Heavy Metal–Soluble Starch Xanthate Interactions in Aqueous Environments

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ABSTRACT: The effectiveness of the water-soluble starch xanthate (SSX) process for removal of heavy metals [Hg(II), Cu(II), Cd(II) and Ni(II)] has been evaluated. Removal of Hg(II) and Cu(II) is effective; Cd(II) and Ni(II), less so. The metal [Hg(II)/Cu(II)] binding capacity remains the same in the pH range 3–7. An optimum metal/SSX ratio is observed for maximum metal removal. The metal removal efficiency of SSX appears to be dependent on a specific chemical interaction between metal and SSX and on separation of the metal–xanthate complex from the aqueous phase. An analogy between the metal–SSX system and the colloid–cationic polyelectrolyte system (coagulation and flocculation in water treatment) is observed. The role of ionic strength for metal–SSX system appears to be analogous to the role of indifferent electrolyte in coagulation and flocculation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1325–1332, 1999

Key words: heavy metal; starch xanthate; precipitation; coagulation and flocculation

INTRODUCTION

Removal of heavy metals from wastewater is achieved by various treatment technologies, which may be classified as available, innovative, and emerging.[1] The starch xanthate process, an emerging technology, appears to be promising based on studies reported in the literature.[2–7] Two distinct approaches of application of starch xanthates—soluble and insoluble—have been advocated. Though attempts[6–8] have been made to compare the two approaches, no definite conclusions regarding the suitability of either could be drawn. This is because several of the factors affecting the performance of the process have not been carefully studied. It is reported that the process performance very much depends on the metal and aqueous environmental conditions. Although Cu–xanthate and Cd–xanthate interactions in the aqueous environment have been studied in some detail,[8] information on other environmentally important metals, such as Hg(II) and Ni(II), is scarce. This investigation was undertaken to improve the state-of-the-art of soluble starch xanthate process, with the aim of improving its performance and ultimately paving the way for realistic comparison of the two suggested application modes of the xanthate process.

One of the major limitations of the soluble starch xanthate (SSX) process is the separation of the metal–starch xanthate precipitate complex from the aqueous phase. This has been achieved either through the addition of cationic polyelectrolyte followed by simple settling[5,9] or through high-speed centrifugation.[8] When centrifugation is used as a mode of separating the metal–SSX complex, an optimum dose of SSX is observed for maximum metal removal.[8,10] Emphasis on the observed anomalous (optimum dose) behavior is lacking in earlier studies. It is not known whether the optimal behavior is associated with the metal–xanthate precipitation/complexation or is due to the limitations of the solid–liquid separa-

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tion technique adopted. This article specifically explores this aspect of the process.

EXPERIMENTAL

Experiments were conducted under controlled aqueous conditions to observe the effect of changes in environmental conditions (such as pH, ionic strength, initial metal concentration, etc.) on the efficiency of metal removal. Hg(II), Cu(II), Cd(II), and Ni(II) were chosen as model heavy metals to study the interaction with SSX. Stock solutions of heavy metals were prepared from metal salts in triple distilled water. The salts used for were $HgCl_2$, $CuSO_4 \cdot 5H_2O$, $3CdSO_4 \cdot 5H_2O$, and $NiCl_2 \cdot 6H_2O$. Universal buffer mixtures were prepared from mixture of acetic, boric, and phosphoric acids and sodium hydroxide.[11] Potassium nitrate solution was used for ionic strength (μ) adjustment. The procedure for synthesis and purification of soluble starch xanthate was similar to that used by Marani et al.[4]

The required amount of experimental solution mixture was prepared using triple distilled water, stock metal solution, buffer, and potassium nitrate stock solution in a corning glass volumetric flask. Then 25 mL of the solution mixture was added to several 100 mL polyethylene bottles. To this appropriate quantities of purified SSX solution (pH adjusted) and triple-distilled water were added to make the reactant mixture volume 50 mL. Mixing was done by an end-over-end shaker at 20 rpm for 15 min. The bottles were then kept for 2 h to allow the precipitation reaction to near completion; this was considered to be an appropriate time to achieve near-equilibrium conditions due the very rapid nature of the metal–SSX reaction.[4] The precipitates (solid phase) were separated by centrifugation at 10,000 rpm for 30 min. The supernatants were stored in 30 mL polyethylene bottles and subsequently subjected to metal analysis. A summary of the experimental conditions used for various precipitation experiments is presented in Table I. Metal concentration in the aqueous phase was estimated using a Varian Spectra AA 20 atomic absorption spectrophotometer. Xanthate groups on SSX (degree of substitution) were estimated using a Varian Model Cary 2200 UV-Vis spectrophotometer. The electrodes used for the measurement of free cadmium and copper were Orion Models 94-48 and 94-29, respectively. These were used in conjunction with Orion Model 90-01 (for cadmium) and Model 90-02 (for copper) reference electrode and an Orion Model 901 meter. Electrophoretic mobility measurements were done using a Mark II particle electrophoresis apparatus supplied by M/S Rank Brothers, Ltd., Bottisham, United Kingdom.

RESULTS AND DISCUSSION

Figures 1 and 2 present the variation of the equilibrium aqueous phase metal [Cd(II) and Ni(II)] fraction [equilibrium aqueous phase metal concentration (Ce)/initial metal concentration (Co)] and concentration of SSX at different pH values.

As shown, there is significant metal removal by SSX, but residual metal concentrations are higher than regulatory effluent standards of many countries. Cadmium removal with increased SSX dose is slightly systematic in the pH range of 4–5, whereas it is random at pH 3, 6, and 7. Cadmium removal of up to 80% of the initial metal concentration is achieved at pH 4 and 5 by SSX. Nickel removal by SSX is less than cadmium removal, and the maximum removal achieved is ~ 50% of the initial nickel concentration.

These observations are at variance with those of Lokesh and Tare[10] for the Cd–SSX system at higher ionic strength (0.3–0.6). Lokesh and Tare[10] also reported an optimum SSX dose for maximum metal removal that is not apparent from Figure 1. It was argued that SSX may have lower affinity for cadmium and nickel, and the xanthate groups on SSX (being a high-molecular-weight polymer) may interact with each other, as was postulated for polyelectrolytes used as coagulant.[12] However, this possibility seemed to be less probable as the color of supernatant resembled the typical color of the metal [Cd(II)/Ni(II)]–SSX complex formed. This coloration was also similar to the metal–EX (metal ethyl xanthate) complex. Estimations of aqueous free cadmium in the supernatant also implied that cadmium was in a complexed form. Based on these observations, it appeared that although Cd(II)– and Ni(II)–SSX complexes were formed, their separation from the aqueous phase was not effectively achieved under the conditions of solid–liquid separation used.

Figures 3 and 4 present variation of the fraction of metal [Hg(II) and Cu(II)] removed with SSX concentration. Irrespective of the pH studied, it is possible to achieve low (< 1 mg/l) residual aqueous phase metal concentration. There appears to be an optimum dose of SSX for maximum

Table I Experimental Conditions Used in Various Precipitation Experiments (Equilibration Time 2 h; Temperature 20°C)

Metal and Its Initial Concentration, Co (mg/L)	Precipitant (SSX) Concentration (m*M*/L)	pH	Ionic Strength (μ)	Concentration of Acetate; Phosphate; Borate in Buffer (g/L)
Cadmium				
Co = 5.6	0.02–1.65	3.1–3.4	0.01	0.60; 0.97; 0.60
Co = 10.8	0.05–2.47	4.2–4.4	0.01	0.57; 0.93; 0.56
Co = 13.0	0.99–1.98	4.3–4.4	0.01	0.57; 0.93; 0.56
Co = 23.0	0.03–2.32	4.3–4.4	0.01	0.57; 0.93; 0.56
Co = 24.0	0.1–1.95	4.0–4.2	0.10	0.57; 0.93; 0.56
Co = 45.0	0.31–4.57	4.0–4.4	0.01	0.57; 0.93; 0.56
Co = 50.0	0.19–2.93	4.0–4.2	0.10	0.57; 0.93; 0.56
Co = 118.0	0.03–2.00	4.2–4.3	0.01	0.57; 0.93; 0.56
Co = 12.0	0.02–1.45	5.1–5.3	0.01	0.53; 0.86; 0.52
Co = 5.6	0.08–1.55	6.2–6.3	0.01	0.50; 0.81; 0.49
Co = 5.5	0.08–1.55	7.1–7.2	0.01	0.46; 0.76; 0.46
Copper				
Co = 19.2	0.28–2.87	3.2–3.6	0.01	0.60; 0.97; 0.60
Co = 4.4	0.02–2.02	4.0–4.3	0.01	0.57; 0.93; 0.56
Co = 19.2	0.11–1.43	4.0–4.1	0.01	0.57; 0.93; 0.56
Co = 47.0	0.20–3.03	3.8–4.0	0.01	0.57; 0.93; 0.56
Co = 102.0	1.42–8.53	4.0–4.4	0.01	0.57; 0.93; 0.56
Co = 19.0	0.28–2.87	4.9–5.1	0.01	0.53; 0.86; 0.52
Nickel				
Co = 19.2	0.10–2.40	3.2–4.0	0.01	0.60; 0.97; 0.60
Co = 9.6	0.22–3.37	4.2–4.5	0.01	0.57; 0.93; 0.56
Co = 19.0	0.11–2.89	4.2–4.5	0.01	0.57; 0.93; 0.56
Co = 48.0	0.58–5.88	4.2–4.8	0.01	0.57; 0.93; 0.56
Co = 89.0	0.99–7.98	4.0–4.7	0.01	0.57; 0.93; 0.56
Co = 19.2	0.10–2.40	5.2–5.5	0.01	0.53; 0.86; 0.52
Co = 19.2	0.11–2.75	6.0–6.5	0.01	0.50; 0.81; 0.49
Co = 19.2	0.11–2.77	7.1–7.4	0.01	0.46; 0.76; 0.46
Mercury				
Co = 16.0	0.06–3.22	3.3–3.4	0.01	0.60; 0.97; 0.60
Co = 18.0	0.06–3.22	4.1–4.5	0.01	0.57; 0.93; 0.56
Co = 48.0	0.12–3.65	4.0–4.3	0.01	0.57; 0.93; 0.56
Co = 105.0	0.24–3.64	4.0–4.3	0.01	0.57; 0.93; 0.56
Co = 19.0	0.07–3.34	5.0–5.4	0.01	0.53; 0.86; 0.52
Co = 20.0	0.07–3.36	6.2–6.3	0.01	0.50; 0.81; 0.49
Co = 20.0	0.07–3.36	7.1–7.2	0.01	0.46; 0.76; 0.46

metal removal. The behavior is systematic over the pH range studied. The optimum dose of SSX is not affected by pH, in the pH range 3–7, for similar initial concentrations of mercury and copper.

Visual observation indicated that the metal–SSX complex of mercury and copper formed flocs that settled well for SSX doses up to optimum. A few random estimation of aqueous metal concentrations exhibited no significant difference between supernatant of settled and centrifugally separated metal–SSX complexes up to the optimum dose of SSX.

In the present study, removal of metal by SSX from the aqueous phase is considered to consist of two steps. The first step is the specific chemical interaction of metal ions with xanthate functional groups on SSX; the second step is separation of the metal–SSX complex from aqueous phase.

Metal ions are in dynamic equilibrium with free xanthate, complexed metal xanthate, and other aqueous specie. The solubility product (K_{sp}) values of metal ethyl xanthate for Hg(II), Cu(II), Cd(II), and Ni(II) are 1.7×10^{-38}, 5.2×10^{-20}, 2.6×10^{-14}, and 1.9×10^{-12}, respectively.[13] The

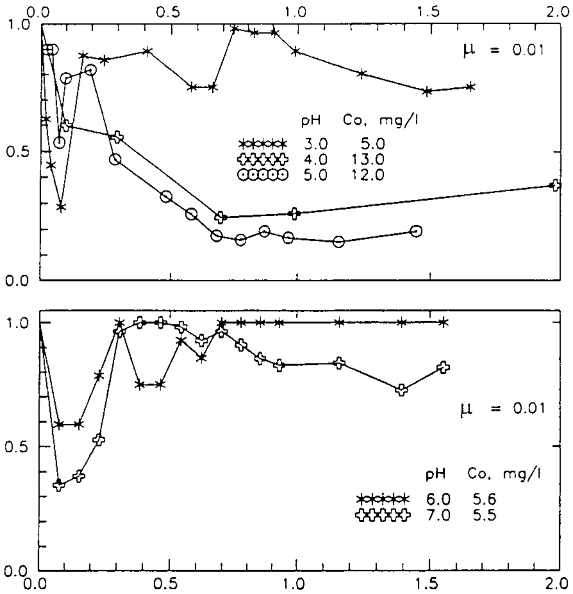

Figure 1 Variation of aqueous phase cadmium fraction with SSX concentration.

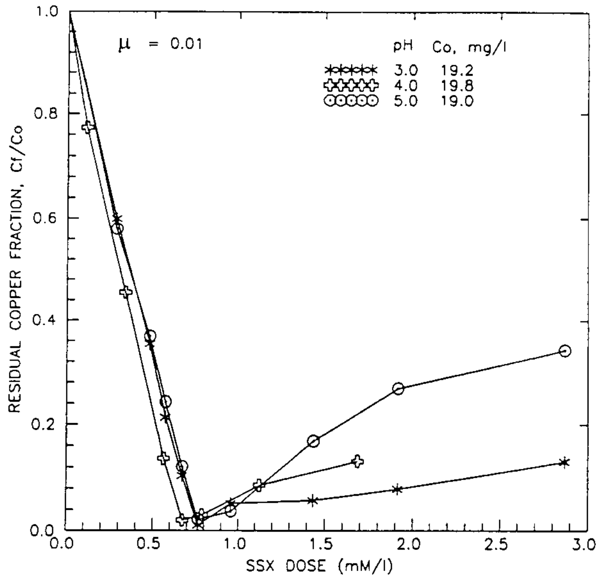

Figure 3 Variation of aqueous phase copper fraction with SSX concentration.

solubility product values for metal starch xanthate would be different than those of metal ethyl xanthate, and thus these are used only for qualitative purpose. The solubility product values for Cd(II) and Ni(II) are much higher than those for Hg(II) and Cu(II). Metal–xanthate complexation in a simplified form could be expressed as

$$M^{+2} + 2X^{-1} = (MX_2)^0$$

$$K_{sp} = [M] \cdot [X]^2,$$

where M represents the metal ion and X represents the xanthate group. It is evident from the above equation that aqueous free xanthate concentration would be higher when K_{sp} is higher

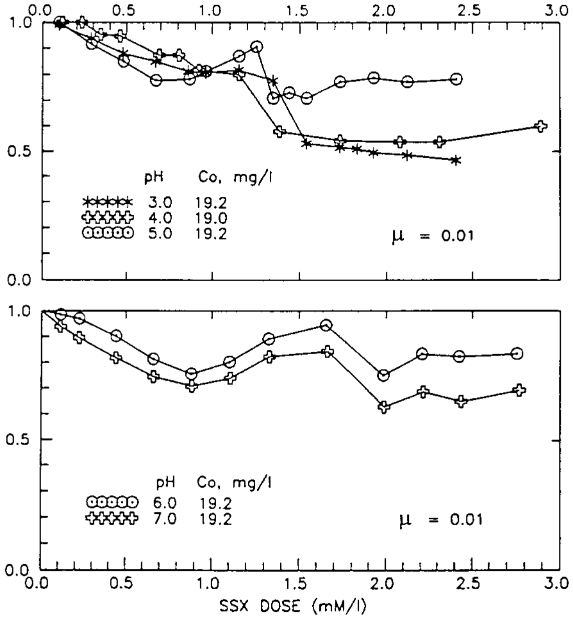

Figure 2 Variation of aqueous phase nickel fraction with SSX concentration.

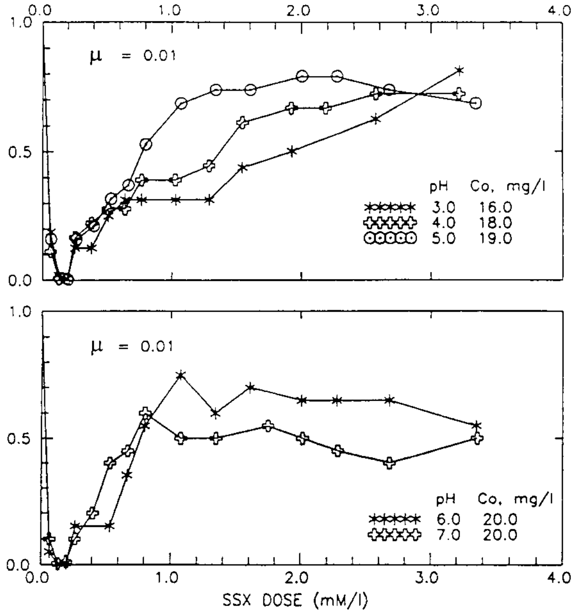

Figure 4 Variation of aqueous phase mercury fraction with SSX concentration.

and vice versa, when other conditions are kept constant. In the context of the metal–SSX system, soluble starch xanthate is considered to be a polymer with several xanthate groups on it, and when metals with high K_{sp} interact, then the residual charge (free xanthate) on SSX molecule left over is significant. This is probably the case for Cd(II)– and Ni(II)–SSX complex. The residual charge on the complex hinders particle aggregation, with consequent low metal removal, whereas low solubility product values for ethyl xanthates of Hg(II) and Cu(II) are an indicator of higher complexation and better charge neutralization, leading to higher removal. Low metal removal at higher doses SSX (beyond optimum) for the same metals could be attributed to the net negative charge prevailing on the metal–SSX complex due to unreacted/free xanthate (formation of negatively charged metal–xanthate specie) hindering particle aggregation. The constant optimum dose of SSX for Hg(II) and Cu(II) over the pH range 3–7 is attributed to no change in charge characteristics of metal ions and SSX in this pH range.

Attempts were made to measure particle charges through electrophoretic mobility measurements using particle electrophoresis apparatus. Due to typical nature of the solids (rapid decomposition of xanthates in dilute solutions and flexible physical structure of the particles) precise quantitative estimates of zeta potentials could not be made. However, the following qualitative observations were made based on the movement of particles under an electric field:

- Particles in SSX, Ni-SSX, and Cd-SSX dispersions had net negative charges.
- Hg-SSX and Cu-SSX dispersions had particles with near-neutral charge up to optimal SSX doses. Beyond optimum doses, these dispersions also had particles with net negative charge.

The observed behavior of the metal–SSX system appears to be similar to the colloid–cationic polyelectrolyte system in water treatment.[14] Thus, separation of the metal–xanthate complex could be considered analogous to that observed in coagulation of colloids by polyelectrolytes in water purification. In the metal–SSX system, positively charged metal species could be considered as colloids and anionic starch xanthate as a polyelectrolyte. The role of ionic strength for the metal–SSX system by the same analogy should be considered to be similar to the role of indifferent electrolytes for colloid–polyelectrolyte system.

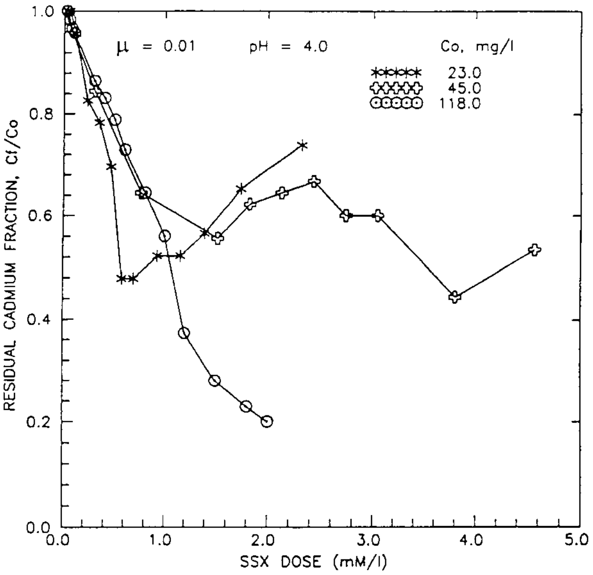

Figure 5 Variation of aqueous phase cadmium fraction with SSX concentration at pH 4.

To justify the analogy considered between the two systems, it was felt that metal removal by SSX for different initial metal concentrations at a particular pH and ionic strength could be studied. This could indicate whether there is any stoichiometric relationship between initial metal concentration and optimum SSX dose, and whether the optimum dose range broadens with an increase in initial metal concentration as observed for the colloid–cationic polyelectrolyte system.

Figures 5–8 present the effect of varying SSX doses for different initial concentrations at pH 4. This pH was chosen as the most suitable value at which to examine the influence of initial metal concentration and ionic strength considering metal speciation (most of the metals are present in free form at this pH) and decomposition of xanthates (xanthate decomposition rate rapidly increases at pH < 3). The amount of SSX required to reduce residual aqueous metal concentrations (precipitation reaction to complete) increases with increase in initial metal concentrations. The efficiency of SSX to remove Cu(II) improves with increasing metal concentrations. Further, at higher initial metal [Hg(II) and Cu(II)] concentrations the optimum dose range of SSX is broader than for low initial metal concentrations, where the optimum dose range almost narrows down to a point. It appears from Figures 7 and 8 (for copper and mercury) that there exists a stoichiometric

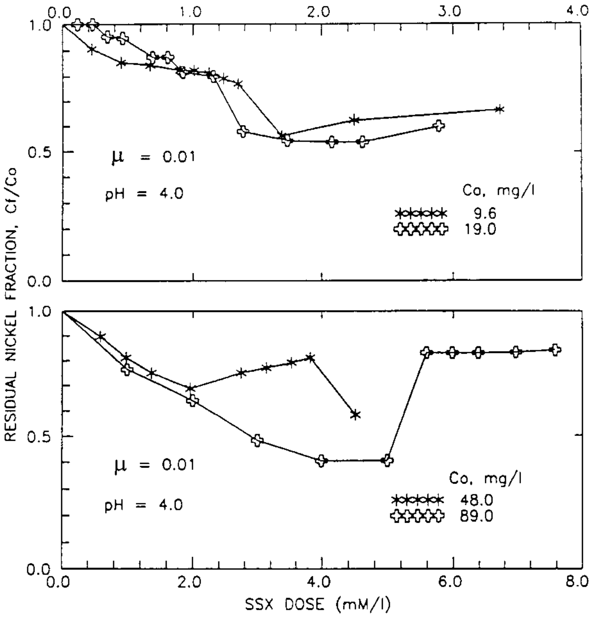

Figure 6 Variation of aqueous phase nickel fraction with SSX concentration at pH 4.

relationship between SSX dose and initial metal concentration for the optimum removal.

The metal–SSX behavior observed in this study appears to be similar to that of the colloid–polyelectrolyte system. When cationic polymers (anionic starch xanthate for the metal–SSX system) are used to destabilize negative colloids (cationic metal ions for the metal–SSX system), destabilization is accomplished by charge neutralization and/or bridging or a combination of these two mechanisms. Both of these methods indicate a stoichiometry between colloid concentration and coagulant dosage, and both predict restabilization by overdosing. The width of the coagulation region (optimum dose range) is narrow for lower colloid concentration (low initial metal concentration), and this region broadens with increasing colloid concentration.[14] These polymers may not be effective coagulants for low turbidity waters; that is, waters containing low concentrations of colloidal particles. This is probably due to the low rate of interparticle contacts in such systems, although other phenomena may be involved. The addition of more colloidal material in the form of a coagulant aid can permit these polymers to function; alternatively Fe(III), Al(III), or lime may be used in conjunction with these polymers.[12]

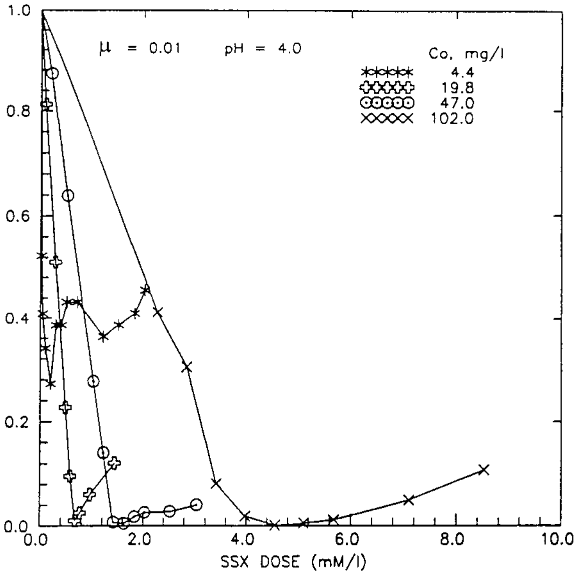

Figure 7 Variation of aqueous phase copper fraction with SSX concentration at pH 4.

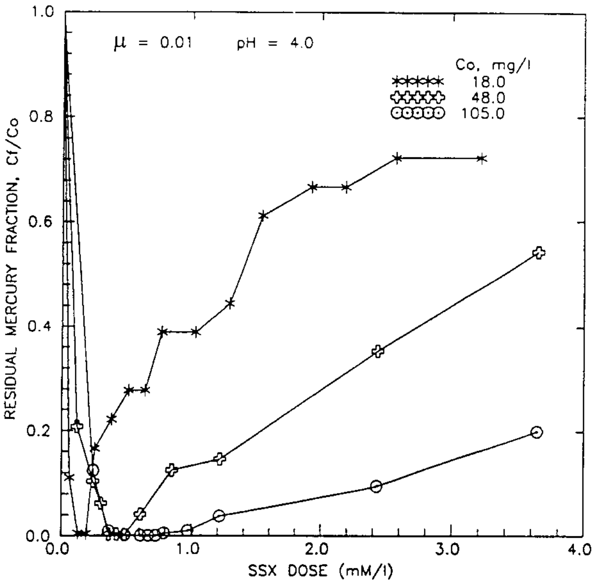

Figure 8 Variation of aqueous phase mercury fraction with SSX concentration at pH 4.

It is established from the aforementioned observations that cadmium and nickel are removed less effectively by SSX, and it would appear that the removal efficiency is associated with the inability of the centrifugation method used to separate the metal–xanthate complex from the aqueous phase. This could be further supported by studying the metal–SSX interaction with different aqueous phase ionic strengths. If the metal removal efficiency of SSX is governed by separation of the colloidal metal–xanthate complex, then it can be expected that an increase in aqueous phase ionic strength would assist in metal–xan-

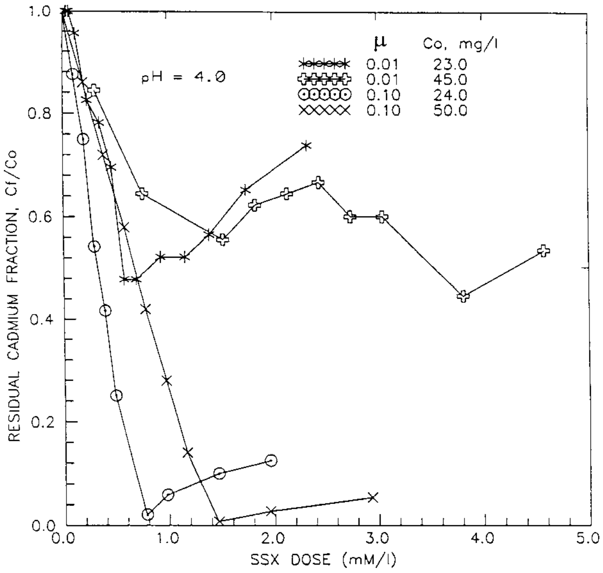

Figure 9 Variation of aqueous phase cadmium fraction with SSX concentration for different ionic strengths at pH 4.

thate complex separation and thereby improve the metal removal efficiency of SSX. However, careful choice of ionic strength is required to ensure that the effect of ionic strength is not to the extent that would alter the behavior of metal–SSX interaction.

Figure 9 presents the variation of the equilibrium aqueous phase cadmium concentration as a function of SSX dose for different ionic strengths at pH 4. Increasing the ionic strength decreases the aqueous phase cadmium concentration and hence increases the cadmium removal capacity of SSX for the optimum dose of SSX. The possible reason for increased metal removal due to high ionic strength may be due to better aggregation of negatively charged cadmium–xanthate complex because destabilization of colloids by counter-ions (potassium ions in the present study) is considered to be accomplished by compressing the diffuse layer surrounding the colloidal particles (cadmium–xanthate complex). High electrolyte concentration in the solution results in correspondingly higher concentration of counter-ions in the diffuse layer. The volume of the diffuse layer to maintain electroneutrality is lowered, and consequently the thickness of the diffuse layer is reduced. The range of repulsive interaction between similar colloidal particle decreases, and the activation energy barrier can disappear.[5,12,15] Results similar to those presented in Figure 9 have been reported by Posselt and coworkers with respect to adsorption and destabilization/restabilization phenomena affected by cationic polyelectrolytes and metal ions in suspensions of manganese dioxide.[16] These investigators studied the effect of polydiallyldimethylammonium polycation having a molecular weight in excess of 5 × 10^4 and the effects of the simple Ca(II) ion in colloidal systems of hydrous MnO at different pH levels. It was observed that destabilization of the colloid did not occur as a result of sorption of the polycation, and that Ca(II) ions also affected destabilization at sufficiently high concentration. The Ca(II) ions did not produce restabilization, whereas an increased polycation concentration beyond that required for destabilization ultimately resulted in restabilization of the suspension.

CONCLUSIONS

Based on the results of the present investigation and the synthesis of the available scientific information derived from review of the relevant literature, the following conclusions may be drawn:

1. Soluble starch xanthate exhibits an optimum metal/xanthate ratio [for Hg(II) and Cu(II)] at which maximum metal removal occurs from the aqueous phase. The optimum is independent of pH in the range of 3–7. The phenomenon of the optimum appears to be associated with the solid–liquid separation method used to separate the metal–xanthate complex from aqueous phase.
2. Cadmium and nickel at low ionic strength ($\mu = 0.01$) are less efficiently removed by SSX as compared to copper and mercury. It is hypothesized that cadmium and nickel complex with xanthate and form colloids that are difficult to remove from aqueous phase. This is probably the reason for lower cadmium and nickel removal. However, metal removal efficiency increases with increased initial metal concentration. Removal efficiency is also promoted by increasing the ionic strength. At higher ionic strength ($\mu = 0.1$), cadmium removal by SSX follows the trend similar to that of copper and mercury-SSX interaction.
3. Efficiency of the process is limited by solid–liquid separation and not by the ability/capacity of the xanthate to bind the metals.

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