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Separation of emulsified crude oil in saline water by dissolved air flotation with micro and nanobubbles

R. Etchepare [1,2], H. Oliveira [1], A. Azevedo, J. Rubio *

Laboratório de Tecnologia Mineral e Ambiental, Departamento de Engenharia de Minas, PPGE3M, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, Setor 6 (Centro de Tecnologia), Prédio 43819, Bairro Agronomia 91501-970 Porto Alegre, RS, Brazil[3]

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ABSTRACT

This work investigates the separation of emulsified crude oil in saline water (30 g L^{-1} NaCl) with microbubbles (MBs, D_{32} = 30–40 μm) and nanobubbles (NBs, D_{32} = 150–350 nm). Bubbles were generated simultaneously by the depressurization of air-saturated water through a flow constrictor (needle valve). The emulsified oil, after gravity separation of the "free" oil, was flocculated with a cationic polyacrylamide (Dismulgan) at pH 7 and removed by: i. Flotation with MBs and NBs; ii. "Floatation" by NBs; and iii. Flotation with MBs and NBs following floc conditioning by NBs. The best oil removal (>99% efficiency) was obtained at 5 bar and 5 mg L^{-1} of Dismulgan, reducing the oil content (feed concentration = 334–484 mg L^{-1}) in the treated water to <1 mg L^{-1}. Furthermore, the use of low saturation pressure (Psat = 3.5 bar), resulted in a treated water with oil concentrations lower than 29 mg L^{-1} (EPA standards for offshore discharge). Best results were obtained at a low energy for bubble formation, followed by efficient precipitation and nucleation, at a fairly low air/feed emulsified oil interfacial tension (55 mN m^{-1}). The flotation was very fast and followed a first-order model, with a flotation kinetic constant of 1.3 and 1.8 min^{-1} for P_{sat} of 3.5 and 5 bar, respectively. The injection of isolated NBs (3×10^8 NBs mL^{-1}), in a conditioning stage after flocculation (with 1 and 3 mg L^{-1} Dismulgan) increased the hydrophobicity of the aggregates, improved the adhesion between bubbles and oily flocs and the overall efficiency of the flotation process from 73 to 84%, and from 92 to 95%, respectively. "Floatation" (simply flocs rising with isolated NBs) resulted in oil removal efficiencies of 75 and 90% with and without NaCl (30g L^{-1}). It is believed that the NBs entrap and adhere inside the flocculated oil droplets, forming aerated oily flocs, which subsequently assist the MBs in the flotation process. This finding appears to have potential in improving oil separation by flotation.

1. Introduction

Flotation is extensively employed in the removal of emulsified oils from aqueous dispersions, after destabilization by flocculation. The size distribution of bubbles and oil droplets plays a key role in flotation efficiency. Small bubbles are preferred because of their large surface areas, which are shown to be very useful in the aggregation of droplets [1,2]. Conversely, larger bubbles tend to rise rapidly, which results in lower collision efficiency. The adhesion between bubble and oil droplet is another key factor for flotation efficiency. The formation of stable bubble-droplets aggregates depends on a number of factors, such as the ratio of bubble / droplet size, their numeric concentration, salinity, oil viscosity, fluid velocity and turbulence. Among these factors, the gas dispersion parameters are considered the most important in oil-water separation [3].

Produced water is wastewater generated in petroleum prospecting that is composed of a mixture of water from wells and process water [4–6]. Flotation is usually applied in its treatment at offshore platforms [7], and the effluent should meet the emission limit (EPA Oil and Gas Effluent Guidelines [8]) of 29 mg L^{-1} total oil concentration average for monthly and 42 mg L^{-1} for daily maximum for offshore disposal.

Recent studies have found that in dissolved air flotation (DAF) microbubbles (MBs) and nanobubbles (NBs) are formed [9,10]. The generation and applications of NBs are an emerging and fast-growing research area because of their physical, chemical and physicochemical properties.

* Corresponding author.
E-mail address: jrubio@ufrgs.br (J. Rubio).
[1] Both authors contributed equally.
[2] Current address: Departamento de Hidráulica e Saneamento, Universidade Federal do Paraná, 81531-980 Curitiba, PR, Brazil.
[3] www.ufrgs.br/ltm.

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Reports and news about flotation with NBs to remove pollutants from waters and wastewaters are scarce. Recent studies have demonstrated the potential of these fine bubbles in solid-liquid separation and mineral treatment [11–15]. Recently, the removal of amine and sulfate precipitates from aqueous solutions using isolated NBs (F-NBs) and DAF assisted by NBs were studied [11,16]. The DAF assisted by NBs consists in the injection of an aqueous dispersion of NBs in a conditioning stage (with or without flocculants) promoting aggregation and hydrophobization of the particles to be removed.

It is believed that NBs may play an important role in the aggregation and stabilization of these aggregates (flocs) by adhering to and/or entraining inside (entrapment) the flocs, generating capillary bridges between oil droplets, and improving their hydrophobicity and the probability of adhesion with MBs [11,17]. The aim of this study was to evaluate the role of NBs on various multi-bubble flotation configurations: MBs and NBs, DAF assisted by NBs, and "floatation" (flotation without lifting power) with isolated NBs (F-NBs), on the removal of emulsified oil after destabilization / flocculation at the bench level.

2. Materials and methods

2.1. Synthetic produced water

Ultrapure (DI) water at room temperature (22 °C ± 1) with a conductivity of 3 μS cm^{-1}, a surface tension of 72.5 ± 0.1 mN m^{-1} and pH 5.5 was used to prepare the synthetic produced water. DI water was obtained by ultrapurification of tap water with a reverse osmosis cartridge and modules of ion-exchange resins and activated carbon.

The petroleum (crude oil) used in this study was supplied by a local oil refinery (REFAP, Petrobras, southern Brazil). This oil was characterized in terms of its physicochemical and interfacial properties (Table 1).

The brine solution for synthetic produced water was made by dissolving 30 g L^{-1} of NaCl (99.5%, Vetec®, Brazil) into 1 L of DI water. Then, 1.6 g of crude oil was slowly dripped into the brine solution for emulsification with an Ultra Turrax mixer (IKA, 24.000 rpm, 10 min). The emulsion was left to stand in an acrylic column for 1 h for the separation of the free oil phase to obtain a well stabilized oil-in-water emulsion. Solutions of 0.1 M NaOH (Vetec®, Brazil) were prepared for pH adjustment in the destabilization/flocculation stage.

The destabilization and flocculation of the emulsion was conducted using Dismulgan V3377 (Clariant®, Rio Grande do Sul, Brazil) (1 to 10 mg L^{-1}), a flocculation polymer (polyacrylamide) widely used on offshore petroleum platforms.

2.2. Flocculation-flotation studies for oil/water separation

The experiments were performed using the system shown in Fig. 1, which consisted of: i. saturator vessel made of acrylic (1) for bubble generation (2.5 L, h = 400 mm, diameter = 110 mm, equipped with a manometer and a needle valve); ii. a glass column (2) for the separation of MBs (2 L, h = 250 mm, diameter = 100 mm) using the technique described by Calgaroto et al. [9,17]; and iii. a glass column (3) for the flocculation and flotation stages (2.5 L, h = 330 mm, diameter = 100 mm) and a mechanical stirrer Fisatom® brand (model 713D).

The glass column (2) had one input receiving the depressurized flow (MBs and NBs) from the saturator vessel and one output connected to the glass column (3), to inject the isolated NBs. With flotation by MBs and NBs together, the glass column (2) was not employed.

Table 1
Crude oil physicochemical and interfacial properties.

Parameters	Value
Density, 25 °C (g mL^{-1})	0.88
API Grade (°API)	23
Viscosity, 25 °C (cP)	42
Superficial tension (oil/water), 25 °C (mN m^{-1})	28

Fig. 1 shows a schematic representation of the bench system for generation and treatment of oily emulsion by flocculation-flotation with MBs and NBs.

2.2.1. Flotation with MBs and NBs

The bubbles formed by depressurization and hydrodynamic cavitation of the flow of air saturated water through the needle valve were injected directly into the glass column (3) (without separation of MBs and NBs). To perform the tests, a volume of 800 mL of the oily emulsion was transferred to the glass column (3). Flocculation was performed using rapid mixing stages (1 min, G = 2400 s^{-1}), followed by slow mixing (5 min, G = 30 s^{-1}) by the use of the mechanical agitator.

The effect of the saturation pressure (P_{sat}) on the oil removal was observed between 2.5 and 6 bar by injecting compressed air and adjusting the relief valve in the saturator vessel over 30 min. Flotation was performed with 200 mL of bubble suspension into the flotation cell, corresponding to a recycle ratio of 25%.

Aliquots of 100 mL were collected for oil concentration analysis after 1 h of separation of the free oil phase, and from the clarified liquid (treated water) after 5 min of flotation. All experimental assays were performed in triplicate and the results were analyzed in terms of oil removal efficiency (%), according to (Eq. (1)).

$$\text{Efficiency}(\%) = 100 - \frac{[(C_f \times F) \times 100]}{C_0} \quad (1)$$

where, C_f is the final oil concentration; F is the dilution factor (1.2) corresponding to the volume (200 mL) of saturated water injected; C_0 is the initial oil concentration.

The air/oil ratio (Eq. (2)) was calculated using the theoretical calculation of air saturation in water (Henry's Law) and the volume of precipitated air per liter of water for different values of Psat calculated by Rodrigues and Rubio [18] using a saturation efficiency of 95% in the saturator vessel.

$$\text{Ratio}\frac{\text{air}}{\text{oil}} = \frac{(v_{air} \times F2) \times 0.95}{(C_{oil} \times F1)} \quad (2)$$

where C_{oil} is the initial oil concentration (mg L^{-1}); F1 is the correction factor corresponding to the volume of liquid (oily emulsion) used (800 mL); V_{air} is the volume of precipitated air (mL L^{-1}); F2 is the correction factor corresponding to the volume of saturated water used (200 mL).

The effect of Psat on flotation kinetics was evaluated at a P_{sat} of 3.5 and 5 bar. Treated water samples were collected at different flotation times (0–300 s) for measuring residual oil concentration. The results were expressed in terms of the percentage of oil removal (Eq. (1)) and flotation kinetic parameter data was adjusted to the first-order flotation model [19]. The flotation kinetic constant k was obtained using (Eq. (3)).

$$\ln\left(\frac{R\infty}{R\infty - R}\right) = kt \quad (3)$$

The García-Zuñiga kinetic model of flotation is given by (Eq. (4)).

$$R = R\infty(1 - e^{-kt}) \quad (4)$$