shape fibers. Therefore, the concentration of the PU solution was 6%.

Coagulation bath influenced the morphology, mechanical and other performances greatly of the fibers which is vital for the wet spinning. In this study, 20% DMF aqueous solution (w/w), 20% THF aqueous solution (w/w) and pure water solution were investigated as the coagulation bath. The fiber could hardly be formed and difficult to spin using 20% THF aqueous solution as the coagulation bath. When pure water solution was selected as the coagulation bath, the syringe needle would be blocked. When 20% DMF aqueous solution was chose as the coagulation bath, the obtained fibers had good shape and good flexibility after drying. Therefore, 20% DMF aqueous solution was chosen as the coagulation bath in this study.

3.2 Effect on the adsorption capacity

3.2.1 Effect of the phytic acid content

The pure and modified PU fibers with different content of phytic acid were prepared, the mass ratio of phytic acid and PU was chosen 1:4, 1:3, 1:2, 5:7 of the modified fibers. The pure or each modified fiber (0.1 g) was added into the Erlenmeyer flask, and 50 mL Pb^{2+} solution with the concentration of 200 mg/L was added into the flask which was treated at 20 °C for adsorption 24 h. The adsorption capacities of the modified fibers with different content of phytic acid are as shown in Figure 2. As can be seen from Figure 2, the adsorption capacity of the modified

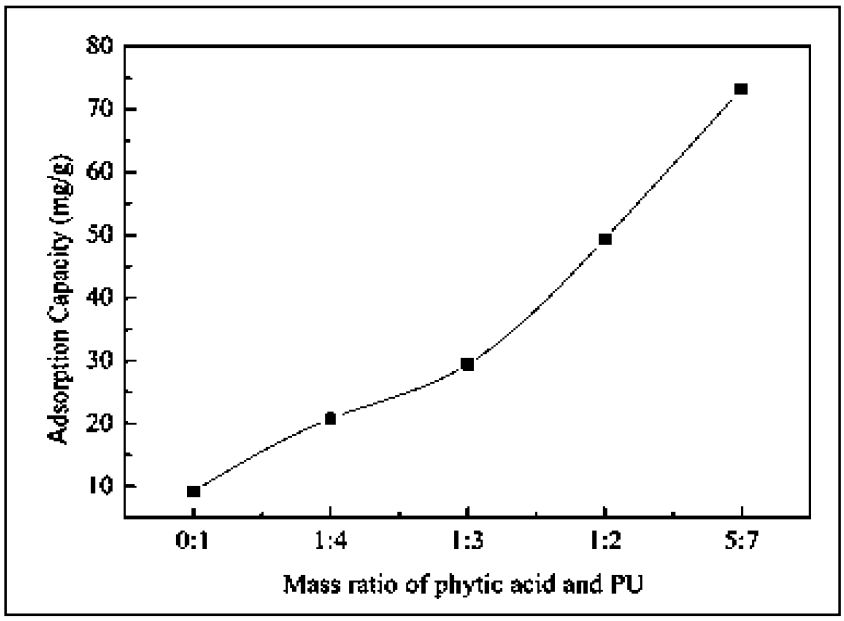

Fig. 2. Adsorption capacity of modified fibers with different mass ratio of phytic acid and PU

fibers increased with the content of phytic acid. The reason about this because the phytic acid molecule has six phosphate functional groups possessing the strong chelate ability of Pb^{2+}. However, the viscosity of the blend solution and spinnability decreased with the increasing of the phytic acid content. When the ratio was higher than 5:7, the fibers could hardly to be formed. Therefore, the mass ratio of phytic acid and PU was chosen 5:7.

3.2.2 Effect of pH value

The modified fiber (0.1 g) with the ratio of phytic acid and PU of 5:7 was added into the 50 mL Pb^{2+} (200 mg/L) solution with different pH value from 1 to 7 which was treated at 20 °C for adsorption 24 h. The adsorption capacity influenced by different pH value is as shown in Figure 3. The adsorption capacity was low only about 29.67 mg/g when the pH value was 1, and it increased with the pH value from 1 to 6. It isn't good for the hydrolysis of the phosphate groups under the strong acid condition. The phosphate groups were hydrolyzed into phosphate anion gradually with the reducing of acidity, thus the chelating capacity of Pb^{2+} gradually increased. While the pH was higher than 7, Pb^{2+} would turn into the $Pb(OH)_2$ precipitation. The result indicated that the optimal pH value of adsorption Pb^{2+} by the modified fibers was 6.

3.2.3 Effect of temperature

The modified fiber (0.1 g) was added into the 50 mL Pb^{2+} (200 mg/L) solution which was treated at different temperature for adsorption 24 h. The adsorption capacity was influenced by different temperature as shows in Figure 4. As it is be seen from Figure 4, the adsorption capacity decreased with the increasing of

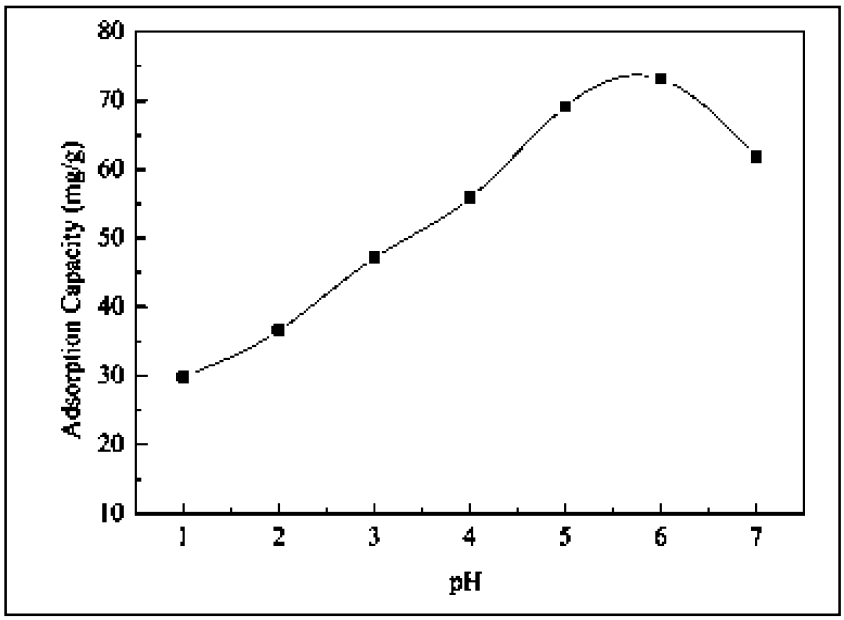

Fig. 3. Effect of pH value on the adsorption capacity of modified fibers

temperature. Increasing temperature is beneficial for the migration of Pb^{2+}, while the desorption of water molecule on surface of the fiber increased. The result demonstrated that the adsorption of Pb^{2+} by phytic acid modified PU fibers was a exothermic process. Therefore the adsorption temperature was chosen 20 °C.

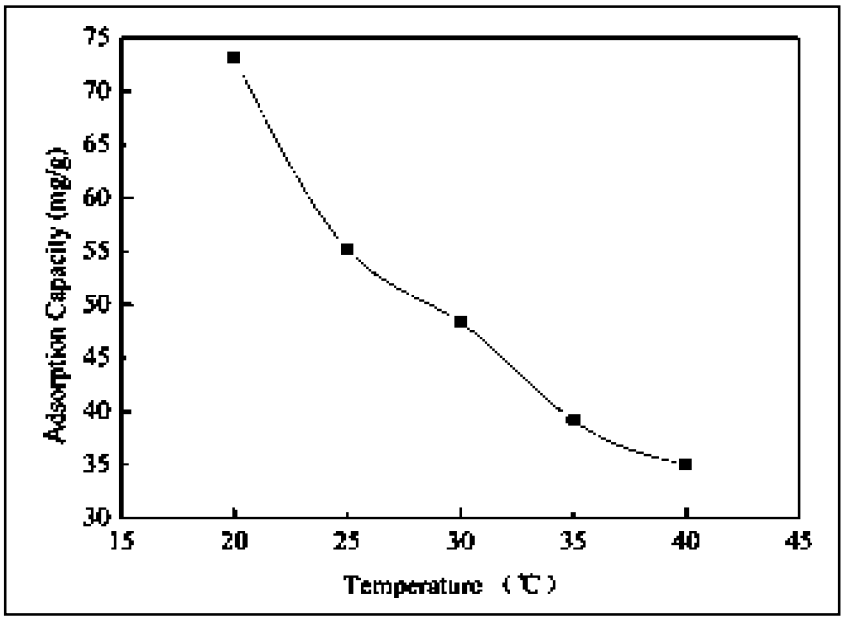

Fig. 4. Effect of temperature on the adsorption capacity of modified fibers

3.3 Adsorption kinetics of phytic acid modified PU fibers

The modified fiber (0.1 g) was added into the 50 mL Pb^{2+} (200 mg/L) solution with pH 6 which was treated at 20 °C for adsorption. The adsorption capacity at different adsorption time (t) was as shown in Figure 5. The adsorption rate was fast at the initial stage, while it was slowed down after 3 h and reached the adsorption equilibrium at 9 h.

The relationship between t/Q_t and t was as shown in Figure 6. As shown in Figure 6, t/Q_t increased linearly with t from 0.5 h to 3 h, the adsorption kinetics equation of t/Q_t and t was $t/Q_t=0.01064t+0.0177$ and the correlation coefficient R^2 was 0.9911 indicating the adsorption process of Pb^{2+} by phytic acid modified PU fibers belongs to monolayer adsorption [33,34]. There are much active binding sites on the fiber surface at the initial adsorption stage, thus the adsorption rate of Pb^{2+} is greater than the desorption rate exhibiting the fast adsorption rate at the initial stage. While the active binding sites on the fiber surface decreased with the increasing of adsorption time, thus the adsorption gradually tend to equilibrium.

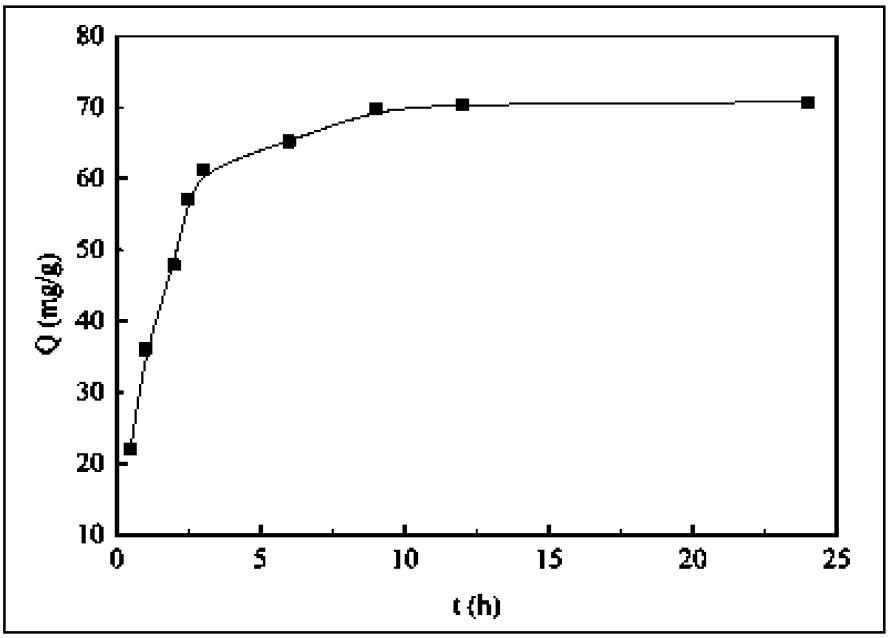

Fig. 5. The relationship between the adsorption capacity and time

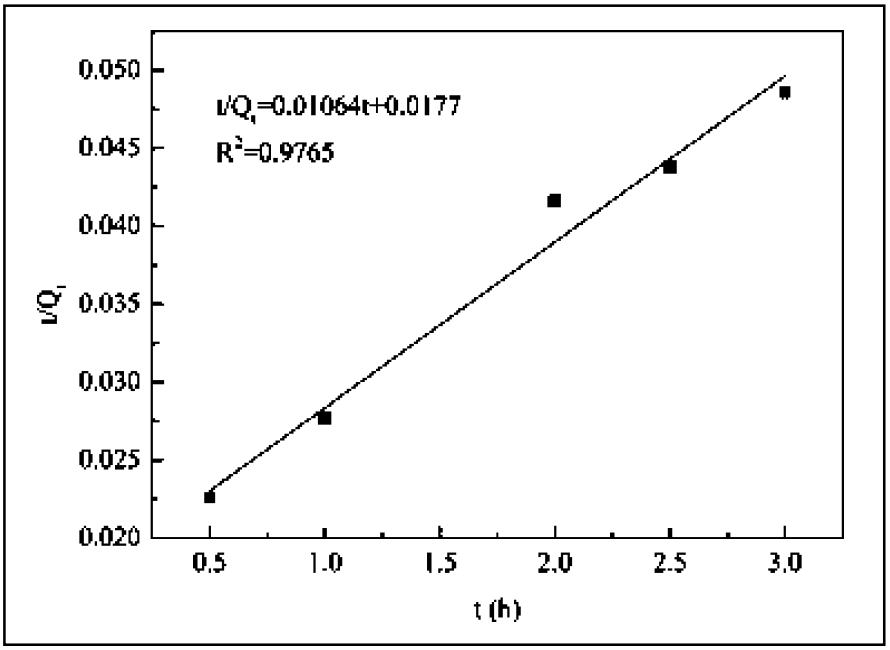

Fig. 6. The relationship between t/Q_t and t

3.4 Saturated adsorption capacity of phytic acid modified PU fibers

The pure or modified PU fibers (0.1 g) was added into the 50 mL Pb^{2+} (pH=6) solution with different concentration which was treated at 20 °C for adsorption 24 h. The adsorption capacities of these two fibers in different concentration Pb^{2+} solution are as shown in Table 1. The adsorption capacity of the fibers increased with the increasing of Pb^{2+} concentration from 100 mg/L to 200mg/L, while the adsorption capacity of the fibers reached saturation when the concentration was higher than 200 mg/L. As can be seen from Table 1, the adsorption capacity of the phytic acid modified PU fibers was greatly higher than that of pure one's. When the concentration of Pb^{2+} solution was 200 mg/L, the saturated adsorption capacity of the phytic acid modified PU fibers was 73.25 mg/g which was 7.28 times of the pure one's (10.05 mg/g). The result revealed that the PU fibers modified by phytic acid could greatly improve the adsorption capacity of Pb^{2+}.

TABLE 1. Saturated adsorption capacities of pure and phytic acid modified PU fibers

Samples		Concentration of Pb^{2+} solution		
		100	200	400
Saturated Adsorption Capacity (mg/g)	Pure PU fibers	9.24	10.06	10.08
	Modified PU fibers	48.67	73.25	73.28

4. CONCLUSION

The phytic acid modified the PU fiber was successfully prepared by wet spinning which was used for adsorption of Pb^{2+}. The concentration of PU in the spinning solution was 6% using 20% DMF aqueous solution as the coagulation bath could obtain the good shape and flexibility PU fibers. The modified fibers achieved the highest adsorption capacity when the the mass ratio of phytic acid and PU was chosen 5:7, at pH 6 and the adsorption temperature was 20 °C. The adsorption process of Pb^{2+} by phytic acid modified PU fibers belongs to monolayer adsorption. The phytic acid modified PU fibers possessed higher saturated Pb^{2+} adsorption capacity than the pure PU. The saturated adsorption capacity of the phytic acid modified PU fibers was 73.25 mg/g which was 7.28 times of the pure PU (10.05 mg/g) when the concentration of Pb^{2+} solution was 200 mg/L. The results demonstrated that phytic acid could be a good modifier for improving the Pb^{2+} adsorption capacity of PU fibers and this modified fibers would achieve the potential application in the fields of the removal of heavy metal ions.

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