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Removal of Heavy Metals from Aqueous Solutions Using Microgas Dispersions

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Abstract

Flotation by means of microgas dispersions was used to remove copper, chromium, nickel, lead, and zinc from aqueous solutions, including an industrial plating effluent. Metal removals of up to 100% were obtained from solutions of the metals ranging in concentration from 2 to 20 ppm.

INTRODUCTION

The presence of heavy metals in our water resources presents problems ranging from being a nuisance to being extremely unhealthy. Many of these metals, even when present in only trace amounts, can be lethal. This contamination of our water supplies renders many sources of water unfit for residential as well as industrial use. The cost of the facilities necessary to purify these polluted resources to a quality acceptable for residential use can be prohibitive for many communities.

Industry is now being required by law to meet discharge standards, even though their wastes may be discharged into municipal sewage treatment systems. In many cases, to achieve these standards will require the installation of new equipment and/or modification of operating processes. For firms thus affected, this represents an added cost which in some cases actually threatens many businesses with serious financial hardship and in some cases collapse. One of these industries in financial difficulty is the jewelry industry.

The jewelry industry must be in compliance with the federal standards shown in Table 1 by October 12, 1982 (*1*). It should be noted that for plants discharging less than 37.9 m^3/d, federal requirements are less stringent. This permits two solutions to the discharge problems. First, plants discharging over 37.9 m^3/d can be subjected to less stringent regulations if they conserve

TABLE 1

Federal Standards (*1*)

Pollutant	Process water less than 10,000 gpd (ppm) 1 d	Process water less than 10,000 gpd (ppm) 30 d	Process water greater than 10,000 gpd (ppm) 1 d	Process water greater than 10,000 gpd (ppm) 30 d
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

enough water to bring them below this figure. Thus conservation is one solution available to some plants. For larger plants which cannot get under 37.9 m^3/d, purification is the solution. Purification can be achieved by either the installation of end-of-pipe treatment equipment, modification of the operating processes, or the use by several plants of a centrally located common treatment facility. The flotation process discussed in this paper can be used for purification of the water.

Flotation achieves a separation by concentrating a substance at a gas–liquid interface. The formation of stable bubbles and the collection of the substance is dependent on the surface properties of either the substance being collected or of some collector ion (*2, 3*). There have been numerous papers written which show the efficiency of the removal of metals from solution by flotation (*4–6*). Recently, microgas dispersions (MGD) have been investigated for the removal of metals from solution by flotation (*7*).

Microgas dispersions were first manufactured by Sebba using a venturi generator (*8*). This generator introduces a gas to a circulating surfactant solution at a region of high velocity and low pressure. This produces a dispersion of small bubbles which range in size from 1 to 50 μm in diameter. These very small bubbles provide a large amount of surface area for a given volume of dispersion. Assuming an average bubble size of 25 μm and perfect packing, which is a reasonable assumption given the small size of the bubbles, 1.00×10^{-6} m^3 of dispersion will provide about 0.24 m^2 of surface area. Furthermore, since these "microbubbles" are attached to each other at the interface, they rise through the solution at a rate more characteristic of larger bubbles. This results in very rapid separations. There are several published papers which discuss the properties and advantages of these dispersions (*8–10*).

There were two basic mechanisms by which removal was effected in this research. First there was an ion-exchange mechanism, and second there was precipitate flotation. In ion flotation, stable bubbles are first formed with a surfactant and then introduced into the solution being treated. As the MGD rises through the solution, the substance being collected, which is of opposite charge to the surfactant, is attracted to the bubble surface. This attraction can be purely coulombic or there can be some chemical bond formed. The insoluble product which is then formed on the bubble surface is then floated to the surface of the solution. The degree of removal is determined by the solubility of the substance in solution and the extent to which it bonds to the bubble surface.

In precipitate flotation, unlike the ion-exchange mechanism where an insoluble product is formed at the interface, precipitation of an insoluble product is carried out before flotation. It is this solid precipitate which is then floated out of solution. A substance can be precipitated by either changing pH to form the oxide or hydroxide, or by the addition of some reagent to form an insoluble compound. Precipitate flotation proved to be the most efficient method for removal of metal ions.

EXPERIMENTAL

Apparatus

Figure 1 is a schematic of the system used to produce the MGD and to effect removal of the various metals. The MGD 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. A Sears Model 563.26461 paddle pump, driven by a Craftsman Model 113.12550, 373 W electric motor was used to circulate the dispersion throughout the system. Since the quality of the dispersion is obviously affected 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, passes through the generator which formed and maintained the dispersion. In the generator, Fig. 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 MGD was formed, the generator acted

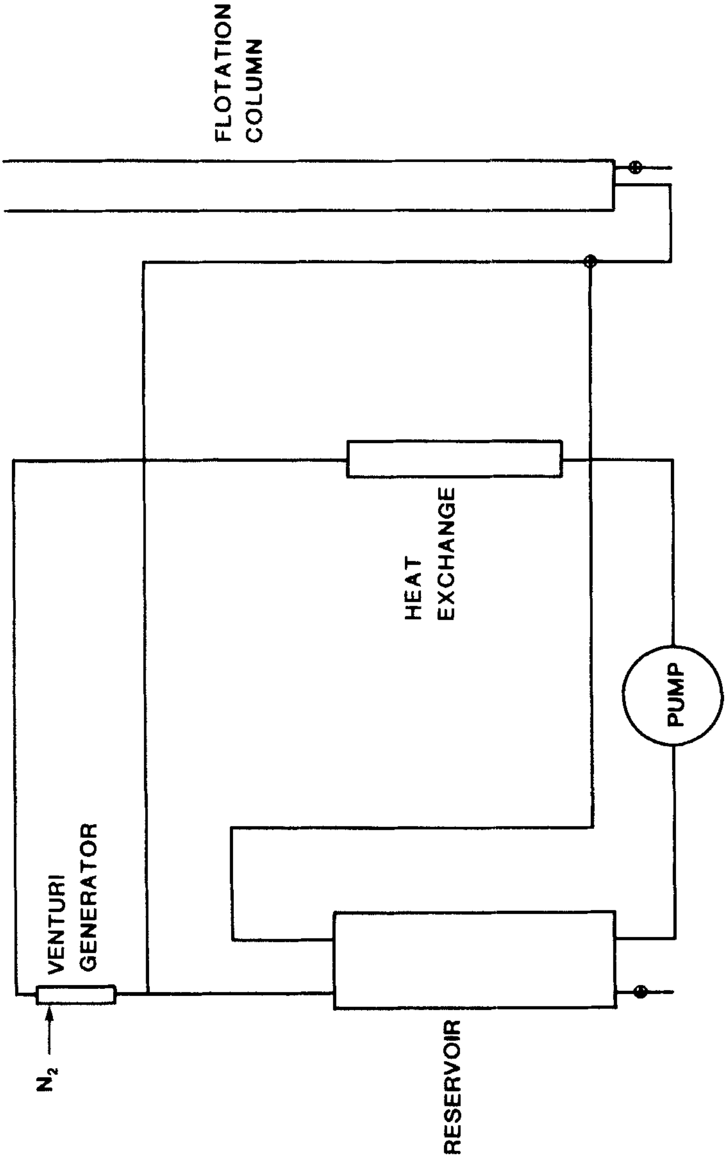

FIG. 1. Microgas dispersion generator.

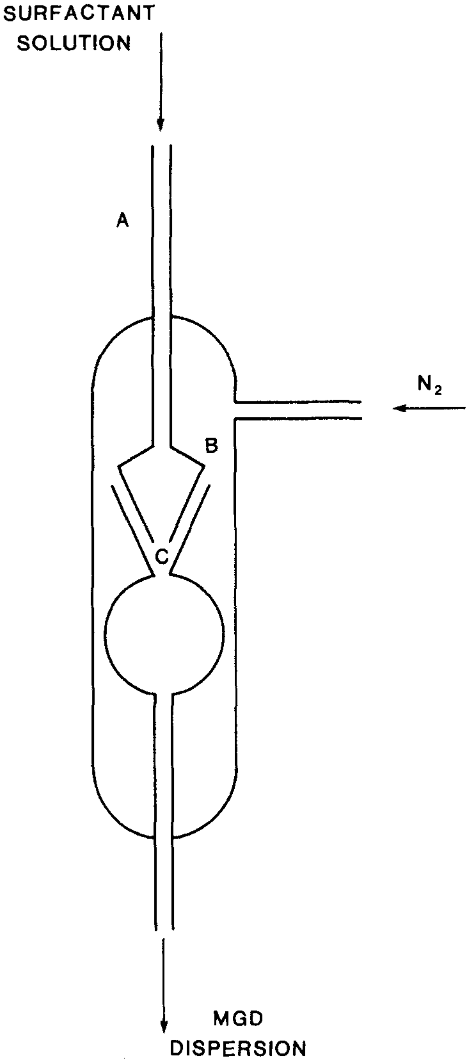

FIG. 2. Venturi generator.

to maintain a constant MGD quality by breaking up larger bubbles as they passed through it. 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

Surfactant solutions were prepared using 300 ppm of either ethylhexadecyldimethylammonium bromide (EHDA), or sodium dodecylbenzene sulfonate (DBSS). These solutions were used to prepare the bubble structure. No further addition of surfactants was required.

Procedure

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. Once the metals were in solution, they were then diluted to 1 L for a final concentration of 2000 ppm. Solutions to be treated were prepared from these stock solutions by making the appropriate dilutions. 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 to the 30-cm mark with the metal solution, and the MGD dispersion was introduced at the bottom of the column for a period of 1 min. Some runs were made using chitosan as a chelating or complexing agent. Chitosan is the deacetylation product of chitin, a long-chain polymer of β-(1, 4)-*N*-acetyl-D-glucosamine. The molecule weight of the chitosan used was unknown. The same procedure was used in these runs except that, prior to pH adjustment, the sample solutions were made up to 6.0 ppm chitosan. The pH was then adjusted and samples were stirred for 5 min. 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 10 to 15 min to assure a constant MGD 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 MGD 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). Introduction of MGD for a period of 1 min gave a typical dilution between 0.88 and 0.91. With this dilution approximately 73 mL of surfactant solution was contacted with the metal solution. This also translates into about 17 m^2 of surface area. Samples of the treated water were withdrawn from an outlet at the bottom of the column, acidified, and analyzed on an atomic absorption unit. Percent removals were obtained as follows:

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

where CI = initial concentration of metal
CF = final concentration of metal
DIL = dilution factor

Analytical

Metal ion concentration was determined using a Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer with background correction. The conditions used were those specified by the manufacturer. The following Perkin Elmer Intensitron lamps were used: chromium, Lamp #303-6021; zinc, Lamp #303-6081; lead, Lamp #303-6039; copper, Lamp #303-6024; and nickel, Lamp #303-6047. A Corning, Model 10C, pH controller was used to read pH.

RESULTS AND DISCUSSION

Percent removals have been calculated and are shown in Figs. 3–7. Operating conditions and initial metal concentrations are also noted. The residual concentrations obtained in each of these runs are presented in Tables 2 and 3.

Individual Metal Ion Solutions

Removal curves for the individual pure solutions of copper, nickel, zinc, lead, and chromium are shown in Fig. 3. At low pH, Cu, Ni, Zn, and Pb are present as the divalent ion. Below pH 6, Cu^{2+} was the stable ion. At pH 7, Cu^{2+}, $CuOH^{+}$, and $Cu(OH)_2$ probably coexist. $Cu(OH)_2$ can exist a a chain structure (*12*). A similar situation exists for nickel except that the $Ni(OH)_2$ precipitate which forms above pH 8.5 can consist of a structure in which each nickel atom is surrounded by six hydroxyl groups (*12*). The lead hydroxide which forms exists as a slightly soluble large molecule with no definite composition (*13*). As the hydroxides and insoluble oxides are formed, the removal mechanism changes from ion to precipitate flotation. This occurs above pH 6 for copper, 6.5 for zinc, 6 for lead, and 9 for nickel. From the literature the point of zero charge is 9.4 for the copper compounds, 11.1 for nickel, 9.8 for lead, and 9.3 for zinc (*11*). These values are close to the pH at maximum removal in each case. Some shifting may occur because of surfactant interaction or anion effects.

Zinc was removed by an anionic surfactant probably because of the

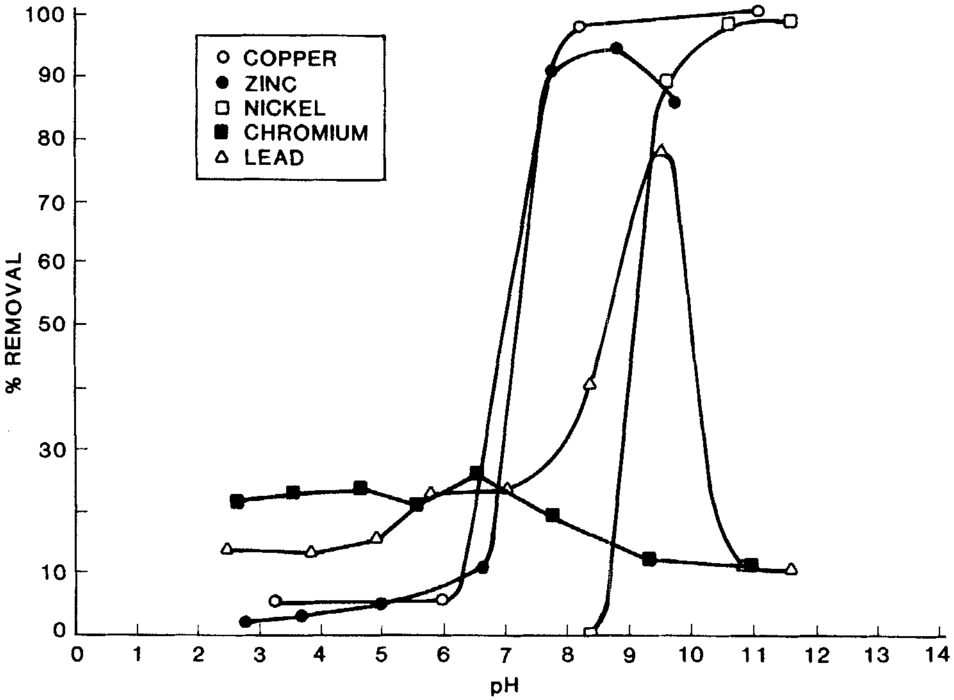

FIG. 3. Individual metal solution removal.

presence of positively charged Zn^{2+} or $Zn(OH)^+$ still associated with the surface of the forming precipitates. Similar results were obtained for manganese removal.

Unlike the other metals, chromium was present as an anion. At pH less than 1, the main species is H_2CrO_4. Between pH 2 and pH 6, H_2CrO_4 and $Cr_2O_3^{2-}$ are in equilibrium. Above pH 8, CrO_4^{2-} is present (*12*). Consequently, over this entire pH range, ion flotation was the removal mechanism.

Mixture

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 4 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 affected by

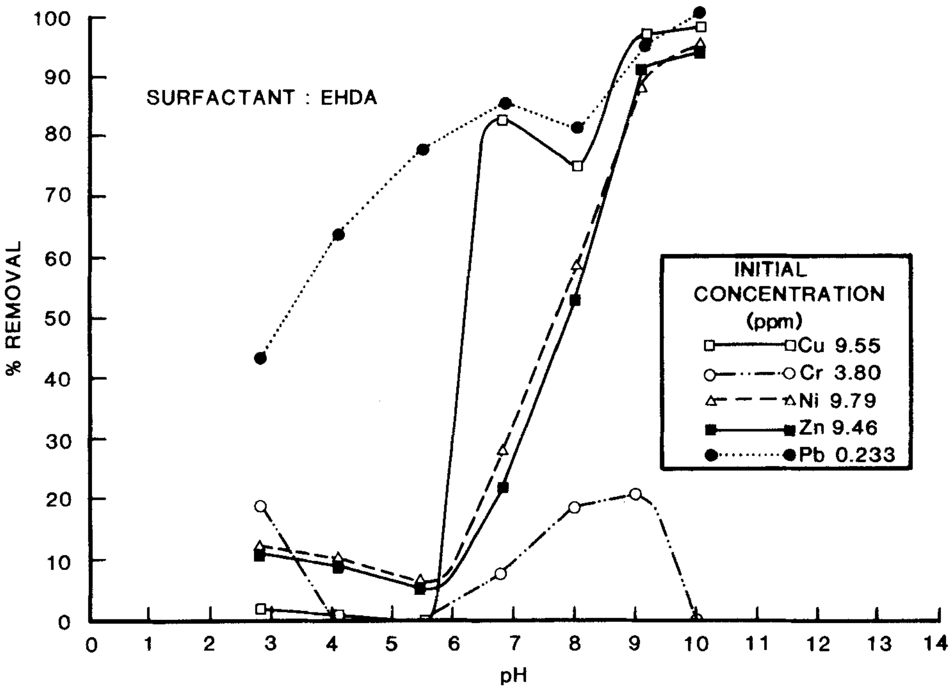

FIG. 4. Mixed ion removal.

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 makes 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 5 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 Fig. 5 and the corresponding curves in Fig. 4 can be noted.

TABLE 2

Metal Removal from Synthesized Solutions of Pure and Mixed Metal Ions[a]

	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[b]	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

[a] Surfactant: EHDA (300 ppm).
[b] Surfactant: DBSS (300 ppm).

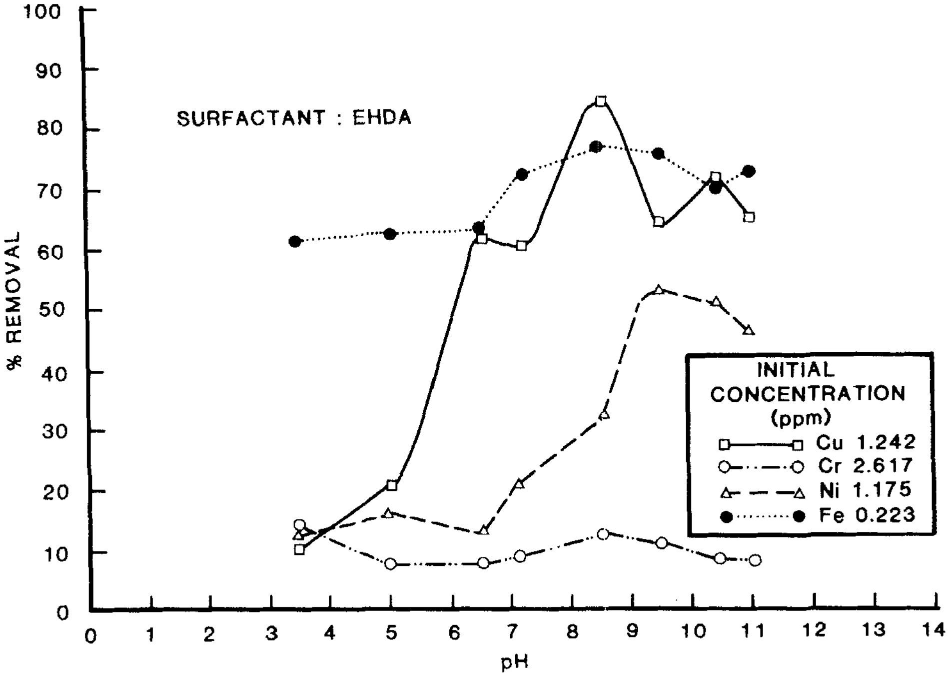

FIG. 5. Purification of wastewater.

TABLE 3

Metal Removal from Industrial Effluent with and without Chitosan[a]

	Industrial effluent			Industrial effluent with chitosan		
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	[b]	[b]	0.372	0.02	94.6

[a] Surfactant: EHDA (300 ppm).
[b] Sample lost.

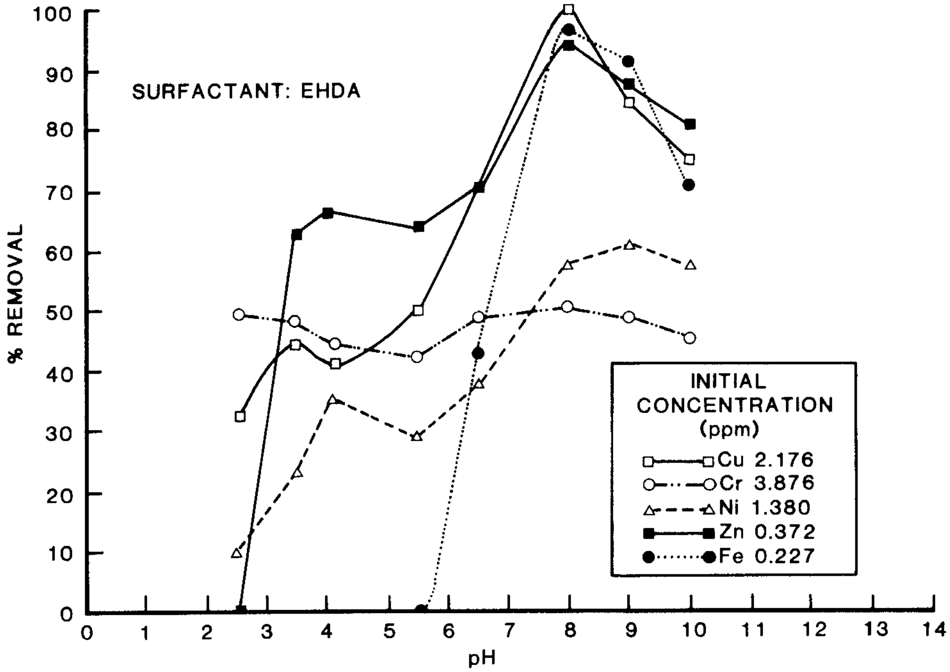

FIG. 6. Purification of wastewater using chitosan.

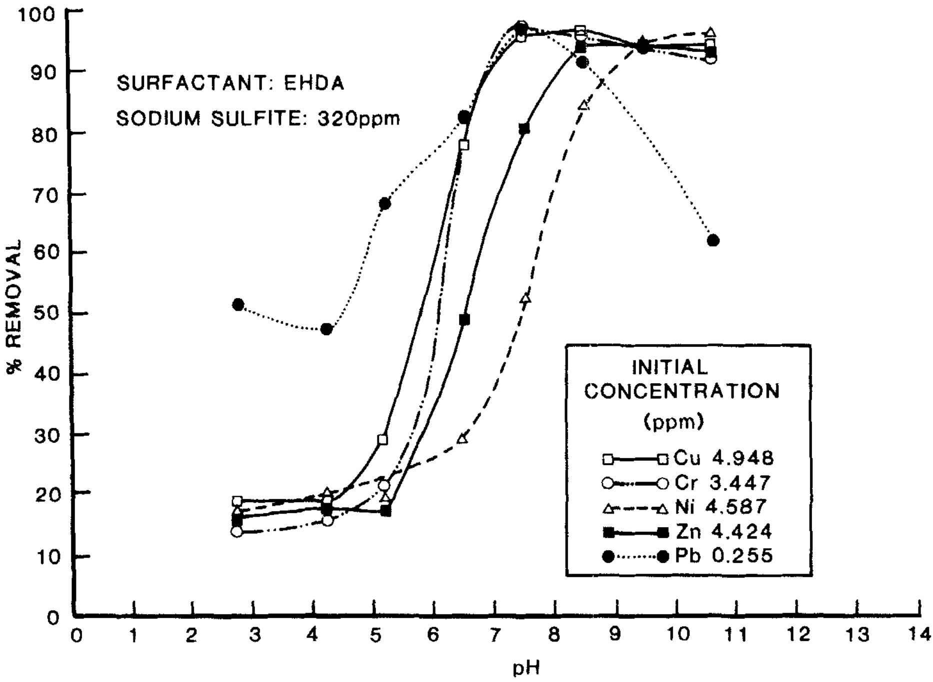

FIG. 7. Mixed ion removal using sodium sulfide.

Wastewater with Chitosan

Figure 6 shows the data obtained for the flotation of metals from a plating firms wastewater using chitosan as a chelating or complexing agent. Comparison of Fig. 6 with Fig. 5 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.

Mixed Ion Removal Using Sodium Sulfite

Since the removal of chromium was very poor when using the standard procedure used for the removal of other metals, a modification was tried. The hexavalent chromium was reduced to the trivalent state by the addition of sodium sulfite under acidic conditions. The resultant trivalent ion can then be precipitated and floated out. The use of sodium sulfite in a mixed ion removal is shown in Fig. 7.

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.

Acknowledgments

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