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

Adsorbing Colloid Flotation of Cu(II) with a Chelating Surfactant

Wesley D. Allen[a]; Mark M. Jones[a]; Wanda C. Mitchell[a]; David J. Wilson[a]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

To cite this Article Allen, Wesley D. , Jones, Mark M. , Mitchell, Wanda C. and Wilson, David J.(1979) 'Adsorbing Colloid Flotation of Cu(II) with a Chelating Surfactant', Separation Science and Technology, 14: 9, 769 — 776

To link to this Article: DOI: 10.1080/01496397908060238

URL: http://dx.doi.org/10.1080/01496397908060238

SEPARATION SCIENCE AND TECHNOLOGY, 14(9), pp. 769–776, 1979

Adsorbing Colloid Flotation of Cu(II) with a Chelating Surfactant

WESLEY D. ALLEN, MARK M. JONES,
WANDA C. MITCHELL, and DAVID J. WILSON*

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

Cu(II) is effectively removed from synthetic mixtures by dodecylamine-*N*,*N*-diacetic acid with $Fe(OH)_3$ and a carrier foam. The effects of pH and ionic strength on the separation are ascertained. Cu(II) is effectively floated at much higher ionic strengths with dodecylamine-*N*,*N*-diacetic acid than with nonchelating surfactants such as sodium lauryl sulfate.

INTRODUCTION

Foam flotation involves the separation of materials (ionic, molecular, colloidal, or macroparticulate) from aqueous solutions by adsorption to the surface of bubbles rising through the liquid. Applications of foam flotation techniques include the treatment of wastewater, the analysis of trace metals, and the recovery of metals from ores. Foam flotation has recently been reviewed by Clarke and Wilson (*1*), Lemlich (*2*), Somasundaran (*3*, *4*), and others. Grieves, Bhattacharyya, and their coworkers have devoted much effort to applying flotation techniques to waste treatment problems (*5–16*). Wilson and his collaborators have used precipitate flotation and adsorbing colloid flotation to treat industrial wastewaters (*17*, *18*). Zeitlin's group has also worked with adsorbing

---

*To whom requests for reprints should be sent.

colloid flotation and has developed a number of analytical methods based on this technique (*19–24*). Flotation separation procedures have also been adapted to remove radioactive substances (*25*).

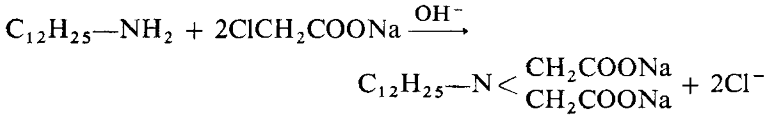
The presence of anions such as phosphates, oxalates, and EDTA in aqueous solutions is a serious obstacle to the successful application of adsorbing colloid flotation techniques (*26*, *27*). The ionic strength of the solution is also important; if it is too high, removal of toxic metals from wastewaters is severely impaired. Many industrial wastewaters are of relatively high ionic strength; furthermore, the detergents found in these wastes often contain phosphates. The negatively charged ions present compete with the surfactant for attachment to the floc surfaces, and surfactants which electrostatically attach to floc particles thus become ineffective at high ionic strengths. The objective of this research is to ascertain the effectiveness of a surface-active chelating agent in the removal of Cu(II) by adsorbing colloid flotation at high ionic strength. Removal of Hg(II) and Cd(II) by ion flotation with a chelating surfactant was previously reported by Okamoto and Chou (*28*).

EXPERIMENTAL

Batch separations were performed using an apparatus similar to one previously described (*29*). The Pyrex glass column was 3.5 cm in diameter by 90 cm in length. Sidearms for a glass pH electrode and for surfactant injection were located 12 cm from the bottom of the column. The bottom of the column was closed by means of a large rubber stopper in which were mounted a stopcock for sample collection, a drain to facilitate rapid emptying and flushing of the column, and a 40–60 mesh fine pore fritted glass sparger for air dispersion.

Air was supplied by a Metaframe aquarium air pump. A microvalve with vernier control regulated the flow of air into a glass tube 3 cm in diameter by 28 cm in length which was packed with Ascarite and glass wool to remove CO_2 and dust particles. The air was then humidified and passed into the column through the sparger. Flow rates were measured with a soap film flowmeter and a stopwatch.

A new chelating surfactant, dodecylimino-*N*,*N*-diacetic acid sodium salt (DIDA) was synthesized by the following reaction (*29*):



$$C_{12}H_{25}{-}NH_2 + 2ClCH_2COONa \xrightarrow{OH^-} C_{12}H_{25}{-}N{<}\begin{matrix}CH_2COONa\\ CH_2COONa\end{matrix} + 2Cl^-$$

A 1000-mg/l stock solution of DIDA in distilled water was prepared. Polyethylene containers and distilled water were used in all experimental procedures. A 1000-mg/l stock solution of laboratory grade sodium lauryl sulfate (NLS) was also prepared; new solutions of NLS were made every 2 to 3 weeks to avoid problems with bacterial growth in the surfactant. ACS reagent-grade nitrate salts were used to make stock solutions of Cu(II) and Fe(III). Stock solutions of other substances were also prepared from reagent-grade chemicals: a 2.0 *M* $NaNO_3$ solution, 1.0 and 0.5 *M* Na_2SO_4 solutions, a 0.1 *M* Na_2HPO_4 solution, a 0.1 *M* HNO_3 solution, and 1.0 and 0.1 *M* NaOH solutions. A 2000-ppm solution of Udylyte, a heavy-duty industrial detergent, was also prepared. A Sargent-Welch Model EP pH meter was used to measure pH in the batch studies. Copper concentrations were measured on a Perkin-Elmer Model 370 atomic absorption spectrophotometer at 324.7 nm.

Visible results of test runs were used to determine areas encouraging further investigation. It was found necessary to use a carrier foam with the chelating surfactant; both ionic and nonionic surfactants (NLS and Tween 20, polyoxyethylene (20) sorbitan monolaurate) were used for this. Runs were of 10 min duration, and surfactant was added only at the beginning of a run, even though distributed surfactant addition during the course of a run has been shown advantageous (*30–34*). The effects of four substances typical of those found in industrial wastewaters ($NaNO_3$, Na_2SO_4, Na_2HPO_4, and Udylyte) on successful Cu(II) removal were studied. Two procedures were used to prepare synthetic mixtures for these experiments:

Method I	Method II
1. Addition of Cu(II) to distilled water	1. Addition of Cu(II) to distilled water
2. Addition of Fe(III)	2. Addition of Fe(III)
3. pH increased to flocculate metals	3. Addition of anions
4. Simultaneous addition of surfactants and anions	4. Addition of surfactants
5. Further adjustment of pH	5. pH adjustment

After each run in which floc removal occurred, samples were taken from the solution for analysis by atomic absorption. The pH was not monitored during the course of a run; however, final pH measurements did not differ from initial values by more than 0.2 pH units.

DATA AND CONCLUSIONS

DIDA proved to be extremely effective in the removal of Cu(II) by precipitate flotation in the presence of $NaNO_3$ (Table 1). The drinking water standard for Cu(II) is 1 ppm (*34*). At a pH of 8.0, even in the presence of 1.0 *M* $NaNO_3$, the residual copper concentration after treatment is less than this level. The ineffectiveness of removal at lower pH's can be attributed to the increased solubility of $Cu(OH)_2$. Removal at lower pH's is achieved by adsorbing colloid flotation with $Fe(OH)_3$, as is shown later. Distribution of surfactant addition during the course of the run and perhaps closer maintenance of optimal pH during flotation would probably further reduce the residual Cu(II) concentration.

Our previous work shows that NLS effectively removes Cu(II) by adsorbing colloid flotation with $Fe(OH)_3$ at $NaNO_3$ concentrations up to 0.25 *M* (*18*). At a pH of 8.0, NLS alone is effective to only 0.075 *M* $NaNO_3$. Thus the chelating surfactant tremendously increases the concentration range of $NaNO_3$ within which efficient flotation can occur.

DIDA also performed quite well in the presence of Na_2SO_4. Removal of Cu(II) to well below the drinking water standard could be obtained by the application of techniques mentioned above. Table 2 shows that good removal can be obtained in the presence of 0.20 *M* Na_2SO_4. Table 3 shows that longer run durations decrease Cu(II) concentrations to below 1 ppm. Wilson and Thackston report that no removal whatsoever can be obtained with NLS above 0.03 *M* Na_2SO_4 (*36*). Thus DIDA is much more effective than NLS at high ionic strengths. We found that Cu removal at pH 9.0

TABLE 1

Precipitate Flotation of Cu(II) with DIDA and NLS[a]

	Residual copper (ppm)					
	Added $NaNO_3$ (*M*)					
pH	0.0	0.20	0.40	0.60	0.80	1.0
5.5	>9	>9	>9	—	--	—
6.0	>9	>9	>9	—	—	—
6.5	>9	>7	>7	>9	—	—
7.0	2.2	2.8	5.3	3.3	3.2	3.9
7.5	1.7	.7	1.4	1.8	.7	.8
8.0	.4	.4	.2	.4	.9	.9

[a] Method 2. Initial Cu(II), 20 ppm; initial Fe(III), 0 ppm; time, 10 min; air flow, ~60 ml/min.

TABLE 2

Adsorbing Colloid Flotation of Cu(II) with $Fe(OH)_3$, DIDA, and NLS[a]

	Residual copper (ppm)				
	Added Na_2SO_4 (M)				
pH	0.0	0.05	0.10	0.15	0.20
6.5	>10	2.6	1.1	1.4	1.4
7.0	1.0	1.8	1.1	1.4	.9
7.5	.5	1.5	1.4	1.1	1.9
8.0	.2	.2	1.2	2.2	1.2
8.5	.1	1.2	.4	1.3	4.4
9.0	.6	>10	1.8	.9	.9

[a] Method 1. Initial Cu(II), 20 ppm; initial Fe(III), 50 ppm; time, 10 min; air flow, ~60 ml/min.

TABLE 3

The Effect of Run Duration on the Adsorbing Colloid Flotation of Cu(II) in the Presence of Na_2SO_4[a] (pH = 8.0)

	Residual copper (ppm)				
	Added Na_2SO_4 (M)				
Time of run (min)	0.0	0.05	0.10	0.15	0.20
10	0.2	0.2	1.2	2.2	1.2
25	0.1	0.8	0.4	0.3	0.8

[a] Method 2. Surfactants: DIDA 25 ppm, NLS 50 ppm. Initial Cu(II), 20 ppm; initial Fe(III), 50 ppm; air flow, ~60 ml/min.

was very erratic; this may be due to adsorption of OH^- on the $Fe(OH)_3$ floc, producing a surface sufficiently negatively charged that the DIDA is not adsorbed.

Table 4 shows that little advantage can be obtained by using one method of mixture preparation over another. Table 5 reveals that Tween 20, a nonionic surfactant, can be used as a carrier foam for DIDA; it seems that no special advantage can be obtained by using an ionic carrier surfactant over a nonionic one.

Table 6 shows that acceptable separation can be obtained with DIDA at a phosphate concentration of 20 ppm; however, at 40 ppm the phosphate has inhibited separation, presumably by adsorption on the floc. We previously reported no removal of Cu(II) with NLS at 0.0025 M Na_2HPO_4 or 4.2×10^{-4} M $(NaPO_3)_6$ (*34*). The concentration of Na_2HPO_4 which prevents separation with DIDA is 4.2×10^{-4} M (40 ppm). Thus

TABLE 4

A Comparison of the Effectiveness of Methods 1 and 2[a]

	Residual copper (ppm)				
	Added Na_2SO_4 (M)				
pH = 8.0	0.0	0.05	0.10	0.15	0.20
Method 1	0.2	0.2	1.2	2.2	1.2
Method 2	0.2	2.3	1.0	0.9	1.6

[a] Surfactants: DIDA 25 ppm, NLS 50 ppm. Initial Cu(II), 20 ppm; initial Fe(III), 50 ppm; time, 10 min; air flow, ~60 ml/min.

TABLE 5

A Comparison of Various Surfactants in the Adsorbing Colloid Flotation of Cu(II) with $Fe(OH)_3$[a] (pH = 8.0)

	Residual copper (ppm)					
	Added $NaNO_3$ (M)					
	0.0	0.20	0.40	0.60	0.80	1.0
NLS	0.2	>10	>10	>10	>10	>10
Tween 20	NR[b]	NR	NR	NR	NR	NR
DIDA and NLS	0.4	0.4	0.2	0.4	0.9	0.9
DIDA and Tween 20	0.0	1.8	0.5	0.9	0.2	0.8

[a] Method 2. Total concentration of surfactants, 75 ppm. Initial Cu(II), 20 ppm; initial Fe(III), 50 ppm; time, 10 min; air flow, ~60 ml/min.

[b] No visible removal.

TABLE 6

The Removal of Cu(II) with DIDA in the Presence of Na_2HPO_4[a]

Method	Duration of run (min)	pH	Phosphate concentration (ppm)	Residual Cu(II) (ppm)
2	10	7.0	20	0.4
2	10	7.5		2.5
2	10	8.0		1.6
2	25	8.0		0.7
2	10	8.0		3.7
1	10	8.0	40	~20
2	10	8.0		~20

[a] Surfactants: DIDA 25 ppm, NLS 50 ppm. Initial Cu(II), 20 ppm; initial Fe(III), 50 ppm; air flow, ~60 ml/min.

TABLE 7

The Removal of Cu(II) with DIDA in the Presence of Udylyte[a]

Duration of run (min)	pH	Udylyte concentration (ppm)	Residual Cu(II) (ppm)
10	7.5	50	2.1
10	8.0		1.0
25	8.0		1.1
10	8.5		1.1
10	7.0	100	1.8
10	7.5		0.5
10	8.0		1.8
10	8.5		0.4
10	7.0	150	1.2
10	7.5		2.9
10	8.0		3.7
25	8.5		2.5
10	8.5		5.8

[a] Surfactants: DIDA 25 ppm, NLS 50 ppm. Method 2. Initial Cu(II), 20 ppm; initial Fe(III), 50 ppm; air flow, ~60 ml/min.

the chelating surfactant does not seem to significantly increase removal of Cu(II) in the presence of Na_2HPO_4. Table 7 shows that DIDA effectively removed Cu(II) in the presence of up to 150 ppm Udylyte, which is promising.

Our results suggest that chelating surfactants may eliminate many of the difficulties from interfering ions which have been noted with NLS. We plan further work with DIDA and $Fe(OH)_3$ with oxalate, carbonate, and fluoride as interfering ions, and we will investigate dodecylmagnesium xanthate as a chelating surfactant.

Acknowledgments

We are indebted to Mr. Ronald P. Robertson for helpful discussions and to Schrader Automotive Products for the use of their atomic absorption spectrophotometer.

REFERENCES

1. A. N. Clarke and D. J. Wilson, *Sep. Purif. Methods*, 7(1), 55 (1978).
2. R. Lemlich (ed.), *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972.
3. P. Somasundaran, *Sep. Purif. Methods*, *1*, 117 (1972).

4. P. Somasundaran, *Sep. Sci.*, *10*, 93 (1975).
5. R. B. Grieves and S. M. Schwartz, *AIChE J.*, *12*, 746 (1966).
6. R. B. Grieves and D. Bhattacharyya, *Sep. Sci.*, *8*, 501 (1973).
7. R. B. Grieves and R. C. Aronica, *Nature*, *210*, 901 (1966).
8. R. B. Grieves and D. Bhattacharyya, *Sep. Sci.*, *1*, 81 (1966).
9. D. Bhattacharyya, J. A. Carlton, and R. B. Grieves, *AIChE J.*, *17*, 419 (1971).
10. R. B. Grieves and D. Bhattacharyya, *J. Appl. Chem.*, *19*, 115 (1969).
11. R. B. Grieves and D. Bhattacharyya, *Sep. Sci.*, *7*, 115 (1972).
12. R. B. Grieves, J. K. Ghosal, and D. Bhattacharyya, *J. Amer. Oil Chem. Soc.*, *45*, 591 (1968).
13. R. B. Grieves and T. E. Wilson, *Nature*, *205*, 1066 (1965).
14. R. B. Grieves and D. Bhattacharyya, *Ibid.*, *207*, 476 (1965).
15. R. B. Grieves and D. Bhattacharyya, *AIChE J.*, *11*, 274 (1965).
16. R. B. Grieves, *Ind. Water Eng.*, *2*, 11 (1965).
17. T. E. Chatman, S. Huang, and D. J. Wilson, *Sep. Sci.*, *12*, 461 (1977).
18. D. J. Wilson, *Foam Flotation Treatment of Heavy Metals and Fluoride-Bearing Industrial Wastewaters*, U.S. Environmental Protection Agency Report, EPA-600/2-77-072, April 1977.
19. Y. S. Kim and H. Zeitlin, *Sep. Sci.*, *7*, 1 (1974).
20. Y. S. Kim and H. Zeitlin, *Ibid.*, *6*, 505 (1971).
21. Y. S. Kim and H. Zeitlin, *Anal. Chem.*, *43*, 1390 (1971).
22. C. Matsuzaki and H. Zeitlin, *Sep. Sci.*, *8*, 185 (1973).
23. D. Voyce and H. Zeitlin, *Anal. Chem. Acta*, *69*, 27 (1974).
24. F. Chaine and H. Zeitlin, *Sep. Sci.*, *9*, 1 (1974).
25. E. Schonfeld and A. H. Kibbey, *Nucl. Appl.*, *3*, 353 (1967).
26. R. P. Robertson, D. J. Wilson, and C. S. Wilson, *Sep. Sci.*, *11*, 569 (1976).
27. B. L. Currin, F. J. Potter, D. J. Wilson, and R. H. French, *Sep. Sci. Technol.*, *13*, 573 (1978).
28. Y. Okamoto and E. J. Chou, *Sep. Sci.*, *10*, 741 (1975).
29. A. N. Clarke and D. J. Wilson, *Ibid.*, *10*, 417 (1975).
30. W. Mitchell, Ph.D. Dissertation, Vanderbilt University, 1975.
31. R. B. Grieves and T. E. Wilson, *Nature*, *205*, 1066 (1965).
32. K. A. Razumov, G. V. Illyuvieva, and T. F. Poltoranina, *Obogashch. Rud.*, *10*, 14 (1965).
33. R. B. Grieves and D. Bhattacharyya, *J. Appl. Chem.*, *19*, 115 (1969).
34. T. E. Chatman, S. Huang, and D. J. Wilson, *Sep. Sci.*, *12*, 461 (1977).
35. *Water Quality Criteria 1972*, *Ecological Research Series*, EPA-R3-73-033, March 1973, p. 64.
36. D. J. Wilson and E. L. Thackston, *Laboratory and Pilot Plant Scale Foam Flotation Treatment of Industrial Wastewaters*, Environmental Protection Agency, Environmental Protection Technology Series.

Received by editor April 9, 1979