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Adsorbing Colloid Flotation of Zn(II) with $Fe(OH)_3$ and Polyelectrolytes

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Abstract

It was found that zinc ion could be removed from aqueous solutions by adsorbing colloid flotation with $Fe(OH)_3$ and sodium lauryl sulfate (SLS) provided that the ionic strength of the solution is low (containing no greater than 0.02 *M* $NaNO_3$). An excess dose of iron resulted in poor separation. Three types of polyelectrolytes were used as the activators to compensate for the effect of increasing ionic strength of the solutions. Betz 1150 (a weakly cationic acrylamide copolymer) was found to be the most effective activator. The separation was effective from a solution containing $NaNO_3$ as high as 0.7 *M* when Betz 1150 was used as the activator.

INTRODUCTION

Foam separation techniques has been found to be very effective in removing various heavy metal ions from dilute aqueous solutions. A number of excellent reviews on foam separation are available (*1*–*5*). When dealing with dilute waste, foam separation techniques appear to possess some distinct advantages: low residual metal concentrations, rapid operation, low space requirements (important where land costs are high), flexibility of application to various metals at various scales, production of small volumes of sludge highly enriched with the contaminant, and moderate cost. However, there is one distinct disadvantage of foam separation: the separation efficiency decreases with

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increasing inert salt concentration of the solution (*6–11*). We have shown that the effect of increasing inert salt concentration on the separation efficiency of adsorbing colloid flotation with $Fe(OH)_3$ as the adsorbing floc can be compensated to quite a large extent with the aid of activators [such as Al(III), Zn(II), and Mg(II) ions] (*8–12*).

Foam separation of Zn(II) has been developed by a number of investigators. These were recently reviewed by Clarke and Wilson (*2*). Rubin and Lapp (*13*) studied the foam fractionation and precipitate flotation of Zn(II) with sodium lauryl sulfate (SLS). Pearson and Shirley (*14*) used a diamine diacetate to float zinc hydroxide from industrial wastes. Mukai et al. (*15*) floated zinc with ferric hydroxide, sodium oleate, and pine oil. Robertson et al. (*16*) investigated the adsorbing colloid flotation of 50 ppm Zn(II) with ferric or aluminum hydroxide and SLS. 200 ppm of Fe(III) or 100 ppm of Al(III) was used to yield the floc. They found that ferric hydroxide was not effective in removing zinc from the solution: the surface potential of ferric hydroxide is negative at pH's high enough to give zinc a low solubility; at a pH of 7.5 the iron was incompletely removed. Aluminum hydroxide was effective at pH's in the 8.0–8.6 range. Effective separation with residual zinc levels less than 1.0 ppm was achieved from solutions containing 0–0.4 *M* $NaNO_3$. Pilot-plant studies (*17*) also reveal that the efficiency of $Al(OH)_3$ for Zn(II) removal is substantially higher than that of $Fe(OH)_3$ with effluent pH at the 7.0 to 7.3 range. Currin et al. (*18*) found that zinc was effectively removed in mixtures with lead and copper by flotation with ferric hydroxide and SLS. We reported recently that zinc was effectively removed in mixtures with chromium and copper or in mixtures with chromium, copper, and nickel with ferric hydroxide and SLS (*19*).

Synthetic organic polyelectrolytes have been extensively used in wastewater treatment (*20*). They are used as a coagulation aid for gravity-type clarification and thickening, and for sludge dewatering. They are also used in the flotation process to incrase the particle size so that bubble–solid attachment can occur, to increase the volume of the air–solid agglomerate which will result in a faster separation rate, and to increase the solid particle density to produce a sludge of higher consistency (*20*).

Ore flotation sometimes involves the use of polyelectrolytes along with a surfactant (*21–26*). Usoni et al. (*23*) showed that polymers can enhance or depress flotation depending on the nature, concentration, and duration of contact of the polymers with the mineral. Somasundaran and Lee examined the role of polymer–surfactant interactions on the flotation of quartz by using both anionic and cationic polymers and surfactants;

the possible mechanisms by which flotation was affected by the polymers were discussed (*27*).

Sasaki et al. reported a series of studies of ion flotation of cations and anions with polyelectrolytes (*28–30*). In the case of ion flotation of Fe(III) and Cu(II), they remarked that the metallic ions removed by this process were presumably in the state of large metallic hydroxide aggregates carrying a few residual positive charges (*30*).

We recently reported that the separation efficiency of floc foam flotation of C(VI) with Fe(II) from aqueous solutions with high ionic strength can be improved by adding a very small amount of polyelectrolytes (either strongly cationic Betz 1160 or weakly anionic Betz 1100) as the activators (*31*). In this paper we report that Zn(II) can be effectively removed from aqueous solutions (50 ppm of zinc initially) by adsorbing colloid flotation with $Fe(OH)_3$ and SLS, provided that the ionic strength of the solution is low (no greater than 0.02 *M* $NaNO_3$). An excess dose of iron results in poor separation. The separation is effective from solution containing $NaNO_3$ as high as 0.7 *M* if Betz 1150 (a weakly cationic acrylamide copolymer) is used as the activator. Betz 1150 is found to be a more effective activator than Betz 1160 or Betz 1100 which were used as the activators in our previous report (*31*).

EXPERIMENTAL

The foam flotation system used was similar to that described in earlier reports (*8*, *11*, *12*). Figure 1 depicts the apparatus used for the batch separations. A soft glass column 90 cm in length with an inside diameter of 3.5 cm was used for the flotation. There was a side arm with a rubber septum near the bottom to inject the collector. The bottom of the column was closed with a rubber stopper with holes for a gas sparger and a stopcock to take samples and to drain the column. The gas sparger was a commercially available gas dispersion tube. A lipped side arm near the top of the column served as a foam outlet.

Compressed air was generated from an air pump, and the gas flow was adjusted with a Hoke needle valve with micrometer control and measured with a soap film flowmeter. The air was purified by passing it through glass wool to remove particulates, Ascarite to remove carbon dioxide, and distilled water for controlled rehumidification.

Laboratory grade sodium lauryl sulfate (SLS) was used as the collector and frother without further purification. The polyelectrolytes used were from Betz (practical grade): Betz 1100 is a weakly anionic acrylamide

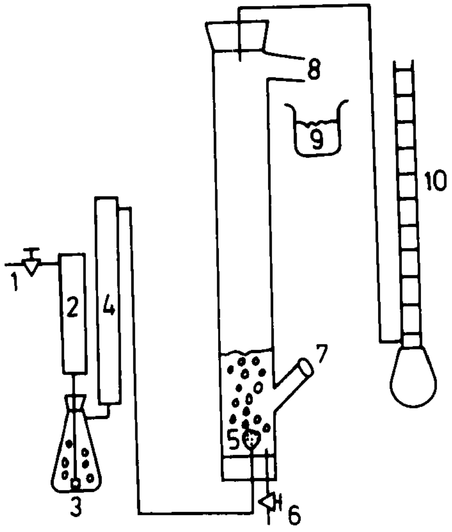

FIG. 1. The apparatus for foam separation. (1) Air needle valve, (2) Ascarite tube for CO_2 removal, (3) humidifier, (4) glass wool column, (5) fritted glass sparger, (6) drain, (7) reagent syringe, (8) foam discharge port, (9) discharged foam, (10) soap film flowmeter.

copolymer, Betz 1160 is a strongly cationic acrylamide copolymer, and Betz 1150 is a weakly cationic acrylamide copolymer. All of them are in powder form. 100 ppm polyelectrolyte stock solutions were prepared by adding 0.1 g polyelectrolyte slowly into 1000 mL distilled water with rapid stirring. The stock solution was prepared fresh each week. Reagent grade $Zn(NO_3)\cdot 4H_2O$, $Fe(NO_3)_3\cdot 9H_2O$. $NaNO_3$, and NaOH were used for sample preparation. The effect of ionic strength variation was studied by adding $NaNO_3$ solution. The air flow rate was maintained at 90 mL/min. All experiments were run using 250 mL solution. The initial concentration of Zn(II) was 50 ppm. After adding SLS, the solution was stirred for 5 mins before flotation. The SLS dose was 80 ppm for all the runs.

The duration of the runs was 10 minutes (although floc separations were complete in 5 mins for many runs). The average values and standard deviations are given for the duplicate runs.

pH measurements were made with a Radiometer PHM63 digital pH meter. Concentrations of zinc were measured with a Perkin-Elmer 5000 atomic spectrophotometer.

RESULTS AND DISCUSSION

The effect of Fe(III) dose and pH on the adsorbing colloid flotation of Zn(II) is shown in Table 1. The table shows that zinc can be effectively removed from the solution by using a 50 mg/L iron dose at pH 8.5. An excess dose of iron results in poor separation, presumably due to a decrease in the surface potential of the floc (mixture of $Fe(OH)_3$ and $Zn(OH)_2$) with an increasing the portion of $Fe(OH)_3$ of the floc. It is probable that Robertson et al. (*16*) could not remove iron effectively from the solution at pH 7.5 because they used a high dose of iron (200 mg/L). The effect of ionic strength variation (adjusted by adding $NaNO_3$ solution) and pH on the separation efficiency is shown in Table 2. The separation efficiency decreases with increasing ionic strength, as expected. Effective separation with residual zinc levels lower than 1.0 ppm was achieved provided that the concentration of $NaNO_3$ in the solution was no greater than 0.02 *M*. The separation of zinc was very poor from the 0.1 *M* $NaNO_3$ solution. Note that Robertson et al. (*16*) showed that zinc can be removed effectively from solutions containing 0–0.4 *M* $NaNO_3$ if $Al(OH)_3$ is used as the adsorbing floc.

The effect of adding polyelectrolytes to the 0.1 *M* $NaNO_3$ solution at pH 8.0 is shown in Table 3. The polyelectrolyte was added to the acidic solution before adding base. The separation was not improved by adding either Betz 1100 or Betz 1160, and improved only a little bit by adding Betz 1150. The separation of zinc from a solution containing 0.07 *M* $NaNO_3$ at pH 8.5 is shown in Table 4. The separation was improved somewhat with the addition of 0.5–2.0 ppm of any one of the polyelectrolytes; while the best separation efficiency was achieved with the

TABLE 1
Effect of pH and Iron Dose on Separation

pH	Fe(III) (ppm)	Residual Zn (ppm)
7.5	50	>10
8.0	50	1.5
8.5	50	0.04
8.5	100	0.07
8.5	200	3.00

TABLE 2
Effect of pH and Ionic Strength on Separation[a]

pH	Residual Zn (ppm) NaNO$_3$ (*M*): 0.00	0.02	0.04	0.06	0.07	0.08	0.10
8.0	1.5	5.4	5.5 ± 0.6	—	—	5.5	6.0 ± 1.5
8.5	0.04 ± 0.02	0.7	1.1	1.6	4.2 ± 1.0	7.9	>10
9.0	—	—	5.3	—	—	>10	>10

[a] Fe(III) = 50 ppm.

TABLE 3
Effect of Polymer on Separation from 0.1 *M* NaNO$_3$ Solution[a]

Polymer type (Betz)	Residual Zn (ppm) Polymer dose: 0.0	0.1	0.5	1.0	2.0	5.0	10.0
1100	6.0 ± 1.5	6.5	7.4	7.5	>10	>10	>10
1160	6.0 ± 1.5	5.5	5.3	5.2	6.6	>10	>10
1150	6.0 ± 1.5	—	5.3 ± 0.9	—	4.5 ± 1.2	—	4.10 ± 0.04

[a] Initial Zn(II) = 50 ppm, Fe(III) = 50 ppm, pH = 8.0, polymer was added before adding base.

TABLE 4
Effect of Polymer on Separation from 0.07 *M* NaNO$_3$ Solution[a]

Polymer type (Betz)	Residual Zn (ppm) Polymer dose: 0.0	0.5	2.0	5.0	10.0
1100	4.2	2.7	3.5	6.3	>10
1160	4.2	4.0	1.8	7.4	>10
1150	4.2	4.5	1.0	1.2	1.4

[a] Initial Zn(II) = 50 ppm, Fe(III) = 50 ppm, pH = 8.5, polymer was added before adding base.

addition of Betz 1150. The reason for the improvement in the separation of zinc by floc foam flotation with the addition of Betz 1100 is proposed to be as follows: The surface potentials of each floc are different; some of the floc may have a net negative charge on the surface even though the average surface potential of the floc is positive (this is especially true when the average surface potential of the floc is low). During the flotation process, the positively charged floc is floated with the anionic surfactant, while the negatively charged (or less positively charged) floc remains in solution. With the addition of Betz 1100, the negatively charged floc (or less positively charged floc) may be coagulated with other positively charged floc by the mechanism of crosslinking (bridging) by the polyelectrolyte; the coagulated floc is then carried out from the solution by flotation and results in better separation efficiency. Furthermore, Betz 1100 is a weakly anionic organic polymer; the hydrophobic part of the polymer may increase the surface activity of the floc and improve its floatability when the polymer is adsorbed onto the floc. The addition of a large excess of Betz 1100 results in poor separation, presumably due to a decrease of the surface potential of the floc by adsorption of the anionic polyelectrolyte, and therefore the affinity for anionic surfactant adsorption on the floc surface is decreased. Coagulation of the floc by the addition of Betz 1100 may also result in poor separation if the floc is too heavy.

The reason for the improvement in separation with the addition of Betz 1160 and Betz 1150 is presumably due to an increase in the surface potential of the floc by the adsorption of the cationic polyelectrolytes, such that the affinity for anionic surfactant adsorption onto the floc is increased. The addition of a large excess (10 ppm) of Betz 1160 results in poor separation, presumably due to extention of part of the strongly ionic polymer chain into the aqueous solution (part of the polymer chain is adsorbed on the floc) such that the floc surface becomes more hydrophilic and less floatable. The increased size of the floc may also cause the floc to be less floatable if the floc is too heavy. The best separation efficiency was achieved with the addition of Betz 1150, the weakly cationic polyelectrolyte. The reason that Betz 1150 is a better activator than Betz 1160 is presumably because Betz 1150 is not as hydrophilic as Betz 1160, as is evident by the effective separation that can be achieved by adding as much as 10 ppm Betz 1150.

More data about the effect of ionic strength variation and the effect of adding polyelectrolytes on separation efficiency are shown in Tables 5 and 6. Betz 1150 was found to be the most effective activator among these three polyelectrolytes. Effective separation with a residual zinc level of 1.3

TABLE 5
Effect of Polymer and Ionic Strength on Separation[a]

Polymer type (Betz)	Polymer dose (ppm)	Residual Zn (ppm)		
		$NaNO_3$ (*M*): 0.07	0.10	0.15
—	0.0	4.2	>10	—
1100	0.5	2.7	7.8	
1100	2.0	3.5	8.2	
1160	0.5	3.4	>10	
1160	2.0	1.8	>10	
1150	0.5	1.2	4.9	>10
1150	2.0	1.0	1.8	6.3

[a] Fe(III) = 50 ppm, pH = 8.5, polymer was added before adding base.

TABLE 6
Effect of Betz 1150 Dose and Ionic Strength on Separation[a]

Betz 1150 dose (ppm)	Residual Zn (ppm)					
	$NaNO_3$ (*M*): 0.07	0.10	0.15	0.20	0.25	0.30
0.0	4.2	>10	—	—	—	—
2.0	1.0	1.8	6.3	>10	—	—
5.0	1.2	1.5	1.1	>10	—	—
10.0	—	1.1	—	1.3	5.0	>10

[a] Fe(III) = 50 ppm, pH = 8.5, polymer was added before adding base.

ppm was achieved from a solution containing 0.2 *M* $NaNO_3$ when 10 mg/L Betz 1150 was added before the addition of base.

Note that all the rsults shown in Tables 3–6 were obtained by adding polyelectrolyte before adding base [Zn(II) + Fe(III) + polyelectrolyte + OH^- + SLS]. The results for runs when the polyelectrolyte was added after the addition of base [Zn(II) + Fe(III) + OH^- + polymer + SLS] are shown in Table 7. The separations were not improved by adding either Betz 1100 or Betz 1160. However, the separation was significantly improved by adding Betz 1150. The amount of Betz 1150 required to improve separation is less if it was added after the addition of base as compared to when it was added before the addition of base. This is

TABLE 7

Effect of Polymer and Ionic Strength on Separation[a]

Polymer type (Betz)	Polymer dose (ppm)	Residual Zn (ppm)							
		NaNO$_3$ (*M*): 0.1	0.2	0.3	0.4	0.5	0.7	0.8	0.9
—	0	>10	—	—	—	—	—	—	—
1100	2	>10	>10	—	—	>10	—	—	—
1100	10	>10	>10	—	—	>10	—	—	—
1160	2	>10	>10	—	—	>10	—	—	—
1160	10	>10	>10	—	—	>10	—	—	—
1150	2	0.7	0.7	0.8	3.3	>10			
1150	10	0.4	0.7	—	—	1.0	0.9	1.5	5.4

[a] Fe(III) = 50 ppm, pH = 8.5, polymer was added after adding base.

probably due to better crosslinking being achieved by adding Betz 1150 after formation of the floc. Effective separation with residual zinc levels of less than 1.0 ppm can be achieved from a solution containing $NaNO_3$ as high as 0.7 *M* if 10 mg/L Betz 1150 is used as the activator.

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