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RESEARCH ARTICLE

Experimental Investigation of Fe_3O_4-Chitosan Nanocomposite as a Nano-Demulsifier for Water in Crude Oil Separation

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ABSTRACT

Nowadays chemical and electrostatic demulsification techniques are typically used to separate water-in-crude-oil emulsions. The need to improve demulsification techniques has led to the use of various additives among which nanoparticles have emerged as a novel alternative. Most of the exploited crude oil exists in an emulsion state, where may cause serious problems during processing. Chemical demulsifiers, bottle tests, and electrostatic desalters are commonly used to separate water from crude oil emulsions but there are some issues involved with these methods. Therefore, using new technologies like nanotechnology can help improve the desalting process. First, Fe_3O_4 and Fe_3O_4-chitosan nanocomposite were synthesized via co-precipitation method. Fe_3O_4-chitosan nanoparticles were characterized by X-ray diffraction and Fourier transform infrared spectroscopy. The results showed that ultrafine Fe_3O_4 nanoparticles were prepared and coated by chitosan. In this study, Fe_3O_4 and Fe_3O_4-chitosan nanocomposite were utilized to improve emulsion destabilization. The effect of different parameters on the separation performance was studied and the best conditions were determined. The results showed that the application of certain nanostructures in crude oil emulsions improves the performance of demulsification up to 86% and decreases the amount of demulsifier consumption in the desalting process.

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INTRODUCTION

Crude oil is mainly produced in the form of stable water-in-oil emulsions [1]. Water droplets in the crude oil flowing through transportation lines and refinery processing equipment entail certain standards to prevent corrosion and catalyst deactivation as a result of high-temperature hydrolysis of water producing an acidic environment. Another reason for corrosion is the inclusion of salts such as $MgCl_2$, NaCl and $CaCl_2$ in the emulsified water, which makes demulsification necessary as an inevitable part of primary crude oil processing. The water content of crude oil has been often < 50 % with a salt content of ~ 400-200000 ppm, bringing about serious problems during crude oil refining. The aim of desalting is generally the reduction of water content down to 10 lb per barrel (10 PTB) [2]. Besides, the emulsified oil-in-water waste is an environmental pollutant, which needs to be discharged to the environment with standard properties [3].

Interfacially-active materials either naturally present in crude oil [4] (asphaltenes, resins and solid particles like clays and waxes) or intentionally added for enhanced oil recovery purposes (surfactant flooding, ASP flooding, etc.) lead to the stabilization of water-in-oil and oil-in-water emulsions by forming active and resilient interfacial layers [1,3]. Asphaltenes are micro-colloidal suspensions in crude oil with a ~ 3 nm diameter, resulting in the stabilization of emulsions through interaction with resins (Pickering

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emulsions) [5]. Studies show that suspended solids prevent the thinning of the film layer by enhancing its resilience. However, inorganic salts are believed to reduce emulsion stability [6].

Various parameters such as water content [7], emulsifier type and concentration [8], mixing rate, temperature [7], the viscosity of the continuous phase and surface tension [7] play role in emulsion stability. Electrical and steric stabilization mechanisms are also considered to be effective in emulsion stability [9].

Several techniques have been proposed for emulsion breaking such as flotation [10], chemical coagulation [11], chemical-electrochemical demulsification [12], membrane separation [13], microwave demulsification [14,15], membrane separation [16,17], thermal demuslification, hydrocyclone separation [18], ultra-sonication [19] and nano-enhanced demulsification [20]. Among these, chemical demulsification is considered as the most prevalent desalting technique currently applied. Demulsifiers possess complicated and harmful components for the environment and researchers have investigated their replacement with more efficient and/or less harmful alternatives. Currently, many chemical demulsifiers are available [21] competitive characters of which include simple, fast oil-water separation, eco-friendliness, and cost-effectiveness.

Demulsifiers are expected to be adsorbed at the oil-water interface to break the stable water-oil interface. This breakdown occurs by replacing emulsion stabilizers which alter surface properties such as interfacial tension, mechanical strength, elasticity, and interfacial film thickness, resulting in enhanced coalescence. Most demulsifiers are non-ionic surfactants with the main components as polypropylene oxide (PPO) as the hydrophobic part and polyethylene oxide (PEO) groups as the hydrophilic part. Alkylphenol ethers, fatty amides, fatty esters and ethoxylated phenols are also used for demulsification.

Recently, new technologies have been successfully studied and tested in laboratory for demulsification of water-in-oil emulsions such as microwave and ultrasonic technologies. In the presence of a microwave field, emulsion temperature is increased resulting in the reduction of viscosity and zeta potential of the water-oil suspension. Microwave radiation causes molecular rotation. So, electrical double bonds between water and oil molecules are destroyed resulting in the reduction of zeta potential and increasing gravitational separation efficiency. Also, in the ultrasonic field, primary and secondary acoustic forces are applied to water emulsions. Due to primary acoustic forces, water droplets move to the pressure nodes of standing ultrasonic wave. Further coalescence of droplets is based on secondary inter-droplet acoustic forces [22, 23].

Khajehesamedini et al. (2018) designed an ultrasound transducer to reduce the consumption of chemical demulsifiers. They examined the effect of ultrasonic radiation time, ultrasonic intensity, and the water content. The results showed that by choosing the appropriate field time duration and intensity, the use of chemical suspensions can be reduced up to 50%. They also proposed a population balance model for the interpretation of experimental data and the proposed model was in good agreement with the experimental results [24].

Another novel technology is the use of nanoparticles [25-29]. Various nanoparticles are proposed as alternative additives for the improvement of demulsifier performance. Nanoparticles can accumulate at the water-oil interfaces, leading to the improvement of demulsification efficiency. Among suggested nanoparticles, magnetic nanoparticles (MNPs) can be regained by an external magnetic field and reused [30]. Magnetic core-shell structures are generally used using magnetite (Fe_3O_4) as the magnetic core due to its low cytotoxicity and biocompatibility modified by various active materials (surfactants or polymers) to improve dispersion characters [30, 31]. Magnetic nanoparticles are synthesized by different techniques such as the co-precipitation and thermal decomposition [32, 33], microemulsion, hydrothermal technique and sono-chemical synthesis [34]. Various magnetic core-shell structures are proposed and utilized for demulsification improvement. Peng et al. (2012) reported a magnetic demulsifier, ethyl cellulose-grafted nano-Fe_3O_4, to separate water droplets from heavy naphtha and diluted bitumen bulks. Lemos et al. [31] synthesized a magnetic amphiphilic composite to remove biodiesel droplets from water. Li et al. [3] used magnetite nanoparticles to enhance the performance of a polyether polyol demulsifier for separating oil in water emulsion. In other study, single-layer oleic acid-coated magnetite (Fe_3O_4-OA) nanoparticles have been synthesized and tested for demulsificaion of cyclohexane-in-water nano-emulsions (CH-NEs)

[35]. These nanoparticles were used for removing oil nano-emulsions from water while evaluating the technical feasibility of a magnetic demulsifier for treatment of extracted crude oil and oily wastewater from oilfields. Nikkhah et al. (2015), suggested nano-titania as an improved chemical demulsifier for water-in-oil emulsions. In their study, sol-gel method was used to synthesize nano-titania particles. The results show that this demulsifier can improve demulsification efficiency by 90 % besides reducing the time taken for water and salt separation [36].

These studies reveal the potential of interfacially-active MNPs in water-oil multiphase separation. However, detailed properties of the protective film around water particles are essential for understanding the mechanisms involved, besides the fundamental knowledge of the chemistry of interacting active components in crude oil. In this study, Fe_3O_4-chitosan nanocomposite particles are synthesized and their ability to destabilize water-in-oil emulsions is investigated. Based on the literature review performed, this material has not been investigated previously as crude oil demulsification agent.

EXPERIMENTAL

Materials and Methods

$FeCl_2.4H_2O$, $FeCl_3.6H_2O$ (Merck; with > 98% purity) as Fe sources and chitosan as polymer stabilizer were used without further purification. Also, HCl and NaOH for pH adjustment were supplied by Merck Co.

Preparation of water in crude oil emulsion

Crude oil was supplied by the GACHSARAN oil field with an industrial chemical demulsifier (FD 7250). Characterization of crude oil is given in Table 1. Water-in-oil emulsions were prepared by adding 5 Vol. % and 10 Vol. % water to crude oil at 50°C and mixed perfectly. The prepared emulsions were stable for about a week without significant phase separation.

Preparation of the Fe_3O_4-Chitosan Nanocomposite

Fe_3O_4 nanoparticles were synthesized by the co-precipitation technique using $FeCl_2$ and $FeCl_3$ as Fe sources. 2 mmol of $FeCl_3.6H_2O$ and 1 mmol of $FeCl_2.4H_2O$ were dissolved in 100 ml HCl at pH = 2 until a homogeneous solution was obtained. Chemical precipitation was induced by gradual addition of a 0.5 mM NaOH solution to the mixture. Vigorous mixing for 30 min at 80 ^{0}C was necessary for precipitation. Centrifugation was used to separate the precipitates. Then, they were washed with water and ethanol so that side products and impurities were removed. The final product was kept in the oven and dried at 60 ^{0}C [37].

In order to produce Chitosan coating on the as-synthesized particles, a 0.01 V/V acetic acid solution was prepared (1 cc acetic acid in 100 cc water) and then 1 g of chitosan was added and dissolved. 1 g of the as-synthesized Fe_3O_4 nanoparticles were dispersed in 100 ml distilled water using ultrasonication and vigorously mixed at 50 ^{0}C. The Chitosan solution was added during a 30 min period. Then magnetic separation was applied to collect the final product, washed with ethanol and water and finally dried in an oven at 50^{0}C. The procedure for the synthesis of Fe_3O_4 nanoparticles is summarized in Fig. 1.

Bottle Test Procedure

Bottle test was employed to evaluate the performance of the as-synthesized nanocomposite particles for demulsification. In the first step, crude oil and freshwater (5 vol. % and 10 vol. %) were mixed perfectly with an electric mixer to dissolve more salt crystals in the added water, and the process water from oil separation is performed with a higher efficiency. Then, the industrial demulsifier was added via a micro-syringe and nanoparticles were added through sonication during 5 minutes. After performing the above steps, the sample was shacked and poured in a graduated cylinder. Then the graduated cylinder was placed in an electric oven and heated to 70°C. Eventually, after 12 hours the demulsification efficiency (DE) was calculated by the following equation:

$$DE(\%) = \frac{V}{V_0} \times 100 \tag{1}$$

Where, V is the the separated water volume and V_0 the initial water volume [17].

Preparation of samples

Bottle test was performed on four different samples. Namely: (1) a sample with 80 ppm of demulsifier (the standard demulsifier concentration in desalting units) named blank80;

(2) A sample with 40 ppm chemical demulsifier named blank40. Both samples were considered as reference samples and were prepared without addition of nanocomposite particles. (3, 4) Two

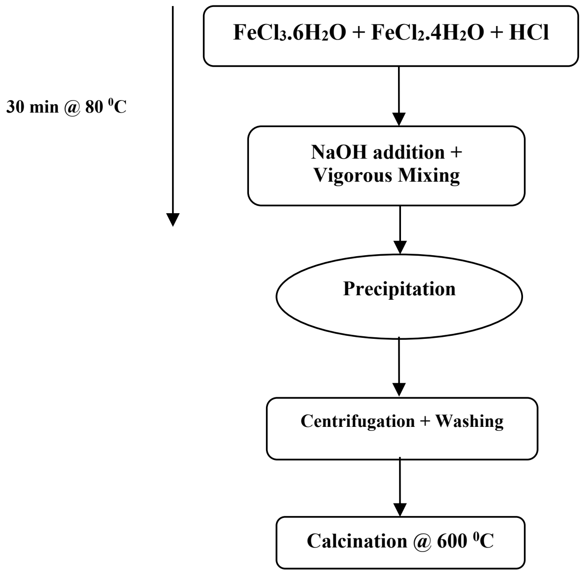


Fig. 1. The procedure for the synthesis of Fe_3O_4 nanoparticles.

other samples containing Fe_3O_4 and Fe_3O_4-chitosan, with equal proportions of NP and blank40.

RESULTS AND DISCUSSION

Particle Size Analysis (PSA)

Fig. 2 shows the PSA of Fe_3O_4 nanoparticles and Fe_3O_4-chitosan nanocomposite using HORIBA LB-550 equipment. Fe_3O_4 nanoparticles show a narrow PSD with an average value of 5 nm in diameter which was enhanced to ~ 90 nm upon coating by chitosan. TEM results from a previous study performed by the authors reveal that the as-produced nanoparticles have a single magnetite nanoparticle covered by a chitosan shell configuration [38]; thus the difference between the graphs can be attributed to the thickness of the chitosan shell.

FTIR Analysis

To realize the binding, FTIR spectra of chitosan-coated Fe_3O_4 nanocomposite is examined as shown in Fig. 3. The Fe-O peak can be observed at the 580 cm^{-1} wavelength which is prevalent for other mineral bonds also and observed in other studies in the same range [39]. Other peaks are also observed in the FTIR for Chitosan which confirms the coating of Fe_3O_4 with chitosan. The wide peak at 3600 cm^{-1} is attributed to the stretching vibration of the amine ($–NH_2$) and hydroxyl (–OH) groups. The absorption bands at 1883 cm^{-1} 1586 cm^{-1} are attributed to –C–O stretching of primary alcoholic group in chitosan. These peaks indicate the Fe bond to the NH_2 group of chitosan [32]. The results indicate that chitosan was coated on Fe3O4 nanoparticles successfully. Due to the negative surface charge of iron oxide an affinity exists toward chitosan and coating can occur by the electrostatic interaction [39].

XRD Analysis

Fig. 4 shows the XRD pattern for Fe_3O_4-chitosan nanocomposite. As expected, six peaks are observed at (220), (311), (040), (422), (511), and (440) which are also confirmed by other synthesis results in the literature [40].

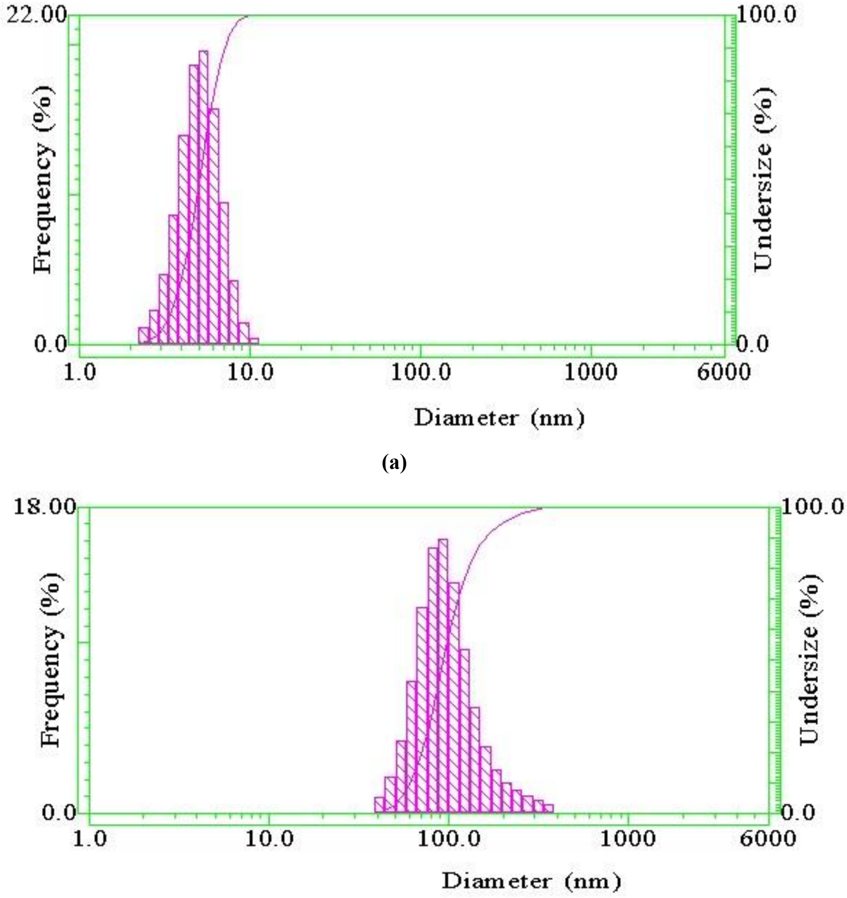
The peak before $2\theta = 20^0$ indicates that Fe_3O_4 nanoparticles were successfully coated by amorphous chitosan.

Parameters affecting the demulsification efficiency

Demulsification efficiency is related to many parameters such as adding freshwater, settling time, temperature, nanoparticle dose and mixing time. The main parameters have been studied in this paper.

Freshwater injection

Bottle tests were performed with 5% and 10% water injection to similar samples to investigate the effect of water addition on the demulsification



(a)

(b)

Fig. 2. (a) PSA of Fe_3O_4 (b) PSA upon chitosan coating.

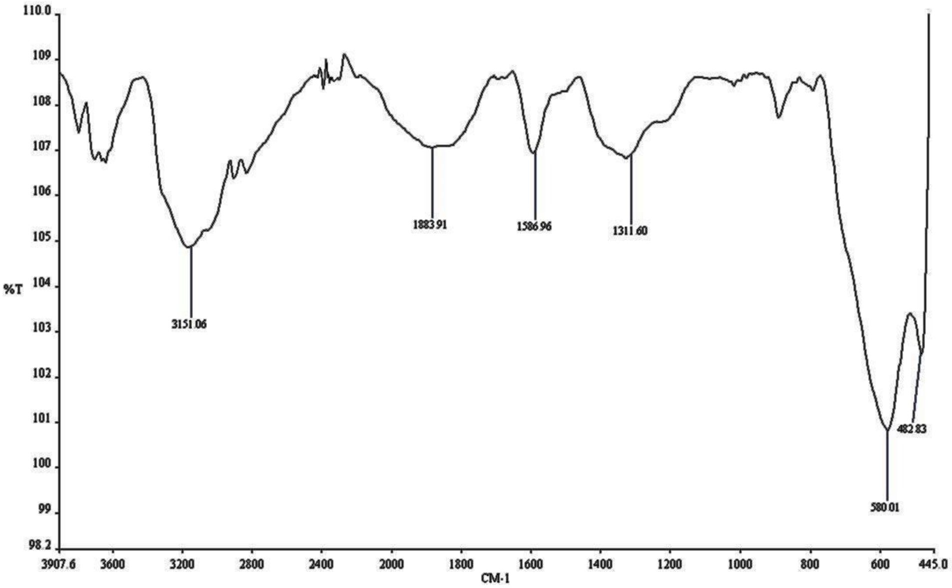


Fig. 3. FTIR spectrum of chitosan-coated Fe_3O_4 nanoparticles.

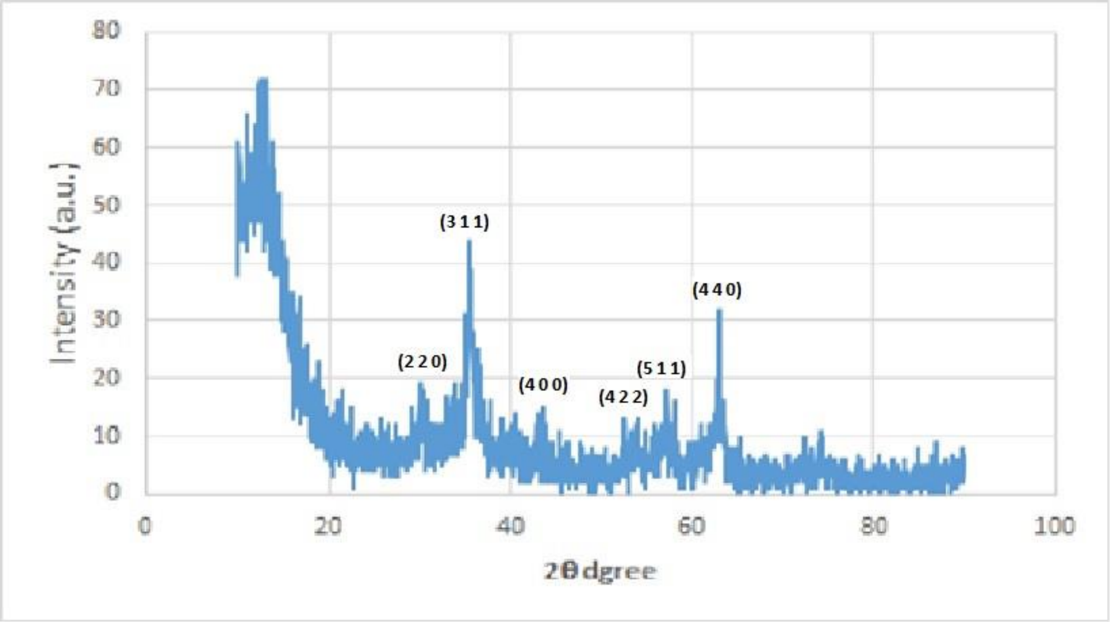


Fig. 4. XRD pattern for chitosan-coated Fe_3O_4 nanoparticles.

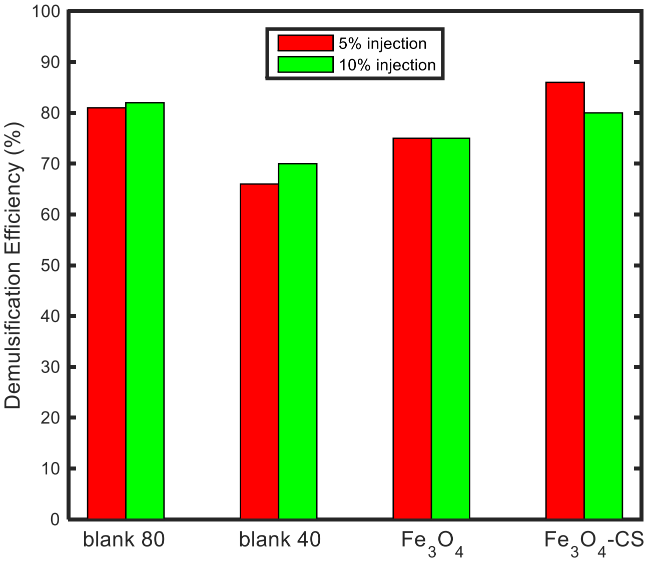


Fig. 5. Bottle test results for 5% and 10% freshwater injection. Other conditions: settling time: 12h, nanoparticles dosage: 0.04%wt, heat temperature: 70ºc, mixing time: 3 min.

efficiency. The results (Fig. 5) show that when 10 wt. % freshwater is added, demulsification performance is not enhanced by the addition of NPs, although demulsifier consumption is reduced by 50%. So, it is affordable to use 5 wt. % freshwater to achieve the highest efficiency.

Effect of Settling Time

The effect of settling time on desalting efficiency is shown in Fig. 6. It is observed that demulsification efficiency is increased by increasing the contact time. Although, the efficiency does not clearly change after 12 h. As can be seen in the figure, Fe_3O_4-

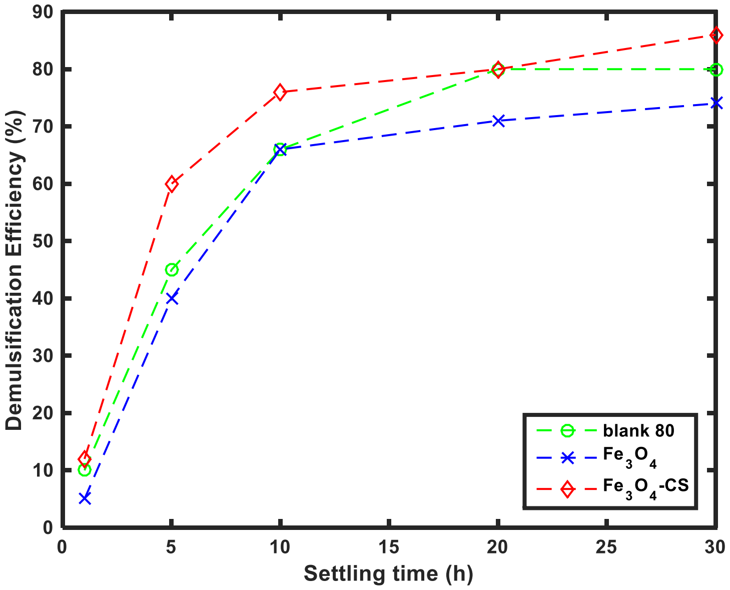


Fig. 6. Effect of settling time on the demulsification efficiency. Other conditions: freshwater: 5%, nanoparticles dosage: 0.04%wt, heat temperature: 70°c, mixing time: 3 min.

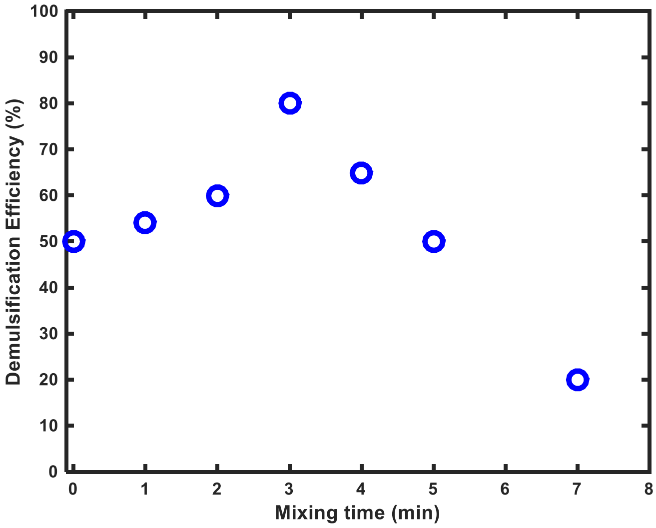


Fig. 7. Effect of mixing time on the demulsification efficiency. Other conditions: freshwater: 5%, nanoparticles dosage: 0.04%wt, heat temperature: 70°c: settling time: 12h.

chitosan nanoparticles have been able to increase the separation efficiency of chemical demulsifier by 15% compared to Fe_3O_4 nanoparticles.

Effect of Mixing Time

Mixing time is varied in the 0-7 min range and according to the results, if other parameters are kept constant, 3 min of vigorous mixing can result in the highest demulsification efficiency. Shorter mixing periods are insufficient to stabilize the water-oil mixture. Longer mixing times lead to very stable emulsions which are hard to separate (Fig. 7). Also, longer mixing times usually causes breakage of water and form smaller droplets, which is not desirable in the crude oil desalting process.

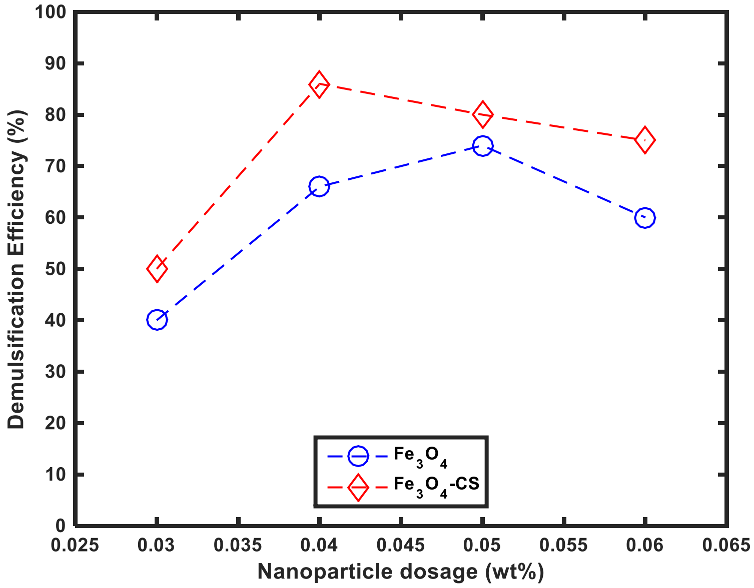


Fig. 8. Effect of nanoparticle dosage on demulsification efficiency. Other conditions: freshwater: 5%, settling time: 12h, heat temperature: 70°c, mixing time: 3 min.

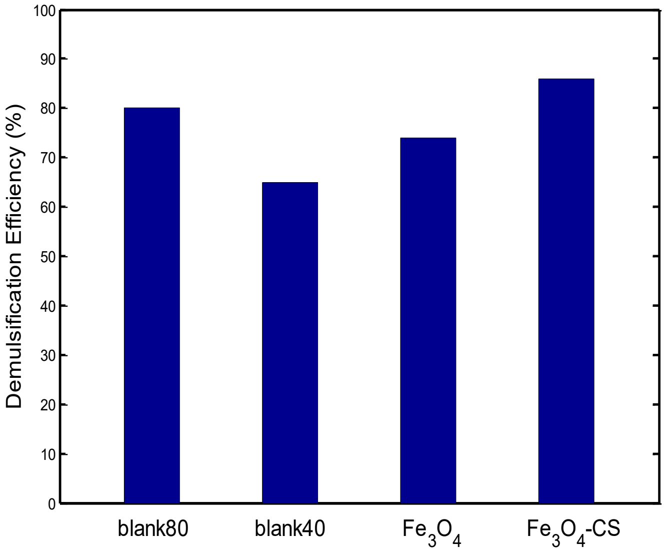


Fig. 9. The demulsification efficiency at the best conditions.

Effect of Nanoparticle Dosage

The effect of NP dose is shown in Fig. 8. This figure shows that there is an optimum value when adding NP at 0.004 wt. %. At higher NP contents, NP interactions are increased which reduce their interfacial activity, leading to lower demulsification efficiencies.

Fig. 9 shows demulsification efficiency at the best conditions by the bottle test method. According to this figure, addition of nanocomposite particles results in a 10 % enhancement of the demulsifier efficiency by reducing the demulsifier consumption up to 50%.

Electrostatic Separation

In this study, the electrostatic desalination pilot

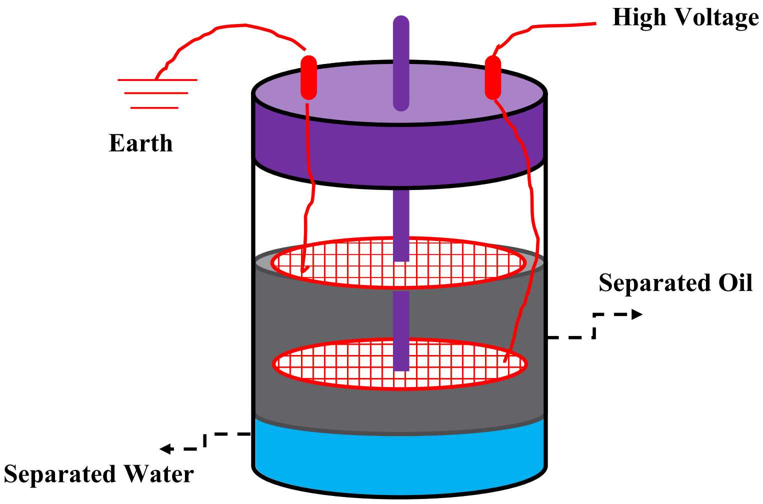


Fig. 10. Electrostatic separation efficiency.

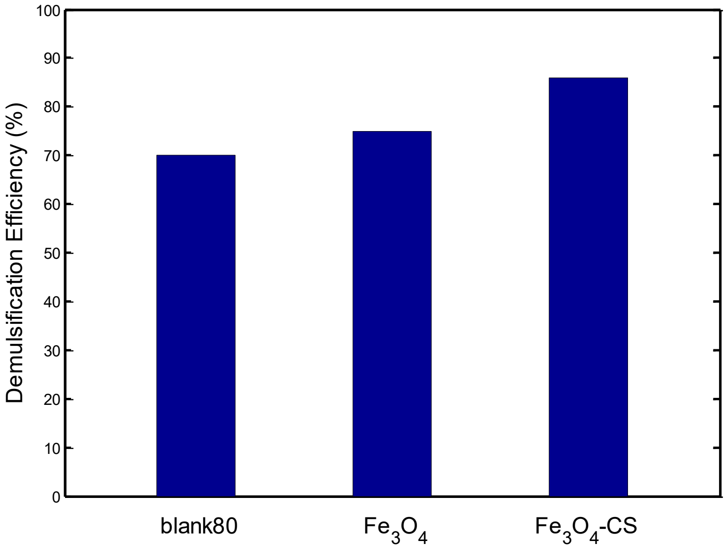


Fig. 11. Electrostatic demulsification efficiency.

was used to check the accuracy of the bottle test results under crude oil desalting plant operating conditions. As shown in Fig. 10, the system consists of two grid electrodes. The upper electrode is an earth electrode while the lower one is a high voltage grid electrode. The distance between the electrodes and device voltage can be adjusted so that the electric field can be set based on the emulsion type.

In the electrostatic test, a certain volume of crude oil is poured into a beaker and heated by a plate magnetic stirrer. Then, nano-particle, chemical demulsifier and freshwater were added respectively and perfectly mixed with the emulsion. Afterward, an electrical field of 1000 v/cm was applied to the produced mixture for 20 min. Finally, the height of separated water was measured to calculate the DE (%).

According to Fig. 11, the results indicate a significant increase in the demulsification efficiency which is higher in case of Fe_3O_4-chitosan nanoparticles. The electric current affects the surface tension and weakens the stable layer around droplets and causes coalescence. As can be seen in this figure, the efficiency of the desalting process with the new Fe_3O_4-chitosan demulsifier is increased by 15% compared to the conventional operating conditions.

Interfacial tension

Interfacial tension was measured for the demulsifier as well as after the addition of NP to the Fe_3O_4-chitosan. Pendant drop technique is used in this regard. The results demonstrate that the reduction of interfacial tension due to NP addition (22.53 mN/m) is almost equal to the industrial demulsifier (23.18 mN/m).

CONCLUSIONS

Bottle tests and electrostatic equipment were used to investigate the effect of magnetic Fe_3O_4 NPs and Fe_3O_4-chitosan nanocomposite on the oil desalting efficiency. NPs were synthesized and used at various concentrations. The as-produced nanocomposite exhibits a higher performance due to chitosan hydrophobicity. According to the bottle test, 5% water is added to crude oil along with 40 ppm injection of the commercial demulsifier as well as the addition of 0.004 wt% NPs provide the highest performance. At similar conditions, it was observed that the electrostatic test with an electric field of 1000 v/cm and 20 min residence time led to a significant improvement in the separation performance.

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The authors declare that they have no conflict of interest.

CONFLICT OF INTEREST STATEMENT

All authors declare that no conflicts of interest exist for the publication of this manuscript.

REFERENCES

1. Peng JX, Liu QX., Xu ZH, Masliyah J. Novel magnetic demulsifier for water removal from diluted bitumen emulsion. Energy Fuels. 2012; 26: 2705–2710.
2. Al-Otaibi M, Elkamel A, Al-Sahhaf T, Ahmed AS. Experimental investigation of crude oil desalting and dehydration. Chemical Engineering Communications. 2003; 190 (1): 65-80.
3. Li SQ, Li NX, Yang SB, Liu FY, Zhou JC. The synthesis of a novel magnetic demulsifier and its application for the demulsification of oil-charged industrial wastewaters. J. Mater. Chem. A. 2014; 2: 94–99.
4. McLean JD, Kilpatrick PK. Effects of asphaltene solvency on stability of water-in-crude-oil emulsions. J. Colloid Interface Sci. 1997; 189: 242-253.
5. Kraft DJ, Luigies B, de Folter JWJ, Philipse AP, Kegel WK. Evolution of equilibrium pickering emulsions-A matter of time scales. J. Phys. Chem. B. 2010; 114: 12257-12263.
6. Abdel-Aal HK, Aggour M, Fahim MA. Petroleum and Gas Field Processing. CRC Press Jul 1 (2003).
7. Ghannam MT. Water-in-crude oil emulsion stability investigation, Petroleum Science Technology. 2003; 23: 652-665.
8. Abdel-Raouf ME. Factors affecting the stability of crude oil emulsions, crude oil emulsions- composition stability and characterization, 2012; 190-194.
9. Lee RF. Agents which promote and stabilize water-in- oil emulsions. Spill Science Technology Bulletin. 1999; 5: 117-126.
10. Maruyama H, Seki H, Satoh Y. Removal kinetic model of oil droplet from o/w emulsion by adding methylated milk casein in flotation. Water Res. 2012; 46: 3094–3100.
11. Santo CE, Vilar VJP, Botelho CMS, Bhatnagar A, Kumar E, Boaventura RAR. Optimization of coagulation–flocculation and flotation parameters for the treatment of a petroleum refinery effluent from a Portuguese plant. Chem. Eng. J. 2012; 183: 117–123.
12. Eow JS, Ghadiri M. Electrostatic enhancement of coalescence of water droplets in oil: a review of the technology. Chem. Eng. J. 2002; 85: 357–368.
13. Zhou JE, Chang QB, Wang YQ, Wang JM, Meng GY. Separation of stable oil-water emulsion by the hydrophilic nano-sized ZrO_2 modified Al_2O_3 micro-filtration membrane. Sep. Purif. Technol. 2010; 75: 243–248.
14. Martínez-Palou R, Cerón-Camacho R, Chávez B, Vallejo AA, Villanueva- Negrete D, Castellanos J, Karamath J, Reyes J, Aburto J. Demulsification of heavy crude oil-in-water emulsions: a comparative study between microwave and thermal heating. Fuel. 2013; 113: 407–414.
15. Nour AH, Anisa ANI, Nour AH. Demulsification of water-in-oil emulsion via microwave irradiation: An optimization. Scientific Research Essays. 2011; 7: 231-243.
16. Nguyen D, Sadeghi N, Houston C. Chemical interactions and demulsifier characteristics for enhanced oil recovery applications. Energy Fuels. 2012; 26: 2742–2750.
17. Razi M, Rahimpour MR, Jahanmiri A, Azad F. Effect of a different formulation of demulsifiers on the efficiency of chemical demulsification of heavy crude oil. J. Chem. Eng. Data. 2011; 56: 2936-2945.
18. Bai ZS, Wang HL. Crude oil desalting using hydrocyclones. Chem. Eng. Res. Des. 2007; 85 (12): 1586-1590.
19. Riera-Franco de Sarabia E, Gallego-Juarez JA, Rodriguez G, Elvira-Segura L, Gonzalez-Gomez I. Application of high-power ultrasound to enhance fluid/solid particle separation processes, Ultrasonics. 2000; 38, 642.
20. Liang J, Du N, Song Sh, Hou W. Magnetic demulsification of diluted crude oil-in-water nanoemulsions using oleic acid-coated magnetite nanoparticles. Colloids and Surfaces A: Physicochem. Eng. Aspects. 2015; 466: 197-202.
21. Duan M, Ma YZ, Fang SW, Shi P, Zhang J, Jing B. Treatment of wastewater produced from polymer flooding using polyoxyalkylated polyethyleneimine. Sep. Purif. Technol. 2014; 133: 160–167.
22. Parvasi P, Khaje Hesamedini A, Jahanmiri A, Rahimpour MR. A comparative study on droplet coalescence in heavy crude oil emulsions subjected to microwave and ultrasonic fields. Separation Science Technology. 2013; 48: 1591-1601.
23. Parvasi P, Khaje Hesamedini A, Jahanmiri A, Rahimpour MR. A novel modeling and experimental study of crude oil desalting using microwave. Separation Science Technology.

2014; 49: 1029-1044.

24. Khajehesamedini A, Sadatshojaie A, Parvasi P, Rahimpour M. R., Naserimojarad M. M. Experimental and theoretical study of crude oil pretreatment using low-frequency ultrasonic waves, Ultrason. Sonochem. 2018; 48: 383-395.
25. Shokri A. Degradation of 4-Nitrophenol from industerial wastewater by nano catalytic Ozonation. Int. J. Nano Dimens. 2016; 7 (2): 160-167.
26. Shokri A, Mahanpoor K. Removal of Ortho-Toluidine from Industrial Wastewater by UV/TiO_2 Process, Journal of Chemical Health Risks. 2016; 6(3): 213-223.
27. Shokri A, Joshagani A H. Using Microwave along with TiO_2 for Degradation of 4-Chloro-2-nitrophenol in Aqueous Environment, Russian Journal of Applied Chemistry. 2016; 89(12): 1985–1990.
28. Saghi M, Shokri A, Arastehnodeh A, Khazaeinejad M, Nozari A. The photo degradation of methyl red in aqueous solutions by α-Fe_2O_3/SiO_2 nano photocatalyst, J. Nanoanalysis. 2018; 5(3): 163-170.
29. Mohadesi M, Shokri A. Treatment of oil refinery wastewater by photo-Fenton process using Box–Behnken design method: kinetic study and energy consumption, International Journal of Environmental Science and Technology. 2019; 16, 7349–7356.
30. Peng JX, Liu QX, Xu ZH, Masliyah J. Synthesis of interfacially active and magnetically responsive nanoparticles for multiphase separation applications. Adv. Funct. Mater. 2012; 22: 1732–1740.
31. Lemos BRS, Teixeira APC, Ardisson JD, Macedo WAA, Fernandez-Outon LE, Amorim CC, Moura FCC, Lago RM. Magnetic amphiphilic composites applied for the treatment of biodiesel wastewaters. Appl. Sci. 2012; 2: 513–524.
32. Lu A, Salabas EL, Schuth F. Magnetic nanoparticles: synthesis, protection, functionalization, and application. Angewanted Chemistry International Ed. 2007; 46: 1222–1244.
33. Hyeon T, Lee S, Park J, Chung Y, Na H. Synthesis of highly crystalline and monodisperse maghemite nanocrystallites without a size-selection process. J. American Chemical Society. 2001; 123: 12798-12801.
34. Wu W, He Q, Jiang C. Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies, Nanoscale Res. Lett. 2008; 3(11): 397–415.
35. Liang JL, Li HP, Yan JG, Hou WG. Demulsification of oleic acid-coated magnetite nanoparticles for oil-in-water nanoemulsions. Energy Fuels. 2014; 28: 6172–6178.
36. Nikkhah M, Tohidian T, Rahimpour MR, Jahanmiri A. Efficient demulsification of water-in-oil emulsion by a novel nano-titania modified chemical demulsifier. Chem Eng Res Des. 2015; 94:164–172.
37. Cuonga ND, Hoa TT, Khieu DQ, Lam TD, Hoa ND, Hieu NV. Synthesis, Characterization and comparative gas-sensing properties of Fe_2O_3 prepared from Fe_3O_4 and Fe_3O_4-chitosan. J. Alloys Compounds. 2012; 523: 120–126.
38. Nasirimoghaddam S, Zeinali S, Sabbaghi S. Chitosan coated magnetic nanoparticles as nano-adsorbent for efficient removal of mercury contents from industrial aqueous and oily samples. J. Industrial Engineering Chemistry. 2015; 27: 79–87.
39. Li GY, Jiang YR, Huang KL, Ding P, Chen J. Preparation and properties of magnetic Fe_3O_4–chitosan nanoparticles. J. Alloys Comp. 2008; 466: 451–456.
40. Nguyen DC, Tran TH, Dinh QK, Tran DL, Nguyen DH,Nguyen VH. Synthesis, Characterization and comparative gas-sensing properties of Fe_2O_3 prepared from Fe_3O_4 and Fe_3O_4-chitosan. J. Alloys Compounds. 2012; 523: 120-126.