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Modified column flotation of adsorbing iron hydroxide colloidal precipitates

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Abstract

A promising technique for the removal of heavy metal ions from wastewater streams involved firstly the ions adsorption on a colloidal precipitate (carrier) and then the separation of the loaded flocs (coagula) by a modified column flotation. Here, the effluent feed and the carrier (ferric hydroxide) enter smoothly by the top of the column through a special diffuser, in counter current with rising bubbles (100–600 μm diameter) generated by using recycled water, surfactant and air suction through a venturi. High separation values of the column flotation of the carrier precipitates were achieved, despite the high superficial flow rate and the high Fe^{+3} concentration utilized (>60 mg L^{-1} Fe). No rupture of colloidal carrier aggregates was observed and a low split was ensured by monitoring the concentrate (floated product) flow rate. Results indicated that best separation was attained by controlling the medium pH (for best heavy metal ion adsorption onto the carrier), followed by sodium oleate, used as "collector" and optimizing operating parameters (conditioning, flow rates, etc.). The column throughput reached 43 m h^{-1} (m^3 m^{-2} h^{-1}), which is about 4 times the normal capacity of DAF-dissolved air flotation unit, the most used floater in wastewater treatment. Various metals (Cu, Ni, Pb, etc.) and molybdate ions present in synthetic and real effluent were successfully removed based on this colloidal adsorbing flotation principle. The process was also applied in a pilot scale to treat an industrial electroplating wastewater. Most of toxic metals (Cu, Ni and Zn) were reduced from initial concentrations of about of 2 to 10 mg L^{-1}, to below 0.5 to 1.0 mg L^{-1}, meeting local municipal discharge limits (but Cd ions). It is believed that flotation separation using medium-sized bubbles has great potential as a clean water and wastewater treatment technology.

Keywords: flotation; environmental; bubbles; wastewater; wasteprocessing

1. Introduction

The treatment of aqueous or oily effluents continues to be a serious environmental issue faced by the minerals and metallurgy industries. Main pollutants are metal ions (Cu, Cd, Pb) and some may be valuable (Au, Pt, Ag). The use of flotation is showing a great potential due to the high throughput of modern equipment, low sludge generation and the high efficiency of the separation schemes already available (Zabel, 1992; Rubio, 2003; Rubio et al., 2002a,b; Mavros and Matis, 1992; Matis, 1995; Voronin and Dibrov, 1999; Rosa et al., 1999; Parekh and Miller, 1999; Rosa and Rubio, 2005;

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Carissimi and Rubio, 2005). It is believed that this process will be soon incorporated as a technology in the minerals industry to treat these wastewaters reusing the process water (Rubio, 2003).

The removal of metal ions by precipitate flotation (such as hydroxides, insoluble salts or complexes with surfactants), adsorbing colloids and adsorbing particulate flotation has been proposed by several authors (Pinfold, 1972; Rubio et al., 2002a,b; Rubio, 2003). The latter method is a variant of the adsorbing colloid flotation process which, instead of colloids, employs particles as carriers and adsorbent material for the metal ions. The carrier may be a mineral particle, a polymeric resin, activated coal or a by-product having good adsorbing properties, large surface area and responsiveness to flotation.

The precipitate flotation process is based on the formation of a precipitate of the ionic species, using a suitable reagent, and its subsequent removal by attachment to air bubbles to form a flotation "concentrate" (Silva et al., 1993; Stalidis et al., 1989a,b; Mummallah and Wilson, 1981). Depending on the concentration of the metal solution, the precipitation may proceed via metal hydroxide formation or as a salt with an specific anion (sulphide, carbonate, etc.). In the case of anion removal, precipitation should proceed through the addition of a metal cation.

The adsorbing colloid flotation method involves the removal of the metal ion by adsorption on a precipitate (coagulum) acting as a carrier. The loaded carrier then floats usually assisted by a suitable "collector" surfactant. The main carriers commonly employed are ferric or aluminium hydroxides collected with the help of sodium oleate or lauryl sulphate (Stalidis et al., 1989a,b; Rubio et al., 2002a,b).

Most of the techniques used for applied flotation to wastewater use DAF, dissolved air flotation, whereby the bubbles are formed by a reduction of pressure of a water stream pre-saturated with air (or some other gas) at pressures usually exceeding 3 atm. In industrial practice, the supersaturated water is forced through needle valves, producing clouds of 30–70 μm diameter bubbles just down stream of the constriction. Yet the problem of using these bubbles is the low carrying capacity and for this reason high throughput column flotation using mid-sized bubble with higher "lifting power" values may be a good solution.

Column flotation is still a subject of great interest in mineral processing with a steadily growing number of research studies and industrial applications (Finch, 1995; Rubinstein, 1994; Finch and Dobby, 1990). In the columns used in the mineral processing area, feed slurry enters about one-third the way down from the top and descends against a rising swarm of bubbles generated by a sparger. In wastewater treatment, feed may enter by the column top in the middle of the "concentrate" product.

New developments in column technology include external gas spargers operating with and without addition of surfactant or frothers, columns with internal baffles and coalescers for oil recovery (Gu and Chiang, 1999). In the presence of the surface-active reagents fine bubbles can be obtained as in the Microcel column (Yoon et al., 1992; Yoon and Luttrell, 1994). Applications of column flotation in the field of oil removal in production waters (Rubio, 2003; Gebhardt et al., 1994) and in the recovery of heavy metals precipitates (Filippov et al., 2000; Filippov and Filippova, 2003) have been reported.

In this work, a technique for the removal of heavy metal ions from wastewater streams was studied using a colloidal ferric hydroxide precipitate (carrier) and then the separation of the loaded flocs (coagula) by a modified column flotation. Column design factors, loading capacity and removal efficiencies were the main parameters studied.

2. Experimental

2.1. Materials

Synthetic solutions were prepared with local tap water and reagent grade metal salts as contaminant models (Cu, Cd, Pb, Ni, etc.). $FeCl_3{\cdot}6H_2O$ was employed as the solute to form the hydroxo-precipitates, the adsorbent and carrier for the heavy metal ions. All the solutions were prepared immediately prior to each set of experimental runs. Dowfroth 1012, a commercial polypropylenglycol methyl ether-based frother, was used to create a stable froth. Sodium oleate, was employed as the carrier (iron precipitate) collector. The solution pH was adjusted using hydrated lime–$Ca(OH)_2$. Mafloc 490 C, a commercial polyacrylamide flocculant, was employed in some experiments to enforce the flocs resistance.

2.2. Methods

2.2.1. Laboratory column pilot tests

Precipitate flotation tests in counter-current mode were run in an open circuit using the pilot column. The experimental setup is shown in Fig. 1.

Main equipment were variable speed peristaltic pumps, centrifugal pumps, air and water rotameters, manual level controllers and pressure regulators. The