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Research article

Electrocoagulation with polarity switch for fast oil removal from oil in water emulsions

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ABSTRACT

An electrocoagulation technique using a 3.5 L reactor, with aluminum electrodes in a monopolar arrangement with polarity switch at each 10 s was used to separate oil from synthetic oily water similar in oil concentration to produced water from offshore platforms. Up to 98% of oil removal was achieved after 20 min of processing. Processing time dependence of the oil removal and pH was measured and successfully adjusted to exponential models, indicating a pseudo first order behavior. Statistical analysis was used to prove that electrical conductivity and total solids depend significantly on the concentration of electrolyte (NaCl) in the medium. Oil removal depends mostly on the distance between the electrodes but is proportional to electrolyte concentration when initial pH is 8. Electrocoagulation with polarity switch maximizes the lifetime of the electrodes. The process reduced oil concentration to a value below that stipulated by law, proving it can be an efficient technology to minimize the offshore drilling impact in the environment.

1. Introduction

Cleaning water using cheaper and less material consuming processes is one of the leading challenges of the 21st century (Mollah et al., 2004). In particular, in the oil industry, during the exploration, drilling and production activities, the produced water (PW) responds by 98% of all generated effluents (Thomas, 2001).

PW comes together with the hydrocarbons and from rock cuttings from drilling. It is a severe environmental problem, especially in offshore drillings and a source of costs since regulations put strict limits on levels of contaminants which can be discharged to the environment (Bakke et al., 2013).

PW is usually in the form of a secondary oil-in-water emulsion (Shin and Kim, 2001a). Due to the presence of surfactants, and cosurfactants, the secondary emulsions are very stable, and the emulsified oil droplets are of the order of few micrometers in diameter. This stability arises from the formation of interfacial films encapsulating the oil droplets. Thus, the electrostatic repulsion forces make the separation by conventional methods difficult (Tir and Moulai-Mostefa, 2008).

Electrocoagulation (EC) have attracted interest because it is simple to mount and operate, low capital and operating cost, demand less space than most techniques, does not demand an injection of chemical coagulants and generates less sludge without compromising the quality of the treated water (Moussa et al., 2017a).

EC is a simple process that uses electrical current supplied by a DC voltage applied to the electrodes located inside the electrochemical

Abbreviations: PW, produced water; SPW, Synthetic Produced Water; EC, Electrocoagulation; SC, salt concentration; DE, distance between electrodes; ElC, electrical conductivity; TS, total solids content; OR%, percent of oil removed.

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reactor. The electrodes are usually made of iron or aluminum since these materials are inexpensive, efficient and readily available on the market.

When subjected to electrical charge and immersed in solution the anode suffers oxidation and releases highly charged polymeric metal hydroxide species that destabilize the colloidal particles in the solution (El-Naas et al., 2009). Such destabilization occurs due to charge balancing of the surfaces and leads to particle aggregation and precipitation (Krystynik and Tito, 2017).

The coagulation of dissolved organic matter by the addition of hydrolyzing metal salts to the waste is a well-known process. It has two mechanisms: a) binding of metal species to the organic molecules, neutralizing their charge and reducing solubility; b) adsorption of the organic material on amorphous metal hydroxide precipitates (Pablo Cañizares et al., 2006).

The theories behind EC and coagulation/flocculation are very similar, and they can have the same efficiency if the conditions are right (Cañizares et al., 2009). Nonetheless, Rincón and La Motta (Rincón and La Motta, 2014) broke oil in water emulsions using EC while conventional coagulation/flocculation using aluminum sulfate failed.

In EC the coagulants are generated *in situ* by the electrolytic oxidation of an appropriate anode material which results in much less sludge generation. Also, the presence of electrical current can contribute to the coalescence of water droplets, increasing the potential application of this technique in oily water treatment (Moussa et al., 2017a).

The EC process can be described as (1) electrolytic oxidation of the anode, formation of coagulants, (2) destabilization of the contaminants, particle suspensions and breaking of emulsions (3) aggregation of the formed phases to form flocs (Mollah et al., 2004).

After coagulation, the material can either float or precipitate, depending on their density and the presence of bubbles or dissolved gas. Hydrogen gas is generated by the cathode (reduction) and helps to float the flocculated particles to the water surface (Moreno-Casillas et al., 2007).

The generation of O_2 and H_2 bubbles due to the reduction of water on the electrode surfaces is one of the advantages of EC (Cañizares et al., 2007). These bubbles promote the coalescence process and the separation of the coalesced droplets. They can float the coalesced pollutant to the top of the solution where it can be more easily concentrated and removed (Fouad, 2014).

Despite the name, electrocoagulation, adopted for this system, flotation by the hydrogen bubbles is often an important component in this technology (Rincón and La Motta, 2014). The combination of EC and electroflotation increases the effectiveness of the process.

Demirci and co-workers (Demirci et al., 2015) tested three configurations of electrodes for the treatment of real textile wastewater: monopolar-parallel, monopolar-serial and bipolar-parallel. The monopolar configuration with cells in parallel was proven to be the most cost-effective.

The monopolar arrangement is also preferred at industrial scale since it allows for a better control of anode consumption and its periodic replacement (Bocos et al., 2016). In this arrangement, the same electrical current passes between each cathode/anode pair (Jiang et al., 2002), allowing current density to be better-controlled through the DC power supply.

Although EC has been used both in laboratory and industry for over a century, there is little in the way of systematic reactor design rules, and almost nothing in the way of a generic *a priori* approach (Moreno-Casillas et al., 2007).

In the present study mathematical models and statistical analysis were used to describe the EC process to separate oil from oil in water (OW) emulsions. A combination of parameters that are not very common in the literature was used, a volume higher than usual for laboratory experiments (3.5 L), a monopolar arrangement of three pairs of aluminum electrodes and polarity switch to preserve the electrodes and increase efficiency.

Following the need for a systematic approach, care was taken to contribute with models and equations relating the input variables: distance between electrodes (DE), salt concentration (SC) and initial pH to the efficiency in oil removal and its variation with time.

Aluminum electrodes were used due to their proven effectiveness in oil in water removal (Emamjomeh and Sivakumar, 2009).

The pH was chosen as an input variable since the solubility of the metal hydroxide complexes formed during EC depends on it (Tezcan Un et al., 2009). Other variables that control the coagulant are electrical current density and temperature. Current density increases the amount of coagulant liberated by the electrode while temperature increases aluminum solubility (El-Naas et al., 2009). Both these variables were kept constant with current density at the higher value possible for the system and temperature kept around 293 K (room temperature).

NaCl was chosen as an electrolyte since the objective was to simulate production water as closely as possible, but it has other advantages. Oil usually has sulfates that will inhibit the oxidation of the electrodes, reducing EC efficiency. The presence of chloride ions reduces the adverse effect of sulfates. Other electrolytes lack this advantage and also may add to the pollutants to be removed in a later step of purification (Moussa et al., 2017b).

2. Materials and methods

2.1. Preparation of synthetic produced water

To prepare 3.5 L of synthetic oily water (SPW), 0.7000 g of crude oil, 0.0700 g of commercial emulsifier Emustab® and salinized with sodium chloride (10 and 14 gL^{-1}). To obtain SPW all components placed in a glass beaker and mixed at 9500 rpm using a rotor-stator mixing device (T18 basic Ultra Turrax model) for 21 min.

According to Motta and co-workers (Motta et al., 2013), oil concentration in PW is in the range of 2–565 mgL^{-1}. All experiments were done maintaining a concentration of 200 mgL^{-1} of crude oil in salted water, close to the center of the concentration range for PW. This methodology to produce SPW was based on Cerqueira and co-workers (Cerqueira et al., 2011). Some of the characteristics of the crude oil used are listed in Table 1.

2.2. Electrocoagulation system

A pilot unit consisting of an electrolytic cell, a set of aluminum electrodes, a polarity inverter and a DC power source was used for electrocoagulation. The electrolytic cell was made of cylindrical recipient made of plexiglass with two taps to collect samples. These taps were positioned at 7 and 14 cm from the bottom. In the top was a lid made of PVC containing two breathers and two orifices for the passage of electrical wiring. The experiments were carried out using 3.5 L of synthetic oily water.

The aluminum electrodes were mounted vertically forming two

Table 1
Characterization of the crude oil used.

Parameter	Value
API Gravity	35.2
Density at 20 °C (gcm^{-2})	0.8450
Salinity ($mg.L^{-1}$ NaCl)	223 ± 6
Viscosity at 20 °C (mm^2s^{-1})	11.52 ± 0.01
Viscosity at 30 °C (mm^2s^{-1})	7.95 ± 0.02
Sulfur content (% mm^{-1})	0.16672 ± 0.00009