Recyclable Amine-Functionalized Magnetic Nanoparticles for Efficient Demulsification of Crude Oil-in-Water Emulsions

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Abstract

Produced water from the oil and gas industry often contains stable crude oil-in-water emulsions that are typically difficult to treat with conventional separation methods. Amine-functionalized nanoparticles have demonstrated effective destabilization of the crude oil-in-water emulsions by associating with the natural surfactants present at the oil-water interface leading to separation of oil from water under an external magnetic field. Effects of magnetic demulsifier concentration, reaction time and initial oil content of emulsion on the demulsification efficiency were investigated. The demulsification efficiency of emulsions by developed magnetic demulsifier can reach as high as 99.7%. Our findings characterize the demulsification process as a function of nanoparticle concentration and elucidate the governing interactions between NH_2 -MNPs and emulsion droplets. Another important feature of this magnetic demulsifier is its capability to be recovered by solvent-washing and reused for subsequent demulsification cycles. The recovered magnetic demulsifier was proven to be effective in demulsifying O/W emulsion for at least 6 cycles, revealing its recyclability. Demulsification of O/W emulsions with NH_2 -MNPs has great potential as an efficient strategy for oil removal from produced water.

1. Introduction

Due to the rapid increase in demand for energy worldwide, produced wastewater generated during gas and oil production has significantly increased¹. Typically, treated produced water is either injected back into spent reservoirs or discharged into water streams as long as the concentration of oil or grease meets onshore or offshore discharge regulations. Because of increasing environmental concerns and the stringent regulations on the discharge of produced water into the surface water streams, efficient produced water treatment has become an important issue for the energy industry. Of the various constituents of produced water, removal of highly dispersed oil droplets in the aqueous phase is extremely difficult. Although water and oil are immiscible, stable oil-in-water (O/W) emulsions are formed during production due to the combination of shear stresses during fluid transport and the presence of naturally present surface-active components, such as inorganic/organic solids and neutralized naphthenic acids commonly found in crude oil.² Enhanced oil recovery (EOR) processes often further the formation of stable O/W emulsions due to the addition of chemicals, such as surfactants and polymers¹⁻². A great deal of effort has been made to develop effective and economic techniques, such as adsorption,³ air flotation,^{4,5} chemical demulsification,⁶⁻⁸ electrochemical methods,⁹ and filtration¹⁰⁻¹² to break these stable emulsions. During the produced water treatment, the majority of crude oil can be removed by methods mentioned above. However, the separation of crude oil at low concentrations from stable O/W emulsions remains a challenge.

Chemical demulsification is one of the most common methods to destabilize emulsions to separate crude oil from O/W emulsions. Chemical demulsifiers^{7,13} operate by removing the surface-active compounds at the O/W interface, thus destabilizing the O/W interface and enhancing the coalescence of oil droplets. Chemical demulsifiers employed for the treatment of

produced water are typically formulated with chemicals that contain solvents, surfactants, flocculants and wetting agents.² Although chemical demulsification has proven to be effective, limitations still exist. For instance, the chemical demulsifier dosage is difficult to control. At low concentrations, chemical demulsifiers may not effectively destabilize the O/W emulsions; versus at high concentrations, demulsifiers are undesirable for the treatment process since an excess amount of the demulsifier may also further stabilize the emulsions. Furthermore, compounds formulating the chemical demulsifier can remain in the oil or water phases, causing further contamination during treatment.² Even though there are significant advances in developing effective demulsifiers, there remains a demand for more environmentally friendly and economically competitive demulsifiers for disrupting crude oil-in-water emulsions during produced water treatment process.

Recently, magnetic demulsifiers have attracted much attention, due to their low cytotoxicity, good biocompatibility, interfacial activity provided by functionalized materials, and rapid response under the magnetic field.^{14–21} Magnetic demulsifiers can migrate to the O/W interface, imparting magnetic properties on the dispersed oil droplets, which makes the magnetic nanoparticle-oil droplet complex easily isolated from the continuous water phase upon the application of a magnetic field. Another important feature of magnetic demulsifiers is that they can be collected, recovered by solvent washing, and recycled for the subsequent cycles. One type of magnetic demulsifier, ethyl cellulose-grafted Fe_3O_4 , was developed and successfully employed to remove water from water-in-heavy bitumen emulsion and water-in-heavy naphtha emulsion.^{14,22} Other functional groups, such as oleic acid,¹⁸ PVP,^{17,23} polyester materials,²⁴ have been used on magnetic nanoparticles and employed to demulsify the oil-in-water emulsions. But the magnetic demulsifiers reported to date generally require harmful organic solvents, high

temperatures (above 200°C) for fabrication, or large concentration to achieve effective separation, which can be costly and environmentally unfriendly. Also, the majority of the magnetic nanoparticle systems mentioned above are designed to attach onto the suspended oil droplet and then removed with a magnetic field.

Amine dendrimer-based demulsifier has been proven to reduce the interfacial tension of the diesel-water interface and demulsify diesel-in-water emulsion successfully.^{25,26} However, appropriate handling the dendrimers with adsorbed oil droplets remains an issue since they cannot be efficiently collected and recovered. In this study, amine groups were coated on the surface of magnetic nanoparticles for demulsification of O/W emulsions. Here, we utilize amine-functionalized magnetic nanoparticles as a magnetic demulsifier to disrupt O/W interfaces at relatively low nanoparticle concentrations. This leads to an O/W separation in which the oil can be skimmed off on the top, and large oil-MNPs complexes can be separated by magnetic attraction. During MNP synthesis, an aqueous coating process was employed to functionalize amine group on the surface of magnetic nanoparticles, making the scale-up process easy, cost-effective and environmentally friendly. NH₂-MNPs were found to be an excellent demulsifier that efficiently separates crude oil from O/W emulsions upon the application of a magnetic field at specific MNP concentrations. Batch experiments were conducted to evaluate the demulsification performance of NH₂-MNPs for O/W emulsions. Effects of magnetic demulsifier concentration, reaction time and initial oil content on the demulsification efficiency were investigated. The highlight of this work is the report of efficient demulsification of contaminated water with as low as 0.12 wt% O/W, which is typically difficult to demulsify due to the stability of small O/W emulsions. Furthermore, the recyclability of the NH₂-MNPs is demonstrated with recovery studies, highlighting the stability of the amine-coating.

2. Experimental Section

2.1 Materials

Deionized water (DI-H₂O) with a resistivity of approximately 18.2 M Ω ·cm was obtained from Barnstead Nanopure water purification system (Thermo Scientific, Waltham, MA, U.S.A.). Iron chloride tetrahydrate (FeCl₂·4H₂O), iron chloride hexahydrate (FeCl₃·6H₂O), citric acid monohydrate, ammonium hydroxide, glacial acetic acid, 3-amino propyltriethoxysilane (APTES), sodium hydroxide (NaOH), hydrochloric acid (HCl), dichloromethane (DCM) and nitric acid were purchased from Sigma-Aldrich (St. Louis, MO, U.S.A.). All reagents were tested as received without further purification.

The model crude oil for this study was randomly selected from in-house oils. The crude oil used has a density of 0.814 g/cm³, API gravity of 41.7, and viscosity of 2.60 cP. Polyacrylic acid coated magnetic nanoparticles (PAS-MNPs) were purchased from Chemicell GmbH (Germany).

The test brine was prepared with 18.2M Ω •cm DI water and ACS grade NaCl ($\geq 99.0\%$) to a salinity of 1180 ppm, with a measured pH = 8.2.

2.2 Fabrication and characterizations of amine-functionalized magnetic demulsifier

Amine-functionalized magnetic demulsifier (NH₂-MNPs) was fabricated according to a procedure reported previously.^{27–30} Initially, magnetic nanoparticles (MNPs) were prepared by aqueous co-precipitation of iron chloride under an alkaline condition. Subsequently, an APTES coating process was employed to functionalize amine group on the surface of MNPs. A detailed methodology for preparation of the magnetic nanoparticles are described in Supporting Information.

To characterize the magnetic nanoparticles, transmission electron microscopy (JEM-1230, JEOL) was employed to observe the morphology of the as-synthesized magnetic nanoparticles. For sample preparation, one drop of the diluted nanoparticles, namely an aqueous nanoparticle suspension of 15 μl , was placed on a carbon-coated copper TEM grid and allowed to be air-dry. TEM images were obtained at a voltage of 80 kV.

Fourier transform infrared spectroscopy (FTIR) was used to characterize the surface chemical state of the as-prepared nanoparticles. FTIR was performed using a Thermo Scientific Nicolet Nexus 670 FT-IR spectrometer and Smart iTR with a diamond window (Thermo Fisher Scientific Inc., Waltham, MA). The powder sample was placed on the diamond window of the Smart iTR, and the spectra were recorded from 400 cm^{-1} to 4000 cm^{-1} .

Thermogravimetric analysis (TGA) was carried out on a Q-600 Simultaneous TGA/DSC from TA Instruments to determine the amount of amine coating on the surface of the fabricated nanoparticles. During measurement, the powder sample was heated from 50°C to 600°C at a constant rate of 10°C/min. The weight loss during heating indicated the decomposition of organic components on the surface of MNPs. The mass fraction of surface coating on MNPs was reported as the percentage loss of weight.

Superconducting quantum interference device (SQUID) was employed to determine the saturation magnetization of the synthesized magnetic nanoparticles. Magnetization measurements were taken at room temperature (300°K) on a Quantum Design MPMSXL SQUID magnetometer. Magnetization (M) as a function of applied magnetic fields (H), varying from -10 KOe to +10KOe, was recorded during the experiments.

Particle size distribution and zeta potential measurements in brine were measured using a Delsamax Pro (Beckman Coulter) dynamic light scattering (DLS) analyzer. The specific surface area of the particles was analyzed using the Brunauer-Emmet-Teller method (Quantachrome Autosorb-iQ-MP/Kr BET Surface Analyzer). All values reported were measured for at least three replicates. The morphology and hydrodynamic size distribution of NH₂-MNPs are presented in Figure 1 (A). According to the TEM images, the amine functionalized magnetic nanoparticles exist as nano-clusters, consisting of many individual nanoparticles. The majority of nanoparticles were polygonal with rough surfaces, which is in agreement with previous observations.³¹ As shown in the DLS result, insert of Figure 1 (A), the average hydrodynamic diameter of the nanoclusters in DI-H₂O is approximately 102.1±1.3 nm. The BET measured surface area was determined to be 132.8 m²/g and the zeta potential of the particles in brine was measured to be +18.5 ± 0.3 mV.

Figure 1. Characterizations of the magnetic demulsifier NH₂-MNPs. TEM images and hydrodynamic size distribution (A), Langevin curves of MNPs and NH₂-MNPs (B), FTIR spectra of MNPs and NH₂-MNPs (C), TGA curves of MNPs and NH₂-MNPs (D)

The Langevin curves of MNPs and NH₂-MNPs were presented in Figure 1 (B). The absence of hysteresis on the Langevin curves indicates that the magnetic nanoparticles are superparamagnetic, which means that the nanoparticles do not retain magnetization in the absence of a magnetic field. The saturation magnetizations (M_s) of MNPs and NH₂-MNPs are 64 emu/g and 55 emu/g, respectively. Compared to MNPs, the M_s value of NH₂-MNPs is reduced due to the non-magnetic surface coating.

As shown in Figure 1 (C), surface chemistry of MNPs and NH₂-MNPs was characterized by ATR-FTIR. A peak appears at the wavenumber of 1610 cm⁻¹, which corresponds to N-H

bending vibrations of the primary amine. Si–O–Si out of plane bending was present in the amine-coated nanoparticles, as evidenced by a broad peak at 530 cm^{-1} . The FTIR result shown above indicates that amine group was successfully grafted onto the surface of MNPs via silane-linking chemistry.

As indicated in Figure 1 (D), the mass fraction of surface coating on magnetic nanoparticles was reported as the percentage of weight loss. A continuous weight loss was observed for both MNPs and NH_2 -MNPs when the temperature ramped from 50°C to 600°C . The overall weight loss of the MNPs is approximately 5.3%, which includes the physically and chemically adsorbed water, as well as the citric acid added to stabilize the magnetic nanoparticles. The total weight loss for NH_2 -MNPs is 8.5% and subtracting the weight loss due to the decomposition of the components conjugated on the MNPs, the mass fraction of the amine functional groups on the magnetic nanoparticles is 3.2%.

2.3 Preparation of crude oil-in-water emulsion

The O/W emulsion consisted of crude oil and brine (salinity=1180 ppm and pH=8.2). During preparation, crude oil and brine were mixed by a Branson probe sonifier at 20% amplitude for 2 minutes. In a typical experiment, the O/W emulsion contain 5 vol.% of crude oil, and any significant change of the average droplet size was observed within the experimental time period. Size distribution and zeta potential measurements of the O/W emulsions were measured using DLS. The emulsion size distribution was determined to be $402.3 \pm 167.5\text{ nm}$ and the zeta potential of the O/W emulsion was measured to be $-33.8 \pm 5.2\text{ mV}$.

2.4 Demulsification test

For the demulsification tests, a prescribed amount of NH_2 -MNPs (NH_2 -MNPs in DI- H_2O) was mixed with freshly prepared O/W emulsion at a volume ratio of 1:1 on a mechanical shaker for 30 minutes at 180 rpm. After applying an external magnetic field, the magnetic nanoparticle tagged oil droplets were separated from the water phase by the magnetic field. One example of a successful demulsification tests is illustrated in Figure 2. The demulsification capability of NH_2 -MNPs was determined by the difference between the initial oil concentration in the O/W emulsion and the residual oil concentration in the separated water. All demulsification tests were conducted at room temperature ($\sim 23^\circ\text{C}$).

Figure 2. The process of O/W-emulsion demulsification by the magnetic demulsifier. Red-O dye was added to the oil phase for better visualization

The initial oil concentration in the emulsion and residual oil concentration in the separated water were measured by gas chromatography with flame ionization detector (GC-FID). Dichloromethane (DCM) was used to extract oil from the separated water phase. GC-FID analysis was performed on an Agilent gas chromatograph Model 7890A equipped with an FID and an autosampler (Agilent 7683B). The analytical column was SUPELCO SPB-5 (60 m $\times$ 0.32 mm I.D., film thickness 1 μm). High-purity helium (99.9%) at a constant flow rate of 3.15 mL/min was the carrier gas. The oven temperature was initially held at 50°C for one minute, and

then ramped to 180°C at a rate of 15°C/min, followed by reaching 320°C at a rate of 30°C/min and held isothermal at 320°C/min for 20 minutes. The duration of the total run was about 35 minutes. Hydrocarbons were monitored before and after the magnetic separation. Peak quantification, counting the total area under the curve, yielded the hydrocarbon concentration in each sample. The demulsification efficiency was calculated from the initial oil concentration in the emulsion (C_0) and the residual oil concentrations in the separated water (C_e) by E_D (%) = $[(C_0 - C_e)/C_0] \times 100$.

2.5 Nanoparticle-Emulsion Interactions

Heterocoagulation describes the aggregation of oppositely charged colloidal dispersions that are either of the same or different sizes and are composed of either the same or different materials.³² Typically, these systems are governed by charge neutralization due to oppositely charged particles. In order to characterize particle-droplet heterocoagulation, the interaction energy between the NH₂-MNPs and the emulsion droplets is calculated using an extended Derjaguin-Landau-Verwey-Overbeek (DLVO) theory described by Hogg et al.³³⁻³⁴ The potential energy for the interaction of two dissimilar spherical electrical double layers, V_{EDL} , corresponding to a separation distance, h is given by:

$$V_{EDL} = \frac{\epsilon_o \epsilon_r}{4} (a_1^{-1} + a_2^{-1})^{-1} (\psi_1^2 + \psi_2^2) \left\{ \frac{2(\psi_2/\psi_1)}{1 + (\psi_2/\psi_1)^2} \ln \left(\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right) + \ln (1 - \exp(-2\kappa h)) \right\} \quad (1)$$

where ϵ_o = permittivity of free space, $8.856 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$, ϵ_r = relative permittivity (80 for water), a_1 and a_2 are the radii of particle and droplet respectively, ψ_1 and ψ_2 are the surface potentials of the particle and droplet respectively, and κ is the Debye-Huckel parameter, which is the inverse Debye screening length (κ^{-1}), defined as:

$$\kappa^{-1} = \left(\frac{\epsilon_0 \epsilon_r k_b T}{e^2 \sum_i c_i z_i^2} \right)^{\frac{1}{2}} \quad (2)$$

Where c_i refers to the concentration in molar units,

k_b = Boltzmann's constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$), T = temperature (298 K), z = valency of ion species, e = charge on electron ($-1.6 \times 10^{-19} \text{ C}$).

The corresponding van der Waals interaction energy is given by:

$$V_{\text{VDW}} = - \frac{A_{121} a_1 a_2}{6h(a_1 + a_2) \left(1 + \frac{14h}{\lambda} \right)} \quad (3)$$

where A_{121} is the Hamaker interaction parameter between two particles interacting across a medium, given by $A_{121} = \left(\sqrt{A_{22}} - \sqrt{A_{11}} \right)^2$, with A_{11} = Hamaker constant for particle (1) and A_{22} = Hamaker constant of the droplet, h = distance of separation, and " λ " is the characteristic wavelength associated with interactions. Gregory showed these effects to be of electromagnetic origin, prevalent at dimensions well below 100 nm.^{35, 36} It is noteworthy that at λ values over 100 nm, h/λ approaches zero and the expression in Eq. 3 reduces to the familiar form for van der

Waals interactions between two spherical colloidal particles^{36, 37}: $V_{\text{VDW}} = - \frac{A_{121} a_1 a_2}{6h(a_1 + a_2)}$. For the

scenario where NH_2 -MNPs are emulsion droplets, $A_{11} \sim 0.9 \times 10^{-20} \text{ J}$ and $A_{22} \sim 4 \times 10^{-20} \text{ J}$. Hence, $A_{121} = 1.1 \times 10^{-20} \text{ J}$.³⁸

2.6 MNP recovery test

To evaluate the reusability of the magnetic demulsifier, NH_2 -MNPs were separated from the aqueous phase by an external magnetic field after the demulsification test, and recovered by solvent washing. The collected NH_2 -MNPs were washed twice with 1 mL ethanol to remove

contaminants and crude oil residues, and washed twice with 1 mL DI-H₂O to remove excess ethanol. The cleaned magnetic nanoparticles were then resuspended in water by ultra-sonication, and used for the subsequent demulsification test. In the current study, 6 cycles were conducted to study the recovery of the magnetic demulsifier.

3. Results and Discussion

3.1 Demulsification of O/W emulsions by magnetic demulsifier

The demulsification capability of magnetic nanoparticles with different surface coatings was compared as shown in Figure 3A. Three types of magnetic nanoparticles with different surface coatings were used in this study, which are MNPs, NH₂-MNPs and polyacrylic acid functionalized MNPs (PAS-MNPs). During demulsification experiments, 5-mg/mL MNP suspension was added to 5 vol.% O/W emulsion with a volume ratio of 1:1. After mixing for 2 hours, the mixture was settled on a permanent magnet at room temperature, and the oil content in the separated emulsion (or water) layer was analyzed by GC-FID. To rule out the effects of mechanical shaking and dilution on emulsion-demulsification, an equal volume of DI-H₂O was added into the O/W emulsion (denoted as shaking), and the oil concentration in the emulsion layer was determined after 2 hours shaking. As indicated in Figure 3B, the oil content of the emulsion layer slightly reduced from 2.57 wt% to 2.01 wt% after 2 hours shaking. With the addition of MNPs and negatively charged PAS-MNPs ($\zeta = -32.1$ mV at pH 8), the oil content in the emulsion layer was reduced to 1.50% and 1.82% respectively, suggesting that MNPs and PAS-MNPs are virtually ineffective for demulsification of crude oil-in-water emulsions. However, followed by adding NH₂-MNPs ($\zeta = +18.5$ mV at pH 8) into the O/W emulsion and mixing for 2 hours, a clear water layer was instantly obtained after applying the external magnetic field. According to GC-FID analysis, the oil content dramatically decreased to 0.03%,

indicating a demulsification efficiency of 98.8%. According to the test results discussed above, NH_2 -MNPs are effective in destabilizing the O/W emulsion, presumably due to the electrostatic attraction between positively charged NH_2 -MNPs and negatively charged oil droplets (carboxyl group on the natural surfactant naphthenic acid in the crude oil).

Figure 3. Demulsification of O/W emulsion by different types of magnetic nanoparticles, including MNPs, PAS-MNPs, and NH_2 -MNPs (A) ; oil content remained in the emulsion layer at each condition (B); Real-time observation of an emulsion-globule destabilized by NH_2 -MNPs (C). Scale bar: 50 μm .

An optical microscopy study was conducted to further prove that the amine groups coated on the nanoparticles are effective at disruption the O/W interface. Prior to the microscopy observation, emulsion was prepared by adding one drop of crude oil into brine followed by vortexing. Due to the presence of natural surfactant and other component like asphalts, the emulsion obtained here might not be the ideal single O/W emulsion. Then the emulsion was diluted by the corresponding brine and placed onto a glass slide, where oil globules containing many aqueous droplets with

different sizes were initially observed. After adding MNP suspension with a concentration of 0.1 mg/mL, destabilization of oil globule occurred as shown in Figure 3C. With the presence of NH₂-MNPs, the oil-globule was found to burst, and a halo of oil appeared at 17 s, indicating that the W/O layer was disrupted and oil-film spread on the air-liquid interface. From 17 s to 33 s, subsequent external coalescence of aqueous droplets progressively decreased the diameter of the emulsion-droplet. All these destabilization phenomena are due to the association between MNPs and natural stabilizer in crude oil.

3.2 Effect of NH₂-MNP-concentration on the demulsification efficiency of crude oil from O/W emulsion

To validate the performance of NH₂-MNPs as a magnetic demulsifier, a crude oil emulsion with 5 vol.% oil content was utilized. The demulsification efficiency of NH₂-MNPs was determined by using GC-FID to examine the crude oil content in the separated water. During this experiment, the NH₂-MNP-concentration with respect to the total volume of O/W emulsion was varied from 0 mg/mL to 1 mg/mL. After mixing for 24 hours, samples were allowed to undergo phase separation, and a permanent magnet was used to recover magnetic nanoparticles with trapped oil droplets. Figure 4A is to indicate the effect of NH₂-MNP-concentration on demulsification efficiency of O/W emulsion at room temperature (~23°C). A concentration increase of the magnetic demulsifier results in a gradual increase of the demulsification efficiency, followed by reaching a plateau. The optimal NH₂-MNP concentration was determined to be 0.4 mg/mL, defined as the lowest concentration at which 98% demulsification efficiency is observed. Since NH₂-MNPs have a high affinity for the natural surfactants on the oil-in-water interface during the demulsification process, the optimal concentration of NH₂-MNPs for O/W-emulsion demulsification is highly dependent on the specific surface area and size of the oil droplets.

Figure 4. Effect of NH_2 -MNP-concentration on a emulsion containing 5 wt% crude oil (A) and mixing time (B) on demulsification efficiency from O/W emulsions. Experiments were conducted at room temperature ($\sim 23^\circ\text{C}$). After mixing the MNP suspension and emulsion, the clear water layer was sampled after magnetic separation, from which the oil contents were extracted by dichloromethane and analyzed by GC-FID.

To further quantify demulsification efficiency as a function of the concentration of NH_2 -MNPs, Langmuir and Langmuir-Freundlich (Sips) isotherms, were adopted to estimate the maximum demulsification of NH_2 -MNPs at the experimental condition.³⁹⁻⁴⁰ As shown by calculations provided in the Supporting Information, the predicted maximum adsorption capacity was estimated to be 1.49×10^5 mg/g, indicating that 1 gram of NH_2 -MNPs can demulsify approximately 149 gram of crude oil. This large value illustrates the superior capability of NH_2 -MNPs for demulsifying oil droplets, which is due to the robust surface functionalization of the nanoparticles.

3.3 Rate of demulsification by NH₂-MNPs

Experiments were performed to investigate the rate of demulsification of O/W emulsion with each curve representing a specific NH₂-MNP concentration. During an experiment, NH₂-MNPs at a prescribed concentration was added into the O/W emulsion with an oil content of 5 vol.% at a volume ratio of 1:1. Followed by mechanically shaking for a period of time varying from 10 minutes to 24 hours, phase separation between the water and oil phases were observed upon application of the magnetic field. The residual crude oil in the separated water was extracted by dichloromethane and analyzed by gas chromatography with flame ionization detector (GC-FID).

As indicated in Figure 4B, for a relatively low NH₂-MNP concentration, e.g. 1.25 mg/mL, the demulsification efficiency is 6.2% and 18.0% for the mixing time of 0.5 and 1 hour, respectively. When the mixing time is extended to 6 hours, the demulsification efficiency of NH₂-MNPs significantly increases to 91.3%, and increased to 98.7% at 24 hours. This is indicative of a contact time required for the MNPs to reach the interface of oil droplets. As the concentration of NH₂-MNPs increases, the contact time decreases and demulsification occurs more rapidly. For a relatively high NH₂-MNP concentration, e.g. 7.5 mg/mL, the demulsification efficiency can reach 98.4% within 10 minutes, and then slowly increases up to 99.7% at 24 hours. These results illustrate how effective NH₂-MNPs are at demulsifying crude oil-in-water emulsions within a short time interval at ambient conditions.

3.4 Effect of initial oil content on the demulsification efficiency of NH₂-MNPs

The effect of the initial oil content on demulsification efficiency upon adding NH₂-MNPs was also studied. Experiments were performed to evaluate the demulsification efficiency using both low oil-content emulsions and high oil-content emulsions. The test results in Figure 5 reveal a

slight removal of crude oil by mechanical shaking (without adding NH_2 -MNPs), as indicated by the difference between the split line and blue square symbol. With mechanical shaking of emulsions for 24 hours, a maximum demulsification efficiency of 28.5% was obtained for all oil concentrations studied. After adding 5 mg/mL MNP aqueous suspension into the crude oil emulsions with a volume ratio of 1:1, a significant reduction in residual oil concentration was observed for both low oil-content emulsions (below 0.1 wt.%) and high oil-content emulsions (up to 30 wt.%), as indicated by the red diamond symbols. For produced water with an initial oil concentration of 0.12 wt%, the demulsification efficiency was 91.7%. Separation efficiencies typically fall off as the initial oil content decreases, due to stable oil droplets with a higher specific surface area. Mechanical methods and many chemical methods are typically unable to separate such low oil fractions from water. These test results further prove that NH_2 -MNP is an effective demulsifier for both low-oil content and high-oil content emulsions.

Figure 5. Effect of initial oil content on demulsification efficiency from the O/W emulsions with NH_2 -MNPs. Both high oil content (2.5 wt.% ~15 wt.%) and low oil content (0.12 wt.% ~2 wt.%) emulsions are studied with 5 mg/mL NH_2 -MNPs addition and without NH_2 -MNPs addition.

3.5 MNP recovery tests

The demulsification efficiency was significantly improved by surface modification of magnetic nanoparticles with amine functional group. Unlike a conventional chemical demulsifier, the functionalized magnetic demulsifier can be recovered and reused, which is environmentally friendly and cost-effective for the treatment of produced water. After each usage of NH_2 -MNPs, the crude oil was separated from the water phase by the application of the magnetic force, recovered, and washed alternatively with ethanol and water two times to remove any crude oil trapped within the MNPs and used for the subsequent demulsification tests. According to our study, the magnetic nanoparticle suspension with the concentration of 1 mg/mL can be used to destabilize 5 vol.% O/W emulsion for at least 6 times. As indicated in Figure 6, for 6 cycles tested by GC-FID, the demulsification efficiency was constant at above 96%, suggesting that NH_2 -MNPs have high demulsification efficiency and reusability after recovery.

Figure 6. Demulsification efficiency of recovered NH_2 -MNPs (NH_2 -MNP concentration=1 mg/mL; 5 vol.% crude oil emulsion; volume ratio of NH_2 -MNP and emulsion=1:1; room temperature)

3.6 Demulsification of emulsion droplets by NH₂-MNPs

The stability of crude oil-in-water emulsions is due to the interfacially active components, such as neutralized naphthenic acid, that provides a strong repulsive interaction between emulsion droplets, hindering coalescences.⁴¹⁻⁴² Analysis of the interaction energy between NH₂-MNPs and the emulsion droplets based on Eqns (1-3) is shown in Figure 7.

Figure 7. Net DLVO Interaction Energy for between NH₂-MNPs and the crude oil emulsion droplets.

At the tested conditions, the net interaction energy is attractive at short distances of separation. Therefore, the key to demulsification of stable O/W emulsions is to diminish the repulsive force between oil droplets, finally leading to oil-water phase separation. Magnetic nanoparticles with amine functionalized group have an excellent stability in the aqueous phase with $\zeta = +18.5$ mV at pH 8, and can be uniformly dispersed in the aqueous phase. Once NH₂-MNPs are added into the emulsion followed by vigorous shaking, the magnetic nanoparticle-oil droplet complex will form due to the electrostatic attraction between the positively charged magnetic nanoparticles and the oil droplets with an opposite surface charge (-32.2 mV at pH 8). The decrease of the repulsive

force will induce the coalescence of small oil droplets to form big ones. After the application of a magnetic field, the magnetic-nanoparticles-tagged oil droplets can be successfully separated from the water phase. However, depending on the quantity of NH₂-MNPs added into the emulsion, the coalesced oil droplets might either migrate to the air/water interface or be entrapped within the magnetic nanoparticle complexes and attracted towards the direction of the magnetic field.

Figure 8. Transport of NH₂-MNPs governed by magnetic, buoyancy, and drag forces. The scale bars in the microscopy images represent 100 μm .

The transport of the NH₂-MNPs is driven by the competition of the forces acting on the oil droplet-MNP complex, shown in Figure 8, and described as⁴³

$$m \cdot a = \overrightarrow{F_b} + \overrightarrow{F_{drag}} + \overrightarrow{F_m} \quad (4)$$

where m is the mass of the MNP-oil droplet complex (g), a is acceleration (m/s^2), F_b is buoyancy force (N), F_{drag} is drag force (N) and F_m is the magnetic force (N) acting on the nanoparticles

adsorbed on the O/W interface. As $F_b - F_{drag} - F_m > 0$, the coalesced oil droplets tend to migrate to the air/water interface since buoyancy dominates. The lower concentration of MNPs in the system results in a less coverage of nanoparticles on the O/W interface. On the other hand, as $F_b + F_{drag} - F_m < 0$, the coalesced oil droplets will move towards the direction of the magnetic field since the coverage of nanoparticles on the O/W interface is large due to a high MNP concentration. For instance, to demulsify 5 vol.% O/W emulsion, when the concentration of NH₂-MNPs is 0.5 mg/mL, a significant amount of oil will separate from the oil after placing the magnet next to the reaction vial, as shown in Figure 8. Here, Red-O, an oil-soluble dye, was added into the oil phase for better visualization. When the MNP concentration is relatively high, e.g. 12.5 mg/mL, the majority of the oil phase will be entrapped inside the MNP-complex and attracted towards the direction of the magnetic field. Therefore, another advantage of functionalized magnetic nanoparticles as demulsifier is that the amount of NH₂-MNPs for oil removal can be manipulated to meet the demands of particular applications. The proposed MNP transport is further confirmed by images taken by an optical microscope. As shown in Figure 8, oil droplets are surrounded by aggregated MNPs to form the network of oil droplets and nanoparticles in the top layer, where the oil droplets and the nanoparticles can be removed by skimming method. For the optical images obtained from the bottom layer, oil droplets were entrapped within larger nanoparticle aggregates, thus allowing the separation of oil droplets from water by magnetic separation instantly.

For the demulsification-recovery process by NH₂-MNPs, experimental results indicate that the functionalized magnetic nanoparticles can have an immediate interaction with oil droplets stabilized by interfacially active components, leading to the rapid separation of oil droplets from the water phase. In the absence of a magnetic field, separation does occur, but at a much slower

timescale (data shown in Supplemental Information). Furthermore, the collected magnetic nanoparticles can be easily recovered by solvent washing and magnetic separation, and therefore recovered and reused for subsequent cycles, indicating that NH₂-MNPs have excellent stability and reusability after recovery. Such proposed process provides an eco-friendly and efficient strategy for oil removal from produced water.

4. Conclusion

The magnetic demulsifier with magnetic nanoparticles as the core and amine as the functional group was synthesized by co-precipitation of iron chloride followed by an aqueous APTES coating process and employed to investigate the demulsification of crude oil-in-water emulsions. It was found that the addition of NH₂-MNPs into the O/W emulsions results in a separation of the oil phase and water phase at a specific nanoparticle concentration upon the application of a magnetic field. Such effective destabilization of O/W emulsions is attributed to the electrostatic repulsion between negatively charged crude oil droplets and the magnetic nanoparticles with an opposite surface charge. The demulsification efficiency can reach as high as 99.7%, and is affected by factors, such as NH₂-MNP concentration, reaction time and initial oil concentration. Another significant feature of NH₂-MNPs as demulsifier is their capability to be recovered by solvent washing and reused for subsequent demulsification processes while remaining effective. In this study, after six cycles of testing, the demulsification efficiency remained above 95%, indicating excellent stability and reusability after recovery. The effective demulsification of crude O/W emulsions and reusability of NH₂-MNPs offers great potential in the treatment of produced or contaminated water from oil and gas processing.

ASSOCIATED CONTENT

Supporting information

Details of fabrication of amine functionalized magnetic nanoparticles and the video of oil and water separation by magnetic nanoparticles are shown in the Supporting Information. The Supporting Information is available free of charge on the website.

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