This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Cadmium from Aqueous Solution Using Adsorptive Bubble Separation Techniques

Shang-Da Huang[a]; Tsen-Fong Wang[a]
[a] DEPARTMENT OF CHEMISTRY, NATIONAL TSING HUA UNIVERSITY, HSINCHU, TAIWAN, REPUBLIC OF CHINA

To cite this Article Huang, Shang-Da and Wang, Tsen-Fong(1988) 'Removal of Cadmium from Aqueous Solution Using Adsorptive Bubble Separation Techniques', Separation Science and Technology, 23: 10, 1083 — 1091
To link to this Article: DOI: 10.1080/01496398808058440
URL: http://dx.doi.org/10.1080/01496398808058440

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 23(10 & 11), pp. 1083-1091, 1988

Removal of Cadmium from Aqueous Solution Using Adsorptive Bubble Separation Techniques

---

SHANG-DA HUANG and TSEN-FONG WANG

DEPARTMENT OF CHEMISTRY
NATIONAL TSING HUA UNIVERSITY
HSINCHU, TAIWAN 30043, REPUBLIC OF CHINA

Abstract

Cadmium ion was removed from aqueous solutions using adsorptive bubble separation techniques. The effect of pH, coagulant and activator concentrations, and ionic strength on separation efficiency was studied. Adsorbing colloid flotation using ferric hydroxide and aluminum hydroxide as the coprecipitant and sodium lauryl sulfate as the collector and frother was found to be very effective provided that the ionic strength of the solution was no greater than 0.01 *M*. The residual cadmium concentration was less than 0.02 ppm after foaming for 10 min from a solution containing 20 ppm cadmium initially. Effective separation can be achieved from solutions containing 0.1 *M* $NaNO_3$ or 0.05 *M* Na_2SO_4 when zinc ion is used as the activator. The results of foam flotation were compared with the zeta potential of the floc. It was found that the zeta potential of the floc decreases with increasing ionic strength of the solution. The zeta potential of the floc is more positive when activators (aluminum and zinc ions) were added, which presumably gives the floc a stronger affinity for anionic surfactant adsorption, resulting in better separation efficiency. Adsorbing colloid flotation becomes less effective with increasing inert salt concentration of the solution; this effect can be compensated for to quite a large extent with the aid of activators, and the applicability of foam separation techniques for heavy metal removal from wastewater is thus greatly extended.

INTRODUCTION

Foam separation techniques, a class of adsorptive bubble separation techniques, have 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*). 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 cheaper anionic surfactant (such as sodium lauryl sulfate), is then added, adsorbs onto the floc particle, and renders it hydrophobic. The floc (with adsorbed metal) is removed by air flotation.

When dealing with dilute wastes, 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 capital costs plus chemical costs of wastewater treatment by adsorbing colloid flotation have been recently estimated and compared with those of lime precipitation (*6–8*). Economics appear to favor adsorbing colloid flotation by a substantial margin.

Foam separation of cadmium has been studied by many investigators. These studies were recently reviewed by Jurkiewicz (*9*) and Wilson et al (*2*). Works of particular relevance to the present one include 1) precipitate flotation of CdS and adsorbing colloid flotation with FeS, using hexadecyltrimethyl ammonium bromide by Ferguson et al. (*10*); 2) precipitate flotation of $Cd(OH)_2$ and adsorbing colloid flotation of Cd with $Al(OH)_3$, $Fe(OH)_3$, and CuS by Huang and Wilson (*11*); 3) foam fractionation and ion flotation of cadmium with sodium lauryl sulfate and sodium laurate by Jurkiewicz (*9*); 4) precipitate flotation of cadmium hydroxide with sodium lauryl sulfate by Jurkiewicz (*12*); 5) selective foam separation of Zn, Cd, Hg, and Au chloride and cyanide complex with hexadecyltrimethylammonium chloride by Walkowiak and Grieves (*13*, *14*); and 6) ion flotation of cadmium stearate, foam fractionation of cadmium with sodium lauryl sulfate, and adsorbing colloid flotation of cadmium with metal hydroxide using sodium tripolyphosphate as the modifier by Wu et al. (*15*).

Among all the methods mentioned above, the adsorbing colloid flotation of cadmium sulfide with FeS or CuS (*10*, *11*) seems to be the most effective one for cadmium removal from wastewater, with the residual cadmium levels lower than 20 ppb. The rate of separation was very fast, and the separation was effective from solutions with a wide range of ionic strengths. However, the toxicity and deterioration problems involved with sulfide led us to seek alternative methods. Foam fractionation of cadmium ion was effective, but the rate of separation was slow. Furthermore, the separation efficiency of foam fractionation was significantly affected by ionic strength variation (*15*, *19*). Ion flotation of cadmium stearate (*15*) was effective from solutions with high ionic strength, but the rate of separation was somewhat slow.

In recent years the most systematic studies on adsorbing colloid flotation processes have been carried out by Wilson et al. (*1*, *2*, *6*, *7*, *11*, *16–19*). These studies mainly concern the flotation of heavy metal hydroxides with $Fe(OH)_3$ or $Al(OH)_3$ as the coprecipitant. One of the authors of this paper has also published the results of adsorbing colloid flotation of Pb (*20*), Cd (*15*), Hg (*21*), Cu (*22*), Zn (*22*), Cr (*23–25*), Sn (*26*), Mn (*27*), Co (*28*), and mixtures of heavy metal ions (*29*, *30*) at various ionic strengths. Previous studies on adsorbing colloid flotation of cadmium with $Fe(OH)_3$ or $Al(OH)_3$ have shown that separation is effective provided that the ionic strength of the solution is no greater than 0.001 *M* (*15*). We have recently shown that the effect of ionic strength variation on the separation efficiency of adsorbing colloid flotation of Cr(VI), Cr(III), Sn(II), and Co(II) with $Fe(OH)_3$ and sodium lauryl sulfate can be compensated for in many cases by using Al(III) as an activator to increase the zeta potential of the floc (*31*). Here we will demonstrate that Al(III) is also a useful activator for cadmium removal by adsorbing colloid flotation with $Fe(OH)_3$ and sodium lauryl sulfate. Furthermore, we will show that Zn(II) is a even more powerful activator for adsorbing colloid flotation of cadmium from solutions of higher ionic strength when Fe(III) and Al(III) are used as the coagulants. The relationship between the separation efficiency and the effect of activators on the zeta potentials of the floc at various ionic strength will be discussed.

EXPERIMENTAL

The foam flotation system used was similar to that described earlier (*24*, *31*). 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 $Cd(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $NaNO_3$, 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. The duration of foam flotation treatment was 10 min for all the runs. The initial cadmium concentration was 20 ppm for all the runs.

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

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 average velocity of particles was 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 (*32*). The typical standard deviation of the zeta potential measured is about 10% of its value.

RESULTS AND DISCUSSIONS

The effect of pH, Fe(III) and Al(III) dosage on adsorbing colloid flotation of cadmium with $Fe(OH)_5$ is shown in Table 1. Separation using $Fe(OH)_3$ as the coagulant was effective (with a residual cadmium level less than 0.1 ppm) at pH 11.0. When Al(III) was used as the activator, the separation was effective at pH 9.5. The residual cadmium level was higher at a pH lower than 9.5, presumably due to incomplete coprecipitation of cadmium ion with the floc. The effect of ionic strength variation (adjusted with $NaNO_3$) and the dosage of Fe(III) and Al(III) on separation are shown in Table 2. The separation was effective provided that the concentration of $NaNO_3$ was no greater than 0.01 *M* and that proper amounts of Fe(III) and Al(III) were used. [Note that the separation was poor from a solution containing $NaNO_3$ greater than

TABLE 1
Effect of pH and Dosage of Fe(III) and Al(III) on Separation[a]

pH	Fe(III) (ppm)	Al(III) (ppm)	Residual Cd (ppm)
8.0	50	25	2.50
8.5	50	25	1.43
9.0	50	25	0.36
9.5	25	0	0.80
9.5	50	0	0.30
9.5	100	0	3.80
9.5	50	10	0.11
9.5	50	25	0.08
9.5	50	30	0.04
9.5	44	25	0.04
9.5	40	20	0.07
10.0	25	0	0.21
10.0	44	25	0.28
10.0	50	30	0.70
10.5	25	0	0.18
10.5	25	8	0.13
10.5	36	8	0.90
11.0	25	0	0.08

[a] NLS = 40–48 ppm.

TABLE 2
Effect of $NaNO_3$ and Dosage of Fe(III) and Al(III) on Separation[a]

Fe(III) (ppm)	Al(III) (ppm)	$NaNO_3$ (*M*)						
		0	0.001	0.005	0.01	0.02	0.05	0.10
		Residual Cd (ppm)						
24	30				0.18		1.03	1.87
32	30				0.26		1.00	9.02
40	30	0.04	0.06	0.03	0.04	0.24	0.91	
50	30				0.42			
32	20				0.25			
32	32				0.05	0.16		
50	35			0.18	0.19	1.28		
40	35				0.15	1.50		

[a] pH = 9.5.

0.001 *M* if Fe(III) was used alone.] The effect of Zn(II) is shown in Table 3. Good separation with a residual cadmium level less than 0.1 ppm and a residual zinc level less than 0.05 ppm could be achieved from a solution containing $NaNO_3$ as high as 0.1 *M* when zinc ion was added as the activator by the following procedure. Proper amounts of Fe(III) and Al(III) were added to the cadmium solution, the pH of the solution was adjusted to 9.5 to produce the floc, the solution of zinc was added (the pH of the solution shifts down a little bit), the solution of sodium lauryl sulfate was then added, and the final adjustment of the pH to 9.5 was made before flotation. The floc was then removed by flotation.

The effect of sulfate and the activators on separation is shown in Table 4. When Fe(III) and Al(III) were used, effective separation with a residual cadmium level at 0.02 ppm was achieved provided that the concentration of Na_2SO_4 was no greater than 0.005 *M*. The separation efficiency was significently improved from a solution containing 0.01 *M* Na_2SO_4 if 2 ppm of zinc ion was added. It was also found that separation could be effective from a solution containing 0.05 *M* Na_2SO_4 using the following procedure: solutions of Fe(III) and Al(III) were added to the sample solution, the pH of the solution was adjusted to 9.8 to produce the floc, a solution of zinc ion was added (which shifted the pH of the solution down to 9.5), and then the floc was removed by flotation with sodium lauryl sulfate. Note that if zinc ion was added with Fe(III) and Al(III) before pH adjustment (to pH 9.8), separation was very poor. Zeta potential measurement (see Table 5) showed that the zeta potential of the floc was highly negative in a solution containing 0.05 *M* Na_2SO_4 if no zinc was added, but the zeta potential of the floc was less negative if zinc ion was added with Fe(III) and Al(III) to produce the floc. The zeta potential of the floc changed to a positive value if zinc ion was added to the solution after the floc of a mixed metal hydroxide [such as $Fe(OH)_3$, $Al(OH)_3$, and $Cd(OH)_2$] had already been produced by pH adjustment.

TABLE 3
Effect of Zn(II) on Separation[a]

Fe (ppm)	Al (ppm)	Zn (ppm)	Residual level	
			Cd (ppm)	Zn (ppm)
48	60	24	0.09	0.04
32	56	70	0.09	0.05
36	56	80	0.09	0.04

[a] $NaNO_3$ = 0.1 *M*, pH = 9.5, NLS = 120 ppm.

TABLE 4
Effect of Sulfate and Activators on Separation[a]

Na_2SO_4 (*M*)	Fe (ppm)	Al (ppm)	Zn (ppm)	Residual Cd (ppm)
0	30	34	0	0.02
0.005	40	30	0	0.29
0.005	36	35	0	0.02
0.01	30	34	0	>2
0.01	36	35	1	0.28
0.01	36	35	2	0.08
0.01	40	35	0	>2
0.01	40	35	2	0.09
0.01	32	40	0	1.86
0.01	32	40	1.5	0.06
0.05	56	80	32[b]	0.08[c]

[a] pH = 9.5.
[b] pH adjusted to 9.8, then add Zn, pH shift to 9.5.
[c] Residual zinc = 0.04 ppm.

The zeta potential of the floc depends on the surface composition of the floc. The zeta potential is more positive if more zinc ion and/or a hydroxylated species of zinc ion is adsorbed on the surface of the floc. If zinc ion is added before the formation of the floc, some zinc ion may be incorporated in the floc by a coprecipitation mechanism. If zinc ion is added after the formation of the floc, more zinc ion is available for adsorption onto the floc surface, and therefore the floc produced may have a higher zinc composition at the floc surface than floc produced by adding zinc ion before the formation of the floc. The zeta potential of the floc produced by adding zinc ion after the formation of the floc is therefore more positive, which presumably gives the floc a stronger affinity for anionic surfactant adsorption, thereby resulting in better separation efficiency. More studies on the relationship between the separation efficiency of foam flotation and the effects of Al(III) and Zn(II) on the zeta potentials of the flocs at various ionic strength are shown in Table 6. The improvement in separation efficiency by activators from solutions with high ionic strength are well explained by their effect on the zeta potential of the floc.

Acknowledgment

We are indebted to the National Science Council of the Republic of China for a grant in support of this work.

TABLE 5
Effect of Zn and Procedure of Zn Addition on Zeta Potential and Separation[a]

Fe (ppm)	Al (ppm)	Zn (ppm)	Procedure	Zeta potential (mV)	Residual Cd (ppm)
56	80	0	—	−40.4	>7
56	80	32	[b]	−23.5	6.5
56	80	32	[c]	9.7	0.09

[a] Final pH = 9.5 for flotation and zeta potential measurement, Na_2SO_4 = 0.05 *M*.
[b] Add zinc together with Fe and Al.
[c] Add zinc after the pH is adjusted to 9.8.

TABLE 6
Effect of Ionic Strength and Activators on Zeta Potential and Separation[a]

Fe (ppm)	Al (ppm)	Zn (ppm)	$NaNo_3$ (*M*)	Na_2SO_4 (*M*)	Zeta potential (mV)	Residual Cd (ppm)
70	0	0	0.01	0	−38 ± 3	>1
40	0	0	0.01	0	9 ± 1	0.34
40	30	0	0.01	0	20 ± 3	0.03
48	60	0	0.10	0	−29 ± 3	>1
48	60	24[b]	0.10	0	10 ± 1	0.09[d]
71	0	0	0	0.005	−38 ± 4	>1
36	35	0	0	0.005	10 ± 1	0.02
56	80	0	0	0.050	−42 ± 6	>1
56	80	32[c]	0	0.050	10 ± 1	0.08[d]

[a] Final pH = 9.5 (for flotation or zeta potential measurement).
[b] The pH of the solution was adjusted to 9.5, followed by adding zinc ion, and the pH was readjusted to 9.5.
[c] The pH of the solution was adjusted to 9.8, followed by adding zinc ion, which shifted the pH of the solution down to 9.5.
[d] The residual zinc level in the solution after flotation is 0.05 ppm.

REFERENCES

1. D. J. Wilson and A. N. Clarke, *Sep. Purif. Methods*, *7*, 55 (1978).
2. D. J. Wilson and A. N. Clarke, *Developments in Foam Flotation*, Dekker, New York, 1983.
3. R. Lemlich (ed.), *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972.
4. R. B. Grieves, *Chem. Eng. J.*, *9*, 93 (1975).
5. P. Somasundaran, *Sep. Sci.*, *10*, 93 (1975).
6. G. T. McIntyre, J. J. Rodriguez, E. L. Thackston, and D. J. Wilson, *Sep. Sci. Technol.*, *17*, 683 (1982).
7. E. L. Thackston, D. J. Wilson, J. S. Hanson, and D. L. Miller Jr., *J. Water Pollut. Control Fed.*, *52*, 317 (1980).

8. M. A. Slapik, "Pilot Plant Study of Lead Removal by Absorbing Colloid Foam Flotation," Master's Thesis, Vanderbilt University, Nashville, Tennessee, 1982.
9. K. Jurkiewicz, *Sep. Sci. Technol., 19,* 1039 (1984–85).
10. B. B. Ferguson, C. Hinkle, and D. J. Wilson, *Sep. Sci., 9,* 125 (1974).
11. S.-D. Huang and D. J. Wilson, *Ibid., 11,* 215 (1976).
12. K. Jurkiewicz, *Sep. Sci. Technol., 19,* 1051 (1984–85).
13. W. Walkowiak, D. Bhattacharyya, and R. B. Grieves, *Anal. Chem., 48,* 975 (1976).
14. W. Walkowiak and R. B. Grieves, *J. Inorg. Nucl. Chem., 38,* 1351 (1976).
15. L.-F. Wu, R.-C. Kuo, and S.-D. Huang, *J. Chin. Chem. Soc., 27,* 165 (1980).
16. D. J. Wilson and R. M. Kennedy, *Sep. Sci. Technol., 14,* 319 (1979).
17. A. N. Clarke, D. J. Wilson, and J. H. Clarke, *Ibid., 13,* 573 (1978).
18. R. P. Robertson, D. J. Wilson, and C. S. Wilson, *Sep. Sci., 11,* 569 (1976).
19. T. E. Chatman, S.-D. Huang, and D. J. Wilson, *Ibid., 12,* 461 (1977).
20. Y.-F. Chiu and S.-D. Huang, *Appl. Surf. Chem., 2*(4), 2 (1979).
21. L.-F. Wu, Y.-F. Chiu, and S.-D. Huang, *Ibid., 3*(1), 2 (1980).
22. S.-D. Huang, T.-P. Wu, C.-H. Ling, G.-L. Sheu, C.-C. Wu, and M.-H. Cheng, Paper Presented at the 6th International Symposium on Surfactant in Solution, New Delhi, India, August 18–22, 1986.
23. S.-D. Huang and C.-F. Fann, *Proc., 2nd World Congr. Chem. Eng., 4,* 329 (1981).
24. S.-D. Huang, C.-F. Fann, and H.-S. Hsieh, *J. Colloid Interface Sci., 89,* 504 (1982).
25. S.-D. Huang and D. J. Wilson, *Sep. Sci. Technol., 19,* 603 (1984).
26. T.-F. Ferng, J.-J. Tzuoo, and S.-D. Huang, *Appl. Surf. Chem., 5*(3), 2 (1982).
27. T.-G. Shing, H.-H. Hsieh, and S.-D. Huang, *Ibid., 4*(2), 2 (1981).
28. J.-Y. Gau and S.-D. Huang, *Surf. Sci., 7*(2), 2 (1984).
29. J.-Y. Gau, Y.-A. Chen, and S.-D. Huang, *Proc. Natl. Sci. Counc., Repub. China, 9*(3), 228 (1985).
30. S.-D. Huang, M.-K. Huang, J.-Y. Gua, T.-P. Wu, and J.-Y. Huang, Paper Presented at the 6th International Symposium on Surfactant in Solution, New Delhi, India, August 18–22, 1986.
31. S.-D. Huang, J.-J. Tzuoo, J.-Y. Gau, H.-S. Hsieh, and C.-F. Fann, *Sep. Sci. Technol., 19,* 1061 (1985).
32. *Zeta-Meter Manual,* 3rd ed., Zeta-Meter Inc., New York, 1975, p. 70.

Received by editor October 13, 1987