



Oil removal efficiency forecast of a Dissolved Air Flotation (DAF) reduced scale prototype using the dimensionless number of Damköhler

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ABSTRACT

The increasingly automated industrial processes are responsible for a large part of the generation of oily effluents, which present great difficulty of treatment due to the complexity of removal of fine particles of oil. The application of biosurfactants and the dimensionless number of Damköhler (Da) in a prototype of dissolved air flotation (DAF) allowed predictions of efficiency of oil removal in oily waters. Two different biosurfactants were used in order to confirm a first-order kinetic law for the DAF process in the water-oil separation. The kinetic behavior of the DAF process was associated by analogy with a perfect blending reactor (Continued Stirred Tank Reactor – CSTR). In this way, a laboratory float was used in order to allow experiments with the biosurfactants produced by the bacteria *Bacillus* sp. and *Pseudomonas aeruginosa*. A first-order kinetic model was fitted to the experimental data, using Quasi-Newton numerical optimization methods. The application of the dimensionless number of Damköhler, together with the use of the biosurfactants, allowed prediction of the oil removal efficiency, around 90%. It has been observed that it is also possible to predict the flotation chamber volume based on a desired value of removal efficiency.

1. Introduction

The development of the world industry in the last hundred years, including the production of noble metals, phosphate for agriculture, among others, would not have been possible without the flotation process discovery. The conventional physical processes of centrifugation and decantation are not efficient in the removal of fine particles. However, techniques such as dissolved air flotation (DAF) allow the appropriate treatment of difficult-to-remove contaminants such as oil-contaminated water, besides of being clean and very efficient technologies [1]. The production or generation of industrial oily waters is an important problem for many industries, since many types of effluents tend to form emulsions difficult to be treated [2].

DAF is an important water-oil separation method based on surface physico-chemical mechanisms. This process basically depends on the creation of an air/liquid/liquid interface, where a part of “oil” binds to gas (air) microbubbles, mainly due to the hydrophobicity of its surface

[3]. The hydrophobicity control in this process can occur through the use of specific chemical reagents in order to separate the particles by polar attraction [4].

In relation of chemical reagents, these are composed, for the most part, of surfactants compounds derived from petroleum [5–7]. However, surfactants from bacteria, yeasts and filamentous fungi have been showing great potential in oily waters treatment [8,9]. These alternative collectors are known by scientific community as biosurfactants. These biomolecules are highly stable when subjected to pH, temperature and salinity variations, allowing their use as auxiliary in controlled processes (DAF) or in oil spills, as in the case of oil platforms [10,11].

In practice, the kinetics of the DAF process is used to study several industrial processes, that from experimental data, can convert the measured time in laboratory, in a non-stationary state, for continuous operations. Kinetic study is a very useful tool to analyze various variables involved in a process, as well as assist the development of industrial projects and equipment design [12].

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Among other benefits, the kinetics knowledge of a vessel that behaves as a reaction system allows a correlation application aiming a reactor or pseudo-reactor scaling, in this case an DAF chamber [13]. For example, after the identification of a kinetic law for a bench, pilot or commercial scale, it is possible to estimate the dimensionless number of Damköhler (Da), for one of these structures [14]. In this case, if the system is of the CSTR type, the solution for the corresponding vessel volume on a given scale can be simplified, since the Da for these structures are identical.

In the present work, the kinetic characteristics were investigated in a flotation chamber, where the water-oil emulsified mixture was separated in a benchtop prototype. In this way, volume predictions were tested for a pilot plant of DAF applied in a water-oil separation in the presence of biosurfactants.

2. Material and methods

2.1. Biosurfactants production

2.1.1. Microorganisms

The microorganisms *Pseudomonas aeruginosa* UCP0992 and *Bacillus* sp. were obtained from the culture collection of the Catholic University of Pernambuco (Brazil) and were used in the production of biosurfactants.

2.1.2. Seed cultures

The microorganisms were maintained in Nutrient Agar (NA), within 0.5% meat extract, 1% peptone, 0.5% NaCl and 0.5% Agar. For inoculum growth, the nutrient broth medium (NB) was used, with the following composition: 0.5% meat extract, 1.5% peptone, 0.5% NaCl and 0.5% K_2HPO_4 .

The biosurfactants production was carried out in mineral medium formulated with 0.1% de K_2HPO_4 , 0.1% de K_2HPO_4 , 0.02% de $MgSO_4 \cdot 7H_2O$, 0.002% de $CaCl_2 \cdot 2H_2O$ and 0.005% $FeCl_3 \cdot 6H_2O$ [15].

For *P. aeruginosa*, 0.6% $NaNO_3$ and 3% glycerol were added to the mineral medium, according to Silva et al. [16], while for *Bacillus* sp., 3% molasses and 3% corn steep liquor were added [17]. These biosurfactants were selected based on the previous results obtained by Rocha e Silva et al. [18].

2.1.3. Preparation of inoculum

Young cultures of the bacteria obtained after 24 h in nutrient agar medium were transferred to an Erlenmeyer containing 50 mL nutrient broth, which was maintained under orbital shaking at 150 rpm for 24 h at 28 °C to obtain na O.D. (Optical Density) of 0.7 (corresponding to an inoculum of 10^7 U.F.C./mL) at 600 nm. This reading was used as inoculum in the concentration of 1% (v/v).

2.1.4. Fermentations

The production of biosurfactants was carried out in Erlenmeyer flasks of 500 mL capacity, containing 100 mL of production medium and incubated with 2% of the pre-inoculum. The flasks were maintained under 200 rpm in orbital shaking for 120 h for *P. aeruginosa* and 200 rpm for 120 h for *Bacillus* sp., both at 28 °C. At the end of cultivation, the cell-free metabolic broth of the two biosurfactants were obtained after cells removal by centrifugation at $5000 \times g$ for 30 min, afterwards, samples were used to determine surface tension.

2.1.5. Determination of surface tension

The surface tension was measured in the cell-free metabolic broth in a KSV Sigma 700 (Finland) tensiometer using the NUOY ring. The platinum ring was immersed in the metabolic fluid, recording the force required to pull it through the air/liquid interface, presenting 29 mN/m for *Bacillus* sp. and 27.4 mN/m for *Pseudomonas aeruginosa*. The instrument was calibrated against Mill-Q-4 ultrapure distilled water (Millipore, Illinois, USA). Prior to use, the platinum plate and all

glassware were sequentially washed with chromic acid, deionized water and acetone and flamed with a Bunsen burner. Samples were read three times for accuracy.

2.2. Determination of kinetic flotation model

It is known that the principle of the flotation phenomenon for effluent treatment is based on contaminant removal, that is, in this case, oil. Thus, the kinetic model attributed to this phenomenon, by analogy with a mixing reactor (CSTR type), must be associated to the decay of oil concentration as a function of flotation time. For this, the expression that represent the reaction velocity is given by:

$$-\left(\frac{dC_o}{dt}\right) = k \cdot C_o^n \quad (1)$$

Where:

C_o – Oil concentration, $mg L^{-1}$

k – Oil removal speed constant, min^{-1}

n – pseudo kinetic order of oil removal in DAF process, -

Lubricating oil was selected as the contaminant oil that is commercially available for use in flex engines (gasoline, VNG and alcohol), type SAE 20W-50, with synthetic guard (Petrobras, Brazil). It consists of a paraffinic base lubricating oil (a complex mixture of hydrocarbons) and performance enhancing additives.

2.3. Damköhler adimensional number (Da)

The dimensionless number of Damköhler (Da) is a parameter that can give a quick estimate of the conversion to be achieved in continuous flow vessels [19]. This number can be interpreted, in a float, as the ratio between the rate of oil removal and the convective transport velocity of this oil, measured at the float input:

$$Da = \frac{k \cdot C_{o0} \cdot V}{q_0 \cdot C_{o0}} \quad (2)$$

In which:

C_{o0} – Oil concentration at the float inlet, $mg L^{-1}$

q_0 – Volumetric flow at the float inlet, L/min

V – Float volume, L

It is important to know that values from the Damköhler number correspond to high and low conversion values [20]. For irreversible transformations a $Da \leq 0,1$ value will correspond to less than 10% for the conversion. A $Da \geq 10$ value will usually correspond to a conversion greater than 90%.

2.4. Flotation chamber

A 15L laboratory-scale dissolved air float was built, applying scale-down laws to the prototype used by Rocha e Silva et al. [8], with the suppression of one of the flotation chambers. The dimensions of the flotation chamber are as follows: 0.262 m high, 0.240 m long and 0.240 m wide. The reduced prototype was also constructed in acrylic in order to allow a better visualization of the air microbubbles distribution. The prototype has a microbubble injector at the bottom of the chamber, allowing the oily foam formed to be collected at the top and back of the chamber, taking advantage of direction flow. At the bottom, opposite entrance of flotation chamber, the treated water follows into a discharge compartment, aiming at the disposal or recirculation for microbubbles production as shown in Fig. 1.

The oily effluent used in the float was produced in a water-oil mixing tank, shaken for 40 min, before entering DAF chamber. The effluent inlet was adjusted to a flow of 3.0 L/min and the air inlet to microbubbles was maintained at 6.5 L/min. The oil concentration in the synthetic effluent was maintained at 500 ppm and monitored with the aid of a samples absorbance calibration.

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