Journal of Environmental Management 147 (2015) 257–263

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Oil removal from produced water by conjugation of flotation and photo-Fenton processes

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ARTICLE INFO

Article history:
Received 5 November 2013
Received in revised form
5 June 2014
Accepted 27 August 2014
Available online 17 September 2014

Keywords:
Oilfield
Produced water
Flotation
Photo-Fenton
Integration

ABSTRACT

The present work investigates the conjugation of flotation and photo-Fenton techniques on oil removal performance from oilfield produced water. The experiments were conducted in a column flotation and annular lamp reactor for induced air flotation and photodegradation steps, respectively. A nonionic surfactant was used as a flotation agent. The flotation experimental data were analyzed in terms of a first-order kinetic rate model. Two experimental designs were employed to evaluate the oil removal efficiency: fractional experimental design and central composite rotational design (CCRD). Overall oil removal of 99% was reached in the optimum experimental condition after 10 min of flotation followed by 45 min of photo-Fenton. The results of the conjugation of induced air flotation and photo-Fenton processes allowed meeting the wastewater limits established by the legislations for disposal.

1. Introduction

Throughout the productive life of an oil field, the simultaneous production of gas, oil and water generally occurs. However, the economic interest is focused on the production of hydrocarbons (oil and gas), thus requiring the separation of these three fluids. The treatment of produced water (aqueous stream) aims to recover the dispersed oil and frame the final effluent for the purpose of reuse or disposal. In Brazil (CONAMA) and USA (USEPA), the maximum concentration of the total of oils and grease (TOG) in effluent disposal in the seabed is 29 ppm.

Several methods are applied to TOG reduction in aqueous effluents, such as liquid–liquid extraction (Moraes et al., 2011), hydrocyclones (Amini et al., 2012), flotation (Santo et al., 2012) and biological treatment (Lu et al., 2009). Among these methods, flotation is widely used because of its high rate of separation in short residence times and low operating cost (Watcharasing et al., 2008; Rattanapan et al., 2011; Le et al., 2013). This unit operation is based on differences in hydrophobicity among substances to be separated (Ding, 2010) and consists of the following steps (El-Kayar et al., 1993): (1) generation of bubbles, (2) contact between generated bubble and dispersed droplet, (3) formation of an aggregate bubble-droplet, (4) aggregate transportation.

The probability of flotation is defined as the product of the collision probabilities, adhesion and transport (Yoon, 2000). Eq. (1) shows that the probability of collision between the oil droplet and the air bubble is lower for small drops of oil.

$$P_C \alpha \left(\frac{D_g}{D_b}\right)^2 \tag{1}$$

where D_g and D_b are the diameters of the droplet and the bubble, respectively. This limitation is important in the treatment of produced water, where the oil could be present in four phases: free oil (droplets of oil >150 μm), dispersed oil (droplets of oil >50 μm), emulsified oil (droplets of oil <50 μm) and dissolved oil (Santander et al., 2011). Moreover, degradation of organic compounds present in effluents by Advanced Oxidation Processes (AOPs) has shown high efficiency even when they are present at low concentrations (Philippopoulos and Poulopoulos, 2003; Masomboon et al., 2010; Paz et al., 2013). Among AOPs, photo-Fenton is one of the most widely used techniques (Moraes et al., 2004a, 2004b; Nogueira et al., 2008; Sakkas et al., 2010; Nagarnaik and Boulanger, 2011). This process can be divided into three major steps (Krutzler and Bauer, 1999) (Eqs. (2)–(5)): (1) generation of hydroxyl radicals (•OH); (2) regeneration of ferrous ions by the action of light, (3)

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http://dx.doi.org/10.1016/j.jenvman.2014.08.021
0301-4797/

oxidation of the organic matter by hydroxyl radicals present in the reaction medium.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} \quad (2)$$

$$[Fe\ (OH)]^{2+} \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet} \quad (3)$$

$$[Fe\ (COOCR)]^{2+} \xrightarrow{h\nu} Fe^{2+} + CO_2 + R^{\bullet} \quad (4)$$

$$HO^{\bullet} + RH \rightarrow \text{oxidation products} \rightarrow CO_2 + H_2O \quad (5)$$

Thus, a photodegradation step subsequent to the flotation process can improve oil removal efficiency in the effluent. Recently, some researchers have suggested the application of integrated processes as being the most appropriate solution for the treatment of various industrial effluents (Zak, 2009; Sena et al., 2009; Silva et al., 2012). Induced air flotation and photo-Fenton processes were integrated to the treatment of residual waters contaminated with xylene, resulting 100% of organic load removal in 20 min (Silva et al., 2012). Significant removal levels of chemical oxygen demand (COD) in treatment of oilfield wastewater containing polymers were obtained using the combination of the advanced oxidation by zerovalent iron/EDTA/air system followed by biodegradation process (Lu and Wei, 2011). Treatment of tannery industrial effluent by integrating the photo-Fenton and electrocoagulation processes resulted in an appreciable improvement in the results of COD removal when compared with the conventional process using a combination of filtration, chemical coagulation and sedimentation (Módenes et al., 2012). The integration of photocatalytic methods with a reverse osmosis unit can lead to complete decolorization of synthetic dye stuff effluent, as well as to a more than 95% reduction of the initial organic content (Berberidou et al., 2009). Oilfield wastewater treatment by combined microfiltration and biological processes may also result in a significant improvement in the effluent quality (Campos et al., 2002). Therefore, different combinations of processes can be applied for removing the several types of contaminants. Herein, the treatment of wastewater containing a real crude oil sample from Potiguar Basin (Natal, Brazil) was investigated with a conjugation of flotation and photochemical processes.

In this context, the aim of this study was to evaluate the integration of induced air flotation (IAF) and photo-Fenton processes for reducing the oil from oilfield produced water. From this integration, the aim was to recover the maximum amount of oil by flotation, and then degrade the remaining oil fraction in the aqueous phase by the photo-Fenton process.

2. Materials and experimental methodology

2.1. Crude oil

This study used a real crude oil sample from Potiguar Basin (Natal, Brazil). The oil was free of dissolved gas and water and its properties are summarized in Table 1.

Table 1
Physical–chemical properties of crude oil.

Physical–chemical property	Value
Density at 25 °C (g mL^{-1})	0.88
API gravity (°API)[a]	27
Viscosity (cP)	65.00
Superficial tension (mN m^{-1})	29.95
Interfacial tension (water/oil) (mN m^{-1})	10.98

[a] Calculated according to the relation °API $= \left(\frac{141.5}{d_{60\ ^\circ F}}\right) - 131{,}5$, where d is the relative density.

2.2. Materials

A surfactant ethoxylated derived from fatty alcohol used as a flotation agent was supplied by Oxiteno®. Hydrophile-lipophile balance (HLB) and molecular mass of surfactant are 6.3 and 274 g mol^{-1}, respectively. The other used reagents were supplied by VETEC: sodium nitrate ($NaNO_3$), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), potassium chloride (KCl), aluminum chloride ($AlCl_3$), magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$), ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), hydrogen peroxide (H_2O_2, 30%) e chloroform ($CHCl_3$).

Experiments were carried out using effluent prepared carefully from the dispersion of real crude oil in a saline aqueous solution containing: 17 ppm ($NaNO_3$), 4229 ppm (NaCl), 204 ppm (Na_2SO_4), 1497 ppm (KCl), 2.35 ppm ($AlCl_3$), 1506 ppm ($MgCl_2$) and 4875 ppm ($CaCl_2$). The selection and concentration of these salts was established from the average values found in the literature for oilfield produced water (USEPA, 2000; Campos et al., 2002; Ahmadun et al., 2009; Dong et al., 2011; Yeung et al., 2011; You and Wang, 2011). This effluent was stirred for 25 min at 33,000 rpm and then kept at rest for 50 min to allow free oil separation. Initial oil concentration in the effluent was 300 ppm and 35 ppm for the stages of flotation and photo-Fenton, respectively. These initial values of oil concentration were established on the basis of the average TOG of the effluents in the primary processing units of Potiguar basin, Brazil.

The determination of the TOG in aqueous samples was performed by liquid–liquid extraction, using chloroform as a solvent, followed by the measurement of the extract in molecular absorption spectrum, at $\lambda = 262$ nm (Varian, Cary 50) (Lima et al., 2008). The efficiency of each individual step (η) was expressed in terms of TOG removal (Eq. (6)), where TOG_o and TOG_t are the initial concentrations of oil and grease at $t = 0$ and time t, respectively. The measurements of oil/water interfacial tension were carried out by the drop method (tensiometer, 100 DAS).

$$\eta(\%) = \left(1 - \frac{TOG_t}{TOG_o} \times 100\right) \quad (6)$$

2.3. Experimental procedure of induced air flotation (IAF)

Flotation experiments were carried out in the flotation column using induced air aeration as a system for generating bubbles. Schematic diagram of column is shown in a previous work (Silva et al., 2012). Diffused air aeration was used, where the compressed air stream passed through a porous plate filter (16–40 μm) to form bubbles. The column with a capacity of 0.9 L has the following dimensions: 0.80 m (height), 0.040 m (inner diameter) and 0.042 m (external diameter). The initial pH (7.0) and the air flow (3.209 cm^3 m in^{-1}) values were kept constant for all the experiments. The addition of surfactant to the effluent was performed immediately before the beginning of the flotation step. At predetermined times (practically at each 2 min), samples were collected from the center of the column in order to determine the TOG value.

2.4. Photo-Fenton experimental procedure

The experiments were carried out in an annular reactor with a capacity of 0.6 L. A mercury vapor lamp was used as source of radiation (high pressure 400 W, FLZ) and located on the longitudinal