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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Husein, Maen M. , Vera, Juan H. and Weber, Martin E.(1998) 'Removal of Lead from Aqueous Solutions with Sodium Caprate', Separation Science and Technology, 33: 12, 1889 — 1904

To link to this Article: DOI: 10.1080/01496399808545911

URL: http://dx.doi.org/10.1080/01496399808545911

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SEPARATION SCIENCE AND TECHNOLOGY, 33(12), pp. 1889–1904, 1998

Removal of Lead from Aqueous Solutions with Sodium Caprate

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ABSTRACT

Lead was removed from aqueous solutions by precipitation using sodium caprate [$CH_3(CH_2)_8COONa$]. For a feed concentration of 7 mM (1450 ppm) lead and a mole ratio of caprate to lead of 2, the percentage removal of lead and the percentage loss of caprate were 99.5 ± 0.2 and 0.8 ± 0.3, respectively. The effects of pH and the concentrations of lead, calcium, chloride, and nitrate in the feed on the removal step were determined. At a mole ratio of caprate to lead of 2.0, the equilibrium concentrations of lead and caprate were independent of the feed concentration of lead. Decreasing the pH of the feed decreased the removal of lead but did not affect the loss of caprate. The presence of calcium, chloride, or nitrate in the feed did not affect the removal of lead. Sodium caprate was regenerated by adding HNO_3 to the lead caprate precipitate to form capric acid from which sodium caprate was recovered by adding NaOH. Based on the amount of caprate used in the lead removal step, a percentage recovery of 98.9 ± 0.3 was achieved.

INTRODUCTION

Heavy metals such as lead, mercury, and cadmium are toxic when absorbed into the body. They can cause accumulative poisoning, cancer, brain damage, etc. (1). Lead is a general metabolic poison and enzyme inhibitor. It can cause mental retardation and semipermanent brain damage in young children. Lead has the ability to replace calcium in the bone to form sites for long-term release (1).

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Wastewater streams of the battery industry and mining activities contain high concentrations of lead. Several techniques, e.g., precipitation as hydroxides, membrane processes, ion-exchange resins, etc. (1), are employed to reduce the concentrations of heavy metals to acceptable levels. The process of choice depends on the cost, the nature of the wastewater (acidity, concentration, etc.), and the target concentration for the treated water.

In this work the precipitation of lead with straight-chain sodium carboxylate reagents was investigated. This technique was developed to overcome some of the disadvantages associated with other techniques, such as the long equilibrium time for the precipitation of heavy metals as hydroxides, the sensitivity of the membrane material to acids or salt solutions for the membrane processes, and the interference of other metal ions, such as calcium and magnesium, by removal of heavy metals in ion-exchange resins (1).

Preliminary experiments were performed using sodium propionate (CH_3CH_2COONa), sodium caprate [$CH_3(CH_2)_8COONa$, or NaR], and sodium oleate [$CH_3(CH_2)_7CH{:}CH(CH_2)_7COONa$]. Sodium propionate did not form a precipitate with lead, while sodium oleate formed a suspension which was very difficult to filter. Since sodium caprate formed an easily filterable precipitate, we studied the removal of lead with this reagent. We determined the effects of the pH of the feed and the concentrations of lead, calcium, chloride, and nitrate in the feed on the removal of lead. Calcium is an alkaline earth metal which exists in almost all water streams. If calcium competes with lead, some caprate may form calcium complexes; consequently, more caprate will be required to remove a given amount of lead. Chloride, which is also present in most water streams, increases the solubility of heavy metals by forming soluble complexes. In the case of lead, these complexes are $PbCl^+$, $PbCl_{2(aq)}$, $PbCl_3^-$, and $PbCl_4^{2-}$ (2). Nitrate was used to account for the effect of the ionic strength. Finally, we devised a procedure to regenerate the sodium caprate reagent.

EXPERIMENTAL METHODS

Removal of Lead

The removal experiments were performed on 35 mL of feed solution at a certain pH, and fixed concentrations of lead, calcium, nitrate, and chloride ions. This feed was mixed with 15 mL of sodium caprate solution as shown in Fig. 1. The chemicals used to prepare the feed solutions were lead nitrate (Acros, Montreal, PQ), lead chloride (Aldrich, Milwaukee, WI), calcium nitrate (Anachemia, Montreal, PQ), and nitric acid (Anachemia, Montreal, PQ). All chemicals were reagent grade and were used without purification. The

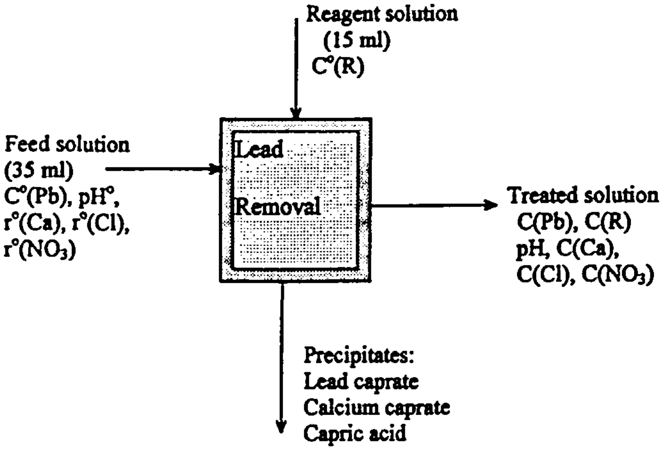

FIG. 1 Flow sheet of lead precipitation by sodium caprate.

reagent solution was prepared by dissolving sodium caprate (Pfaltz & Bauer, Waterbury, CT) in distilled water.

After mixing, the samples were allowed to equilibrate for 24 hours at a constant temperature of 24 ± 1°C. The precipitate was filtered with Fisherbrand fast flow filter paper or with 0.45 μm Millipore filter paper to obtain a clear filtrate. The finer filter paper was required when treating a solution of $Pb(NO_3)_2$ at a mole ratio of caprate to lead above 2.0. The precipitate was dried and saved for the regeneration of the caprate reagent. The following measurements were made on the filtrate: pH and the concentrations of lead, calcium, and caprate.

The pH was measured using a Metrohm Brinkmann 691 pH meter. The lead and calcium were measured using atomic absorption spectroscopy (Model SH11, Thermo Jarrell Ash, Waltham, MA). The detection range of this instrument was from 1 to 25 ppm for both lead and calcium. Standard solutions of lead and calcium containing 5, 10, 15, 20, and 25 ppm were used to calibrate the instrument. If the concentration of lead or calcium exceeded 25 ppm, the samples were diluted.

The concentration of caprate was measured using a total organic carbon analyzer (Model DC-183 with DC-85 NDIR detector, Dohrmann, Santa Clara, CA). The detection range of the instrument was from 1 to 2000 ppm of carbon. The instrument readings were converted from the concentration of carbon to the concentration of caprate by dividing by 0.701, the weight fraction of carbon in the caprate ion. Additional details are given by Husein (3).

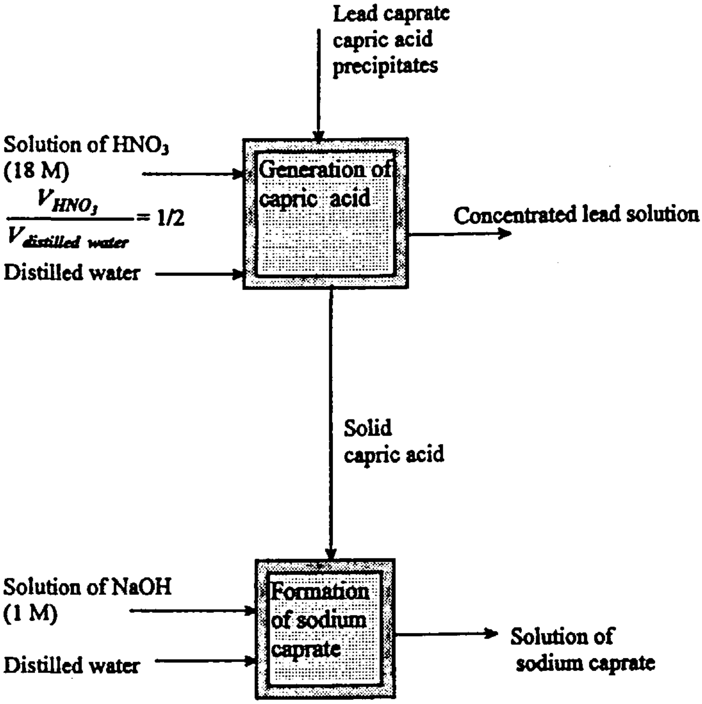

FIG. 2 Flow sheet of the regeneration of sodium caprate.

Regeneration of Sodium Caprate

The regeneration of sodium caprate was achieved in two steps as shown in Fig. 2. In the first step the lead caprate precipitate was treated with 18 M HNO_3 to produce capric acid as a precipitate. This precipitate was filtered using Fisherbrand fast flow filter paper. In the second step the solid capric acid was treated with 1.0 M NaOH solution to regenerate the sodium caprate. The number of moles of NaOH added was equal to the number of moles of capric acid. Distilled water was added to adjust the concentration of sodium caprate solution to the value used in the lead removal process.

Determination of the Solubility Products for Lead Caprate and Capric Acid

The values of the solubility products of lead caprate and capric acid were determined experimentally by dissolving lead caprate and capric acid precipitates in distilled water. The equilibrium pH and the equilibrium concentrations of lead and caprate were measured. The activity of hydrogen was assumed to be unity, and lead was assumed to exist at equilibrium in the form of Pb^{2+}. The values of the solubility products for lead caprate and capric acid were calculated from Eqs. (3) and (8) below.

RESULTS AND DISCUSSION

The composition of the feed is specified by its pH value, pH^0, the concentration of lead, $C^0(Pb)$, and the mole ratios of calcium to lead, $r^0(Ca)$, nitrate to lead, $r^0(NO_3)$, and chloride to lead, $r^0(Cl)$. The amount of caprate in the reagent solution is expressed as the mole ratio of caprate to lead, $r^0(R)$.

The major results of the removal experiments are reported as percentage removals of lead $R(Pb)$ or calcium $R(Ca)$, and percentage loss of caprate $L(R)$. The removal of lead or calcium was computed as

$$R(M) = \left(1 - \frac{C(M)}{C^*(M)}\right) \times 100\% \qquad (1)$$

where $C(M)$ is the total concentration of the metal in the treated solution, and $C^*(M)$ is the total concentration of the metal in a solution containing the mass of the metal in the feed in a volume equal to the sum of the volumes of the feed and the added reagent, i.e., 50 mL.

The percentage loss of caprate to the treated solution was calculated from

$$L(R) = \frac{C(R)}{C^*(R)} \times 100\% \qquad (2)$$

where $C(R)$ is the total concentration of caprate in the treated solution, and $C^*(R)$ is the total concentration of caprate in a solution containing the mass of caprate added to the feed in a volume equal to the sum of the volumes of the feed and the added reagent.

Three replicates were run for each experiment. Typical values of the 95% confidence intervals for the removal of lead and the loss of caprate were ±0.5% and ±0.4%, respectively.

Lead Removal

Figure 3 shows the percentage removal of lead, the percentage loss of caprate, and the equilibrium pH as functions of the mole ratio of caprate to lead. The feed solution contained 7 mM (1450 ppm) lead added as $Pb(NO_3)_2$. No acid was added, resulting in pH^0 4.4. This low pH resulted from the hydrolysis of Pb^{2+} according to

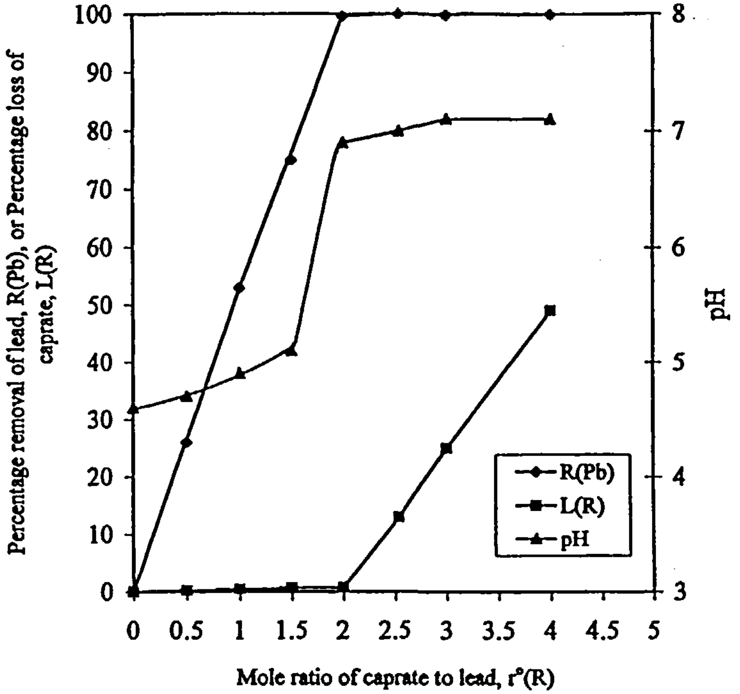

FIG. 3 Effect of caprate-to-lead ratio on the removal of lead, loss of caprate reagent, and equilibrium pH. $C^0(\text{Pb}) = 7.0$ mM, $\text{pH}^0 = 4.4$, $r^0(\text{Ca}) = 0$, $r^0(\text{NO}_3) = 2.0$, $r^0(\text{Cl}) = 0$.

$$\text{Pb}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{PbOH}^+ + \text{H}^+ \qquad \text{(R1)}$$

Since all of the nitrate came from $\text{Pb(NO}_3)_2$, $r^0(\text{NO}_3) = 2.0$. Neither calcium nor chloride was added, hence $r^0(\text{Ca}) = r^0(\text{Cl}) = 0$. The mole ratio of caprate to lead, $r^0(\text{R})$, was changed by adjusting the concentration of sodium caprate in the reagent solution.

The removal of lead increased linearly with an increasing mole ratio of caprate up to a mole ratio of 2, where the percentage removal of lead was 99.5 ± 0.2. At this condition the percentage loss of caprate was 0.8 ± 0.3. At higher mole ratios the percentage removal increased slightly while the percentage loss of caprate increased linearly. Beyond $r^0(\text{R}) = 2.0$, the added caprate formed only a small amount of lead caprate precipitate while the remainder was lost in the solution. As the removal of lead increased, less lead remained in solution to be hydrolyzed and thus the pH increased. After most of the lead was removed, the pH reached a value of about 7.0.

The linear increase in the percentage removal with increasing mole ratio of caprate to lead, and the fact that a mole ratio of 2.0 gave the highest percentage removal with the lowest reagent loss, suggest that the following reaction describes the precipitation:

$$PbR_{2(S)} \leftrightarrow Pb^{2+} + 2R^- \tag{R2}$$

Effect of Feed Concentration of Lead

For a mole ratio of caprate to lead of 2.0, the concentration of lead in the feed was varied from 0.35 to 7.0 mM (72.5 to 1450 ppm). Figure 4 shows the results plotted as the percentage removal of lead and the percentage loss of caprate versus the concentration of lead in the feed. The concentrations of lead and caprate in the treated solution are also shown. The equilibrium concentrations of lead and caprate were independent of the feed concentration

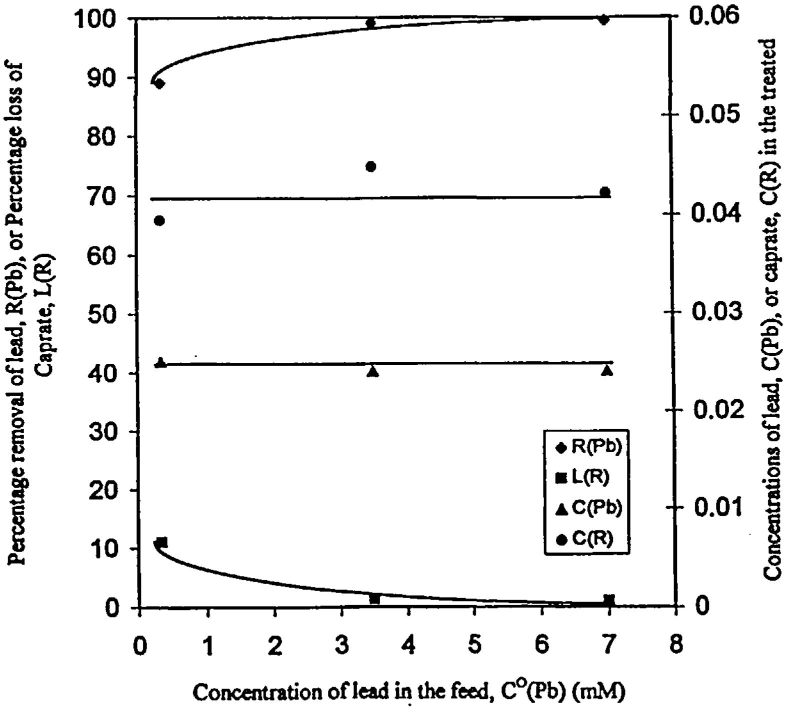

FIG. 4 Effect of feed concentration of lead on the removal of lead, the percentage loss of caprate, and the equilibrium concentrations of lead and caprate. $pH^0 = 4.4$, $r^0(Ca) = 0$, $r^0(NO_3) = 2.0$, $r^0(Cl) = 0$, $r^0(R) = 2.0$.

of lead. This explains the increase in the percentage removal of lead, and the decrease in the percentage loss of caprate, with increasing feed concentration of lead. These constant equilibrium concentrations suggest that a solubility product equation for lead caprate can be written following Reaction (R2) as

$$K_{SP} = C(Pb^{2+}) \times [C(R^-)]^2 \tag{3}$$

assuming that all lead at equilibrium exists as Pb^{2+} and all caprate exists as R^-.

Effect of Feed pH

Figure 5 shows the effect of decreasing the pH of the feed at a mole ratio of caprate to lead of 2.0. For a feed containing 7 mM $Pb(NO_3)_2$, pH^0 was decreased from 4.4 to 1.7 by adding HNO_3. Adding HNO_3 increased the mole

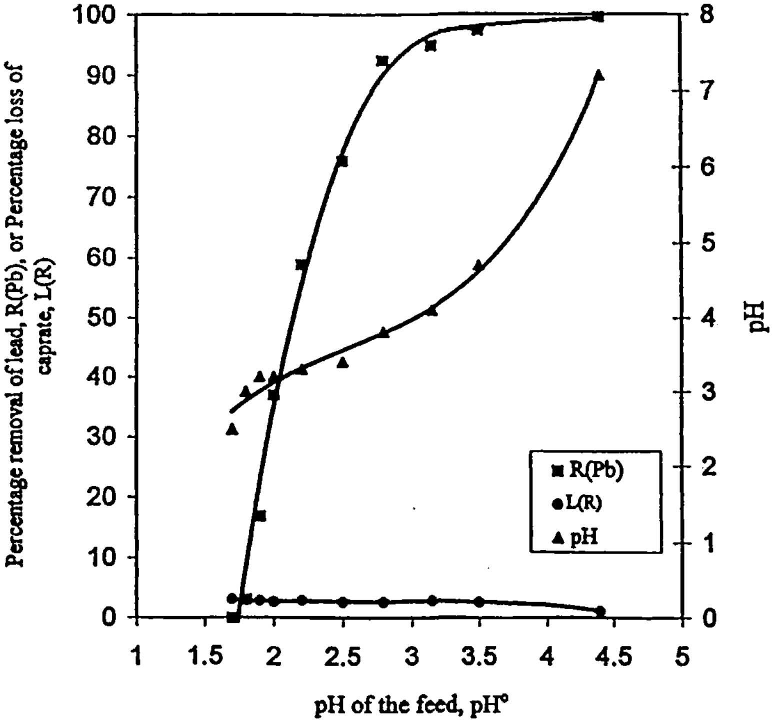

FIG. 5 Effect of feed pH on the removal of lead, the percentage loss of caprate, and the equilibrium pH. $C^0(Pb) = 7.0$ mM, $r^0(Ca) = 0$, $r^0(Cl) = 0$, $r^0(R) = 2.0$.

ratio of nitrate to lead, $r^0(NO_3)$, from 2 at pH^0 4.4 to 6 at pH^0 1.7. The percentage removal of lead, the percentage loss of caprate, and the equilibrium pH are plotted against pH^0 in Fig. 5. The percentage removal of lead decreased with decreasing pH^0 while the percentage loss of caprate was essentially constant (2.8 ± 0.4%) for pH^0 values of 3.5 or less. The equilibrium pH was always higher than the pH of the feed.

The decrease in the percentage removal of lead, the constancy of the percentage loss of caprate, and the difference between pH^0 and pH can be explained by Reactions (R2), (R3), and (R4):

$$RH_{(aq)} \leftrightarrow H^+ + R^- \tag{R3}$$

$$RH_{(S)} \leftrightarrow RH_{(aq)} \tag{R4}$$

Capric acid is a weak acid, hence it is present in un-ionized form in solution. Since it has a relatively long carbon chain, it also precipitates. The competition between hydrogen and lead ions for the caprate ion decreased the removal of lead and increased the equilibrium pH. Since a certain concentration of soluble capric acid is in equilibrium with the precipitated form of the acid, a constant equilibrium concentration of caprate and a constant percentage loss in the filtrate resulted. At pH^0 4.4, hydrogen ion could not compete with lead and so a little capric acid formed, thus giving a lower percentage loss of caprate at this pH^0.

Effect of Caprate to Lead Ratio at Low pH^0

Figure 6 shows the effect of increasing the amount of caprate for a feed at pH^0 1.8 containing 7 mM $Pb(NO_3)_2$. The percentage removal of lead, the percentage loss of caprate, and the equilibrium pH are plotted against the mole ratio of caprate to lead. At a mole ratio of 2.0 the percentage removal of lead was 3 ± 1. As $r^0(R)$ increased from 2.0 to 4.0, the percentage removal of lead increased linearly, and the percentage loss of caprate decreased slightly. The equilibrium concentration of caprate was constant at 40 ± 4 ppm while the equilibrium pH increased with the addition of caprate. Reactions (R2)–(R4) explain these results.

Effect of Calcium in the Feed

The selectivity of sodium caprate for lead versus calcium was determined by adding $Ca(NO_3)_2$ to the feed. For a feed concentration of 7 mM $Pb(NO_3)_2$ and $r^0(R) = 2.0$, the mole ratio of calcium to lead in the feed, $r^0(Ca)$, was varied from 0.5 to 4.0.

The percentage removal of lead and the percentage loss of caprate were independent of the mole ratio of calcium to lead. No calcium was removed

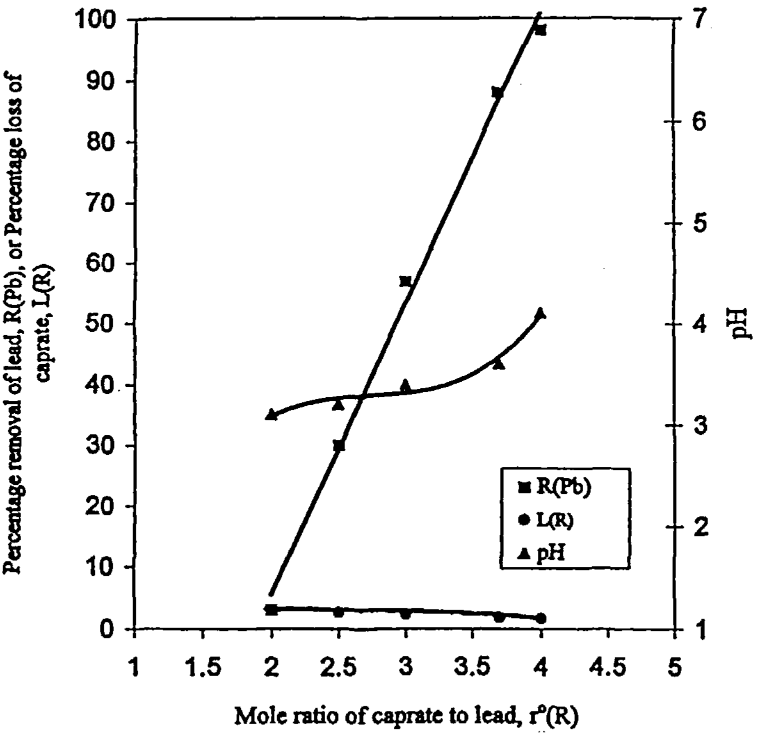

FIG. 6 Effect of mole ratio of caprate to lead on the removal of lead, the loss of the caprate, and the equilibrium pH. $C^0(\mathrm{Pb}) = 7.0$ mM, $\mathrm{pH}^0 = 1.8$, $r^0(\mathrm{Ca}) = 0$, $r^0(\mathrm{NO_3}) = 4$, $r^0(\mathrm{Cl}) = 0$.

for any value of $r^0(\mathrm{Ca})$. The caprate reagent precipitated lead selectively; however, when added to a solution containing only $\mathrm{Ca(NO_3)_2}$, caprate formed a precipitate with calcium.

Effects of Chloride and Nitrate in the Feed

The effect of chloride concentration on the removal of lead was investigated by adding NaCl to the feed solution. For a feed concentration of 7.4 mM $\mathrm{PbCl_2}$ (1533 ppm lead) and $r^0(\mathrm{R}) = 1.9$, the mole ratio of chloride to lead, $r^0(\mathrm{Cl})$, was increased from 2 to 200 by adding NaCl. To account for the effect of the ionic strength, a second set of experiments was carried out in nitrate media since nitrate is considered an inert ion. In these experiments, lead nitrate was the source of lead in the solution, and $\mathrm{NaNO_3}$ was added to adjust the concentration of $\mathrm{NO_3^-}$ to achieve similar values of $r^0(\mathrm{NO_3})$.

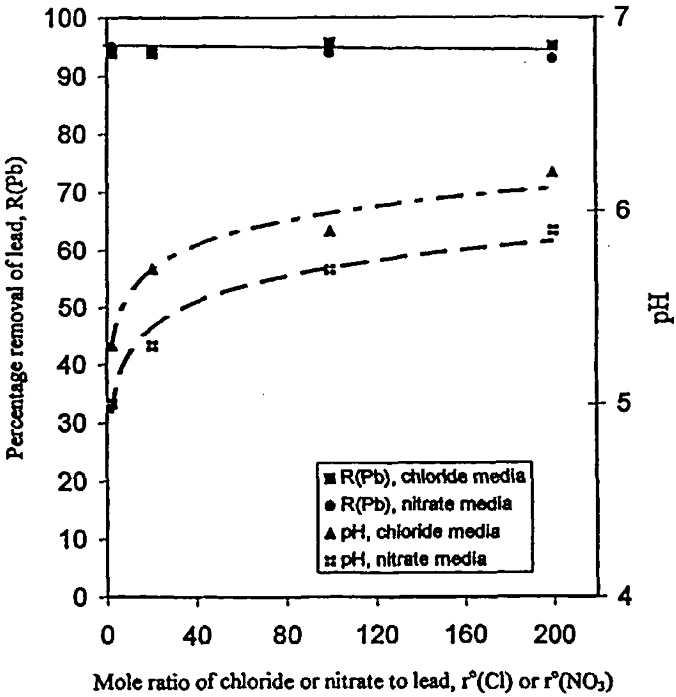

FIG. 7 Effect of chloride and nitrate on the removal of lead and the equilibrium pH. C^0(Pb) = 7.4 mM, r^0(Ca) = 0, r^0(R) = 1.9.

Figure 7 shows the results of the two sets of experiments. The percentage removal of lead and the equilibrium pH are plotted against the mole ratio of chloride to lead, r^0(Cl), or the mole ratio of nitrate to lead $r^0(NO_3)$. For both media, the percentage removal of lead was essentially independent of $r^0(NO_3)$ or r^0(Cl), and thus of the ionic strength of the solution.

Figure 7 also shows that the equilibrium pH of the solution increased with increasing concentrations of chloride or nitrate. This increase is attributed to the effect of the ionic strength of the solution on the activity coefficient of hydrogen (4, 5). As the ionic strength increased, the activity coefficient of hydrogen ion decreased. For the same ionic strength, the higher equilibrium pH in chloride media resulted from the following reaction:

$$PbOH^+ + Cl^- \leftrightarrow PbCl^+ + OH^- \qquad (R5)$$

Regeneration of Sodium Caprate

The overall percentage regeneration of sodium caprate, Γ, was based on the amount of caprate used in the removal step:

$$\Gamma = \frac{\text{moles of caprate in the regenerated solution}}{\text{moles of caprate added to the feed in the removal step}} \times 100\% \tag{4}$$

The number of moles of caprate added to the feed was calculated from the values of $C^*(\mathrm{R})$, and the number of moles of caprate in the regenerated solution was calculated from the concentration of total carbon in the regenerated solution. Following the procedure summarized in Fig. 2, a percentage regeneration of 98.9 ± 0.3 was achieved, and lead was concentrated to 50 mM, seven times its feed concentration

MODELING LEAD REMOVAL

A chemical equilibrium model was derived to describe the lead removal, caprate loss, and the equilibrium pH. The three major assumptions were: 1) the activity coefficients of all species were unity, 2) nitrate and sodium ions were inert, and 3) the feed and reagent solution volumes were additive. In addition to Reactions (R2) and (R3), the following reactions were assumed to occur:

$$\mathrm{PbOH^+} \xleftrightarrow{K_1} \mathrm{Pb^{2+}} + \mathrm{OH^-} \tag{R6}$$

$$\mathrm{H_2O} \xleftrightarrow{K_w} \mathrm{H^+} + \mathrm{OH^-} \tag{R7}$$

$$\mathrm{RH_{(S)}} \xleftrightarrow{K_{spA}} \mathrm{H^+} + \mathrm{R^-} \tag{R8}$$

Following the procedure outlined earlier, K_{SP} was calculated from Eq. (3) to be 1.1×10^{-13}, and K_{spA} from Eq. (8) below. The values of K_1 and K_w were taken from the literature (6, 7). The value of K_a was assumed to be equal to the value reported for hexanoic and octanoic acids (8), because the value of K_a for straight-chain carboxylic acids does not vary much with the chain length of the acid (7). The equations and the values of the stability constants for the reactions taking place are given below.

$$K_1 = \frac{C(\mathrm{Pb^{2+}}) \times C(\mathrm{OH^-})}{C(\mathrm{PbOH^+})} = 1.7 \times 10^{-7} \tag{5}$$

$$K_w = C(\mathrm{H^+}) \times C(\mathrm{OH^-}) = 10^{-14} \tag{6}$$

$$K_a = \frac{C(\mathrm{H}^+) \times C(\mathrm{R}^-)}{C(\mathrm{RH}_{(aq)})} = 1.4 \times 10^{-5} \tag{7}$$

$$K_{spA} = C(\mathrm{H}^+) \times C(\mathrm{R}^-) = 2.6 \times 10^{-9} \tag{8}$$

where $C(i)$ is the molar concentration of species i.

The feed solution consists of $Pb(NO_3)_2$ and HNO_3 in water. This solution is specified by its lead concentration, $C^0(\mathrm{Pb})$, and its pH, pH^0. The pH of the feed was related to the number of moles of lead nitrate and nitric acid through a material balance on lead and a charge balance, assuming that Reactions (R6) and (R7) occur. The material balance and the charge balance are written in terms of the equilibrium concentrations of Pb^{2+} and H^+ as follows:

$$\frac{n_{\mathrm{Pb(NO_3)_2,\,feed}}}{V_f} = C(\mathrm{Pb}^{2+}) + \frac{K_w}{K_1}\frac{C(\mathrm{Pb}^{2+})}{C(\mathrm{H}^+)} \tag{9}$$

$$2C(\mathrm{Pb}^{2+}) + \frac{K_w}{K_1}\frac{C(\mathrm{Pb}^{2+})}{C(\mathrm{H}^+)} + C(\mathrm{H}^+) = \frac{2n_{\mathrm{Pb(NO_3)_2,\,feed}}}{V_f} + \frac{n_{\mathrm{HNO_3,\,feed}}}{V_f} + \frac{K_w}{C(\mathrm{H}^+)} \tag{10}$$

where $n_{\mathrm{Pb(NO_3)_2,\,feed}}$ and $n_{\mathrm{HNO_3,\,feed}}$ are the number of moles of lead nitrate and nitric acid used to prepare the feed, and V_f is the volume of the feed. For a fixed V_f, these equations have two inputs, $n_{\mathrm{Pb(NO_3)_2,feed}}$ and $n_{\mathrm{HNO_3,\,feed}}$, and two unknowns, $C(\mathrm{Pb}^{2+})$ and $C(\mathrm{H}^+)$, the latter giving pH^0.

Upon adding sodium caprate, NaR, additional species are formed, including capric acid and lead caprate precipitates. The amount of sodium caprate added is specified by the mole ratio of caprate to lead, $r^0(\mathrm{R})$. In addition to the hydrolysis reaction of Pb^{2+} and the dissociation of water, the precipitation reactions of lead caprate and capric acid and the dissociation reaction of capric acid were assumed to take place. The material balances on lead and caprate and the charge balance are written in terms of the equilibrium hydrogen ion concentration as follows:

$$\frac{n_{\mathrm{Pb(NO_3)_2,\,feed}}}{V} = \frac{n_{\mathrm{PbR_{2(S)}}}}{V} + \frac{K_{SP}}{K_{spA}^2}[C(\mathrm{H}^+)]^2 + \frac{K_{SP}K_w}{K_1K_{spA}^2}C(\mathrm{H}^+) \tag{11}$$

$$\frac{n_{\mathrm{NaR,\,added}}}{V} = \frac{2n_{\mathrm{PbR_{2(S)}}}}{V} + \frac{n_{\mathrm{RH_{(S)}}}}{V} + \frac{K_{spA}}{K_a} + \frac{K_{spA}}{C(\mathrm{H}^+)} \tag{12}$$

$$2\frac{K_{SP}}{K_{spA}^2}[C(\mathrm{H}^+)]^3 + \left(\frac{K_{SP}K_w}{K_{spA}^2K_1} + 1\right)[C(\mathrm{H}^+)]^2 + \left(\frac{n_{\mathrm{NaR,\,added}}}{V} - \frac{n_{\mathrm{HNO_3,\,feed}}}{V} - \frac{2n_{\mathrm{Pb(NO_3)_2,\,feed}}}{V}\right)C(\mathrm{H}^+) - \left(\frac{K_w}{K_1} + K_{spA}\right) = 0 \tag{13}$$

where $n_{\mathrm{NaR,\,added}}$ is the number of moles of sodium caprate added to the feed solution, $n_{\mathrm{PbR}_{2(S)}}$ is the number of moles of lead caprate precipitate, $n_{\mathrm{RH}_{(S)}}$ is the number of moles of capric acid precipitate, and V is the volume of the feed plus the volume of the reagent solution. Equations (11)–(13) have three inputs, $n_{\mathrm{Pb(NO_3)_2,\,feed}}$, $n_{\mathrm{HNO_3,\,feed}}$, and $n_{\mathrm{NaR,\,added}}$, and three unknowns, $n_{\mathrm{PbR}_{2(S)}}$, $n_{\mathrm{RH}_{(S)}}$, and $C(\mathrm{H}^+)$.

The percentage removal of lead, and the percentage loss of caprate were calculated from:

$$R(\mathrm{Pb}) = \frac{n_{\mathrm{PbR}_{2(S)}}}{n_{\mathrm{Pb(NO_3)_2,\,feed}}} \times 100\% \tag{14}$$

$$L(\mathrm{R}) = \frac{(n_{\mathrm{NaR,\,added}} - 2n_{\mathrm{PbR}_{2(S)}} - n_{\mathrm{RH}_{(S)}})}{n_{\mathrm{NaR,\,added}}} \times 100\% \tag{15}$$

Comparison of Model Prediction to Data

The model predictions for the effect of pH^0 are compared to the experimental data in Fig. 8 for a caprate to lead ratio of 2.0. There is good agreement

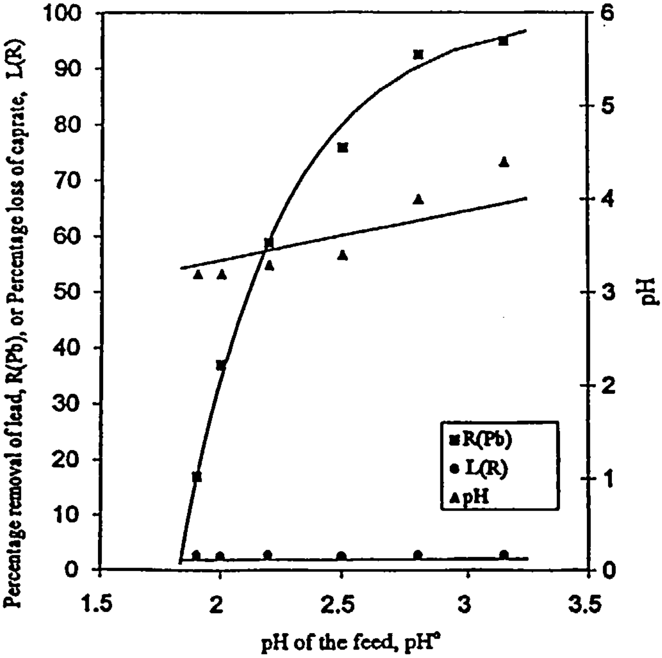

FIG. 8 Effect of pH^0 on the removal of lead, the loss of the caprate, and the equilibrium pH. $C^0(\mathrm{Pb}) = 7.0$ mM, $r^0(\mathrm{Ca}) = 0$, $r^0(\mathrm{Cl}) = 0$, $r^0(\mathrm{R}) = 2.0$. Points: experiments. Lines: model.

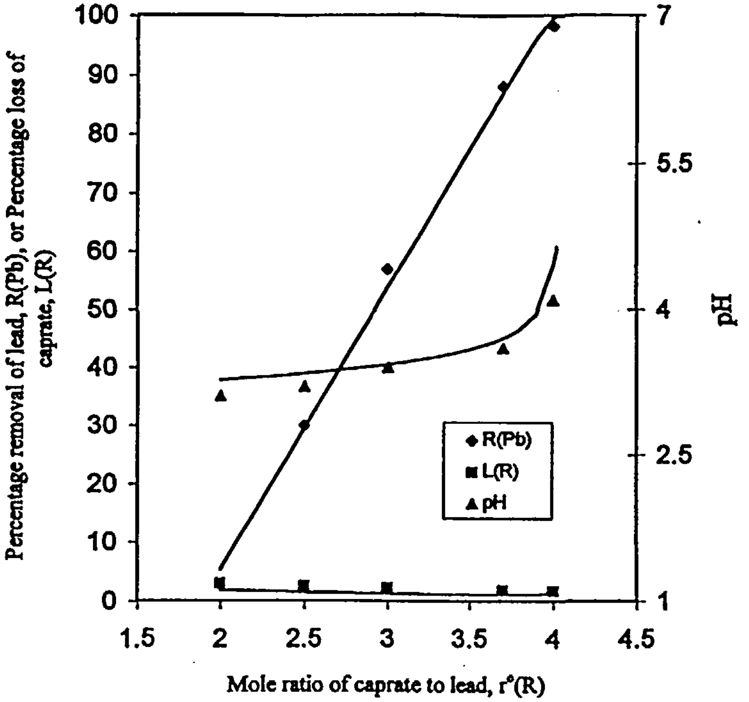

FIG. 9 Effect of the mole ratio of caprate to lead on the removal of lead, the loss of caprate, and the equilibrium pH. $C^0(\mathrm{Pb})$ = 7.0 mM, pH^0 = 1.8, $r^0(\mathrm{Ca})$ = 0, $r^0(\mathrm{NO_3})$ = 4.0, $r^0(\mathrm{Cl})$ = 0. Points: experiments. Lines: model.

between the experimental results and the model predictions for both the percentage removal of lead and the percentage loss of caprate. The experimental equilibrium pH data were below the predictions at low pH^0 and above at higher pH^0, but the differences were generally within 0.2 pH unit.

The model predictions for the effect of the mole ratio of caprate to lead, $r^0(\mathrm{R})$, at pH^0 1.8 are compared with experiments in Fig. 9. There is good agreement between the predictions and the experimental results for the percentage removal of lead, the percentage loss of caprate, as well as the equilibrium pH.

CONCLUSIONS

Sodium caprate formed an easily filterable precipitate of lead caprate with a high percentage removal of lead from solutions initially containing between 72 and 1450 ppm lead. For a feed of 1450 ppm lead and a mole ratio of caprate to lead of 2.0, the percentage removal of lead was 99.5 ± 0.2 and the percentage loss of caprate was 0.8 ± 0.3. At a mole ratio of caprate to lead of 2.0, the equilibrium concentrations of lead and caprate in the supernatant were 5 ± 2 and 7 ± 1 ppm, respectively, independent of the feed concentration of lead. Decreasing the pH of the feed decreased the percentage removal of lead but did not change the equilibrium concentration of caprate. The constant concentration of caprate resulted from the equilibrium established between the solid and soluble forms of capric acid. At a low pH of the feed, adding more caprate increased the percentage removal of lead but did not affect the equilibrium concentration of caprate. The presence of calcium, chloride, or nitrate in the feed solution had no effect on the removal of lead.

A model was developed based on the chemical reaction equilibria between different solutes and the assumption that all activity coefficients are unity. The model predicted the experimental results with good accuracy without fitted parameters.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada and from McGill University through the Max Stern Fellowship awarded to M.M.H.

REFERENCES

1. B. Volesky, "Removal of Heavy Metals by Biosorption," in *Biosorption of Heavy Metals* (B. Volesky, Ed.), CRC Press, Boca Raton, FL, 1990.
2. H. Hahne and W. Kroontje, "Significance of pH and Chloride Concentration on the Behavior of Heavy Metal Pollutants: Mercury(II), Cadmium(II), Zinc(II), and Lead(II)," *J. Environ. Qual.*, *2*, 444–450 (1973).
3. M. Husein, "Removal of Lead from Aqueous Solutions with Compounds Having the Sodium Carboxylate Group," M.Eng. Thesis, McGill University, Montreal, Canada, 1996.
4. H. Meissner, "Prediction of Activity Coefficient of Strong Electrolytes in Aqueous Systems," in *Thermodynamics of Aqueous Systems with Industrial Applications* (S. Newman, Ed.), American Chemical Society, Washington DC, 1980.
5. G. Demopoulos and V. Papangelakis, "Hydrogen Ion Activities and Species Distribution in Mixed Metal Sulfate Aqueous Systems," *AIChE J.*, *41*, 171–184 (1995).
6. M. Schock, "Response of Lead Solubility to Dissolved Carbonate in Drinking Water," *J Am. Water Works Assoc.*, *72*, 695–704 (1980).
7. G. Solomons, *Organic Chemistry*, 6th ed., Wiley, New York, NY, 1996.
8. N. Allinger, M. Cava, D. Jongh, C. Johnson, N. Lebel, and C. Steven, *Organic Chemistry*, Worth Publisher, New York, NY, 1971.

Received by editor August 5, 1997
Revision received January 1998