Separation of emulsified crude oil in saline water by flotation with micro- and nanobubbles generated by a multiphase pump

H. A. Oliveira, A. C. Azevedo, R. Etchepare and J. Rubio

ABSTRACT

The flocculation-column flotation with hydraulic loading (HL, >10 m h⁻¹) was studied for the treatment of oil-in-water emulsions containing 70–400 mg L⁻¹ (turbidity = 70–226 NTU) of oil and salinity (30 and 100 g L⁻¹). A polyelectrolyte (Dismulgan, 20 mg L⁻¹) flocculated the oil droplets, using two flocc generator reactors, with rapid and slow mixing stages (head loss = 0.9 to 3.5 bar). Flotation was conducted in two cells (1.5 and 2.5 m) with microbubbles (MBs, 5–80 μm) and nanobubbles (NBs, 50–300 nm diameter, concentration of 10⁶ NBs mL⁻¹). Bubbles were formed using a centrifugal multiphase pump, with optimized parameters and a needle valve. The results showed higher efficiency with the taller column reducing the residual oil content to 4 mg L⁻¹ and turbidity to 7 NTU. At high HL (27.5 m h⁻¹), the residual oil concentrations were below the standard emission (29 mg L⁻¹), reaching 18 mg L⁻¹. The best results were obtained with high concentration of NBs (apart from the bigger bubbles). Mechanisms involved appear to be attachment and entrapment of the NBs onto and inside the flocs. Thus, the aggregates were readily captured, by bigger bubbles (mostly MBs) aiding shear withstanding. Advantages are the small footprint of the cells, low residence time and high processing rate.

Key words | centrifugal multiphase pump, column flotation, nanobubbles, oil removal

INTRODUCTION

Dissolved air flotation (DAF) is a solid–liquid separation method widely employed in emulsified oily wastewater treatment (Zouboulis & Avranas 2000; Al-Shamrani et al. 2002a, 2002b; Rubio et al. 2002; Santander et al. 2011; Santo et al. 2012; Saththasivam et al. 2016). The process consists of the rapid depressurization of air-saturated water from pressurized tanks for the generation of bubbles and subsequent solid–liquid and/or liquid–liquid separation. Recently (Calgaroto et al. 2014; Azevedo et al. 2016), the presence of nanobubbles (NBs) in DAF operation was discovered, a fact unknown for years. The role of these NBs in flotation, together with microbubbles (MBs), is being studied extensively by our research group (Calgaroto et al. 2015, 2016; Amaral Filho et al. 2016; Etchepare et al. 2016; Azevedo et al. 2017a, 2017b). An upcoming and promising alternative for the saturation of air in water in DAF applications is open-end saturation (Lee et al. 2007; Pioltine & Reali 2011; Etchepare 2016; Azevedo et al. 2017), so-called flotation with a multiphase pump (F-MP), in which air is continuously injected into the low-pressure suction side of a special centrifugal multiphase pump (CMP). This unit provides efficient air dissolution into the liquid, and a high generation of MBs (50–100 μm) and NBs (100–850 nm) is attained due to the depressurization of the multiphase flow, the hydrodynamic cavitation caused by the flow constrictor and by the shearing effects inside the pump chamber impellers.

Etchepare et al. (2017c) investigated the generation of NBs by a CMP and its operating parameters to obtain a high concentration of these bubbles in the F-MP (approximately 4 × 10⁶ NBs mL⁻¹ at 5 bar). These authors reported that the mechanisms of hydrodynamic cavitation inside the pump chamber and downstream of the flow constrictors are responsible for a high concentration of NBs in these systems. This technique was compared to other methods of NBs generation (Ushikubo et al. 2010; Liu et al. 2012;

Recent studies of emulsified oil removal by flotation at bench scale (Etchepare 2016; Etchepare et al. 2017b) showed an increase in the oil removal by conditioning oily aggregates (flocs) with NBs, followed by flotation with MBs. The authors discussed the role of NBs in the oil flotation phenomena, after the entrapment of NBs into flocs and a reduction of their relative density. Other studies have also demonstrated that NBs improve the aggregation of colloids and fine particles and increase the contact angle at the solid–liquid–air interface, which increases the probability of flotation due to an improvement in the bubble–particle adhesion mechanism and stability of these aggregates (Fan et al. 2013).

Most of the technologies available for petroleum produced water (PW) treatment, such as membrane filtration, centrifugation and biological treatment, present many limitations due to operational costs, high footprint (low hydraulic loadings – HLs) and low efficiency (Fakhru’l-Razi et al. 2009). The most conventional PW treatment in offshore platforms consists of a gravimetric separation stage (hydrocyclone) followed by flotation (Zheng et al. 2016). The treated effluent must meet the emission limit standards determined by many agencies, namely the US Environmental Protection Agency (EPA) effluent guideline for oil and gas extraction (CFR 40.435; EPA 1979). For offshore water disposal the limit is about 29 mg L⁻¹ of oil for a monthly average and 42 mg L⁻¹ for a daily maximum. The PW treatment on offshore platforms presents technical challenges due to the limitations of available area, equipment weight and low residence time, which usually does not exceed 15 min (Gabardo et al. 2011). Thus, there is a need to develop and improve treatment processes with high processing rates, especially in compact units that occupy reduced areas (low footprint).

Carissimi & Rubio (2005a) developed a helical coiled hydraulic flocculator, a so-called flocs generator reactor (FGR®). This type of flocculator has been used in aerated floc formation by the injection of air bubbles upstream of the reactor; it presents high processing rates and requires low residence times and a small footprint area for installation (Carissimi & Rubio 2005b). Aerated flocs are structures composed of flocs and bubbles which are fairly light and rapidly rise in flotation systems (Carissimi & Rubio 2005b; Da Rosa & Rubio 2005; Rodrigues & Rubio 2007; Oliveira & Rubio 2012). Another important feature of these structures is the high shear resistance during turbulent conditions. It is believed that NBs generated at a high rate by the CMP may play an important role in aerated floc resistance due to capillary forces inside these structures.

Column flotation technologies appear as alternatives for high rate DAF utilities in offshore platforms. Zaneti et al. (2011, 2012) studied flocculation–column F-MP for the treatment and reuse of vehicle wash wastewater (high suspended solids concentrations) and reported the use of HL higher than 20 m h⁻¹. The main advantages of column flotation for wastewater treatment are its high throughput and flux pattern (plug flow), which allows better contact between bubbles and particles and requires lower residence times, leading to higher HL (Rubio & Zaneti 2009).

Filippov et al. (2000) reported that by increasing the relation of height/diameter of the column in precipitate flotation, the turbulence caused by liquid flow and bubble rising movement may be reduced, thereby improving flotation efficiency.

In this work, MBs and NBs were generated by a CMP feed column with bubbles for oil removal in a semi-continuous pilot rig. This process utilized flocculation in an FGR and column flotation for the separation of the oily flocs. The objectives of the study were to evaluate the generation of bubbles in a multiphase pump and the influence of operating parameters (reagent concentration, column height and HL) on oil removal efficiency.

**EXPERIMENTAL**

**Materials**

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

For the generation of the oil-in-water emulsion, tap water and industrial salt (iodine-free NaCl, Mossoró®, Brazil) were employed.

A commercial cationic polyacrylamide (Dismulgan V3377, Clariant®) was employed for oil emulsion destabilization and Table 1 | Crude oil physicochemical and interfacial properties

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, 25 °C (g mL⁻¹)</td>
<td>0.88</td>
</tr>
<tr>
<td>API Grade (°API)</td>
<td>23</td>
</tr>
<tr>
<td>Viscosity, 25 °C (cP)</td>
<td>42</td>
</tr>
<tr>
<td>Superficial tension (oil/water), 25 °C (mN m⁻¹)</td>
<td>28</td>
</tr>
</tbody>
</table>
flocculation after adjusting medium pH to 7 with a solution of NaOH 1% w/w (Vetec®, Brazil).

Oil concentration analyses were performed by spectrometry using a Horiba OCMA-350 device. Tetrachloroethylene (C₂Cl₄, Sigma Aldrich®) was used for the extraction of the oil from the samples and hydrochloric acid (HCl 5% v/v, Dinâmica Química®) was used for pH adjustment. Anhydrous sodium sulfate (Na₂(SO)₄; Sigma Aldrich) was employed to remove residual humidity from the organic phase.

Methods

Oil-in-water emulsion generation system

The oily emulsion generation system (Figure 1) was composed of: (i) a tap water feed tank; (ii) a helical high-pressure pump (Netzsch, NEMO®); (iii) a dosing piston pump (OMEL® DMP-02) for inline oil injection; (iv) a flow constrictor (needle valve) with manometers upstream and downstream of the pipe; and (v) an oily emulsion storage tank (1 m³) with a centrifugal pump for mixing the salt (Schneider® BCR 2000).

The process consisted of the injection of crude oil at high pressure through the depressurizing needle valve, followed by a pressure drop (12 bar) and high shear caused by the passage of the oily water mixture through the flow constrictor. This procedure allowed the formation of a stable oily emulsion with oil contents ranging from 60 to 450 mg L⁻¹. According to Santander et al. (2021) the oil droplet volumetric mean diameter (D₃₂) is inversely proportional to the pressure drop, and the application of 12 bar resulted in oil droplets with a D₃₂ of 10–15 μm. NaCl (50 to 100 g L⁻¹) was added into the oil wastewater storage tank and dissolved by recirculation with a centrifugal pump.

Feed oil concentrations (<200 mg L⁻¹) were obtained by diluting the oily emulsion with tap water (1:1).

Bubble generation

The bubble generation unit consisted of a CMP (Schneider ME-1315 or ME-1420), operating with a pressure of 4 bar and liquid flow varying between 1 and 3 m³ h⁻¹. The injection (air/liquid ratio 7.5%) was controlled by an air rotamer (ASA®) positioned in the suction line of the CMP, with a vacuum meter gauge (Fabre Primar®). A PVC pressure vessel (external diameter = 110 mm, height = 0.95 m), with a pressure gauge (NuovaFima®) was employed to relieve the excess air and increase the air in water saturation and dissolution time to about 27 s. A needle-type valve was used as a flow constrictor for hydrodynamic cavitation and the formation of MBs (5–80 μm) and NBs (50–300 nm). The liquid flow was measured by a liquid rotamer (AppliTech®) positioned downstream of the pressure vessel.

Flocculation

The flocculation unit was composed of two FGRs (details in Table 2) that use the kinetic energy of the liquid flow along the helical tubular reactors. The system was composed of a rapid mixing stage (low residence time and high velocity gradient – G) for dispersion of the flocculant.
and NaOH, and a slow mixing stage (high residence time and reduced $G$) for the formation of stable flocs.

Bubbles generated upstream of the reactor adhere to and entrap aggregates, forming large aerated flocs with low density. These flocs floated very rapidly (high flotation kinetics), similar to the results published by Oliveira & Rubio (2012). The head loss in the system was measured by manometers which were positioned in the inlet and outlet of the reactor.

Reactants (floculation polymer and NaOH) were injected by two diaphragm-dosing pumps (EXATTA) located downstream of bubble injection.

The effect of the floculation reagent (Dismulgan V3377) on oil removal by flotation was studied in the range of 5–30 mg L$^{-1}$ in duplicate tests.

### Flotation

The flotation column had a variable height (1.5 and 2.5 m) and a square section with 33 cm edges (Table 2). The treated water outlet was positioned in the lower third part of the column, and the sludge removed from the top of the column was disposed of in a drying bed that consisted of alternating layers of gravel, and coarse and fine sands amounting to 0.5 m$^3$ total volume.

Schematic images of the oily emulsion treatment system by floculation–column flotation with CMP are shown in Figures 2 and 3.

The results were analyzed in terms of oil removal efficiency ($\%$), calculated according to Equation (1).

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

where $C_f$ is the final oil concentration and $C_0$ is the initial oil concentration.

The effect of the HL on oil removal by flotation was studied varying the feed liquid flow (1–3 m$^3$ h$^{-1}$), with HL values in the range of 10–27.5 m$^3$ h$^{-1}$.

### Table 2 | Design and operation parameters of the floculation–flotation units for oily water treatment

<table>
<thead>
<tr>
<th>Flocculation unit</th>
<th>Rapid mixing</th>
<th></th>
<th>Slow mixing</th>
<th></th>
<th>Flotation unit</th>
<th>Column</th>
<th></th>
<th>CMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (m)</td>
<td>6</td>
<td></td>
<td>24</td>
<td></td>
<td>Height (m)</td>
<td>1.5–2.5</td>
<td></td>
<td>Air/liquid ratio</td>
</tr>
<tr>
<td>Inner diameter (m)</td>
<td>0.011</td>
<td></td>
<td>0.035</td>
<td></td>
<td>Edges (m)</td>
<td>0.33</td>
<td></td>
<td>7.5%</td>
</tr>
<tr>
<td>Volume (m$^3$)</td>
<td>0.0006</td>
<td></td>
<td>0.023</td>
<td></td>
<td>Inner area (m$^2$)</td>
<td>0.11</td>
<td></td>
<td>Operating pressure (bar)</td>
</tr>
<tr>
<td>Residence time (min)</td>
<td>0.03–0.01</td>
<td></td>
<td>1.4–0.47</td>
<td></td>
<td>Volume (m$^3$)</td>
<td>0.16–0.27</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>$G^2$ (s$^{-1}$)</td>
<td>663–2300</td>
<td></td>
<td>30–102</td>
<td></td>
<td>Residence time (min)</td>
<td>16–5.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The residence times and $G$ were calculated for the flows of 1 and 3 m$^3$ hour$^{-1}$, respectively.

*Mixture $G$ was calculated by the following equation (Tchobanoglous et al. 2003): $G = \sqrt{\gamma HF/\mu}$, where $G$ – velocity gradient (s$^{-1}$); $\gamma$ – specific weight of liquid mass (kgf m$^{-3}$); $H$ – head loss (m); $\mu$ – absolute viscosity of liquid mass (N s m$^{-1}$); $t$ – residence time (s).

Figure 2 | Oily emulsion treatment system by floculation–column flotation. (1) Oily emulsion storage tank; (2) air injection; (3) CMP; (4) flow-meter; (5) manometer; (6) pressure vessel; (7) needle valve; (8) manometer; (9) chemicals (floculation polymer and NaOH) tanks; (10) dosing pumps; (11) rapid mixing FGR; (12) slow mixing FGR; (13) sampling point; (14) flotation column; (15) treated water outlet; (16) sludge outlet.
RESULTS AND DISCUSSION

Effect of the flocculant concentration

Figure 4 shows the effect of the Dismulgan concentration on oil removal and turbidity reduction efficiencies, using a flotation column 1.5 m in height. Best results were obtained with a flocculant concentration of 20 mg L\(^{-1}\), wherein the mean residual turbidity and oil concentration were 17 NTU and 20 mg L\(^{-1}\), respectively.

These results are similar to those obtained by Santander et al. (2011), in our research group, who flocculated the crude oil emulsion (oil feed <200 mg L\(^{-1}\)) with 10 mg L\(^{-1}\) of Dismulgan and 3 mg L\(^{-1}\) of a non-ionic polymer (polyvinyl acetate) as flocculants. In that work, the flocs were then removed from water by a modified ‘jet’ flotation process at a high HL (24.7 m h\(^{-1}\)), resulting in residual oil contents between 20 and 30 mg L\(^{-1}\) in the treated water.

Effect of flotation column height

Figure 5 shows the results obtained with different flotation column heights. Increasing from 1.5 m to 2.5 m resulted in higher oil removal efficiency at the same process conditions. This effect proved to be more relevant in the treatment of oily emulsions with higher initial oil feed (above 200 mg L\(^{-1}\)), where the mean residual oil concentrations were reduced from 17 mg L\(^{-1}\) to 4 mg L\(^{-1}\), comparing the two column heights at an HL of 10 m h\(^{-1}\).

Similar results were obtained by Da Rosa (2002) for emulsified crude oil removal in flotation columns; higher oil separation efficiency was obtained with taller columns. The author explains the results in terms of less overflow of the oily flocs towards the treated water outlet, located in the bottom of the 4.2 m high column.

Filippov et al. (2000) showed that the limiting factor for metal-organic precipitate flotation in a column is the level of aggregate stability under the turbulence created by the rising bubbles. The hydrodynamic conditions in a 75 mm diameter pilot column were optimized by using different bubble spargers to control the air hold-up, the gas flow rate and the feed flow rate in the column. This led to less turbulence and less entrainment of the floating particles. In a tall flotation column, this aggregate breakage under turbulence would certainly be reduced compared to a short cell.

These results can also be related to studies on column flotation for ore beneficiation. Yianatos et al. (1988) observed an improvement in mineral recovery efficiency by increasing the column height/diameter (H/D), due to the longer fluid and particle residence time in the system, which provides a higher probability of collision, adhesion and flotation of particle–bubble aggregates.
In this work, with respect to cell design, if the H/D relation increased from 4 to 6.7 for the taller column, better oil removal efficiencies were obtained.

Therefore, results obtained in this work appear to indicate that increasing the distance between the floated sludge collection zone and the outlet of treated water is responsible for the improvement in the efficiency of oil–water separation, due to reduced drag of flocs.

Table 3 presents the oil concentration and turbidity values of the emulsion and the treated effluent, obtained in each experiment assayed, with a 2.5 m column height and an HL of 10 m h\(^{-1}\). Additional experiments with higher NaCl concentrations (100 g L\(^{-1}\)) were conducted. Excellent separation was obtained, attaining oil contents of 1 mg L\(^{-1}\) in the treated water (>99% efficiency). Residual turbidity may be related to the salinity that ranged from 30 to 100 g L\(^{-1}\).

**Effect of hydraulic loading**

Figure 6 shows the results for the different HLs studied. Discharge limits of these substances in PW emanating from offshore petroleum plants are usually regulated at a monthly average of 29–34 mg L\(^{-1}\) with a daily maximum of 39–42 mg L\(^{-1}\) (Rawlins 2009). Oil and gas production plants in the northeast Atlantic are required to meet the 30 mg L\(^{-1}\) oil and grease discharge standards set by the OSPAR convention (Atarah 2011). Herein, residual oil concentration values obtained were below the emission standards set by the US EPA for oil and gas extraction (monthly average = 29 mg L\(^{-1}\)) (EPA 1979) with all the HLs lower than 27.5 m h\(^{-1}\).

At HL lower than 18 m h\(^{-1}\), the treated effluent reached a residual oil content less than 10 mg L\(^{-1}\). Filippov et al. (2000) evaluated the influence of hydrodynamic conditions on the stability of colloidal precipitate flotation in the process of column flotation (diameter = 75 mm). It was found that with high HL, the breakage of the precipitates by shearing forces may occur. Yet, the author showed that, by decreasing the residence time by increasing the superficial velocity of the liquid, these flocs (broken) are more easily drawn, decreasing the efficiency of solid/liquid separation. These effects may be related to the flotation of oily flocs, explaining the decrease in separation efficiency at high HL. The good results obtained with high HL on oil removal appear to be due to the high flotation kinetics and the shear resistance of the aerated oily flocs formed in the flocculation step.

The FGR presented head-loss (Hf) values from 0.9 to 3.5 kgf cm\(^{-2}\), measured from the pressure difference on gauges positioned upstream and downstream of the reactor. Da Rosa & Rubio (2005) evaluated different hydraulic flocculators in oil emulsion treatment by flocculation–flotation and found that the results obtained do not depend on the geometrics of the reactor, but on the Hf provided in the system, obtaining lower oil concentrations in the treated water (10–15 mg L\(^{-1}\)) when the Hf reached values between 0.5 and 1.0 kgf cm\(^{-2}\). For higher values of Hf, the oil concentration has not decreased significantly.

**FINAL REMARKS**

The flotation process has been used for many years in the treatment of oily liquid effluents (removal of oil and water...
reuse). In these applications, the reported size and size distribution of bubbles have been 40–100 μm. Yet, the contribution of NBs has been ignored and unknown (until recently) to most engineers, researchers and flotation professionals, due to the absence and/or lack of knowledge of analytical techniques capable of characterizing and identifying NBs.

Thus, by taking advantage of the upcoming nanotechnology and the development of more advanced particle/bubble analysis techniques, our research group was able to evaluate the generation of NBs and understand some properties that improve flotation efficiency, notably, the discovery that hydrodynamic cavitation using CMPs generates a high concentration of these NBs (Azevedo et al. 2017; Etchepare et al. 2017c).

This flocculation-column flotation process, using RGF for aerated floc formation and CMP for MBs and NBs generation, appears to present a great potential for oily wastewater treatment. Future applications for pollutant removal at high rates may be possible where small areas are required for equipment installation, namely, for industrial emulsified oils such as petroleum PWs from offshore platforms.

The advantages of this proposed process are:

i. efficient generation of bubbles with wide size distributions and a high concentration – MBs with a size distribution of 5–80 μm and air hold-up in the range of 5–6%, and NBs sizing between 50 and 300 nm and a concentration of about 10^9 NBs mL^-1 (Etchepare 2016; Etchepare et al. 2017c);

ii. continuous generation of oil–bubble clusters (aerated flocs) in the FGR;

iii. a highly efficient separation process with high rates, obtaining low oil contents in the treated water;

iv. small footprint area for equipment installation.

Regarding mechanisms involved, it is believed that NBs entrapped into flocs exert a strong bridging force, assisting oil droplet entrapment allowing the action of hydrophobic forces. These structures have a strong shear resistance and low density, avoiding the breakage and dragging the oil towards the treated water outlet.

CONCLUSIONS

Excellent results removing emulsified crude oil to levels below EPA standard emissions for offshore disposal (29 mg L^-1) were obtained at pilot scale, at high HL (27.5 m h^-1) by flocculation–column flotation with MBs and NBs. The bubbles were generated by a novel hydrodynamic cavitation method using a CMP, and flocculation was conducted in an FGR. Two sizes of column flotation units were employed (1.5, 2.5 m tall). Best results (high oil removal and low residual oil content in the treated water) were attained at an HL of 10 m h^-1 with a flotation column 2.5 m in height, yielding treated water with an oil content <5 mg L^-1. Results validated the role of the NBs assisting the separation process and maximizing the plant treatment capacity. Further advantages are the low footprint required and the high efficiency of the pumps generating the NBs (4 × 10^9 NB mL^-1; D32 = 150–300 nm). The whole process appears to have great potential in the treatment of oily wastewaters.

ACKNOWLEDGEMENTS

The authors would like to thank Alberto Pasqualini refinery (REFAP/Petrobras) and Hidrocicle for partnership in this study, and all Brazilian research institutions: CNPq, Fapergs, UFRGS. Special thanks to all the students at our laboratory, especially Alex Rodrigues, Luciana Kaori, Luisa Neves and to Marcelo Ferrmann and Rafael Zaneti (Hidrocicle) for their technical support.

REFERENCES


EPA 1979 *EPA Effluent Guideline for Oil and Gas Extraction* (CGR 40.455). US Environmental Protection Agency, USA.


First received 5 May 2017; accepted in revised form 18 July 2017. Available online 1 August 2017