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Effect of Al(III) as an Activator for Adsorbing Colloid Flotation

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Abstract

The effect of Al(III) on adsorbing colloid flotation using $\text{Fe}(\text{OH})_3$ as the coprecipitant and sodium lauryl sulfate as the collector was studied, and the results of foam separation were compared with the zeta potential of the floc before and after Al(III) being added to the solution. It was found that when Al(III) is used as an activator, the zeta potential of the floc is more positive, which presumably gives the floc a stronger affinity for anionic surfactant adsorption, resulting in better separation efficiency. The working range of pH for an effective separation is extended and good separation efficiency can be achieved at pH values closer to neutral with the aid of Al(III). Furthermore, the separation efficiency is significantly improved for solutions containing interfering ions, such as sulfate, by using Al(III) as an activator.

INTRODUCTION

Numerous techniques exist to remove metal ions from aqueous solutions. The most common method is chemical precipitation (often with lime or NaOH). This may be rather costly; requires relatively large amounts of space for the clarifier; often produces a very wet, bulky sludge; and usually requires final filters for polishing if very low residual levels of metals are desired. Other available technologies include ion exchange, reverse osmosis, adsorption on active carbon, and solvent extraction. These methods are usually relatively expensive, involving either elaborate and costly equip-

ment or high operating costs and energy requirements. Ultimate disposal of the contaminant(s) may also be a problem with some of these techniques.

Foam separation processes have been utilized to separate or concentrate a variety of constituents from dilute aqueous solution. A number of excellent reviews on foam separation are available (1–5). These techniques are based on the fact that surface-active material tends to concentrate at the gas–liquid interface. On bubbling the air through the solution, one adsorbs the surface-active material at the surface of the rising bubble, which then separates it from the solution. The substance to be removed, if not surface active, can be made surface active through union with or adsorption of a surface-active material. For instance, adsorbing colloid flotation involves the addition of a coagulant (alum or ferric chloride) to produce a floc. The dissolved metal is adsorbed onto the floc particle and/or coprecipitated with it. A surfactant, usually a relatively cheap anionic surfactant (such as sodium lauryl sulfate), is then added, adsorbs onto the floc particle, and renders it hydrophobic, and the floc (with adsorbed metal) is removed by air flotation.

When dealing with dilute waste, foam flotation appears 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. The chemical costs and capital costs of wastewater treatment by adsorbing colloid flotation have been recently estimated and compared with those of lime precipitation (6–8). For instance, estimated costs (capital cost plus chemical costs) for lead removal from dilute wastewater by adsorbing colloid flotation were \$0.75/1000 gal, while the corresponding costs by lime precipitation were \$1.47/1000 gal. Economics appear to favor adsorbing colloid flotation by a substantial margin (7, 8).

Both Fe(III) and Al(III), as the coagulant for metals removal by adsorbing colloid flotation, have been used by us (9–11) and other investigators (12, 13, 16–21) for some time. Development of a successful separation depends highly on the complete coprecipitation of the contaminant metal ions with the floc, and on sufficient adsorption of the surfactant (usually an anionic surfactant) on the floc to render the surface of the floc hydrophobic. The pH of the solution should be adjusted to a value high enough to get essentially complete coprecipitation of the contaminant metal ions with the floc. However, if the pH value is adjusted to too high a value, the surface of the floc will be negatively charged, which prevents the adsorption of the anionic surfactant. (The attractive force between the anionic surfactant and the hydroxide floc is presumably due in large part to coulombic interactions.) Therefore, the pH of the solution requires careful

control within a certain range for an effective separation. The adsorption of the surfactant on the floc may also be affected by various interfering ions in the solution. Doubly charged anions, such as sulfate ion, have been found to decrease the efficiency of the separation to a greater extent than singly charged anions (such as Cl^- and NO_3^-) do (7, 9, 11).

We have reported that the separation efficiency of the adsorbing colloid flotation of chromium(VI) and tin(II), using $\text{Fe}(\text{OH})_3$ as the adsorbing floc, can be improved by adding a certain amount of Al(III) as an activator (9, 11). Here we demonstrate the effect of Al(III) on adsorbing colloid flotation by giving a couple of examples of foam flotation and correlating the results of foam flotation with zeta potential measurements of the floc before and after the addition of Al(III). It was found that when Al(III) is used as the activator, the zeta potential of the floc is more positive, which presumably gives the floc a stronger affinity for anionic surfactant adsorption, thereby resulting in better separation efficiency. The working range of pH values yielding effective separation is extended and good separations can be achieved at pH values closer to neutral with the aid of Al(III). Furthermore, the separation efficiency is significantly improved for solutions containing sulfate ion by using Al(III) as an activator.

EXPERIMENTAL

The foam flotation system used was similar to that described earlier (9). 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. The air flow rate 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, through Ascarite to remove carbon dioxide, and through distilled water for controlled rehumidification.

Laboratory grade sodium lauryl sulfate (NLS) was used as the collector and frother without further purification. Reagent grade $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, SnCl_2 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Na_2SO_4 were used for sample preparation. The air flow rate was maintained at 80 mL/min. All experiments were run using 250 mL of solution.

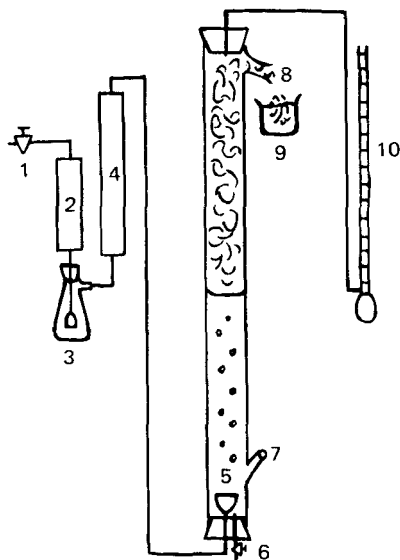


FIG. 1. The apparatus for foam separation. (1) Air needle valve, (2) ascarite tube for CO_2 removal, (3) humidifier, (4) glass wool column, (5) fritted glass sparger, (6) drain, (7) reagent syringe, (8) foam discharge port, (9) discharged foam, (10) soap film flowmeter.

The pH measurements were made with a Radiometer PHM63 digital pH meter. Concentrations of iron, cobalt, tin, and chromium were measured with two Perkin-Elmer 5000 and 303 atomic absorption spectrophotometers. Hexavalent chromium was also determined by the formation of the red-purple colored complex with diphenyl-carbazide in weak acid; the absorbance at $540 \text{ m}\mu$ was measured and compared with standards (14).

Zeta potentials of particles were measured with a Zeta Meter (Zeta-Meter, Inc.) consisting of a cell across which a potential can be applied which will cause the charged particles to move. The time needed for a colloid particle to pass across a certain distance was measured. Ten to 20 particles were tracked. The timer did not reset after each particle was tracked. Instead, the time was accumulated. The average tracking time was calculated by dividing the total time by the number of colloid particles tracked. The average velocity of the particles is calculated at a known applied voltage to determine the zeta potential. A graph prepared from the Helmholtz-Smoluchowski formula was used to determine the zeta potential (15). The marks (\circ , \times , etc.) on the figures represent the zeta potential of the floc as actually measured under various conditions.

RESULTS AND DISCUSSIONS

The zeta potentials of the floc produced by 50 ppm Fe(III) at various pHs are shown in Fig. 2. The effect of Al(III) on zeta potential is also shown in the same figure. The point of zero charge of the iron floc is 7.3. When 10 ppm of Al(III) is added, the point of zero charge (PZC) shifts to 8.8. This is partly due to the floc containing some amount of Fe(OH)₃ with PZC at pH 7.3 and some amount of Al(OH)₃ with PZC at pH about 9. The extensive compilation of data on the PZC and surface charge of oxides and hydroxides in aqueous solution can be found in the excellent reviews by Parks (22, 23). The zeta potential of the floc is generally significantly increased by the addition of Al(III). Note that the coprecipitation of metal ions with the ferric hydroxide floc is usually more complete at higher pH values. Thus, one can carry out adsorbing colloid flotation at higher pH values and get more complete separation by using Al(III) as an activator,

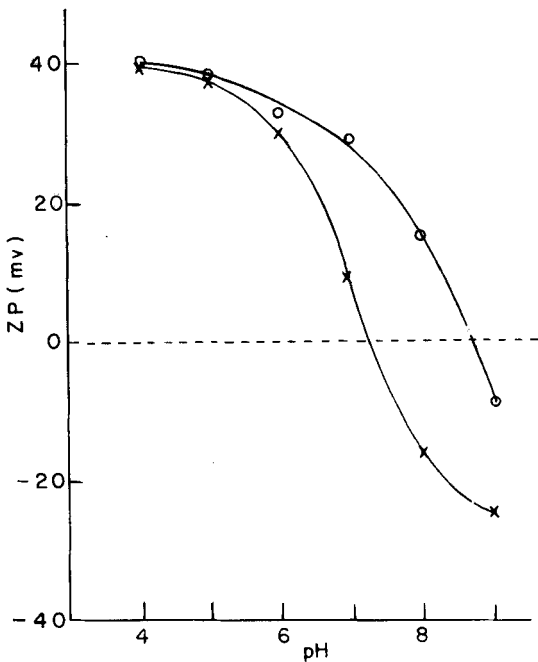


FIG. 2. Zeta potential of Fe(OH)₃ floc. Fe(III) = 50 ppm, (x) without Al(III), (o) with 10 ppm Al(III).

which causes the zeta potential of the floc to be sufficiently positive for anionic surfactant adsorption even at more alkaline pHs. Furthermore, the efficiency of adsorbing colloid flotation decreases with increasing ionic strength (9–11); presumably this is due to the decrease of zeta potential caused by the interfering ions. This effect might be compensated somewhat by using Al(III) as an activator.

We have shown that chromium (VI) can be removed from aqueous solution by adsorbing colloid flotation with $\text{Fe}(\text{OH})_3$ as the adsorbing colloid and coprecipitant and with sodium lauryl sulfate (NLS) as the collector (9, 10). The separation is very poor from solutions containing 0.01 M Na_2SO_4 . However, when a small amount of Al(III) is added, 98% of the chromium (VI) can be removed by a two-stage flotation. The effect of Al(III) and sulfate ion on the zeta potential of Cr(VI)– $\text{Fe}(\text{OH})_3$ floc is shown in Fig. 3. The zeta potential of the floc is decreased by introducing sulfate ion and increased by introducing Al(III). The zeta potential of the floc is negative in the solution containing 0.01 M Na_2SO_4 and positive in the solution which contains the same amount of sulfate ion and a small amount of Al(III). This supports our previous conjecture that the improvement of Cr(VI)– $\text{Fe}(\text{OH})_3$ floc removal from sulfate solution by adding Al(III) is due to the increase of the zeta potential of the floc by those Al(III) species. We note that when aluminum hydroxide is used as the adsorbing colloid flotation for Cr(VI) removal (no iron being added), the floc of Cr(VI)–

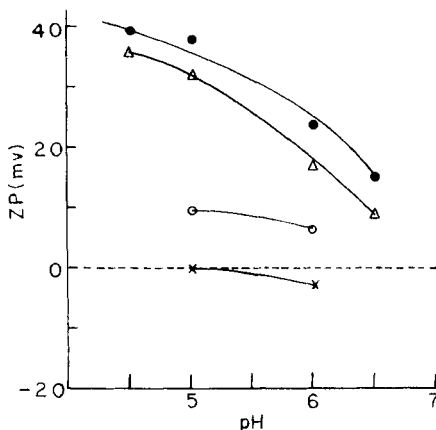


FIG. 3. Zeta potential of Cr(VI)– $\text{Fe}(\text{OH})_3$ floc. Cr(VI) = 50 ppm, Fe(III) = 750 ppm. (×) 0.01 M Na_2SO_4 without Al(III), (○) 0.01 M Na_2SO_4 with 50 ppm Al(III), (Δ) without Na_2SO_4 and Al(III), (●) without Na_2SO_4 with 10 ppm Al(III).

$\text{Al}(\text{OH})_3$ cannot be separated from the solution containing 0.001 M Na_2SO_4 by foam flotation.

Chromium (VI) can also be separated from aqueous solution by reducing chromium (VI) with ferrous ion. The floc (mixture of $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$) was then removed from the solution by foam flotation using NLS as the collector (9, 10). The separation of the floc by foam flotation was incomplete from the solution containing 0.02 M Na_2SO_4 . Good separation of the floc from the above solution was achieved by adding a certain amount of Al(III) to the solution. The effects of pH, sulfate ion, and Al(III) on the zeta potential of the $\text{Cr}(\text{OH})_3$ - $\text{Fe}(\text{OH})_3$ floc are shown in Fig. 4. The zeta potential of the floc decreases with increasing sulfate concentration and pH. The zeta potential of the floc is zero to negative (pH 5.0 to 5.5) in

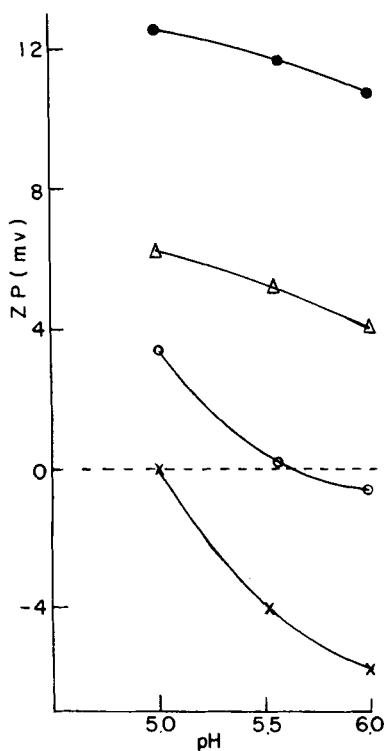


FIG. 4. Zeta potential of $\text{Cr}(\text{OH})_3$ - $\text{Fe}(\text{OH})_3$ floc. Initial $\text{Fe}(\text{II}) = 175$ ppm, initial $\text{Cr}(\text{VI}) = 50$ ppm, (x) 0.02 M Na_2SO_4 without Al(III), (o) 0.02 M Na_2SO_4 with 60 ppm Al(III), (Δ) 0.001 M Na_2SO_4 without Al(III), (\bullet) 0.001 M Na_2SO_4 with 60 ppm Al(III).

the 0.02 *M* Na₂SO₄ solution; it becomes positive on the addition of Al(III).

The details of the adsorbing colloid flotation of Sn(II) with Fe(OH)₃ and NLS were described in our recent report (11). The data directly related to our interest here are listed in Table 1. The separation of the floc by foam flotation was incomplete from the solution containing 0.1 *M* Na₂SO₄. The decrease in separation efficiency by the influence of sulfate ion can be compensated somewhat by the treatment of the floc with Al(III). Good separation was achieved from the solution containing as much as 0.025 *M* Na₂SO₄ if Al(III) was added. Figure 5 shows the effect of sulfate ion and Al(III) on the zeta potential of the floc. The zeta potential of the floc is negative for solutions containing more than 0.01 *M* Na₂SO₄. When Al(III) was added to the solutions, the zeta potentials of the flocs were positive for the solutions containing less than 0.025 *M* Na₂SO₄. The effect of sulfate ion and Al(III) on the foam separation of the floc can be well explained by their effect on the zeta potential of the floc.

Results of the precipitate flotation of Co(OH)₂ and the adsorbing colloid flotation of Co(II) with Fe(III) and/or Al(III) are shown in Table 2. The zeta potentials of the flocs produced by 50 ppm Co(II) and 20 ppm Fe(III) at various pHs and various amounts of Al(III) are shown in Fig. 6. The floc is primarily a mixed metal hydroxide which bears a charge dependent on the relative amount of each metal hydroxide. The initial concentration of Co(II) was 50 ppm for all runs. The solubilities of Co(II) at various pHs were tested by filtering the floc of Co(OH)₂ through a Whatman #2 filter paper, and the Co(II) concentrations in the filtrates were measured. The Co(II) concentrations of the filtrates are listed in the top line in Table 2. The

TABLE 1
Adsorbing Colloid Flotation of Sn(II) with Fe(OH)₃, Al(III), and NLS^a

Na ₂ SO ₄ (<i>M</i>)	Fe(III) (ppm)	Al(III) (ppm)	pH	Residual tin (ppm)
0	100	0	5.0	0.6
0.010	100	0	5.0	>10
0.010	200	0	4.5	5.5
0.025	200	0	4.5	>10
0.010	100	30	5.5	0.5
0.025	100	30	5.5	0.7
0.050	100	40	5.5	>10

^aAll runs made with 50 ppm Sn(II) initially; duration of run = 10 min.

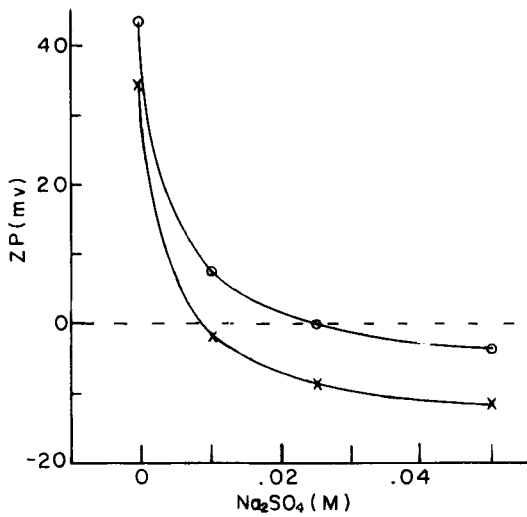


FIG. 5. Zeta potential of Sn(II)–Fe(OH)₃ floc. Sn(II) = 50 ppm, Fe(III) = 100 ppm, (×) without Al(III), pH = 4.5; (O) with 30 ppm Al(III), pH = 5.5.

TABLE 2
Adsorbing Colloid Flotation of Co(II) with Fe(OH)₃, Al(OH)₃, and NLS^a

Fe(III) (ppm)	Al(III) (ppm)	pH	7	8	9	10	11	12
		Residual Co(II) (ppm)						
0	0	—	>10 ^b	5.3 ^b	0.5 ^b	0.5 ^b	0.4 ^b	
0	0	—	>10	1.6	0.8	0.1	7.0	
0	100	—	>10	>10	0.1	0.3	1.1	
20	0	>10	>10	1.8	0.3	0.3	>10	
100	0	>10	3	0.6	0.4	2.4	—	
20	10	>5	0.5	0.4	0.6	0.6	>10	

^aAll runs made with 50 ppm Co(II) initially, duration of run = 10 min.

^bResidual Co(II) in the filtrate.

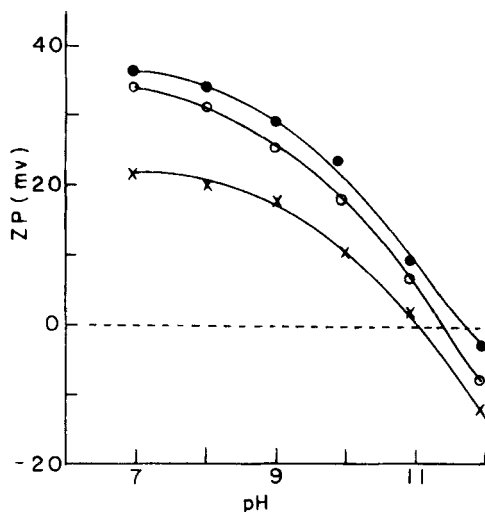


FIG. 6. Zeta potential of $\text{Co(OH)}_2\text{-Fe(OH)}_3$ floc. $\text{Co(II)} = 50$ ppm, $\text{Fe(III)} = 20$ ppm, (x) without Al(III) , (○) $\text{Al(III)} = 5$ ppm, (●) $\text{Al(III)} = 10$ ppm.

Co(II) concentration at pH 8 or 9 were rather high, presumably due to the high solubility of Co(OH)_2 . Precipitate flotation of Co(OH)_2 was very effective at pH 10 or 11, and was poor at either higher or lower pH. Using Al(OH)_3 as the coprecipitant didn't improve the separation at pH 9 or 8. Using Fe(OH)_3 as the coprecipitant improved the separation at pH 9. When both Fe(III) and Al(III) were added to the Co(II) solution, good separation was achieved even at pH 8, presumably due to the more complete coprecipitation of Co(II) with the mixed floc of Fe(OH)_3 and Al(OH)_3 than that with either Fe(OH)_3 or Al(OH)_3 alone. Al(III) not only increases the zeta potential of the floc, which presumably increases the affinity of the floc for anionic surfactant adsorption, it also enhances the coprecipitation of Co(II) ion with the floc, such that the flotation can be run over a wider pH range.

The effect of sulfate ion on the adsorbing colloid flotation of Co(II) is shown in Table 3. The separation of Co(II) from the solution containing 0.3 M Na_2SO_4 by adsorbing colloid flotation with either Fe(OH)_3 or Al(OH)_3 is incomplete. However, if both Fe(III) and Al(III) were used, good separation was achieved from the solution containing Na_2SO_4 at concentrations as high as 0.5 M.

TABLE 3
Effect of Sulfate on Adsorbing Colloid Flotation of Co(II)^a

Na ₂ SO ₄ (M)	Fe(III) (ppm)	Al(III) (ppm)	pH ^b	Residual cobalt (ppm)
0.3	0	0	—	>10
0.3	20	0	10.5	2
0.3	0	50	—	>10
0.3	30	10	9.0	0.3
0.5	30	10	9.0	0.9

^aAll runs made with 50 ppm Co(II) initially, duration of run = 10 min.

^bOptimum pH for separation.

CONCLUSION

Fe(III) has been used extensively in adsorbing colloid flotation for metal ions removal from aqueous solutions. An anionic surfactant, such as NLS, is usually used as the collector. Note that some of the works by Zeitlin et al. (18), Wilson et al. (2, 24), and Huang et al. (9) indicate that actual coprecipitation is an important mechanism in the scavenging of an ion from solution by ferric hydroxide floc. For systems which must be run under acidic conditions in order to make the surface of the floc positively charged for anionic surfactant adsorption, good separation can probably be achieved at higher pHs by the treatment of the floc with Al(III), presumably due to an increase of the zeta potential of the floc by the adsorption of Al(III) species ($\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^{2+}$, Al^{3+}) and by incorporation of $\text{Al}(\text{OH})_3$ into the floc. On the other hand, for systems which must be run under basic conditions in order to get more complete coprecipitation of the metal ions with the floc, good separation can probably be achieved at lower pH with the aid of Al(III), presumably due to the improvement of coprecipitation and/or due to create a larger surface area for adsorption or coprecipitation. Generally a wider pH range can be used, which reduces the difficulty and the costs of pH control during the run. Since the flotation can be run at pH conditions closer to neutral, the effluent may be discharged without further pH adjustment.

Adsorbing colloid flotation becomes less effective with increasing inert salt concentration of the solution, presumably due to the decrease of the zeta potential of the floc at higher ionic strength. This problem can be compensated for in many cases by using Al(III) to increase the zeta potential of the floc.

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