Advances in the adsorptive particulate flotation process

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Abstract

The removal of contaminants from liquid effluents by the adsorptive particulate flotation (APF) process, including new adsorbents and flotation devices, are reported. Herein, contaminants are adsorbed (and/or absorbed) onto the surface of a particulate carrier and both are separated attached to rising bubbles. The adsorbents were coal, charcoal, coal beneficiation tailings, modified Brazilian smectites and barite. Emulsified oils in water, dyes and metal ions present in synthetic and industrial effluents were successfully removed using various carrier and DAF, induced air flotation, IAF or jet flotation for the separation of the loaded carrier. Process efficiency was found to be a function of the carrier/contaminant mass ratio, size distribution of the carrier and system hydrodynamics. Results and mechanisms involved are discussed in terms of adsorption and flotation phenomena.

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Keywords: flotation; adsorption; pollutants; alternative adsorbents

1. Introduction

Mining, metallurgical, petroleum and chemical industries generate huge amounts of wastewater usually polluted by solid powders, process chemicals, organic and other compound (Rubio, 1998; Smith, 1989). Accordingly, the search for efficient and reliable technologies to remove and control these effluents is increasing.

Different authors have proposed flotation since its application to wastewater treatment has showed technical and economical advantages (Rubio et al., 2002). The APF or carrier flotation process is a variant of the adsorbing colloid flotation process, and employs particles as carrier-sorbing (absorbing and/or adsorbing) material for the pollutants. APF resembles oxide flotation activation by metal ions, sulfide depression by anions and coal flotation with oils. Conversely, the target here is the ions, flotation reagents and oils. The carrier can be minerals, polymeric resins, activated carbon, by-products, biomass or microorganisms and must have a high surface area, high reactivity with the pollutant to be removed and good characteristics of...
coagulation/flocculation and flotation (Rubio and Tessele, 1997; Zouboulis et al., 1992; Matis et al., 1989; Matis and Zouboulis, 1994; Zouboulis and Matis, 2000). Basically, the APF process includes the following stages: (a) contaminant adsorption; (b) flocculation or collector adsorption (optional) to aggregate or hydrophobize the loaded solid sorbent; (c) bubble–particle (or flocs) interactions; and (d) flotation of the loaded carrier. Several authors have proposed the removal of metal ions and others by APF process but no industrial plant has been installed yet. Table 1 summarizes some reported studies at bench and pilot scales.

Table 1

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Pollutants removed</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBT</td>
<td>Ni, Cu, Zn</td>
<td>Féris, 1998</td>
</tr>
<tr>
<td>Zeolites</td>
<td>Ni, Cu, Zn</td>
<td>Rubio and Tessele, 1997</td>
</tr>
<tr>
<td>Zeolites</td>
<td>Hg, As, Se</td>
<td>Tessele et al., 1998</td>
</tr>
<tr>
<td>Pyrite</td>
<td>Cu, As</td>
<td>Zouboulis et al., 1992</td>
</tr>
<tr>
<td>Red sludge</td>
<td>Cu</td>
<td>Zouboulis et al., 1993</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Pb</td>
<td>Zouboulis et al., 1993</td>
</tr>
<tr>
<td>Fly ash</td>
<td>Ni</td>
<td>Zouboulis et al., 1993</td>
</tr>
<tr>
<td>Ion exchange resin</td>
<td>Cu</td>
<td>Duyvesteyn and Doyle, 1995</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>Cd</td>
<td>Zouboulis et al., 1997</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Rhodamine B</td>
<td>Schneider et al., 1999</td>
</tr>
<tr>
<td>Streptomyces riomonus</td>
<td>Ni, Cu, Zn</td>
<td>Zouboulis et al., 2000</td>
</tr>
<tr>
<td>Nonliving digested activated sludge</td>
<td>Cd</td>
<td>Zouboulis et al., 2000</td>
</tr>
</tbody>
</table>

Metal ions carrier: CBT.

Dye carrier: CBT and Smectite (Bentonite). Samples of Na⁺ bentonite (<74 μm) (Paraiba, Brazil) modified with 1.1 ortho-phenanthroline (OP) (De Leon et al., 2001). The residual concentration of dyes was determined using spectrophotometry.

2.2. Emulsions and solutions

Petroleum emulsions: These were prepared to simulate offshore petroleum effluents, in a salty medium (NaCl) using a heavy oil, crude petroleum, having a specific gravity (ρ) of 0.933 g cm⁻³. The droplets size distribution (100% < 20 μm) was monitored with a Malvern Sizer, Model System 3601 and residual oil concentration measured by UV spectroscopy.

Dyes: brilliant green, and methylene blue in concentrations of about 40–50 mg l⁻¹.

Heavy metal solutions: NiSO₄·6H₂O, CuSO₄·5H₂O and ZnSO₄·7H₂O were used for the synthetic solution using tap water. An electroplating effluent had about 90 mg l⁻¹ total Zn, Ni, Cu ions (among others), a fraction being complexed with process reagents.

2.3. Flotation studies

IAF studies were performed in a Denver D-12, 1 L cell. Thus, 0.8 l of emulsion or dyes were conditioned in the same cell at 1450 rpm during 1 min, with the carrier and frother. Flotation proceeded introducing an air flow-rate of 15 l min⁻¹ during 2 min while keeping system stirring. Finally, the system was allowed to stand during 5 min before sampling.

Modified jet flotation, MJF. A Jameson type cell here has been redesigned placing an internal cylinder which receive the downcomer suspension allowing all particles to enter the separation zone by the
This artifact highly improved process efficiency (Fig. 1).

Dissolved air flotation (DAF) studies were conducted at bench and pilot (0.6–1 m$^3$ h$^{-1}$) scale (see Fig. 2). Process efficiency was evaluated by measuring the residual content of metal, oils, dyes and supernatant turbidity.

3. Results and discussion

3.1. Oils removal by APF-IAF

Table 2 shows results of oil separation by IAF with different oil sorbent materials. Results show that best oil sorbents were coal and CBT. Using coal, separation recovery of the oil reached 96%, yielding 19 mg l$^{-1}$ oil content in the treated water (20 mg l$^{-1}$, the target). Results with CBT yielded 94% removal and 26 mg l$^{-1}$ oil. However, after addition of a frother (16 mg l$^{-1}$ “Dowfroth 1012”), to improve froth stability, the removal with the tailing reached 98% and only 10 mg l$^{-1}$ in the treated water.

Fig. 1. Modified Jet flotation-MJF, used in the oil removal from petroleum/water emulsions (loading capacity, 25 m/h).

Fig. 2. Dissolved air flotation pilot unit (0.6–1 m$^3$/h).
The hydrophobic adsorbents such as coal and the CBT interact with the oil droplets by hydrophobic association (forces) as in coal froth flotation. Yet, barite may adsorb the oil via chemical and/or electrostatic mechanisms between the carrier surface sites and anionic groups present in this type of oils. Eventually, silanol groups “activated” with ferric or aluminum ions, present at the surface of quartz or clays (coal cleaning tailings) may also serve as adsorption sites.

3.2. APF-jet flotation of oils

Fig. 3 shows results of removal of highly difficult-to-treat emulsified oils (petroleum) using coal as the oil carrier and a high capacity jet, continuous flotation unit. Values attained 74% oil removal yielding final oil concentrations of about 40 mg l\(^{-1}\) in one stage and using a coal/oil ratio of about 1. These results are lower than those obtained in batch IAF tests whereby most parameters are optimized. Jet type of cells, like the Jameson cells, are very rapid flotation units with very low residence time, which, in one-stage operations, are usually accompanied with short circuits or low recoveries. Yet, new upcoming devices are endowed with recycling systems to enhance residence time thus solving these recovery problems.

Here, with less difficult-to-treat emulsified feeds (603 mg l\(^{-1}\) oil) and enhancing the retention time (optimal conditions), the removal was found to be normally greater than 80% regardless of the initial oil content. It is believed that this type of flotation cell has a great potential for oil or organic solvent removal at high throughput values (>25 m h\(^{-1}\)).

3.3. Removal of heavy metal ions APF-DAF (bench and pilot)

Fig. 4 shows comparative results between APF of metal-loaded CBT at bench and pilot scale and Brazilian emission limit concentration for wastewater discharge. Mechanisms involved in the sorption depend on the surface characteristics of the various compounds present in this coal tailing. Interfacial complexation between the hydrolyzed species and the negatively charged silicate surface and hydroxide precipitation at surfaces are considered the most important ones. Because of the high values of surface area, sorption capacity and price, CBT appears to have

<table>
<thead>
<tr>
<th>Oil adsorbents</th>
<th>(Oil)(i) (mg l(^{-1}))</th>
<th>(Oil)(f) (mg l(^{-1}))</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>445</td>
<td>105</td>
<td>76</td>
</tr>
<tr>
<td>Coal</td>
<td>440</td>
<td>19</td>
<td>96</td>
</tr>
<tr>
<td>Coal shale</td>
<td>478</td>
<td>40</td>
<td>92</td>
</tr>
<tr>
<td>Charcoal</td>
<td>476</td>
<td>40</td>
<td>92</td>
</tr>
<tr>
<td>CBT</td>
<td>438</td>
<td>26</td>
<td>94</td>
</tr>
<tr>
<td>CBT(^{a})</td>
<td>493</td>
<td>10</td>
<td>98</td>
</tr>
<tr>
<td>Barite</td>
<td>474</td>
<td>29</td>
<td>94</td>
</tr>
<tr>
<td>Barite(^{a})</td>
<td>447</td>
<td>29</td>
<td>94</td>
</tr>
</tbody>
</table>

\(R = \text{oil removal} = \{(1 - (Oil)\(f\)/(Oil)\(i\))\}100\).

\(^{a}\) With 16 mg l\(^{-1}\) frother (“Dowfroth 1012”).
an attractive potential as a low cost treatment of metal bearing liquid effluents.

3.4. Removal of oils, dyes and heavy metals—APF-DAF (pilot)

Fig. 5 shows the removal of oil, methylene blue and heavy metals by the APF-DAF process using CBT as carrier. Removal values higher than 85% was found for heavy metals and methylene blue and about 75% were found for oil removal.

The same figure shows that a separation efficiency of about 70% was reached for the heavy metal removal from the electroplating industrial effluent. This can be explained by the presence of other ions which also adsorb and reduce available adsorption sites and complexes which interfere and do not adsorb. Only the presence of these substances may explain the high amount of “soluble” ions and possess a huge problem for the treatment of this effluent.

3.5. Removal of dyes by APF-IAF using bentonites

Bentonites were modified with ortophenanthroline and ethylenediamine as sorbing material for oils, metal ions and dyes (De Leon et al., 2001). After this treatment, adsorption characteristics enhanced nearly 10 times, and when compared to ion exchange resins, these modified bentonites are quite similar in terms of adsorption capacity for metal ions.

In this work, the adsorption capacity for brilliant green, (BG) showed to be strongly dependent of solids concentration (MB-OP), achieving almost 100% efficiency with 1000 mg l\(^{-1}\) solid. The flotation of this loaded carrier is not straight due to the fineness, high surface area and hydrophilicity. Thus, a flocculant to reduce the number of particles (and surface area) and sodium oleate to gain hydrophobicity, were added. Best flotation results showed that IAF of dye-loaded bentonite intercalated with ortho-phenanthroline was successful, yielding 95–100% with the polyelectrolyte Nalco\textsuperscript{R} 440C. After the addition of flocculant (only 0.2 mg l\(^{-1}\)) and the surfactant (sodium oleate, 40 mg g\(^{-1}\)) to the solution, and 1 min of mixing at 1000 rpm, the formation of flocs took place rapidly. These hydrophobic flocs adhere readily to bubbles resulting in a high flotation rate.

4. Conclusions

1. High separation values were found for oil droplets—emulsified in water by APF (IAF or jet) using mineral particles or coal wastes as carrier. Treated solutions had very low content of oil, lower than emission limits. Best carriers were
the hydrophobic adsorbents, coal and coal beneficiation tailings.

2. The present investigation shows high removal efficiencies by APF (jet, IAF or DAF) using coal jigging tailings and modified bentonites. These carrier showed to possess good adsorbing and flotation characteristics for oils, dyes and heavy metal ions removal such as copper, zinc and nickel.

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References


