Removal of Lead from Aqueous Solutions with Compounds Having the Sodium Carboxylate Group

by

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In the name of God

To my parents

Abstract

Lead was removed from aqueous solutions using reagents having the sodium carboxylate group. For sodium acrylate and sodium polyacrylate, the removal of lead increased, and the reagent loss decreased when using sodium polyacrylate compared to the monomer, and when using a polymer with higher molecular weight. Sodium propionate did not precipitate lead. Sodium oleate formed a suspension with lead. Sodium caprate formed an easily filterable precipitate For a feed concentration of 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 $99.5 \pm 0.2\%$ and $0.8 \pm 0.3\%$, respectively. The effects of pH, concentrations of lead, calcium, chloride and nitrate in the feed on the removal step were determined. For a certain amount of added caprate, 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 or nitrate in the feed did not affect the removal of lead. At high chloride concentration, $C^{o}(Cl^-) > 0.7$ M, the loss of caprate increased slightly. Sodium caprate was recovered by adding HNO_3 to form capric acid. The sodium caprate was regenerated by adding NaOH. A percentage regeneration of $98.9 \pm 0.3\%$ was achieved.

Résumé

L'utilisation de réactifs possédant le groupe carboxylate de sodium a permis d'enlever du plomb de solutions aqueuses. Avec des systèmes acrylate et polyacrilate de sodium, les résultats obtenus ont été : l'extraction du plomb a augmenté et la perte en réactifs a diminué en utilisant le polyacrylate de sodium par rapport au monomère. Ceci s'est confirmé avec l'utilisation d'un polymère à poids moléculaire plus élevé. Le propionate de sodium ne précipite pas le plomb, l'oléate de sodium forme une suspension avec le plomb, tandis que le caprate de sodium forme un précipité facilement filtrable. Pour une concentration d'alimentation de 1450 ppm en plomb et une fraction molaire en caprate de sodium de 2.0 par rapport au plomb, le taux d'extraction du plomb et le pourcentage de perte en caprate de sodium obtenus ont été respectivement $99.5\pm0.2\%$ et $0.8\pm0.3\%$. Les effets du pH, des concentrations d'alimentation en plomb, calcium, chlorure et nitrate sur le processus d'extraction ont été déterminés pour le système du caprate. Pour une certaine quantité de caprate ajoutée, les concentrations à l'équilibre en plomb et caprate se sont avérées indépendantes de la concentration d'alimentation en plomb. Abaisser le pH au niveau de l'alimentation diminue l'extraction du plomb mais n'affecte pas la perte en caprate. La présence de calcium ou de nitrate dans l'alimentation n'a pas affecté l'extraction du plomb. A des concentrations élevées en chlorure $C^{\circ}(Cl^-) > 0.7$ M, la perte en caprate a augmenté légèrement. Le caprate de sodium a été régénéré en formant, dans un premier temps, de l'acide caprique par addition de HNO_3, transformé ensuite en caprate de sodium par ajout de soude. Un taux de régénération de $98.9\pm0.3\%$ a été obtenu.

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Nomenclature

$C(Ca)$	:	equilibrium concentration of total calcium.
$C^o(Ca)$	:	feed concentration of total calcium.
$C^o(Cl)$	:	feed concentration of total chloride.
$C^o(NO_3)$	:	feed concentration of total nitrate.
$C(Pb)$	:	equilibrium concentration of total lead.
$C^o(Pb)$	:	feed concentration of total lead.
$C(R_2COO)$	:	equilibrium concentration of total acrylate.
$C^*(R_2COO)$	:	blank concentration of total acrylate.
$C(R_9COO)$	:	equilibrium concentration of total caprate.
$C^*(R_9COO)$	:	blank concentration of total caprate.
$C(R_{17}COO)$	:	equilibrium concentration of total oleate.
$C^*(R_{17}COO)$	:	blank concentration of total oleate.
$L(R_2COO)$	:	percentage loss of acrylate.
$L(R_9COO)$	:	percentage loss of caprate.
$L(R_{17}COO)$	:	percentage loss of oleate.
$n_{HNO_3, feed}$	:	moles of nitric acid in the feed.

Nomenclature

$n_{Pb(NO_3)_2,\ feed}$: moles of lead nitrate in the feed.

$n_{R_9COONa,\ added}$: moles of sodium caprate added to the feed in the removal step.

pH : equilibrium pH.

pH° : pH of the feed.

$r^\circ(Ca)$: mole ratio of total calcium to total lead, in the feed.

$r^\circ(Cl)$: mole ratio of total chloride to total lead, in the feed.

$r^\circ(NO_3)$: mole ratio of total nitrate to total lead, in the feed.

$r^\circ(R_2COO)$: mole ratio of the added acrylate to the total lead, in the feed.

$r^\circ(R_9COO)$: mole ratio of the added caprate to the total lead, in the feed.

$r^\circ(R_{17}COO)$: mole ratio of the added oleate to the total lead, in the feed.

$R(Ca)$: percentage removal of calcium.

$R(Pb)$: percentage removal of lead.

$\Gamma(R_2COO)$: percentage regeneration of acrylate.

$\Gamma(R_9COO)$: percentage regeneration of caprate.

Nomenclature

Chapter 1: Introduction

1.1 Motivation

The term heavy metals refers to all metals in the periodic table, except the metals of the first two groups. Heavy metals like mercury, cadmium, and lead are toxic when absorbed into the body. They can cause accumulative poisoning, cancer, brain damage. etc. (13). This work aimed at the removal of lead from wastewaters.

Lead is a general metabolic poison and enzyme inhibitor. It can cause mental retardation and semipermanent brain damage for young children. Lead has the ability to replace calcium in the bone, and form sites for long term release (13). The main source of lead in the atmosphere, is the burning of leaded gasoline. Eventually, the atmospheric lead dissolves and contaminates the water sources, sea water, and soil systems (10). In addition, wastewater streams of the battery industry and mining activities contain high concentrations of lead. The concentrations of lead and other heavy metals in industrial wastewater streams should be reduced to levels imposed by government regulations. Table 1.1 shows the effluent limitations on three heavy metals in some Canadian provinces, and cities in the United States.

Table 1.1 Effluent limitations for some heavy metals.

	Quebec[*]	Ontario[*]	Los Angeles[**]	Detroit[**]
Hg	0.001	-	-	0.005
Cd	0.001	0.001	1.5	2.0
Pb	0.2	0.2	5.0	1.0

All values in ppm.
[*] Environment Canada, 1993.
[**] Reference 3.

1.2 Removal of heavy metals from industrial wastewaters

Many techniques are employed to reduce the concentrations of heavy metals to acceptable levels. Which one is best, depends on the cost, nature of the wastewater stream (acidity, salt concentration, etc.), and the maximum accepted level in that specific region. A brief discussion of some of these techniques is provided below.

1.2.1 Precipitation at an optimum pH

This technique is often employed for high flow rate wastewater streams. Heavy metals precipitate as hydroxides, and the solid precipitate is removed. However, it may not be suitable to meet recent limitations on effluent streams. Furthermore, the time required to reach equilibrium may be long (around a month, from my experience), and fine precipitates may be produced, making filtration difficult.

1.2.2 Liquid-liquid extraction

In this technique, an immiscible organic phase is brought into contact with aqueous phase containing a chelating agent which forms a complex with the heavy metal ions. This complex is much more soluble in the organic phase than in the aqueous phase.

This technique is not feasible for treatment of large volumes of wastewater with low metal content. The loss of the organic solvent and the chelating agent in the aqueous phase may also be a problem. However, extraction is widely used for the recovery of valuable metals from concentrated solutions.

1.2.3 Membrane processes

Reverse osmosis, dialysis, and electrodialysis have been used, but they are expensive. Some of their disadvantages are low membrane flux rates and membrane instability in salt and acid-containing solutions.

The combination of water soluble polymers and ultrafiltration may be promising (4). In this technique, the metal ions form complexes with a polymer, like polyethyleneimine (4,7). The polymer cannot pass through the membrane, thus removing the metal. However, this process also suffers from low flux rates.

1.3 Thesis objectives

1. To investigate the precipitation of lead from aqueous solutions with compounds having the sodium carboxylate group.
2. To study the effects of the following variables on the removal of lead:
   a. concentration of lead in the feed,
   b. pH of the feed,
   c. concentration of calcium in the feed, and

    d. concentrations of chloride and nitrate in the feed.

3. To develop a procedure to regenerate the reagents.

4. To develop a simple model to predict the lead removal and the reagent loss.

Chapter 2: Experimental Work

This chapter illustrates the procedures followed to perform the lead removal and the reagent regeneration experiments. Definitions of the percentage removal of lead, the percentage loss of the reagent, and the percentage regeneration of the reagent are provided.

2.1 Removal of lead

The removal experiments were performed by treating a volume of 35 ml of the feed solution at certain pH, lead, calcium, and chloride or nitrate concentrations, with 15 ml of the reagent solution at a certain concentration. Figure 2.1 gives a schematic diagram of the removal step. The chemicals used to adjust the concentrations of lead, calcium, chloride or nitrate, and the pH are listed in Table 2.1. All chemicals used were reagent grade and were used without purification. The feed was prepared by adding certain volumes of solutions of these chemicals to the lead solution to make a volume of 35 ml.

Reagent solution
(15 ml)
C^o(reagent)

Feed solution
(35 ml)
C^o(Pb), pH^o,
r^o(Ca), r^o(Cl),
r^o(NO$_3$)

Lead

Removal

Treated solution
C(Pb), C(reagent)
pH, C(Ca),
C(Cl), C(NO$_3$)

Precipitates:
Lead-reagent
Calcium-reagent
Acid form of the reagent
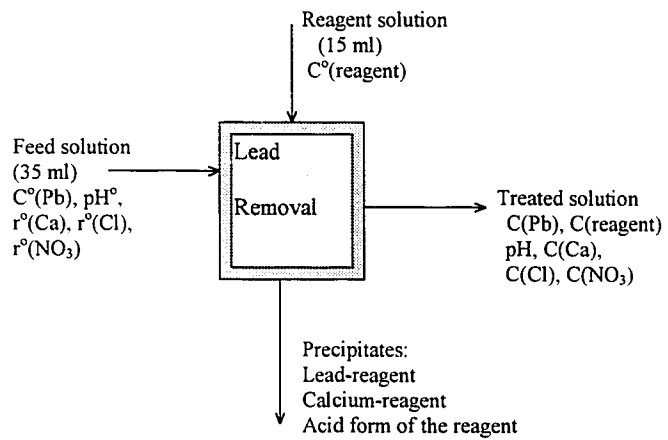
Figure 2.1: Schematic diagram of the removal of lead.

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Table 2.1: Chemicals used in the experimental work.

Chemical	Chemical Formula	MW (gm/mole)	Company
Calcium Nitrate	$Ca(NO_3)_2$	236.2	Anachemia (Canada)
Lead Chloride	$PbCl_2$	278.1	Aldrich (USA)
Lead Nitrate	$Pb(NO_3)_2$	331.2	Acros (USA)
Nitric Acid	HNO_3	63.0	Anachemia (Canada)
Sodium Carbonate	Na_2CO_3	106.0	Anachemia (Canada)
Sodium Chloride	$NaCl$	58.4	Anachemia (Canada)
Sodium Hydroxide	$NaOH$	40.0	A & C (Canada)
Sodium Nitrate	$NaNO_3$	85.0	Anachemia (Canada)

When the effect of calcium was studied, volumes of 1.0 M $Ca(NO_3)_2$ were added to the feed to give 35 ml of lead and calcium solutions at the required feed concentration of lead, $C^o(Pb)$, and mole ratios of calcium to lead, $r^o(Ca)$. When the effects of chloride and nitrate concentrations were studied, volumes of 1.0 M NaCl or $NaNO_3$ were added to the feed to give 35 ml of lead solutions at the required $C^o(Pb)$, and mole ratios of chloride to lead, $r^o(Cl)$, or mole ratios of nitrate to lead, $r^o(NO_3)$. The pH of the feed, pH^o, was adjusted using HNO_3, or NaOH.

The reagents used in the removal of lead were organic compounds having the carboxylate functional group. A list of these reagents is shown in Table 2.2.

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Table 2.2 Reagents used for lead removal.

Reagent	Chemical Formula	Symbol	MW (g/mole)	f	Company
Sodium acrylate	$CH_2\!=\!CHCOONa$	R_2COONa	94.0	0.51	Aldrich (USA)
Sodium polyacrylate	$-\!\!\left[CH_2\!-\!CH\right]_n\!\!-$ COONa	-	12 000 30 000	0.51	Aldrich (USA)
Sodium propionate	CH_3CH_2COONa	-	96.0	0.49	Aldrich (USA)
Sodium caprate	$CH_3(CH_2)_8COONa$	R_9COONa	194.0	0.70	Pfaltz & Bauer (USA)
Sodium oleate	$CH_3(CH_2)_7CH\!=\!CH(CH_2)_7COONa$	$R_{17}COONa$	304.0	0.77	Pfaltz & Bauer (USA)

The factor f is defined as:

$$f = \frac{g\ carbon\ /\ mole\ of\ the\ reagent}{MW\ of\ the\ anionic\ part\ of\ the\ reagent\ (g\ /\ mole)} \qquad (2.1)$$

The molecular weight of the anionic part of the reagent rather than the molecular weight of the reagent was used, because sodium did not participate in the reactions and its concentration remained constant. The factor f was used to convert the concentration of total carbon measured to the concentration of the anionic part of the reagent, as discussed later.

For sodium acrylate, precipitation occurred and a clear upper phase formed when the mole ratio of carboxylate to lead was lower than 10. For sodium polyacrylate of average molecular weights of 1 200 and 30 000, precipitation occurred and a clear upper phase formed when the mole ratios of carboxylate to lead were lower than 3 and 2.5, respectively. The samples were left for 24 hours at

a constant temperature of 24 ± 1 °C. Then, the clear upper phase was removed for analysis and the precipitate was left at the bottom. Filtration could not be achieved, because the precipitate passed through the 0.22 μm Millipore filter paper. The volume of the collected upper phase was 45 ml.

For sodium propionate, no precipitation occurred. The solution stayed clear for different mole ratios of propionate to lead. A mole ratio from 1 to 20 was tested.

For sodium caprate, precipitation occurred and clear upper phase formed when the mole ratio of caprate to lead was equal to 2, or lower. After the samples were left for 24 hours at constant temperature of 24 ± 1 °C, the precipitate was easily filtered with Fisherbrand fast flow filter paper. For mole ratios of caprate to lead higher than 2, cloudiness appeared in the upper phase. A 0.45 μm Millipore filter paper was used to perform the filtration. The volume of the collected filtrate was 49.5 ml.

For sodium oleate, a suspension was formed for all mole ratios of oleate to lead in a range from 0.5 to 6. The suspension was left for 24 hours at constant temperature of 24 ± 1 °C before it was separated using 0.45 μm Millipore filter paper. The filtration step was very slow, and samples of only 10 ml were collected.

The collected treated volumes were used for analysis. The concentration of lead and calcium were measured using a TJA (Thermo Jarrell Ash) model SH 11 Surface Beam atomic absorption spectrophotometer. The detection range of the instrument is from 1 to 25 ppm for both lead and calcium with a precision of $\pm5\%$. Standard solutions of 5, 10, 15, 20, 25 ppm lead concentration were used to calibrate the instrument for lead measurements. Standard solutions of the same concentrations of calcium were used to calibrate the instrument for calcium

measurements. Whenever the concentration of lead or calcium exceeded 25 ppm, the samples were diluted. Blank solutions containing the same mass of lead as the feed solutions were prepared. The volume of the blank solution was the sum of the feed and the added reagent volumes. The concentration of lead in the blank solution is defined as follows:

$$C^*(Pb) = M^o(Pb)/(V_f + V_a) \tag{2.2}$$

where $M^o(Pb)$ is the mass of lead in the feed solution (mg), V_f is the volume of the feed (l), and V_a is the volume of the added reagent (l).

The percentage removal of lead was defined as follows:

$$R(Pb) = \frac{(C^*(Pb) - C(Pb))}{C^*(Pb)} \times 100\%. \tag{2.3}$$

where $C(Pb)$ is the concentration of lead in the treated solution.

Similarly, blank solutions for calcium were prepared, and the concentration of calcium in the blank was defined as follows:

$$C^*(Ca) = M^o(Ca)/(V_f + V_a) \tag{2.4}$$

where $M^o(Ca)$ is the mass of calcium added to the feed solution (mg), and V_f and V_a are the same as in equation 2.2.

The percentage removal of calcium was defined as follows:

$$R(Ca) = \frac{(C^*(Ca) - C(Ca))}{C^*(Ca)} \times 100\% \tag{2.5}$$

where $C(Ca)$ is the concentration of calcium in the treated solution.

The concentration of the reagent was measured using the Dohrmann DC-183 Total Carbon Analyzer (Boat Sampler module), in combination with the Dohrmann DC-85 NDIR detector module. The detection range of the instrument is from 1 ppm to 2000 ppm of total carbon with a precision of $\pm2\%$. To convert the instrument readings from the concentration of total carbon, in ppm, to the

concentration of the anion part of the reagent, in ppm, the factor f presented in Table 2.2 was used.

The concentration of the anion part of the reagent in the blank solution was defined as follows:

$$C^*(reagent) = M^o(reagent)/(V_f + V_a) \qquad (2.6)$$

where $M^o(reagent)$ is the mass of the anionic part of the reagent added the feed solution (mg), and V_f and V_a are the same as in equation 2.2.

The percentage loss of the reagent was defined as follows:

$$L(reagent) = \frac{C(reagent)}{C^*(reagent)} \times 100\% \qquad (2.7)$$

where C(reagent) is the concentration of the anion part of the reagent in the treated solution.

2.2 Regeneration of the reagents

The regeneration of sodium acrylate, sodium polyacrylate, and sodium caprate was achieved using the experimental procedures described below.

2.2.1 Regeneration of sodium acrylate and sodium polyacylate

Sodium acrylate and sodium polyacrylate were regenerated by precipitating the lead in the complex as lead carbonate with the addition of sodium carbonate. Figure 2.2 presents a scheme for the regeneration step. The volume of sodium carbonate added was such to give a mole ratio of carbonate to lead of 2.0. Lower mole ratios were tested, but they gave lower percentages of regeneration. Distilled water was added to adjust the concentration of sodium acrylate or sodium polyacrylate in the regenerated solution. Lead carbonate precipitate was filtered using 0.45 μm Millipore filter paper.

Lead acrylate, or
lead polyacrylate
precipitates

Solution of Na_2CO_3
(1 M)

Regeneration
of sodium
acrylate, or
sodium
polyacrylate

Concentrated solution
solution of sodium
acrylate, or sodium
polyacrylate
containing Na_2CO_3

$PbCO_3$ precipitate
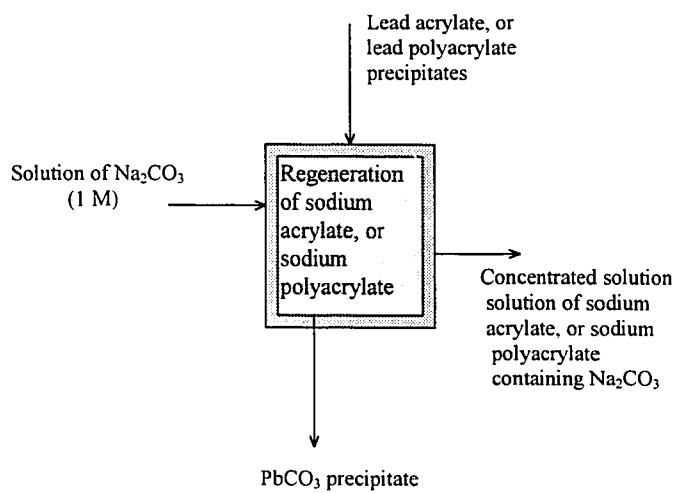
Figure 2.2: Regeneration of sodium acrylate or sodium polyacrylate with
sodium carbonate at moles carbonate/ moles Pb= 2.0.

The percentage regeneration of sodium acrylate or sodium polyacrylate was defined as follows:

$$\Gamma(R_2COONa) = \frac{moles\ of\ acrylate\ in\ the\ regenerated\ solution}{moles\ of\ acrylate\ added\ to\ the\ feed\ in\ the\ removal\ step} \times 100\% \qquad (2.8)$$

The moles of acrylate added to the feed were calculated from the values of $C^{\bullet}(R_2COO)$, and the moles of acrylate in the regenerated solution were calculated from the concentration of total carbon in the regenerated solution. To avoid the interference of carbonate in the total carbon analysis, the samples were acidified, and then degassed with O_2.

2.2.2 Regeneration of sodium caprate

The regeneration of sodium caprate was achieved in two steps. The first step, was the regeneration of capric acid. Lead caprate precipitate was treated with 18 M HNO_3, and distilled water. Water was added to provide the necessary dilution. The volume ratio of HNO_3 to distilled water was 0.5. Figure 2.3 presents a schematic view of the regeneration of sodium caprate. Hydrogen replaced the lead on caprate, and solid capric acid formed at the surface of the solution. Then it was filtered using Fisherbrand fast flow filter paper.

In the second step, the solid capric acid was treated with 1.0 M NaOH solution. The number of moles of NaOH added were equal to the number of moles of capric acid. Distilled water was added to adjust the concentration sodium caprate solution.

Lead caprate
capric acid
precipitates

Solution of HNO₃
(18 M)

$$\frac{V_{HNO_3}}{V_{distilled\ water}} = 1/2$$

Distilled water

Regeneration
of capric
acid

Concentrated

lead solution

Solid
capric acid

Solution of NaOH
(1 M)

Distilled water

Formation
of sodium
caprate

Solution of
sodium caprate
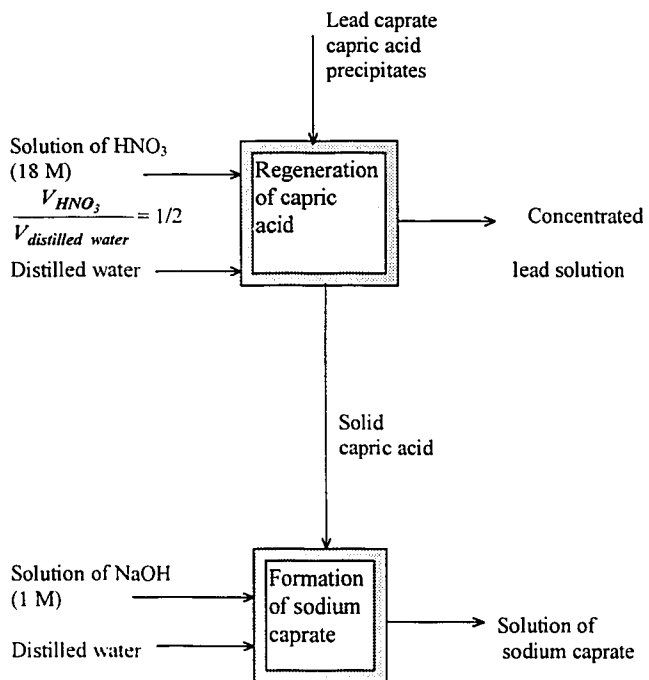
Figure 2.3: Regeneration of sodium caprate

The percentage regeneration of sodium caprate was defined as follows:

$$\Gamma(R_9COONa) = \frac{\text{moles of caprate in the regenerated solution}}{\text{moles of caprate added to the feed in the removal step}} \times$$

$$100\% \qquad (2.9)$$

The number of moles of caprate added to the feed was calculated from the values of $C^*(R_9COO)$, and the number of moles of caprate in the regenerated solution was calculated from the concentration of total carbon in the regenerated solution.

Chapter 3: Experimental results and discussion

This chapter is divided into three sections. The first section presents the results obtained using different types of reagents. The second section, shows the effects of some variables, including calcium and chloride concentrations, on the removal of lead using sodium caprate. The third section describes processes for removing lead using sodium polyacrylate or sodium caprate. Section three also includes the results of the regeneration experiments for sodium acrylate, polyacrylate, and sodium caprate.

3.1 Removal of Lead

Sodium acrylate precipitated lead with law percentage removal and high reagent loss. The main reason is the relatively high solubility of the complex. To reduce the solubility of reagents having the carboxylate functional group, the molecular weight of the reagent was increased. Sodium polyacrylate, and straight carbon chain sodium carboxylate reagents with different chain lengths were used.

3.1.1 Sodium acrylate and sodium polyacrylate

Sodium acrylate and sodium polyacrylates having average molecular weights of 1 200 and 30 000 were used to remove lead from solutions containing

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1450 ppm lead at pH^o= 4.4. Three replicates were run for each point, and the 95% confidence interval is given. Figure 3.1 shows the percentage removal of lead as a function of the ratio of the moles of acrylate group to the moles of lead $r^o(R_2COO)$. The moles of the acrylate rather than polymer were used in order to present the results for sodium acrylate and sodium polyacrylate on the same graph.

For sodium acrylate, an increase in $r^o(R_2COO)$, increased the percentage removal of lead. The increase was linear up to a mole ratio of 6. The loss of acrylate was $70\pm1\%$ for runs with $r^o(R_2COO)\le 6$. At $r^o(R_2COO)$= 8.0, the removal fell below an extrapolation of the linear relation and the loss of acrylate increased to $77\pm1\%$. At $r^o(R_2COO)$= 10, the aqueous phase became cloudy. For even higher mole ratios, both the cloudiness and the precipitate disappeared.

When sodium polyacrylate of average molecular weight of 1 200 was used, lead removal increased linearly with the mole ratio. The reagent loss was $11.4\pm0.3\%$. The aqueous phase was clear up to a mole ratio of 2.5, at which the removal was $96.0\pm0.2\%$ as shown in Figure 3.1. When the mole ratio was increased to 3, cloudiness appeared. For $r^o(R_2COO)\ge 4$, both the cloudiness and the precipitate disappeared. The polymer with the average molecular weight of 30 000 behaved similarly. The loss was $2.4\pm0.5\%$, and the removal was $84\pm1\%$, at a mole ratio of 2. When the mole ratio was increased to 2.5, cloudiness appeared. For $r^o(R_2COO)\ge 3$, both the cloudiness and the precipitate disappeared.

As expected, increasing the molecular weight of sodium acrylate reagent increased the percentage removal of lead, and reduced the reagent loss.

The disappearance of the lead-acrylate precipitate at higher ratios of acrylate to lead is attributed to the formation of soluble complexes. For the polymer, a second reason might be that, as the mole ratio was increased, too few carboxylic acid groups were combined with lead to precipitate the polymer.
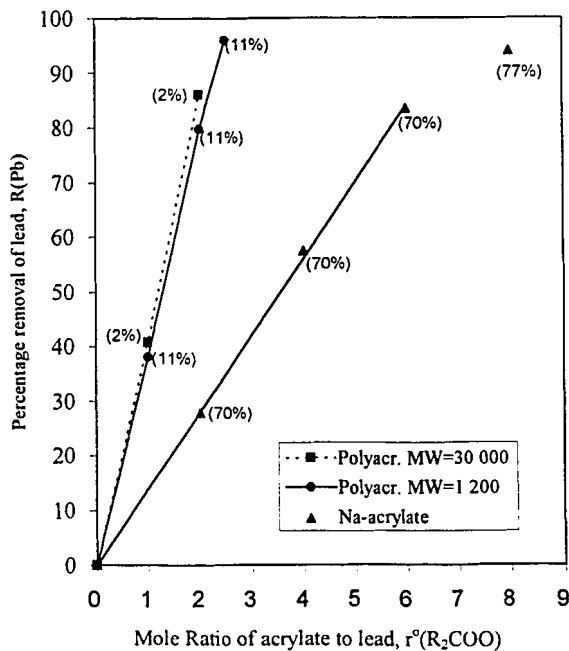
Figure 3.1: Removal of lead by sodium acrylate and sodium polyacrylate. $C^{\circ}(Pb)= 1450$ ppm, $pH^{\circ}= 4.4$, $r^{\circ}(Ca)= 0$, $r^{\circ}(NO_3)= 2.0$, $r^{\circ}(Cl)= 0$. Values in parenthesis are percentage acrylate loss, $L(R_2COO)$.

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3.1.2 Sodium carboxylate reagents with straight carbon chains

The second type of reagent was straight chain sodium carboxylate. Increasing the chain length was expected to reduce the solubility of the lead complex. Three different straight chain sodium carboxylates were tested: sodium propionate, sodium caprate, and sodium oleate.

3.1.2.1 Sodium propionate

Sodium propionate did not remove lead. Propionate $(CH_3CH_2COO^-)$ did not form a precipitate with lead. The only difference between the propionate and acrylate groups is the double bond in acrylate. Lead acrylate was found insoluble to some extent, while lead propionate was soluble. Acrylate is hypothesized to form a five member ring complex with lead as shown in Figure 3.2. The contribution of the double bond makes the complex more stable (4), and thus precipitation occurs.
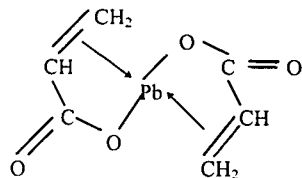

Figure 3.2: Suggested structure for lead acrylate complex.

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3.1.2.2 Sodium caprate

Sodium caprate $(CH_3(CH_2)_8COONa,$ or $R_9COONa)$ was used to remove lead from a feed solution of 1450 ppm of lead, at $pH^° = 4.4$. Figure 3.3 shows the percentage removal of lead and the percentage loss of caprate as functions of the mole ratio of caprate to lead. The maximum values of 95% confidence intervals were $\pm1\%$ for the percentage removal of lead, and $\pm2\%$ for the percentage loss of caprate.

The removal increased linearly with increasing mole ratio of caprate to lead up to a mole ratio of two, where the percentage removal of lead was $99.5\pm0.2\%$, and the percentage loss of caprate was $0.8\pm0.3\%$. At higher mole ratios, the percentage removal increased very slightly with an increasing loss of caprate.

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

$$Pb^{2+} + 2R_9COO^- \leftrightarrow (R_9COO)_2Pb_{(S)} \tag{2.1}$$
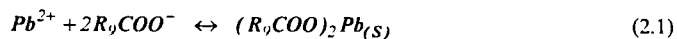
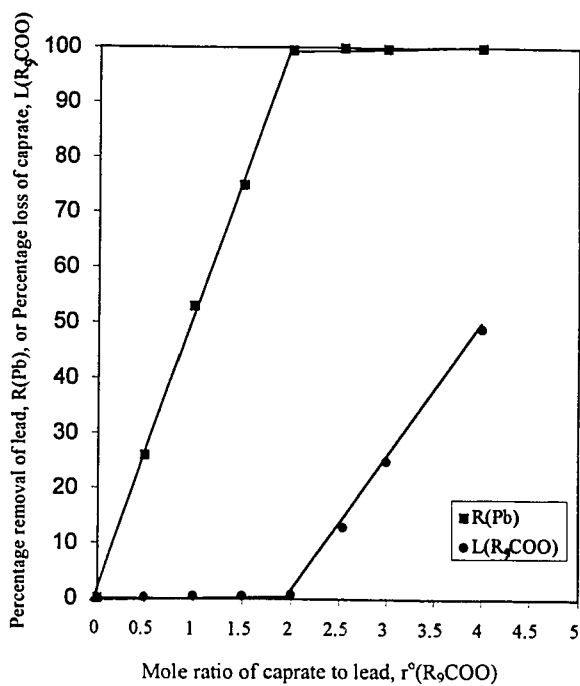**Figure 3.3:** Removal of lead and loss of caprate using sodium caprate reagent. $C^o(Pb)$= 1450 ppm, pH^o= 4.4 , $r^o(Ca)$= 0, $r^o(NO_3)$= 2.0, $r^o(Cl)$= 0.

3.1.2.3 Sodium oleate

To study the effect of longer chain carboxylate, sodium oleate $(CH_3(CH_2)_7CH=CH(CH_2)_7COONa$, or $R_{17}COONa)$ was used. The removal of lead from feed solutions of two different concentrations, 725 ppm and 1450 ppm, was tested. The mole ratio of oleate to lead, $r^o(R_{17}COO)$, was kept 2. Table 3.1 shows the percentage removal of lead and the percentage loss of oleate for the two feed concentrations of lead. The tabulated results show 95% confidence intervals for three replicates per run.

Table 3.1 Removal of lead and loss of oleate at two different feed concentrations of lead using sodium oleate reagent. $r^o(R_{17}COO)= 2.0$, $pH^o= 4.4$, $r^o(Ca)= 0$, $r^o(NO_3)= 2$, $r^o(Cl)= 0$.

$C^o(Pb)$ (ppm)	Percentage removal of lead, R(Pb)	Percentage loss of oleate, $L(R_{17}COO)$
725	82 ± 6	14 ± 6
1450	97.5 ± 0.3	2.5 ± 0.4

At the same mole ratio and feed concentration of lead, the removal was lower with oleate than with caprate. With sodium oleate, a suspension rather than a precipitate was formed, possibly due to the presence of a double bond in oleate. This suspension was very difficult to filter, and it is suspected that some of the lead detected in the filtrate was suspension that come through the 0.45 μm filter paper pore, thus giving lower percentage removal.

3.2 Effect of some variables on lead removal using sodium caprate

Among all the reagents tested, sodium caprate gave the highest percentage removal of lead, the lowest reagent loss, and produced an easily filterable precipitate. The effects of feed variables (lead concentration, pH, calcium concentration, as well as chloride and nitrate concentrations) on the removal of lead and loss of reagent were studied for sodium caprate.

3.2.1 Effect of feed concentration of lead

For a mole ratio of sodium caprate to lead of 2, and a feed pH of 4.4, the concentration of lead in the feed was varied from 72.5 to 1450 ppm (0.35 mM to 7.0 mM). Figure 3.4 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 equilibrium concentrations of lead and caprate are also shown. The maximum values of 95% confidence intervals for the percentage removal of lead, and the percentage loss of caprate were $\pm1\%$, $\pm4\%$ respectively. The values for the equilibrium concentration of lead and caprate were ±2 ppm and ±2 ppm respectively.

Figure 3.4 shows that the equilibrium concentrations of lead and caprate were independent of the feed concentration 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 equation (3.1) as:

$$K_{SP} = C(Pb^{2+}) \times C^2(R_9COO^-) \qquad\qquad (3.2)$$

assuming that all lead at equilibrium exists as Pb^{2+}, and all caprate exists as R_9COO^-.
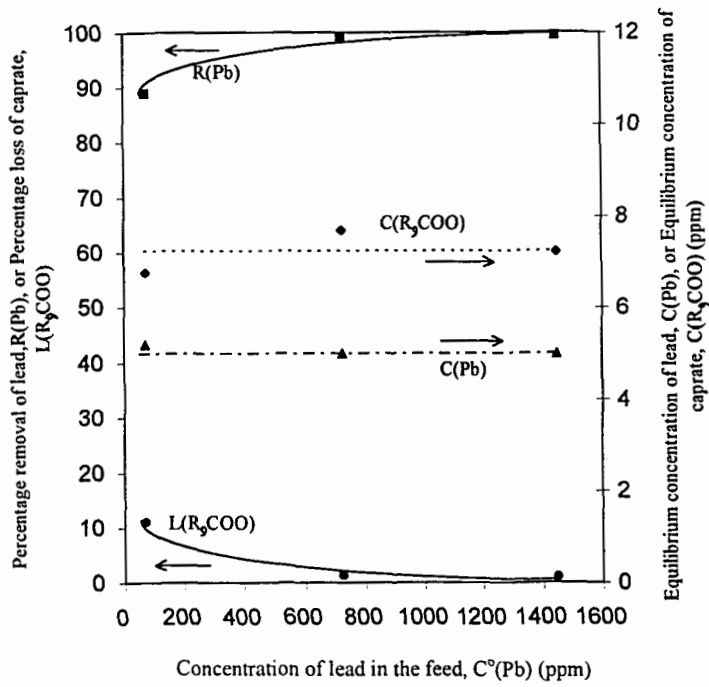
Figure 3.4: Effect of feed concentration of lead on the removal of lead, the percentage loss of reagent, and the equilibrium concentrations of lead and caprate using sodium caprate. $r^o(R_oCOO)= 2.0$, $pH^o= 4.4$, $r^o(Ca)= 0$, $r^o(NO_3)= 2.0$, $r^o(Cl)= 0$.
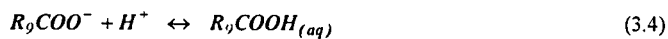
3.2.2 Effect of feed pH

Two sets of experiments were conducted: the first shows the effect of decreasing pH°, at constant mole ratio of caprate to lead, $r°(R_9COO)$. The second shows the effect of increasing $r°(R_9COO)$ at constant pH° value.

3.2.2.1 Decreasing pH°

For a feed concentration of 7 mM $Pb(NO_3)_2$, $C°(Pb)= 1450$ ppm, the pH of the feed was decreased from 4.4 to 1.7 by adding HNO_3. When HNO_3 was added, the ratio of nitrate to lead, $r°(NO_3)$, increased from 2 at pH°= 4.4 to 6 at pH°= 1.7. The mole ratio of caprate to lead was fixed at 2.

Figure 3.5 shows the percentage removal of lead, the percentage loss of caprate, and the equilibrium pH plotted against pH°. Three replicates were run for each condition. The maximum values of the 95% confidence intervals for the percentage removal of lead, $\pm 3\%$, and for the percentage loss of caprate, $\pm 0.9\%$ - see Table A.4 Appendix A for details. The percentage removal decreased with decreasing pH°. The percentage loss of caprate was essentially constant $(2.8\pm 0.4\%)$ for all the samples to which acid was added. 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° and pH, can be explained by the following equilibrium reactions:

$$2R_9COO^- + Pb^{2+} \leftrightarrow (R_9COO)_2Pb_{(S)} \qquad (3.3)$$

$$R_9COO^- + H^+ \leftrightarrow R_9COOH_{(aq)} \qquad (3.4)$$

$$R_9COOH_S \leftrightarrow R_9COOH_{(aq)} \qquad (3.5)$$
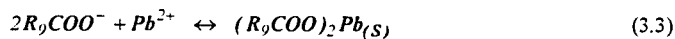
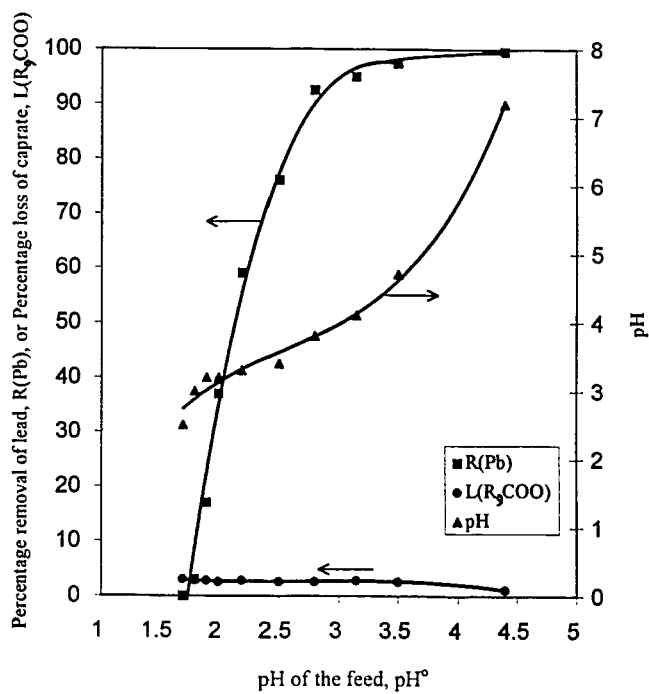**Figure 3.5:** Effect of feed pH on the removal of lead, the percentage loss of reagent, and the equilibrium pH using sodium caprate. $C^o(Pb)= 1450$ ppm, $r^o(R_9COO)= 2.0$, $r^o(Ca)= 0$, $r^o(Cl)= 0$.

Capric acid is a weak acid, hence it may be present in solution and since it has a relatively long carbon chain, it may precipitate. The competition between hydrogen and lead ions decreased the removal of lead and increased the equilibrium pH. Since a certain concentration of soluble capric acid is in equilibrium with the solid form of the acid, a constant equilibrium concentration of caprate and a constant percentage loss resulted.

Without acid addition, the initial pH of a 7 mM $Pb(NO_3)_2$ solution was 4.4. This low pH resulted from the hydrolysis of Pb^{2+} (2):

$$Pb^{2+} + H_2O \leftrightarrow Pb(OH)^+ + H^+ \tag{3.6}$$

When almost all the lead was removed with caprate, the pH of the solution returned to a value around 7 as shown in Figure 3.5 and described by the following reactions:

$$Pb(OH)^+ + 2R_9COO^- \leftrightarrow (R_9COO)_2Pb_{(S)} + OH^- \tag{3.7}$$

$$OH^- + H^+ \leftrightarrow H_2O \tag{3.8}$$
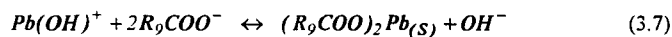
At $pH^\circ = 4.4$, hydrogen ion could not compete with lead, and little capric acid formed, Thus giving a lower percentage loss of caprate at this pH°.

3.2.2.2 Increasing $r^\circ(R_9COO)$

For a feed concentration of 7 mM $Pb(NO_3)_2$, $C^\circ(Pb) = 1450$ ppm, and $pH^\circ = 1.8$, the mole ratio of caprate to lead, $r^\circ(R_9COO)$, was increased from 2 to 4. The percentage removal of lead, the percentage loss of caprate, and the equilibrium pH are plotted against the mole ratio of sodium caprate to lead in Figure 3.6. Three replicates were run for each point.
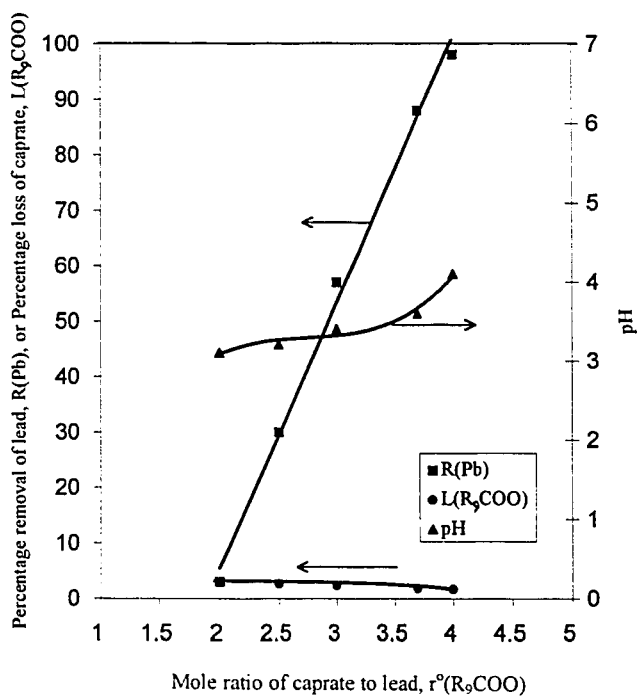
Figure 3.6: Effect of mole ratio of caprate to lead on the removal of lead, the loss of the reagent and the equilibrium pH using sodium caprate. $C^o(Pb)= 1450$ ppm, $pH^o= 1.8$, $r^o(Ca)= 0$, $r^o(NO_3)= 4$, $r^o(Cl)= 0$.

The maximum values of the 95% confidence intervals for the percentage removal of lead, and the percentage loss of caprate of $\pm 2\%$, and $\pm 0.4\%$, respectively.

The percentage removal of lead increased linearly, and the percentage loss of caprate decreased slightly with increasing $r^o(R_9COO)$. The equilibrium concentration of caprate was constant at 40 ± 4 ppm - see Table A.5 in Appendix A. Equations 3.3 to 3.5, together with their related argument explain these results.

3.2.3 Effect of calcium

Calcium is an alkaline earth metal which exists in almost all water streams. If calcium competes with lead, some sodium caprate will be consumed to form calcium complexes. Consequently, more sodium caprate will be required to remove a given percentage of lead. The selectivity of sodium caprate for lead against calcium was determined by adding $Ca(NO_3)_2$ to the feed. For a feed concentration of 7 mM $Pb(NO_3)_2$, $C^o(Pb)= 1450$ ppm, and $r^o(R_9COO)= 2.0$, the mole ratio of calcium to lead in the feed, $r^o(Ca)$, was varied from 0.5 to 4.0.

The results are presented in Table 3.2. The percentage removal of lead and calcium, and the percentage loss of caprate are tabulated for several $r^o(Ca)$. Three replicates were run and 95% confidence intervals are given. 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 for any value of $r^o(Ca)$. The caprate reagent precipitated lead selectively.

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Table 3.2 Effect of calcium on the removal of lead using sodium caprate. $C^o(Pb)$= 1450 ppm, $r^o(R_9COO)$= 2.0, $r^o(Cl)$= 0..

$r^o(Ca)$	$r^o(NO_3)$	Percentage removal of lead, R(Pb)	Percentage removal of calcium, R(Ca)	Percentage loss of caprate, L(R₀COO)
0.0	2.0	99.5±0.2	0	0.8±0.3
0.5	3.0	99.4±0.4	0	1.1±0.5
1.0	4.0	99.6±0.4	0	1.1±0.4
2.0	6.0	99.4±0.6	0	1.1±0.5
3.0	8.0	99.3±0.6	0	0.8±0.4
4.0	10.0	99.4±0.5	0	1.2±0.5

To study the removal of calcium alone, sodium caprate was added to lead-free solutions containing 3.5 mM and 7 mM $Ca(NO_3)_2$. Table 3.3 shows the percentage removal of calcium, and the percentage loss of caprate as well as the 95% confidence intervals computed from three replicates. The percentage removal of calcium increased from 44% to 75% as the concentration of calcium was increased from 140 ppm to 280 ppm. These values are well below those of lead shown in Figure 3.4.

Table 3.3 Removal of calcium from solutions of $Ca(NO_3)_2$ using sodium caprate. The mole ratio of sodium caprate to calcium was 2.0.

$C^o(Ca)$ (ppm)	Percentage removal of calcium, R(Ca)	Percentage loss of caprate, L(R₀COO)
140	44±10	19.5±0.1
280	75±2	12.7±0.4

3.2.4 Effects of Chloride and Nitrate

Chloride, which present in most water streams, increases the solubility of heavy metals by forming soluble complexes. In the case of lead, these complexes are: $PbCl^+$, $PbCl_{2(aq)}$, $PbCl_3^-$, $PbCl_4^{2-}$ (8). 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 $PbCl_2$, $C^o(Pb)$= 1530 ppm, and $r^o(R_9COO)$= 1.9, the mole ratio of chloride to lead, $r^o(Cl)$, was increased from 2 to 200 by adding NaCl. To eliminate the effect of the ionic strength, the same experiment was repeated in nitrate media since nitrate is considered an inert ion. Lead nitrate was the source of lead in the solution, and $NaNO_3$ was added to adjust the concentration of NO_3^- to achieved similar values of $r^o(NO_3)$.

Figure 3.7 shows the percentage removal of lead and the equilibrium pH plotted against the mole ratio of chloride to lead, $r^o(Cl)$, or the mole ratio of nitrate to lead $r^o(NO_3)$. For three replicates for each point, the maximum values of the 95% confidence intervals for the percentage removal of lead in both chloride and nitrate media were $\pm 1\%$. For both media, the percentage removal of lead was essentially independent of $r^o(NO_3)$ or $r^o(Cl)$ and thus the ionic strength of the solution. For chloride media, there was a slight increase in the percentage loss of caprate, with increasing $r^o(Cl)$ - see Table A.8 in Appendix A. This increase in caprate loss is attributed to the formation of $PbCl_2$ precipitate at high $r^o(Cl)$ thus leaving some caprate in the solution.

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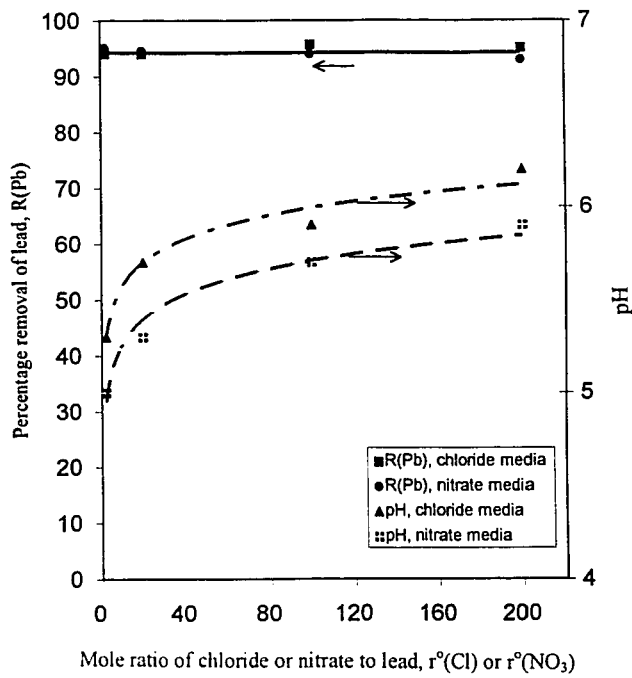
Figure 3.7: Effect of chloride and nitrate on the removal of lead and the equilibrium pH using sodium caprate. $C^o(Pb)= 1530$ ppm, $r^o(R_9COO)= 1.9$, $r^o(Ca)= 0$.

Figure 3.7 also shows that the equilibrium pH of the solution 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 (5,8). As the ionic strength increased, the activity coefficient of hydrogen ion decreased. For the same ionic strength, the difference in the equilibrium pH between chloride and nitrate media resulted from the following reaction:

$$Pb(OH)^+ + Cl^- \leftrightarrow PbCl^+ + OH^- \tag{3.9}$$

As a result, the equilibrium pH values of the chloride media were higher.

3.3 Process concepts for the removal of lead and regeneration of the Reagents

In this section, the results of regeneration of sodium acrylate, sodium polyacrylate, and sodium caprate is described. Conceptual flowsheets are shown for the two step process involving the removal of lead and the regeneration of the reagent for two reagents: sodium polyacrylate (MW=1 200) and sodium caprate.

3.3.1 Regeneration of sodium acrylate and sodium polyacrylate

Following the procedure outlined in Chapter 2, the percentage regeneration of sodium acrylate and sodium polyacrylate were 99.8% with a 95% confidence interval of ±0.2% (based on three replicates).

Figure 3.8 is a conceptual flowsheet of a process for removal of lead using sodium polyacrylate of average molecular weight of 1 200. The flows are based on 100 ml of a feed solution containing 1450 ppm lead from $Pb(NO_3)_2$. No acid, calcium, or chloride were present in the feed. The mole ratio of acrylate to lead,

Make-up solution, V= 1.54 ml
(9 230 ppm polyacrylate)

V_a= 13.46 ml
r°(R$_2$COO)= 2.5
(9 230 ppm polyacrylate)

Feed solution V_f= 100 ml
C°(Pb)= 1450 ppm,
pH°= 4.4, r°(Ca)= 0,
r°(NO$_3$)= 2, r°(Cl)= 0.

Lead removal

Treated solution
103.5 ml, C(Pb)= 41 ppm,
C(R$_2$COO)= 101 ppm

Lead-polyacrylate
precipitate

Solution of 1 M
Na$_2$CO$_3$, V= 1.92 ml

$$\frac{moles\ CO_3^{2-}}{mole\ Pb} = 2.0$$

Regeneration of sodium polyacrylate

Solution of sodium
polyacrylate, V= 11.92 ml
(9 230 ppm polyacrylate)

PbCO$_3$ precipitate

Figure 3.8: Flowsheet for a lead removal process using sodium polyacrlate of average molecular weight 1 200. C°(Pb)= 1450 ppm, r°(R$_2$COO)= 2.5, pH°= 4.4, r°(Ca)= 0, r°(NO$_3$)= 2, r°(Cl)= 0.

$r^o(R_2COO)$, was 2.5. The volume added to the feed in the removal step was 13.46 ml of 9 230 ppm polyacrylate solution. In the removal step, the percentage removal of lead, $R(Pb)$, was 96%, and the percentage loss of acrylate, $L(R_2COO)$, was 11.4%. The concentration of lead in the treated solution, $C(Pb)$, was 41 ppm, and the concentration of acrylate, $C(R_2COO)$, was 101 ppm. In the regeneration step, lead polyacrylate precipitate was treated with 1.92 ml of 1 M sodium carbonate solution. The percentage regeneration, $\Gamma(R_2COO)$, was 99.8%. The concentration of polyacrylate in the regenerated solution was 9 230 ppm. Assuming that the reagent make-up stream also contained 9 230 ppm polyacrylate, a volume of 1.54 ml was sufficient to compensate for the loss of sodium polyacrylate in the removal step.

3.3.2 Regeneration of sodium caprate

Sodium caprate was regenerated in two steps. The first step, was the regeneration of capric acid by treating lead caprate precipitate with HNO_3. The second step, was the formation of sodium caprate by treating capric acid precipitate with NaOH (see Chapter 2 for details). The percentage regeneration, $\Gamma(R_oCOO)$, was 98.9% with a 95% confidence interval of $\pm0.3\%$ based on three replicates.

Figure 3.9 is a conceptual flowsheet of a process for removal of lead from 100 ml feed solution of 1450 ppm lead concentration. No acid, calcium, or chloride were present in the feed. The mole ratio of caprate to lead in the removal step was 2.0.

Make-up solution,
(25 400 ppm caprate)
V= 0.18 ml

V_a= 9.43 ml
$r°(R_9COO)$= 2.0

Feed solution
100 ml
$C°(Pb)$= 1450 ppm,
$pH°$= 4.4, $r°(Ca)$= 0,
$r°(NO_3)$= 2, $r°(Cl)$= 0.

Lead removal

Treated solution
$C(Pb)$= 5 ppm
$C(R_9COO)$= 7 ppm
V= 99.5 ml

Precipitate
$(R_9COO)_2Pb_{(S)}$

Solution of HNO_3
(18 M), V= 4.64 ml

Distilled water
V= 9.29 ml

Regeneration of capric acid

Concentrated lead solution
$C(Pb)$= 10 350 ppm
$C(R_9COO)$= 19 ppm
V= 13.9 ml

Solid capric acid
$R_9COOH_{(S)}$

Solution of NaOH
(1 M)
V= 1.37 ml

Distilled water
V= 7.88 ml

Formation of sodium caprate

Solution of sodium caprate
(25 400 ppm caprate)
V= 9.25 ml

Figure 3.9: Flow sheet for a process of removing lead using sodium caprate. $C°(Pb)$= 1450 ppm, $r°(R_9COO)$= 2.0, $pH°$= 4.4, $r°(NO_3)$= 2.0, $r°(Cl)$= 0.

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In the removal step, the percentage removal of lead was 99.5%, and the percentage loss of caprate was 0.8%. The concentration of lead and caprate in the treated solution were 5 ppm and 7 ppm, respectively.

To regenerate capric acid, 18 M HNO_3 was added. Solid capric acid was formed, and concentrated lead solution was produced. Lead was concentrated to 10 350 ppm, seven times the concentration in the original feed. The percentage loss of caprate in this step was 1.1% of the caprate originally added to the feed.

The solid capric acid was treated with NaOH to form sodium caprate. The concentration of the caprate in the regenerated solution was 25 400 ppm. This stream was recycled to the removal step. A make-up stream of sodium caprate of the same caprate concentration was added to compensate for the 1.9% loss of caprate in the removal and the regeneration steps. A volume of 0.18 ml of this stream was required. Distilled water was added to adjust the concentration of sodium caprate in the added solution.

Chapter 4: Modeling the Removal of Lead By Sodium Caprate

4.1 Introduction

The model was used to predict the experimental results for the effect of different lead concentrations in the feed, and the effect of pH on the removal step using sodium caprate. The inital system, shown in Figure 4.1.a, consists of $Pb(NO_3)_2$ and HNO_3 in water. Feed solution is specified by its lead concentration, $C^o(Pb)$, and its pH, pH^o. Upon adding sodium caprate, R_9COONa, additional species are formed, including capric acid and lead caprate precipitates as shown in Figure 4.1.b. The amount of sodium caprate added is specified by the ratio of the moles of caprate to moles of lead, $r^o(R_9COO)$. Considering Na^+ and NO_3^- as inert ions, their numbers of moles at equilibrium are equal to the Na^+ added as R_9COONa, and to the NO_3^- added as $Pb(NO_3)_2$ and as HNO_3. Eight unknowns remain: the number of moles of: Pb^{2+}, $PbOH^+$, $(R_9COO)_2Pb_{(S)}$, R_9COO^-, $R_9COOH_{(aq)}$, $R_9COOH_{(S)}$, OH^-, and H^+. Therefore, eight independent equations are needed. Five of these equations are the equilibrium constant equations of the reactions taking place between different solutes. The three remaining equations are

the lead material balance, the caprate material balance, and charge neutrality in the equilibrium liquid. A detailed derivation is given in Appendix B.

$Pb(NO_3)_2$ _____   _____ HNO_3

| Pb^{2+} | OH^- | H^+ |
| NO_3^- | $PbOH^+$ | |
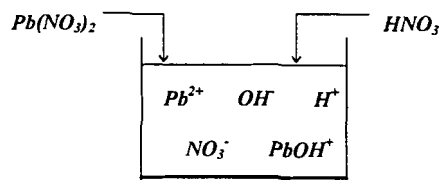
Figure 4.1.a: Feed solution of $Pb(NO_3)_2$ in water at $pH°$.

R_9COONa _____

Pb^{2+}	OH^-	H^+
NO_3^-	R_9COOH_{aq}	$PbOH^+$
Na^+	R_9COO^-	

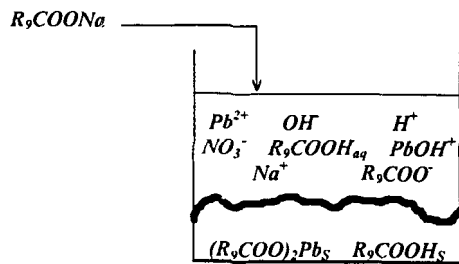$(R_9COO)_2Pb_S$ R_9COOH_S

Figure 4.1.b: Equilibrium upon adding R_9COONa.

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4.2 Equilibrium reactions

Five reactions are assumed to occur in the pH range from 2.0 to 7.0. The equilibrium constant equations are given below each reaction. The activity coefficients for all species are assumed to be unity.

$$PbOH^+ \xrightleftharpoons{K_1} Pb^{2+} + OH^- \qquad\qquad (4.1)$$

$$K_1 = \frac{[Pb^{2+}][OH^-]}{[PbOH^+]} \qquad\qquad (4.2)$$

$$(R_9COO)_2Pb_{(S)} \xrightleftharpoons{K_{SP}} Pb^{2+} + 2R_9COO^- \qquad\qquad (4.3)$$

$$K_{SP} = [Pb^{2+}][R_9COO^-]^2 \qquad\qquad (4.4)$$

$$R_9COOH_{(aq)} \xrightleftharpoons{K_a} H^+ + R_9COO^- \qquad\qquad (4.5)$$

$$K_a = \frac{[H^+][R_9COO^-]}{[R_9COOH_{(aq)}]} \qquad\qquad (4.6)$$

$$R_9COOH_{(S)} \xrightleftharpoons{K_{spA}} H^+ + R_9COO^- \qquad\qquad (4.7)$$

$$K_{spA} = [H^+][R_9COO^-] \qquad\qquad (4.8)$$

$$H_2O \xrightleftharpoons{K_w} H^+ + OH^- \qquad\qquad (4.9)$$
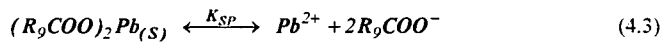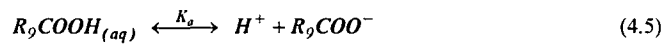
$$K_w = [H^+][OH^-] \qquad\qquad (4.10)$$

where [i] is the equilibrium concentration of species i in molar (M).

4.3 Material Balances

4.3.1 Lead balance

Lead added to the solution, either precipitates as lead caprate, or remains soluble as Pb^{2+}, or $PbOH^+$. The material balance is:

$$n_{Pb(NO_3)_2, \ feed} = n_{(R_9COO)_2Pb_{(S)}} + n_{Pb^{2+}} + n_{PbOH^+} \qquad (4.11)$$

where n_i is the equilibrium number of moles of species i, and $n_{Pb(NO_3)_2, \ feed}$ is the number of moles of lead nitrate in the feed.

Expressing the equilibrium number of moles of Pb^{2+}, and $PbOH^+$ in terms of the equilibrium constants and the equilibrium hydrogen concentration, $[H^+]$, the following equation can be written:

$$n_{Pb(NO_3)_2, \ feed} = X + C_1 Z^2 + C_2 Z \qquad (4.12)$$

where the number of moles of lead caprate precipitate, $n_{(R_9COO)_2Pb_{(S)}}$, is X, and Z is the equilibrium concentration of hydrogen ion, $[H^+]$. The constans C_1 and C_2 are constants, which depend on the reaction equilibrium constants and the volumes of feed and reagent solution.

This equation has one input ($n_{Pb(NO_3)_2, \ feed}$), and two unknowns, X and Z.

4.3.2 Caprate balance

Caprate added to the system, either precipitates as lead caprate, $(R_9COO)_2Pb_{(S)}$, or capric acid, $R_9COOH_{(S)}$, or remains as soluble capric acid, $R_9COOH_{(aq)}$, or caprate ion, R_9COO^-. The material balance is:

$$n_{R_9COONa, \ added} = 2n_{(R_9COO)_2Pb_{(S)}} + n_{R_9COOH_{(S)}} + n_{R_9COOH_{(aq)}} + n_{R_9COO^-}$$

$$\qquad (4.13)$$

where $n_{R_9COONa, \, added}$ is the number of moles of sodium caprate added to the feed.

Expressing the equilibrium number of moles of $R_9COOH_{(aq)}$, and R_9COO^- in terms of the equilibrium constants and the equilibrium hydrogen concentration, $[H^+]$, the following equation can be written:

$$n_{R_9COONa, \, added} = 2X + Y + C_3 + C_4 \, / \, Z \qquad (4.14)$$

where Y is the number of moles of capric acid in the precipitate at equilibrium, and C_3 and C_4 are constants, which depend on the reaction equilibrium constants and the volumes of the feed and reagent solutions.

This equation has one input ($n_{R_9COONa, \, added}$), and three unknowns, X, Y, and Z.

4.4 Charge Balance

The ions expected to exist in the aqueous phase at equilibrium are: Pb^{2+}, $PbOH^+$, H^+, Na^+, OH^-, NO_3^-, and R_9COO^-. For electroneutrality, the number of equivalents of positive ions equals the number of equivalents of negative ions:

$$2n_{Pb^{2+}} + n_{Na^+} + n_{H^+} + n_{PbOH^+} = n_{NO_3^-} + n_{R_9COO^-} + n_{OH^-} \qquad (4.15)$$

Assuming that sodium and nitrate do not participate in the reactions:

$$n_{Na^+} = n_{R_9COONa, \, added} \qquad (4.16)$$

$$n_{NO_3^-} = 2n_{Pb(NO_3)_2, \, feed} + n_{HNO_3, \, feed} \qquad (4.17)$$

where $n_{HNO_3, \, feed}$ is the number of moles of nitric acid in the feed.

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Expressing the equilibrium moles of the other ions in equation 4.15, in terms of the equilibrium constants and the equilibrium hydrogen concentration, the following equation can be written:

$$2C_1Z^3 + (C_2 + C_5)Z^2 + (n_{R_9COONa,\ added} - n_{HNO_3,\ feed} - 2n_{Pb(NO_3)_2,\ feed})Z$$
$$-(C_4 + C_6) = 0 \qquad (4.18)$$

where C_5 and C_6 are constants which depend on the reaction equilibrium constants and the volumes of the feed and reagent solution.

This equation has three inputs: $n_{R_9COONa,\ added}$, $n_{HNO_3,\ feed}$, and $n_{Pb(NO_3)_2,\ feed}$, and only one unknown, $[H^+]$. The solution to this cubic equation gave one positive root, and two negative or complex roots.

Moles of HNO_3 in the feed, $n_{HNO_3,\ feed}$, were the input to the model. The model predictions were plotted against the feed pH, pH°. The values of pH° were calculated from the concentration of nitric acid in the feed, assuming complete dissociation of nitric acid, activity coefficient of hydrogen ion to be unity, and no hydrolysis of Pb^{2+}. The last assumption is only valid when pH°< 4.0 (8). The model predictions were restricted to values of pH°< 4.0. With the above assumptions, pH° is related to $n_{HNO_3,\ feed}$ by:

$$pH° = -\log(n_{HNO_3,\ feed} / V_f) \qquad (4.19)$$

Figure 4.2 shows the calculated values of pH°, and the values of pH° determined experimentally using the pH meter, both plotted versus the moles of HNO_3 in the feed, $n_{HNO_3,\ feed}$. There is good agreement between the calculated and measured values.
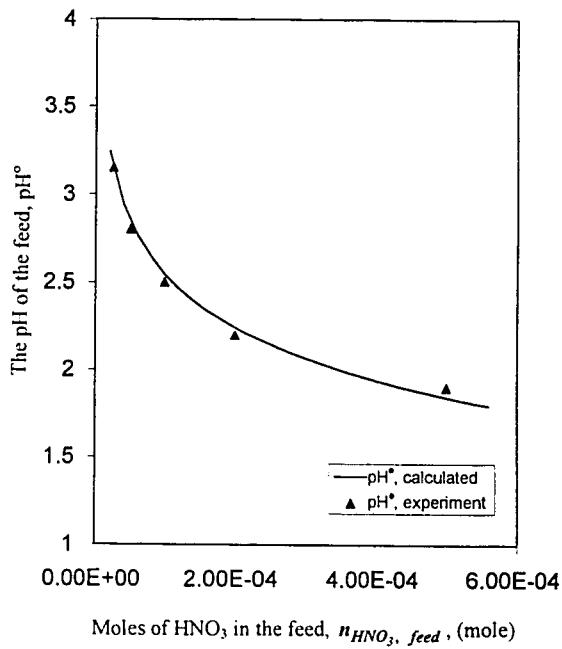
Figure 4.2: Feed pH, pH°, calculated from the concentration of HNO_3, and measured with the pH meter versus the moles of HNO_3 in the feed, $n_{HNO_3, feed}$.

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4.5 Model Prediction

The values of K_1 and K_w were taken from literature (11). The value of K_a for capric acid was assumed to be equal to the values reported for hexanoic and octanoic acids (1) because the value of K_a for straight chain carboxylic acids does not vary much with the chain length of the acid (12). The values of the solubility product for lead caprate and capric acid were detemined experimentally - see Appendix C for details. The values of the equilibrium constants and the constants appearing in equations (4.12), (4.14), and (4.18) are listed below.

$K_1 = 1.7 \times 10^{-7}$ M, $K_{sl} = 1.1 \times 10^{-13}$ M³, $K_a = 1.4 \times 10^{-5}$ M, $K_{spA} = 2.6 \times 10^{-9}$ M²,

$K_w = 10^{-14}$ M², $C_1 = 831.5$ 1/M, $C_2 = 4.9 \times 10^{-5}$ 1, $C_3 = 9.3 \times 10^{-6}$ 1·M, $C_4 = 1.3 \times 10^{-10}$ 1·M², $C_5 = 35 \times 10^{-3}$ 1, $C_6 = 3.5 \times 10^{-16}$ 1·M².

Calculating the equilibrium hydrogen concentration from equation 4.18, the moles of lead caprate precipitate, $(R_9COO)_2Pb_{(S)}$, and capric acid precipitate, $R_9COOH_{(S)}$, can be calculated from equations 4.12, and 4.14 respectively, i.e. the three equations can be solved in series.

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

$$R(Pb) = \frac{(n_{Pb(NO_3)_2, \, feed} - n_{(R_9COO)_2Pb_{(S)}})}{n_{Pb(NO_3)_2, \, feed}} \times 100\% \qquad (4.20)$$

$$L(R_9COO) = \frac{(n_{R_9COONa, \, added} - 2n_{(R_9COO)_2Pb_{(S)}} - n_{R_9COOH_{(S)}})}{n_{R_9COONa, \, added}} \times 100\% \qquad (4.21)$$

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4.5.1 Effect of feed concentrations of lead

Figure 4.3 shows the model prediction for the effect of different feed concentration of lead. The lines are the model prediction while the points are the experimental results. The model predicts constant equilibrium concentrations of both lead and caprate, independent of the concentration of lead in the feed. The small differences between the experimental values and the model predictions generally fall within the experimental error. Overall, there is a good agreement between the model results and the experimental data.
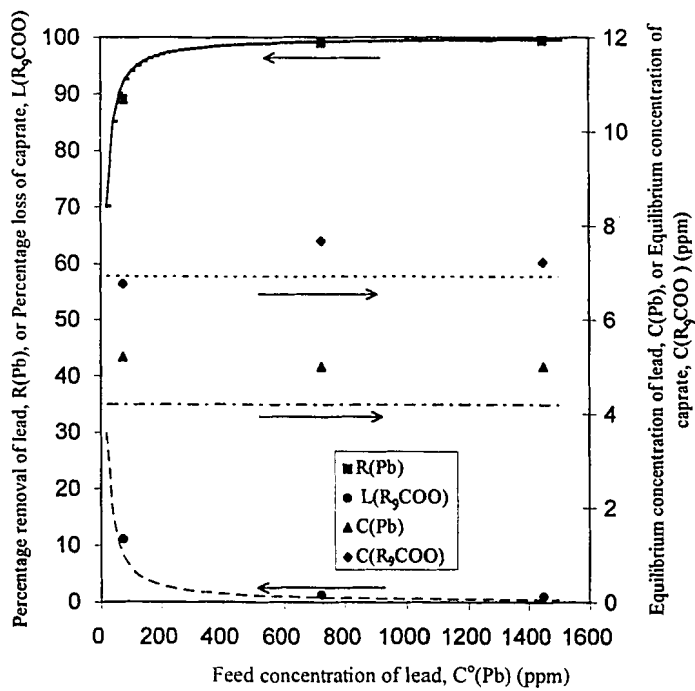
Figure 4.3: Effect of feed concentration of lead on the removal of lead, the loss of reagent, and the equilibrium concentration of lead and caprate using sodium caprate. $r^\circ(R_9COO)$= 2.0, pH$^\circ$= 4.4, $r^\circ(Ca)$= 0, $r^\circ(NO_3)$= 2.0, $r^\circ(Cl)$= 0. Points-experiments; Lines-model.

4.5.2 Effect of feed pH

The model predictions for the effect of pH^o are shown in Figure 4.4. There is good agreement between the experimental results and the model predictions for both the percentage removal of lead and the percentage loss of caprate. For the equilibrium pH, the experimental points fell above and below the model predictions with deviations generally fall within the experimental error.

4.5.3 Effect of ratio of caprate to lead

The model predictions for the effect of the mole ratio of caprate to lead, $r^o(R_oCOO)$, at $pH^o= 1.8$, are compared with experiments in Figure 4.5. There is a good agreement between the model predictions and the experimental results for the percentage removal of lead, the percentage loss of caprate, and the equilibrium pH.
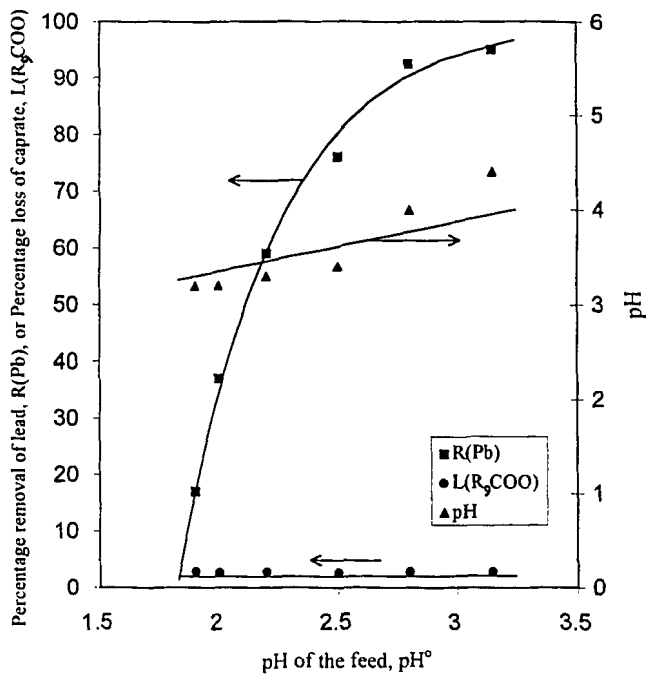
Figure 4.4: Effect of pH° on the removal of lead, the loss of the reagent, and the equilibrium pH using sodium caprate. C°(Pb)= 1450 ppm, r°(R_9COO)= 2.0, r°(Ca)= 0, r°(Cl)= 0. Points-experiments; Lines-model.
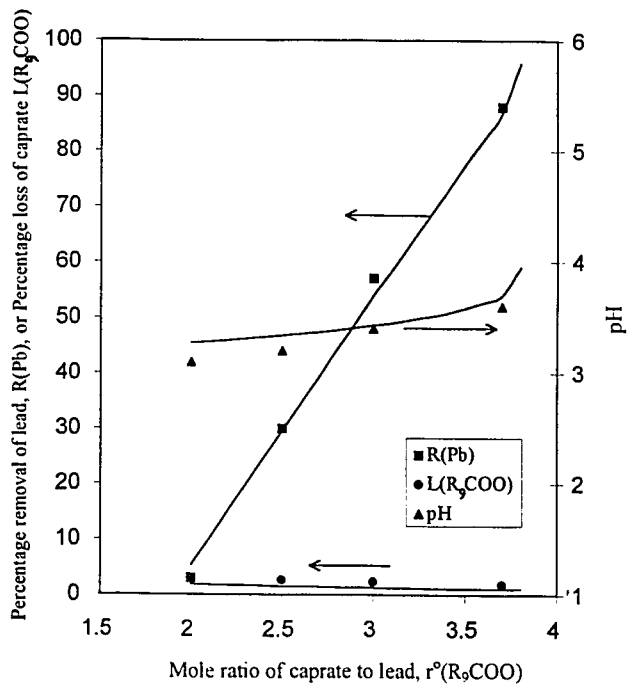
Figure 4.5: Effect of the mole ratio of the reagent to lead on the removal of lead, the loss of caprate, and the equilibrium pH using sodium caprate. $C^{\circ}(Pb)$= 1450 ppm, pH°=1.8. $r^{\circ}(Ca)$= 0. $r^{\circ}(NO_3)$= 4.0, $r^{\circ}(Cl)$= 0. Points-experiments; Lines-model.

Chapter 5: Conclusions and Recommendations

The following conclusions and recommendations are drawn from this work.

5.1 Conclusions

Passing from the monomer sodium acrylate to the polymer sodium polyacrylate, increased the percentage removal of lead and reduced the percentage loss of the reagent. Increasing the average molecular weight of sodium polyacrylate increased the percentage removal and reduced the reagent loss.

A short chain length carboxylate, sodium propionate, did not precipitate lead, but a moderate chain length carboxylate, sodium caprate, formed an easily filterable precipitate with a high percentage removal of lead ($\approx 99.5\%$) and a low loss of the reagent ($\approx 0.8\%$). A long chain carboxylate, sodium oleate, formed a suspension, which was difficult to filter.

5.1.1 Sodium caprate

At a certain mole ratio of caprate to lead, the equilibrium concentrations of lead and caprate were independent of the feed concentration of lead. Decreasing the pH of the feed, decreased the percentage removal of lead. It did not affect the

equilibrium concentration of caprate, because of the equilibrium established between the solid and soluble forms of capric acid. At a certain pH of the feed, increasing the amount of the added caprate increased the percentage removal of lead, but did not affect the equilibrium concentration of caprate, because of the above mentioned reason.

The presence of calcium in the solution had no effect on the removal of lead in the studied range of mole ratio of calcium to lead, from 0 to 4.0. At high values of chloride concentration, $C^{o}(Cl^-)> 0.7$ M, the percentage loss of caprate, increased slightly, due to the formation of $PbCl_2$ precipitate.

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.

5.2 Recommendations

Using sodium caprate, the concentration of lead can be reduced to a minimum value of 5 ± 2 ppm. This value is above the recently imposed limits. To reduce the lead further, saturated straight chain sodium carboxylate with ten or more carbon atoms in the backbone should be tested. As well, carboxylate reagents should be tested for the removal of other heavy metals like Hg, Cd, and Zn.

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Appendix A: Tabulated Experimental Results

Three replicates were run for each experimental point. The 95% confidence interval is given as ±----.

Table A.1 Removal of lead from using sodium caprate. [$C^*(Pb)$=1110±16 ppm, pH°=4.4, $r^\circ(Ca)$= 0, $r^\circ(NO_3)$= 2.0, $r^\circ(Cl)$= 0].

$r^\circ(R_9COO)$	C (Pb) (ppm)	R(Pb)	$C^*(R_9COO)$ (ppm)	$C(R_9COO)$ (ppm)	$L(R_9COO)$
1	523±15	53±1	530±12	2.8±0.7	0.5±0.3
2	5±3	99.5±0.2	1190±8	9.7±0.7	0.8±0.3
2.5	1.0±0.5	99.9±0.1	1325±9	213±6	13±1
3	2.0±0.5	99.8±0.1	1642±8	460±19	25±2
4	1.2±0.5	99.9±0.1	1946±5	970±12	49±1

Table A.2 Removal of lead using sodium oleate. $[r^o(R_{17}COO)= 2.0,$ $pH^o=4.4, r^o(Ca)= 0, r^o(NO_3)= 2.0, r^o(Cl)= 0].$

$C^o(Pb)$ (ppm)	$C^*(Pb)$ (ppm)	$C(Pb)$ (ppm)	$R(Pb)$	$C^*(R_{17}COO)$ (ppm)	$C(R_{17}COO)$ (ppm)	$L(R_1\text{-}COO)$
72.5	47±2	9±3	82±6	100±18	14±7	14±6
1450	985±30	24±4	97.5±0.3	2135±40	53±7	2.5±0.4

Table A.3 Effect of feed lead concentration on the removal using sodium caprate. $[r^o(R_9COO)= 2.0, pH^o= 4.4, r^o(Ca)= 0, r^o(NO_3)= 2.0, r^o(Cl)= 0].$

$C^o(Pb)$ (ppm)	$C^*(Pb)$ (ppm)	$C(Pb)$ (ppm)	$R(Pb)$	$C^*(R_9COO)$ (ppm)	$C(R_9COO)$ (ppm)	$L(R_9COO)$
72.5	47±1	5.2±0.5	89±1	55±6	7±1	11±4
725	485±10	5±2	99.1±0.5	580±5	8±1	1.3±0.8
1450	985±30	5±2	99.5± 0.4	1190±30	7±2	1.0±0.2

Table A.4 Effect of pH° on the removal of lead using sodium caprate. [C*(Pb)= 990±10 ppm, C*(R$_9$COO)= 1190±18 ppm, r°(R$_9$COO)= 2.0, r°(Ca)= 0, r°(Cl)= 0]

pH°	C(Pb) (ppm)	R(Pb)	C(R$_9$COO) (ppm)	L(R$_9$COO)	pH
4.4±0.1	4±3	99.6±0.4	13±5	1.1±0.4	7.2±0.1
2.5±0.1	235±17	76±2	31±5	2.6±0.5	3.4±0.1
2.2±0.1	400±35	59±3	34±7	2.8±0.6	3.3±0.1
2.0±0.1	620±25	37±3	32±7	2.6±0.6	3.2±0.1
1.9±0.1	816±13	17±1	33±8	2.8±0.9	3.2±0.1
1.8±0.1	960±24	3±2	34±5	2.8±0.4	3.0±0.1
1.7±0.1	990±12	0	36±4	3.0±0.4	2.5±0.1

Table A.5 Effect of mole ratio of caprate to lead on the removal of lead from a solution at low pH° using sodium caprate. [C*(Pb)= 990±13 ppm, pH°= 1.8, r°(Ca)= 0, r°(NO$_3$)= 4, r°(Cl)= 0].

r°(R$_9$COO)	C(Pb) (ppm)	R(Pb)	C*(R$_9$COO) (ppm)	C(R$_9$COO) (ppm)	L(R$_9$COO)	pH
2.0	960±22	3±1	1180±20	36±2	3.0±0.1	3.1±0.1
2.5	693±18	30±1	1490±23	39±3	2.6±0.3	3.2±0.1
3.0	426±23	57±2	1793±18	41±4	2.3±0.2	3.4±0.1
3.7	120±20	88±2	2190±22	40±5	1.8±0.2	3.6±0.1
4.0	19±5	98.1±0.5	2360±27	40±10	1.7±0.4	4.1±0.1

Table A.6 Effect of calcium on the removal of lead using sodium caprate. [C^*(Pb)= 970±25 ppm, C^*(R_9COO)= 1180±40 ppm, $r°$(R_9COO)= 2.0, $r°$(Cl)= 0].

$r°$(Ca)	C(Pb) (ppm)	R(Pb)	C(R_9COO) (ppm)	L(R_9COO)
0.50	6±4	99.4±0.4	13±7	1.1±0.5
1.0	4±3	99.6±0.4	13±5	1.1±0.4
2.0	6±5	99.4±0.6	13±5	1.1±0.5
3.0	7±6	99.3±0.6	10±5	0.8±0.4
4.0	6±5	99.4±0.5	13±6	1.2±0.5

Table A.7 Removal of calcium from feed solutions of different concentrations of Ca(NO$_3$)$_2$, using sodium caprate with mole ratio of caprate to calcium in the feed of 2.0.

$C°$(Ca) (ppm)	C^*(Ca) (ppm)	C(Ca) (ppm)	R(Ca)	C^*(R_9COO) (ppm)	C(R_9COO) (ppm)	L(R_9COO)
280	200±14	48±1	75±2	1185±17	150± 4	12.7±0.4
140	100±10	55±10	44±10	600±16	116±2	19.5±0.1

Table A.8 Effect of chloride on the removal of lead using sodium caprate. $[C^*(R_9COO)=1185\pm6$ ppm, $r^\circ(R_9COO)= 1.9$, $r^\circ(Ca)= 0$, $r^\circ(NO_3)= 0]$.

$r^\circ(Cl)$	pH°	$C^*(Pb)$ (ppm)	$C(Pb)$ (ppm)	$R(Pb)$	$C(R_9COO)$ (ppm)	$L(R_9COO)$	pH
2	4.3±0.1	1080±25	60±10	94±1	9±4	1.0±0.8	5.3±0.1
20	4.7±0.1	1080±40	60±16	94±1	19±2	1.4±0.7	5.7±0.1
100	5.1±0.1	1079±6	47±6	95.7±0.5	24±5	2.1±0.8	5.9±0.1
200	5.5±0.1	1075±30	53±5	95.1±0.6	33±7	2.7±0.6	6.2±0.1

Table A.9 Effect of nitrate on the removal of lead using sodium caprate. $[C^*(R_9COO)= 1185\pm16$ ppm, $r^\circ(R_9COO)=1.9$, $r^\circ(Ca)= 0$, $r^\circ(Cl)= 0]$.

$r^\circ(NO_3)$	pH°	$C^*(Pb)$ (ppm)	$C(Pb)$ (ppm)	$R(Pb)$	$C(R_9COO)$ (ppm)	$L(R_9COO)$	pH
2	4.2±0.1	1080±30	60±17	95±0.1	20±12	2±1	5.0±0.1
20	4.5±0.1	1075±14	59±4	94.5±0.4	20±12	2.0±0.9	5.3±0.1
100	4.7±0.1	1080±22	60±10	94±1	22±9	1.9±0.7	5.7±0.1
200	4.8±0.1	1070±25	75±13	93±1	20±4	1.7±0.4	5.9±0.1

Appendix B: Model Derivation

Material Balances:

a. Lead Balance:

At equilibrium, lead in the feed appears as lead caprate precipitate, Pb^{2+}, and $Pb(OH)^+$ in the solution:

$$n_{Pb(NO_3)_2,\ feed} = n_{(R_9COO)_2Pb_{(S)}} + n_{Pb^{2+}} + n_{PbOH^+} \qquad (B.1)$$

Combining equations (4.4) and (4.8) gives

$$[Pb^{2+}] = \frac{K_{SP}[H^+]^2}{K_{spA}^2} \qquad (B.2)$$

For equilibrium solution volume, V:

$$n_{Pb^{2+}} = V \times [Pb^{2+}] \qquad (B.3)$$

Substituting (B.2) into (B.3):

$$n_{Pb^{2+}} = V \times \frac{K_{SP}[H^+]^2}{K_{spA}^2} \qquad (B.4)$$

Combining equations (4.2) and (4.10) gives

$$[PbOH^+] = \frac{K_{SP}K_w[H^+]}{K_1 K_{spA}^2} \qquad (B.5)$$

The moles of lead hydroxide in the solution is

$$n_{PbOH^+} = V \times [PbOH^+] \qquad (B.6)$$

Combining (B.5) and (B.6) yields

$$n_{PbOH^+} = V \times \frac{K_{SP}K_w[H^+]}{K_1 K_{spA}^2} \qquad (B.7)$$

Define:

$$X = n_{(R_9COO)_2 Pb_S} \qquad (B.8)$$

$$Z = [H^+] \qquad (B.9)$$

Substituting (B.6), (B.7), (B.8), and (B.9) into (B.1) gives:

$$n_{Pb(NO_3)_2, \, feed} = X + C_1 Z^2 + C_2 Z \qquad (B.10)$$

where $C_1 = V \times \dfrac{K_{SP}}{K_{spA}^2} = 831.5$ \qquad (B.11)

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$$C_2 = V \times \frac{K_{SP} K_w}{K_1 K_{spA}^2} = 4.9 \times 10^{-5} \tag{B.12}$$

assuming the volumes are additives, i.e., $V = 35 \times 10^{-3} + 15 \times 10^{-3} = 50 \times 10^{-3}$ l

b- Caprate Balance:

At equilibrium, caprate added to the feed appears as lead caprate precipitate, capric acid precipitate, R_9COO^-, and $R_9COOH_{(aq)}$ in the solution:

$$n_{R_9COONa,\ added} = 2n_{(R_9COO)_2 Pb_S} + n_{R_9COOH_S} + n_{R_9COOH_{aq}} + n_{R_9COO^-} \tag{B.13}$$

From equation (4.8):

$$[R_9COO^-] = \frac{K_{spA}}{[H^-]} \tag{B.14}$$

The moles of caprate ion in the solution is

$$n_{R_9COO^-} = V \times [R_9COO^-] \tag{B.15}$$

Combining equations (B.14) and (B.15) gives

$$n_{R_9COO^-} = V \times \frac{K_{spA}}{[H^-]} \tag{B.16}$$

Combining equations (4.6) and (4.8) yields

$$[R_9COOH_{aq}] = \frac{K_{spA}}{K_a} \qquad (B.17)$$

The moles of soluble capric acid in the solution is

$$n_{R_9COOH_{aq}} = V \times [R_9COOH_{aq}] \qquad (B.18)$$

Substituting (B.17) into (B.18) gives

$$n_{R_9COOH_{aq}} = V \times \frac{K_{spA}}{K_a} \qquad (B.19)$$

Define:

$$Y = n_{R_9COOH_S} \qquad (B.20)$$

Substituting (B.8), (B.16), (B.19), and (B.20) into (B.13) gives

$$n_{R_9COONa, \; added} = 2X + Y + C_3 + \frac{C_4}{Z} \qquad (B.21)$$

where $C_3 = V \times \dfrac{K_{spA}}{K_a} = 9.3 \times 10^{-6} \qquad (B.22)$

$$C_4 = V \times K_{spA} = 1.3 \times 10^{-10} \qquad (B.23)$$

Charge Balance:

To attain electroneutrality in the solution, the number of moles of positive ions at equilibrium has to be equal to the number of moles of negative ions at equilibrium:

$$2n_{Pb^{2+}} + n_{Na^+} + n_{H^+} + n_{PbOH^+} = n_{NO_3^-} + n_{R_9COO^-} + n_{OH^-} \qquad (B.24)$$

Considering Na^+, and NO_3^- inert ions (do not contribute to the reactions taking place), the following can be written:

$$n_{Na^+} = n_{R_9COONa, \ added} \qquad (B.25)$$

$$n_{NO_3^-} = 2n_{Pb(NO_3)_2, \ feed} + n_{HNO_3, \ feed} \qquad (B.26)$$

From equation (4.10)

$$[OH^-] = \frac{K_w}{[H^+]} \qquad (B.27)$$

The moles of hydroxide ion in the solution

$$n_{OH^-} = V \times [OH^-] \qquad (B.28)$$

Substituting (B.27) into (B.28) gives:

$$n_{OH^-} = V \times \frac{K_w}{[H^+]} \qquad (B.29)$$

The moles of hydrogen ion in the solution

$$n_{H^+} = V \times [H^+] \qquad (B.30)$$

Substituting (B.4), (B.7), (B.9), (B.16), (B.19), (B.25), (B.26), (B.29), B(30) into (B.24) gives:

$$2C_1 Z^3 + (C_2 + C_5)Z^2 + (n_{R_9COONa,\ added} - 2n_{Pb(NO_3)_2,\ added} - n_{HNO_3,\ added})Z -$$

$$(C_6 + C_4) = 0 \qquad\qquad (B.31)$$

where $C_5 = V = 35 \times 10^{-3}$ $\qquad\qquad$ (B.32)

$\qquad C_6 = V \times K_w = 3.5 \times 10^{-16}$ $\qquad\qquad$ (B.33)

$\qquad C_1$, C_2, and C_4 are defined in equations (B.11), (B.12), and (B.23).

The procedure to solve the material balances and the charge balance equations is as follows:

1- Solve for Z, $[H^+]$, from the charge balance.

2- Knowing Z, solve for X, $n_{(R_9COO)_2Pb_S}$, from material balance on lead.

3- Knowing Z and X, solve for Y, $n_{R_9COOH_S}$, from material balance on caprate.

Appendix C: Determination of the Solubility Product for Lead caprate and Capric acid

a. Solubility product of lead caprate

     The solubility product of lead caprate was determined experimentally by dissolving lead caprate precipitate in distilled water. The equilibrium concentration of lead was measured using the atomic absorption spectrophotometer. All the lead was assumed to be in the form of Pb^{2+}. The equilibrium concentration of caprate was calculated from the measurements of the total carbon using the total carbon analyzer. All the caprate was assumed to be in the form of capric ion, R_9COO^-. The K_{Sp} value of lead caprate was calculated from equation 4.4, and the value reported, $1.1 \pm 0.3 \times 10^{-13}$, shows a 95% confidence interval for three replicates.

b. Solubility product of capric acid

     The solubility product for capric acid was also determined experimentally by dissolving capric acid precipitate in distilled water. The equilibrium hydrogen ion concentration was measured using a Metrohm Brinkmann 691 pH meter (the activity coefficient of hydrogen was assumed to be unity). The equilibrium caprate

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concentration was calculated from the measurements of the total carbon content using the total carbon analyzer. This concentration represents the total solubility of caprate as $R9COO^-$, and $R_9COOH_{(aq)}$. The equilibrium concentration of capric ion, $[R_9COO^-]$, was determined from the K_a equation for capric acid, equation 4.6, as follows:

Defining S_t as the total solubility of caprate calculated from the total carbon content.

$$S_t = [R_9COO^-] + [R_9COOH_{(aq)}]$$ (C.1)

and $X = [R_9COO^-]$ (C.2)

Combining equations (4.6), (C.1), and (C.2), the K_a equation becomes:

$$K_a = \frac{X \times [H^+]}{(S_t - X)} = 1.4 \times 10^{-9}$$ (C.3)

Measuring the equilibrium hydrogen ion concentration, $[H^+]$, with a pH meter, and the total solubility of caprate, S_t, using the total carbon analyzer, the value of X can be calculated from equation (C.3). The solubility product for capric acid, K_{spA}, can be calculated from equation (4.8). The K_{spA} value obtained was $2.6 \pm 0.6 \times 10^{-9}$, with a 95% confidence interval for three replicates.