Adsorbing colloidal flotation removing metals ions in a modified jet cell

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ABSTRACT

The removal of Cu²⁺, Zn²⁺ and Ni²⁺ ions from synthetic wastewater with a modified Jameson cell (MJC) was studied using adsorption colloidal flotation (ACF). A colloidal dispersion of Fe (OH)₃ (formed in situ from FeCl₃) at pH 11 was used as an adsorbent colloid to ensure full adsorption and precipitation. The precipitates were flocculated with polyacrylamide and hydrophobised with sodium oleate and pine oil as a frother during the flotation stage. In the modified jet cell, the downcomer was sealed at the bottom with a diffuser, and the re-flotation of detached flocs and the probability of bubbles/particles capture was enhanced, which improved the recovery rate. As a result, the modified Jameson cell was more efficient (higher loaded carrier recoveries) than the conventional jet cell (CJC) in removing heavy metals ions. The physico-chemical characteristics, cell design and operating parameters were studied, and the removal efficiency was evaluated by monitoring the final concentration of ions in the treated effluent. The results indicated that the removal efficiencies of the MJC were approximately 95% and 98% for dilute (Cu²⁺, Zn²⁺ and Ni²⁺ concentration of 2 mg/L) and concentrated wastewater (25 mg/L of each ion), respectively. The optimal parameters included a Fe⁺³/ion ratio of 0.5 and a minimum air flow-rate/feed flow-rate ratio of 0.18. The results are discussed in terms of the physical and physico-chemical parameters, and the findings suggested that the proposed flotation technique has great potential for the treatment of wastewater.

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1. Introduction

The extraction, purification and processing of ores involves the use of large amounts of water, which generates contaminated effluents. The pollutants associated with these effluents can include colloidal and suspended solids, residual chemical reagents, heavy metal ions, toxic anions, oils used in machines and lubrication (emulsified or non-emulsified) organic waste (frothers, collectors and surfactants), flocculants, flotation modifiers, organic solvents, and others. (Rubio, 1998; Rubio et al., 2002; Carissimi et al., 2007; Rodrigues and Rubio, 2007).

When liquid wastes are generated in abandoned mining sites, tailing deposits and tailing dams, the solution may be acidic (pH is less than 7) and contain significant amounts of dissolved metals such as nickel, copper, zinc, lead, mercury, manganese and sulphate, among other ions (Silveira et al., 2009).

The conventional method for the removal of ions (mainly heavy metals) is precipitation-settling, followed by thickening, deposition and sludge filtration. Other methods that can be used to treat effluents containing anions and dissolved heavy metals are micro/nano/ultrafiltration, reverse osmosis, ion exchange, flotation and biosorption (absorption and/or adsorption). Some of these processes have high operating costs, whereas others are inefficient (Silveira et al., 2009).

Among novel toxic waste removal techniques, methods based on flotation and the immobilisation of pollutants as precipitates or adsorbates have potential in wastewater treatment. Some alternative methods for heavy metal ion removal are precipitate flotation, adsorbing colloid flotation (ACF) and adsorbing particle flotation (APF).

ACF involves the removal of metal ions by adsorption onto a precipitate (coagula), which acts as an adsorbing carrier. The loaded carrier is then floated by adding a flocculant and/or a suitable collector surfactant. Carriers that have been employed in ACF include ferric or aluminium hydroxides and sodium oleate or lauryl sulphate (Rubio, 1998; Alexandrova and Grigorov 1996; Stalidis et al., 1989; McIntyre et al., 1982; Carissimi et al., 2007; Rodrigues and Rubio, 2007). Several examples of studies on ACF are summarised in Table 1.

Dissolved air flotation (DAF) devices are widely used for solid/liquid separation. However, when large volumes of effluent must be treated, this equipment presents several limitations due to its low
throughput (approximately 7 m$^3$/m$^2$/h). In DAF, particles, oils and precipitate-loaded adsorbents are removed by flotation via fine bubbles or microbubbles.

Flotation devices (and their applications) differ based on the volume of air introduced during the process and the concentration of solids to be separated. For instance, compared to mineral separation (30–40% weight basis), DAF processes can be used to separate solids that are present in relatively low concentrations (1–3% weight basis) (Rubio et al., 2002). DAF microbubbles are used to catch only small, light solids, such as metal-ion hydroxide flocs and bacteria, which have a specific weight that is similar to that of water. Namely, bubbles generated in ore flotation machines (600–2500 μm diameters) are not applicable for separating the aforementioned materials (Solari and Gochin, 1992; Rubio, 2003; Rubio et al., 2002).

Nowadays, non-conventional flotation technologies such as Jameson cells, columns and centrifuge cells that are used for the concentration of minerals are potential alternatives for the removal of ion-loaded precipitates (Clayton et al., 1991; Santander and Rubio, 1998; Santander et al., 1999). However, the mechanical strength of adsorbing colloids is too low to withstand turbulent hydrodynamic conditions. Thus, a flocculant must be added to increase the mechanical strength and resistance of the colloids to shear stress (Pavez et al., 2000; Rubio et al., 2002).

Jameson cells have shown great potential, in mineral processing solid/liquid separation and liquid/liquid separation (Jameson and Manlapig, 1991; Cowburn et al., 2005). The main advantage of

<table>
<thead>
<tr>
<th>Adsorbing-carrier colloids</th>
<th>Contaminants</th>
<th>Author(s)</th>
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<tr>
<td>Fe(OH)$_3$</td>
<td>Cu</td>
<td>Choi et al. (2000)</td>
</tr>
<tr>
<td>Polyaluminum chloride (PAC)</td>
<td>Zn, Pb, Cu, Ni</td>
<td>Huang et al. (2000)</td>
</tr>
<tr>
<td>FeCl$_3$, 6H$_2$O</td>
<td>Zn, Cu, Cd, Pb</td>
<td>Sabti et al. (2002)</td>
</tr>
<tr>
<td>Fe(OH)$_3$ or Al(OH)$_3$</td>
<td>Zn, Cd</td>
<td>Jurkiewicz (2005)</td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
<td>Cu, Cd, Pb, Ni</td>
<td>Matisi et al. (2005)</td>
</tr>
<tr>
<td>Polyaluminum chloride silicate (PAX-XL60 S)</td>
<td>Cu</td>
<td>Ghazy et al. (2006)</td>
</tr>
<tr>
<td>ZnHCF</td>
<td>$^{137}$Cs</td>
<td>Shakir et al. (2007)</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of Jet (Jameson) flotation cells (a) CJC-Conventional and (b), (c) MJC-Modified Jameson cell.
Jameson cells is their high efficiency and moderate equipment costs (Clayton et al., 1991; Harbort et al. 1994). Nevertheless, in some cases, the rupture of fragile coagula or flocs has been observed in the downcomer. However, these problems have been recently overcome by applying low-shear mixing heads, recycling of treated water and adding polymeric flocculants to the downcomer. As a result, Jameson cells can be used in wastewater treatment and the recovery of solvent extraction liquors (Readett and Clayton, 1993), municipal waters (Yan and Jameson, 2004) and the treatment of wastes from a variety of industries, such as dairy factories, abattoirs, metal finishing, rolling mills and coke ovens.

The Jameson cell provides many advantages such as a compact design, low capital cost, no moving parts, low power consumption, low maintenance costs, low residence times (<3 min), high throughput and high efficiency.

The objective of the present work was to modify the design of a jet flotation cell and study the removal efficiency of heavy metals (Cu, Ni and Zn) using ferric hydroxide as a model colloid of a carrier adsorbent. The work is a continuation of a series on applications of a rapid flotation to remove pollutants (Santander et al., 2011).

2. Experimental

2.1. Materials

Synthetic effluents containing copper, nickel and zinc ions were obtained by dissolving analytical grade CuSO₄·5H₂O; NiSO₄·7H₂O and ZnSO₄·6H₂O in water at pH 2. Fe³⁺, which was obtained by dissolving FeCl₃·6H₂O in water, was used as a co-precipitant, and its hydrolysis product (Fe (OH)₃) was used as an adsorbing colloidal precipitate.

Sodium polyacrylate (molecular weight = 1000,000) was used as a flocculant (Alcotac FE4 from Ciba Specialty Chemicals), and sodium lauryl sulphate and pine oil were used as a flocs collector and frother, respectively. The pH of the medium was modified with sodium hydroxide (NaOH), and de-mineralised water was used to prepare the reagents.

2.2. Flotation cells

The removal of loaded colloid was achieved using a conventional jet cell and a modified jet cell. Both lab flotation cells possessed a capacity of 0.42 m³/h and consisted of a downcomer, a flotation tank and a level control system. The cell tank (acrylic) possessed a diameter and height of 0.145 m and 0.55 m (9 L capacity), respectively, and the froth launder was 0.3 m in diameter and 0.2 m in height. Synthetic wastewater was pumped at a flow rate of 0.13 m³/h and was fed to the cells using a helical pump with a capacity of 0.5 m³/h.

2.3. Conventional Jameson cell

Fig. 1a shows a schematic diagram of the conventional Jameson cell system. The cell consisted of a downcomer (contact tube), a 50-L PVC flotation tank (phase separation) and a level control system. The downcomer possessed a height and diameter of 1.8 m and 25 mm, and was equipped with an air injector (a nozzle constrictor 3 mm). The level control system was made of PVC and was used to adjust the height of the liquid in the flotation tank (height of the froth layer).

2.4. Modified Jameson cell

Fig. 1b shows a schematic representation of the modified cell. As shown in the figure, a bottom blind diffuser was placed at the end of the downcomer, which allowed air bubbles/flocs to move in an upward direction towards the frothy phase. If flocs break, the detached units can be recaptured by the rising bubbles.
2.5. Methods

The model effluent was prepared by dissolving different metal salts and varying the concentration of Cu$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$ in a 50-L tank of tap water (acidic medium, pH 3). Next, predetermined concentrations of FeCl$_3$·6H$_2$O were added, and the pH of the solution was adjusted to 11 to generate colloidal precipitates (Fe(OH)$_3$), which adsorb heavy metal ions. The performance of the flotation cells in the removal of copper ions were compared, and the MJC was used to separate loaded carriers from dilute (2 mg/L Cu, Zn and Ni ions) and concentrated synthetic effluent (about 24 mg/L Cu, Zn and Ni ions). Finally, the effects of the Fe/metal ion concentration and the air flow-rate/feed flow-rate ratio were studied. The results were expressed as the mean, which was obtained by conducting 20-min tests in triplicate. The standard error of the mean was ±5%, and the confidence interval was 95%.

The pH of the solution was not increased in the absence of Fe salts; otherwise, metal ions would precipitate (especially in concentrated solutions). In fact, whether or not precipitation would occur was difficult to ascertain due to kinetic reasons. A pH of 11 was selected because the colloids were larger and more consistent under these conditions; however, the colloids could not withstand shearing. Thus, 10 mg/L of flocculant was added to prevent precipitate shearing and breakage problems in the injector.

Thereafter, a collector and a frother were added at a concentration of 50 and 10 mg/L, respectively. The collector was required because the loaded colloids, now in the form of flocs, were fairly hydrophilic, and the frother was used to prevent the formation of large bubbles, which create turbulence in the downcomer and phase separation tank. The time required to achieve colloid formation and floc adsorption was established in preliminary studies and was equal to 5 and 10 min, respectively.

In both cells, the collection (collision–adhesion) of aggregates/flocs via air bubbles occurs in the downcomer, and separation occurs in the flotation tank. The mixture falls, and light aerated flocs rise to the froth layer. Alternatively, treated water is discharged at the bottom of the tank. Table 2 summarises the operating parameters of both cells.

3. Results and discussion

Fig. 3 shows the removal efficiency of copper ions in the CJC and MJC. As shown in the figure, the removal rates of the MJC were higher for the entire concentration range of Cu$^{2+}$ ions. With the CJC, the removal rates were always <90%. In contrast, with the MJC, nearly complete removal was achieved.

The inferior performance of the CJC was due to the fact that some air bubbles/flocs units are discharged in the jet and break apart in the separation tank. As a result, flocs are carried by entrainment towards the discharge of the clarified effluent (short circuit). The detached flocs cannot be re-collected and are trapped by the turbulent flow-rate of the treated water.

Alternatively, floc breakage appears to be diminished in the MJC. Herein, the jet is diverted in an upward direction, dispersing air bubbles/flocs throughout the separation tank, decreasing the probability of bubble/floc detachment and allowing re-flotation.

The results shown in Fig. 3 suggested that concentration effects were not as pronounced in the MJC, and the removal rates fluctuated between 95% and 99%. At an initial copper dosage of 25 mg/L, the final concentration of the effluent was 0.15 mg/L, which is within the analytical error of the atomic absorption spectrometer. The same effect was observed when the copper concentration was equal to 2 mg/L; however, the concentration of copper in the treated effluent was only 0.10 mg/L. Thus, compared to that of the CJC, a 19% higher removal efficiency was attained with the MJC.

Table 3 shows the adsorbing colloidal flotation results for the removal of ions in dilute and concentrated solutions (Cu, Ni and Zn) with the MJC, and Fig. 4 provides a detailed depiction of the loaded froth.

The removal efficiencies were slightly higher for the dilute solution than the concentrated effluent because the (Fe$^{3+}$/Cu$^{2+}$, Zn$^{2+}$, Ni$^{2+}$) ratio was fairly low (approximately 0.26 for the loaded samples). Nevertheless, as shown in Table 4, at higher (Fe$^{3+}$/Cu$^{2+}$, Zn$^{2+}$, Ni$^{2+}$) ratios, superior performance was observed. Thus, a minimum ratio of 0.5 was required to attain removal rates >98%. Under the optimal conditions, the residual content of the ions in the treated effluent was always lower than those permitted by the emission standards of Brazil for the discharge of wastewater into reservoirs.

The results indicated that both flocculant and collector were necessary to achieve good separation. In the absence of these reagents, incomplete separation was observed due to the destruction of colloids under shearing (results not shown).

The effect of the air flow-rate/feed flow-rate ratio on the metal (Cu, Zn and Ni) ion removal rate (25 mg/L of each metal ion) in the MJC was studied under constant operating conditions. The feed flow-rate was maintained at 2140 mL/min, and the air flow rate was varied between 133 and 862 mL/min.

As shown in Table 5, a minimum ratio of 0.18 was required to attain optimal performance (>97% metal ion removal). Namely, when the ratio was less than 0.18, the removal efficiencies decreased to 67%. Moreover, when the air flow-rate/feed flow-rate ratio was >0.35, a slight decrease in the performance was observed.

At low air flow-rates, the Sb value, or the superficial bubble surface area flux and carrying capacity of the device were fairly low,
which reduced the overall recovery rate (low capture and low flotation probabilities). As a result, the metal ion loaded-floc carrier recovery rate increased with an increase in the air flow-rate/feed flow-rate ratio and reached an optimal value at 0.18–0.25. Thereafter, when high Sb values or air flow-rates were employed, the degree of turbulence inside the downcomer increased, causing the jet to fall downwards rapidly, which increased the amount of drag on the loaded precipitates, especially those that were not flocculated or weakly attached to air bubbles. As a result, the overall carrier and metal ion removal rate decreased.

4. Conclusions

The results of the present study showed that the modified jet flotation (MJC) was more efficient than the conventional jet cell (CJC) in the removal of heavy metals ions by adsorption onto iron hydroxide colloidal precipitates. To achieve good flotation separation, metal ion loaded-precipitates must be flocculated (using polyacrylamide) to withstand shearing and hydrophobised with sodium oleate to improve bubble capture. Moreover, pine oil must be used as frother to stabilise bubbles and to achieve froth formation. With the MJC, removal efficiencies of 95% were obtained for synthetic wastewater contaminated with low concentrations of heavy metal ions (2 mg/L of Cu^{2+}, Zn^{2+} and Ni^{2+}), and removal efficiencies of 98% were obtained for solutions with high concentrations of heavy metal ions (25 mg/L of Cu^{2+}, Zn^{2+} and Ni^{2+}). The residual concentration of metal ions in the treated water was lower than those permitted by Brazilian legislation. To achieve the desired removal efficiencies, a minimum (Fe^{3+}/ion) ratio of 0.5 and a minimum air flow-rate/feed flow-rate ratio of 0.18 are required. Thus, the proposed technique can be used to rapidly remove heavy metals ions from contaminated water or wastewater.

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