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Foam Separation of Mercury(II) and Cadmium(II) from Aqueous Systems

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Abstract

Mercury(II) and cadmium(II) were separated from aqueous systems by a number of batch-type precipitate flotation and adsorbing colloid flotation techniques. HgS, CdS, and $Cd(OH)_2$ were removed by precipitate flotation; $Fe(OH)_3$, $Al(OH)_3$, FeS, and CuS were used as adsorbing colloids. Sodium lauryl sulfate and hexadecyltrimethylammonium bromide (HTA) were used as collectors. Dependence of separation efficiency on pH and ionic strength was investigated. Floc foam flotation of both metals with CuS and HTA was found to be quite effective, resulting in residual Hg(II) levels as low as 5 ppb and residual Cd(II) levels as low as 20 ppb. Floc foam flotation of Cd(II) with FeS and HTA yielded residual Cd(II) levels as low as 10 ppb.

INTRODUCTION

The serious health problems presented by environmental contamination with cadmium and mercury have been extensively reviewed elsewhere (*1–3*). The use of foam flotation techniques for the removal of heavy metals from aqueous systems is well documented in a number of texts and reviews (*4–7*). Mercury has been separated by flotation of the nitrate or chloro complexes with hexadecyltrimethylammonium bromide (*8*, *9*), and cadmium has been removed by flotation of CdS and by adsorbing colloid flotation with FeS (*10*). Of all the various foam flotation techniques, it would appear that adsorbing colloid flotation is capable of reducing residual concentrations of a wide range of metals and nonmetals to the lowest levels with the greatest speed (*11–13*).

We report here adsorbing colloid flotation batch separations of mercury and cadmium from aqueous systems; these separations are capable of reducing the concentrations of these toxic metals down to the 20 parts per billion (ppb) level with the proper choice of floc and surfactant.

EXPERIMENTAL

The foam flotation system used was quite similar to that described by Ferguson et al. (*10*). House compressed air was reduced to about 5 psig and the gas flow was then adjusted with a Hoke needle valve with micrometer control and measured with a soap film flowmeter. The air was prepared by passage through concentrated sulfuric acid, ascarite, water, and a glass wool filter. Fisher Scientific laboratory grade sodium lauryl sulfate (NLS) and Eastman Kodak practical grade hexadecyltrimethylammonium bromide (HTA) were used without further purification. Other chemicals used were all reagent grade. The pH's of the solutions were adjusted with 0.1 *N* sodium hydroxide (or in a few cases, sodium carbonate) and 0.1 *N* nitric acid, and ionic strengths were varied by the addition of sodium nitrate. The pH measurements were made with a Sargent-Welch microcombination electrode and Sargent-Welch LSX pH meter; these were calibrated at pH's 4.01, 7.00, and 10.00.

Analyses for cadmium, iron, and copper were done by atomic absorption (Aztec model Mark II) at 228.8, 248.33, and 324.75 nm, respectively. Mercury was determined on a Perkin-Elmer 305 B instrument at 253.7 nm with a flameless atomic absorption system. Cadmium concentrations at low levels were measured to ±10 ppb; mercury to ±2 ppb; copper and iron to 0.1 ppm.

All experiments were run in the batch mode using 500 ml of solutions. Gas flow rates of 60 ml/min were used; a few runs made at a flow rate of 150 ml/min. with NLS and $Fe(OH)_2$ yielded very wet foams. At 60 ml/min flow rates the volume of collapsed foamate was less than 5 ml. Five milliliter samples were taken for analysis during the course of the runs. All runs were made at approximately 25 °C.

RESULTS

Initially a number of runs were made using simple precipitate flotation of mercuric sulfide ($pK_{sp} = 53.8$), cadmium sulfide ($pK_{sp} = 28.0$), and

TABLE 1

Hg(II) Removal by Precipitate Flotation of Mercuric Sulfide

S^{2-} (*M*)	pH	Ionic strength (*M*)	Time (min)	Surfactant	Hg (ppm)
0.0001	10, 7, 4	0.001	60	NLS	>5
0.001	10, 7, 4	0.002	60	NLS	>5
0.0001	10, 7	0.001	30	HTA	>0.5
0.0005	10, 7	0.001	30	HTA	>0.5
0.001	10, 7	0.002	30	HTA	>0.5
0.0003	3.5	0.001	60	HTA	0.2
0.002	1.8	0.01	60	HTA	0.12
0.002	1.8	0.01	30	HTA	0.30
0.002	0.8	0.1	30	HTA	0.10
0.001	0.8	0.1	30	HTA	0.11

cadmium hydroxide ($pK_{sp} = 13.9$). Mercuric sulfide was not removed by the anionic surfactant NLS at any pH, but was removed by cationic HTA, with the best results being obtained under highly acidic conditions. Initial Hg(II) concentrations of 20 ppm were reduced in 30 min to about 0.1 ppm at pH 0.8. Sulfide ion concentrations ranging from 10^{-4} to 2×10^{-3} *M* had no effect on removal rates or amount of mercury removed. The data are summarized in Table 1.

Ferguson's and Hinkle's results on the precipitation flotation of CdS (*10*) were verified; Cd concentrations between 0.1 and 0.3 ppm were obtained at low ionic strengths over a wide pH range.

Precipitation flotation of $Cd(OH)_3$ from solutions initially containing 10 ppm Cd(II) was carried out with HTA at pH 11.5; after 30 min of flotation 0.8 ppm Cd(II) remained in solution.

Adsorbing colloid flotation of Hg(II) and Cd(II) with $Al(OH)_3$ or $Fe(OH)_3$ was attempted using solutions containing 20 ppm Hg(II) or 10 ppm Cd(II). By and large, these separations were not very effective, as summarized in Table 2. Use of Na_3CO_2 as the neutralizing base yielded no better results than use of NaOH. Addition of 50 ppm PO_4^{3-} to a run with 100 ppm Al(III), NLS, and pH 7.5 resulted in a final Cd(II) concentration of 2 ppm.

At low ionic strengths (<0.01 *M*), $Fe(OH)_3$ was found to be rather effective in removing Cd(II) by a combination of precipitation and flotation in the pH range of 11 to 12. Solutions treated contained 10 ppm Cd(II) and 100 ppm Fe(III) initially. The pH was adjusted to 12 and 20 ppm HTA was added, which speeded coagulation. After 30 min the super-

TABLE 2

Hg(II) and Cd(II) Removal by Adsorbing Colloid Flotation

Hg with $Al(OH)_3$

Al(III) (ppm)	pH	Ionic strength (M)	Time (min)	Surfactant	Hg (ppm)
50	7.2–7.5	0.006	60	NLS	>5
50	7.5–8.0	0.006	60	NLS	>5
50	7.6–7.5	0.006	60	HTA	>5
50	7.5–8.2 (with Na_2CO_3)	0.006	45	HTA	>5

Hg with $Fe(OH)_3$

Fe(III) (ppm)					
100	10, 12	0.01	30	HTA	>5
100	10	0.005	30	NLS	>5
100	8	0.005	30	NLS	>5

Cd with $Al(OH)_3$ or $AlPO_4$

Al (ppm)	PO_4^{-3} (ppm)					Cd (ppm)
100	0	6.5–6.8	0.01	30	NLS	>5
100	0	7.5	0.01	20	NLS	4.5
100	100	6.5	0.01	25	NLS	5
100	50	7.5	0.01	25	NLS	5
100	50	7.5	0.01	45	NLS	2

TABLE 3

Effect of Ionic Strength and pH on Cd(II) Removal by Adsorbing Colloid Flotation with $Fe(OH)_3$

Ionic strength:	0.006	0.016	0.03	0.056	0.1
pH	Cd (ppb)				
9.5	100				
10.0	60				
10.5	50				
11.0	10	100	200	220	220
11.5	10	70	100	120	220
12.0	10	70	80	100	220

TABLE 4

Cd(II) Removal by Adsorbing Colloid Flotation with $Fe(OH)_3$[a]

Fe(III) (ppm)	pH	I (*M*)	Time (min)	Surfactant	Cd (ppm)
100	8.5, 10	0.005	30	HTA	>5
100	8.5, 10 (with Na_2CO_3)	0.005	30	HTA	>5
100	11.6 (with Na_2CO_3)	0.01	40	HTA	1
100	5.5 (with Na_2CO_3)	0.005	30	NLS	>5
100	7.7	0.005	30	NLS	3.5

[a] Floc and supernatant were transferred to the flotation column.

natant contained 250 to 500 ppb Cd(II); it was decanted into the flotation column and treated for 30 min, with HTA being added in small amounts as needed to maintain a stable foam. After treatment, the solutions contained as little as 10 ppb Cd(II), as indicated in Table 3.

Inclusion of the precipitate with the decantate in the flotation column drastically reduces the separation efficiency, as is shown in Table 4.

Ferguson et al. (*10*) have shown that Cd(II) is quite efficiently removed by adsorbing colloid flotation with FeS and HTA at alkaline pH's. We have checked their results and obtained residual Cd(II) concentrations of about 12 ppb. The same technique is rather effective for mercury, as indicated in Table 5. Initial Hg(II) concentrations were 20 ppm; our results indicate that approximately 130 ppm of S^{2-} and 50 ppm of Fe(II) are needed to reduce the mercury concentration below 100 ppb, and that the separation is not seriously affected by ionic strengths ≤ 0.1 *M*. Best results were obtained at pH 9.0; under acidic conditions the FeS floc was not removed effectively.

TABLE 5

Hg(II) Removal by Adsorbing Colloid Flotation of HgS with FeS

Fe(II) (ppm)	S^{2-} (*M*)	pH	I (*M*)	Time (min)	Surfactant	Hg (ppb)
20	0.0008	9	0.002	30	HTA	>200
20	0.0008	5	0.002	30	HTA	>300
50	0.004	9	0.001	30	HTA	50
50	0.004	9	0.1	30	HTA	70

The most effective foam flotation procedure we found for the removal of Hg(II) and Cd(II) is adsorbing colloid flotation with cupric sulfide and HTA. This method is effective even at ionic strengths as high as 2.0 *M*, it is insensitive to large pH variations, and it can yield final Hg(II) concentrations as low as 5 ppb and Cd(II) concentrations as low as 20 ppb. It functions well at neutral pH. The details of the procedure are as follows. Ten milliliters of 0.2 *M* Na_2S solution is added to 490 ml of solution containing 100 ppm Cu(II) and 20 ppm Hg(II) or 10 ppm Cd(II). Ionic strength is adjusted with sodium nitrate, and pH with sodium hydroxide and nitric acid. HTA (40 ppm) is added to coagulate the colloid and the solution is allowed to stand for 10 min; solution and floc are then poured into the flotation column. An air flow rate of 80 ml/min is used, and 10 ppm HTA is added by injection into the liquid pool every 6 min. The foam is rather dry; volumes of collapsed foamate from 30-min runs were always less than 10 ml. The results for mercury are summarized in Table 6.

Increasing ionic strength did not affect the maximum ultimate removal of mercury, but it did decrease the rate of removal. Variation of pH within the range of 1 to 8 affected neither maximum removal nor rate of removal. Residual Cu(II) concentrations were always less than 0.5 ppm.

Data on Cd(II) removal by this technique are presented in Table 7. Varying the pH and the ionic strength does have some effect on the maximum ultimate removal of cadmium; at an ionic strength of 0.5 *M*, we found that separation was most complete at pH 7.0 to 8.5. Even at this

TABLE 6

Hg(II) Removal by Adsorbing Colloid Flotation of HgS with CuS

Cu(II) (ppm)	S^{2-} (*M*)	pH	I (*M*)	Time (min)	Hg (ppb)
12	0.0008	9.5	0.002	30	200
12	0.0008	6	0.002	30	200
12	0.0008	4	0.002	30	200
12	0.0008	2	0.01	30	100
12	0.0008	1	0.1	30	90
60	0.002	1	0.1	20	5
60	0.002	0.8	0.2	20	5
60	0.002	0.8	0.6	60	500
100	0.003	0.8	0.6	20	5
100	0.004	6–6.7	0.01	20	5
100	0.004	6–7	0.1	20	5
100	0.008	6–7	0.5	25	5
100	0.008	7–8	2.0	40	5

TABLE 7

Effect of pH and Ionic Strength Variation on Cd(II) Removal by Adsorbing Colloid Flotation of CdS with CuS: $[S^{2-}] = 0.004$ *M*, $[Cu^{2+}] = 100$ ppm Initially

pH:	3.0–3.1	4.0–4.1	5.0–6.5	6.0–7.8	7.0–8.5
Ionic strength (*M*)	Cd (ppb)				
0.1	20	20	40	20	20
0.5	70	70	120	70	50

pH	I (*M*)	Time (min)	Cd (ppb)	Residual Cu (ppm)
7–8	0.1	30	20	<0.5
7–8	0.5	30	50	<0.5
7–8	1.0	30	150	<0.5
7–8	1.5	45	250	0.5
7–8	2.0	45	250	0.5

optimum pH, however, about 250 ppb of Cd(II) remained in solution after 45 min of treatment when the ionic strength was 2 *M*. As with mercury, residual Cu(II) concentrations were always less than 0.5 ppm.

The effect of interference from doubly charged ions was examined. Neither 0.1 *M* Na_2SO_4 or 0.1 *M* $Ca(NO_3)_2$ had any effect on the maximum removal of Hg(II), but they decreased the effectiveness of the Cd(II) separation. In 0.1 *M* Na_2SO_4 solution, 80 ppb Cd(II) and <0.5 ppm Cu(II) remained in solution after a 45-min run at pH 7.8 to 8.5. In 0.1 *M* $Ca(NO_3)_2$ solution, 180 ppb Cd(II) and 2.0 ppm Cu(II) remained after similar treatment.

Residual sulfide was determined on some of the runs by titration with $KMnO_4$. With an initial sulfide ion concentration of 4×10^{-3} *M* (before addition of the cadmium and copper salts), a typical residual sulfide level is about 8×10^{-5} *M* when the pH is in the range of 6 to 7.

Sorption of Cd and Hg on the glass walls of the column in the presence of sulfide was tested for by rinsing the column with acid and analyzing the rinsings. No evidence of sorption was found, in marked contrast to our earlier work on lead (*10*).

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