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Removal of oil from oil-in-saltwater emulsions by adsorption onto nano-alumina functionalized with petroleum vacuum residue

Camilo A. Franco [a], Nashaat N. Nassar [b,*], Farid B. Cortés [a,*]

[a] Grupo de Investigación en Yacimientos de Hidrocarburos, Facultad de Minas, Universidad Nacional de Colombia Sede Medellín, Kra 80 No. 65-223, Medellín, Colombia
[b] Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada

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ABSTRACT

Formation water from oilfields is one of the major environmental issues related to the oil industry. This research investigated oil adsorption onto nanoparticles of hydrophobic alumina and alumina nanoparticles functionalized with a petroleum vacuum residue (VR) at 2 and 4 wt% to reduce the amount of oil in oil–saltwater emulsions at different pH values (5, 7 and 9). The initial concentration of crude oil in water ranged from 100 to 500 mg/L. The change in oil concentration after adsorption was determined using a UV–vis spectrophotometer. The results indicated that all of the systems performed more effectively at a pH of 7 and using Al/4VR material. The oil adsorption was higher for neutral and acid systems compared with basic ones, and it was improved by increasing the amount of VR on the surface of the alumina. Additionally, the amount of NaCl adsorbed onto nanoparticles was estimated for different mixtures. The adsorption equilibrium and kinetics were evaluated using the Dubinin–Astakhov model, the Brunauer–Emmet–Teller model, and pseudo-first- and pseudo-second-order models, with a better fitting to the Brunauer–Emmet–Teller model and pseudo-second-order model.

1. Introduction

The demand for energy is increasing rapidly worldwide, and consequently, oil production from conventional and unconventional resources is growing. Accordingly, significant amounts of produced brine waters are generated during the exploitation and production processes [1]. Typically, these wastewaters are discharged back into the spent reservoir or into water bodies or tailing ponds [2,3]. Further, these wastewaters contain an appreciable amount of free oil and emulsified hydrocarbons, which contain many toxicity/phytotoxicity-associated compounds [1,4,5]. Accordingly, the effects of discharging produced water into the environment have recently become a significant environmental concern [1]. Therefore, to meet environmental regulations and to promote the reuse and recycling of produced water, many scientific researchers and decision makers have focused their attention on treating oily, saline produced water [6]. A number of conventional treatment methods to handle such effluent streams have been reported, including reinjecting produced water into spent oil wells, directly discharging it and reusing it in applications such as thermal loops [7]. Of these methods, the reinjection technique is the most efficient way of handling produced water. However, the disposal costs, which include transportation costs, capital costs and infrastructure maintenance costs, may be as much as $4.00 per barrel of water [7]. In addition, the disposal of produced water that contains toxicity-associated compounds may impact underground water. Therefore, the treatment of these effluents may improve oil/water separation, oil recovery, water quality and water reuse while protecting downstream facilities and enhancing environmental permit compliance [8]. Various methods have been reported for removing oil from oil in water (o/w) emulsions, including adsorption [7], filtration [9,10], reverse osmosis [11], biological processes [10], air flotation [12,13], membrane bioreactors [14], chemical coagulation, electrocoagulation and electroflotation [15]. Among these methods, adsorption is the most commonly used method for produced water treatment due to its simplicity and cost effectiveness [4,8]. Typical adsorbents used in the treatment of produced water are activated carbon, organoclay, copolymers, zeolite and resins [4,5]. The combination of activated carbon and organoclays has proven to be efficient in removing total petroleum hydrocarbons (TPH) [4]. Copolymers reduced the oil content by up to 85% [7]. However, these types of adsorbents do not effectively remove oil at small droplet scales (stable o/w emulsions) and are therefore not efficient in meeting environmental regulations

* Corresponding authors. Address: 2500 University Drive NW, Calgary, Alberta, Canada (N.N. Nassar). Address: Kra 80 N. 65-223, M3-100A, Colombia. Fax: +57 4 2341002 (F.B. Cortés).
E-mail addresses: nassar@ucalgary.ca (N.N. Nassar), fbcortes@unal.edu.co (F.B. Cortés).

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[8]. Thus, the identification of alternative adsorbents or the improvement of available adsorbents is of paramount importance. Many researchers have dedicated themselves to the study and development of advanced adsorbent materials that provide high sorption capacity and affinity, efficient mass transfer rates and favorable sorption equilibrium [8,16]. Silica aerogel particles functionalized with $CF_3(CH_2)_2$ were successfully employed as adsorbents for removing crude oil from saltwater and a Prudhoe Bay crude oil mixture [4,5]. For a single-phase oil in water (o/w) emulsion at the macro level, the functionalized aerogels removed all the oil from the original emulsion, with a mass ratio of 3.5 oil/aerogel. For an oil-to-aerogel ratio of 4.6–14, an emulsion, which was easily separated from water, was formed. For two phase emulsions with a mass ratio of oil to aerogel greater than 16, only a small portion of oil was adsorbed onto the silica particles, indicating that the stability of o/w emulsions plays a role in the adsorption mechanism. A very high adsorption capacity was obtained for silica functionalized with methyltrimethoxysilane (MTMS) [7]. These adsorbents showed a very high uptake of non-polar "hydrocarbon" molecules (9.83–20.64 g/g) [7]. A silica aerogel (Cabot nanogel with a pore diameter of 16 nm and a size range of 0.7–1.2 mm) was successfully used as an adsorbent to remove different types of oils (vegetable oil, motor oil and light crude oil) from o/w emulsions [1]. The adsorption of liquid oil onto silica aerogel seems to be dependent on the viscosity and molecular weight of the oil, both of which directly impact flow through nanoporous or aerogel pores due to capillary forces. In addition, the surfactant concentration and the stability of o/w emulsions play an important role in adsorption; the adsorption capacity was shown to decrease as the amount of surfactant used to stabilize an emulsion increased, and an even lower sorption capacity and a slower sorption rate were attained due to the high stability of the oily wastewater emulsion [1]. Recently, nanoparticle technology has promised many benefits through nano-enabled applications in multiple sectors, including wastewater treatment [17–30]. Nanoparticles exhibit unique catalytic and sorption properties due to their exceptionally high surface-area-to-volume ratio, dispersability and functionalizable surface. Nanoparticle adsorbents (nanoadsorbents) could be employed effectively not only at very low pollutant concentrations but also at very high concentrations for which other techniques are ineffective, time-consuming, or costly [21,31]. Different metal oxide nanoadsorbents have been used successfully for the adsorptive removal of organic and inorganic pollutants from wastewater [20–24]. Due to their rapid adsorption, cost effectiveness and in-situ application potential, these nanoadsorbents could be used as an alternative to the commonly used granular and powder activated carbons or activated alumina [22]. Commercially available hydrophobic nano-silica (Aerosil R812, particle size of 7 nm) was as an effective adsorbent in the treatment of wastewater contaminated with gasoline and diesel, with a high adsorption rate and a 99% removal efficiency [12]. In a recent study we have shown that nano-alumina functionalized with petroleum vacuum residue (VR) could be employed successfully for removing oil from fresh water emulsions [32]. However, the presence of salt in oil-in-fresh water emulsion can have dramatic effect on the oil removal. Therefore, this study continues our previous work aiming at investigating the adsorptive removal of oil from emulsions of oil–saltwater onto nanoparticles of silica and alumina functionalized with VR. The effect of various operating and experimental conditions, including the chemical nature of the nanoparticles (silica and alumina), contact time, solution pH, temperature, salt concentration and VR content, on adsorptive removal was evaluated. Nanoparticles were functionalized with VR because covering the nanoparticle surface with VR is expected to make the surface more hydrophobic and subsequently improve the kinetics and adsorptive capacities compared to conventional adsorbents. The kinetic data were described by the first- and second-pseudo-order models, and the adsorption isotherms were described by the Polanyi-theory-based Dubinin–Ashtakhov (DA) model and the Brunauer–Emmet–Teller (BET) model. Furthermore, a simplex-centroid mixture design (SCMD) was used to optimize the operational and experimental parameters to favor the adsorption capacity and affinity of nanoparticles. To the best of our knowledge, no research has been conducted on the removal of oil from oil–saltwater emulsions by virgin and functionalized alumina nanoparticles using a design of experiments (DOE) with mixtures for the simultaneous measurement of salt and oil adsorption by following two different variables (i.e., conductivity and absorbance). This approach holds great promise for the oil and gas industry, as the low-cost method could be used to treat produced water.

2. Materials and methods

2.1. Materials

A Colombian light crude oil (33°API), deionized water and NaCl (99%, Merck KGaA, Germany) were used for preparing oil in brine emulsions. HNO_3 (65%, CARLO ERBA Reactifs-SDS, Italy) and NaOH pellets (anhydrous, 98%, Sigma Aldrich, USA) were used for pH adjustment. Alumina nanoparticles purchased from Petroraza, Colombia were used as adsorbent. Silica nanoparticles purchased from Sigma Aldrich was used as adsorbent as well for comparison. A petroleum vacuum residue (VR), with an approximate content of 15 wt% of asphaltenes, supplied by a local refinery (Barrancabermeja-Colombia) was used to functionalize the alumina nanoparticles aiming at increasing their affinity for non-polar components, and improving kinetic and adsorptive capacities in comparison with conventional materials. Elemental analysis showed that virgin VR sample has 78.28 wt% carbon, 14.32 wt% hydrogen, 1.14 wt% sulfur, 4.37 wt% nitrogen and 1.82 wt% oxygen. Toluene (99.5%, Merk KGaA, Germany) was used for washing the alumina nanoparticles functionalized with the VR. All chemicals were used as received without further purifications.

2.2. Methods

2.2.1. Preparation of oil-brine emulsions

Saltwater (brine) was prepared by mixing NaCl and deionized water at 600 rpm and a temperature of 298 K to obtain a concentration of 500 mg/L. Oil-brine emulsions were prepared by mixing crude oil and brine at 16,000 rpm for 20 min. Neutral emulsions were acidified and basified by adding aliquots of 0.1 N HNO_3 and 0.1 N NaOH, respectively. The stability of the emulsions was monitored for 72 h by observing changes in the size of oil drops using a RPL3B optical microscope Rotating Stage Bertrand Lens Mica and Gypsum Plates (Microscopes INDIA, India) [33] and changes in absorbance using UV–vis spectrophotometer Genesys 10S (Thermo scientific, United States). Properties of crude oil, brine and oil-brine emulsion were reported in our previous study [32] and are presented in Table 1 as a reference.

2.2.2. Preparation of nanoparticle functionalized with VR

The alumina nanoparticles were functionalized with VR at different loadings following a procedure developed in our previous

Table 1
Crude oil, brine and emulsion properties at 298 K.

Sample	Density (g/mL)	Viscosity (cP)	pH
Crude oil	0.860	3.02	7.88
Brine	1.034	1.500	7.32
Oil in brine emulsion	1.017	1.475	7.38