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Recovery of Process Water of Effluent from Metallurgical Industry by Association of Dissolved Air Flotation and Biodemulsifier

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A method of treating a metalworking industry effluent composed by water, cutting fluid and graphite has been developed. The recovery of components of an effluent from the machining process becomes complex due to the existence of solid materials mixed to water-oil emulsions, as is the case of graphite. The graphite is distributed in the form of very small particles emulsified in water and distributed in both phases (aqueous and organic), making the treatment process very difficult. In general, treatment of an effluent of this type requires a preliminary step to breaks the emulsion so that the graphite dispersed in the liquid medium can be recovered. Thus, the treatment was performed in a laboratory-scale phase separation prototype, constructed with recirculation tanks, pumps, hydrocyclones and a continuous decanter. Initially, the effluent was acidified with sulfuric acid to break the solid-liquid emulsion. Subsequently, the solid phase was recovered with the aid of a hydrocyclone that originated a discharge by the equipment overflow of a mixture of oily wastewater and cutting fluid. Then the water-oil mixture was separated in the continuous decanter, yielding a cutting fluid stream and an aqueous phase containing residual oil contaminated with 120 ppm of oil. The aqueous phase was then subjected to a dissolved air flotation (DAF) process with a biodemulsifier as the collector in a laboratory prototype. To define appropriate conditions to obtain an aqueous phase with a level of contamination that would allow its return to the process, the conditions of application of DAF were determined with experiments outlined by a Central Composite Rotational Design (CCRD) technique. A statistical model for the DAF prototype operating conditions was obtained by response surface methodology (RSM). Concentrations of residual oil 12% below the Brazilian environmental agency regulations for disposal in water bodies, which is 20 ppm, were found. The separation efficiency reached values higher than 97%.

1. Introduction

In metallurgical industries, the use of cutting fluids, lubrication and cooling media, when appropriately chosen and applied, brings benefits. The fluid must be applied in such a way as to allow its action as close as possible to the cutting edge at the part / tool / chip interfaces, in order to ensure that its functions are properly exercised. However, despite the benefits presented, the use of cutting fluid in machining processes generates costs associated with acquisition, storage, preparation, in-service control and disposal. Within the industry, environmental issues involve damage to the health of the operator due to the contact of these fluids with the skin and the respiration and / or ingestion of pollutants derived from them. Outside industry, when discarded, care must be taken not to affect soil, water, and sometimes air itself (Groover, 2010).
A cutting fluid should reduce production costs by reducing tool wear and improving the surface of the machined component. Secondary functions include transporting the chip out of the working region and cooling the cutting region and part, since for a greater dimensional tolerance requirement too much heating leads to a thermal expansion of the component, and this should be avoided (Birat, 2016).

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The reduction of friction is one of the factors that increase the useful life of a cutting tool in machining, because the effects of the wear on the tool decrease. One way of reducing such effects is the introduction of a low shear rate lubricating layer between the surfaces of the tool and the workpiece. Depending on the application, the solid lubrication is the one that has the greatest advantages in relation to the reduction of the friction, once when the lubricant layer is formed, it can remain between the parts in contact. Another advantage of the solid lubricant over the liquid is in relation to the operating temperature, which can reach the range of 1000 °C, keeping the coefficient of friction relatively low. Among the solid lubricants, the best known are graphite, molybdenum disulfide (MoS2) and polytetrafluoroethylene (Chelgani, et al., 2015). However, the use of water-emulsified cutting fluids with the presence of solid lubricant (graphite, for example) makes it difficult the dispose of this effluent to the environment, since all the fluids components are reusable (Karhu et al., 2014).
Thus, the present work developed a methodology for the separation of these components and recovery of the aqueous effluent, the latter with the aid of the Dissolved Air flotation (DAF) technique assisted by a biosurfactant as an alternative collector to the synthetic collectors (Silva et al., 2015; Albuquerque et al. 2012; Menezes et al., 2011; Brasileiro et al., 2015; Sarubbo et al., 2015).

2. Materials and Methods

The general strategy adopted was the chemical destabilization of the three-phase emulsion, followed by recovery of each component through simple, efficient and low-cost implantation techniques.

2.1 Chemical emulsion acid destabilization

Chemical emulsions are created when a surface-active chemical or other chemicals are used, such as alkaline cleaning fluids containing surfactants, soaps and detergents with ionic and non-ionic characteristics. These chemicals interfere with natural coalescence of oil droplets and generally create a permanently stabilized emulsion with little chance of breaking (Akcil and Koldas, 2006). In the present work the graphite added to the cutting oil was mixed with the water-oil cutting mixture with the aid of an emulsifier. The breaking of a graphite-water-oil type cutting emulsion can be facilitated by altering the pH (acid / caustic). The chemical to be used depends in particular on the emulsion. These chemicals alter the electrical charges of particles (oil droplets) by the effect of their own charges, which are usually cationic. This manipulation of the charge allows the oil droplets to become free and let them float, thus favoring coalescence (Karhu, et al., 2014).

2.2 Bench Prototype for Preliminary Separations

This preliminary treatment was performed in a phase separation prototype in laboratory scale (Figure 1), counting on recirculation tanks, pumps, hydrocyclone and continuous decanter.

Figure 1: Bench prototype using a continuous decanter and hydrocyclone to separate the free graphite and water-oil mixture in the effluent from an industrial machining unit

The degree of turbulence is a criterion used to evaluate the efficiency of the liquid-liquid separation process, based on the Reynolds number of the turbulence (Schweitzer, 1979):

$$Re_t = \frac{v_C D_H \rho_C}{\mu_C} \tag{1}$$

Where:

v_C - Sedimentation rate of the continuous phase;

D_H - Continuous phase hydraulic diameter;

ρ_C - Specific mass of the continuous phase;

μ_C - Absolute viscosity of the continuous phase

For the judgment of the operating conditions of the equipment we have for $Re_t < 5000$, recommend condition; $5000 < Re_t < 20000$, some problems may arise; $20000 < Re_t < 50000$, some problems should occur and $Re_t > 50000$, process not recommended.

2.3 Bench DAF Prototype

The oily water with 120 ppm of residual oil was subjected to treatment in a Dissolved Air Flotation (DAF) prototype (Rodrigues and Rubio, 2007) at a bench scale, as shown in Figure 2. The prototype was operated with the aid of a biosurfactant produced by the yeast *Candida sphaerica*, as described by (Luna et al., 2013) as a collector. As shown in Figure 2, a centrifugal pump (1) is responsible for feeding the oily aqueous phase stored in a tank (2). The flow of the oily aqueous phase to be treated passes through the flotation cell (3), with a volumetric flow rate adjusted by the opening of a valve (4). The control variables of the operating conditions of the system, such as levels and volumetric flow rates of the fluid, are recorded with the aid of an electronic circuit (5). Part of the treated water is sucked in by a centrifugal pump (6), saturated with air microbubbles. The dispersed oil droplets are surrounded by air microbubbles and float, giving rise to a kind of oily foam, which falls into a foam collector (7). A third centrifugal pump (8) sucks the remaining treated water and sends it for reuse. A Level Sensor Control System (9) keeps the prototype operating at steady state.

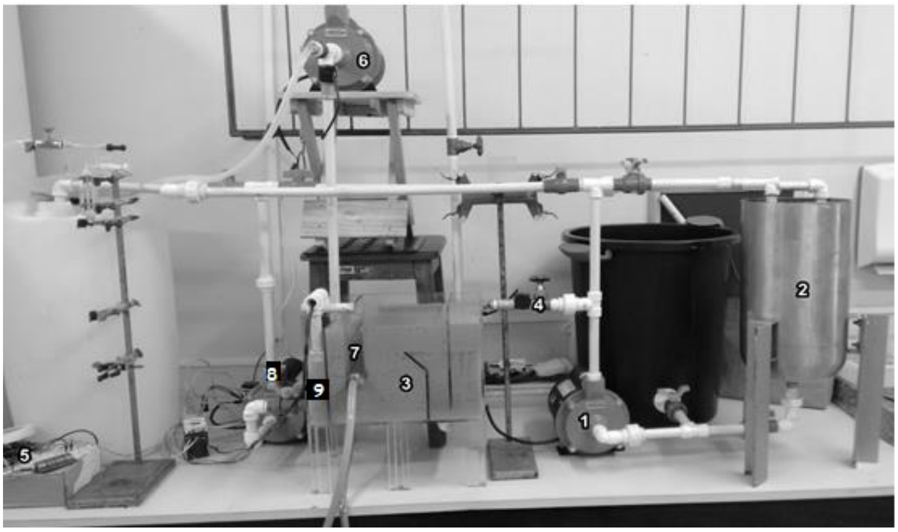

Figure 2: Bench DAF Prototype used for treating the oily aqueous phase

3. Results and Discussion

In preliminary laboratory tests the crude effluent containing water, shear oil and graphite, of pH around 6.8, it took about 10 hours until it was possible to detect the total separation between water and oil. The graphite particles were distributed in both liquids. A liter of this effluent was then brought to different acid pH levels and the height variations of the water-oil interface were monitored with aid of a graduated test tube containing an effluent column of 35 cm in height. Different degrees of demulsification were monitored according to water-oil interface, in function of pH values. Figure 3 illustrates this dependence for pH values of 5.8, 4.8, 3.8 and 2.8. These pH values were monitored once they promote the higher water-oil interface displacement speeds. It is observed that the more acidic the pH of the contents of the test tube, the greater the speed of variation of the height of the water column, signaled by the water-oil interface. The time spent for a total destabilization of the graphite-water-oil emulsion cut was 650 seconds. As a result of the separation of the constituents of the

emulsion from the metallurgical industry, 56.4% v/v water, 39.6% v/v cutting oil and 4.1% v/v particulate graphite were identified.
The presence of graphite in the underflow of the hydrocyclone was monitored with the aid of a laser particle analyzer. To illustrate the efficiency of oily water recovery, the numerical simulation in CFD used the FLUENT software (Version 12.0). The hydrocyclone geometry was created in the Gambit preprocessor and a non-structured type mesh was built. A test of this mesh indicated that 600,000 elements were sufficient to not interfere in the results of the simulation. Turbulence and Multi-Phase Mixing Models were used for the continuous phase (oily water - 130 ppm). Reynolds Stress Model (RSM) was used for the graphite particles as dispersed phase (Nopens et al., 2005). Figure 4 shows the volumetric concentration distribution of the oily water along the axial and radial lengths of the hydrocyclone. The red color represents a volumetric fraction very close to the unit, passing through yellow, green, light blue and, finally, dark blue, the latter of null value. Details with horizontal cuts on the top of the hydrocyclone illustrate that for a feed velocity of 0.4 m/s of the oil-graphite water suspension it is observed that the liquid accumulates at the top of the cylindrical body of the equipment.

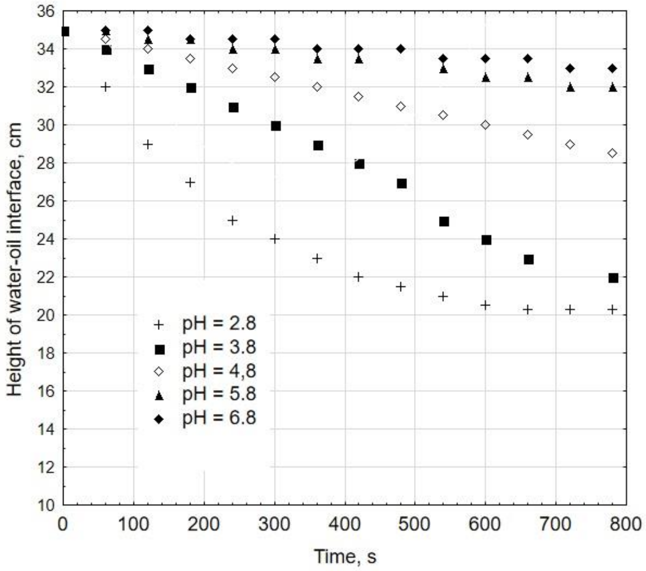

Figure 3: Initial height of water-oil interface as function of the time for different values of pH in determining of the solid-liquid destabilization conditions

The operation of the continuous decanter of the bench prototype was maintained at steady state, with a feed composed of 58.8% water and 41.2% shear fluid. A Reynolds number of turbulence of the order of 2200 was maintained and as can be seen in Figure 5, the liquid-liquid separation efficiency was of the order of 96.0%. Oily water was detected at the top outlet of the decanter with a cutting fluid content of 5.2 ppm.

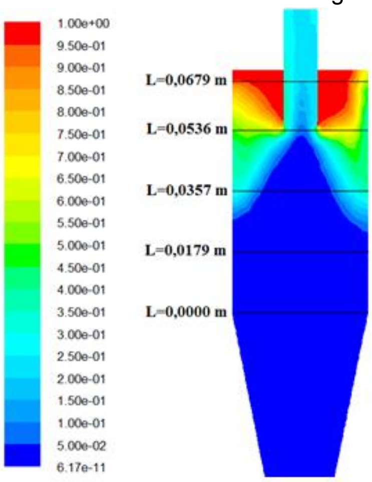

Figure 4: Distribution of volumetric fraction of oily water simulated in the hydrocyclone with the aid of software fluent in CFD

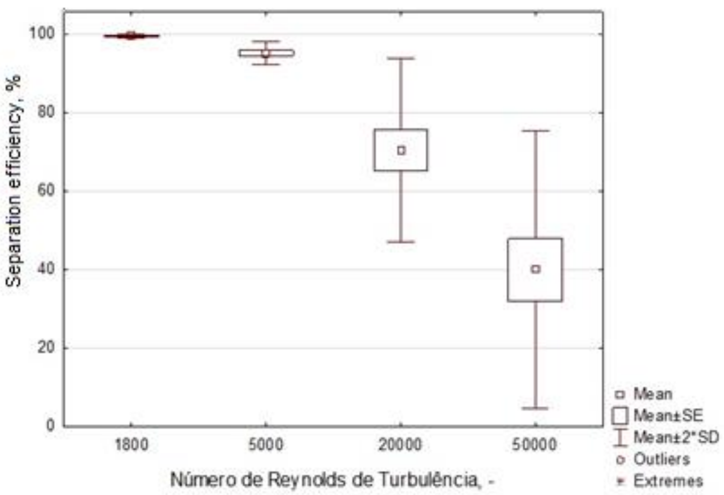

Figure 5. Box plot of the influence of the Reynolds number of the turbulence on the separation efficiency in a continuous horizontal decanter

For recovery of the residual oily water from the hydrocyclone and continuous decanting processes, this liquid mixture was floated in the bench unit shown in Figure 2. The efficiency of residual water-oil separation was evaluated, with the addition of biosurfactant as a collector, according to Silva et. al. (2015). A Central Composite Rotational Design - CCRD (Montgomery, 2005) was used as a statistical tool in the separation process. The ratios between the volumetric flow rates of air and water for the production of microbubbles [X_1: (0.3 - 1.71) $.10^3$] and the ratio between the volumetric dosage flows of biosurfactant and the affluent of the bench prototype [X_2: (1.71 - 2.21) $.10^4$] were the factors considered. The response variable for the CCRD was the water-oil separation efficiency. Figure 6 presents the response surface obtained using the Statesoft® STATISTICA, Version 12 software, through Eq (2), demonstrating the operating conditions of the bench prototype that gave a separation efficiency of about 96.0%.

$$Y=-216,83+210,43*X_1-95,25*X_1^2+258,65*X_2-78,25*X_2^2-10,00*X_1*X_2 \quad (2)$$

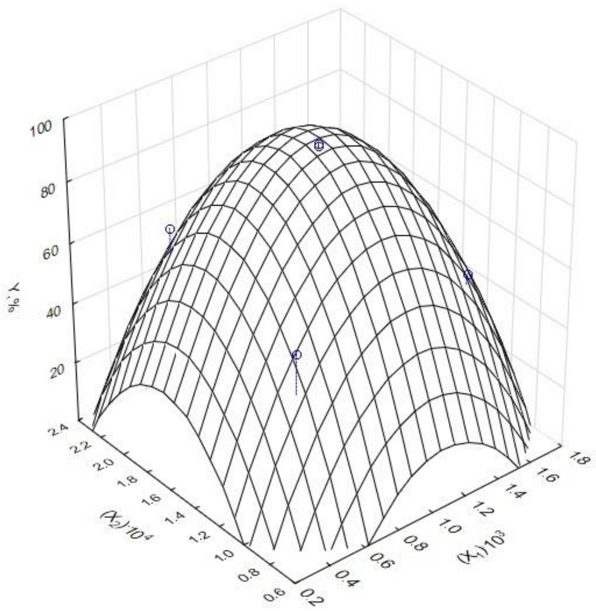

Figure 6: Response surface showing the separation efficiency as a function of the CCRD factors

4. Conclusions

This paper reports a successful strategy to recover water from an effluent from a metalworking industry. Initially, acid destabilization of the liquid-liquid-solid emulsion, followed by separations of the different components with hydrocyclone, continuous decantation and biodemulsifier-assisted DAF. In this sequence, the resulting aqueous phase reached specifications (< 20 ppm) required by the Brazilian environmental monitoring agency – CONAMA, to return to water resources.

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