Colloids and Surfaces A: Physicochem. Eng. Aspects 466 (2015) 197–202

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Magnetic demulsification of diluted crude oil-in-water nanoemulsions using oleic acid-coated magnetite nanoparticles

Jiling Liang[a], Na Du[b], Shue Song[b], Wanguo Hou[a,b,*]

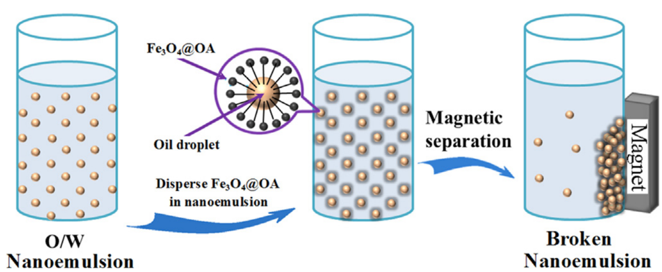
[a] Environment Research Institute, Shandong University, Jinan 250100, PR China
[b] Key Laboratory of Colloid & Interface Chemistry (Ministry of Education), Shandong University, Jinan 250100, PR China

HIGHLIGHTS

- Oleic acid-coated magnetite nanoparticles are a potential magnetic demulsifier.
- The demulsifier can magnetically break diluted crude oil-in-water nanoemulsions.
- The demulsification efficiency of the demulsifier is influenced by its wettability.
- Multistep demulsification shows a higher efficiency than the single-step operation.
- The magnetic demulsifier exhibits a good reusability.

GRAPHICAL ABSTRACT

Single-layer oleic acid-coated magnetite (Fe_3O_4@OA) nanoparticles show potential for magnetically demulsifying diluted crude oil-in-water nanoemulsions from oilfields. The demulsification efficiency was influenced by the dosage and wettability of the nanoparticles, the pH and the demulsification operation process.



ARTICLE INFO

Article history:
Received 24 September 2014
Received in revised form 19 November 2014
Accepted 28 November 2014
Available online 5 December 2014

Keywords:
Magnetic nanoparticle
Emulsion
Demulsification
Oleic acid
Magnetite
Crude oil

ABSTRACT

Most produced crude oil and oily wastewater from oilfields typically exist in the form of emulsions; this makes their demulsification a very challenging process. Chemical demulsifiers are commonly employed to enhance demulsification efficiency (E_D). However, there is still an urgent need to develop more efficient techniques and demulsifiers to meet eco-friendly and economically competitive requirements. In this study, magnetic demulsification of single-layer oleic acid-coated magnetite (Fe_3O_4@OA) nanoparticles as a demulsifier for cyclohexane-diluted crude oil-in-water nanoemulsions (denoted as CO-NEs) was investigated under an external magnetic field. The effects of the dosage and wettability of the demulsifier, the pH of the CO-NEs, and the demulsification operation process on the E_D were examined. The E_D increased with increasing Fe_3O_4@OA dosage and a high E_D of ~97% was reached, which demonstrates the potential of Fe_3O_4@OA nanoparticles as a magnetic demulsifier for crude oil-containing emulsions from oilfields. The E_D is related to the wettability (or water contact angle) of the magnetic nanoparticles, and a maximum E_D was observed at a water contact angle of ~90°. The E_D was almost unchanged in the pH range of 4.0–7.5, while it gradually decreased as the pH rose from 8.0 to 11.0. Multistep demulsification exhibited a higher E_D than the single-step operation when the same amounts of demulsifier were used. The Fe_3O_4@OA nanoparticles exhibited good recyclability; no significant change in the E_D of the recycled Fe_3O_4@OA after demulsification was observed over five cycles. This work improves the understanding of demulsification behaviors of magnetic demulsifiers.

* Corresponding author at: Key Laboratory of Colloid & Interface Chemistry (Ministry of Education), Shandong University, Jinan 250100, PR China. Tel.: +86 531 88365460; fax: +86 531 88564750.
E-mail address: wghou@sdu.edu.cn (W. Hou).

http://dx.doi.org/10.1016/j.colsurfa.2014.11.050
0927-7757/

1. Introduction

Most crude oil is initially produced in the form of water-in-oil (W/O) or oil-in-water (O/W) emulsions in oilfields [1]. Moreover, significant amounts of oily wastewater in the form of O/W emulsions are also generated during crude oil production [2]. All these emulsions need to be demulsified to meet the requirements of the crude oil transportation and refinery processes, as well as wastewater discharge. However, these crude oil-containing emulsions are highly stable due to the presence of interface-active substances that are either naturally present or intentionally added to enhance oil production [1,2]. Thus, the emulsions are hard to treat, especially those containing nano-sized droplets. Several techniques have been developed to break emulsions, including flotation [3], chemical coagulation coupled with flotation [4], chemical and electrochemical demulsification [5], membrane separation [6], microwave demulsification [7], freeze/thaw treatment [8], combined demulsification and reverse osmosis [9] and biotechnology [10]. Many chemical demulsifiers have also been developed to enhance demulsification efficiency [11–13]. However, there is still an urgent need to design alternative techniques and demulsifiers that can realize simple, fast oil–water separation and possess eco-friendly and economically competitive features. Recently, a magnetic oil–water multiphase separation technique using functionalized magnetic nanoparticles (MNPs) as a demulsifier has received considerable attention [1,2,14–17]. The magnetic substrate used usually is magnetite (Fe_3O_4) because of its low cytotoxicity and good biocompatibility [18,19]. The MNPs commonly need to be modified with active substances (surfactants or polymers) to improve their interfacial activity and dispersibility [1,2,14,15]. This magnetic demulsifier can accumulate at oil–water interfaces, imparting its magnetic properties on the dispersed droplets. Therefore, under an external magnetic field, the droplets that have been magnetically tagged by the demulsifier can rapidly coalesce, and be isolated from the continuous phase. Magnetic demulsifiers can be recovered by magnetic separation, and can be reused with or without regeneration; thus they have the advantages of simple operation, recyclability, and low cost [1]. Peng et al. [1,14] first reported a magnetic demulsifier, ethyl cellulose-grafted Fe_3O_4 nanoparticles, used to remove water from water-in-heavy naphtha and water-in-diluted bitumen emulsions, by an external magnetic field. Lemos et al. [15] fabricated a magnetic amphiphilic composite, used to separate oil droplets from a biodiesel-in-water emulsion. Li et al. [2] modified magnetite nanoparticles using a polyether polyol demulsifier, to remove oil droplets from an O/W emulsion, using an external magnetic field. These previous studies [1,2,14,15] have revealed the potential of interface-active MNPs in oil–water multiphase separation. However, there remains a need to fully understand their behavior during magnetic demulsification.

Most recently, we synthesized single-layer oleic acid-coated magnetite (Fe_3O_4@OA) nanoparticles, and investigated their demulsification efficiency for cyclohexane-in-water nanoemulsions (CH-NEs) [17]. The results showed that the Fe_3O_4@OA nanoparticles have the potential to demulsify O/W emulsions. As part of our ongoing research, the Fe_3O_4@OA nanoparticles were applied to remove oil droplets from cyclohexane-diluted crude oil-in-water nanoemulsions (CO-NEs) to evaluate the technical feasibility of using the magnetic demulsifier for treating produced crude oil and oily wastewater from oilfields. The effects of the dosage and wettability of the Fe_3O_4@OA nanoparticles, the pH of the CO-NEs, and the demulsification operation process on the oil removal efficiency from the nanoemulsion were investigated. While the synthesis and characterization of Fe_3O_4@OA nanoparticles has received much attention [20–28], to the best of our knowledge, there are no reports concerning the nanoparticles being used to demulsify crude oil emulsions. This work will improve understanding of magnetic demulsification.

2. Experiments

2.1. Materials

A bare Fe_3O_4 sample and a Fe_3O_4@OA sample were synthesized in our laboratory, as described in our previous work [17]. These magnetic samples were spherical in shape, and the average diameters of the bare Fe_3O_4 and Fe_3O_4@OA nanoparticles, measured using JEM-1011 transmission electron microscope, were ~11 and 13 nm, respectively. The amount of oleic acid (OA) coating (A_O) and water contact angle (θ_W) of the Fe_3O_4@OA, measured using SDT-Q-600 thermal analysis system and DSA10 contact angle goniometer, were 0.11 g g^{-1} and 110°, respectively. In addition, to examine the effect of the wettability of Fe_3O_4@OA nanoparticles on the demulsification efficiency, a further five Fe_3O_4@OA samples with different θ_W values (47–124°) were also used in this work. Details about these five Fe_3O_4@OA samples were given in our previous work [17].

Cyclohexane (analytical grade) was purchased from Damao Chemical Reagent Co., China. Tween 60 (chemically pure) was purchased from Kermel Chemical Reagent Co., China. These two chemicals were used as received. Dehydrated crude oil with a viscosity of 21 Pa s, determined at a shear rate of 100 s^{-1} and a temperature of 25 °C, was supplied by Shengli Oilfield, Sinopec, China. Deionized water was obtained from a Hitech-Kflow water purification system (Hitech, China).

2.2. Preparation of cyclohexane-diluted crude oil-in-water nanoemulsion

The crude oil was first diluted with cyclohexane at a crude oil/cyclohexane mass ratio of 1:2, to produce the cyclohexane-diluted crude oil used as the oil phase in this work. A mixture of 10 wt% cyclohexane-diluted crude oil, 10 wt% Tween 60, and 80 wt% deionized water was stirred using a GJ-2S high-speed mixer (Qingdao Haitongda Dedicated Instrument Co., China) at 9500 rpm for 20 min, yielding a cyclohexane-diluted crude oil-in-water mother emulsion.

The mother emulsion was diluted by 1:30 with deionized water, to produce the CO-NE used for the demulsification tests. This tested emulsion had a mean droplet size (D_m) of 76 nm (Fig. S1 in the Supporting Information), thus belongings to the category of nanoemulsions. It was very stable; no significant changes in droplet sizes were observed by dynamic laser light scattering analysis over a period of 10 days.

The natural pH of the tested nanoemulsion was 6.3. To investigate the effect of pH on the demulsification efficiency, the mother emulsion was diluted with deionized water, whose pH had previously been adjusted using NaOH and HCl.

2.3. Demulsification tests

The demulsification ability of the Fe_3O_4@OA nanoparticles was determined by measuring the residual oil content of nanoemulsions after settling on a hand magnet. A given amount (0.10–1.00 g) of Fe_3O_4@OA nanoparticles and 10 mL of freshly prepared CO-NE samples were thoroughly mixed in a 40 mL glass vial. The mixture was shaken in a THZ-82 thermostatic water-bath shaker (Wuhan Grey Mo Lai Detection Equipment Co., China) at 240 cycles·min^{-1} for 12 h at 25 °C. Oil removal kinetic tests indicated that 12 h of shaking was sufficient to achieve equilibrium (Fig. S2 in the Supporting Information). The magnetic particles along with their adhered oil were then removed by a 5000 Gs NdFeB magnet (Zibo Dry Magnetic Industry Science and Technology Co., China). The