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The Adsorbing Colloid Flotation of Lead(II) and Zinc(II) by Hydroxides

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Abstract

The effects of pH, ionic strength, and specific ions on the adsorbing colloid flotation of lead(II) and zinc(II) with $Al(OH)_3$ and $Fe(OH)_3$ with sodium lauryl sulfate (NLS) as collector are reported. Floc foam flotation of lead with $Fe(OH)_3$ and gelatin, with MnO_2 and NLS, and with $CaCO_3$ and NLS or hexadecyltrimethylammonium bromide was studied. Lead is efficiently removed with $Fe(OH)_3$ and NLS; zinc with $Al(OH)_3$ and NLS. A theoretical study was made of the effect of the charges of ions present as inert electrolyte; separations decrease in efficiency with increasing charge at constant ionic strength.

INTRODUCTION

A number of excellent reviews on foam flotation are available (*1–3*). Experimental papers of particular relevance to the present work include the studies of Rubin and his co-workers on lead(II) (*4*) and zinc(II) (*5*), Kim and Zeitlin's extensive work on the use of adsorbing colloid flotation to remove trace metals from seawater (*6–8*) and our previous work on the separation of lead(II) and cadmium(II) by precipitate or adsorbing colloid flotation of sulfides (*9*). The theoretical work presented here is built upon our earlier applications of the Gouy-Chapman model of the double layer to precipitate and adsorbing colloid flotation (*10–14*). The problems involved in the removal of trace toxic metals from industrial wastes are discussed in a recent EPA report (*15*).

We report here experimental results on batch floc foam flotation of lead(II) and zinc(II) with aluminum and ferric hydroxides, with sodium lauryl sulfate (NLS) as collector. Dependence of the separations on pH and ionic strength was studied in some detail, and specific ion effects on the separation of zinc(II) with $Al(OH)_3$ were investigated. Lead removals with $CaCO_3$ and NLS or hexadecyltrimethylammonium bromide (HTA), with $Fe(OH)_3$ and gelatin, and with MnO_2 and NLS were also studied. The effect of the charge of the ions in the double layer was studied theoretically, and it was also shown that varying the geometry of the model (planar or cylindrical) does not vary the trends observed in the calculated adsorption isotherms.

EXPERIMENTAL

The equipment used was two batch columns essentially identical to the apparatus described by us earlier (*16*). House air was passed through ascarite, water (for rehumidification), and glass wool, then through a "fine" glass gas dispersion tube at the bottom of the column. Laboratory grade NLS or HTA was used as the collector; all other chemicals were of reagent grade. Stock solutions (1.000 g/l) of the metal ions and surfactant were mixed in the desired amount and diluted with deionized water to nearly 200 ml; ionic strength was adjusted by the addition of sodium nitrate solution, and the pH adjusted by addition of dilute NaOH and HNO_3. The sample was diluted to 200 ml and added to the column. The air flow rate was measured with a soap film flowmeter. Air flow rates of approximately 85 ml/min were used in the lead work; for zinc, 65 ml/min was normally used. The pH was monitored during the course of each run, and 7 ml samples were withdrawn from the bottom of the column at 5-min intervals. Lead and zinc analyses were carried out by atomic absorption spectroscopy.

RESULTS

Ferguson's earlier work (*9*) showed that it was feasible to remove lead from dilute solutions by flotation of ferrous sulfide flocs with HTA. The cost of HTA compared to NLS and the toxicity and deterioration problems involved with sulfides led us to seek alternative methods. As is shown in Tables 1 and 2, lead is removed rather effectively with either $Al(OH)_3$–NLS or $Fe(OH)_3$–NLS.

TABLE 1

Floc Flotation of Lead with $Al(OH)_5$ and NLS[a]

	Added $NaNO_5$ (mole/l)				
	0	0.025	0.050	0.075	0.100
pH	Residual lead (ppm)				
6.0	2.4	6.1	7.6	9.1	10.0
6.5	2.3	6.2	6.4	8.3	10.0
7.0	1.2	2.9	4.4	6.2	21
7.5	2.2	6.5	7.2	16	20
8.0	8.2	15	14	23	26

[a] All runs made with 50 ppm Pb(II), 100 ppm Al(III), and 30 ppm NLS initially; initial volume = 200 ml, air flow rate = ~85 ml/min; duration of run = 20 min.

TABLE 2

Floc Foam Flotation of Lead with $Fe(OH)_3$[a]

	Added $NaNO_5$ (mole/l)				
	0	0.025	0.050	0.075	0.100
pH	Residual lead (ppm)				
6.0	1.4	1.4	1.5	1.3	2.1
6.5	0.0	0.0	0.10	1.0	1.1
7.0	0.1	0.14	0.42	0.7	5.8
7.5	0.0	0.20	0.56	2.2	2.6
8.0	0.1	1.1	2.8	6.3	19

[a] All runs made with 50 ppm Pb(II), 100 ppm Fe(III), and 30 ppm NLS initially; initial volume = 200 ml, air flow rate = ~85 ml/min, duration of run = 15 min.

These results indicate that increasing ionic strength does interfere with the separations, that pH should be controlled to within about 1 pH unit, and that $Fe(OH)_3$ is a more effective floc for lead removal than is $Al(OH)_3$. The volume of foamate obtained from a typical run was about 1 to 2 ml, 0.5 to 1% of the volume of solution being treated. It was found that Na_2CO_3 was less suitable as a neutralizing agent than NaOH. The poorer results are probably due to the stronger adsorption of divalent CO_3^{2-} on the positively charged floc particles, reducing their electric charge and zeta potential and thereby weakening their attraction to the negatively charged film surface. A few runs were made using $Fe(OH)_3$ with samples 0.0141 *M* in Na_2SO_4 (ionic strength 0.0423) and containing 50 ppm lead; 10-min runs at pH 6.0 reduced the lead concentration to 0.2 ppm. These results suggest that carbonate is more strongly adsorbed on the surface of the $Fe(OH)_3$ floc than is sulfate.

Calcium carbonate was used as the adsorbing floc with both NLS and HTA in several runs. HTA did not remove $CaCO_3$ or lead in the pH range of 9.0 to 10.5. NLS reduced the lead concentration from 50 ppm down to about 0.2 ppm [100 ppm Ca(II), 30 ppm NLS] at pH 7.0, but the efficiency of removal decreased very markedly as pH was changed (14 ppm residual lead at pH 6.5, 8.6 ppm at pH 7.5). We felt this sensitivity to pH was a serious handicap, and therefore did not pursue the use of $CaCO_3$ further.

A few runs were made using $Fe(OH)_3$ and gelatin. Occasional good separations were obtained (reductions from 50 ppm lead down to approximately 0.1 ppm), but the results were erratic and seemed to depend fairly critically on the details of the preparation of the gelatin solution. Best results were obtained using 250 ppm gelatin and 100 ppm Fe(III) at a pH of 7. In view of the difficulties in obtaining reproducible results and the large quantity of gelatin needed, we felt that further work on this method was unwarranted.

Batch runs with MnO_2 and NLS were quite effective in reducing lead concentrations from 25 ppm down to approximately 0.2 ppm in 5 to 10 min; the optimal pH was approximately 8.0, and 25 ppm NLS and 100 ppm Mn(II) were used. In this approach the Mn(II) is rapidly air oxidized in alkaline solution, and the surfactant is then added to effect flotation. Increasing ionic strength interferes with the separation, as expected. This method does not appear to have advantages over the use of $Fe(OH)_3$ and NLS.

Kim and Zeitlin's studies (*8*) on the removal of zinc from seawater with dodecylamine and ferric hydroxide at pH 7.6 resulted in 94% recovery from an initial concentration of 3.2 ppb. Our work was carried out at a substantially higher initial concentration of zinc; ferric or aluminum hydroxide was used as floc, NLS was used as the collector, and pH and ionic strength were varied.

Ferric hydroxide is speedily removed by foam flotation with NLS at pH 5.5, but with pH's as high as 7.5 the separation was found to be slow and incomplete. The precipitation point for $Zn(OH)_2$ is roughly at pH 8 (*5*), so one could not expect ferric hydroxide and NLS to be an optimum system for zinc removal. Runs made with solutions initially containing 50 ppm NLS and 50 ppm Zn(II) are listed in Table 3 and bear out this surmise; inclusion of 200 ppm Fe(III) appears to interfere with the separation. The air flow rates in all of the work on zinc are 60 to 68 ml/min unless otherwise specified. The samples listed in Table 3 were taken after

TABLE 3

The Effect of $Fe(OH)_5$ on Zn(II) Removal

Fe(III) concn (ppm)	pH	Final Zn(II) concn (ppm)
0	6.6	20
0	7.1	7.2
200	6.6	25
200	7.1	19

TABLE 4

The Effect of pH on Zn(II) Removal with Fe(III) and NLS

pH	Final Zn(II) concn (ppm)
5.5	42
6.2	37
6.6	25
7.1	25
7.5	8

5 min of treatment, at which time $Fe(OH)_3$ removal was essentially complete. There appears to be a competition between the Zn(II) ions and the ferric hydroxide floc for the collector. The effect of pH on Zn(II) removal is shown in Table 4. Initial concentrations were 50 ppm Zn(II), 200 ppm Fe(III), and 50 ppm NLS. At a pH of 7.5 the iron was incompletely removed.

It was found that pulse additions of $Fe(OH)_3$ floc during the course of the runs did not significantly improve the separations, nor did varying the air flow rate. Increasing the duration of the run and/or the amount of NLS added during the course of the run resulted in some improvement in separation, presumably through an ion flotation mechanism. Our results indicate that this is not an industrially feasible technique for removal of zinc from wastewaters, inasmuch as the use of long time periods and high collector concentrations resulted in final Zn(II) concentrations of about 3 ppm.

Huang (*17*) and Clarke (*16*) have removed $Al(OH)_3$ with NLS at pH's close to 8, the precipitation point of $Zn(OH)_2$. We therefore attempted the removal of Zn(II) with $Al(OH)_3$ and NLS. The data listed in Table 5 indicate that zinc is effectively floculated with $Al(OH)_3$ at pH's at which $Al(OH)_3$ is removed by foaming with anionic surfactants such as NLS. In these runs the initial Zn(II) concentration was 50 ppm and the run duration was 15 min. Final Zn(II) concentrations of less than 0.5 ppm are

TABLE 5

The Effect of Al(III) on Zn(II) Removal

pH	Al(III) (ppm)	NLS (ppm)	Final Zn(II) concn (ppm)
6.9	0	150	19.6
	200	150	4.7
7.4	0	150	5.5
	200	150	0.7
7.7	0	150	8.3
	100	100	0.39
	200	150	0.2
8.0	0	100	6.2
	100	100	0.20
8.3	0	100	4.8
	100	100	0.17
	200	100	0.0
8.6	0	100	6.0
	100	100	0.16
8.9	0	100	1.1
	100	100	0.41
9.2	0	100	1.6
	100	100	0.42

TABLE 6

Floc Flotation of Zinc with $Al(OH)_5$ and NLS. Effect of Ionic Strength

	Added $NaNO_3$ (mole/l)						
	0	0.05	0.10	0.15	0.20	0.30	0.40
pH	Residual zinc (ppm)						
9.2	0.06	1.18	4.1	9.2	11.2		
8.9	0.03	0.59	0.33	1.9	2.8		
8.6	0.09	0.11	0.11	0.15	0.60	1.2	4.7*
8.3	0.07	0.13	0.13	0.12	0.9	0.21*	2.3*
8.0	0.10	0.22	0.21	0.42	0.40	0.42*	0.9*
7.7	0.27*	0.32*	0.37*	0.50*	0.56*	0.41*	0.77*
7.4	1.1*				1.3*		1.2*

attained at pH's between 7.7 and 9.2 by adsorbing colloid flotation, and the residual Zn(II) concentrations are roughly an order of magnitude lower than those obtained by ion flotation alone with a similar quantity of surfactant.

The effect of increasing ionic strength at various pH's is shown in Table 6. All runs lasted 30 min; the initial Zn(II) concentration was 50 ppm; the initial Al(III) concentration was 100 ppm; in most of the runs (not starred) the initial NLS concentration was 100 ppm, with 50 ppm added after 15 min. The starred runs had an initial NLS concentration of 150 ppm. We see the usual pattern of decreasing separation efficiency with increasing ionic strength, but good separations can be obtained at ionic strengths below 0.15 mole/l of sodium nitrate.

The effects of different electrolytes on the separation of zinc with NLS and $Al(OH)_3$ are illustrated in Table 7. In all these runs the initial Al(III), NLS, and Zn(II) concentrations were 100, 150, and 50 ppm, respectively; the pH was adjusted to 8.3, 50 ppm of NLS was added after 15 min; the air flow rate was 60 to 68 ml/min; and samples were taken for analysis after 30 min of treatment. At pH 8.3 equilibrium calculations indicate that ~93% of the phosphate is present as HPO_4^{2-}, 7% as $H_2PO_4^-$, 10^{-2}% as PO_4^{3-}, and 10^{-5}% as H_3PO_4. For arsenate at this pH, 96% is present as $HA_5O_4^{2-}$, 4% as $H_2PO_4^-$, 0.1% as $A_5O_4^{3-}$, and 10^{-6}% as $H_3A_5O_4$. (For details see Ref. *18*.)

The decreased removal of zinc with sulfate, as opposed to nitrate as the added anion, is probably due to the increased negative charge on the anion, as is indicated by the theoretical results below. The effects of phosphate and arsenate are much too large to be due to merely a change in the charge of the anion; presumably these effects are due to strong adsorption of

TABLE 7

Floc Flotation of Zinc with $Al(OH)_3$ and NLS. Effect of Electrolyte Identity

Electrolyte identity	Ionic strength (mole/l)				
	0.05	0.10	0.15	0.20	0.30
	Residual zinc (ppm)				
$NaNO_3$	0.13	0.13	0.12	0.22	3.4
Na_2SO_4	0.6	2.2		3.6	3.1
Na_2HAsO_4	47	48			
Na_2HPO_4	46	>45			

these anions onto the floc, which presumably neutralized the charge of the floc.

THEORETICAL

The noticeable differences between Na_2SO_4 and $NaNO_3$ at the same ionic strengths suggested that we examine the effect of ionic charge of the inert salt used to establish the ionic strength of the solution being treated. We were also interested in the effect of model geometry on the results of theoretical calculations. We use here an approach described in more detail previously (*14*).

Let us first calculate the distribution of floc particles in a long cylindrical column of liquid of radius R and surface potential ψ_s. We start by calculating the electric potential within the liquid column by use of the Poisson-Boltzmann equation, as before:

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\psi}{dr}\right) = \frac{A \sinh \beta'\psi}{1 + B \cosh \beta'\psi} \tag{1}$$

where $\beta' = ze/kT$

ze = magnitude of charge on an ion of our 1–1 electrolyte

$A = 8\pi zec_\infty/(1 - 2c_\infty/c_{\max})D$

c_∞ = concentration of inert salt, "molecules" per cm^3

$c_{\max}$ = maximum possible concentration of inert salt (a nonideal, excluded volume effect)

D = dielectric constant of water

$B = 2c_\infty/(c_{\max} - c_\infty)$

We have here assumed that the anion and cation of the inert salt are of the same size. The boundary conditions on the solution of Eq. (1) are

$$\frac{d\psi}{dr}(0) = 0 \tag{2}$$

$$\psi(R) = \psi_s$$

We solve Eq. (1) by numerical integration:

$$\psi_{n+1} = \frac{2}{1 + \Delta r/2r_n}\psi_n - \frac{1 - \Delta r/2r_n}{1 + \Delta r/2r_n}\psi_{n-1} + \frac{(\Delta r)^2}{1 + \Delta r/2r_n}\frac{A \sinh \beta'\psi_n}{1 + B \cosh \beta'\psi_n} \tag{3}$$

where $r_n = n\Delta r$
$\psi_n = \psi(r_n)$

Our boundary conditions become

$$\psi_n = \psi_s$$
$$\psi_1 = \psi_0 + \frac{(\Delta r)^2}{2} \frac{A \sinh \beta'\psi_0}{1 + B\cosh \beta'\psi_0} \tag{4}$$

It is necessary to solve Eq. (3) iteratively in order to simultaneously satisfy both boundary conditions; this is accomplished by initially setting $\psi_0 = 4\psi_s \exp(-R/a)$, where a is the Debye length, calculating ψ_n from Eq. (3), multiplying ψ_0 by ψ_s/ψ_n, and repeating until ψ_n has converged to ψ_s. Convergence is generally quite rapid.

The concentration of the floc partides is then given by

$$c'(r) = \frac{c'_\infty \exp[-\beta q\psi(r)]}{1 + (c'_\infty/c'_{\max})[\exp(-\beta q\psi) - 1]} \tag{5}$$

where q = charge on floc particle
c'_∞ = bulk concentration of floc
$c'_{\max}$ = maximum possible concentration of floc
$\beta = 1/kT$

The net excess of floc per unit volume of collapsed foamate then is

$$c'_{\text{excess}} = \frac{1}{\pi R^2}\int_0^R 2\pi r[c'(r) - c'_\infty]\,dr$$
$$= \frac{2}{R^2} c'_\infty\left(1 - \frac{c'_\infty}{c_{\max}}\right)\int_0^R \frac{r[\exp(-\beta q\psi) - 1]\,dr}{1 + (c'_\infty/c'_{\max})[\exp(-\beta q\psi) - 1]} \tag{6}$$

A similar but slightly simpler analysis can be carried out assuming a planar film of thickness $2l$; the left-hand side of Eq. (1) is replaced by $d^2\psi/dx^2$, boundary conditions are $d\psi(0)/dx = 0$, $\psi(l) = \psi_s$, and Eq. (3) becomes

$$\psi_{n+1} = 2\psi_n - \psi_{n-1} + \frac{(\Delta x)^2 A \sinh \beta'\psi_n}{1 + B\cosh \beta'\psi_n} \tag{7}$$

The net excess of floc per unit volume of collapsed foamate is

$$c'_{\text{excess}} = \frac{c'_\infty}{l}\left(1 - \frac{c'_\infty}{c'_{\max}}\right)\int_0^l \frac{[\exp(-\beta q\psi) - 1]\,dx}{1 + (c'_\infty/c'_{\max})[\exp(-\beta q\psi) - 1]} \tag{8}$$

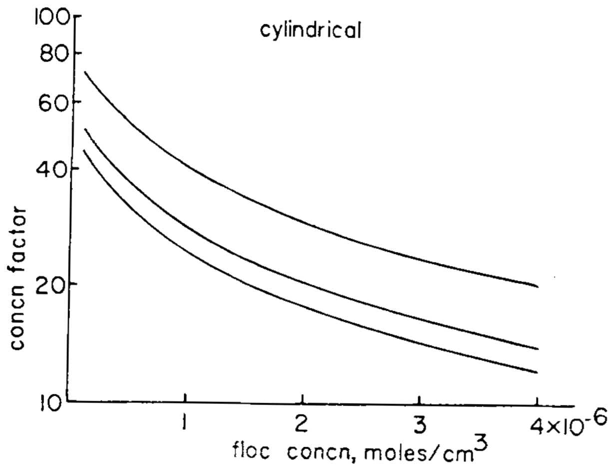

FIG. 1. Plot of concentration factor against floc concentration, cylindrical geometry. Effect of ionic charge of inert salt. $\psi_s = -100$ mv; $c_{\max} = 10^{-3}$ mole/cm; $T = 298$ °K; $R = 10^{-6}$ cm; $c'_{\max} = 10^{-3}$ mole/cm^3; floc charge $= +2$; |inert salt ion charge| $= 1, 2, 2.5$; $c_\infty = 10^{-4}, 2.5 \times 10^{-5}, 1.6 \times 10^{-5}$ mole/cm^3 from top to bottom.

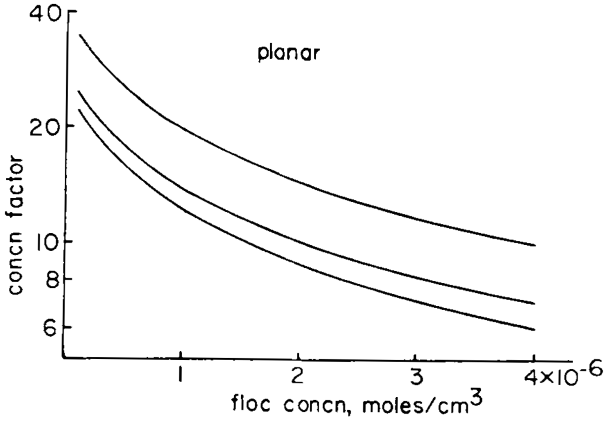

FIG. 2. Plot of concentration factor against floc concentration, planar geometry. Effect of ionic charge of inert salt. The half-thickness of the film is 10^{-6} cm; all other parameters are as in Fig. 1.

We present our results in terms of a separation factor, $c'_{\text{excess}}/c'_{\infty}$, for both geometries.

Typical results for the two geometries are shown in Figs. 1 and 2. We found that, while the isotherms are changed in detail, the trends with temperature, ionic strength, charge of ions and of floc, etc. are the same for the two models. This gives us some confidence that our results are not critically dependent on the geometrical details of the model.

Also of interest is the fact that adsorption decreases *at constant ionic strength* with increasing ionic charge of the inert salt. This is consistent with our findings on sodium sulfate as compared to sodium nitrate, but the effect is much too small to account for the profound impact of HPO_4^{2-} and $HAsO_4^{2-}$, both of which completely ruin the separation of zinc with $Al(OH)_3$ and NLS. According to theory (*14*), the increased size of these anions (as compared to sulfate) should result in a very slight increase in floc adsorption. We speculate that both HPO_4^{2-} and $HAsO_4^{2-}$ may be strongly chemisorbed onto the aluminum hydroxide floc, thereby changing its charge from positive to negative, or possibly just neutralizing the charge. Preliminary work indicates that $Fe(OH)_3$ flocs "poisoned" with HPO_4^{2-} or $HAsO_4^{2-}$ are slowly removed on flotation with hexadecyltrimethylammonium bromide, which tends to support this interpretation.

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