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Adsorptive removal of oil spill from oil-in-fresh water emulsions by hydrophobic alumina nanoparticles functionalized with petroleum vacuum residue

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

[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*
[c] *Department of Chemical Engineering, An-Najah National University, Nablus, Palestine*

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ABSTRACT

Oil spills on fresh water can cause serious environmental and economic impacts onshore activities affecting those who exploit freshwater resources and grassland. Alumina nanoparticles functionalized with vacuum residue (VR) were used as a low-cost and high hydrophobic nanosorbents. The nanomaterial resulting showed high adsorption affinity and capacity of oil from oil-in-freshwater emulsion. The effects of the following variables on oil removal were investigated, namely: contact times, solution pH, initial oil concentrations, temperature, VR loadings and salinity. Kinetic studies showed that adsorption was fast and equilibrium was achieved in less than 30 min. The amount adsorbed of oil was higher for neutral system compared to acidic or basic medium. Increasing the VR loading on nanoparticle surface favored the adsorption. Results of this study showed that oil removal for all systems evaluated had better performance at pH value of 7 using nano-alumina functionalized with 4 wt% VR. Adsorption equilibrium and kinetics were evaluated using the Polanyi theory-based Dubinin–Ashtakhov (DA) model, and pseudo-first and pseudo-second order-models, respectively.

1. Introduction

Oil spills, which are the release of different types of crude oil into the environment, is a form of pollution that is facing freshwater worldwide [1,2]. Despite the fact that oil spills in the freshwater bodies involved significant volumes, however, they do not attract the attention of local or international media as the marine oil spills [1–3]. Oil spills on freshwater can cause serious environmental and economic impacts, as they can influence the aquatic and non-aquatic life [2,4]. Further, the properties and chemistry of the crude oil is strongly dependent on its origin and sources. Accordingly, its behavior in the water body is complex and cannot be easily predicted. For instance, some constituents of crude oil are noted for its tendency to float on water and vaporize; while others prefer binding to solid surfaces [2]. Further, some hydrocarbon compounds of oil constituents could form oil-in-water (o/w) emulsion with freshwater stream due to flow turbulence like flow in rivers and consequently the emulsions change the properties and characteristics of oil spills [1,2], and hence can become dangerous substances with different toxicological effects on the aquatic life and human being [2,3,5]. Hedtke and Puglisi [3] evaluated the toxicity of five oils (Lloydminister crude oil, mixed blend sweet crude oil, No. 1 fuel oil, waste oil, and No. 2 fuel oil) on four freshwater species. The oils were evaluated in two ways as emulsioned and floating layers. The results of the short-term mortality tests indicated wide differences in the toxicity of oils. These differences are affected by a number of factors, such as the chemical nature of oil, the differences between the way of emulsions was made and the changing nature of oils with time, and the exposure time. This o/w emulsions can badly hamper the treatment and disposal processes [4]. Water cleanup and recovery from oil spills is difficult and depends on several factors, including the type of oil spilled, the water body (i.e., shoreline, beaches, rivers, etc.) and its turbulence and temperature [4]. Several physical, chemical and biological methods have been reported for removal of oil from produced water from onshore activities [6]; including bioremediation, controlled burning, skimming, solidifying, and vacuum and centrifugation [6]. These methods have proven to be expensive,

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* Corresponding authors. Address: Kra 80 No. 65-223, M3-100a, Colombia (F.B. Cortés). Address: Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada (N.N. Nassar).

E-mail addresses: fbcortes@unal.edu.co (F.B. Cortés), nassar@ucalgary.ca (N.N. Nassar).

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time-consuming and/or in effective in meeting stringent environment regulations. Owing to their simplicity and applicability at the industrial scale adsorption process could be employed as an alternate technology for oil spill treatment and recovery. Different types of adsorbents have been widely used for water treatment and recyclability, such as activated carbon, copolymers, organoclay, zeolite and resins [7–9]. The combination of activated carbon and organoclays showed high efficiency in removing total petroleum hydrocarbons [10]. Silica aerogel was successfully used as adsorbents for removal of different types of oils, such as vegetable oil, motor oil and light crude oil from o/w emulsion stabilized by surfactant. The presence of surfactant could impact the removal efficiency [11]. Hydrophobic silica (SH) functionalized with methyltrimethoxysilane (MTMS) showed high adsorption for non-polar compounds [12].

Recently, nanoparticle technology is emerging as an alternative for the currently available techniques for water and wastewater purifications [13–21]. Owing to their unique properties over the conventional adsorbents/catalysts, nanoparticles are expected to outperform the conventional adsorbents in wastewater treatment. These properties include high surface area to volume ratio, dispersibility, high adsorption affinity, and possibility of in situ treatment, etc. [13,15,19]. Cho et al. [22] coated silica nanoparticles with polydimethysiloxane (PDMS) for increasing their surface hydrophobicity, which subsequently were successfully used for selectively removing gelating oils from the oil/water mixture, allowing easy separation and removal of oil from water. Hydrophobized silica nanoparticles are shown to be able to gelate rotary pump oil and could be used as remediation treatment of the water [22]. Iron oxide nanoparticles coated with polystyrene could be used for oil spills treatment by adsorptive removal of floating oil on water [23]. However, despite the fact that nanoparticles have been successfully used as adsorbents/catalysts for removing various organic and inorganic pollutants from wastewater, little work has been employed in using nanoparticles for removing of oil from oily freshwater bodies. Therefore, the aim of this work is to develop a low-cost nanoadsorbent that can be used in the adsorptive removal of oil from oily emulsioned freshwater (i.e., o/w stable emulsion), which is one of the challenges for the spilled oil treatment. In this study, a new nanoadsorbent of alumina functionalized by vacuum residue, to increase their affinity towards non-polar compounds, have been tested for adsorptive removal of oil from oily freshwater. The following variables have been investigated to enhance the removal efficiency namely, adsorption time, loading of VR, temperature, salinity and solution pH. In addition, the kinetic data were described by the first and second pseudo order models and the adsorption isotherm were described by the Polanyi theory-based Dubinin–Ashtakhov (DA) model.

2. Materials and methods

2.1. Materials

Alumina nanoparticles of 35 nm diameter purchased from Petroraza S.A.S, Colombia, were used as adsorbents in this study. A petroleum vacuum residue (VR) sample supplied by a local refinery (Barrancabermeja, Colombia) was used for modifying the surface hydrophobicity of the nanoparticles. The elemental analysis of the selected VR is presented in Table 1. NaCl (99%, Merck KGaA, Germany) was used as salt source to study the salinity effect on adsorption. A Colombian light crude oil (33°API) was used as the oil source in the emulsions, and deionized water was used as the continuous phase in the emulsions. HNO_3 (65%, CARLO ERBA Reactifs-SDS, Italy) and NaOH pellets (anhydrous, 98%, Sigma Aldrich, USA) were used for pH adjustment. Toluene (99.5%, Merk KGaA, Germany) was used for washing the functionalized nanoparticles.

Table 1
Elemental analysis of Barrancabermeja refinery vacuum residue.

Element	C	H	S	N	O	Metal
Mass ratio (%)	78.28	14.32	1.14	4.37	1.82	0.07

2.2. Methods

2.2.1. Emulsion preparation

The oil in water (o/w) emulsions were prepared using a Colombian crude oil (33°API) and freshwater. The emulsions were prepared by mixing the oil and freshwater at 16000 rpm for 20 min at 298 K. The mixture pH was around 7. To adjust the pH of the mixture, HNO_3 or NaOH, was used in a range from 4 to 10. The stability of the emulsions was monitored by the size of the oil drop using a RPL3B optical microscope Rotating Stage Bertrand Lens Mica and Gypsum Plates (Microscopes INDIA, India) [24] and the absorbance using UV–vis spectrophotometer Genesys 10S (Thermo scientific, USA). Stability measurements were performed for 36 h (the approximate time for phase separation to occur) which was the time for drop size and absorbance remained unchanged. For the salinity effect studies, NaCl was added to the papered emulsion to obtain a concentration of 500 mg/L. The properties of the oil–freshwater and salt–water emulsions are shown in Table 2.

2.2.2. Nanoparticles preparation

Fresh alumina nanoparticles were washed and posteriorly dried at 393 K for 3 h. To enhance their surface functionality and hydrophobicity, the alumina nanoparticles were aged using a solution of VR in toluene at different concentrations (2 and 4 wt% regard to the amount of nanoparticles) for two weeks at 298 K and constant stirring at 200 rpm. During the aging process, diffusion and physical adsorption of the VR occur on the alumina nanoparticle surface forming an egg-shell profile [25–28]. This adsorption process is fast because the considered alumina nanoparticles are non-porous and hence there was no intraparticle diffusion limitation. As alumina surface can be considered an array of Brönsted acid–base sites [29,30], other mechanisms of VR anchoring on the alumina surface could be due to strong ionic interactions (i.e., Brönsted acid–base interactions) between the organic compounds present in the VR and the surface of alumina nanoparticles [26,30,31]. Ionic interactions are preferred over dipole–dipole interactions as their bonding energy is about ten times larger [30]. After the ageing process, the functionalized alumina nanoparticles were collected after decanting the supernatant. After that, the nanoparticle functionalized with VR were left to dry for a period of 6 h at 393 K for eliminating any remaining solvent and allowing the dissolved VR transportation throughout the alumina surface [25]. Then, the functionalized nanoparticles were washed with toluene several times until the UV–vis absorbance of effluent matched the blank. The resultant functionalized nanoparticles were left to dry at 298 K until no change in mass was observed. It should be noted here that the samples were labeled based on the initial concentration of VR used for the preparation. Two samples having different loads of VR were performed and the samples were labeled as Al/2VR and Al/4VR for an initial concentration of 2 and 4 wt%, respectively.

Table 2
Crude oil, neutral brines and emulsion properties at 298 K.

Sample	Density (g/mL)	Viscosity (cP)	pH
Crude oil	0.860	3.020	7.88
Oil in freshwater emulsion (500 ppm)	1.017	1.475	7.38
Saltwater emulsion (500 ppm)	1.034	1.500	7.32