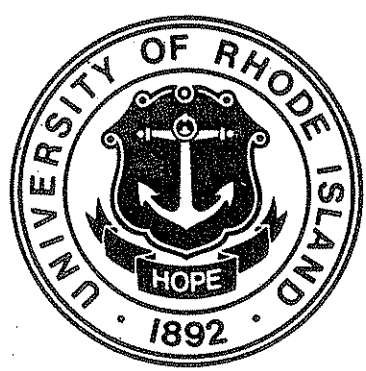


RI A-073
1981

WATER REUSE by METAL REMOVAL
from
INDUSTRIAL PLATING EFFLUENTS



RHODE ISLAND
WATER RESOURCES CENTER

COMPLETION REPORT

Water Reuse by Metal Removal from Industrial Plating Effluents

Project No. A-073-RI

Agreement No.: 14-34-0001-1142

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Research Category: VF

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WATER REUSE BY METAL REMOVAL FROM INDUSTRIAL PLATING EFFLUENTS

Objective

The purpose of this project was to study the removal of various metals in solution (chromium, cadmium, zinc, nickel, etc.) from liquid wastes discharged from the metal-plating and jewelry industries. The process which was used for this investigation employed microgas dispersions for flotation of the various metals. The process had been successfully used in a previous project (A-067-RI) for the removal of manganese from potable water.

Background

The metals found in the metal-plating and jewelry industry waste-waters can contribute significantly to stream pollution either directly or indirectly. Their direct effect is to destroy the stream flora and fauna. Indirectly, they may destroy the various organisms essential to the operation of a conventional sewage treatment plant and thereby render the plant ineffective. Since many of these metals are not removed by conventional processes used by municipal sewage treatment plants and since many of these metals in fact destroy the effectiveness of conventional processes, the wastewaters from plating and jewelry-making processes, in many instances, are not allowed to be discharged directly to municipal sewer systems. This means that these wastewaters must be pre-treated for removal of the metals and other possible toxic materials prior to discharge to the municipal sewer system.

Although technology is available for treating these wastewaters for reduction of the metals to any desired concentration, the cost of treatment is relatively high and therefore only the larger industrial plants can afford to employ this technology. There is a great need for a more economical system

of treatment, particularly for the smaller plating and jewelry facilities. Many of the smaller plants are still discharging directly into municipal sewer systems, but municipal, state, and federal regulations will soon put an end to this practice. The jewelry industry must be in compliance with the federal standards shown in Table 1 in the near future. This means that pre-treatment to a desirable level must be accomplished before discharge to a municipal system.

On the local level, the City of Providence sewage treatment facility has been accepting wastes from a large number of plating and jewelry companies without pretreatment for many years. High concentrations of metals from these industrial wastes have been found in the Providence River and Narragansett Bay waters and sediments. Therefore, the Environmental Protection Agency will soon require that a maximum concentration level be set on various metals contained in the effluent discharged from the Providence treatment plant. The only way this result may be obtained is by pretreating the plating and jewelry wastewaters for removal of the metals before discharge to the sewer system. Since most of the companies involved in the industry are small, this means a more economical method of treatment than is currently available must be found if the companies are to survive.

Experimental Methods

Figure 1 is a schematic of the system used to produce the MGD and to effect removal of the various metals. The foam producing equipment consisted of a reservoir, paddle pump, heat exchanger, and venturi generator. A surfactant solution was made up to the desired concentration (usually 300 ppm) and was then added to the reservoir. The pump was used to circulate the dispersion throughout the system. Since the quality of the dispersion is

Table 1
Federal Standards(1)

<u>Pollutant</u>	Process Water Less than 10,000 GPD (PPM)		Process Water Greater than 10,000 GPD (PPM)	
	<u>1 day</u>	<u>30 days</u>	<u>1 day</u>	<u>30 day</u>
Total Cyanide	-	-	0.8	0.23
Amenable cyanide	5.0	1.5	-	-
Copper	-	-	4.5	1.8
Nickel	-	-	4.1	1.8
Total chromium	-	-	7.0	2.5
Zinc	-	-	4.2	1.8
Lead	0.6	0.3	0.6	0.3
Cadmium	1.2	0.5	1.2	0.5
Silver	-	-	1.2	0.5
Total Metals	-	-	10.5	5.0

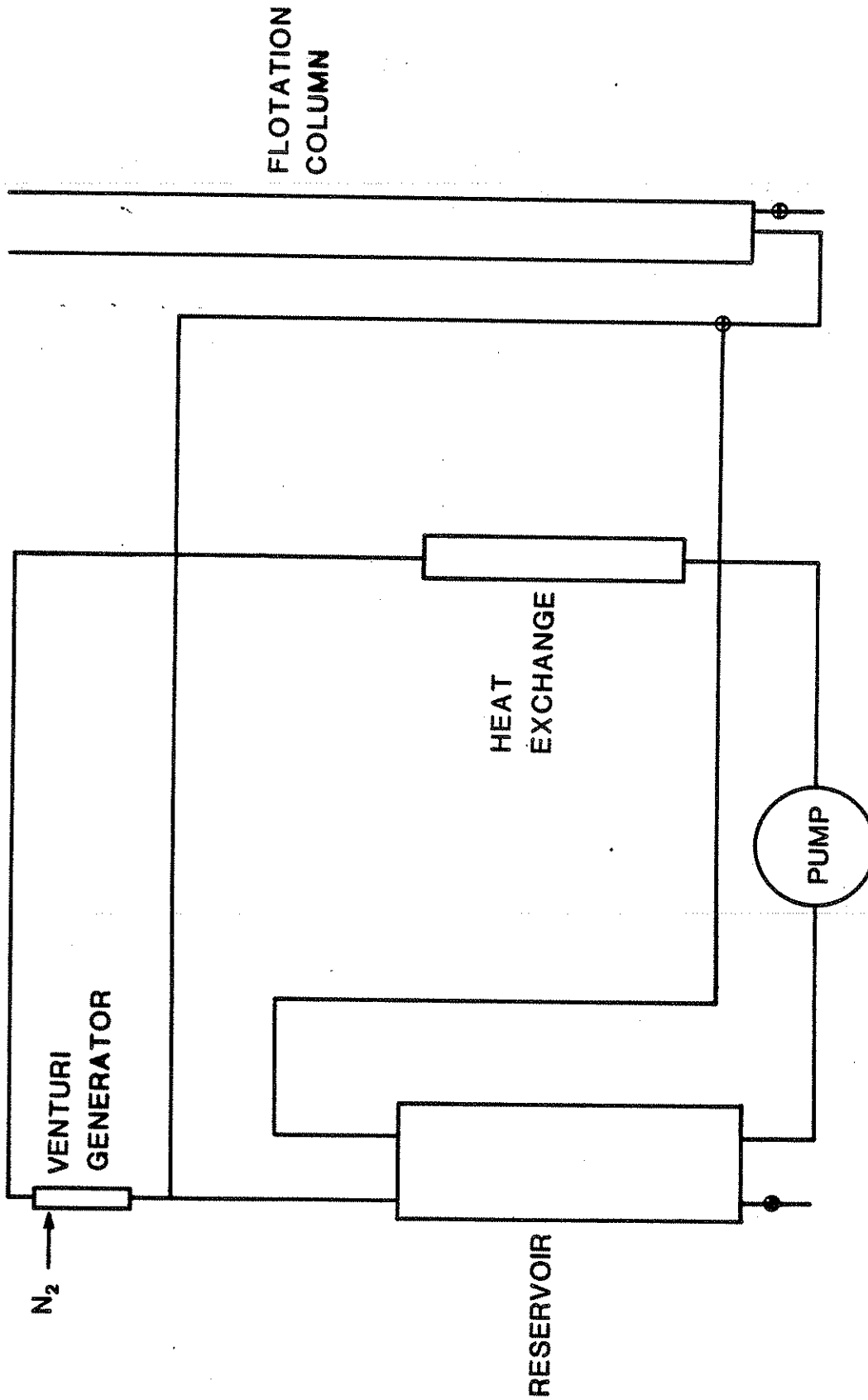


FIGURE 1. MICROGAS DISPERSION GENERATOR

obviously effected by temperatures much above room temperature, it was necessary to include a heat exchanger in the system. From the heat exchanger the dispersion, or surfactant solution at startup, passed through the generator which formed and maintained the dispersion. In the generator, Figure 2, the surfactant passed from an area of low velocity and high pressure, A, to a point of high velocity and low pressure, C. At point C, nitrogen gas or air was introduced and passed through the space, B. The space B, is similar to a loose ground-glass fitting. By this mechanism, the dispersion was formed. Once the foam was formed, the generator acted to maintain a constant foam quality by breaking up larger bubbles as they passed through. From the generator, the dispersion was circulated back to the reservoir. A baffle was present in the reservoir to evenly distribute the dispersion back into the reservoir. A secondary loop fed the MGD dispersion to a flotation column where sample solutions to be treated had been added. The flotation column measured 5.1 cm I.D. and 90 cm in height. The MGD foam entered the bottom of the column through a constriction (eyedropper).

Surfactant solutions which were used had a concentration of 300 ppm of either ethylhexadecyldimethylammonium bromide (EHDA), or sodium dodecylbenzene sulfonate (DBSS). These solutions were used to form the bubble structure. No further addition of surfactants was required.

Solutions of the metals were prepared by adding nitric acid to appropriate amounts of copper sulfate, chromium trioxide, lead nitrate, nickel nitrate, and zinc metal. Adjustments to pH were made under constant stirring, by adding required amounts of either sodium hydroxide or nitric acid. The flotation column was then filled with the metal solution and the MGD dispersion was introduced at the bottom of the column. Some runs were made using chitosan as a chelating or complexing agent. The same procedure was used in these runs except that prior to pH adjustment, the sample solutions

**SURFACTANT
SOLUTION**

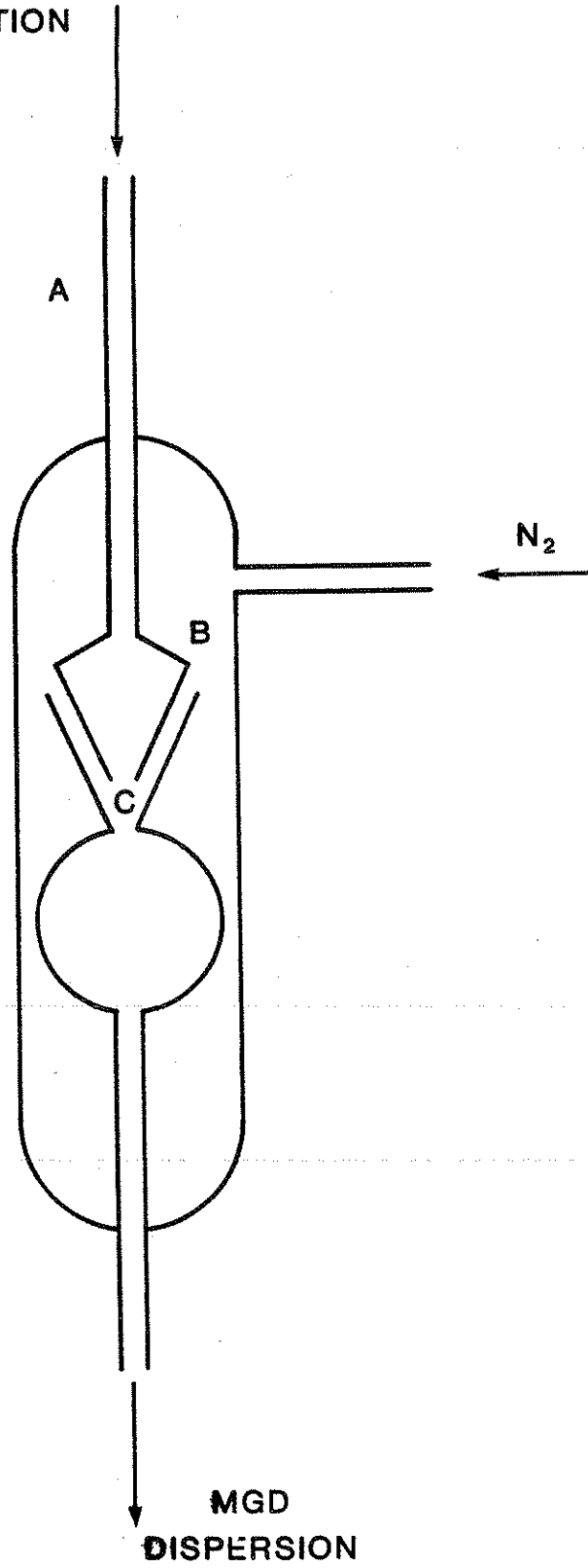


FIGURE 2. VENTURI GENERATOR

were made up to 6.0 ppm chitosan. For each run, a sample of MGD dispersion was taken to determine the quality which was defined as the percent entrained gas in the dispersion. Before making the initial run of each series of runs, it was necessary to circulate the MGD dispersion for about ten to fifteen minutes to assure a constant foam quality. A good MGD dispersion typically entrained about 50-65% gas. Nitrogen gas was introduced into the generator at about 25°C and 24 psig at a rate of 0.29 l/min. No difference in foam quality was found when air was used in place of the nitrogen gas. After the dispersion passed through the liquid column, a final liquid height was read, from which a dilution factor was calculated (initial height/final height). Samples of the treated water were withdrawn from an outlet at the bottom of the column, acidified, and quantified on an atomic absorption unit. Percent removals were obtained as follows.

$$\% \text{ Re} = \frac{\text{CI} - \text{CF}}{\text{DIL}} (100)$$

CI = Initial concentration of metal

CF = Final concentration of metal

DIL = Dilution factor

Results

Percent removals have been calculated and are shown in Figures 3-11. Operating conditions and initial metal concentrations are also noted. The residual concentrations obtained in each of these runs are presented in Tables II and III.

Copper (Cu)

In aqueous solution at low pH, the cupric ion (Cu^{++}) was the stable ion present. This ion is highly soluble in water so the main mechanism of

removal at low pH was ion flotation. In Figure 3, this can be seen as the pH region less than about 6. As alkali was added to the solution, the hydroxide was formed, $\text{Cu}(\text{OH})_2$. This species corresponds to the pH region greater than approximately 6 or 7. As shown in Figure 3, 100% removal was attained at high pH. The vertical portion of the curve at pH 7 corresponds to the point where the removal mechanism changes from ion to precipitate flotation.

Nickel (Ni)

Removal of nickel is plotted in Figure 4. In aqueous solution nickel is present in the plus two state, Ni^{++} . When the pH is less than about 9, nickel is highly soluble, and ion flotation is the predominant mechanism of removal. As alkali is added to increase the pH, insoluble nickel hydroxide, $\text{Ni}(\text{OH})_2$, is formed. The vertical portion of the curve, located at a pH of about 8.5 to 10, represents a change from ion to precipitate flotation.

Zinc

At low pH, less than 6.5, zinc exists in solution as Zn^{++} ions, and therefore ion flotation is the predominant mechanism of flotation in this pH range. Removal is plotted in Figure 5. The vertical portion of the curve is where the removal mechanism changes from ion to precipitate flotation. At a pH of about 8.5, $\text{Zn}(\text{OH})_2$ is the main species present. Increasing the pH beyond 8.5 resulted in lower removal, since the precipitate became more soluble. This increased solubility is due to the formation of anionic hydroxo complexes such as $\text{Zn}(\text{OH})_3^-$, and $\text{Zn}(\text{OH})_4^{=}$ (1).

Lead (Pb)

Figure 6 shows the percent removal obtained for lead. At pH less than 6 lead is present as Pb^{++} ions. In this pH region, ion flotation is

the main mechanism of removal. As alkali is added lead hydroxide is formed. This hydroxide is slightly soluble and exists as a giant molecule with no definite composition (2). The concentration of the solution, along with any impurities which may be present will effect both the composition and solubility of the precipitate. Consequently, there can be a reproducibility problem with this metal. Again, the vertical portion of the curve represents a change in mechanism from ion to precipitate flotation. Maximum removal was attained at pH 9.5. As the pH is increased, removal decreases due to the formation of soluble plumbites (2).

Chromium (Cr)

Figure 7 shows percent removal vs. pH for the flotation of chromium. Chromium, unlike the other metals studies, is present in solution as an anion, the species present being dependent on pH. At a pH less than 1, the main species present is H_2CrO_4 . In the pH range between 2 and 6 $HCrO_4^-$ and $Cr_2O_7^{2-}$ are in equilibrium and above a pH of about 8, CrO_4^{2-} is present (1). All of these species are soluble in water and nowhere in the pH range is there any precipitation. Consequently, the main mechanism of removal throughout the entire pH range was ion flotation, and as shown, removal of only 26% was achieved. Maximum removal was attained in a pH range between 2.5 and 6.5. Beyond this, removals fell off, possibly due to the formation of the unfavorable CrO_4^{2-} ion, which will require a stoichiometric ratio of 2:1 surfactant to metal ion. There may also have been competition for the surfactant by the hydroxyl groups which were now in high concentration.

Since the removal of chromium was very poor when using the procedure used for the removal of the other metals, a modification was tried. The hexavalent chromium was reduced to the trivalent state by the addition of sodium sulfite under acidic conditions. Results are shown in Figure 11.

Mixture of Metals

Since it is unlikely that only one metal will exist in a waste to be treated, a mixture of several metals was examined to determine the effect on removal. Figure 8 shows the percent removal obtained from a mixture of Cu, Cr, Ni, Zn, and Pb. It can be seen that although the same general trend was followed, with higher removal being obtained at higher pH, the shapes of the curves differ from those of the pure components. This result was to be expected, since in a mixture of these metals, each metal species can be effected by every other metal in solution. Each metal is being removed from an environment different from that of the pure solution. There are also several anions present which have an effect on removal. As alkali is added and precipitation occurs, the composition of the precipitate is no longer easily described. The possibility of complexes between different metals and different anions make it impossible to guess the composition of the resulting precipitate. One obvious reaction, however, is that between chromium and lead, which gives precipitates of insoluble lead chromates. This may possibly explain the high removal of lead obtained in the mixture.

Wastewater Sample

Figure 9 shows the percent removal obtained from an actual wastewater sample obtained from a local plating firm. Again, the same general trend is observed with increased removals being realized as precipitate flotation begins. A slight similarity between the curves in Figure 9 and the corresponding curves in Figure 8 can be noted.

Wastewater with Chitosan

Figure 10 shows the data obtained for the flotation of metals from a plating firms wastewater using chitosan as a chelating or complexing agent.

Comparison of Figure 10 with Figure 9 indicates a much more efficient removal is obtained using chitosan as a chelating agent. Peak removals were obtained at a pH of 7.9 for all the metals except nickel which peaked at pH 9. Removal of copper, iron and zinc exceeded 90% with removal of Cu reaching 100%. Removal of chromium reached 50% as compared to only 15% obtained without chitosan.

Conclusions

It has been demonstrated that batch flotation of various metals from aqueous solution is an effective method for removal of these metals from wastewater. Solutions of single metals as well as solutions containing several metals have been treated and significant removal has been obtained. In addition, actual plating wastes containing several metals have been successfully treated. The most efficient system employed the use of a cationic surfactant with precipitate flotation.

Recommendations

Further study should be undertaken to determine the effect of operating conditions such as bubble feed rate, column size, and the use of other surfactants upon the degree of removal of the various metals. The use of chitosan and possibly other complexing agents should also be further investigated. The possibility of using the MGD dispersion in a continuous flow process should be investigated.

Publications

A paper based upon the work done during this project has been accepted for publication in Separation Science and Technology. The title of the paper is "Removal of Heavy Metals from Aqueous Solutions Using Microgas Dispersions."

Table II
Metal Removal from Synthesized Solutions of
Pure and Mixed Metal Ions.***

	Individual Solutions			Synthesized Mixture		
	Initial Conc.	Final Conc.	% Removal	Initial Conc.	Final Conc.	% Removal
Cu	8.46	0.00	100.0	9.55	0.15	98.4
Ni	19.50	0.30	98.5	9.79	0.46	95.3
Zn**	18.11	0.90	95.1	9.46	0.48	94.9
Cr	10.10	7.40	26.7	3.80	3.01	20.8
Pb	10.92	2.28	79.1	0.233	0.00	100.0

**Surfactant: DBSS (300 ppm)

***Surfactant: EHDA (300 ppm)

Table III
Metal Removal from Industrial Effluent with
and without Chitosan***

	Industrial Effluent			Industrial Effluent with Chitosan		
	Initial Conc.	Final Conc.	% Removal	Initial Conc.	Final Conc.	% Removal
Cu	1.242	0.19	84.5	2.176	0.00	100.0
Ni	1.175	0.55	53.2	1.380	0.54	60.7
Fe	0.223	0.052	76.7	0.227	0.008	96.5
Cr	2.617	2.25	14.1	3.876	1.90	50.9
Zn	0.139	*	*	0.372	0.02	94.6

*Sample Lost

***Surfactant: EHDA (300 ppm)

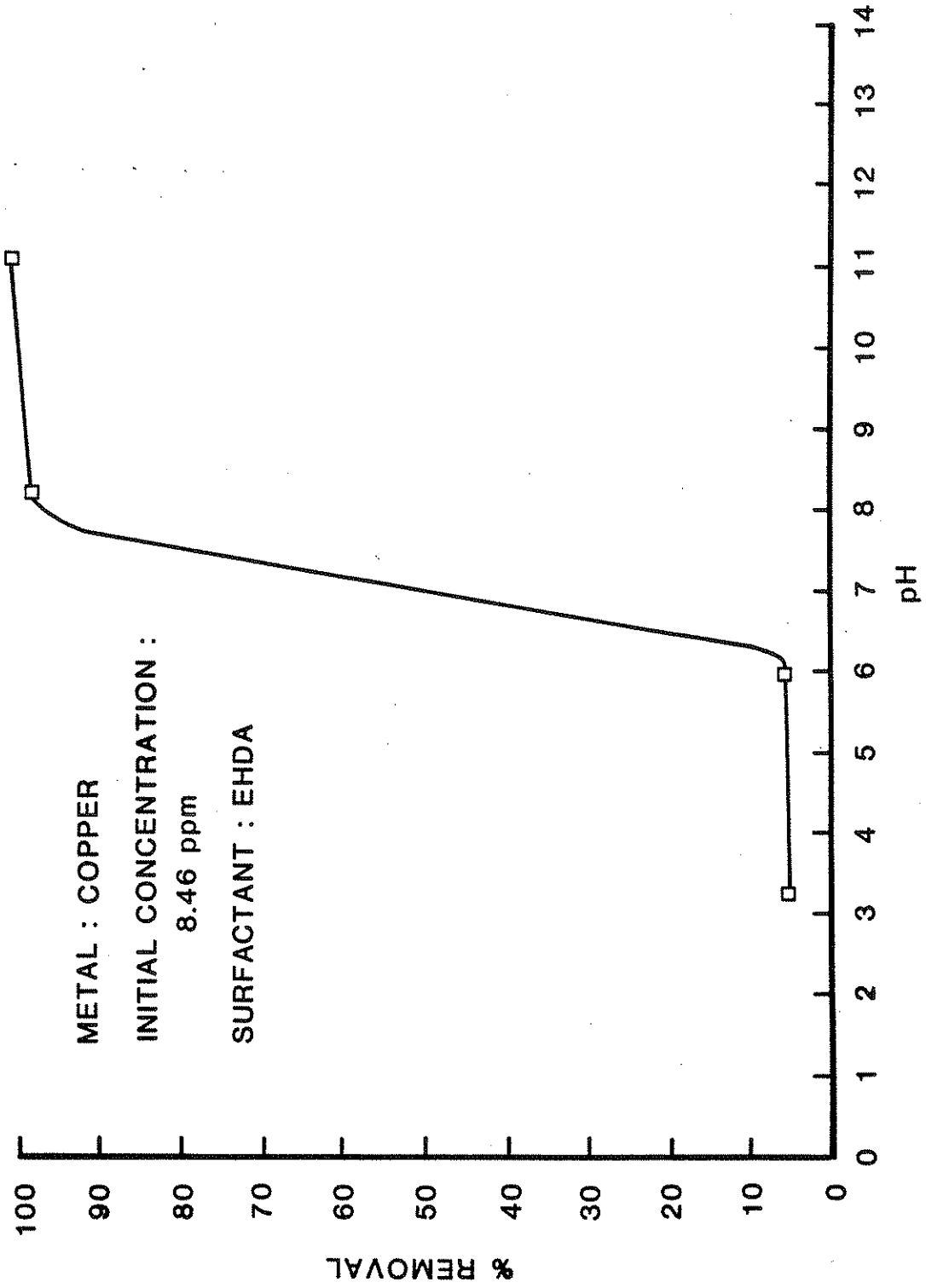


FIGURE 3. COPPER REMOVAL

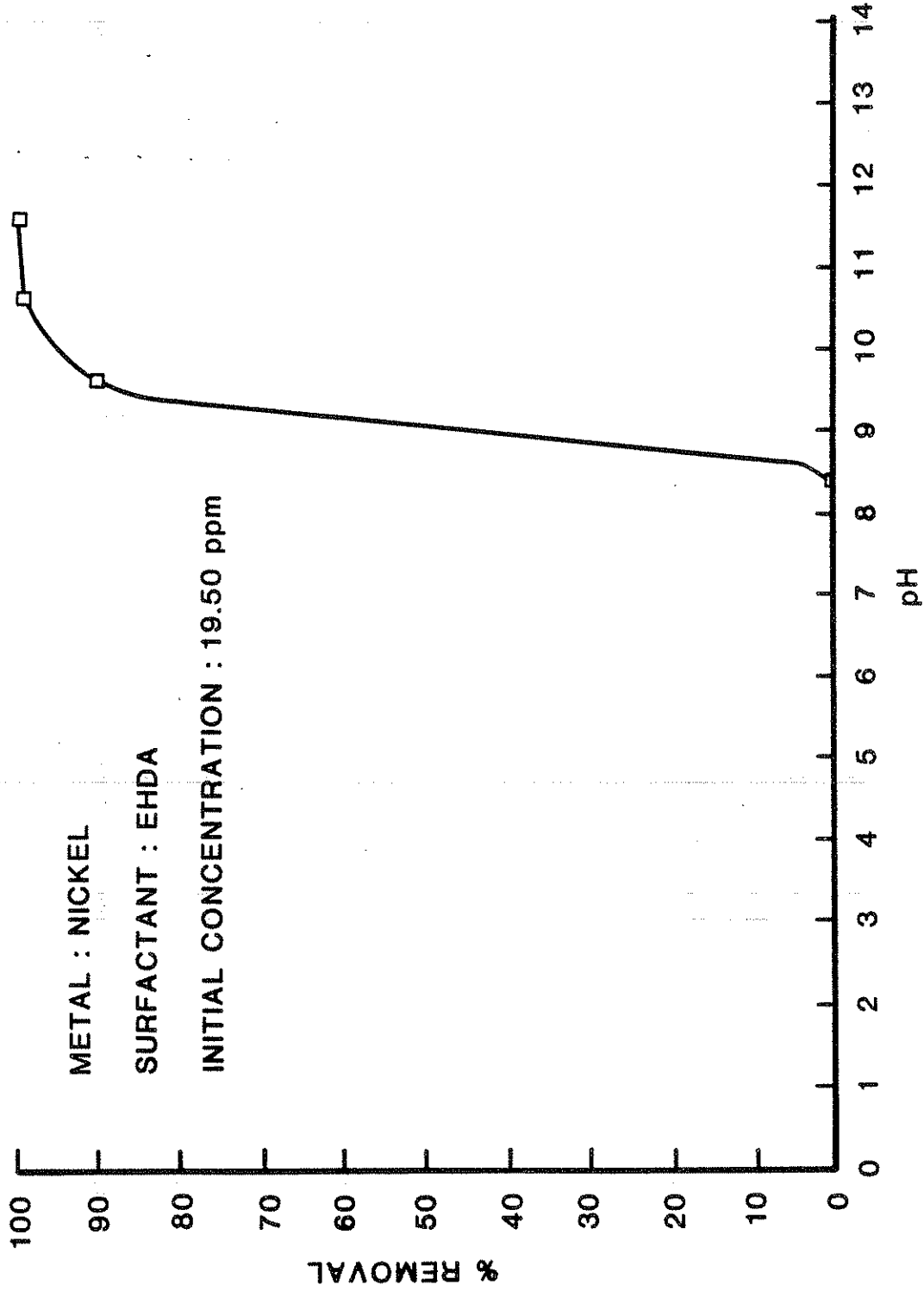


FIGURE 4. NICKEL REMOVAL

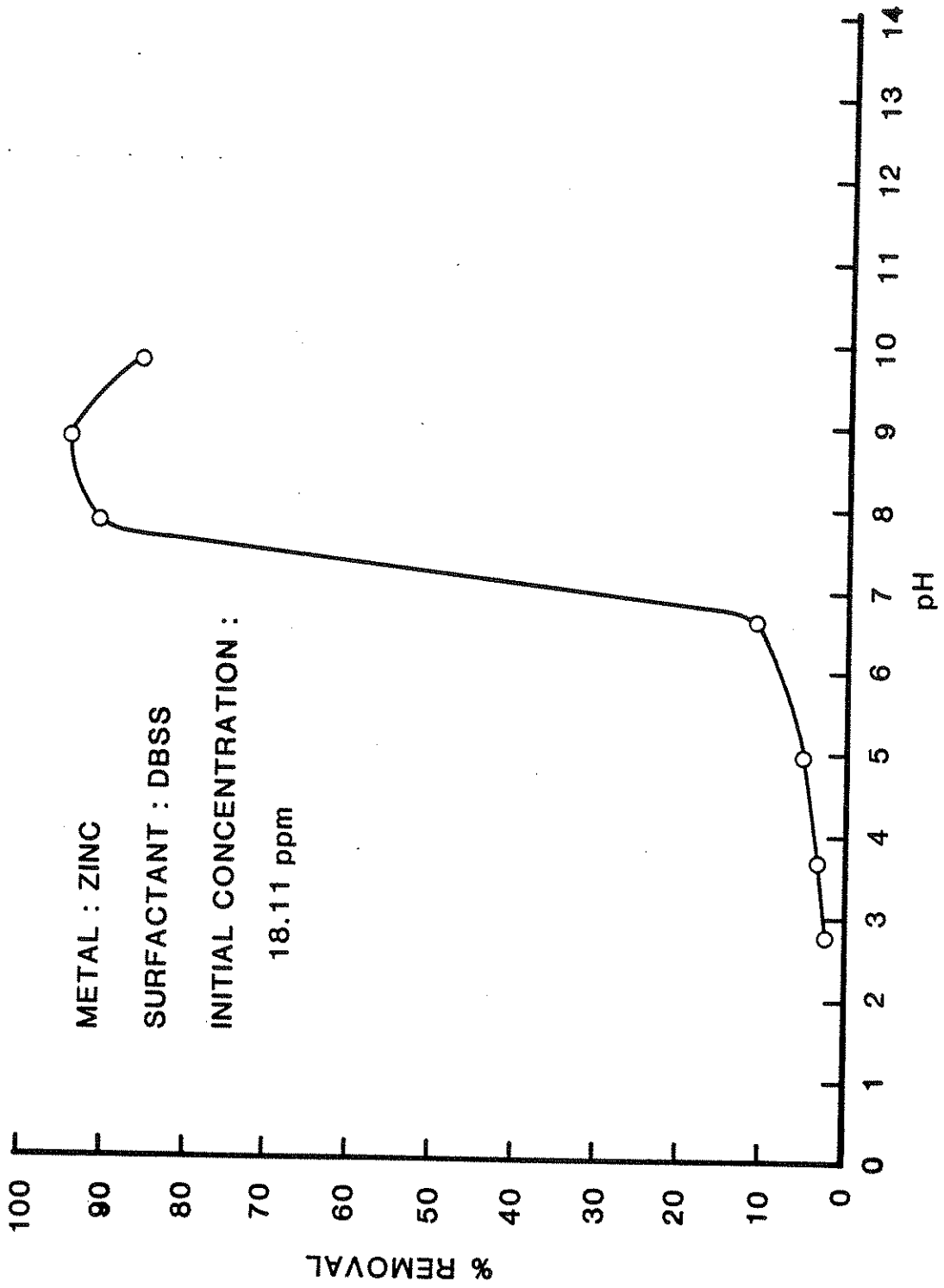


FIGURE 5. ZINC REMOVAL

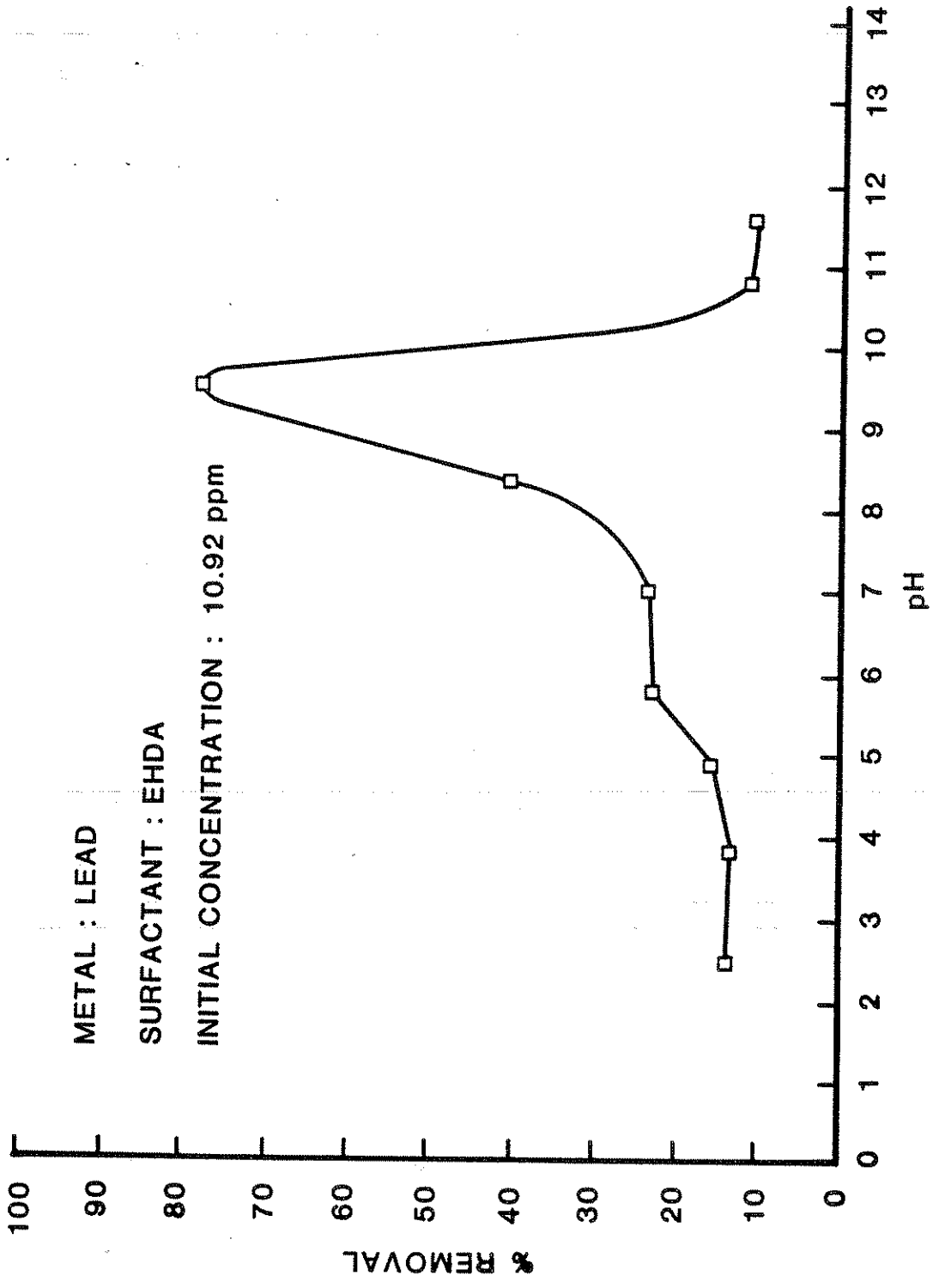


FIGURE 6. LEAD REMOVAL

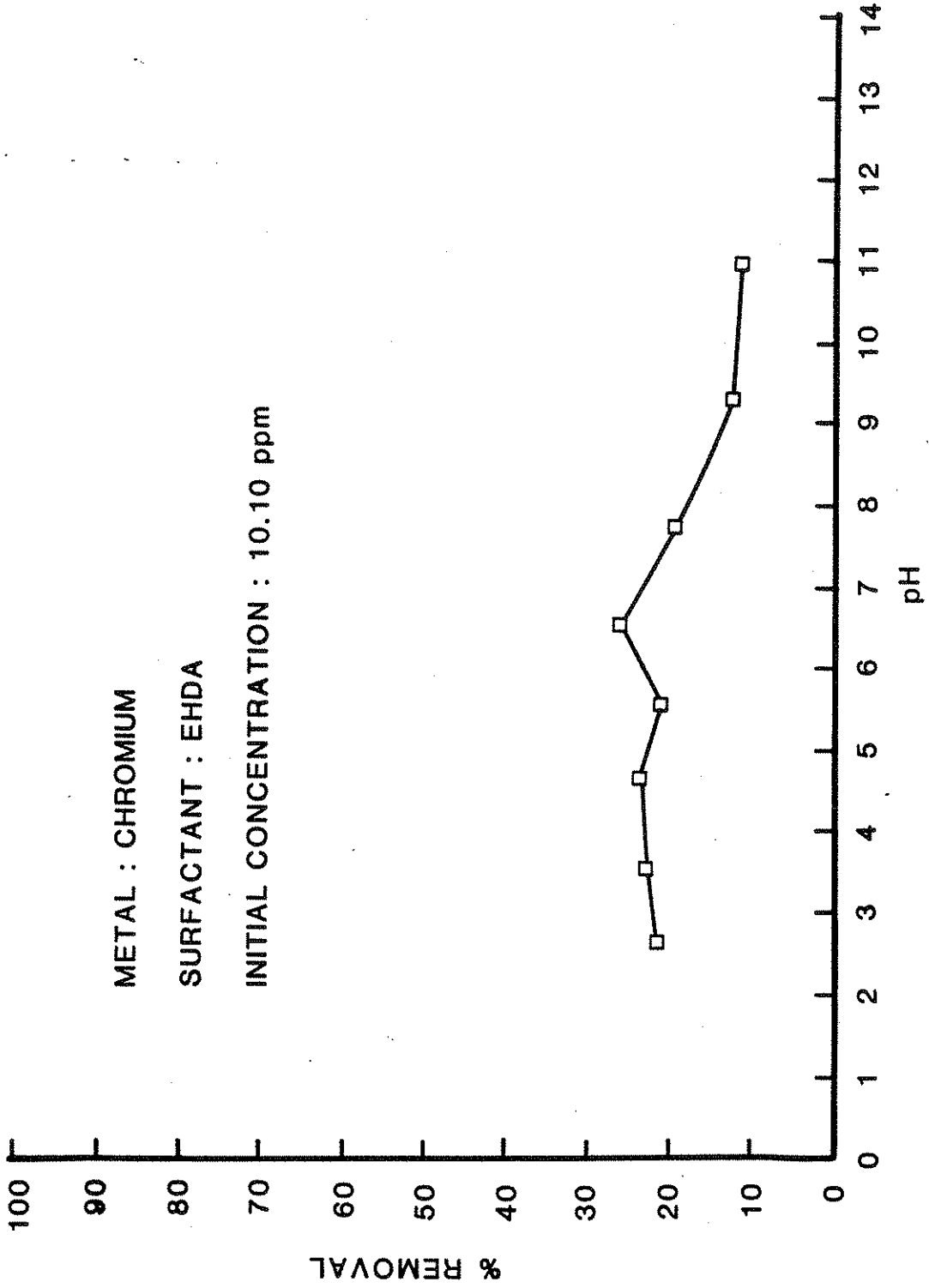


FIGURE 7. CHROMIUM REMOVAL

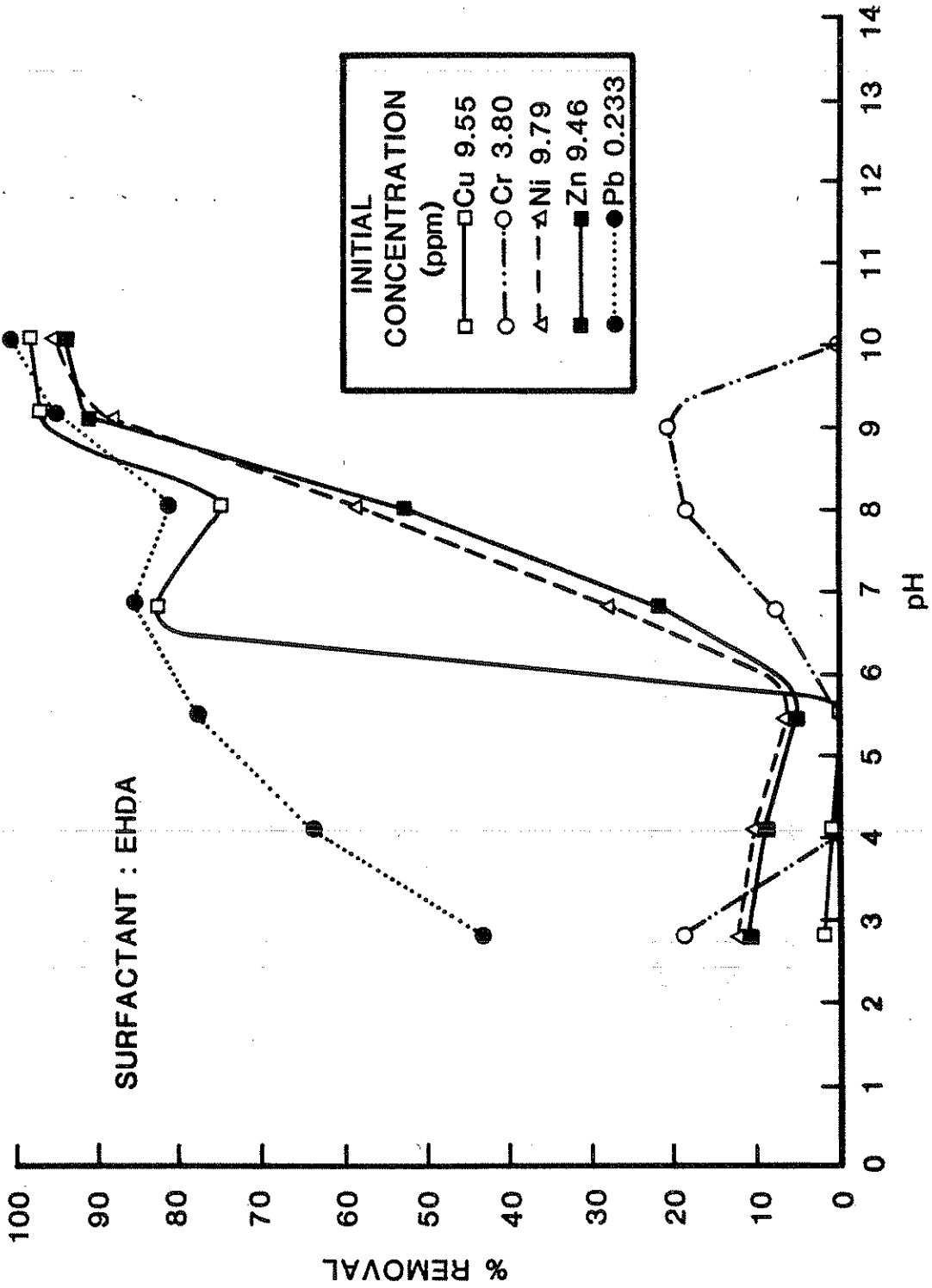


FIGURE 8. MIXED ION REMOVAL

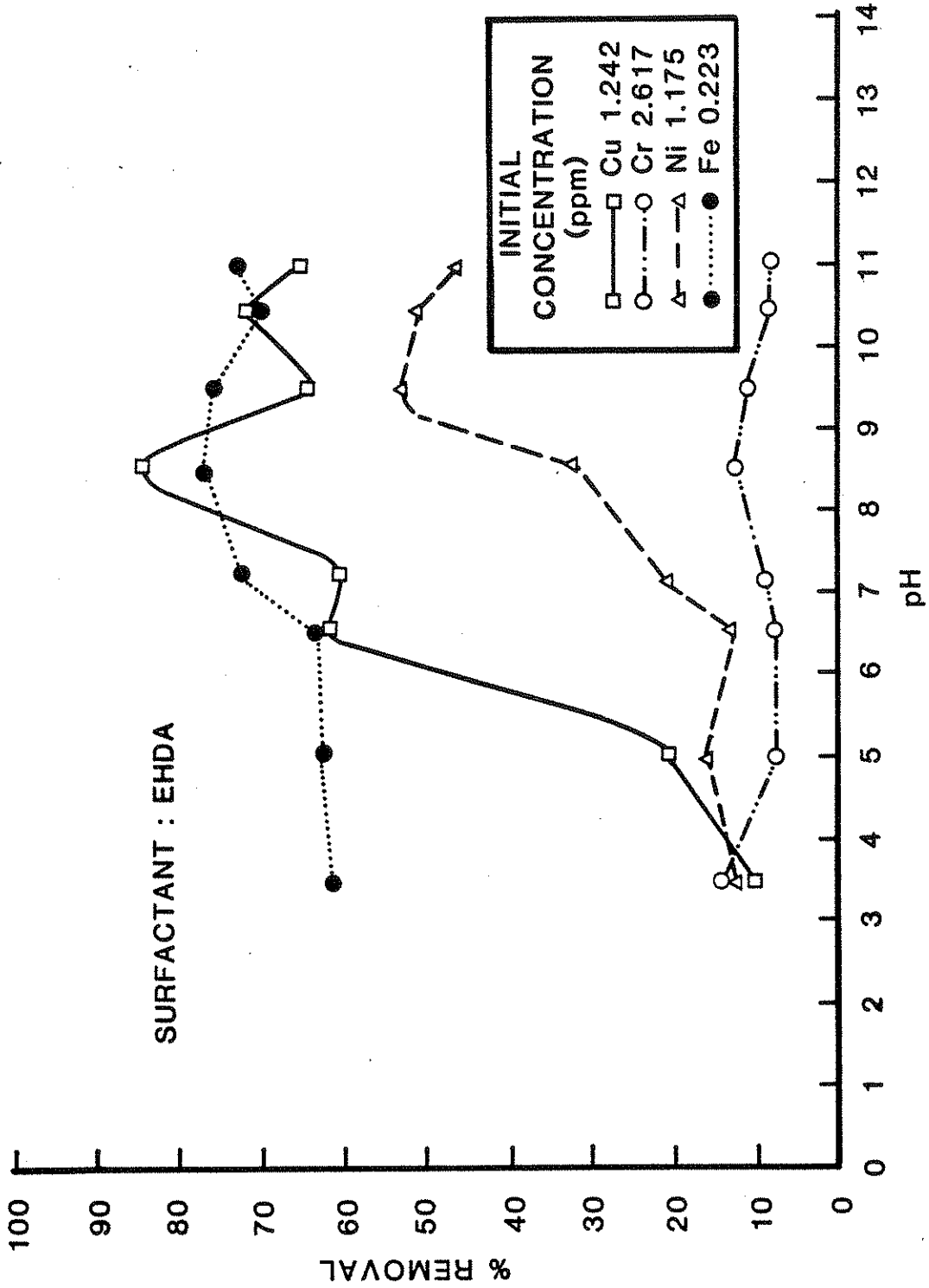


FIGURE 9. PURIFICATION OF WASTEWATER

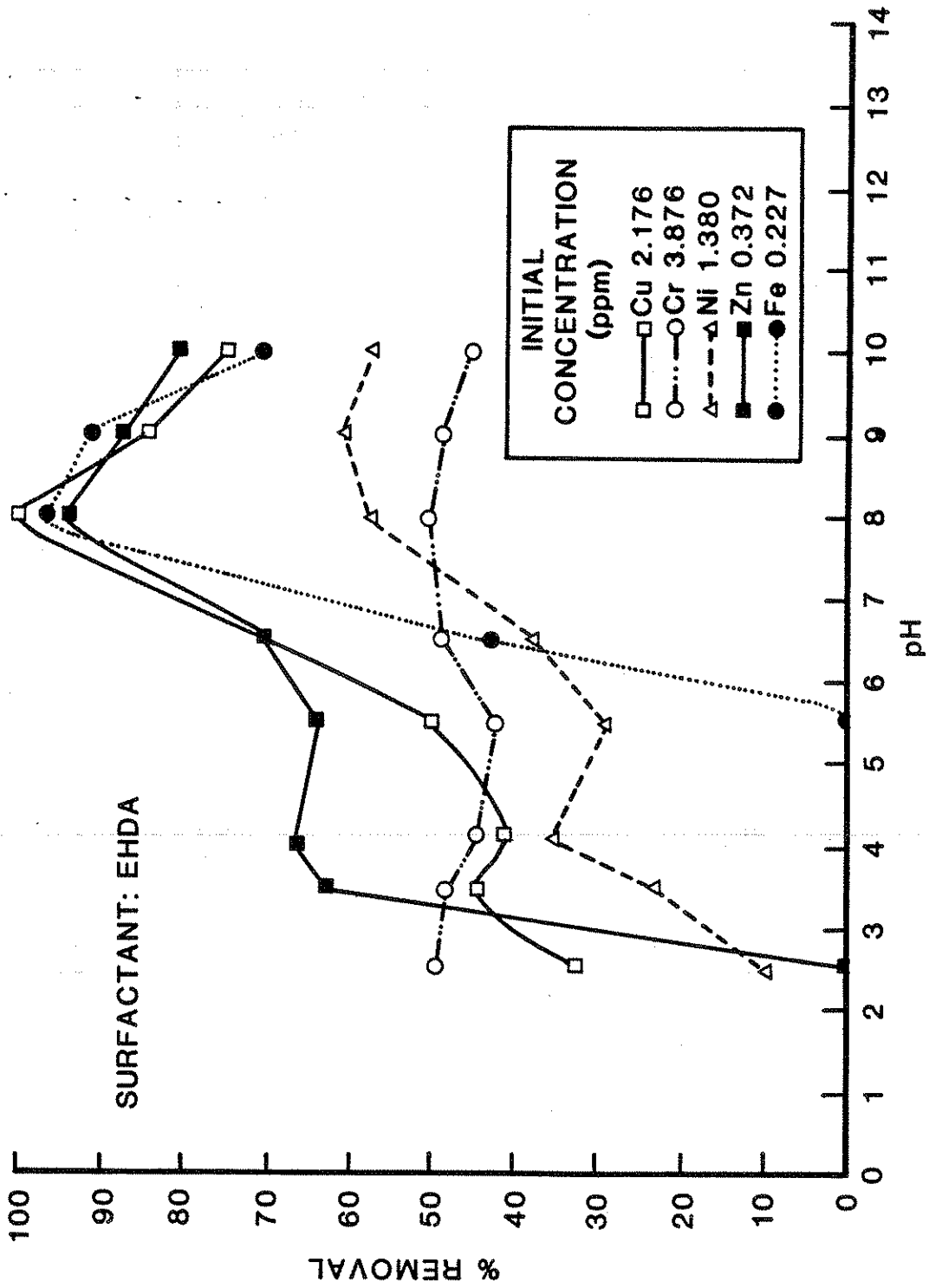


FIGURE 10. PURIFICATION OF WASTEWATER USING CHITOSAN

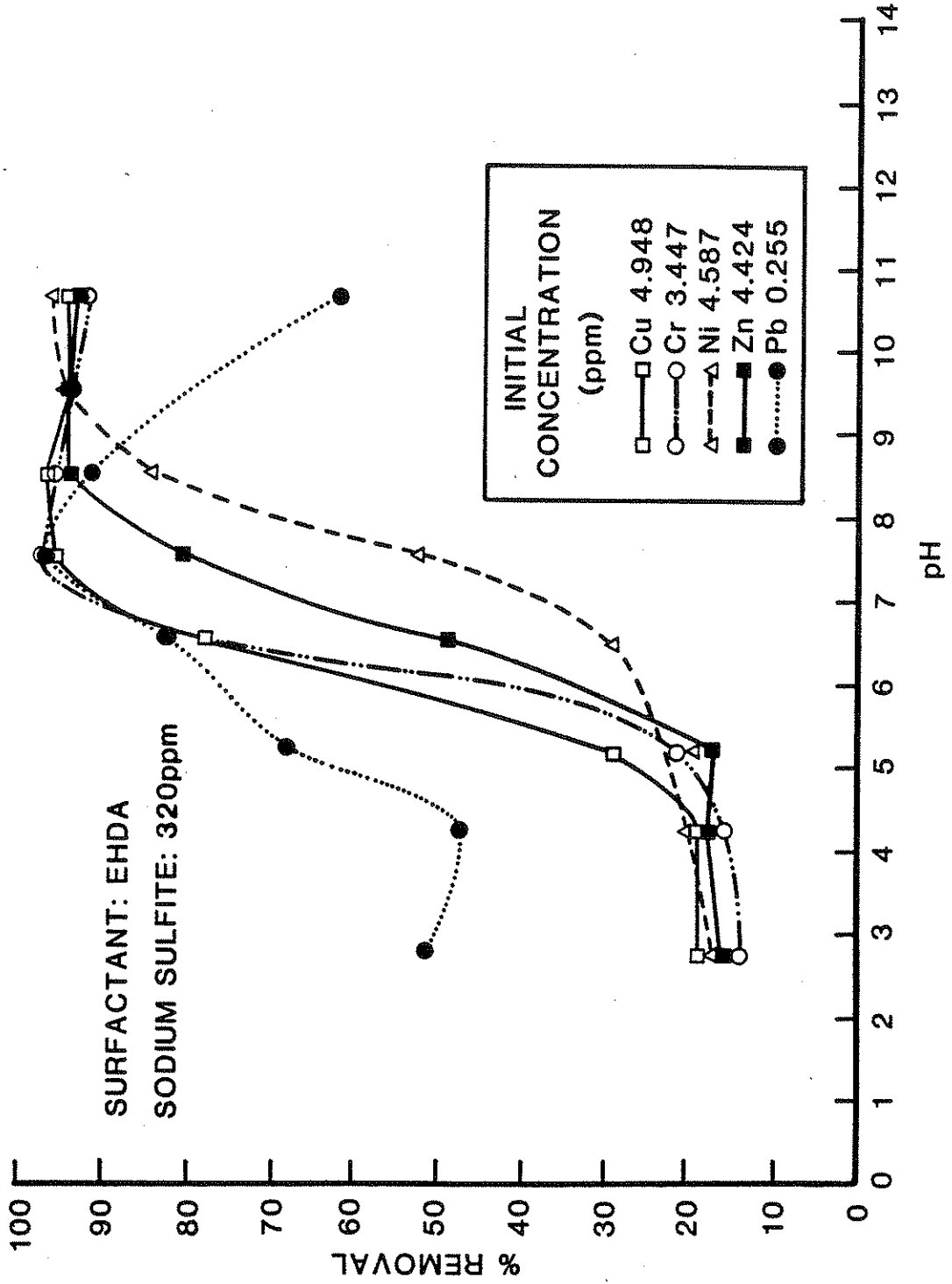


FIGURE 11. MIXED ION REMOVAL USING SODIUM SULFITE

Bibliography

1. J. C. Bailar, H.J. Emeleus, Sir Ronald Nyholm, A.F. Trotman-Dickenson, "Comprehensive Inorganic Chemistry," Vol. 3, Pergamon Press Ltd., Headington Hill Hall, Oxford, 1973.
2. P.J. Durrant, B. Durrant, "Introduction to Advanced Inorganic Chemistry," 2nd Edition, John Wiley & Sons, Inc., New York, 1970.
3. Manufacturing Jewelers & Silversmiths of America, Inc., "Environmental Technical Report #5, Nov. 30, 1979.
4. R. Lemlich, "Adsorptive Bubble Separation Techniques," Academic Press, New York, 1972.
5. F. Sebba, "Ion Flotation," Elsevier, New York, 1962.
6. B.B. Ferguson, C. Hinkle, and D.J. Wilson. Foam Separation of Lead (II) and Cadmium (II) from Wastewater, Sep. Science 9(2), 125-145, 1974.
7. Yoshiyuki Okamoto, E.J. Chou, Chelation effect of Surfactants in Foam Separations: Removal of Cadmium and Copper Ions from Aqueous Solutions, Sep Science, 11(1) 79-87 (1976).
8. Alan J. Rubin and Wilbert L. Lapp, Foam Fractionation and Precipitate Flotation of Zn(II), Sep. Science, 6(3) 357-363, 1971.
9. O.J. Gregory, S.M. Barnett, and F.J. DeLuise, Manganese Removal from Water by a Precipitate Flotation Technique, Sep. Science (In Press).