Industrial Reuse of Water from Chemical Washing of Residual Frying Oil

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The residual frying oil (RFO) is part of one of the residues generated daily in homes, industries and public offices. Uncontrolled disposal of waste frying oils, in sinks or thrown directly into the water, entails a series of environmental damages, such as clogging of pipes in sewage systems and increases the costs of treatment processes, in addition to pollution. The collection and reuse of these waste oils prevents their improper disposal and brings benefits to the environment. The percent recovery of residual oil from fried food depends largely on the washing operations. These operations are also responsible for the effective separation of the organic and aqueous emulsified waste phases, so that they have the lowest oil content, while the oil can be further used for the production of soaps and detergents. In this work, operating conditions to improve the chemical wash process of the RFO by industries were improved to generate a suitable effluent to subsequent physicochemical treatment by Dissolved Air Flotation (DAF). After packaged in capped collectors, the RFO was washed by the addition of chemical reagents ($HCLO_3$, NaOH and NaCl). The material was then treated via DAF, with a biosurfactant acting as a biodegradable collector in a laboratory scale prototype operating in a continuous modus. The experiments were carried out according to a Central Composite Rotational Design (CCRD) in the form of 2^2. The factors were the ratio of the flow of the effluent to be treated and the flow of biosurfactant and the ratio between the flow of air and the effluent recirculated for producing microbubbles. As a result, it was recovered the aqueous phase with aid of flotation efficiency of 95.5 %, giving a statistical model prediction for the optimum condition of a recovery process of water that can be reused in the actual industrial process.

1. Introduction

Brazil recycles about 98% of aluminum cans, while only 2% of residual frying oil (RFO) is reused. It is known that the incorrect disposal of this waste degrades the environment and generate negative impacts on the economy, although research shows that a liter of cooking oil infects about one million liters of water, which is equivalent to the consumption of a person during 14 years (ABRASI, 2013).

The RFO is a heterogeneous material containing, besides oil, hydrogenated fat, breadcrumbs and water, among other constituents (Juarez et al., 2011). It is estimated that 25% of the collected oil is formed by water with impurities. The percent recovery of residual oil from fried food depends largely on the washing operations. These operations are also responsible for the effective separation of the organic and aqueous emulsified waste phases, so that they have the lowest oil content, while the oil can be further used for the production of soaps and detergents (Jamaly et al., 2015). A common practice adopted by several companies that collect residual oil is the use of detergent or soap powder for the washing of the containers and subsequent addition of the effluent resulting from this washing to the general effluent, hindering a subsequent recovery of the aqueous phase due to the formation of very stable emulsions (Matos et al., 2011).

Decantation, centrifugation, ultrafiltration and flotation are examples of physical∕chemical processes effectively used for the separation of oil-water mixtures in industries (Younker and Walsh, 2014). The addition of

coagulants has favored the use of dissolved air flotation (DAF) in the removal of oil from wastewater (Rubio et al., 2002), showing good results. Coagulants are used to improve the efficiency of separation and flotation of the oil droplets. They can be of chemical origin generally derived from petroleum, or of microbial origin, in which case the biosurfactants are promising coagulants and/or dispersants (Silva et al., 2015). These surface-active molecules of biological origin also have several advantages over synthetic surfactants such as higher biodegradability, higher foaming, less toxicity, better environmental compatibility, more tolerant to pH, salt, and temperature variation, and higher selectivity for metals and organic compounds and can be synthesized from renewable feedstocks (Sarubbo et al., 2015; Santos et al., 2016). Recently, novel surface-active biomolecules with attractive properties have been isolated from *Candida* species. These compounds have an anionic nature and are capable of reducing the surface tension of water from 70 to 28 mN/m, with a critical micelle concentration of 300 mg/L, which compares favorably with other known surface-active agents (Albuquerque et al., 2012; Silva et al., 2015).Thus, in this work, we defined operating conditions to improve the chemical wash process of the RFO, obtaining a suitable effluent to subsequent physicochemical treatment by Dissolved Air Flotation (DAF), so that the aqueous phase can be reused in the industrial process itself.

2. Material and Methods

2.1 Collection of Residua Frying Oil (RFO)

The residual frying oil was collected in establishments that generate oil directly as bars, restaurants and canteens, or indirectly, as voluntary delivery points (public and mixed-economy companies). After being packed in capped containers, the RFO was transported to the laboratory where the collectors were washed and the generated effluent was stored for further physic-chemical treatment. The removal of the oil from the collectors was carried out mechanically by pouring its contents into a tank. Subsequently, the residual oil remaining in the vessel was recovered with the aid of a jet of vapor water inside the manifold positioned with the opening down. This entire effluent was then passed through a 0.015 m aperture loop for removal of particulate solids. For the complete recovery of the oil in the form of fouling in the lid of the collectors, a jet of water vapor with absolute pressure higher than 5.0 kPa was applied, replacing washing with soap or detergent that would favor the stabilization of water-oil emulsions.

2.2 Chemical Effluent Washing

The collected residual oil (raw effluent) was discharged and placed in a purification tank. $HClO_3$, NaCl and NaOH were added to the treatment tank in predetermined proportions under heating and constant stirring (Hosny et al., 2016). Soda adjusted the pH of the medium, while hypochlorite and NaCl precipitated the iron (clarification) and destabilized the water-oil emulsion, respectively. After the chemical treatment, the mixture was allowed to stand for about 48 hours. After this period, the material turned separated into three parts, one part consisting by the washed oil, that was sent to a clarification tank; a second part consisting of water and emulsified oil (aqueous effluent), and a third part consisting of water and free oil. The aqueous effluent, at a concentration of 310 ppm oil, was then treated via DAF, with a biosurfactant acting as a collector in a laboratory scale prototype operating in continuous modus.

2.3 Pilot Scale Dissolved Air Flotation System

The aqueous effluent was treated in a DAF pilot system, as described by Silva et al. (2015) and Henauth et al. (2017). The pilot scale DAF system was constructed in clear and transparent acrylic to allow visualization of most of the fluid dynamic phenomena. The supporting metallic structure of the DAF system was made of angles "L" carbon steel 1 inch, interspersed with some flat bars 1 inch wide and 4 mm thick. The system was operated at ambient temperature (28∘C) and pressure. The DAF set up can be seen in Figure 1. At the entrance of the pilot scale system there are two tanks receiving synthetic wastewater to be treated. The first chamber, fitted with three propeller type agitators, homogenizes the addition of biosurfactant and separates the oil free of water by gravitational sedimentation. The second chamber is equipped with static mixers plates to improve the effect of homogenization of biosurfactant. The two DAF chambers arranged in series, after antechambers, process the affluent, which comes into contact with a microbubbles flow in each chamber. In both chambers the oil droplets form the emulsion with the water coming into contact with air microbubbles, yielding dispersed particles with lower average density than water, that are floated. Since these chambers operate completely filled, a layer of the floated material is collected with the aid of a baffle, yielding two flows, one of the oily foam above and the other of the treated water below. The oily foam is collected. The flow of treated water is directed to a final collector chamber. In this last chamber two pumps distribute the treated water. Part of the water is used in the production of microbubbles while the other part is discarded.

Together with the treated water a suitable amount of atmospheric air is admitted to the pump suction line for the microbubbles production. Similarly to a saturation tank of a DAF conventional process, the treated water

and the air suffer agitation, pressurization, and friction, this last near the walls of the pump and pipes, originating the microbubbles.

Microbubbles clouds chapped flows are injected into the base of each DAF chamber. This type of microbubbles production mechanism reduces the number of components compared to the conventional DAF process, which uses a compressor for compressed air producing and a tank for saturation of the treated water. In the early extensions of the two injection pipes of the microbubbles to the DAF chambers, a gate valve was installed to control the pressure and the flow rates required to obtain the microbubbles.

The measure instrumentation of the operating parameters for the pilot scale DAF system comprised four flow meters' rotameter type and a Bourdon manometer type. A rotameter is installed in suction pump microbubbles measuring the flow rate of the treated water. This rotameter is placed on the top of the vertical section of the suction line of the pump to allow measurements of water flow rate without interference from the amount of air admitted in this section. A second rotameter measures the feed water flow rate of the DAF prototype. A third flow meter measures the flow rate of air admitted to the system for the production of microbubbles. The Bourdon type pressure gauge was installed in the discharge line from the microbubbles pump to give information about the work pressure.
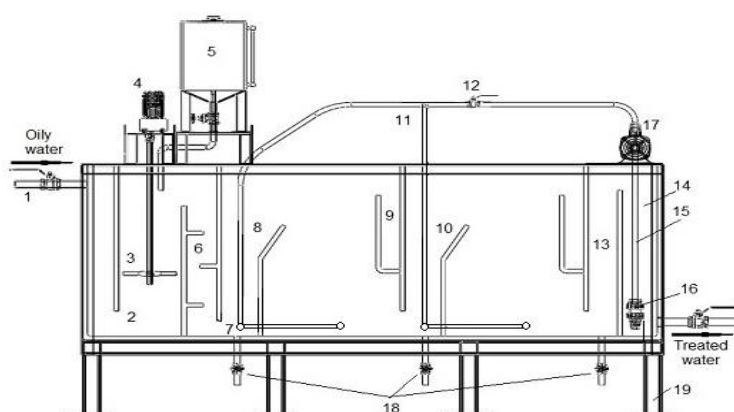
1 - Entrance; 2 - Mixing chamber inlet; 3 - Stirrer; 4 - Agitator motor; 5 - Surfactant tank; 6 - Static mixer; 7 - Microbubbles diffuser; 8 - Flotation chamber 1; 9 - Collector oily foam; 10 - Flotation chamber 2; 11 - Microbubbles tubes; 12 - Flow control valve; 13 - Treated water separator; 14 - Treated water chamber; 15 - Suction pipe; 16 - Check valve; 17 - Microbubbles pump; 18 - Drain valves; 19 - metal structure.

Figure 1: Scheme of pilot scale DAF system showing redistribution of microbubbles diffusers.

2.4 Production of the Biosurfactant

Biosurfactant production was conducted as described by Rufino et al. (2014). *Candida lipolytica* UCP 0988 was obtained from the culture collection of the Catholic University of Pernambuco, Brazil. The microorganism was maintained at 5∘C on yeast mould agar slants containing (w∕v) yeast extract (0.3 %), malt extract (0.3 %), tryptone (0.5 %), d-glucose (1.0 %), and agar (5.0 %). Transfers were made to fresh agar slants each month to maintain viability. The *C. lipolytica* inoculum was prepared by transferring cells grown on a slant to 50 ml of yeast mold broth. The seed culture was incubated at 28 °C and 150 rpm for 24 h. The yeast was cultivated in a submerged culture in a Tecnal Ltda. (Brazil) shaker. The basal medium was composed of 0.1 % NH_4NO_3, 0.02 % KH_2PO_4 and 0.02 % $MgSO_4 \times 7H_2O$. The medium was supplemented with 6 % soybean oil refinery residue and 1 % glutamic acid. The refinery residue was obtained from ASA Indústria e Comércio LTDA (Recife-PE, Brazil). The medium was sterilized by autoclaving at 121∘C for 20 min. The final pH of the medium was 5.3 and the surface tension prior to inoculation was 55 mN∕m. The inoculum (1%, v∕v) was added to the cooled medium at the amount of 10^4 cells∕ml. Fermentation was carried out in Erlenmeyer flasks at 28°C and 150 rpm for 72 h. Separation studies were performed using the cell-free broth (crude biosurfactant) obtained by centrifuging the cultures at 5000×*g* for 20 min.

2.5 Experimental Factorial Design and Response Surface Methodology

The efficiency of the oily water separation obtained after the treatment from the chemical washing of the residual frying oil was evaluated by the application of a Central Composite Rotating Design (CCRD) (Montgomery, 2005). Table 1 presents the factors used by CCRD with the addition of biosurfactant as a flotation aid. The Ratios between the air and water flow rates for microbubbles production (X_1) and between the biosurfactant and feed oily water flow rates (X_2) were tested. The independent variables were coded at five

levels (-1.41, -1, 0, +1, +1.41) and the complete design consisted of 12 experimental points including 4 replications of the central points. The coded levels of the independent variables used in the RSM design are listed in Table 1.

The response variable was the separation efficiency of the pilot prototype calculated according to Eq. (1):

$$\eta = 1 - \frac{C_{in}}{C_{out}} \tag{1}$$

Where η is the percent separation efficiency, while C_{in} and C_{out} are the oil concentrations in the inlet and outlet flow in ppm, respectively.

Table 1: Experimental range and levels of independent variables for separation efficiency in the pilot scale DAF system with use of the biosurfactant

Tested variables	Range and levels				
	-1.41	-1.00	0.00	+1.00	+1.41
X_1 - Ratio between the air and water flow rates $\cdot 10^3$, (X_1)	0.30	0.50	1.00	1.5	1.71
X_2 - Ratio between the biosurfactant and feed oily water flow rates $\cdot 10^4$, (X_2)	1.71	1.00	1.50	2.00	2.21

2.6 Flotation Experiments

Each set of experiments of the prototype was started after the water level inside the discharge of the treated water chamber allowed pushing the production of microbubbles pump. The second step was to feed the unit and to adjust the necessary conditions to the production of the synthetic influent. After about 2 averages elapsed time from the beginning of the operation of the prototype, four samples were collected in the treated water chamber. Finally, a flow of air at the inlet of the pump microbubbles had been reached. After the establishment of each new experimental condition displayed in Table 1, new samples of wastewater or treated water were collected again in the outlet prototype chamber to calculate the separation efficiency according to Eq. (1). The oil was extracted from the synthetic effluent samples with an equal volume of hexane (1:1, v/v). The mixture was vigorously shaken for 15 min and allowed to set until phase separation. The organic phase was removed and the operation was repeated twice. The product was concentrated from the pooled organic phases using a rotary evaporator. The amount of oil residing was gravimetrically determined.

3. Results and Discussion

Table 2 presents the results of the runs performed to analyze the influences of the factors that composed the experimental design on the separation efficiency of the water-oil mixture. In the mentioned table it is observed that the maximum values of separation efficiency are located in the central region, that is, for average values of both independent variables. ANOVA, the determination of regression coefficients and the construction of graphs were performed using the Statistica program, version 12.0 (Statsoft Inc, USA).

Based on these results, the Analysis of Variance (ANOVA) was obtained, as shown in Table 3. The ANOVA allowed the following observations on the fragility of the statistical prediction model for adequate operational conditions of the DAF prototype: (a) the explained variance of the model was of R^2 equal to 84 % and (b) the model showed no adjustment. On the other hand, other items analyzed showed advantages, since all factors can be considered statistically significant, that is, p values are less than 0.05 and the experimental error was less than 1.0 %.

Table 2: Central composite (non-factorial) surface design matrix and experimental values of observed factors on separation efficiency (Y) in the pilot scale DAF prototype

Run	$(X_1) \cdot 10^3$	$(X_2) \cdot 10^4$	Y(%)
1	0.50(-1)	0.7(-1)	44.00
2	0.50(-1)	1.4(+1)	88.00
3	1.50(+1)	0.7(-1)	45.00
4	1.50(+1)	1.4(+1)	65.00
5	0.30(-1.41)	1.05(0.0)	30.00
6	1.71(+1.41)	1.05(0.0)	62.00
7	1.00(0.0)	0.56(-1.41)	33.00
8	1.00(0.0)	1.54(+1.41)	60.00
9	1.00(0.0)	1.05(0.0)	96.00
10	1.00(0.0)	1.05(0.0)	94.00
11	1.00(0.0)	1.05(0.0)	98.00
12	1.00(0.0)	1.05(0.0)	97.00

Table 3: Analysis of variance (ANOVA) for oil-water separation efficiency in the pilot scale DAF prototype

Factor	Square sum (SS)	Degree of freedom	Mean square (MS)	*F*-value	*p*-value
X_1 (L)	117,030	1	117,030	73,913	0,003308
X_1 (Q)	2673,225	1	2673,225	1688,353	0,000032
X_2 (L)	1166,396	1	1166,396	736,671	0,000110
X_2 (Q)	2295,225	1	2295,225	1449,616	0,000040
X_1 by X_2	42,250	1	42,250	26,684	0,014073
Lack of fit	894,199	3	298,066	188,252	0,000651
Pure Error	4,750	3	1,583	-	-
Total SS	6368,000	11	-	-	-

As a way to illustrate the contributions of the factors to the quadratic model obtained, a Pareto diagram was developed, as shown in Figure 2. According to the Pareto Diagram, for the quadratic model tested, all effects are statistically significant and are near 95% confidence level, confirming the information provided by ANOVA. In this case, the removal of any parameter will not improve the adjustment quality. The quadratic prediction model for the water-oil separation efficiency is shown by Eq. 2:

$$Y = -247.258 + 203.064 \cdot X_1 - 85.000 \cdot X_1^2 + 295.296 \cdot X_2 - 84.000 \cdot X_2^2 - 19.000 \cdot X_1 \cdot X_2 \tag{2}$$

This model represents the percentage efficiency of water-oil separation, involving two linear effects, two quadratic effects and an interaction between the factors adopted. A plot of these effects on the separation efficiency, constructed with Eq. 2 is shown in Figure 3.
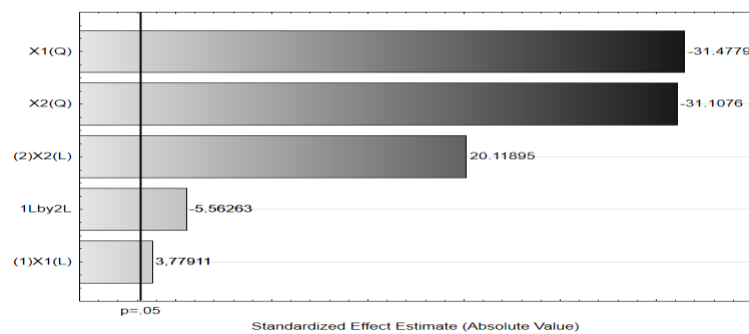

Figure 2: Pareto chart showing the effects of observed factors and their combined impact on separation efficiency in the pilot scale DAF prototype
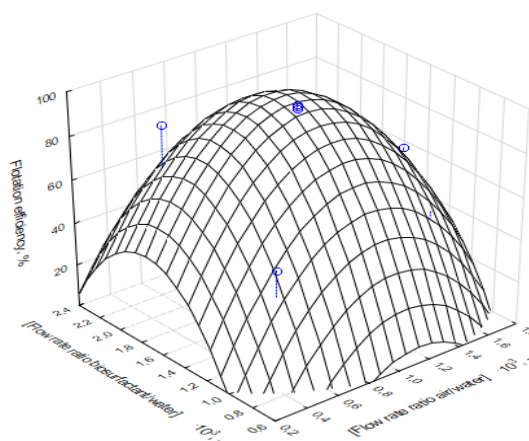

Figure 3: Three-dimensional surface plot of the combined effect of observed factors on separation efficiency in the pilot scale DAF prototype

In this figure, a peak of efficiency of 95.5 % is observed for the average values of the adopted factors. The final oil concentration of 12.4 ppm reached after the treatment is below 20 ppm, which is the concentration

allowed by the Brazilian legislations (CONAMA, 2007). These conditions of operation favorable to the indication of optimum conditions confirm the expected effects by Silva et al. (2015), since a biosurfactant and the same DAF prototype were used, with small adjustments in the physical structure of the experimental arrangement.

4. Conclusion

The water-oil separation by means of the dissolved air flotation, applied with the aid of an experimental design of CCRD type, was an excellent methodology for the recovery of oily waters generated from chemical washes of residual frying oils. Oil and grease quantities well below standards specifications requested by the Brazilian Environmental Agency regulations allow the return of recovered water to water sources around the industry or even to the production process that gave rise to this type of effluent.

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