

REMOVAL OF CHROMIUM SPECIES FROM LIQUID EFFLUENTS BY FLOTATION – PART II – Cr³⁺

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ABSTRACT

The necessity of preservation of water quality standards and the maintenance of life conditions constrain the industries to treat their effluents, in order to reach the legislation limits of pollutants concentrations.

The aim of this paper is the removal of Cr³⁺ by precipitate flotation from dilute solutions.

The removal of Cr³⁺ using sodium dodecylsulfate (SDS) 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 6.0 and 9.0 reaching removal levels of around 85%, using SDS (10⁻⁴ mol.dm⁻³) as collector, for initial concentration of 0.5x10⁻⁴ mol.dm⁻³ of Cr³⁺. To study the influence of the other variables on the precipitate flotation was chosen the pH 8.0, where Cr(OH)₃ precipitate is the predominant species.

The increase of the ionic strength decreased significantly the removal of chromium species to the range between 64% and 42%. The presence of ethanol did not play an important role on precipitate flotation of chromium species.

INTRODUCTION

The necessity of preservation of water quality standards claims for the development of new cleaning techniques of industrial effluents, which are contaminated with a sort of pollutants, including heavy metals.

In this way, the maintenance of life conditions obliges the industries to treat their effluents, in order to reach the legislation limits of pollutants concentrations.

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,1994). 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 this type of separation are not efficient (Zouboulis et al,1991).

As an option, comes the precipitate flotation technique that is feasible to be a good option for the removal of species in very low concentrations.

The goal of the precipitate flotation is remove precipitated ionic species from dilute solutions with a suitable collector, then a gas phase is bubbled in the aqueous solution containing the precipitate, when occurs the interaction between the gas phase and the precipitate. (Scorzelli,1999)

This technique can be classified in two categories:

-First type precipitate flotation: consists in precipitate the ionic species with an appropriate reagent; after the precipitating occurs, the collector is added. The formed product can be floated through the preferential adsorption in the interface gas-liquid. (Matis et al,1991)

-Second type precipitate flotation: In this case, two hydrophilic ions are precipitated to form a hydrophobic compound. Due to that, its not necessary the utilization of collectors. (Matis et al,1991).

Figure 1 shows the speciation diagram for Cr³⁺ (logC as a function of pH) based on the equilibrium reactions proposed by Pourbaix (apud Deltombe et al,1974).

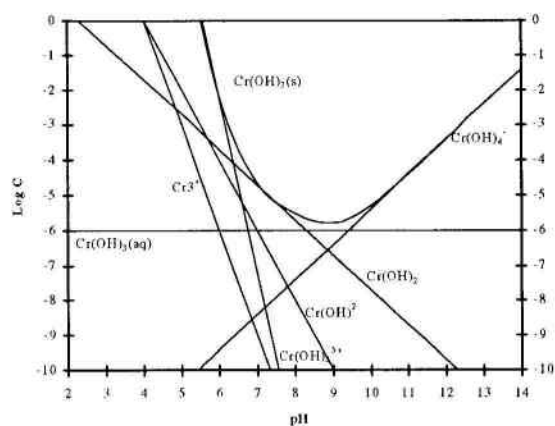
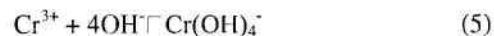
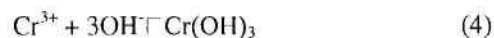
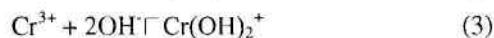
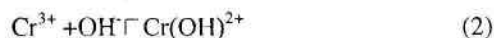


Figure 1 –Cr³⁺ speciation as a function of pH.

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 ≥ 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 ≤ 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, Cr³⁺ is less toxic than Cr⁶⁺. Trivalent chromium is a possible mutagenic agent. (Moore et al,1984) Epidemiological studies have shown a positive relationship between occupational exposure to

chromates and cancer incidence. (apud Moore et al,1984)

The aim of this paper is the removal of Cr³⁺ by precipitate flotation from dilute solutions, studying the influence of the following physical and chemical parameters:

- Solution pH,
- Flotation time.
- Initial collector concentration.
- Initial Cr³⁺ 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.

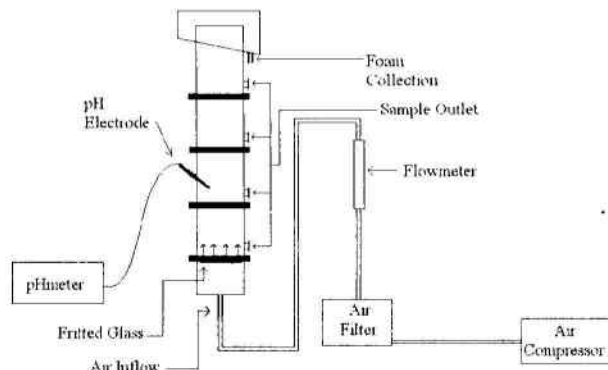


Figure 2 – Schematic diagram of the experimental apparatus.

The 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 ml.s⁻¹. Each experiment used an initial volume of 1 liter, filling approximately half column.

Reagents

The following reagents were used: chromium trichloride hexahydrated (CrCl₃.6H₂O) from Vetec, as metal ion font; sodium dodecylsulfate (SDS: C₁₂H₂₅NaO₄S) from Henkel, as collector; ethanol

(C₂H₅OH) from Merk, as frother; sodium chloride (NaCl) from Vetec, sodium sulfate (Na₂SO₄) from Vetec and sodium phosphate (Na₃PO₄) from Henkel, to alter the ionic strength; sulphuric acid (H₂SO₄, 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 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):

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

RESULTS AND DISCUSSION

In this study, the experiments were carried out varying solution pH, flotation time, initial collector, frother and Cr³⁺ concentrations and ionic strength in order to study their influence in ionic flotation of Cr³⁺.

Figure 3 shows the effect of solution pH on precipitate flotation recovery. It can be seen that in the pH range between 6 and 9, the flotation has the highest performance. The literature (Zouboulis et al,1991) suggests that the formation of Cr(OH)₃ precipitate can explain the recovery increase for pH values higher than 5.5. This precipitate is positively charged for pH values below 9.0; in this way it can be easily removed in the presence of anionic collector. Zouboulis (Zouboulis et al,1992) has presented similar results for the removal of Cr³⁺ in the presence of SDS as collector.

For more alkaline pH solutions, the decrease on Cr³⁺ removal can be explained by the change in the superficial charge of the precipitate, from positive to negative, what hinders the precipitate flotation using anionic collector. (Zouboulis et al,1992)

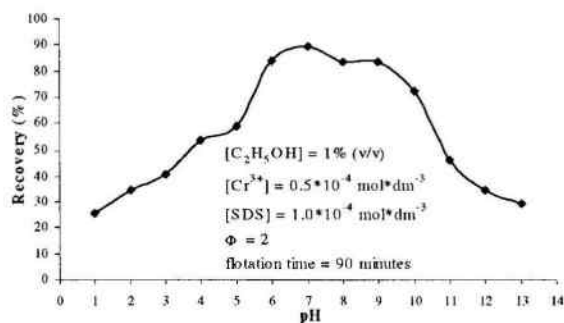


Figure 3 - Effect of solution pH on precipitate flotation recovery.

Figure 4 shows the recovery of Cr³⁺ as a function of flotation time. 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.

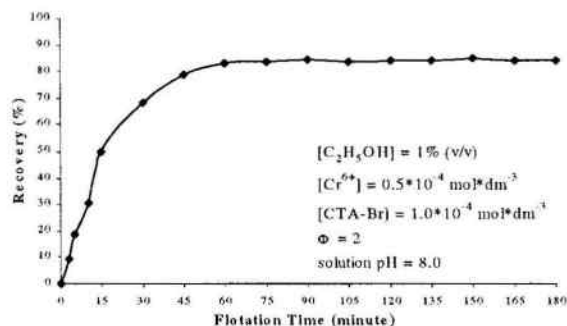


Figure 4 - Effect of flotation time on precipitate flotation recovery.

Figure 5 presents the behavior of precipitate flotation within the variation of initial collector concentration. For SDS concentrations less than 1.0×10^{-4} mol.dm⁻³ there was a low recovery. Pinfold (Pinfold,1972) has suggested that reduced collector concentrations may be not sufficient to provide hydrophobic characteristics to all Cr(OH)₃ precipitate particles.

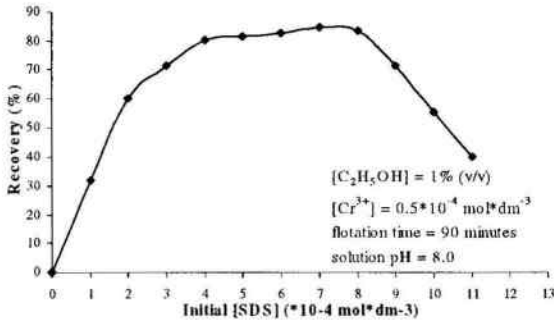


Figure 5 – Effect of initial concentration of collector (SDS) on recovery of Cr³⁺ precipitate flotation.

For SDS concentrations between $1.0 \cdot 10^{-4}$ and $6.0 \cdot 10^{-4}$ mol.dm⁻³ the recovery was higher than 70%.

There is a decrease in recovery for SDS concentrations above $6.0 \cdot 10^{-4}$ mol.dm⁻³. As reported in the literature (Sebba,1962) the decrease on precipitate removal due to the increase on collector concentration may be related to the change of the amphipatic characteristics of the precipitate (hydrophobic to hydrophilic).

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

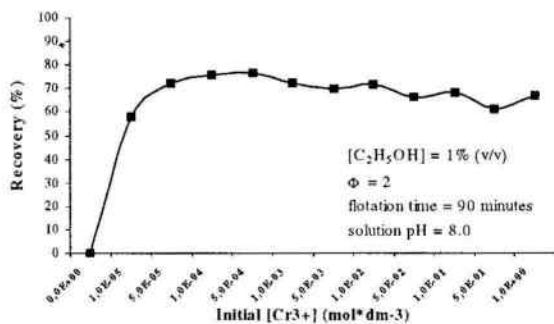


Figure 6 – Effect of initial concentration of the metallic ion (Cr³⁺) on the recovery of Cr³⁺ precipitate flotation.

Figure 7 shows the recovery results of precipitate flotation in which the presence of different salts change the ionic strength. For values of salt concentration until $5.0 \cdot 10^{-3}$ mol.dm⁻³ there is no significant recovery decrease, Above this value there is a decay on precipitate removal. The major decrease occurred within the addition of the trivalent salt, than those derived by the addition of divalent and monovalent salts. In this

case, the salt anions may have adsorbed on the particles surface.

As reported in literature (Pinfold,1972), the presence of salts in solution may interfere in the electrostatic interactions between surfaces of the precipitated particles and the collector ions. Zouboulis (Zouboulis et al,1992) obtained similar results for Cr³⁺ precipitate flotation in the presence of phosphate ions, particularly, in concentrations higher than $1.0 \cdot 10^{-3}$ mol.dm⁻³, which depicts the important role of the ionic strength that, in general, imparts the flotation process.

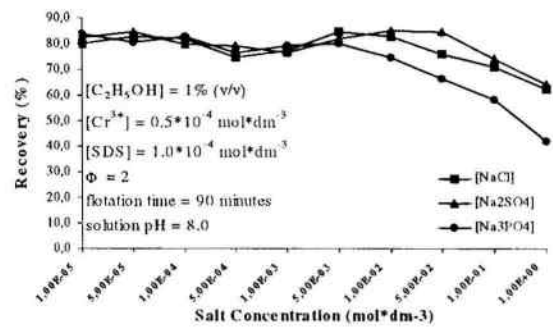


Figure 7 – Effect of ionic strength on the recovery of Cr³⁺ precipitate flotation.

Figure 8 illustrates the influence of the initial ethanol concentration on Cr³⁺ precipitate flotation recovery. The results show that the frother does not affect significantly the Cr³⁺ precipitate flotation.

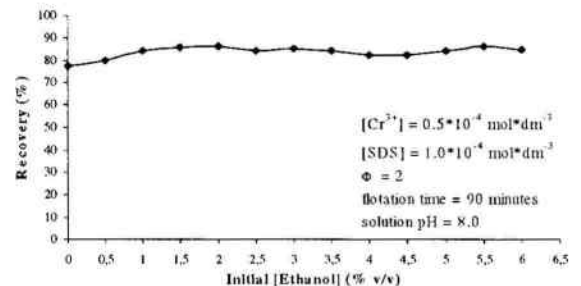


Figure 8 – Effect of frother (ethanol) concentration on the recovery of Cr³⁺ precipitate flotation.

CONCLUSIONS

- Cr³⁺ can be removed from aqueous solutions (as Cr(OH)₃ precipitate) by precipitate flotation in the following conditions.
 - pH: 8.0;
 - Flotation time: 90 minutes;

- Collector / metal ratio (Φ): 2
- For the same collector / metal ratio, the use of 1% (v/v) improves the removal of Cr^{3+} from a value of around 77 % to a value of around 80%.
- In the experimental conditions of this work, the increase of ethanol concentration did not improve the recovery of Cr^{3+} . It could be concluded that, in this case, the frother does not affect the precipitate flotation.
- The increase of ionic strength affects the recovery of $\text{Cr}(\text{OH})_3$ precipitate, particularly, the addition of the phosphate anion.

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