

REMOVAL OF CHROMIUM SPECIES FROM LIQUID EFFLUENTS BY FLOTATION – PART I – Cr⁶⁺

M.L. Torem, N.C.A.S. Braga, G.V. Macedo

Department of Materials Science and Metallurgy/ Catholic University of Rio de Janeiro
Rua Marquês de São Vicente, 225 – Gávea, 22453-900
Rio de Janeiro - RJ, Brazil
Telephone: +5521 529-9491 Fax: +5521 511-2196
e-mail: torem@dcm.puc-rio.br

ABSTRACT

The growing need for development of new methods in chemical technology represents a major challenge facing industries in the next century. The implementation of stricter waste treatment regulation constrain industries to lower the limits of allowable discharges.

The aim of this paper is the removal of Cr⁶⁺ by ion flotation from dilute solutions.

The removal of Cr⁶⁺ using cethyltrimethyl ammonium bromide (CTA-Br) as collector was studied at laboratory scale.

The effect of flotation time, solution pH, concentration of collector and frother (ethanol), initial chromium concentration and ionic strength (NaCl, Na₂SO₄, Na₃PO₄) on the removal of chromium species was evaluated.

The variation of solution pH showed that the best flotation pH was in the range of 3.0 and 7.0 reaching removal levels of around 90%, using CTAB (10⁻⁴ mol.dm⁻³) as collector, for initial concentration of 0.5x10⁻⁴ mol.dm⁻³ of Cr⁶⁺. To study the influence of the other variables on the ion flotation was chosen the pH 4.0, where HCrO₄⁻ is predominant.

The increase of the ionic strength decreased significantly the removal of chromium species to the range between 49% and 33%. The presence of ethanol did not play an important role on ion flotation of chromium species.

INTRODUCTION

The growing need for development of new methods in chemical technology represents a major challenge facing mineral, metallurgical and mineral processing industries in the next century. The implementation of

stricter waste treatment regulation constrain industries to lower the limits of allowable discharges, so that they often must treat large volumes of effluents that contain very dilute concentration of toxic metals.

The pollution caused by heavy metals in water used for animal or human consumption and irrigation, is very harmful for the society, due to their intoxication effects in living beings (Silva,1991). Sometimes, the presence of heavy metals in bodies of water can have noxious consequences, even their eutrophication.

There are several techniques, related to the treatment of industrial effluents that can be applied to the removal of heavy metals. The most common process is chemical precipitation, as hydroxides, which are formed controlling the pH of the medium. Nevertheless, for very dilute solutions these kinds of separation are not efficient (Zouboulis et al,1991).

As an alternative, comes the ion flotation technique that is feasible to be a good option for the removal of different metal species in very low concentrations (Torem et al,1999).

The ion flotation is one of the bubble adsorption separation techniques that best fits the treatment of very dilute solutions, which concentrations are, normally, in the range of 10⁻⁷ mol.dm⁻³ to 10⁻⁴ mol.dm⁻³ (Pinfeld,1972).

The main disadvantage of this technique is the effect of the ionic strength that appears to have a negative influence in its mechanism.

The goal of the ion flotation is remove ionic species from dilute solutions with a surfactant. Its mechanism consists in bubbling a gas phase in an aqueous solution, when occurs the interaction between the gas phase and the substrate, which is a complex formed between the interest species and the surfactant (Filipov et al,1997).

Figure 1 shows the speciation diagram for Cr⁶⁺ (logC as a function of pH) based on the equilibrium reactions that were proposed by Pourbaix (apud Deltombe et al,1974).

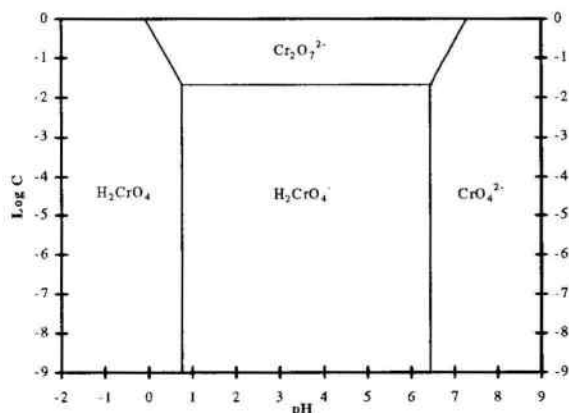
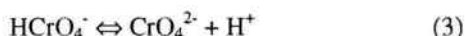
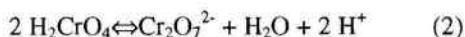
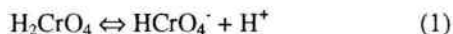


Figure 1 - Cr⁶⁺ speciation as a function of pH.

The toxicity of chromium in aquatic organisms is generally low, in comparison with other heavy metals as mercury, cadmium, copper, lead, nickel and zinc. The presence of chromium in water affects the growth of aquatic plants. The toxicity to plants depends on the pH of the media and hence the availability of free and chelated ions; other factors may influence toxicity to plants. Sub lethal/chronic effects of chromium intoxication include decreased growth and body size. There may also be a significant reduction in the rate of reproduction and survival progeny. (Moore et al,1984)

Fishes are generally less susceptible to the toxic effects of chromium than invertebrates. However, the extent and nature of effect is species dependent. The site of toxic action in fish may depend on pH of media. A pH \geq 7.5, the exposure to chromium results in histological damage to kidney and stomach. Although there appears to be little damage to gills, treatment with chromium at pH \leq 6.5 results in significant hyperplasia. This in turn causes a decrease in plasma osmolarity and an increase in hematocrit. (Moore et al,1984)

Due to the high stability of natural chromium complexes in abiotic matrices, it is not acutely toxic to humans. Nevertheless, Cr⁶⁺ is more toxic than Cr³⁺, because of its high rate of adsorption through intestinal tracts. In the natural environment, Cr⁶⁺ is likely to be reduced to Cr³⁺, thereby reducing the toxic impact of chromium discharges. Based on experimental evidence, it was concluded that hexavalent chromium has mutagenic properties. (Moore et al,1984)

Epidemiological studies have shown a positive relationship between occupational exposure to chromates and cancer incidence. (apud Moore et al,1984) Slightly soluble hexavalent chromium salts, specifically calcium chromate, are the most potent carcinogens. These compounds have induced high levels of chromosomal aberrations in cultures of mammalian cells. (Moore et al,1984)

The aim of this paper is the removal of Cr⁶⁺ by ion flotation from dilute solutions, studying the influence of the following physical and chemical parameters:

- Solution pH.
- Flotation time.
- Initial collector concentration.
- Initial Cr⁶⁺ concentration.
- Ionic strength.
- Initial frother concentration.

EXPERIMENTAL

Experimental Apparatus

The experiments were carried out utilizing the schematic diagram of experimental apparatus that is shown in figure 2.

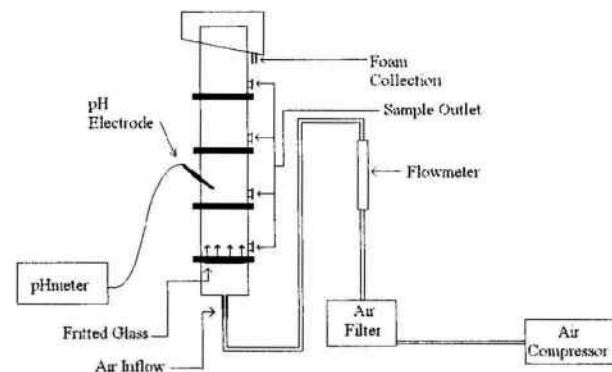


Figure 2—Schematic diagram of the experimental apparatus.

The dispersed air flotation column consists in a 95 cm high acrylic cell with internal diameter of 5.7 cm. Bubbles were generated by sparging air through a sintered glass frit (10 to 15 μm , porosity 4) at a controlled flow rate of 0.4 $\text{ml}\cdot\text{s}^{-1}$. Each experiment used an initial volume of 1 liter, filling approximately half column.

Reagents

The following reagents were used: potash dichromate ($K_2Cr_2O_7$) from Vetec, as metal ion font; cethyltrimethyl ammonium bromide (CTA-Br: $C_{19}H_{32}BrN$) from Henkel, as collector; ethanol (C_2H_5OH) from Merk, as frother; sodium chloride ($NaCl$) from Vetec, sodium sulfate (Na_2SO_4) from Vetec and sodium phosphate (Na_3PO_4) from Henkel, to alter the ionic strength; sulphuric acid (H_2SO_4 , 0.1 N) and sodium hydroxide ($NaOH$, 0.1 N) from Merk, to adjust solution pH.

The ratio of concentrations of the collector to that of the chromium was denoted by Φ .

Methods

Each test solution was prepared by combining the required amount of metal salt stock solution, CTA-Br stock solution, and the necessary frother with distilled water to make up one liter of solution.

The pH of the solution was adjusted and the solution was stirred for approximately 10 minutes to ensure consistent mixing of the reagents. The solution was then introduced into the column with the air flowing through the sparger. With exception for the flotation time test, each test was run for 90 minutes with solution samples taken at 0, 15, 30, 45, 60, 75 and 90 minutes. The metal content of the samples taken from the bulk solution was determined by Inductively Coupled Plasma (ICP). The metal removal at each time interval was calculated based upon the metal content of the initial solution.

The results expressed as percentage removal (recovery) of the chromium species, were calculated using the formula (Zouboulis et al,1991):

$$Re\% = [1 - (C/C_0)] \times 100 \quad (6)$$

RESULTS AND DISCUSSION

In this study, the experiments were carried out varying solution pH, flotation time, initial collector, frother and Cr^{6+} concentrations and ionic strength in order to study their influence in ion flotation of Cr^{6+} .

Figure 3 shows that in the pH range between 4 and 6, the ion flotation achieved recoveries higher than 85%. The results obtained in figure 3 are in accord with the literature (Zouboulis et al,1992), in those registered variations in Cr^{6+} recovery varying the pH media, in the presence of cethyltrimethyl ammonium chloride as collector.

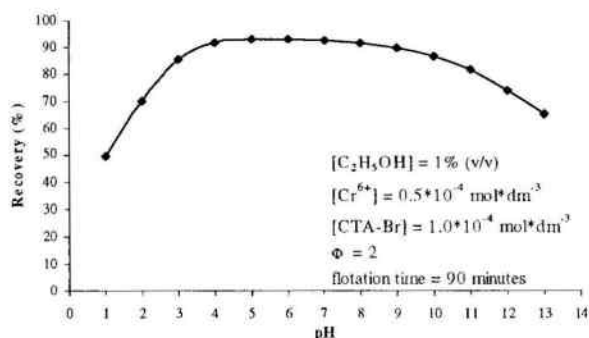


Figure 3 – Effect of solution pH on the recovery of Cr^{6+} ion flotation.

Figure 4 shows the recovery of Cr^{6+} as a function of flotation time.

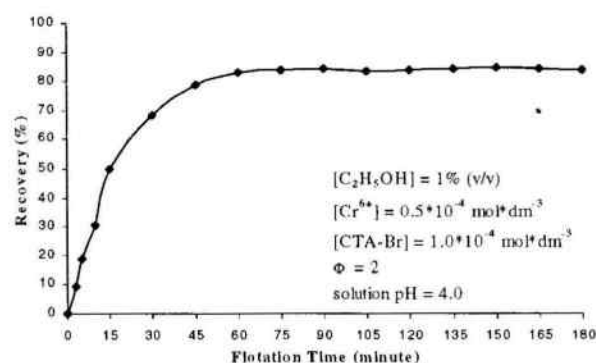


Figure 4 - Effect of flotation time on recovery of Cr^{6+} ion flotation.

One can realize that for flotation time above 60 minutes, the removal reaches a value of 85%, which remains almost steady for the time range analyzed in this work.

The flotation time for the others experiments was chosen at 90 minutes, to ensure the total removal.

Figure 5 presents the behavior of ion flotation within the variation of initial collector concentration. It can be verified in the literature (Zouboulis et al,1991) that the amount of added collector has a strong influence on the flotation of Cr^{6+} . The slight decrease on recovery of Cr^{6+} ion flotation, in the presence of CTA-Br concentrations higher than $10 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ is, probably, due to the formation of collector micelles.

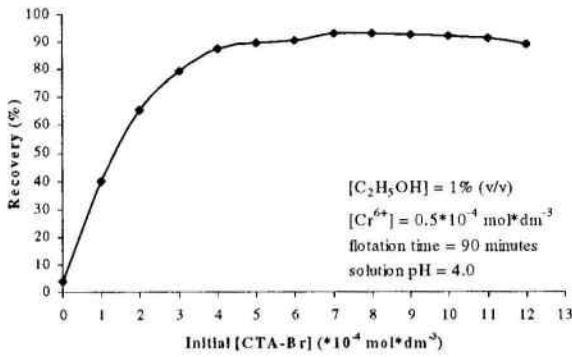


Figure 5 – Effect of initial concentration of collector (CTA-Br) on recovery of Cr^{6+} ion flotation.

Studying the influence of the initial concentration of the heavy metal ion in ion flotation (figure 6), it can be observed that the highest recovery was obtained for the chromium concentration of $5 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$. For concentrations above this one, the recovery decreases, probably because the flotation time is not sufficient to remove all species.

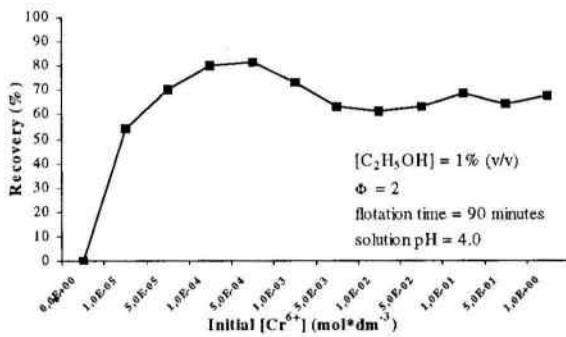


Figure 6 – Effect of initial concentration of the metallic ion (Cr^{6+}) on the recovery of Cr^{6+} ion flotation

Figure 7 shows the recovery data of ion flotation in which the presence of different salts changes the ionic strength. The increase on salt concentration led a consequent decrease on recovery. The major decrease occurred within the addition of the trivalent salt, than those derived by the addition of divalent and monovalent salts.

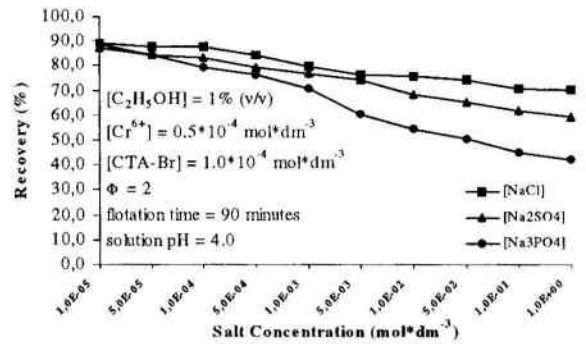


Figure 7 – Effect of ionic strength on the recovery of Cr^{6+} ion flotation.

As suggested in the literature (Pinfold,1972), salt anions, in solution, can be associated to collectors, which become unable to get in contact with interest metallic species.

Similar results were obtained by Zouboulis (Zouboulis et al,1991) for ion flotation of Cr^{6+} in the presence of sodium, sulfate and phosphate chloride, with solution pH = 4.2.

Figure 8 illustrates the influence of the initial ethanol concentration on ion flotation recovery. The initial ethanol concentration of 1% (v/v) is sufficient enough to reach the highest recovery. That occurs probably due to the frothing nature of the collector used in these experiments.

Nevertheless, the increase of the initial frother concentration did not affect significantly the recovery (removal) of Cr^{6+} which remained stable in the range of 83%.

These results are in accordance with the ones obtained by Zouboulis and Goetz (Zouboulis et al,1991).

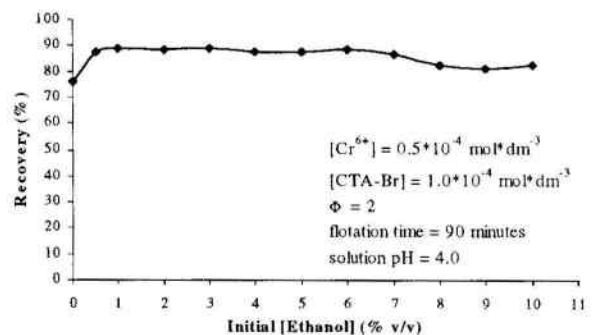


Figure 8 – Effect of frother (ethanol) concentration on the recovery of Cr^{6+} ion flotation.

CONCLUSIONS

- Cr^{6+} can be removed from aqueous solutions (as H_2CrO_4^- species) by ion flotation in the following conditions.
 - pH: 4.0;
 - Flotation time: 90 minutes;
 - Collector / metal ratio (Φ): 2
- For the same collector / metal ratio, the use of frother in a concentration of 1% (v/v) improves the removal of Cr^{6+} from a value of around 76 % to a value of around 87%.
- In the experimental conditions of this work, the increase of ethanol concentration did not improve significantly the recovery of Cr^{6+} .
- The increase of ionic strength deeply affects the recovery of Cr^{6+} species and is related to the charge of anion species of the salt added.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge CAPES, FAPERJ and CNPq for financial assistance.

REFERENCES

- Deltombe, E., Zoubov, N. and Pourbaix, M.; Chromium. In Atlas of Electrochemical Equilibria in Aqueous Solutions, p.256-271, 1974.
- Filippov, L.O., Houot, R. and Joussement, R.; Physicochemical Mechanisms and Ion Flotation Possibilities Using Columns for Cr^{6+} Recovery from Sulfuric Solution, International Journal of Mineral Processing, p.229-239, 1997.
- Macedo, G.V.; Removal of Cr^{3+} e Cr^{6+} by Ion and Precipitate Flotation (in Portuguese), MSc Dissertation - PUC-RJ, 1999.
- Moore, J.W. and Ramamoorthy, S.; Heavy Metal in Natural Waters – Applied Monitoring and Impact Assessment, Springer – Verlag (Editor), p. 58-77, 1984.
- Pinfold, T.A.; Ion Flotation. In: Adsorptive Bubble Separation Techniques, R. Lemilch, Academic Press (Editor): Johannesburg – South Africa, p.53-73, 1972.
- Scorzelli, I.B.; Removal of Cadmium and Zinc From Very Dilute Solutions by Ionic Flotation (in Portuguese), DSc Thesis - PUC-RJ, 1999.
- Silva, M.E.M.C.; Treatment of Industrial Effluents Containing Heavy Metals Through the Method of Precipitate Flotation (in Portuguese), MSc Dissertation - UFMG, 1991.
- Torem, M.L., Scorzelli, I.B., Fragomeni, A.L.; Removal of Cadmium From a liquid Effluent by Ion Flotation. In: Minerals Engineering, Vol. 12, No. 8, p.905-917, 1999.
- Zouboulis, A.I. and Goetz, L.; Ion Flotation as a Tool for Speciation Studies Selective Separation in the System $\text{Cr}^{3+}/\text{Cr}^{6+}$. In: Toxicological and Environmental Chemistry, p.539-547, 1991.