

## Technical note

## The removal of zinc from liquid streams by electroflotation

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## Abstract

The removal of heavy metals from dilute aqueous solutions (in the range of  $10^{-7}$ – $10^{-4}$  mol dm<sup>-3</sup>) is often not acceptable using classical methods, which do not achieve levels in accordance with environmental quality standards. Electroflotation has certain desirable characteristics, compared to dissolved and dispersed air flotation, particularly in regard to the small bubble size distribution of the process. The aim of this work was to develop an electroflotation (EF)/electrocoagulation (EC) cell to study this combined process and the influence of some relevant parameters/variables, such as collector concentration, tension and current density variation, on the removal of zinc from synthetic solutions containing 20 mg l<sup>-1</sup> of the metal. A platinum gore (5 mm) anode and stainless steel mesh cathode were used in the electroflotation cell. The work showed that it was possible to remove zinc by electroflotation, 96% removal being achieved using sodium dodecyl sulfate (SDS) as collector in the stoichiometric ratio 1:3, current density of around 8 mA/cm<sup>2</sup> and an inlet pH of about 7.0.

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## 1. Introduction

## 1.1. Electroflotation

Electroflotation (EF) is a simple process that floats pollutants (or other substances) by their adhesion onto tiny bubbles of hydrogen and oxygen generated from electrolysis of aqueous solutions (Srinivasan and Subbaiyan, 1989; Hosny, 1996; Burns et al., 1997; Jung and Han, 2002; Casqueira et al., 2002; Chen, 2004). The electrochemical reactions at the cathode and anode are therefore mainly hydrogen and oxygen evolution, respectively.

Considering the increasing importance of EF as a tool for environmental applications, the aim of this work was to develop and build an experimental apparatus, operating

continuously, in order to treat any liquid effluent, combining two unit operations (EF and EC) into a single device and, in particular, to electrofloat Zn<sup>2+</sup> from a synthetic solution which contained an initial concentration of 20 mg l<sup>-1</sup> of zinc, at bench scale. The cell design was based on various cell projects found in the literature (Fukui and Yuu, 1984; Jung and Han, 2002; Srinivasan and Subbaiyan, 1989; Chen et al., 2002, 2000; Burns et al., 1997; Ibrahim et al., 2001; Chen, 2004; Gao et al., 2005; Poon, 1997; Manohar et al., 1982; Ibanez et al., 1998).

## 1.2. EF operation – main parameters

The performance of an EF system is assessed by the pollutant removal efficiency and the power and/or chemical consumptions.

## 1.2.1. pH effect

The bubble size distribution depends on the solution pH as well as the electrode material (Chen et al., 2002). The

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hydrogen bubbles are smallest at neutral pH. The size distribution of oxygen bubbles increases with pH. It should be pointed out, however, that the cathode materials affect the size of the hydrogen bubbles, as do the anode materials. The bubble size obeys a log-normal distribution (Fukui and Yuu, 1984).

Using a buffer solution, Llerena et al. (1996) showed that the recovery of sphalerite fines was optimal at a pH range between 3 and 4. It was also observed that, within this pH range, the hydrogen bubbles were smaller, about  $16 \pm 2 \mu\text{m}$ . At pH 6, the mean hydrogen bubble diameter was  $27 \mu\text{m}$ . At pH 2, the mean diameter of the hydrogen bubbles was about  $23 \mu\text{m}$  when the current density was fixed at  $500 \text{ A/m}^2$  using a 304 stainless steel wire mesh.

### 1.2.2. Effect of current density

The gas bubbles are also influenced by the current density (Ketkar et al., 1988, 1991). Moreover, the bubble swarm flux, defined as the number of gas bubbles available per second per unit cross-section area of the flotation cell, also plays an important role in the recovery of fine particles and colloidal matter (Ketkar et al., 1991). A decrease of gas

bubble size distribution was achieved with increase in current intensity, as also observed by Shen et al. (2003).

### 1.2.3. Effect of collector type and concentration

The key to floatability of chemical species in liquid streams is hydrophobicity, the ratio of collector to metal ion being an important factor. The amount of collector used in ion flotation should be at least stoichiometric if it has frother properties (Casqueira and Torem, 2003). Usually a small excess of collector is added to guarantee maximum removal of the metallic ions in solution.

## 2. Experimental apparatus

Fig. 1 shows the experimental device. The main advantages of this equipment are the continuous flow and the reactor capacity and design, compared with other devices (Fukui and Yuu, 1984; Jung and Han, 2002; Srinivasan and Subbaiyan, 1989; Chen et al., 2002, 2000; Burns et al., 1997; Ibrahim et al., 2001; Chen, 2004; Gao et al., 2005; Poon, 1997; Manohar et al., 1982; Ibanez et al., 1998). The apparatus can be used for EF and/or EC. This work deals only with the EF chamber and its components.

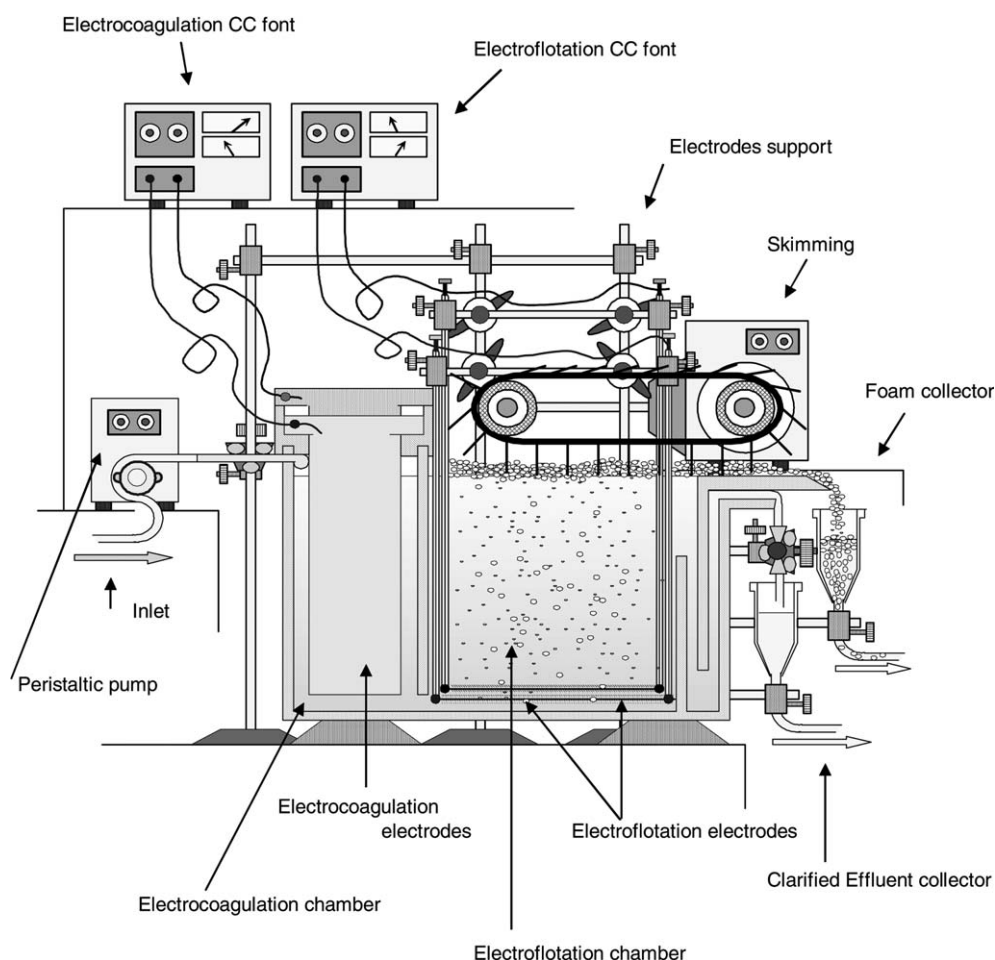


Fig. 1. Experimental apparatus.

Electrodes of platinum gore (5 mm) and stainless steel mesh were used as anode and cathode, respectively. The complete device is shown in Fig. 1.

### 2.1. Experimental procedure

The complete procedure has been described elsewhere (Casqueira, 2004).

The reagents used in the experiments were:

- Zinc sulfate ( $\text{ZnSO}_4$ ).
- Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ).
- Sodium dodecylsulfate (SDS) ( $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$ ).
- Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) (0.1%).
- $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ .

Stock solutions containing zinc sulfate (20 mg/l) were used for all experiments. SDS was utilized as collector, in stoichiometric ratios equal to 1, 2 and 3. Ethanol (0.1% vol.) was used in all tests.

## 3. Results and discussion

### 3.1. Effect of tension and current density

Fig. 2 shows the effect of the current density on the removal of zinc by EF. Although almost constant, an average removal of around 92% was achieved. Comparing the results obtained in this study with similar ones described by Burns et al. (1997), Hosny (1996) and Chen et al. (2000), it can be observed that the current density did not prove to give meaningful results in the studied range. The electrochemical reaction was found to be limited, probably by diffusion, resulting in a linear relationship between the current density and the zinc removal, as shown in Fig. 2. The increase of tension promoted

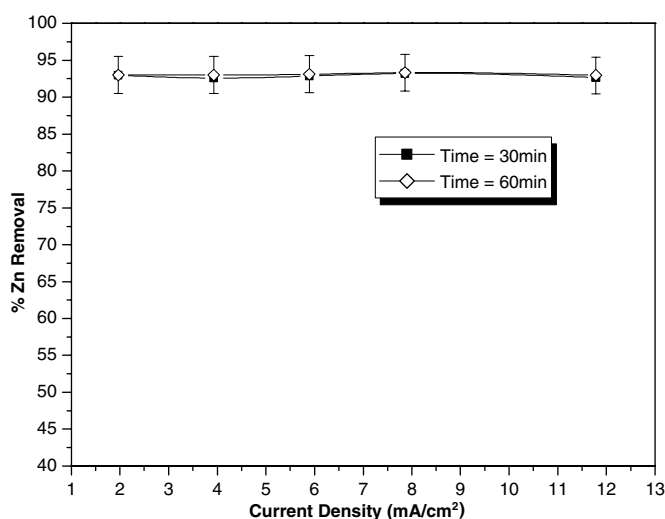


Fig. 2. Removal of zinc by EF as a function of the current density (Zn:SDS ratio = 3).

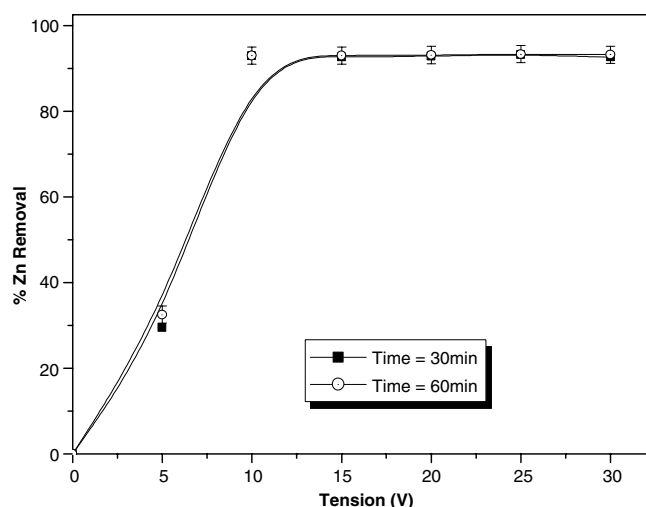


Fig. 3. Removal of zinc by EF as a function of the tension between the electrodes (Zn:SDS ratio = 3).

an increase in bubbles swarm, nevertheless insufficient to increase the Zn removal.

Fig. 3 shows the effect of the tension on the removal of zinc by EF. It was observed that tension values above 10 V promoted a dense and homogeneous bubble swarm, suggesting that, under these conditions, there are enough bubbles available to be attached to the metal-collector species, unlike when 5 V was applied. The results are in very good agreement with the literature related to the EF of solid particles, oil and grass or turbidity removal (Chen et al., 2000; Jung and Han, 2002).

Srinivasan and Subbaiyan (1989) also studied the removal of cadmium and zinc (among other metals) using an EF reactor. In their work, they also observed a small variation in the removal at different pH values and other physical conditions.

### 3.2. Collector concentration

Previous work on ion flotation have indicated that the use of specific stoichiometric ratios of collectors (Zouboulis et al., 1990; Scorzelli, 1999; Scorzelli et al., 1999; Huang et al., 1995) plays an important role in the removal performance.

It is observed (Fig. 4) that high Zn removal, around or higher than 90%, was achieved when the metal:collector ratio increased. When 1:1 collector:colligant ratio was used a very thin and unstable foam layer was formed at the top of the cell.

Similar results can be found elsewhere. Sreenivasarao et al. (1993) studied the removal of Pb and Cu from dilute aqueous solutions using SDS as collector. Operating a non-continuous 45 ml reactor, they obtained up to 75% removal after 60 min tests.

Fig. 5 shows the effect of pH on the removal of zinc by EF. The optimum conditions of zinc removal were carried out under several pH values. It was seen that is possible to

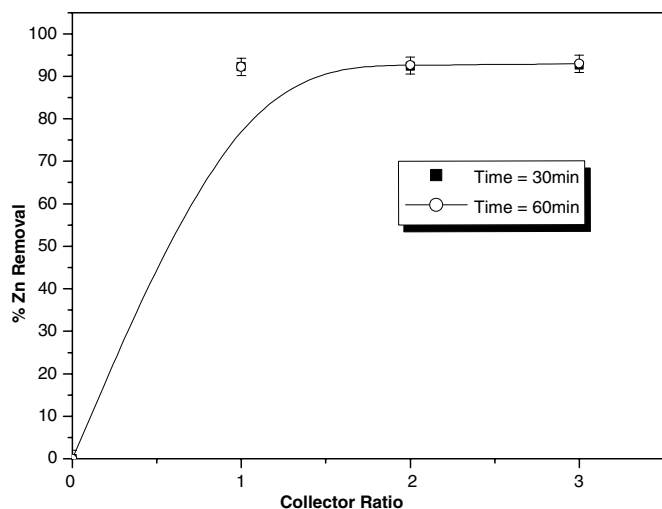


Fig. 4. Removal of zinc by EF as a function of the collector ratio (current density: 8 mA/cm<sup>2</sup>).

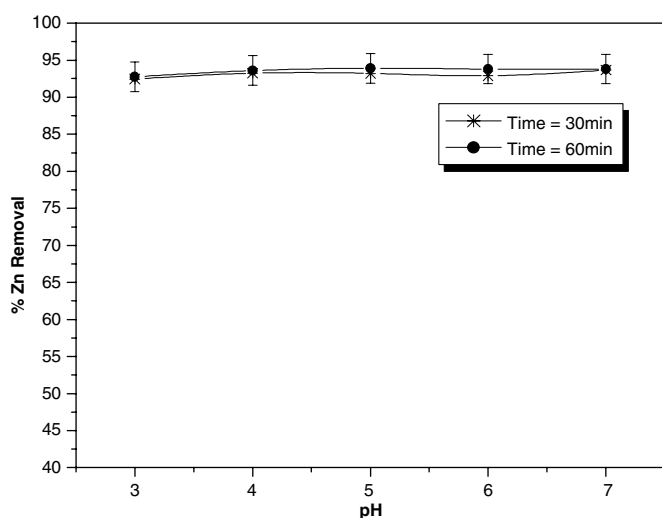


Fig. 5. Removal of zinc by EF as a function of the pH (collector:metal ratio equal to 3:8 mA/cm<sup>2</sup> as current density; voltage: 15 V).

remove Zn<sup>2+</sup>, as the predominant species, in the pH range around 7.0, which is in accordance with most of the general environmental rules or procedures.

#### 4. Conclusions

It was feasible to remove up to 96% of the zinc by EF. The predominant zinc ionic species, Zn<sup>2+</sup>, in the aqueous solution interacts with the sodium dodecyl sulfate collector by electrostatic interaction. The optimum conditions were as follows: tension 15 V, current 400 mA, 150 mg/l Na<sub>2</sub>SO<sub>4</sub> as an electrolytic support, inlet pH around 7.0, initial amount of zinc 20 mg/l, 0.1% ethanol (as a frother), 8 mA/cm<sup>2</sup> current density and molar ratio 3:1 SDS:zinc.

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