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Biosurfactant Application as Alternative Collectors in Dissolved Air Flotation System

Elias J. Silva [a], Marcos J. Chaprão [a], Ivison A. Silva [a], Pedro P.F. Brasileiro [c], Darne G. Almeida [b,c], Juliana M. de Luna [b,c], Raquel D. Rufino [b,c], Valdemir A. Santos [b,c], Leonie A. Sarubbo [*a,b,c]

[a] Northeast Biotechnology Network, Federal Rural University of Pernambuco –Recife – Pernambuco, Brazil
[b] Catholic University of Pernambuco, Rua do Príncipe, n. 526, Boa Vista, Cep: 50050-900, Recife-Pernambuco, Brazil
[c] Advanced Institute of Technology and Innovation (IATI), Rua Joaquim de Brito, n. 216, Boa Vista, CEP: 50070-280, Recife, Pernambuco, Brazil
leonie@unicap.br

The effluent production of oily water type has generated many environmental problems for several industries. The use of flotation as a separation process of oily waters has been described, although it has been sometimes criticized due to the toxicity of collectors. The development and use of biodegradable surfactants may enhance the further acceptance of this separation technology. In this sense, the dissolved air flotation (DAF) process continues to be widely used in industries, both for water and wastewater supplies. The use of collectors is essential to improve the efficiency of the process, due to its specific characteristics that facilitate the adhesion of the particles and, consequently, the separation of the pollutants. 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. The aim of this study was to investigate a water-oil separation by DAF, with and without the addition of biosurfactant produced by *Pseudomonas cepacia* CCT 669 in mineral medium and formulated with 2.0% of corn steep and 3.0% of canola waste frying oil at 28°C for 60 h under 200 rpm. The experiments used to compare the effects of the addition of biosurfactant followed an experimental planning CCRD, where the response variable was the separation efficiency. Results indicated the biosurfactant added a considerable value to the process, increasing from 41.0% to 98.0% the separation efficiency, presenting potential of application as a collector of oily contaminants in the DAF process form.

1. Introduction

Petroleum industry and related industries unavoidably generates large volumes of oily wastewater which has become an urgent challenge for most oilfield and petroleum company focusing attention toward efficient treatment techniques. Effluent production of oily water type has generated many environmental problems for several industries (Yu et al., 2013).
Separation technologies such as centrifugation, ultrafiltration, decantation, flotation, and flocculation are examples of physical/chemical processes effectively used for the separation of oil-water mixtures (Painmanakula et al., 2010). In this context, the flotation process has proven to be quite efficient, with the capability of removing a larger amount of oil in comparison to other methods (Albuquerque et al. 2012).
Flotation is a bubbles adhesion based particle separation process. The oil particle-bubble union has less density than the aqueous medium and floats to the surface of the flotation chamber, where the oil particles are removed (Bahadori et al. 2013). Flotation was first used in mineral processing and has long been employed in solid/liquid separation processes that involve the use of stable foams to recover mineral particles (Peng et al. 2009).
With the industrial sector development, the flotation process application was improved, leading to the emergence of dissolved air flotation (DAF), which involves solute removal through adsorption, co-precipitation

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or occlusion in a floc transporter and subsequent release by the addition of an adequate tensioactive agent (Beneventi et al. 2009). With DAF, the water is saturated with pressurised air through a nozzle, forming bubbles that reach the flotation chamber, which is at atmospheric pressure. The air becomes supersaturated and precipitates from the solution in the form of small bubbles (Babaahmadi, 2010; Rocha e Silva et al. 2015).
The use of flotation as a separation process of oily waters have been widely employed wastewater treatments, of oil industries (Bahadori et al., 2013; Rocha e Silva et al. 2015). The dissolved air flotation may be considered as a clean technology since it uses small quantities of coagulant and air to promote separation. The size, speed, and bubbles, along with the velocity gradient are important parameters to control the efficiency of the process and operating costs (Babaahmadi, 2010). On the other hand, this technique has been sometimes criticized due to the toxicity of the synthetic surfactants used as collectors in this process (Menezes et al., 2011). Surfactants are compounds composed of amphipathic molecules with a hydrophilic portion and a hydrophobic portion that partition at the oil/water or air/water interface. The apolar portion is often a hydrocarbon chain, whereas the polar portion may be ionic (cationic or anionic), non-ionic or amphoteric. These characteristics enable surfactants to reduce surface and interfacial tension and form microemulsions, in which hydrocarbons can be solubilised in water or vice versa (Almeida et al. 2016).
Currently, the development and use of biodegradable surfactants (biosurfactants) has helped to increase acceptance of this separation technology (Rocha e Silva et al., 2015). Biosurfactants are amphipathic molecules that reduce the surface and interfacial tensions of liquids. Such compounds have a predilection for interfaces of dissimilar polarities (liquid–oil) and are soluble in both organic (non-polar) and aqueous (polar) solvents (Silva et al., 2014). 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 (Menezes et al., 2011).
The aim of this study was to investigate a water-oil separation by DAF, with addition of biosurfactant, in a pilot-scale DAF system. The experiments used to evaluate the effects of biosurfactant addition followed an experimental planning CCRD, where the response variable was the oil removal efficiency.

2. Materials and Methods

2.1 Materials

All chemicals were of reagent grade. Growth media were purchased from Difco Laboratories, USA. Canola waste frying oil was received from a local restaurant in Recife-PE, Brazil and was stored according to supplier's recommendations and used without any further processing. Corn steep liquor was obtained from the Ingredion Brasil factory, Cabo de Santo Agostinho-PE, Brazil.

2.2 Bacterial strain and inoculum preparation

A strain of *P. cepacia* CCT6659 was provided from the culture collection of the Fundação André Tosello de Pesquisa e Tecnologia, Campinas city, São Paulo, Brazil. The microorganism was maintained in nutrient agar slants at 4°C. For pre-culture, the strain from a 24-h culture on nutrient agar was transferred into 50 ml nutrient broth to prepare the seed culture. The cultivation condition for the seed culture was 28°C, 200 rpm, and 24h of incubation time.

2.3 Biosurfactant production

The fermentation for the biosurfactant production was carried out in distilled water containing 2% of canola oil residual, 3% of corn steep liquor, 0.2% $NaNO_3$, 0.05% KH_2PO_4, 0.1% K_2HPO_4, 0.05% $MgSO_4 .7H_2O$, 0.01% KCl and 0.001% $FeSO_4 .7H_2O$. After media preparation, the pH was adjusted to 7.0 and these were autoclaved at 121°C for 20 minutes. The culture was incubated in a rotary Marconi MA832 shaker (Marconi Laboratory equipment, SP, Brazil) for 60 h at 200 rpm (Silva et al., 2013).

2.4 Surface tension measurement

Surface tension was determined in the cell-free broth obtained by centrifuging the cultures at 10,000 × g for 15 min. Surface tension was determined with a Tensiometer (Sigma 700, KSV Instruments Ltd., Finland), using the Du Nouy ring method at room temperature (Silva et al., 2014).

2.5 CCRD Experimental factorial design

In order to study biosurfactant potential as an alternative collector on the oil-water separation in a DAF pilot scale system prototype (Figure 1), central composite rotational design (CCRD) application was performed. The independent variables were coded at five levels (-2.00, -1.00, 0.00, +1.00, +2.00) and the complete design consisted of 28 experimental points including 4 replications of the central points. The coded levels of the independent variables used in the experimental design are listed in Table 1. The response variable was the oil removal efficiency of the pilot prototype. All determinations were performed at least three times. ANOVA, regression coefficients and the construction of graphs were performed using the Statistica® program, version 10.0 (Statsoft Inc, USA).

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

Levels	Oily Water Flow (X_1)*	Microbubble Flow (X_2)*	Biosurfactant Flow (X_3)*	Biosurfactant Concentration (X_4)**
-2.00	2.50	5.00	0.50	0.05
-1.00	5.00	5.50	1.00	0.15
0.00	7.50	6.00	1.50	0.25
1.00	10.00	6.50	2.00	0.35
2.00	12.50	7.00	2.50	0.45

** (L/min); ** (g/L)*

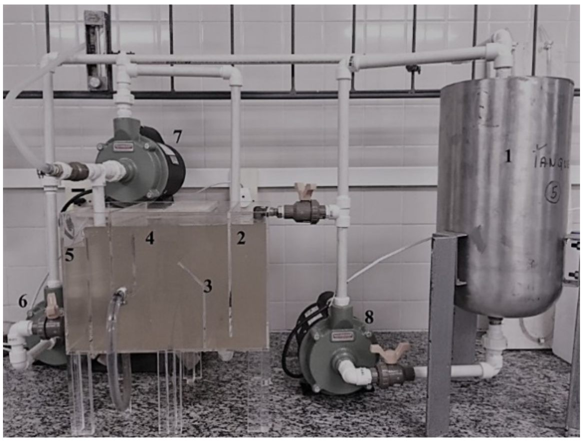

Figure 1: Three dimensional scheme of pilot scale DAF system. Oily water storage tank (1); Flotation chamber (2); Second section where separation between treated water and oily foam formed (3); Oily foam collectors (4); Chamber of treated water collection (5); Return pump for treated water (6); Microbubble production pump (7); and oily water production pump and DAF chamber feed (8)

3. Results and Discussion

3.1 Biosurfactant production

The properties and integrity of the biosurfactant produced were verified prior to the tests for the study of its potential as an alternative collector. The biosurfactant produced was able to reduce the surface tension of the culture medium from 55.0 mN/m to 28.0 mN/m corroborating with the results obtained by Soares da Silva et al (2017) under the same conditions evaluated.

3.2 Evaluation of water-oil separation efficiency using biosurfactant in the DAF system

The CCRD matrix and corresponding results are given in Table 2.
As a result, the effluent flow rate of 5.00 L/min, microbubble water flow of 5.50 L/min, biosurfactant flow rate of 1.00 L/min and biosurfactant concentration of 0.35 g/L were the more favorable parameters for the oil removal process using this type of biosurfactant, reaching a percentage of removal of 98.25% (Run 2), compared with 41.20% of oil removal without the use of the biosurfactant as an alternative collector. The results were not favorable for biosurfactant action of the in the DAF process occurred in the tests 10 and 11 (11.08 and 12.09%, respectively), which was probably due to the considerable increase of the effluent flow (oily water) and low concentration of the biosurfactant which must have influenced negatively in the micelles formation and compromised the collision between the microbubbles and the particles of the oil.

Table 2: Experimental design results matrix and values of observed factors on separation efficiency in the pilot scale DAF system with use of biosurfactant

Runs	Oily Water Flow (X_1)	Microbubble Flow (X_2)	Biosurfactant Flow (X_3)	Biosurfactant Concentration(X_4)	Removal efficiency (%)(Y)
1	5.00	5.50	1.00	0.15	63.20
2	5.00	5.50	1.00	0.35	98.25
3	5.00	5.50	2.00	0.15	85.18
4	5.00	5.50	2.00	0.35	73.83
5	5.00	6.50	1.00	0.15	65.38
6	5.00	6.50	1.00	0.35	49.76
7	5.00	6.50	2.00	0.15	37.82
8	5.00	6.50	2.00	0.35	80.86
9	10.00	5.50	1.00	0.15	80.20
10	10.00	5.50	1.00	0.35	11.08
11	10.00	5.50	2.00	0.15	12.09
12	10.00	5.50	2.00	0.35	71.74
13	10.00	6.50	1.00	0.15	63.95
14	10.00	6.50	1.00	0.35	36.36
15	10.00	6.50	2.00	0.15	29.59
16	10.00	6.50	2.00	0.35	30.39
17	2.50	6.00	1.50	0.25	51.38
18	12.50	6.00	1.50	0.25	19.08
19	7.50	5.16	1.50	0.25	34.13
20	7.50	6.84	1.50	0.25	42.42
21	7.50	6.00	0.50	0.25	40.00
22	7.50	6.00	2.50	0.25	51.37
23	7.50	6.00	1.50	0.05	38.89
24	7.50	6.00	1.50	0.45	73.44
25	7.50	6.00	1.50	0.25	51.88
26	7.50	6.00	1.50	0.25	46.61
27	7.50	6.00	1.50	0.25	47.29
28	7.50	6.00	1.50	0.25	50.54

The Pareto diagram shown in Figure 2 shows the statistical significances of the studied variables at p-values (< 0.05). As can be observed, the Oily Water Flow (X_1) was the most significant variable for the process and its increase causes a decrease in the efficiency of oil removal by the system. The Biosurfactant Flow did not present statistical significance (X_3), however, its concentration (Biosurfactant Concentration) was positively correlated with the oil removal efficiency.

Figure 3 displays the fitted response surface plots for oil removal efficiency shown by Pareto diagram of the statistically significant interactions. The combination of greater oily water flow and greater microbubble flow led to maximum oil removal efficiency (Fig. 3A) and the elliptic curve found in the graph indicates a high degree of interaction of these variables. Figure 3B shows that high oil removal efficiency was also achieved when both oily water flow and biosurfactant concentration were maintained at their maximum levels. Better oil removal efficiency was found when the biosurfactant flow and biosurfactant concentration was maintained at its maximum level (Fig. 3C), however, these interactions were weak and did not produce well-defined regions in the graphs.

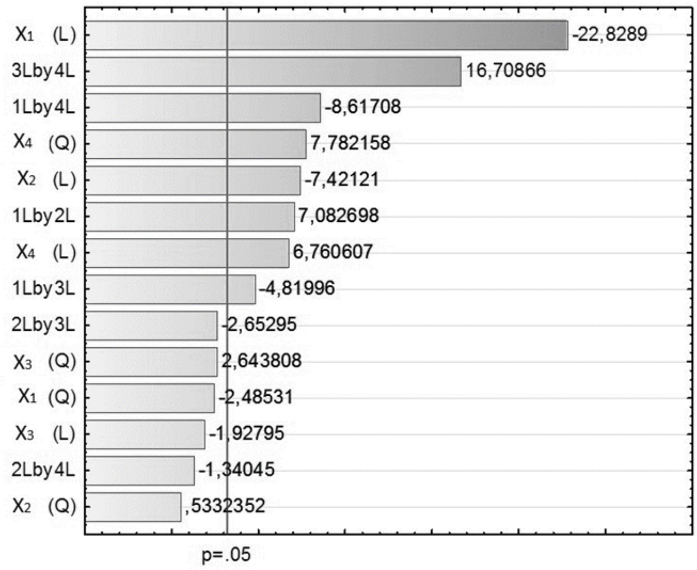

Figure 2: Pareto's Chart of the Central Composed Rotate Design.

In another study conducted by Rocha e Silva et al (2015), a biosurfactant obtained from *Candida sphaerica* UCP 0995 also promotes an improvement of the oil removal in the DAF system. The authors reported increasing separation efficiency from 80.0 to 98.0% in the presence of biosurfactants. The results demonstrate a better performance of the bench scale system using the biosurfactant as a coadjuvant in the DAF process, compared to the action of the microbubbles only without the use of this alternative collector. This confirms the potential of these microbial biomolecules as an aid in the removal of hydrophobic compounds in Dissolved Air Flotation. In addition, it is important to highlight that the biosurfactant from *P. cepacia* CCT 669 was produced in a culture medium prepared only with industrial waste products, which further reduces the process costs, since substrates used in the production of biosurfactants account for 20 to 30% of the production cost (Hazra et al., 2012; Santos et al., 2016). The low cost of the proposed DAF process is evident by the small amount of biosurfactant (350 ppm) required to achieve maximum efficiency (run number 2 in Table 2). As many industries generate huge amounts of oily waters that require adequate treatment before being discarded or reused, the benefits of treating oily waters with the system developed herein demonstrates its considerable market potential. Therefore, biosurfactants are promising coagulants and/or dispersants capable of increasing the efficiency of this technique.

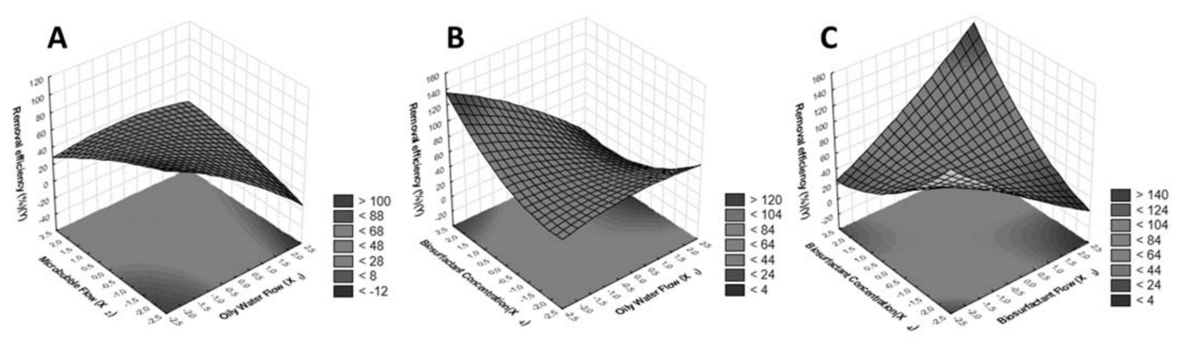

Figure 3: Response surface plots and contour plots for maximum removal efficiency for the 28 experimental runs carried out under conditions established by CCRD; removal efficiency as function of (A) oily water flow and microbubble flow; (B) oily water flow and biosurfactant concentration; (C) biosurfactant flow and biosurfactant concentration.

4. Conclusions

The present study demonstrated the effectiveness of using a central composite rotational design to identify the optimum parameters for increase oil removal efficiency in DAF system. The above results confirm the great potential of the biosurfactant to be used as an alternative collector, since these microbial surfactants act as true "molecular glues", interacting with the oil and the air bubbles, facilitating the oil transportation during the process flotation, as evidenced by the results presented.

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