



REMOVAL OF HEAVY METAL IONS BY ADSORPTIVE PARTICULATE FLOTATION

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ABSTRACT

The removal of Zn, Cu and Ni ions, from diluted solutions, by the adsorptive particulate flotation (APF) process, was studied at laboratory scale. Zeolite (Chabazite) fines, in small concentrations, were used as the particulate sorbing for the metal ions and dissolved air flotation was employed for the solid/liquid separation of the loaded "carrier". Results showed almost complete removal (>98 %) of the heavy metal ions using $Fe(OH)_3$ precipitates to "aggregate" the carrier (coprecipitation). The process efficiency depended on solution and interfacial chemistry and aggregation effectiveness. The potential of APF in the field of effluent treatment is discussed. © 1997 Published by Elsevier Science Ltd

Keywords

Environmental; froth flotation; flocculation

INTRODUCTION

Mining and metallurgical operations handle large volumes of process water which are invariably contaminated with fines, chemicals, metal ions, oils and others. Aqueous streams containing heavy metals are frequently encountered in industrial effluents and sources of Ni, Cu and Zn are very common in the electroplating, electrolytic refining plants [1] and in acid mine waters.

The conventional method for heavy metal removal has been, for many years, the precipitation-settling of the metal hydroxides followed by thickening or filtration of the sludge. Most of the zinc electroplating industries in the United States and all in Brazil, for example, treat their effluents by precipitation [2].

This method, from a technical point of view, presents several limitations, such as incomplete precipitation, chemical instability of the precipitates and formation of large volumes of difficult to filter sludges.

On the other hand, the removal of metal ions by flotation has been proposed by several authors through various methods and techniques but not many industrial applications have been reported [3]. The main ones are precipitate flotation (as hydroxides, insoluble salts or complexes with surfactants), adsorbing colloid flotation [4–5] and adsorbing particulate flotation [6]. The latter is a variant of the adsorbing colloid

flotation process which, instead of colloids, employs particles as carrier and sorbing material for the metal ion. The carrier can be a mineral particle, a polymeric resin, activated coal or a by-product having good sorbing properties, high surface area and amenability for flotation [7–9]. Using mineral particles, the flotation process resembles the metal “activation” process, a very well known technique utilised in the mineral processing field [6].

Despite the fact that dissolved air flotation, DAF, also known as pressure flotation, has been recognised as a method of separating particles with micro-bubbles since the early 1900s, this process continues to grow and is finding new applications, but in heavy metals removal. For example, DAF is now being employed for the clarification of paper mill and refinery wastewaters, tertiary treatment of municipal waters, recycled paper de-inking, wastewater reclamation and recently in drinking water clarification [10].

The main objective of this work is to present a basis for the removal of heavy metal ions, in diluted solutions, by dissolved air flotation after being adsorbed in a “carrier” such as a natural zeolite (chabazite).

Most of the zeolites (including chabazite) are rich in Na^+ , K^+ and Ca^{++} [11], which are usually exchangeable with metal ions [12]. They are naturally occurring aluminosilicates which have unique sorption properties that can be used for adsorption and ion-exchange reactions. Although zeolites have been known for over two hundreds years, their value as adsorbent material was only realised 40 years ago. The discovery of abundant deposits of sedimentary zeolites has, in the last 30 years, provided industry a further input to control and recycle waste pollutants [13–14]. The word sorption will be used here to mean metal uptake by either absorption or adsorption phenomena.

Regarding flotation of zeolites following metal-ion sorption, the studies are fairly recent [15] and this work represents a contribution to this line of metal-sorption-flotation, adsorptive (or sorptive) particulate flotation or simply the carrier flotation approach.

EXPERIMENTAL

Materials and reagents

Sorbing material. Lumps of a natural Chabazite (Nevada-USA) were sampled and ground in a Tema mill to 100 % < 74 microns, and used as the metal ion sorber and carrier.

Reagents. FeCl_3 , p.a. from Spectrum Chem. MFG Corp. was used as coagulant. Reagents used for the make up of synthetic metal containing solutions were of analytical grade and were as follows: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Solution pH adjustment was made using reagent grade NaOH and HCl. Deionized water was used throughout the work. Bufloc 606, a polymer flocculant from Buckman and commercial sodium oleate were used occasionally.

Methods

Sorption of the metal ions

Sorption experiments were performed in a 0.25 liter Erlenmeyer having 100 mL of the target ion solution and 500 ppm of Chabazite. For determining the abstraction of the metal ions by the sorbing, the set heavy metal containing solution was stirred for 30 minutes. The concentration of heavy metal ions in solution was determined both before the introduction of the sorber and after the reaction with the metal containing solution. Filtration was performed in filters which do not uptake the metal ions. The amount of heavy metal ions abstracted from solution was determined using atomic absorption spectroscopy, by the difference in metal ion concentration from the two analyses performed before and after introduction of the chabazite.

Electrokinetic studies

The electrokinetic properties (zeta potential) of the chabazite particles were studied as a function of pH

using a laser based Zeta-meter (microelectrophoresis apparatus), in the absence and/or presence of the heavy metal ions. The pH was adjusted with addition of NaOH and HNO₃. For each pH value 15 readings were measured and averaged. The zeta potential values were calculated from the electrophoretic mobilities using the Smoluchowski equation [16].

Dissolved air flotation, DAF

In the DAF process, micro-bubbles (0.01–0.1 mm in diameter) are generated by a reduction of pressure of a water stream saturated with air at high pressure [17–18]. Batch, bench scale, DAF tests were carried out in a system composed of a pressure vessel (saturator) for water saturation (4 liters capacity) and a flotation cell (1.5 liter capacity). The two parts of the system were connected via a release needle valve for depressurization (Figure 1). The solids concentration (0.5 g/L) was established from the sorption capacity studies. Process efficiency was evaluated by measuring the residual metal content and turbidity (NTU units) in supernatants and by the rate of displacement of the solid/solution interface. For the turbidity measures, a nephelometer, from HF Instruments (DRT-100B), was used. The time of flotation unless otherwise quoted, was 1 min. After flotation, an aliquot of the supernatant was sampled through a side outlet. Before each test, 20 mL of solution were taken as a blank, leaving 980 mL as the final feed volume for the DAF tests.

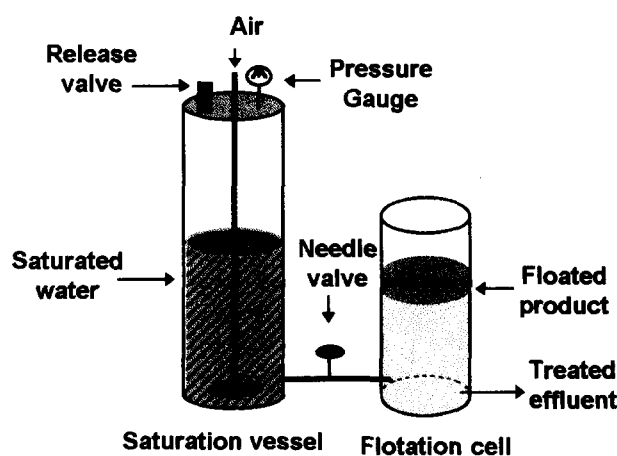


Fig.1 Dissolved air flotation (DAF) laboratory unit.

RESULTS AND DISCUSSION

Electrokinetic studies

Figure 2 shows the zeta potential values of the chabazite, in the presence and absence of metal ions, as a function of pH. The curve indicates that, with no addition of metal ions, the iep lies at about pH 2.0 with particles very negatively charged at neutral and basic pH values. However, the metal ions reversed the zeta potential values of chabazite, in the pH range 2.5–6.5. Similar phenomena have been observed in numerous other systems. For instance, limited adsorption of ions such as calcium, copper, iron, etc., occurred at low pH values onto quartz (mainly oxygen bearing minerals). However, adsorption increases at intermediate or basic pH, causing reversal of the zeta potential. For this to happen, hydrogen bonding of the hydroxy metal complex with the surface; chemisorption of the hydrolysed species and formation and adsorption of the metal hydroxide on the solid surface have been suggested [19].

Metal sorption as a function of pH

Experiments of sorption of mixtures of Cu, Ni and Zn ions onto chabazite fines were performed at various values of pH, and the results are shown in Figure 3.

The sorption of Ni, Cu and Zn was found to be very efficient (>90%) at pH values higher than 5.5, although the metal uptake started at pH 3.5. These results followed the same trend of the zeta potential reversal observed in Figure 2. Similar uptake values were found when the metal ions were added separately.

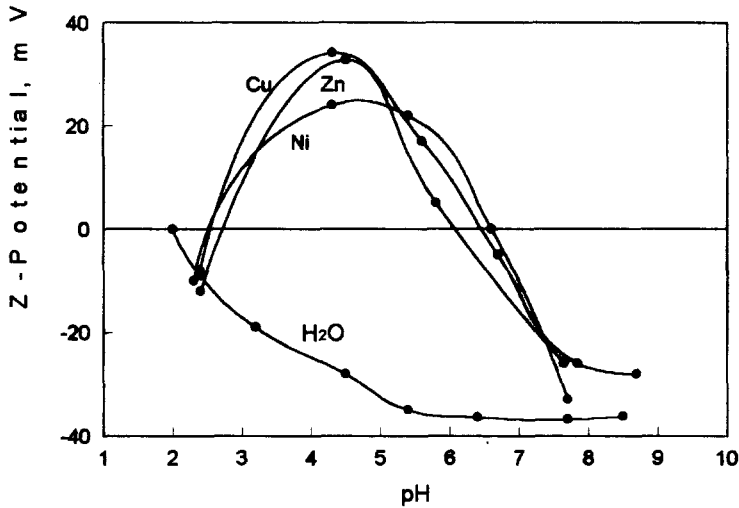


Fig.2 Zeta Potential - pH values for chabazite in the absence and presence of metal ions. Conditions: 2 mg/L Cu, Zn or Ni and 10^{-3} M NaNO_3 , 5g/L of chabazite.

At low pH values, the higher H^+ concentration drastically reduced the heavy metals removal, probably because of the chemical equilibrium of the ions in the aqueous solution. Species which are more amenable for sorption onto chabazite were the hydrolysed, $\text{Me}[(\text{OH})_n]^{+n}$. This metal uptake by the solid proceeds independently of the surface charge of the sorbing particles and is believed to obey a chemisorption reaction.

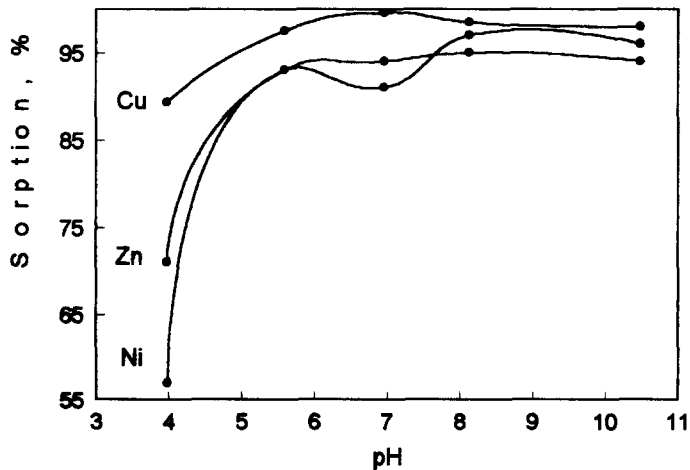


Fig.3 Sorption of dissolved metals species (mixture) on chabazite as a function of pH. Conditions: 5 g/L of solids, 2 mg/L of each metal ion. Sorption time, 70 min.

Figure 4 shows that the sorption kinetics is a very fast process reaching high uptake values within the first 5 minutes. This process advantage appears to be a result of the chemical sorption mechanism already discussed.

Figure 5 shows the sorption capacity of chabazite for copper ions. After about 40 mg/g, which is considered to be very high, no copper ions are released into the solution system. Thereon, accumulation continues and copper hydroxide begins to be formed and coprecipitates with the sorbing solid.

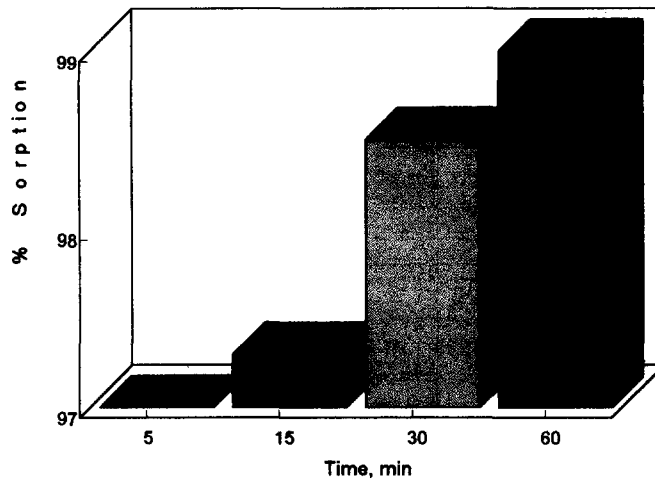


Fig.4 Kinetics of sorption of copper ions onto chabazite.
5 g/L solids, initial $[Cu^{++}] = 6$ mg/L, pH = 6.5

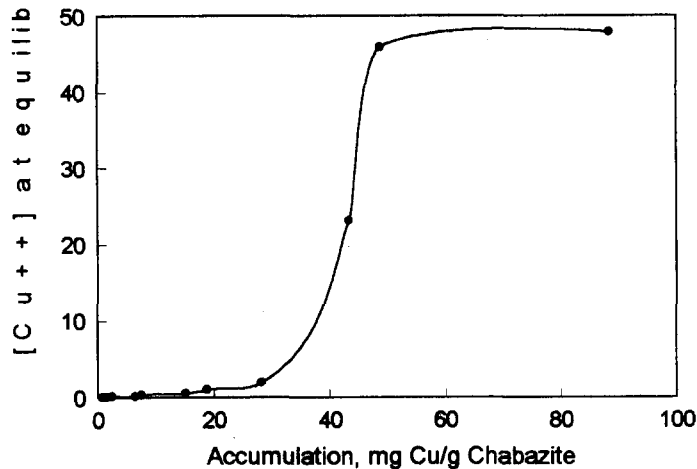


Fig.5 Sorption capacity of copper ions by chabazite.
5g/L solids, pH = 6.5

Adsorptive particulate flotation studies

Different flotation reagents were studied and the best results for the loaded carrier separation were obtained using $FeCl_3$ as coprecipitant when hydrolysed. Most of "aggregates" formed with Cu/Chabazite and $Fe(OH)_3$ are fairly large, well structured and are readily settled or floated. However, because of the presence of a few soft and fairly small flocs, the solid/liquid separation by simple sedimentation is not complete in short times (up to 30 min), and requires a further stage of filtration.

Results of flotation of copper-chabazite aggregates by DAF are shown in Table 1. Similar results, not reported here for the sake of simplicity, were also found in the case of zinc and/or nickel ions. Results showing that the separation depended on feed iron concentration are explained in terms of the

aggregation phenomena. It was observed that a minimum amount of $\text{Fe}(\text{OH})_3$ (20 ppm of Fe^{3+} , in this case) was required to “aggregate” the Cu bearing chabazite particles to produce “floatable” units (Figures 6 and 7). Solutions treated in this way were very clear, yielding turbidities similar to distilled water.

TABLE 1 Effect of Fe^{3+} concentration on removal of Cu by sorption-aggregation-DAF process. pH 7.7, 0.5 g/L of chabazite, 3.5 mg/L of Cu^{++} , 4.5 atmospheres-saturation pressure and 30 % recycle ratio

$[\text{Fe}^{3+}]$, ppm	$[\text{Cu}]$ final, ppm	% Removal	Turbidity, NTU
10.3	1.68	51.72	36.00
20.6	0.39	88.79	8.85
30.9	0.06	98.26	1.04

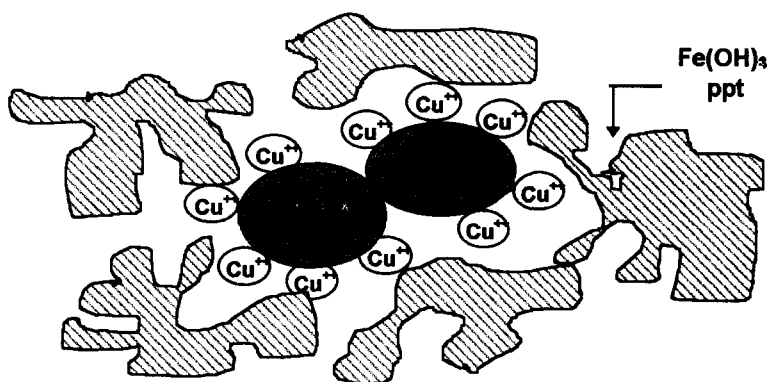


Fig.6 Floatable aggregates formed between the Cu^{++} -chabazite and the $\text{Fe}(\text{OH})_3$ precipitates.

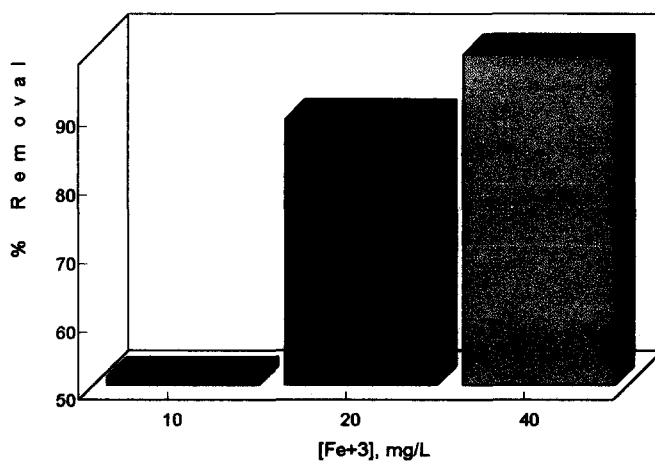


Fig.7 Effect of $[\text{Fe}^{3+}]$ on copper removal by DAF. Conditions in Table I.

Separation of ions in admixtures

Simultaneous separation of the heavy metal ions was studied to measure the DAF removal efficiency and comparison with the sorption performance described in Figure 3. The results obtained are shown in Table 2. Adsorptive particulate flotation, using small quantities of chabazite as carrier, was found to be very effective for the treatment of solutions containing mixtures of heavy metals such as copper, zinc and nickel. Results followed the sorption trend and showed a high separation rate.

TABLE 2 Separation of mixtures of heavy metals by DAF.
Conditions: 0.5 g/L of Chabazite, pH 7.5, feed concentration,
2 ppm each one (Ni, Cu and Zn), 30% recycle ratio
and 30 ppm Fe⁺³, 0.06 ppm Bufloc.

Ion	Final concentration, ppm	Removal, %
Cu	0.05	98.6
Ni	0.05	98.6
Zn	0.05	98.6

Further, a very small amount of polymer was added to improve separation performance because of the following:

1. The use of micro-bubbles is optimised by the provision of more hydrophobic sites, the probability of micro-bubble-particle attachment after collision thereby being increased, increasing the flotation kinetics [20–21].
2. Flocculation provides a suitable number of floating units, and the limitation imposed by the feed solids concentration on micro-bubbles flotation could be partially solved.
3. Floccs are more resistant to shearing and allow the use of macrobubbles instead of micro-bubbles broadening the possibilities of the use of other flotation techniques. This will be the theme of our future work in this area.

Finally, it is believed that the concept of adsorptive particulate flotation, APF, should be stressed by using other pollutants sorbing materials [6, 15, 22, 23, 24] and high capacity flotation techniques. Regarding the sorbing carrier this should have a high surface area, must be very reactive with the solutes to be removed and easy to float. The use of microorganisms as sorbing materials (biosorption or biosorptive flotation) has been proposed and may be another alternative [25, 26]. Some of these processes may lead to an alternative future technology in the field of inorganic and organic contaminants removal.

CONCLUSIONS

The results obtained allowed us to conclude that adsorbing particulate DAF flotation using chabazite, a natural zeolite, is particularly attractive for the removal of metal ions. This process, which employs a small concentration of sorbing carrier, was found to be fast and efficient in the almost quantitative removal of Cu, Zn and Ni ions, yielding very low solution turbidities. Advantages when compared with settling were observed in terms of process kinetics and quality of the supernatants. Because of the high sorption capacity of the zeolites, the amount required to efficiently remove the metal ions was found to be very small (0.5 g/L or less).

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