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The use of DAF (dissolved air flotation) as an alternative treatment for red mud wastewater

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ABSTRACT

The flotation process, largely used for mineral concentration processes, which is based on air bubble adhesion to the dispersed solid phase, is also being used for wastewater treatment purposes. Dissolved air flotation (DAF) is based on the separation of the solid-liquid phases with the aid of small air bubbles (10–100 μm), with high values of interfacial contact area, improving the process efficiency. In the process, the air bubbles and particles or flocs form aggregates, which rise to the surface of the flotation cell to be collected. The advantage of producing small bubbles is directly related to the fact that smaller bubbles result in greater bubble-particle interaction.

Wastewater produced in alumina refinery – from the red mud filtration step – has a red colored aspect due to the presence of very fine particles of red mud and also dissolved matter that still remain in the filtrate. This wastewater might be treated, aiming to reuse the water in the refinery or discharge it properly in the environment.

The aim of this study was to evaluate the DAF process efficiency for the treatment of red mud wastewater in order to decrease suspended particles and dissolved solids contents, in addition to mitigate the high causticity of this wastewater. The process efficiency was evaluated by comparing turbidity removal and total solids concentration in the treated wastewater to the feed. The influence of important variables of the DAF process as type and concentration of coagulant and flocculant were evaluated.

It was possible to obtain good turbidity removal efficiencies (up to 90%) using low concentrations of coagulant (50 mg/L) and flocculant (0.5 -1.0 mg/L). In addition, for most of the experiments, the specification for effluent diposal, according to the Brazilian environmental regulation 430 (Conama, 2011): pH range 5 to 9 and turbidity < 40 NTU, was attained. These results emphasize the possibility of using the DAF as an alternative technique to settling and filtration process, that are traditionally used, for treating wastewater from the alumina industry, allowing the reuse of water in the plant or adequate discharge with less environmental impact.

INTRODUCTION

The flotation process has been used since the beginning of the twentieth century in the selective separation of minerals, and more recently, in industrial-scale wastewater treatment. This process is based on adhesion of air bubble to the dispersed phase (particles), in which the bubble-particle aggregate entrained rises to the top of the flotation cell, where the recovery of particles occurs.

Dissolved Air Flotation (DAF) has the advantage to produce small bubbles (10–100 μm), which is considered an interesting characteristic for the flotation process. This, because the smaller the bubble size, the greater the bubble-particle interfacial contact area and the process efficiency. Bubble generation through DAF is carried out by saturating with air part of the treated wastewater (or water) in tanks under moderate manometric pressures (400–600 kPa). The liquid suffers a sudden decompression after being freed in a needle valve or in flow constriction devices, which promotes the release of the supersaturated air as microbubbles (plus saturation at atmospheric pressure).

This process has greater applicability when the difference in the phases' specific gravity (particulate and continuous) is small. Thus, a stage of wastewater pre-treatment (coagulation/flocculation) is required to form flocks of greater size and smaller specific gravity compared to the original particles, which is of great importance to the DAF process, especially for mineral wastewater which carry particles with a relatively high specific gravity.

In the last decades, DAF has been widely studied and used to remove contaminants and recover products in industrial wastewater (Couto, Melo & Massarani, 2003; Couto, Sant`Anna & Massarani, 2005; Capponi, Sartori & Souza, 2006, Couto et al., 2009; Silva, Rodrigues & Rubio, 2010). Nowadays, there are several DAF industrial plants operating in the world including in Brazil, where some of the world's biggest drinking water treatment plants are established (Edzwald, 1995; Caríssimi & Rubio, 2005).

In this context, the aim of this work was to evaluate the DAF process to treat the aluminum refinery wastewater, generated by refining of bauxite for alumina production (Bayer process), in order to reuse the water in the plant. The importance and influence of the inherent physical variables to the DAF process, such as type and concentration of chemical additives (coagulant and flocculant), recycle ratio and the stage of bubble generation will be evaluated and discussed aiming to verify the efficient application of the DAF for treatment of this type of wastewater.

Waste in the Bayer process – red mud

Red mud is a very fine-grained material, produced during the causticization of bauxite to dissolve aluminum minerals forming sodium aluminate. Typical values for particle size distribution are 90% weight below 20 microns. The specific surface area (BET) of red mud is between 10-15 m^2/g and real density of 3.30 g/cm^3 (Samal, Ray & Bandopadhyay, 2013). The environmental concern about the red mud is it disposal and the big amount of associated caustic water. As a general reference, up to two tons of liquid with a significant alkalinity of 5-20 g/L caustic (as Na_2CO_3) accompany every ton of red mud solids produced (Rai, Wasewar & Mukhopadhyay, 2012).

Once the bauxite residue is highly alkaline (pH > 12) and contains oxides and salts of six major oxides of Fe, Al, Ti, Si, Na and Ca, plus a large variety of trace elements, most of these compounds and ions must be dissolved in the associated water. The possibility of water treatment for this residue could improve the recirculation and reuse of this water in the process or reduce its impact when discarded to the environment. A literature review on the production of the red mud, its characteristics, methods of final disposal, environmental problems from an inadequate disposal and alternative applications for its economic utilization were well reported by Silva Filho, Alves & da Motta (2007) and Aldi (2009).

METHODOLOGY

Materials

Sample

The effluent studied was the supernatant liquid phase (overflow) of a red mud pulp from an alumina refinery, in northern Brazil. The particles contained in the sample were characterized with respected to particle size distribution with Mastersizer 2000SM® equipment from Malvern Instruments (UK), based on light scattering (laser diffraction) technique and the result is presented in the Figure 1.Is can be noticed that 90% of the particles are below 19.2 µm, that was considered the fine fraction to be used in the dissolved air flotation process, and the mean diameter is close to 3.6 µm.

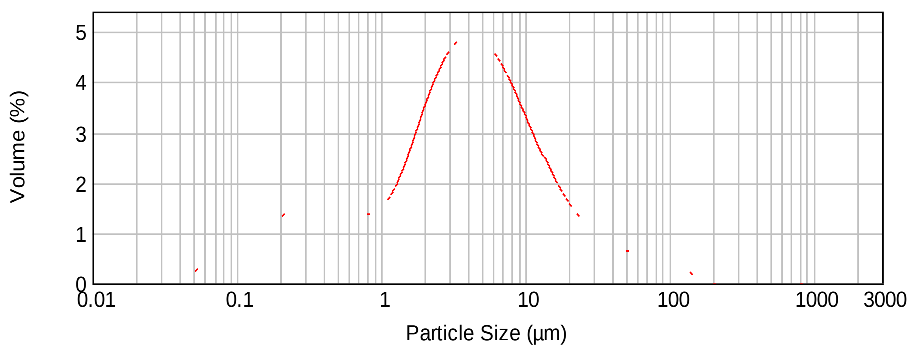

Figure 1. Particle size distribution for the red mud sample

The chemical analyses of the red mud, conducted by X-ray fluorescence, are present in Table 1. The sample used in this work is a typical Brazilian red mud, with almost half of its chemical composition constituted by aluminum and iron oxides (Antunes, Conceição & Navarro, 2011).

Table 1 Chemical composition of red mud

Content (%)												
Na_2O	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	ZrO_2	HfO_2	Al_2O_3	LOI*
13.07	17.7	0.12	0.20	0.31	1.20	6.0	0.15	28.7	0.78	0.21	22.6	8.8

*LOI - loss on ignition

The mineral composition of the red mud was determined by Bruker-D4 endeavor X-rays diffractometer. The X-ray diffractogram revealed the presence of different minerals, like gibbsite, iron and titanium bearing minerals (goethite, hematite, anatase, ilmenite and rutile) and zircon. Sodalite is the main silicate identified; no peaks of kaolinite.

Reagents

The chemical reagents used in the pre-treatment of the wastewater were: ferric chloride ($FeCl_3$) and Nalco® N-99-005B commercial polymer flocculant (polyacrylamide). A VETEC sodium hydroxide solution – NaOH (5% m/v) and hydrochloric acid – HCl (10% m/v) were used as a pH regulators.

Methods

Determination of pH, turbidity and total suspended solid of the effluent

pH measurements were obtained through a Digimed DM-2 pH meter and turbidity measurements through a Hach® 2100P turbidimeter. The total suspended solid (TSS) was calculated by measuring the mass of dry solid material remaining after vacuum filtration of a known sample volume (20 mL). Samples were filtered through a 0.45μm filter membrane according to the procedure described in Standard Methods (Apha, 2005).

DAF experiments

Batch DAF tests were run at CETEM´s laboratory using the experimental set-up shown in Figure 2. The column was previously loaded with the red mud effluent and immediately stirred at a rotation of 300 rpm (rapid mixing step). Next, the coagulant was added, keeping rapid stirring for 1 minute, and the suspension pH was adjusted to 7.0, since the natural pH of the red mud wastewater was around 12.

The stirring speed was then reduced to 100 rpm in the slow mixing step for 10 minutes and the flocculant was added at 5 min. After this step, agitation was interrupted and the air-saturated water, originating from the pressurization tank, was discarded to the column, promoting the flotation process.

Air saturation pressure in the saturation vessel was 4.5 bar (450 kPa). The flow of air-saturated water was controlled according to the recycle ratio of 30%. After 5 minutes, clarified liquid were sampled for turbidity and total suspended solids (TSS) determination and subsequent calculation of removal efficiency.

(a) (b) (c)

Figure 2 Bench unit for dissolved air flotation: (a) effluent before, (b) during and (c) after the DAF treatment

Determination of process efficiency

Particle removal efficiency was calculated based on the turbidity (η_T) and total suspended solid - TSS (η_{TSS}) measurements in the feed (T_o, TSS_o) and in the clarified product (T_f, TSS_f) on the flotation column, as shown in the Equations below:

$$\eta_T\,(\%) = \left(1 - \frac{T_f \cdot V_f}{T_o \cdot V_o}\right) \cdot 100 \qquad (1) \qquad\qquad \eta_{TSS}\,(\%) = \left(1 - \frac{TSS_f \cdot V_f}{TSS_o \cdot V_o}\right) \cdot 100 \qquad (2)$$

The ratio between final (V_f) and initial (V_o) volumes is used to correct the process efficiency due to the effluent dilution with air-saturated water, thus considering the efficiency obtained only by the flotation process.

The amount of air-saturated water introduced into the flotation column, in relation to the amount of effluent to be treated, is quantified by the recycle ratio (R_r). The recycle ratio is the fraction of the final effluent produced which is returned and saturated under pressure before entering the flotation vessel where the pressure is subsequently released and the bubbles are generated. This variable can depend on the application and for water and wastewater treatment application the values of recycle ratio are in the range of 15-50% (Kiuru & Vahala, 2001).

Experimental design

To investigate effects of process variables on the DAF process performance a 2^k factorial design was planned, considering the following variables: coagulant concentration (C_c), flocculant concentration (C_f), recycle ratio (R_r) and separation efficiency (η, response variable), as shown in Tables 2 and 3.

Tables 2 and 3 show the range of variation of investigated variables and their corresponding normalized levels (-1, 0, 1). Three experiments (triplicate) were performed under experimental design central point conditions, for standard deviation measurement purposes, as shown in Table 4.

In the experiments presented in Table 2, the flocculant polyacrylamide was added directly in the flotation column (Figure 2), whereas in Table 3 the polyacrylamide was previously added to the air saturation tank. This form of flocculant conditioning, prior to the formation of the DAF microbubbles, seeks to minimize the coalescence of bubbles, with a consequent reduction of their size and improvement of the DAF process efficiency (Couto et al., 2009; Couto, França & Santos, 2011). In addition, lower flocculant concentration and recycle ratio values were used in experiments planned in Table 3, based on the results obtained in Table 2.

Table 2 Experimental conditions: ferric chloride as a coagulant and polyacrylamide as a flocculant (added directly in the flotation column)

Levels	Cc (mg/L)	Cf (mg/L)	Rr (%)
-1	50	0	20
0	100	1,0	30
+1	150	2,0	40

Table 3 Experimental conditions: ferric chloride as a coagulant and polyacrylamide as a flocculant (previously added to the air saturation tank)

Levels	C_c (mg/L)	C_f (mg/L)	R_r (%)
-1	50	0	10
0	100	0,5	20
+1	150	1,0	30

Table 4 Experimental arrangement: 2^k factorial design and central point conditions

Experiments	C_c (mg/L)	C_f (mg/L)	R_r (%)
1	-1	-1	-1
2	-1	-1	+1
3	-1	+1	-1
4	-1	+1	+1
5	+1	-1	-1
6	+1	-1	+1
7	+1	+1	-1
8	+1	+1	+1
9, 10, 11	0	0	0

Four more experiments were performed under the conditions planned in Table 3, according to experiments 3, 4, 7 and 8 in Table 4, but using the flocculant (at 1 mg/L) in the flotation column. This procedure aimed to compare the results reached by different ways of addition of flocculant: directly in the flotation column and previously into the air saturation tank. Finally, in order to evaluate the effect of the pH, a triplicate at central point conditions (experiments 9, 10 and 11) under natural pH, were performed.

RESULTS AND DISCUSSION

DAF process results

The Tables 5 and 6 present the results of DAF efficiency, according to experimental arrangement in Table 3, and operational conditions shown in Tables 2 and 3, respectively The additional experiments (12 to 15) using flocculant directly in the flotation column and at natural pH of the red mud suspension (16 to 18) are also presented in Table 6.

It can be noted in Table 5, that good efficiencies of TSS removal, up to 85% for all tests (reaching up to 95% in some cases) were obtained, motivating to run a new experimental design using lower values of coagulant and flocculant concentration (Cc and Cf) and recycle ratio (Rr).

Table 5 DAF process efficiency for tested conditions using the experimental design in Table 2

Experiments	TSS_o (mg/L)	TSS_f (mg/L)	η_{TSS} (%)
1	2320	250	87.1
2	2175	210	86.5
3	2315	250	87.0
4	2260	85	94.7
5	2215	190	89.7
6	2215	80	94.9
7	2180	65	96.4
8	2250	180	88.8
9	2240	120	93.0
10	2220	180	89.5
11	2285	240	86.3

In Table 6, showing the results for all experiments planned in Table 3 (1 to 11), it can be observed that TSS and turbidity removal up to 90% were obtained, with a considerable result for experiment 8 (high level of tested conditions +1), in terms of turbidity and TSS reduction and, in other words, a higher removal efficiency was reached.

Table 6 DAF process efficiency for experimental design in Table 3 (1 to 11) and additional experiments (12 to 18)

Experiments	T_o (NTU)	T_f (NTU)	TSS_o (mg/L)	TSS_f (mg/L)	η_T (%)	η_{TSS} (%)	pH (final)
1	3980	105	990	50	97.1	94.4	7.30
2	3090	12.8	780	5	99.5	99.2	7.00
3	3605	140	1050	10	95.7	99.0	7.00
4	4115	9.92	1090	35	99.7	95.8	7.30
5	4350	222.5	1035	85	94.4	91.0	7.20
6	3885	35.9	1055	15	98.8	98.2	7.10
7	3955	83.1	1050	45	97.7	95.3	6.90
8	3990	8.21	1085	5	99.7	99.4	7.00
9	3785	23.85	1000	10	99.2	98.8	7.10
10	4010	17.6	1035	10	99.5	98.8	7.30
11	3755	41.55	1050	20	98.7	97.7	7.00
12	3695	208	1000	120	92.7	84.4	7.10
13	3545	15.5	1060	15	99.4	98.2	6.90
14	3555	439.5	1015	180	83.9	76.9	7.00
15	3990	23.1	1025	20	99.2	97.5	7.20
16	-	-	1010	345	-	55.6	-
17	-	-	1030	345	-	56.5	-
18	-	-	950	395	-	45.9	-

Probably, the higher flocculant concentration led to the formation of a more stable froth, promoting an increase in the flocs' hydrophobic characteristics (Oliveira & Rubio, 2012), in addition to the higher employed recycle ratio that, enabled to obtain a larger amount of bubbles available to promote the adhesion and removal of the solids. In the same context, from some experiments, such as 3, 12, 14 (including the additional experiments), it can be observed that the lowest values of removal efficiency that were obtained can be attributed to the lower values of recycle ratio used, since this parameter is proportional to the amount of bubbles in the flotation cell.

Comparing the results obtained from the experiments performed with the addition of flocculant previously into the air saturation tank (3, 4, 7 and 8) and directly in the flotation column, after microbubbles formation (12, 13, 14 and 15), it was clearly demonstrated that the former experiments were more effectives than the later. This is probably related to the minimization of bubble coalescence and a beneficial effect on the process due to the decrease of the bubbles size and the increase of the bubble-particle interfacial contact area, as already demonstrated by other authors (Féris & Rubio, 1999; Rodrigues & Rubio, 2007; Couto et al., 2009; Couto, França & Santos, 2011).

With respect to the effect of pH on the process efficiency it was noted that in the experiments under natural pH (~12) lower performances of turbidity and TSS removal (45 – 55%) were obtained, when compared with the experiments run under the same conditions, but with pH adjustment (Experiments 9, 10 and 11). These results can be attributed to the influence of pH in the dissociation and adsorption of reagents in alkaline media.

The Brazilian environmental regulation 430 (Conama, 2011) determines the following characteristics for effluents disposal: pH range 5 to 9 and turbidity < 40 NTU. Considering the results obtained in this study, most of the experiments reached the specification for effluent disposal using experimental conditions: flocculant concentration in the range of 0.5-1.0 mg/L and recycle ratio of 20-30% (levels 0 and +1 in the experimental design). Hence, the DAF can be considered an alternative treatment to reduce the environmental impact of red mud and to promote industrial water recycling.

CONCLUSION

The DAF process applied to the red mud wastewater treatment was effective on the total suspended solids (TSS) and turbidity removal, wherein efficiencies up to 99% were obtained.

In general, the addition of the flocculating agent previously in the air saturation tank (before microbubbles generation), was more effective than adding it to the flotation column (after microbubble formation), where the air-saturated water was injected, explained by the improvements related to the minimisation of bubble coalescence.

The DAF can be considered an alternative treatment to reduce the environmental impact of red mud and to promote industrial water recycling, once that the treated effluent attends to the Brazilian environmental regulation.

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