

Research Article

Absorbed Pb^{2+} and Cd^{2+} Ions in Water by Cross-Linked Starch Xanthate

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A cross-linked starch xanthate was prepared by graft copolymerization of acrylamide and sodium acrylate onto starch xanthate using potassium persulfate and sodium hydrogen sulfite initiating system and N,N' -methylenebisacrylamide as a cross-linker. As this kind of cross-linked potato starch xanthate can effectively absorb heavy metal ions, it was dispersed in aqueous solutions of divalent heavy metal ions (Pb^{2+} and Cd^{2+}) to investigate their absorbency by the polymer. Factors that can influence absorbency were investigated, such as the ratio of matrix to monomers, the amount of initiator and cross-linker, pH, and the concentration of metal ions. Results were reached and conclusion was drawn that the best synthetic conditions for the polymer adsorbing Pb^{2+} and Cd^{2+} were as follows: the quality ratio of matrix to monomers was 1:12 and 1:11, the amount of initiator was 2.4% and 3.2% of matrix, and the amount of cross-linker was 12 mg and 13 mg. When the initial concentration of ions was 10 mg/L, the highest quantities of adsorption of Pb^{2+} and Cd^{2+} were 47.11 mg/g and 36.55 mg/g. Adsorption mechanism was discussed by using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDS) test, and adsorption kinetic simulation.

1. Introduction

Modern society is perplexed with water pollution, especially pollution caused by heavy metals. It is vital to remove heavy metals such as lead, cadmium, copper, and mercury before they are drained into the ecosystem, as it will be of great difficulty to remove them from food chains and extremely toxic living organisms [1]. Several techniques have been utilized for the removal of heavy metals from water, such as precipitation, flotation, solvent extraction, adsorption, membrane processing, and electrolysis [2]. Adsorption, with advantages of high efficiency, easy handling, and availability of different adsorbents, is generally preferred. Studies make efforts to search for cost-effective adsorbents. Among the various adsorbents, starch has been considered as one of the best choices for the preparation of low-cost adsorbents and can be used for the separation of pollutants from waste water [3, 4].

Adsorbents based on starch are receiving increasing attention since starch is abundant, renewable, and biodegradable. However, the hydrophilic nature of starch is a major

drawback that limits the development of starch-based materials [5]. Previous studies have shown that some starch derivatives may be effective in removing heavy metals from water. For example, Kweon et al. [6] investigated the adsorption of divalent metal ions by succinylated and oxidized corn starches, Xu et al. [7] studied the adsorption process of Pb^{2+} by cross-linked amphoteric starch with quaternary ammonium and carboxymethyl groups, and Popuri et al. [8] investigated cross-linked starch graft copolymers containing amine groups as the adsorbents for Pb^{2+} and Cu^{2+} .

The modified starch is nontoxic and biodegradable with low cost. Starch can be modified by several ways and the preparation of cross-linked starch is widely used because it contains many functional groups such as $-COOH$, $-OH$, $-SO_3H$, $-CONH_2$ etc. that have strong chelating ability with heavy metal ions. Therefore the cross-linked starch materials can be used on adsorption of heavy metal ions, meaning important values on helping solve current environmental problems—water pollution caused by the heavy metal discharges [9, 10].

In this study, we describe the use of cross-linked starch xanthate as a complexing agent that can absorb Pb^{2+} and Cd^{2+} through grafted copolymerization with acrylamide and sodium acrylate and focus on its adsorption properties and its potential for recycling the heavy metal ions.

2. Experimental Section

2.1. Materials. Potato starch, food grade, was purchased from Inner Mongolia Ke Xinyuan Co., Ltd., China. The sodium hydroxide was obtained from Tianjin North Fine Chemicals Co., Ltd., China. Carbon disulfide was purchased from Chinese Medicine Group Chemical Reagent Co., Ltd., China. Absolute ethanol was purchased from Tianjin North Fine Chemicals Co., Ltd., China. Acrylic acid was purchased from Chinese Medicine Group Chemical Reagent Co., Ltd., China. Acrylamide was obtained from Chinese Medicine Group Chemical Reagent Co., Ltd., China. Potassium persulfate was purchased from Chinese Medicine Group Chemical Reagent Co., Ltd., China. The sodium bisulfite was obtained from Tianjin North Fine Chemicals Co., Ltd., China. $\text{N,N}'$ -Methylenebisacrylamide was purchased from Beijing Chemical Reagent Company, Co., Ltd., China. All the above ingredients except potato starch were of analytical grades.

2.2. Preparation of Starch Xanthate. 5.0 g native starch was dispersed in 25 mL of distilled water and the concentration of 1.4% sodium hydroxide solution was added to the resulting slurry in room temperature. Then, 3.5 mL carbon disulfide was added to the system. To control the reaction temperature, the reactor was placed in a water bath preset at 30°C for 2 h.

The reaction product was precipitated in an excess of ethanol and separated by filtration. Then we dried it in a vacuum oven at 40°C for two days. Moreover the desired starch xanthate was milled and sifted through a 60-mesh sieve to prepare samples.

2.3. Synthesis of Cross-Linked Starch Xanthate. 2.5 g starch xanthate was dispersed in 50 mL of distilled water and stirred for a period of time; then 40 mL sodium acrylate and a selected amount of acrylamide were poured into the solution followed by potassium persulfate (20 mg/mL) and a selected amount of $\text{N,N}'$ -methylenebisacrylamide. They were reacted under a nitrogen gas atmosphere by heating the solution as to make graft copolymerization reaction occur. The product was dried for 12 h and finally ground to powder.

2.4. Metal Adsorption and Procedure for Quantitative Analysis. Aqueous solutions of Pb^{2+} (Pb 10 mg/L) and Cd^{2+} (Cd 10 mg/L) ions were prepared by dissolving 0.7993 g $\text{Pb}(\text{NO}_3)_2$ and 0.6861 g $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 500 mL deionized water. 0.2 g cross-linked starch xanthate was, respectively, added in the lead solution (1000 mL, 10 mg/L) and cadmium solution (1000 mL, 10 mg/L). The saturated adsorption of metal ions on cross-linked starch xanthate was 50 mg/g. The polymer-metal complex was removed by filtration after static adsorption for 4 hours and the filtrate was used for the residual

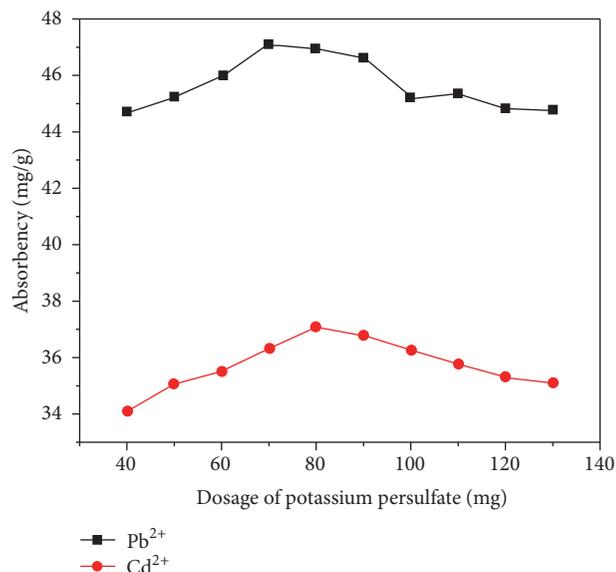


FIGURE 1: Effect of potassium persulfate amount on Pb^{2+} and Cd^{2+} adsorption capacity.

metal analysis. The adsorption capacity was calculated from the following expressions [11, 12]:

$$Q = \frac{(C_0 \times V_0 - C_1 \times V_1)}{m} \quad (1)$$

In this formula, Q (mmol/g) is the adsorption capacity of the adsorbent and C_0 and C_1 (moles per liter) are the initial and final concentrations of Pb^{2+} and Cd^{2+} ions in the adsorption solution. Respectively, V_0 and V_1 (milliliters) are the initial and final volume of Pb^{2+} and Cd^{2+} ions in the adsorption solution and m (grams) is the dose of the cross-linked starch xanthate.

3. Results and Discussions

The cross-linked starch xanthate that was prepared under the different synthesis conditions would be expected to have different absorbency for the metal ions. So the effects of different synthesis conditions on the absorbency of the cross-linked starch xanthate were investigated.

3.1. Effect of Dosage of the Initiator Potassium Persulfate.

The effect of dosage of the initiator potassium persulfate was investigated by changing the dosage of the initiator potassium persulfate under the conditions that the starch quality and other factors were constant, to study its effect on the adsorption amount of metal ions. As shown in Figure 1, the trends of absorbing Pb^{2+} and Cd^{2+} were similar. It can be seen that the absorbency increased totally with the dosage of $\text{K}_2\text{S}_2\text{O}_8$ increasing. When the amount of $\text{K}_2\text{S}_2\text{O}_8$ was higher than the optimum point, the change of the absorbency decreased. The maximal absorbencies of Pb^{2+} and Cd^{2+} were 47.11 mg/g and 36.55 mg/g when the dosages of potassium persulfate were 70 mg and 80 mg, respectively. The cause

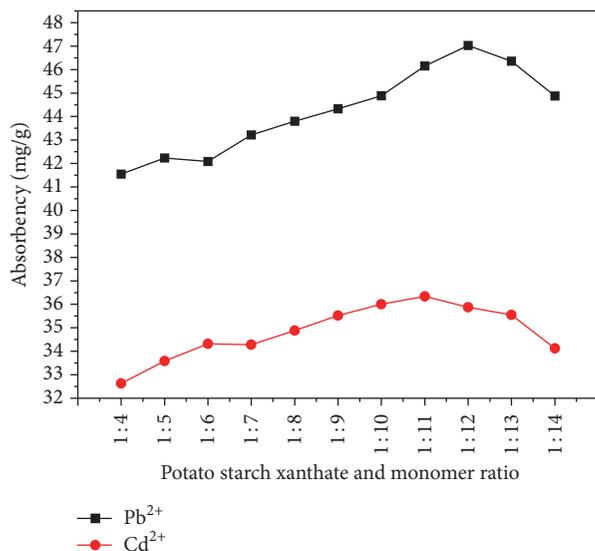


FIGURE 2: Effect of starch xanthate and monomer ratio on polymer adsorbed Pb²⁺ and Cd²⁺.

was related to the relationship between average chain length and concentration of the initiator in the copolymerization [13]. More graft copolymerization occurred between the monomers and the starch xanthate leading to the formation of more stable network structures, which was helpful for the increase of the adsorbency. On the one hand, when the concentration of the initiator was too high, there would be a strong reaction with the starch molecules, resulting in the decrease of the main chain length [14, 15]. On the other hand, with the increase of K₂S₂O₈, the copolymerization rate became so fast that the polymeric heat could not transfer in time, led to the higher temperature of the system, and enhanced the chance of chain transfer and chain cessation. Consequently, the adsorbency of the polymer decreased [16].

3.2. Effect of Mass of Starch Xanthate and Monomer Ratio.

The effect of the weight ratio of starch xanthate to monomers (ranging from 1:5 to 1:14) on the adsorbency was investigated. As shown in Figure 2, the trends of absorbing Pb²⁺ and Cd²⁺ were also similar. The adsorbency increased with the ratio of matrix to monomers increasing and reached a maximum; then it slowly decreased with increasing of the amount of monomers. The maximal adsorption amount of Pb²⁺ was 47.02 mg/g when the weight ratio of starch xanthate to monomers reached 1:12; the adsorbency of Cd²⁺ was 36.33 mg/g when the ratio reached 1:11. It can be explained as follows: on the one hand, as the weight ratio of matrix to monomers increased, more and more functional groups such as -COONa, -CONH₂, and -CONH were grafted onto the starch xanthate, these groups enhanced the capacity of the cross-linked starch xanthate chelated with metal ions, and the chemical adsorption improved. On the other hand, the grafted rate increased and the branch chain grafted in starch became long, which was conducive to the formation of the ideal network structure and the grafted products

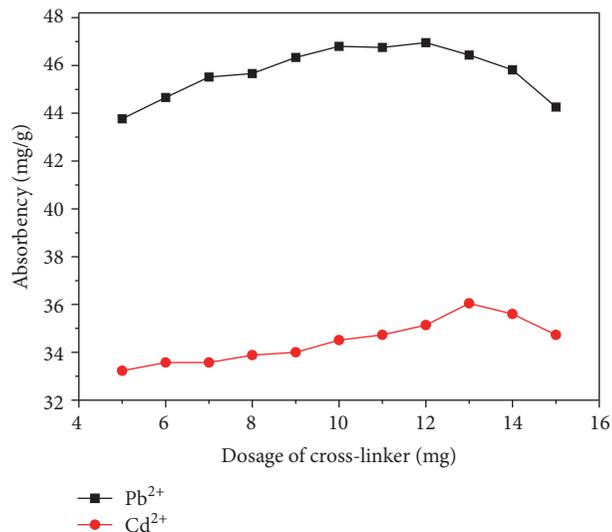


FIGURE 3: Dosage of cross-linker on polymer adsorbed Pb²⁺ and Cd²⁺.

formed appropriate holes so that the physical adsorption improved. The acrylic acid's self-polymerization enhanced with the monomers increased. Although the polyacrylic acid has a mass of carboxyls, these carboxyls were packaged inside the polyacrylic acid and hard to chelate with metal ions. Meanwhile the compactness of the cross-linked starch xanthate increased so that the polymeric network became closer [17] and thus the adsorbency decreased.

3.3. Effect of Dosage of Cross-Linker. The effect of the amount of N,N'-methylenebisacrylamide, which was used as the cross-linker in the copolymerization, was studied and the result was shown in Figure 3. When the amount of cross-linker was lower than 12 and 13 mg, the adsorbency of Pb²⁺ and Cd²⁺ was increased with the amount of cross-linker rising. However, it began to decrease when it was higher than 12 and 13 mg. Therefore, the maximal adsorbency of Pb²⁺ and Cd²⁺ was up to 46.95 mg/g and 36.05 mg/g when the dosage of cross-linker was 12 and 13 mg, respectively. According to Flory's theory, increasing cross-linker addition could increase the number of nodes of the network and the cross-linker density, which was favorable to the cross-linked starch xanthate absorbing. Low concentration of the cross-linker led to low degree of cross-linking, and it was hard for network structure to form, so the adsorbency of metal ions was low. However, when it was higher than the best value, there were more cross-linking points and the pores became smaller in the network, which caused the macroscopic decrease of the adsorbency [18].

3.4. Effect of Solution pH. The pH of aqueous solution is an important controlling parameter in the heavy metal ions adsorption process [19, 20]. The cross-linked starch xanthate samples were put into the Pb²⁺ and Cd²⁺ solutions over a pH range of 2–9 at room temperature to investigate the influence of pH on Pb²⁺ and Cd²⁺ ions adsorption property.

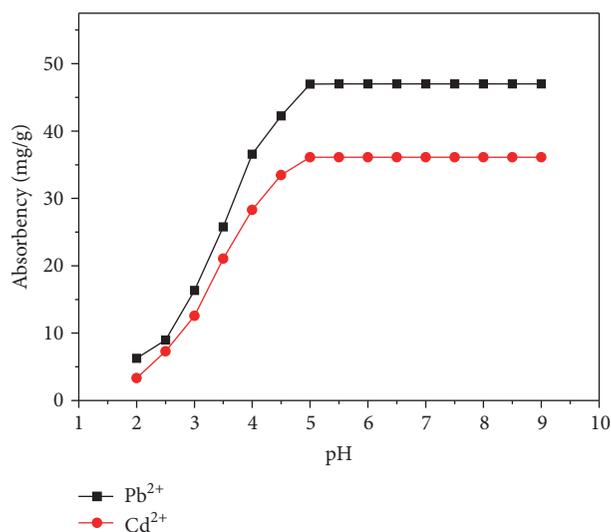


FIGURE 4: Effect of solution pH on adsorbed Pb²⁺ and Cd²⁺.

Figure 4 shows the effect of pH values on the Pb²⁺ and Cd²⁺ ions adsorption properties of the adsorbents. It is observed that the adsorption capacity of cross-linked starch xanthate is pH dependent and shows a weak adsorption capacity at low pH values. The adsorption capacity is increased with increasing pH values and the maximum capacity (47 mg/g and 36.12 mg/g) is achieved around pH of 5.0. The effect of pH value on the removal of Pb²⁺ and Cd²⁺ ions can be explained by the surface charge of the adsorbents in acidic and basic medium [21]. On the one hand, in acidic medium, the pH value is very low, and the competitive capacity of H⁺ is much stronger than metal ions. On the other hand, it may also be because H⁺ can react with active groups and the electrostatic repulsion increases between active groups and metal ions. Then the coordination process between active groups and metal ions is blocked [22]. The S on the cross-linked starch xanthate prefer to chelate with hydrogen ions rather than Pb²⁺ and Cd²⁺ ions due to the protonation as shown in



Therefore, the cross-linked starch xanthate displays the positive surface charge. In basic medium, the cross-linked starch xanthate has the negative surface charge due to the attraction between the base and the H⁺. Thus, the adsorption ability was enhanced significantly with increasing pH values due to the electrostatic attraction.

3.5. Effect of the Initial Concentration of Pb²⁺ and Cd²⁺. The effects of the initial concentration of Pb²⁺ and Cd²⁺ were studied and the result was shown in Figure 5. The absorbency increased with the increasing concentration of metal ions and the tendency of absorbency became slow. It can be explained as follows: when the concentrations of metal ions were low, the amounts of metal ions were far lower than the saturated adsorption capacity of cross-linked starch xanthate. The polymeric absorbent has many vacant sites, so the concentration gradient took place in the solution that it can

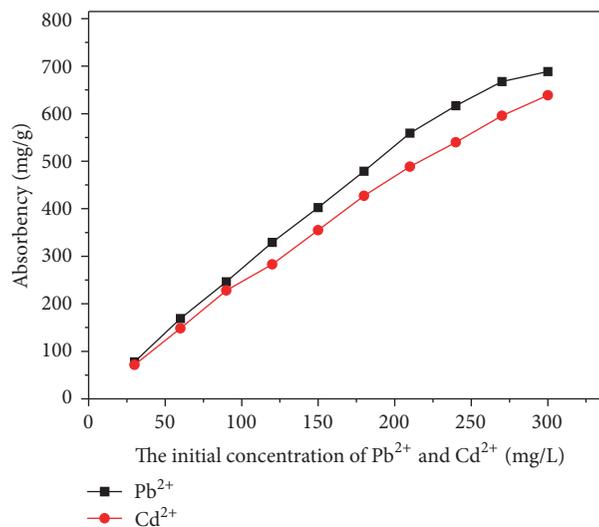


FIGURE 5: Effect of the initial concentration on adsorbed Pb²⁺ and Cd²⁺.

constantly absorb Pb²⁺ and Cd²⁺. The adsorption capacity increased rapidly with the increasing of concentration. The vacant site was constantly filled with increasing concentration of metal ions and the concentration gradient decreased which resulted in the slower tendency of absorbency [23, 24], and finally there was a balance that was achieved.

3.6. FTIR Spectra. The various spectral bands along with respective frequencies of the native starch, starch xanthate, and cross-linked starch xanthate are shown in their spectra, according to Figure 6. Native starch spectra showed that the 3443 cm⁻¹ was the stretch vibration adsorption band of the hydroxyl. Other adsorption bands appeared at 2927 cm⁻¹ as a result of methylene stretching vibrations. The adsorption band of 1639 cm⁻¹ comes from the hydroxyl flexural vibration. The starch xanthate's intensity of the -OH band decreased and the peak became narrower compared with native starch because the hydroxyl took part in the process of the synthesis of starch xanthate. 1204 cm⁻¹ was C=S and C-S band stretching of starch xanthate. The spectra prove that the starch reacted with carbon disulfide under alkaline conditions and generated starch xanthate. The reason why the adsorption peak becomes wider and the intensity increases at 1640 and 1620 cm⁻¹ was the stretch vibration of C=O in -CONH₂ and the symmetrical and asymmetrical stretching vibration of -COONa and -COONH₄. It indicated that the starch xanthate had graft copolymerization reaction with the acrylamide and sodium acrylate as expected.

3.7. X-Ray Diffraction. Figure 7 shows the X-ray diffractograms of native starch, starch xanthate, and cross-linked starch xanthate. The sharp peaks diffraction is the crystalline region of native starch and the dispersion diffraction also represents the amorphous region of native starch. The diffraction pattern of native starch shows several sharp peaks at 15–25°, indicating the crystalline structure of native

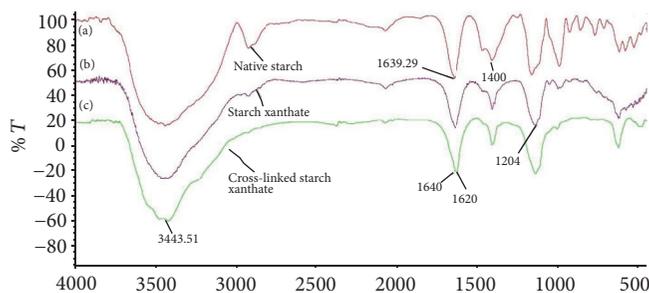


FIGURE 6: IR spectrum of starch, starch xanthate, and cross-linked starch xanthate.

TABLE 1: Quantitative data of EDX measurement for cross-linked starch xanthate adsorbed Pb^{2+} .

ELAN series unn.	C norm. [wt.%]	C Atom. [wt.%]	C Error	(1 Sigma) [at.%]	K fact.	Z corr. [wt.%]	A corr.	F corr.
C 6 K-series	63.72	63.72	70.47	11.68	0.865	0.737	1.000	1.000
O 8 K-series	26.91	26.91	22.35	8.30	0.186	1.448	1.000	1.000
N 7 K-series	7.45	7.45	7.06	5.53	0.054	1.391	1.000	1.000
Pb 48 L-series	1.92	1.92	0.12	0.07	0.110	3.641	1.000	1.133

TABLE 2: Quantitative data of EDX measurement for cross-linked starch xanthate after adsorbed Cd^{2+} .

ELAN series unn.	C norm. [wt.%]	C Atom. [wt.%]	C error	(1 Sigma) [at.%]	K fact.	Z corr. [wt.%]	A corr.	F corr.
C 6 K-series	66.05	66.05	71.74	12.58	0.872	0.757	1.000	1.000
O 8 K-series	28.07	28.07	22.89	9.22	0.190	1.475	1.000	1.000
N 7 K-series	5.75	5.75	5.36	5.39	0.040	1.435	1.000	1.000
Cd 48 L-series	0.13	0.13	0.01	0.07	0.001	2.443	1.000	1.275

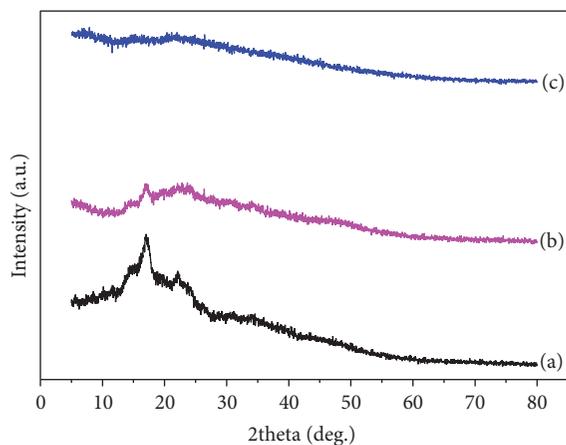


FIGURE 7: The X-ray diffractogram of native starch (a), starch xanthate, (b) and cross-linked starch xanthate (c).

starch [25–27]. The crystalline structure of native starch was destroyed on account of the chemical cross-linking and physical cross-linking when synthesizing the cross-linked starch xanthate. The cross-linked network also prevented the crystallization capacity of starch xanthate, so the diffracted intensity becomes weaker.

3.8. Scanning Electron Microscopy. The scanning electron microscope images of native starch, starch xanthate, and

cross-linked starch xanthate that absorbed Pb^{2+} and Cd^{2+} were shown in Figure 8. The native starch granules are oval in shape with smooth surface. The starch xanthate has a coarse surface rather than a smooth surface with loose structure because of the chemical reaction that happened on the surface [28, 29]. Figures 8(c) and 8(d) indicate that the surface of cross-linked starch xanthate covers a large number of white spots with irregular shapes. That is because the space network structure is completely braced after it absorbed Pb^{2+} and Cd^{2+} . And when the gel was dried, though each network structure on the cross-linked starch xanthate surface returns to its close state before water adsorption, the stains remain to be seen. These irregularly shaped white spots explain that the copolymerization and cross-linking may have some degree of heterogeneity [30].

3.9. Energy Dispersive X-Ray Spectroscopy. Figures 9 and 10 show that the corresponding characteristic peak appeared on the Energy Dispersive X-Ray Spectroscopy graphs after the adsorption of Pb^{2+} and Cd^{2+} by the cross-linked starch xanthate. It can be seen in Tables 1 and 2 that the cross-linked starch xanthate absorbed Pb^{2+} and Cd^{2+} successfully and the absorbency of Pb^{2+} was higher compared to Cd^{2+} . The reasons were various. Firstly, different chelate ability led to the difference of absorbency. The chelate ability of Pb^{2+} is better compared to Cd^{2+} . Secondly, the different adsorption dominant mechanisms lead to the difference of absorbency [3, 31].

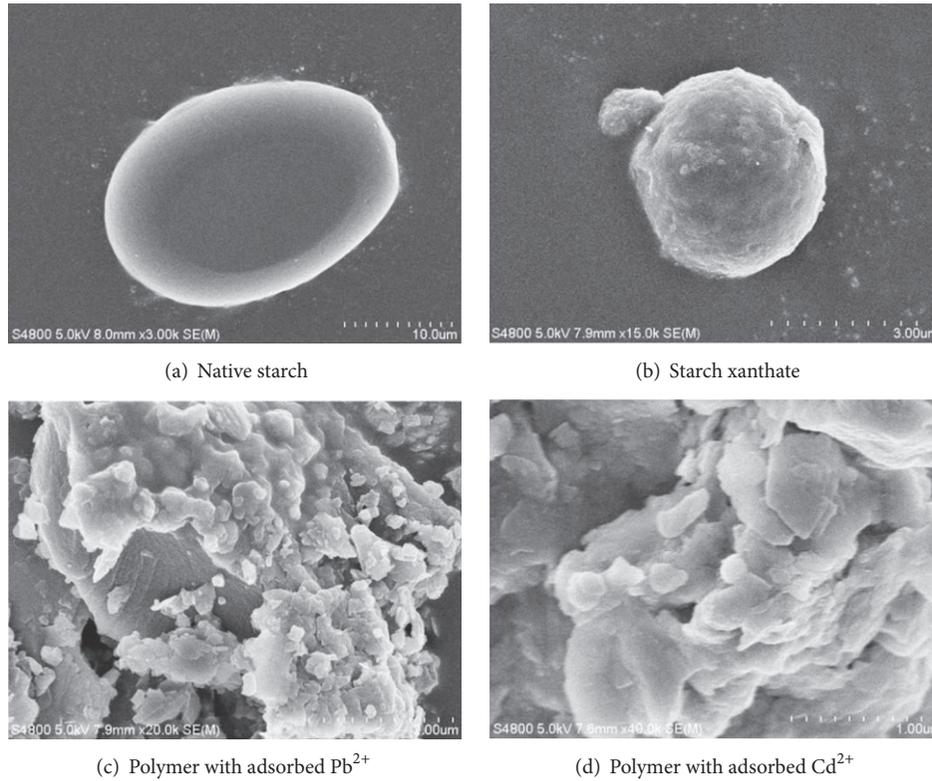
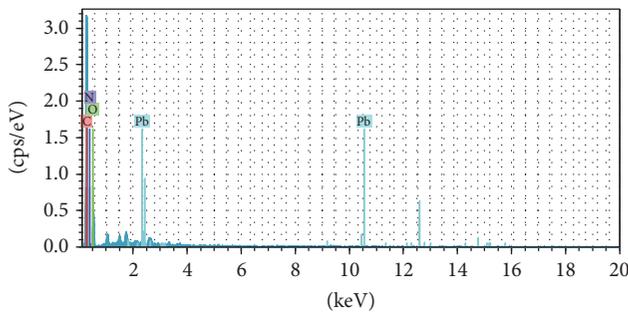
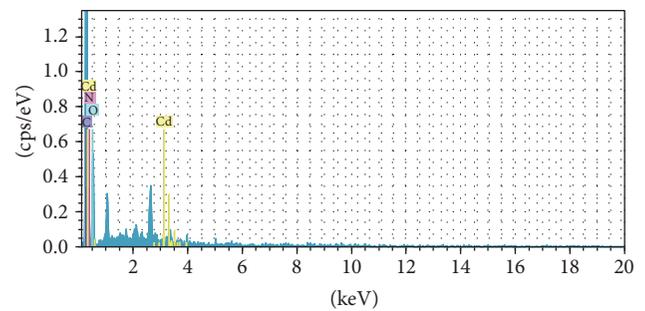


FIGURE 8: Scanning electron micrographs.

FIGURE 9: EDX measurement of cross-linked starch xanthate that absorbed Pb²⁺.FIGURE 10: EDX measurement of cross-linked starch xanthate that absorbed Cd²⁺.

4. Adsorption Isotherms

The analysis of the isotherm data is an important way to accurately represent the relationship between adsorbent and adsorbate [32]. A typical adsorption isotherm for Pb²⁺ and Cd²⁺ is presented in Figures 11 and 12. In this paper, the isotherms of Pb²⁺ and Cd²⁺ adsorption on the cross-linked starch xanthate were studied by calculating adsorption capacity as a function of Pb²⁺ and Cd²⁺ equilibrium concentration. The analysis of obtained experimental data is based on the Langmuir and Freundlich isotherm models. The Langmuir model assumes a homogeneous surface with respect to the energy of adsorption, in which no interaction existed between adsorbed species, and all the adsorption sites are equally

available to the adsorbed specie [33]. Langmuir adsorption model can be described as

$$\frac{C_e}{q_e} = \frac{1}{K_e q_m} + \frac{C_e}{q_m}. \quad (3)$$

In this formula, q_e is the adsorbed amount of the Pb²⁺ and Cd²⁺ at equilibrium (mg/g), C_e is the adsorbate concentration at equilibrium in aqueous solution (mg/L), K_e (L/mg) is the Langmuir adsorption constant related to the energy of adsorption, and q_m (mg/g) is the maximum monolayer adsorption capacity.

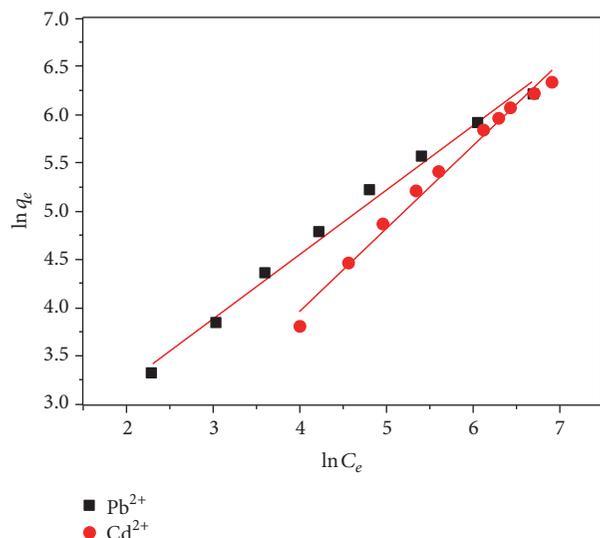


FIGURE 11: Freundlich isotherm curve fitting of Pb^{2+} and Cd^{2+} adsorption for cross-linked starch xanthate.

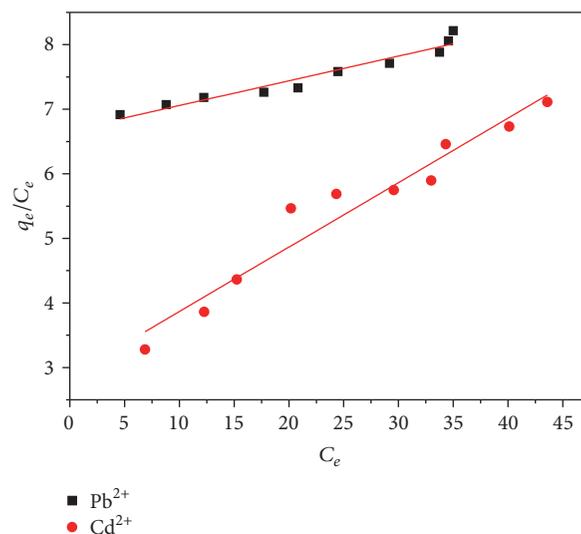


FIGURE 12: Langmuir isotherm curve fitting of Pb^{2+} and Cd^{2+} adsorption for cross-linked starch xanthate.

TABLE 3: Isotherms constants and correlation coefficients for the adsorption of Pb^{2+} and Cd^{2+} on cross-linked starch xanthate.

	Langmuir equation		Freundlich equation		
K_e	Pb^{2+}	7.950	n	Pb^{2+}	2.236
	Cd^{2+}	3.576		Cd^{2+}	1.857
R^2	Pb^{2+}	0.969	R^2	Pb^{2+}	0.998
	Cd^{2+}	0.977		Cd^{2+}	0.994
q_m	Pb^{2+}	50 mg/g	K_f	Pb^{2+}	0.586
	Cd^{2+}	50 mg/g		Cd^{2+}	0.527

Freundlich isotherm model can be applied to the nonideal adsorption on heterogeneous surfaces as well as multilayer adsorption [34], and it is described as [35]

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e. \quad (4)$$

In this formula, q_e is the equilibrium solute concentration on adsorbent (mg/g), C_e is the equilibrium concentration of the solute (mg/L), K_f (mg/g) is the Freundlich constant being indicative of the extent of adsorption, and “ n ” is the heterogeneity factor as an indicator of adsorption effectiveness. The parameters for these two isotherms are calculated. The results indicate that the correlation coefficient values of Freundlich isotherm (Pb^{2+} $R^2 = 0.998$; Cd^{2+} $R^2 = 0.994$) were higher than those of the Langmuir isotherm (Pb^{2+} $R^2 = 0.969$; Cd^{2+} $R^2 = 0.977$), which implies that the Freundlich model is better fitted to the experimental data than Langmuir model. The adsorption characteristics of Pb^{2+} and Cd^{2+} were multilayer adsorption [36, 37]. Isotherms constants and correlation coefficients for the adsorption of Pb^{2+} and Cd^{2+} on cross-linked starch xanthate were shown in Table 3.

5. Conclusion

A cross-linked starch xanthate was prepared by graft copolymerization of acrylamide and sodium acrylate onto starch xanthate using potassium persulfate and sodium hydrogen sulfite initiating system and $\text{N,N}'$ -methylenebisacrylamide as a cross-linker. The adsorption capacity to Pb^{2+} and Cd^{2+} ions of the polymer synthesis under different conditions was studied. The highest quantities of Pb^{2+} and Cd^{2+} adsorption were 47.11 mg/g and 36.55 mg/g, respectively. Freundlich model is better fitted to the experimental data than Langmuir model.

Competing Interests

The authors declare that they have no competing interests.

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