Korean J. Chem. Eng., **16**(3), 298-302 (1999)

Application of Insoluble Cellulose Xanthate for the Removal of Heavy Metals from Aqueous Solution

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(Received 5 August 1998 • accepted 1 March 1999)

Abstract−Insoluble cellulose xanthate (ICX), O-alkyl dithiocarbonate of cellulose, was synthesized and used for the removal of heavy metal ions from aqueous solutions. ICX possessed carbon disulfide (CS_2) as a functional group, which was obtained by esterification of the hydroxyl group on cellulose polymer matrix with CS_2. CS_2 could form complexes with divalent transition metal ions, and the resulting ICX-metal complex was water-insoluble and settled easily. The optimum composition for ICX synthesis was cellulose/NaOH/CS_2=1 : 2 : 2.3 in mole base, which showed the highest removal capacity. The selectivity and binding capacity of ICX for heavy metals were in the order of Pb^{2+}>Cd^{2+}>Ni^{2+} and Cd^{2+}>Pb^{2+}>Ni^{2+}, respectively. More than 90 % of the initial amount of heavy metals was removed within 30 min. The optimum pH was neutral or slightly alkaline, and more than 40 % of initial heavy metals was removed even in the acidic range of pH 2 to 3.

Key words : Cellulose Xanthate, Heavy Metal Removal, Nickel, Lead, Cadmium

INTRODUCTION

One of the advanced processes proposed for the removal of heavy metals from wastewater is that of utilizing xanthates, O-alkyl dithiocarbonate, which can be synthesized by the esterification reaction of alcoholic hydroxide with carbon disulfide (CS_2) in a caustic medium [Morrison and Freiser, 1957; Matis and Mavros, 1991]. Xanthates form complexes with various transition metals through the mechanism of coordinated complex formation. Most of the xanthates of short chain alcohols are soluble in water and thus have been used in flotation processes and analytical extraction for metal recovery [Morrison and Freiser, 1957; Matis and Mavros, 1991]. Xanthates of long chain alcohols can form insoluble complexes with transition metals, and their sludges have been reported to be easily settleable and dewaterable [Peters et al., 1985; Noyes, 1994].

Wing et al. [1975, 1978, 1983] have developed an insoluble xanthate process based on starch, an inexpensive natural polysaccharide biopolymer, for the removal and possible recovery of heavy metals. Although both soluble starch xanthate (SSX) and insoluble starch xanthate (ISX) proved fairly efficient in heavy metal removal from wastewaters [Marani et al., 1980; Mazzi et al., 1985; Campanella et al., 1986; Jawed and Tare, 1991], ISX was preferred for the development of continuous packed-bed process because it could be used repeatedly. However, ISX preparation has not been so simple mainly because of high viscosity of the starch slurry in aqueous phase. A mixer-reactor with screw extruder or high shear mechanical impeller has been employed to overcome difficulties of mixing in large scale production of ISX [Swanson et al., 1961, 1973]. Cross-linking agents are often required prior to xanthation of starch to obtain highly crosslinked starch and to reduce the solubility of ISX in aqueous solution [Wing et al., 1975; Tare and Chaudhari, 1987].

Cellulose is the most abundant and inexpensive natural biopolymer. Substantial amounts of cellulose are also found in wastes and byproducts from industries making cotton, pulp, sugar, etc. [Shreve and Brink, 1977; Kim et al., 1995]. Cellulose can be xanthated since the structure of cellulose is similar to that of starch [Tare and Chaudhari, 1987; Zeng et al., 1994]. Cellulose itself is insoluble and does not form viscous solution in aqueous phase. Therefore the preparation of insoluble cellulose xanthate (ICX) can be less complicated than that of ISX, and resulting ICX can be efficiently utilized in heavy metal treatment in both batch and continuous modes. In this article, ICX has been prepared by the reaction of cellulose with CS_2 in alkaline solution. The effects of preparation condition of ICX on the removal of selected heavy metals as well as its performance are discussed.

MATERIALS AND METHODS

1. Xanthation of Cellulose

Cellulose xanthate was synthesized basically according to Wing's [1975] procedure with some modifications. A commercial α-cellulose (Sigma C8002) was slurried in water in a 500 mL three-neck flask equipped with a condenser, mechanical stirrer, and temperature controller. Sodium hydroxide solution was added and the mixture was stirred for 30 min at 65 °C. The mixture was cooled to 30 °C, then carbon disulfide was added and the mixture was stirred for 6 hrs. The reaction volume was 400 mL. The slurry was filtered through a coarse fritted-glass funnel under vacuum and the filtered paste was

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washed successively with water, acetone, and ether. After drying in an oven at 30 °C overnight, the dried solid was stored at 4 °C in a closed container. Since the density of CS_2 used for xanthation was 1.26 g/cm^3, the molar ratio of cellulose/NaOH/CS_2 in the reaction mixture was 1 : 2 : 1 when the reaction composition was 16.2 g of cellulose, 100 mL of 2 N NaOH, and 6 mL of CS_2. Molar ratio of cellulose/NaOH for xanthation was fixed at 1 : 2, but the CS_2 content was varied. One mole of cellulose was defined as 162 g, which is the molecular weight of the repeating sugar unit of cellulose chain.

2. Heavy Metal Removal

The batch adsorption equilibrium experiments were carried with aqueous solutions of nickel, lead, and cadmium. Heavy metal solutions with different concentrations were prepared by dissolving $Ni(NO_3)_2$, $Pb(NO_3)_2$, or $Cd(NO_3)_2$ in deionized distilled water. Solution pH was adjusted with HCl and NaOH, or maintained by a suitable buffer at desired values : KCl-HCl buffer for pH 2, acetate buffer for pH 3 to 5, phosphate buffer for pH 6 to 8, and carbonate buffer for pH 9 and 10 [Kim and Lee, 1998]. The ionic strength of buffer solutions was kept constant as 0.2 mol/L before dissolving heavy metal. The solution containing a heavy metal was contacted with a weighed amount of dried xanthation product, ICX, at 20 °C under continuous magnetic stirring in a flask. After an appropriate equilibrium time, which was determined from kinetic experiments, the mixture was filtered and the residual concentration of heavy metal in liquid phase was measured. Heavy metal concentrations were determined by AAS (Aurora AI1100GF, Canada).

RESULTS AND DISCUSSION

1. Equilibrium Distribution of Heavy Metals

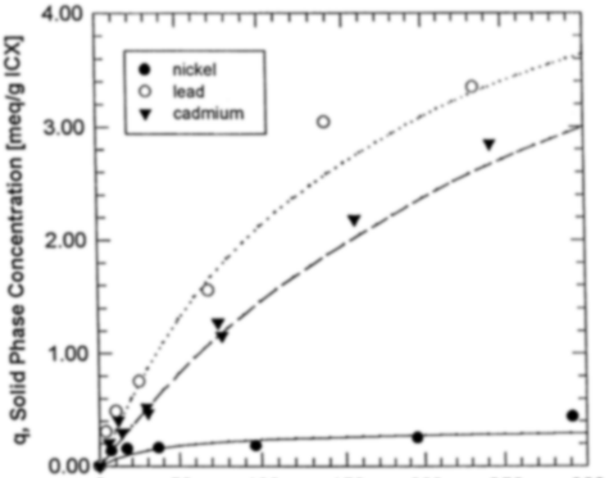

Fig. 1. Equilibrium distribution of heavy metals at 20 °C between aqueous phase and ICX.

Table 1. Langmuir parameters of heavy metals for ICX

Langmuir equation : $q=\frac{aC}{1+bC}$

	Lead	Cadmium	Nickel
a [L/g]	0.034	0.019	0.008
b [L/meq]	0.006	0.003	0.024
a/*b* [meq/g]	6.0	7.4	0.34

Since the xanthation product of cellulose in heavy metal solution settled rapidly and did not show any coagulating behavior or viscosity increase, the dried xanthation product of cellulose is referred to as ICX from here on. Fig. 1 shows adsorption isotherm data for Ni^{2+}, Pb^{2+}, and Cd^{2+} at 20 °C obtained from the batch equilibrium tests with ICX. The ICX used throughout all the experiments was synthesized with a molar ratio 1 : 2 : 2.3 of cellulose/NaOH/CS_2. Four hours of equilibration was enough. The initial pH values were all 6.5 in unbuffered condition. The pH values after equilibrium were not changed significantly and mostly 0.2-0.4 units were lowered. Lines in Fig. 1 represent curves fitted with Langmuir parameters, which are shown in Table 1. The parameters of the Langmuir isotherm for each heavy metal, in Table 1, were estimated from Fig. 1 by assuming that only monolayer adsorption took place by ICX. Since the parameter *a* represents the adsorption equilibrium constant or selectivity, it can be seen that the selectivities of ICX for heavy metal ions were in the order of Pb^{2+}> Cd^{2+}>Ni^{2+}. Heavy metal binding capacities of ICX were in the order of Cd^{2+}>Pb^{2+}>Ni^{2+} from the *a*/*b* ratio. The estimated capacity of ICX for Pb^{2+} was 6.0 meq/g, which is higher than that of the commercial cation exchange resins with styrene-divinylbenzene matrix and sulfone group as a functional group-mostly around 5 meq/g [Bio-Rad, 1997]. The reason why the binding capacities of ICX were not identical for three heavy metals could be explained with two possible mechanisms of heavy metal uptake by ICX : complex formation and ordinary ion exchange. By ion exchange, two negatively charged sulfur atoms of ICX participate in capturing one divalent metal ion. However, complex formation occurs between four sulfur atoms and one divalent metal ion. It is postulated that each heavy metal used in this study could undergo both ion exchange and complex formation with ICX and that the fractions of those two mechanisms were different for the three metals, although the major mechanism would be the complex formation as in primary alcohol xanthates [Morrison and Freiser, 1957].

Xanthation reaction and mechanisms of heavy metal uptake by ICX can be assumed to be similar with those by starch xanthate. In xanthation reaction, the hydroxyl group of cellulose undergoes the following esterification reaction with CS_2, in presence of NaOH, to form the cellulose xanthate sodium salt [Morrison and Freiser, 1957; Wing and Doane, 1978; Kim and Lee, 1998] :

$$\text{cellulose-OH+NaOH} \rightarrow \text{cellulose-ONa+H}_2\text{O}$$

$$\text{cellulose-ONa+CS}_2 \rightarrow \text{cellulose-OCSS}^-\text{Na}^+$$

The sodium salt of cellulose xanthate can bind transition metal ions by the formation of the coordination complex in which four sulfur atoms are associated with one divalent metal ion. Also there may exist an ordinary ion exchange in which two sulfur atoms are associated with one divalent metal ion [Jawed and Tare, 1991; Kim and Lee, 1998]. Therefore, if the frac-

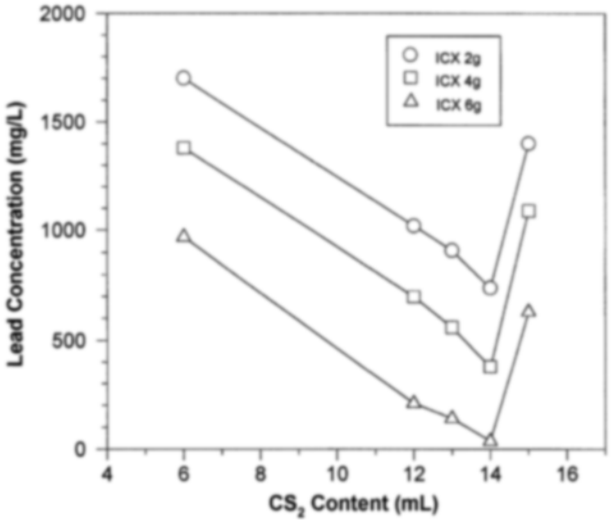

Fig. 2. Effects of CS$_2$ content used in ICX synthesis and ICX dosage on lead removal for 100 mL of 10 mM Pb^{2+} and pH 6.5.

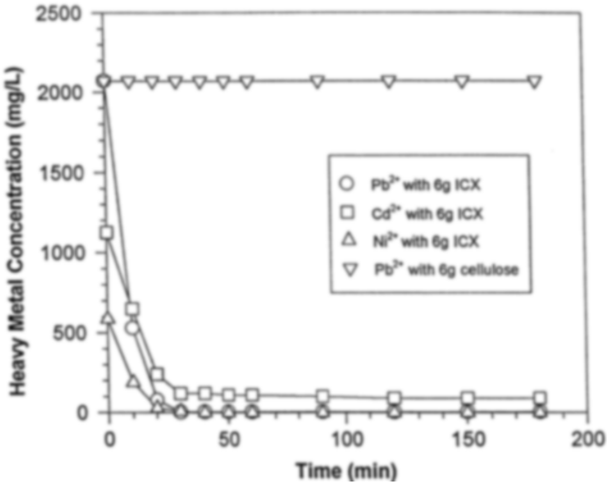

Fig. 3. Effect of equilibrium time on the removal of heavy metals by ICX for 100 mL of 10 mM heavy metals, pH 6.5, and 6 g of ICX dosage.

tion of complex formation for a metal ion (Pb^{2+}) is greater than that of ion exchange, ICX capacity for Pb^{2+} removal can be smaller than that of other metal ion (Cd^{2+}) which has a lower fraction of complex formation, although ICX selectivity is greater for Pb^{2+} than for Cd^{2+}.

2. Effects of Xanthation Composition

Fig. 2 shows the effects of CS$_2$ content used in ICX synthesis and ICX dosage on lead removal. Lead solution was 100 mL of 10 mM Pb(NO$_3$)$_2$, which is 2,072 mg/L as Pb^{2+}. Residual concentrations were measured at four hours of equilibriation after ICX dosage. The molar ratios of cellulose/NaOH/CS$_2$ were 1 : 2 : 1 and 1 : 2 : 2 when CS$_2$ contents used in xanthation reaction were 6 mL and 12 mL, respectively. The ICX made with 14 mL of CS$_2$, which molar ratio of cellulose/NaOH/CS$_2$ was 1 : 2 : 2.3, showed maximum removal of lead. If CS$_2$ content was higher or lower than this ratio, lead removal was decreased. The reason for decreased removal efficiency at lower CS$_2$ content is obvious in terms of the number of available functional groups in unit quantity of ICX. However, the reason for the decreased removal at higher CS$_2$ content is not clear. This trend was also observed in experiments with nickel and cadmium (data not shown). We speculate that some CS$_2$ molecules might be adsorbed physically on the hydrocarbon backbone of ICX if we use an excess amount of CS$_2$ in ICX synthesis. Some of them remaining after washing and drying were released into aqueous phase during stirring and thus formed free CS$_2$-metal complex in liquid phase. This complex of heavy metal and free CS$_2$ is highly soluble and interferes with the normal metal removal by ICX [Morrison and Freiser, 1957].

3. Kinetic Behavior of ICX in Heavy Metal Removal

Fig. 3 shows time course changes of residual metal concentration after ICX addition. Initial metal solution was 100 mL of 10 mM Pb^{2+} (2,072 mg/L), Cd^{2+} (1,124 mg/L), or Ni^{2+} (587 mg/L) at pH 6.5. ICX dosage was 6 g made of cellulose/NaOH/CS$_2$=1 : 2 : 2.3. The residual concentrations decreased rapidly and more than 90 % of initially loaded heavy metals were removed within 30 min. During the first 30 minutes, the residual concentration changes were from 2,072 to 15 mg/L for Pb^{2+}, from 1,124 to 130 mg/L for Cd^{2+}, and from 587 to 8 mg/L for Ni^{2+}. The rate of Pb^{2+} removal was the highest among three heavy metals in terms of mg/L. The removal of Ni^{2+} was the least compared to Pb^{2+} and Cd^{2+}. The result of a control experiment with cellulose showed that unmodified cellulose did not have metal binding capability.

Later, we carried out breakthrough experiments with a column packed with ICX to develop a process for continuous heavy metal removal and to find an effective regeneration method. According to the preliminary results, ICX proved fairly stable showing that the ICX column maintained 82 % of its original capacity for Pb^{2+} after 8th service when the regeneration was carried out with 5 mM HNO$_3$ (data not shown).

4. Effect of pH

Figs. 4-6 show the results of metal removal by ICX over the pH range of 2 to 10. Hydroxide precipitation with NaOH in the absence of ICX were also carried out as a reference. The initial heavy metal solutions were 100 mL of 10 mM concentration, and 6 g ICX (cellulose/NaOH/CS$_2$= 1 : 2 : 2.3) was added. Residual concentrations were measured at four hours of equilibriation after ICX dosage. Unbuffered solution was prepared by properly mixing HCl and NaOH. Buffered pH solutions were prepared by using specific buffer composition [Kim and Lee, 1998]. Metal removal was increased as pH increased, but hydroxide precipitation began taking place at pH around 7, 7, and 8 for Ni^{2+}, Pb^{2+}, and Cd^{2+}, respectively. Therefore the cause of metal disappearance below these pH values was considered only by ICX. The optimum pH for the removal of heavy metals by ICX was slightly alkaline pH before precipitation started. Heavy metal removal was better in unbuffered solutions than in buffered solutions for acidic or neutral pH range. It is noteworthy that more than 40 % of initial heavy metals was removed even at strong acidic condition like pH 2 to 3. Especially, more than 90 % of lead was removed at pH 2 (Fig. 5). Metal binding capabilities of general absorbents such

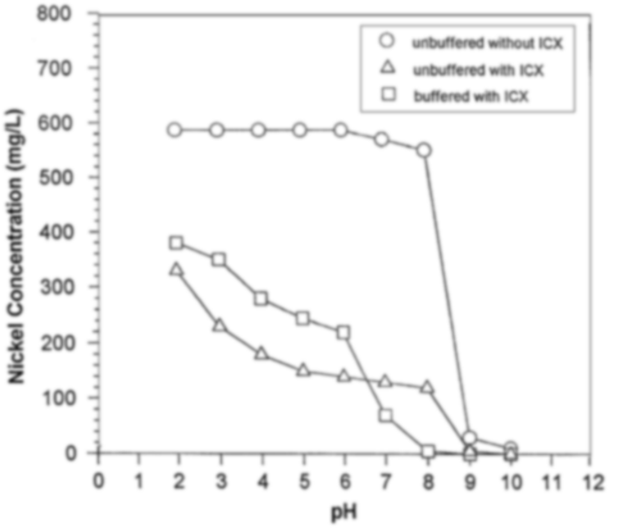

Fig. 4. Effect of pH on nickel removal with ICX for 100 mL of 10 mM Ni^{2+} and 6 g of ICX dosage.

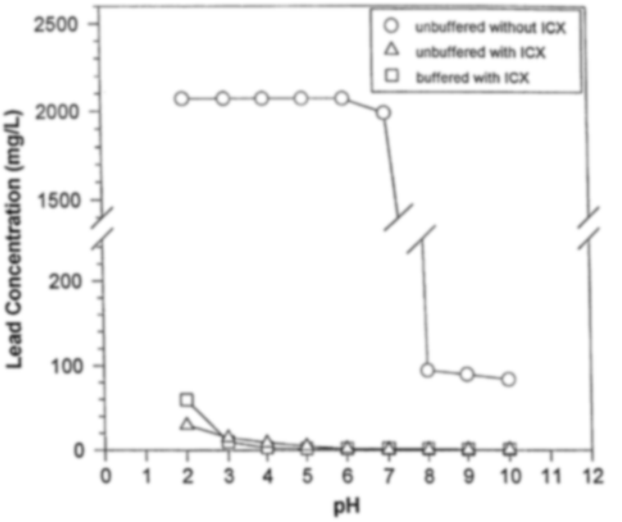

Fig. 5. Effect of pH on lead removal with ICX for 100 mL of 10 mM Pb^{2+} and 6 g of ICX dosage.

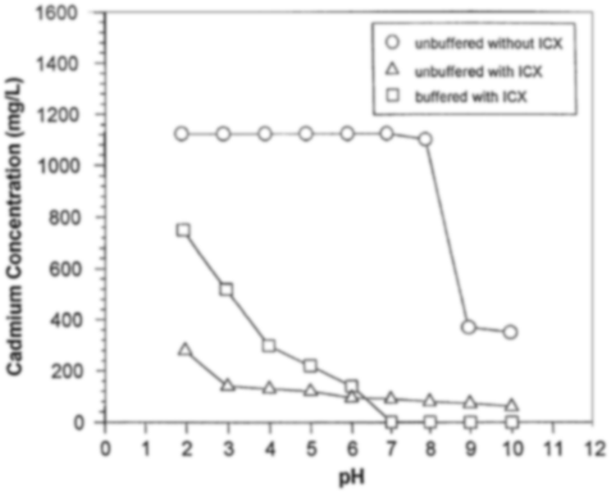

Fig. 6. Effect of pH on cadmium removal with ICX for 100 mL of 10 mM Cd^{2+} and 6 g of ICX dosage.

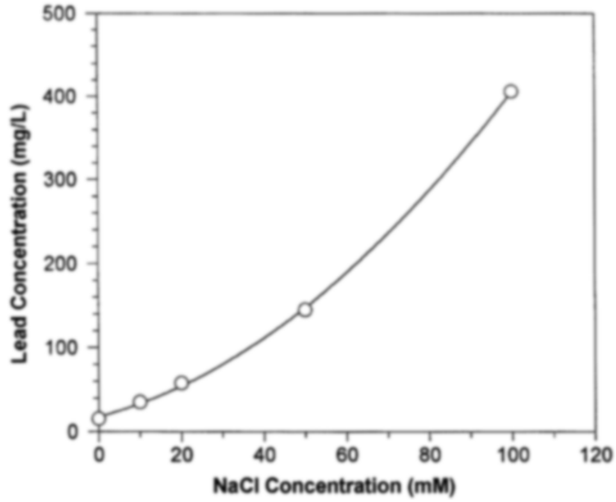

Fig. 7. Effect of ionic strength on lead removal for 100 mL of 10 mM Pb^{2+}, pH 6.5, and 6 g of ICX dosage.

as ion exchange resin, silica, alumina, or activated carbon were known to significantly decrease at acidic pH [Helfferich, 1962].

5. Effect of Ionic Strength

Effect of ionic strength on Pb^{2+} removal was examined in 100 mL of 10 mM Pb^{2+} solution (2,072 mg/L) with 6 g of ICX at different NaCl concentrations. Equilibrium time was 4 hours. Fig. 7 shows that residual Pb^{2+} concentration is increasing as NaCl concentration increases. This is because Na^+ is competing with Pb^{2+} for adsorption to ICX functional site, maybe through the ion exchange mechanism. Therefore, high concentration of NaCl reduces removal efficiency of Pb^{2+} and a similar result was observed in the cases of Cd^{2+} and Ni^{2+}, too.

Residual Pb^{2+} concentration was around 15 mg/L without NaCl after 4 hours of equilibrium, whereas 420 mg/L remained for 100 mM NaCl, which was about 80 % of removal efficiency (Fig. 7). However, the degree of reduction of removal efficiency was fairly small compared with a conventional strong acidic cation exchange resin with St-DVB (styrene-divinylbenzene) matrix and sulfone group as a functional group. St-DVB cation exchanger with sulfone group exhibited more than 50 % reduction of Pb^{2+} removal under the same condition, which is the general tendency when only ion exchange is employed for metal removal. The reason for the less reduction of removal efficiency by ICX is probably because of complex formation, which is specific to divalent transition metal ions.

CONCLUSIONS

Insoluble cellulose xanthate (ICX) with CS_2 group could form complex with transition metal ions, and the resulting ICX-metal complex was water-insoluble and settled readily. The ICX synthesized with cellulose/NaOH/CS_2=1 : 2 : 2.3 in mole base showed the highest removal capacity. The metal removal efficiency decreased when CS_2 content was higher than this ratio probably because of complex formation in liquid phase between metals and free CS_2.

The heavy metal binding capacities of ICX were in the order of $Cd^{2+}>Pb^{2+}>Ni^{2+}$. The reason why the binding capacities of ICX were not identical for three heavy metals is that each heavy metal used in this study could undergo both ion exchange and complex formation with ICX. It is postulated that the fractions of those two mechanisms were different for the three metals. The selectivities for heavy metals were in the order of $Pb^{2+}>Cd^{2+}>Ni^{2+}$. The optimum pH for the removal of heavy metals by ICX was slightly alkaline before hydroxide precipitation started. More than 90 % of the initial amount of heavy metals was removed within 30 min at neutral pH. Heavy metal removal was better in unbuffered solutions than in buffered solutions for acidic or neutral pH range. More than 40 % of heavy metals was removed even in strong acidic pH 2 to 3.

ACKNOWLEDGEMENTS

This research was financially supported by the Regional Research Center of Korea at Myongji University.

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