Removal of Zinc by Adsorbing Colloid Foam Flotation: Pilot Plant Study

Gregory McIntyre[a]; Juan J. Rodriguez[a]; Edward L. Thackston[a]; David J. Wilson[a]
[a] DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING, VANDERBILT UNIVERSITY NASHVILLE, TENNESSEE

To cite this Article McIntyre, Gregory , Rodriguez, Juan J. , Thackston, Edward L. and Wilson, David J.(1982) 'Removal of Zinc by Adsorbing Colloid Foam Flotation: Pilot Plant Study', Separation Science and Technology, 17: 5, 673 — 682
To link to this Article: DOI: 10.1080/01496398208068559
URL: http://dx.doi.org/10.1080/01496398208068559

SEPARATION SCIENCE AND TECHNOLOGY, 17(5), pp. 673–682, 1982

Removal of Zinc by Adsorbing Colloid Foam Flotation: Pilot Plant Study

GREGORY McINTYRE, JUAN J. RODRIGUEZ,
EDWARD L. THACKSTON,* and DAVID J. WILSON

DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

Zinc was removed from simulated industrial wastewater in a pilot scale foam flotation plant. Sodium lauryl sulfate was used as the carrier surfactant, and $Al(OH)_3$ was found to be preferable to $Fe(OH)_3$ as the adsorbing floc. Optimum pH was 7.5–7.8, at which effluent zinc concentrations below 1 mg/L are easily achieved. The effects of varying the hydraulic loading rate, the surfactant concentration, Al(III) concentration, and ionic strength were studied. Surfactant could be displaced from the sludge in the collapsed foamate by addittion of sodium carbonate.

INTRODUCTION

The removal of trace levels of heavy metals is one of the current problems in the area of advanced waste treatment. Their presence interferes with the efficient operation of biological treatment plants as well as with the disposal of biological sludge, expecially by land application. Furthermore, waste discharges carrying heavy metals can cause serious problems in the receiving waters. Most of these metals are toxic to humans at very low concentrations and, therefore, their maximum admissable concentrations in drinking water supplies are quite small.

The most common method for removal of metal ions is chemical precipitation. There are also a number of other techniques, such as ion exchange, reverse osmosis, electrodialysis, solvent extraction, and foam flotation methods. When one is dealing with dilute wastes, foam flotation appears to possess some advantages; low residual metal concentrations, rapid opera-

*To whom correspondence should be addressed.

tion, low space requirements, flexibility of application at different scales, production of small volumes of sludge highly enriched in the contaminant, and low cost.

For some years we have studied adsorbing colloid foam flotation methods for metals removal. This process involves the addition of a floc-forming substance, usually $FeCl_3$ or alum, to collect the dissolved heavy metals by adsorption and/or coprecipitation as the metal hydroxide is formed by the addition of base. The flocs are subsequently removed by flotation in a column using a surfactant, such as sodium lauryl sulfate (NLS). Previous work has been carried out with different heavy metals at laboratory scale (*1*) and in pilot plant scale equipment using simulated lead-bearing wastewaters (*2*, *3*). Recent work with copper in a pilot plant scale showed excellent results (*4*). In this paper we present the results of a pilot plant study on zinc removal with this technique.

Zinc occurs in the waste streams from steel galvanizing operations, zinc and brass works, electroplating, pigments, mine drainage, etc. Reported concentrations in wastewaters range between 5 and 3000 mg/L. A typical value is about 50 mg/L (*5*).

Much information about the effects of zinc on aquatic life has been reported by different authors. Lloyd (*6*) indicates that, at a zinc concentration of 20 mg/L, cytological breakdown of the gill epithelium of trout occurs in about $2\frac{1}{2}$ h. Cytological changes were also detected in fish exposed to 3 mg/L for about 48 h. Morphological and growth changes in guppies were observed by Crandall and Goodnight working at 1.15 mg/L of zinc (*7*). Mathiessen and Bradfield (*8*) describe the pathological effects of zinc salts and the recovery of fish that have been replaced in clean water.

BPT guidelines for zinc range from 0.1 to 5 mg/L and BATEA effluent limitations range between 0.15 and 3 mg/L. The recommended standard for BPT-equivalent control technology is 1 mg/L and the BAT-equivalent effluent value is 0.5 mg/L (5).

The most common practice in treating zinc wastewaters is alkaline precipitation. Precise pH control is important because of the amphoteric character of zinc. The lowest solubility occurs at pH 10–10.5, but some factors, such as the presence of complexing agents, such as ammonia, seem to displace the optimum pH from the value indicated above (*9*, *10*). Typical final concentrations obtainable through lime or caustic precipitation are in the range of 0.5 mg/L (*10*), even though values of 0.1 to 0.2 mg/L have been reported for influent concentrations between 7 and 10 mg/L (*11*).

The literature reports the use of precipitate and adsorbing colloid flotation techniques for zinc (*12*, *13*). Kim and Zeitlin (*14*) recovered zinc from seawater by this procedure, using $Fe(OH)_3$ flocs and the cationic surfactant dodecylamine; 94% recovery was obtained at pH 7.5.

Laboratory experiments with simulated zinc-bearing wastewaters showed that residual zinc levels in the range of 0 to 0.2 mg/L could be obtained with adsorbing colloid foam flotation, using alum and NLS, in a pH range between 7.7 and 8.3 (*1, 13*).

EXPERIMENTAL PROCEDURES

The foam flotation pilot plant used in this work has been fully described in earlier papers (*2, 3*). The apparatus is diagrammed in Fig. 1.

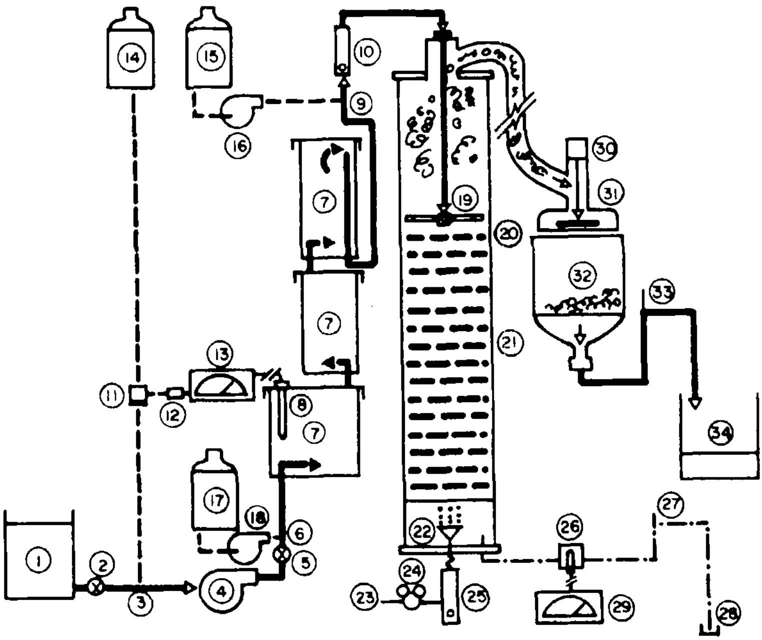
Simulated wastewater containing Zn(II) is pumped through the system at the desired flow rate. Floc-forming reagent and surfactant are fed at the required rate by means of two Masterflex feed pumps; pH is adjusted by adding 0.25 *N* NaOH solution which flows through a solenoid valve connected to a Horizon 5650 pH controller. Air is supplied at the bottom of the column through a porous glass dispersion head at a measured flow rate. Effluent leaves the column from the bottom, and the foam flows from the top through a rotating disk foam breaker. Effluent pH is continuously measured using a glass electrode placed in the exit pipeline and connected to a Sargent Welch LS model pH meter. Simulated wastewaters are prepared by dissolving $ZnSO_4 \cdot 7H_2O$ in tap water in a 1-m^3 storage tank. $Al(OH)_3$ is used as adsorbent, Al(III) being supplied to the system as $Al_2(SO_4)_3 \cdot 18H_2O$ solution. $Fe(OH)_3$ was also tested as an adsorbent; $FeCl_3$ was used to prepare the Fe(III) feed solution. NLS is used as the surfactant.

Effluent samples are collected and analyzed for zinc by atomic absorption using an Aztec Mark II atomic absorption spectrophotometer at a wavelength of 213.8 mm. NLS analyses were also performed in some samples by the methylene blue–chloroform extraction method for anionic surfactant (*15*).

RESULTS AND DISCUSSION

A series of runs was performed to determine the optimum operating parameters for Zn(II) removal. First of all, selection of adsorbent was required. Although previous work in batch laboratory scale demonstrated that $Fe(OH)_3$ was not successful in that respect (*1, 13*), this was checked at pilot plant scale; $Al(OH)_3$ was also checked. Table 1 shows the results of these preliminary tests for adsorbent selection. As observed, the efficiency of $Al(OH)_3$ for Zn(II) removal is substantially higher than that of $Fe(OH)_3$, and in the rest of this work $Al(OH)_3$ was used as adsorbent.

Optimum pH for Zn(II) removal with $Al(OH)_3$ and NLS was found to be in the range of 7.5 to 7.8 as Table 2 shows; in this, pH values refer to the effluent pH. Zn(II) levels in the effluent below 1 mg/L are easily achievable



1. Waste Tank
2. Waste Tank Valve
3. NaOH Injection Tee
4. Main Pump
5. Flow Control Valve
6. $FeCl_3$ Injection Tee
7. Mixing Chamber
8. Control pH Electrode
9. NLS Injection Tee
10. Waste Flow Rotometer
11. NaOH Solenoid Valve
12. Electrical Junction Box
13. Control pH Meter
14. NaOH Tank
15. NLS Tank
16. NLS Feed Pump
17. $FeCl_3$ Tank
18. $FeCl_3$ Feed Pump
19. Flow Dispersion Head
20. Column
21. Baffles
22. Air Diffuser
23. Air Supply Line
24. Air Pressure Regulator
25. Air Flow Rotometer
26. Monitoring pH Electrode
27. Column Liquid Level Control
28. Effluent Line
29. Monitoring pH Meter
30. Foam Breaker Motor
31. Foam Breaker
32. Clarifier
33. Clarifier Liquid Level Control
34. Broken Foam Container

FIG. 1. Schematic diagram of 30-cm pilot plant.

in this range, with 0.5 mg/L obtained at 7.6 pH; higher pH values lead to a decrease in system efficiency because of poorer flotation of the flocs.

Table 3 shows the influence of increasing hydraulic loading on Zn(II) removal. A NLS concentration of 40 mg/L was used in these runs. As can be

TABLE 1

Adsorbent Colloid Selection for Zn(II) Removal[a]

Adsorbent	Effluent pH	Residual Zn(II) (mg/L)
$Fe(OH)_3$	7.00	6.2
$Fe(OH)_3$	7.10	5.9
$Fe(OH)_3$	7.20	5.8
$Al(OH)_3$	7.00	2.5
$Al(OH)_3$	7.10	2.1
$Al(OH)_3$	7.30	1.2

[a]All runs made with initial Zn(II) at 20 mg/L, Fe(III) or Al(III) at 100 mg/L, NLS at 30 mg/L, influent flow rate at 6.9 $m^3/m^2 \cdot h$ (2.8 gal/min·ft^2), and air flow rate at 12.9 $Nm^3/m^2 \cdot h$ (30 SCFH).

seen, doubling the hydraulic loading had very little effect on the system performance. Zn(II) levels below 1 mg/L were consistently obtained at the maximum hydraulic loading achievable in the pilot plant.

Increasing NLS concentration above 30 mg/L seems to have some beneficial effect on Zn(II) removal, although this is not very substantial, as shown in Table 4. A NLS concentration below 30 mg/L leads to a decrease of the flotation system efficiency.

Figure 2 shows the influence of Al(III) dose on effluent zinc concentration for three different Zn(II) influent concentrations. A general correlation between the amount of zinc removed per unit mass of aluminum, $x =$ mg Zn/mg Al(III), and the residual zinc concentration, C (mg Zn/L), can be

TABLE 2

Effect of pH on Zn(II) Removal with $Al(OH)_3$ and NLS[a]

Effluent pH	Residual Zn(II) (mg/L)
7.00	2.5
7.10	2.1
7.30	1.2
7.60	0.5
7.80	0.8
8.00	1.2
8.20	2.1
8.50	3.3

[a]All runs made with initial Zn(II) at 20 mg/L, Al(III) at 100 mg/L, NLS at 30 mg/L, influent flow rate at 6.9 $m^3/m^2 \cdot h$ (2.8 gal/min·ft^2), and air flow rate at 12.9 $Nm^3/m^2 \cdot h$ (30 SCFH).

TABLE 3

Effect of Increasing Hydraulic Loading on Zn(II) Removal[a]

Hydraulic loading ($m^3/m^2 \cdot h$)	Effluent pH	Residual Zn(II) (mg/L)
6.9	7.30	0.9
10.4	7.30	1.4
13.8	7.30	1.5
6.9	7.50	0.6
13.8	7.50	0.8

[a]All runs made with initial Zn(II) at 20 mg/L, Al(III) at 100 mg/L, NLS at 40 mg/L, and air flow rate at 12.9 $Nm^3/m^2 \cdot h$ (30 SCFH).

established from the experimental data presented in Fig. 2. These data conform closely to a power law, $x = aC^b$, for $a = 0.3$ and $b = 0.8$, giving a correlation coefficient, r, of 0.974. The value of r that can be expected at a 1% level of significance from observations drawn by chance when there is no corrleation is 0.798. Then, our correlation coefficient, which is substantially higher, allows us to conclude, with a probability higher than 99%, that these data conform to the equation. This equation can be used to calculate the Al(III) dose required to obtain a specified residual Zn(II) concentration, knowing the influent Zn(II) concentration, provided this is not substantially different from the range studied and the operating pH is close to the one used in these experiments (7.6).

The effect of Fe(III) dose on effluent copper concentration is shown in Fig. 3 for three influent Cu(II) concentrations; the same trends are observed here

TABLE 4

Effect of NLS Concentration on Zn(II) Removal[a]

NLS Concentration (mg/L)	Effluent pH	Residual Zn(II) (mg/L)
20	7.30	2.5
30	7.30	1.2
40	7.30	0.9
30	7.60	0.5
40	7.50	0.6

[a]All runs made with initial Zn(II) at 20 mg/L, Al(III) at 100 mg/L, NLS at 30 mg/L, influent flow rate at 6.9 $m^3/m^2 \cdot h$ (2.8 $gal/min \cdot ft^2$), and air flow rate at 12.9 $Nm^3/m^2 \cdot h$ (30 SCFH).

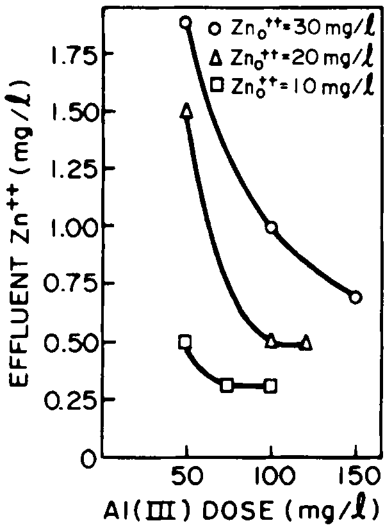


FIG. 2. Effluent Zn^{2+} concentration vs Al(III) dose.

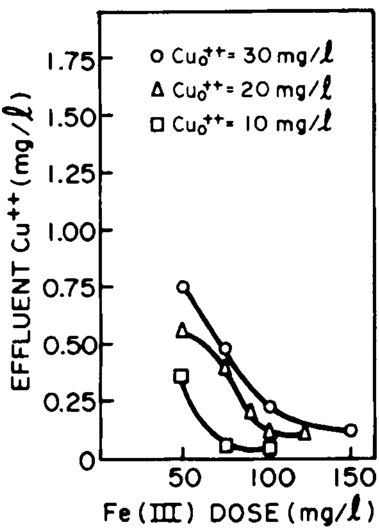


FIG. 3. Effluent Cu^{2+} concentration vs Fe(III) dose.

as were seen with the investigation of the effect of Al(III) concentration on zinc removal.

Ionic strength has a detrimental effect on Zn(II) removal, although this effect is not significant for a 0.05 *M* NaCl concentration. Table 5 summarizes the results for these experiments.

NLS analyses were also performed on some effluent samples. Values ranging from 12 to 16 mg/L were obtained when the plant was operating at 30 mg/L NLS and 100 mg/L Al(III) in the optimum pH range. The amount of foamate was typically about 12% that of the influent wastewater, on a mass basis. The foamate consisted of a clear liquid subnatant and a floating white scum. Samples were treated with different amounts of 0.25 *N* Na_2CO_3 solution, stirred, and allowed to settle. The final pH was controlled because of its influence on the solubility of zinc and aluminum hydroxides, both of which were amphoteric. One hundred mililiters of carbonate solution per liter of foamate was found to be enough to treat it. This yielded a settled sludge and a clarified·liquid with practically no Zn(II) (zero values were found by AA) when the pH was maintained close to 10.

CONCLUSIONS

Removal of Zn(II) by adsorbing colloid foam flotation using $Al(OH)_3$ and NLS was carried out at a pilot plant scale. Zn(II) levels around 0.5 mg/L were obtained under optimum conditions for an influent concentration of 20 mg/L; at 10 mg/L influent concentration, residual Zn(II) levels of 0.3 mg/L were achieved.

Table 6 lists the optimum operating parameters as determined in our 30-cm continuous flow pilot plant.

TABLE 5

Effect of Increasing Ionic Strength (I.S.) on Residual Zn(II) (mg/L)[a]

	I.S.		
Effluent pH	0 *M*	0.05 *M*	0.1 *M*
7.00	2.5	2.7	4.2
7.30	1.2	1.4	2.9
7.60	0.5	0.5	1.3

[a]All runs made with initial Zn(II) at 20 mg/L, Al(III) at 100 mg/L, NLS at 30 mg/L, influent flow rate at 6.9 $m^3/m^2$4 § h (2.8 gal/min · ft^2), and air flow rate at 12.9 $Nm^3/m^2 \cdot h$ (30 SCFH). NaCl was used to increase ionic strength.

TABLE 6

Optimum Operating Parameters for 30-cm Pilot Plant

Parameter	Value
pH	7.50–7.80
Al(III) (mg/L)	100 [for 20 mg/L influent Zn(II)]
NLS (mg/L)	30–40
Hydraulic loading ($m^3/m^2 \cdot h$)	6.9–13.8 (2.8–5.7 gal/min·ft^2)
Air flow rate ($Nm^3/m^2 \cdot h$)	12–13 (30 SCFH)

Acknowledgment

This work was supported by a grant from the Office of Water Research and Technology.

REFERENCES

1. D. J. Wilson and E. L. Thackston, *Foam Flotation Treatment of Industrial Wastewaters: Laboratory and Pilot Scale*, EPA-600/2-80-138, June 1980.
2. E. L. Thackston, D. J. Wilson, J. S. Hanson, and D. L. Miller, Jr., "Lead Removal with Adsorbing Colloid Flotation," *J. Water Pollut. Control Fed.*, *52*(2), 317 (1980).
3. M. A. Slapik, E. L. Thackston, and D. J. Wilson, "Improvements in Foam Flotation for Lead Removal," in *Proceedings, 35th Industrial Waste Conference*, Ann Arbor Science, Publishers, Ann Arbor, Michigan, 1980, p. 694.
4. G. T. McIntyre, J. J. Rodriguez, E. L. Thackston, and D. J. Wilson, "Copper Removal by an Adsorbing Colloid Foam Flotation Pilot Plant," *Sep. Sci. Technol.*, *17*, 359 (1982).
5. J. W. Patterson, "Control of Inorganic Priority Pollutants," in *Design for the Eighties*, Vanderbilt University Engineering School, Nashville, Tennessee, March 1980.
6. R. Lloyd, "The Toxicity of Zinc Sulfate to Rainbow Trout," *Ann. Appl. Biol.*, *48*, 84 (1960).
7. C. A. Crandall and C. J. Goodnight, "Effects of Sublethal Concentrations of Several Toxicants on Growth of the Common Guppy, *Lebistes reticulatus*," *Trans. Am. Microsc., Soc.*, *82*, 59 (1963).
8. P. Matthiessen and A. E. Bradfield, "The Effects of Dissolved Zinc on the Gills of the Stickleblack, *Gasterosteus aculeatus*," *J. Fish. Biol.*, *5*, 607 (1973).
9. W. W. Eckenfelder, Jr., *Principles of Waste Water Quality Management*, CBI, Boston, 1980.
10. K. H. Lanouette, "Heavy Metals Removal," *Chem. Eng.*, *84*(22), 73 (1977).
11. Y. Argaman and C. L. Weddle, "Fate of Heavy Metals in Physical-Chemical Treatment Processes," *AIChE Sym. Ser.*, *70*(136), 400 (1977).
12. A. J. Rubin and W. L. Lapp, "Foam Fractionation and Precipitate Flotation of Zinc(II)," *Sep. Sci.*, *6*(3), 357 (1971).
13. R. P. Robertson, D. J. Wilson, and C. S. Wilson, "The Adsorbing Colloid Flotation of Lead(II) and Zinc(II) by Hydroxides," *Ibid.*, *11*(6), 569 (1976).

14. Y. S. Kim and J. Zeitlin, "The Separation of Zinc and Copper from Seawater by Adsorbing Colloid Flotation," *Ibid.*, *7*(1), 1 (1972).
15. *Standard Methods for the Examination of Water and Wastewater*, 14th ed., APHA, AWWA, WPCF, Washington, D.C., 1976.

Received by editor July 23, 1981