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Removal of Pb (II) by crosslinked amphoteric starch containing the carboxymethyl group

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Abstract

The adsorption process of Pb (II) ions from aqueous solution by crosslinked amphoteric starch with quaternary ammonium and carboxymethyl groups was investigated. The adsorption capacity is found to be dependent on the pH of the solution, the dose of the crosslinked amphoteric starch, and the initial concentration of Pb (II) ion. Moreover, the adsorption capacity increases with the increasing degree of substitution (DS) of carboxymethyl groups. The Langmuir adsorption isotherm gave a satisfactory fit of the equilibrium data. The adsorption process is endothermic, and thermodynamic parameters were calculated at different DS.

Keywords: Adsorption; Amphoteric starch; Metal ion; Carboxymethyl

1. Introduction

Removal of heavy metal ions from sewage and industrial wastewater has been given considerable attention over recent years. Precipitation, ion exchange (Huang, Si, & Li, 1997; Ji, 1999; Karakisla, 2003), solvent extraction, and adsorption on activated carbon, as well as synthetic polymers (Egawas, Nonaka, Abe, & Nakayama, 1992; Lee & Hong, 1995; Piskin, Keenci, & Satiroglu, 1996; Rivas, Pereira, Gallegos, & Geckeler, 2002) are the conventional methods for removing the heavy metal ions from aqueous solutions. However, these methods are limited to a certain degree, due to possible recontamination and high cost.

Starch is renewable and biodegradable, and modified starch is capable of adsorbing heavy metal ions. Low-cost modified starch for removal of heavy metal ions has been previously reported. Crosslinked starch xanthate, and carboxyl-containing starch products have been shown to remove heavy metal cations effectively from wastewater (Kim & Lim, 1999; Kweon, Choi, Kim, & Lim, 2001; Rayford, Wing, & Doane, 1979; Wing, Rayford, Doane, & Russell, 1978). Chan reported (Chan & Wu, 2001) the mass transport process for the adsorption of Cr (VI) onto crosslinked cationic starch, as well as the adsorption of Cu^{2+} and Ga^{2+} onto insoluble amphoteric starch containing quaternary ammonium and phosphate groups (Chan, 1993; Chan & Ferng, 1999). However, the relationship between the adsorption capacity and the degree of substitution (DS) of modified starch, which is very important in actual applications, has not been reported. Moreover, the adsorption behavior between Pb (II) and amphoteric starch with carboxymethyl groups, which are obtained by hemi-dry processes, have not been investigated so far in the literature.

Recently, the adsorption processes of metal anions by amphoteric starch with quaternary ammonium and carboxymethyl groups have been investigated by our Laboratory (Xu, Zhang, & Lu, 2003). In the present study, removal of Pb (II) from aqueous solution by adsorption on a series of crosslinked amphoteric starches with different DS was investigated. Adsorption isotherms and thermodynamic parameters of the adsorption are also presented.

2. Experimental

2.1. Materials

Food grade corn starch was dried at 105 °C before use. 3-Chloro-2-hydroxypropyltrimethylammonium chloride

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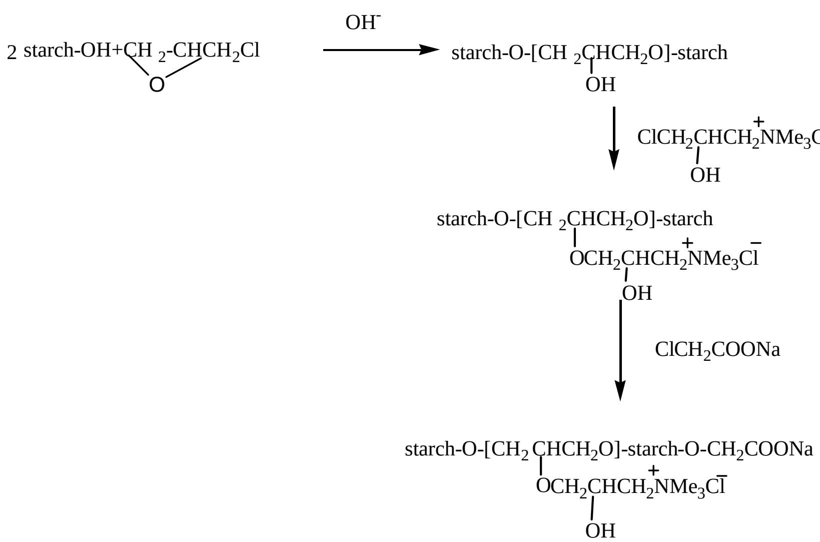
(65% aqueous solution), epichlorohydrin, and chloroacetic acid (A.R.) were used as received. Atomic adsorption spectrometry was carried out using an AAnalyst 300 instrument (P.E Company)

Crosslinked amphoteric starches (CAS) were prepared by a hemi-dry process according to the previously published work (Xu et al., 2003). Nitrogen content, and hence the DS of quaternary ammonium cationic groups in the CAS, were measured with the Kjeldahl method; the amount and DS of carboxymethyl anionic group was measured by alkaline titration (Mattisson & Legendre, 1952). Three kinds of CAS were used, which were designated as CAS1, CAS2, and CAS3, respectively. Their DS of quaternary ammonium cationic groups were all 0.3, while the DS of carboxymethyl anionic groups were 0.12, 0.20, and 0.33, respectively.

The proposed reactions involved in the above process are shown in the following scheme:



2.2. Adsorption procedure

The adsorption experiments in this study were carried out in a series of 100 mL Erlenmeyer flasks containing the desired dose of CAS and 50 mL of aqueous $Pb(NO_3)_2$ solution at the desired concentration and initial pH (adjusted with 0.1 N hydrochloric acid or 0.1 N NaOH) in a shaking bath. After shaking for a certain time, the supernatant was removed and the concentration of Pb (II) was analyzed by atomic adsorption spectrophotometry. All results were performed in triplicate and the data were recorded as a mean (C.V. < 5%). The adsorption capacity of the CAS was calculated by the following expression

$$Q = \frac{(C_0 - C_t)V}{m}$$

where Q is the adsorption capacity of the CAS (mg/g), C_0 and C_t (mg/L) are the concentration of Pb (II) ions at the initial time and time t, respectively, V is the total volume of the aqueous solution (L) and m is the weight of CAS (g).

3. Results and discussion

3.1. Effect of initial pH

The effect of the initial pH of the solution on the residual Pb (II) concentration (initial [Pb 2+] = 50 mg/L) at $T = 20$ °C is shown in Fig. 1.

Since at the initial Pb^{2+} concentration, $Pb(OH)_2$ can precipitate at pH 5.5 (pKsp = 14.93), we carried out the experiment at or below pH 5.5. It is shown that the residual concentration of Pb^{2+} markedly decreases from pH 2 to 4, then decreases gradually until it reaches a stable value at pH = 4–5. The same trends are indicated at different DS of the carboxymethyl groups. At the same pH value, the adsorption capacity of the adsorbent augments with the increase of DS of the anionic groups, i.e. $Q_{CAS1} < Q_{CAS2} <$

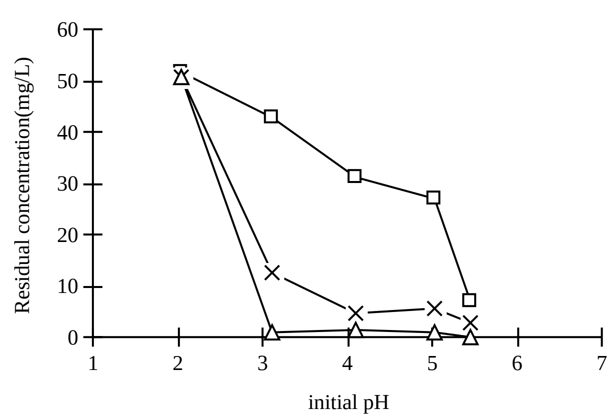


Fig. 1. Effect of initial pH value of solution on residual concentration (□) CAS1; (×) CAS2; (△) CAS3 ([Pb^{2-}] = 50 mg/L; t = 1 h; T = 20 °C; the dose of CAS1, CAS2, CAS3 all are 40 mg).

Q_{CAS3}. The ionic interaction between the negative carboxymethyl groups in the CAS and positive Pb^{2+} ion is the main factor in the adsorption procedure, so the adsorption is more effective when the DS of carboxymethyl groups is higher. At low pH, the carboxymethyl groups exist predominately in the form of $-CH_2COOH$, and this prevents Pb^{2+} ions from adsorbing on the CAS. However, when the pH value continued to increase up to 5.5, the residual concentration decreased abruptly, especially for CAS1. This is probably because Pb^{2+} precipitates out in the form of $Pb(OH)_2$ at pH > 5, and flocculation acts as a dominant role instead of the ionic interaction.

3.2. Effect of dose of CAS

It was supposed that the residual concentration of Pb (II) would decrease under the higher dose of the absorbents, because the active sites increase with the increasing dose. The experimental results that higher DS of the anionic group results in more effective adsorption further confirm this conclusion. In Fig. 2, the effect of varying the CAS dose on the residual Pb(II) concentration is shown, and it is seen that the residual concentration plateaus at 20.87, 1.22, and 0.77 mg/L for CAS1, CAS2 and CAS3, respectively, at a 50 mg dose. If only the ionic interaction is concerned, the adsorption capacity of CAS2 should be equal to that of 1.5 times of CAS1 because the DS value of the former is 0.20, and the latter is 0.12, but the results do not support this at higher dose. It can possibly be interpreted that the interaction between absorbent molecules becomes stronger under a higher dose. So it is concluded that to increase the DS of the absorbent is more effective and economical than to increase the dose of absorbents under a certain initial concentration of metal ions.

3.3. Effect of initial concentration

Fig. 3 shows the relation between the initial concentration and the residual concentration of Pb (II) ions.

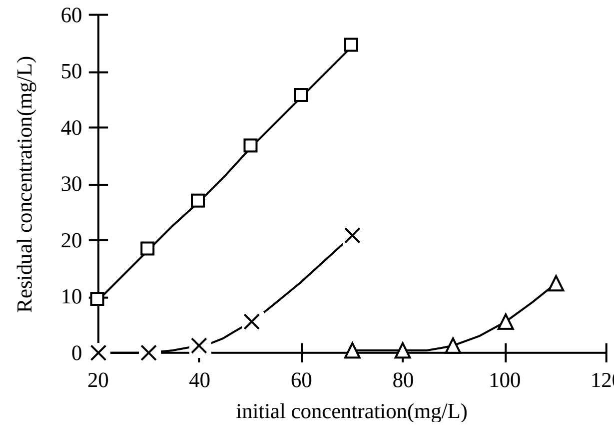


Fig. 3. Effect of initial concentration of Pb^{2+} on residual concentration (□) CAS1; (×) CAS2; (△) CAS3. (The dose of CAS1, CAS2 and CAS3 are 40 mg; t = 1 h; T = 20 °C; pH = 4.)

As seen from Fig. 3, the residual concentrations of Pb (II) of CAS1, CAS2 and CAS3 increase, respectively, from 9.36 to 54.64 mg/L, almost 0 to 20.67 mg/L, and 0.51–12.19 mg/L with increasing initial concentration of Pb (II) from 20 to 70 mg/L for CAS2 and CAS1, and 70–10 mg/L for CAS3. The experimental adsorption capacities of CAS1, CAS2 and CAS3 are 19.2, 61.66 and 152.74 mg/g, while the DS values indicate that the starches theoretically will adsorb 76.7, 127.9 and 191.7 mg/g Pb (II) for CAS1, CAS2 and CAS3, respectively. The adsorption capacities in the experiments show a value less than their theoretical value, especially, at lower concentration. It could be interpreted that the lower initial concentration, as well as the electrostatic repulsion and steric hindrance of the cationic groups in the amphoteric starches, leads to an unsaturated adsorption. The three curves of residual concentration of Pb (II) vs. initial concentration of Pb (II) are all concave upwards. Moreover, they have a common trend, which implies that the type of adsorption isotherms for the three adsorbents would be the same.

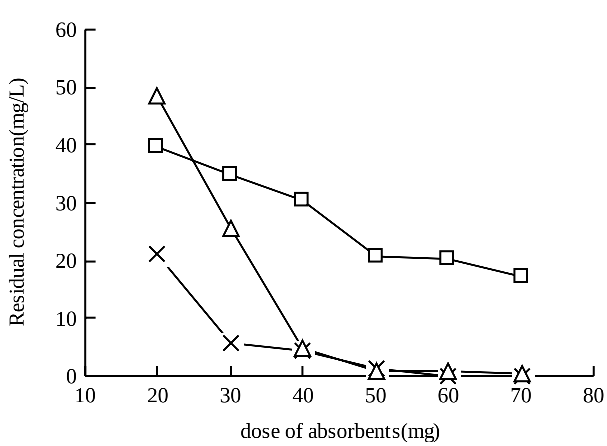


Fig. 2. Effect of dose of CAS on residual concentration (□) CAS1; (×) CAS2; (△) CAS3 ($[Pb^{2-}]$ = 50 mg/L for CAS1 and CAS2, $[Pb^{2-}]$ = 100 mg/L for CAS3; t = 1 h; T = 20 °C; pH = 4).

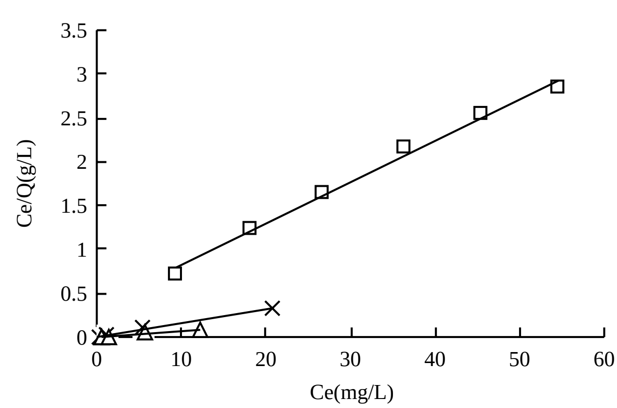


Fig. 4. Langmuir adsorption isotherm for CAS1, CAS2 and CAS3 (□) CAS1; (×) CAS2; (△) CAS3 (pH = 4; t = 1 h; T = 20 °C; the dose of CAS1, CAS2, CAS3 all are 40 mg).

Table 1
Langmuir parameters for three kinds of CAS

	Q_0 (mg/g)	b (L/g)	r^a
CAS1	21.01	0.063	0.9964
CAS2	62.11	16.79	0.9996
CAS3	156.25	48.83	0.9981

[a] The relative coefficient.

3.4. Adsorption isotherm

A typical adsorption isotherm for Pb (II) is presented in Fig. 4. As seen from the figures, the experimental data of the adsorption fit much better to the Langmuir isotherm. The Langmuir adsorption isotherm can be expressed in the following simple model in which the attachment of adsorbate to the surface is represented

$$\frac{C_e}{Q} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

where C_e is equilibrium concentration of the metal ion in solution (mol/L), Q is adsorption capacity (mg/g), Q_0 is the maximum capacity (mg/g), and b is Langmuir constant (mg/L). The Langmuir parameters are shown in Table 1. The conclusion that the adsorption capacity increases with increasing DS of carboxymethyl group can be drawn from the Langmuir constant b: b increases from 0.063 to 16.79 to 48.83 L/g, when the DS of the anionic groups increase from 0.12 to 0.20 to 0.33.

3.5. Thermodynamic studies

In order to explain the effect of temperature on the adsorption, the residual concentrations of Pb^{2+} with varying temperature (20–60 °C) were determined. A plot of the relation of the two variables shows a downward trend (Fig. 5), which implies that the adsorption process is endothermic. To verify the conclusion, Q/C_e is plotted

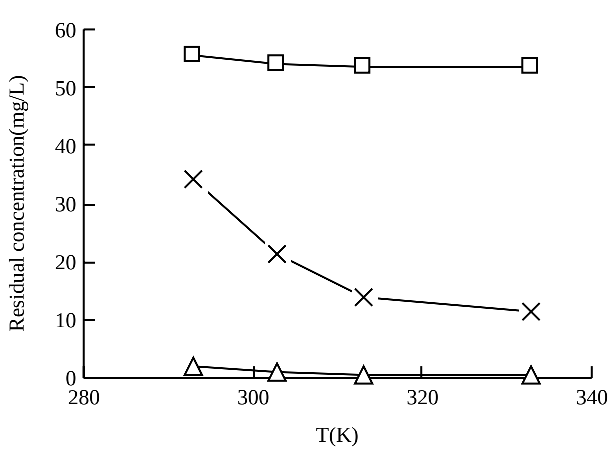


Fig. 5. Effect of temperature on residual concentration (□) CAS1; (×) CAS2; (△) CAS3 ([Pb^{2-}] = 50 mg/L, the dose of CAS1, CAS2 and CAS3 are 40 mg; t = 1 h; pH = 4).

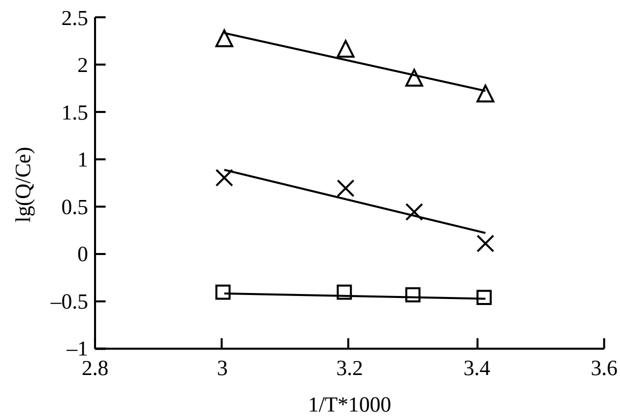


Fig. 6. Log (Q/C_e) ~ $1/T \times 10^3$ for CAS1, CAS2 and CAS3 (□) CAS1; (×) CAS2; (△) CAS3 ([Pb^{2-}] = 50 mg/L, the dose of CAS1, CAS2 and CAS3 are 40 mg; t = 1 h; pH = 4).

against $1/T$ (Fig. 6) to give ΔH^θ, ΔS^θ according to the equation as follows:

$$\lg\frac{Q}{C_e} = -\frac{\Delta H^\theta}{2.303RT} + \frac{\Delta S^\theta}{2.303R}$$

The change of apparent enthalpy (ΔH^θ), free energy (ΔG^θ), and entropy (ΔS^θ) are calculated using the relationship below and are listed in Table 2:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$$

It can be observed that the residual concentration decreases as the temperature increases, with CAS2 being the most dependent on the temperature. The positive values of ΔH^θ indicate that the adsorption of Pb (II) is endothermic, and higher temperature makes the adsorption easier. The negative ΔG^θ for CAS2 and CAS3 show the spontaneous nature of the process, while the slightly positive ΔG^θ for CAS1 indicates that the adsorption is more difficult, perhaps because more cationic groups in CAS1 interfere with the normal adsorption process.

Table 2
Thermodynamic parameters for CAS1, CAS2 and CAS3

Sample	Temperature (°C)	Q (mg/g)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol)
CAS3	20	55.39	−9.69	28.56	130.53
	30	54	-10.99		
	40	53.79	-12.29		
	60	53.75	-14.91		
CAS2	20	34.08	−1.23	31.47	111.59
	30	21.3	−2.34		
	40	13.79	−3.46		
	60	11.38	−5.69		
CAS1	20	1.74	2.60	2.43	−0.58
	30	1.17	2.61		
	40	0.58	2.61		
	60	0.46	2.62		

4. Conclusion

The adsorption between Pb (II) ion and crosslinked amphoteric starches (CASs) with quaternary ammonium and carboxymethyl groups is found to be dependent on the pH of the solution, the dose of absorbents, the initial concentration of Pb^{2+} ion, as well as the adsorption temperature. The adsorption follows the Langmuir isotherm. The adsorption capacity increases with the increasing DS of the anionic group in the CASs, and reaches to 19.2 and 61.66 mg/g, respectively, for CAS1 and CAS2 (20–70 mg/L initial concentrations) and 152.74 mg/g for CAS3 (70–110 mg/L initial concentrations).

The adsorption processes are endothermic, the apparent enthalpies (ΔH^{θ}) are 2.43, 31.47 and 28.56 kJ/mol for CAS1, CAS2 and CAS3, respectively, and negative ΔG^{θ} for CAS3 and CAS2 indicates that adsorption happens more readily when the CAS has a higher DS of carboxymethyl groups. Moreover, the adsorption for CAS2 is more dependent on the temperature.

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