



Full Length Article

Recyclable magnetic graphene oxide for rapid and efficient demulsification of crude oil-in-water emulsion



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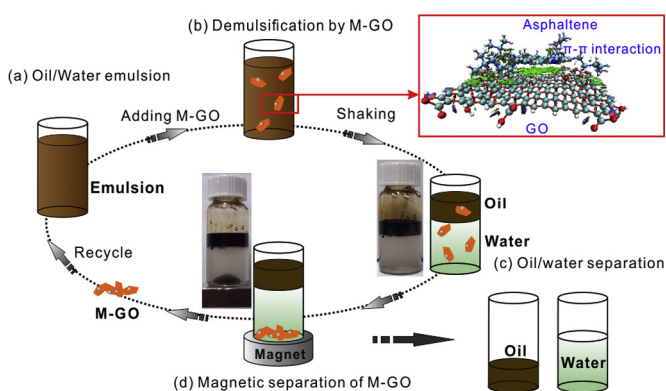
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HIGHLIGHTS

- The M-GO was a high efficiency demulsifier which could be reused for 6–7 times.
- The non-covalent interaction analysis proved that π - π and σ - π interactions between GO materials and asphaltene molecules are the major driven forces for demulsification.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene oxide (GO) nanosheets have been experimentally proved to be a highly efficiency, rapid and universal demulsifier to break up the crude oil-in-water emulsion and/or the emulsified oily waste water in our previous study. To recycle the GO nanosheets and avoid the possible contamination of GO for crude oil, in this work, the magnetic graphene oxide (M-GO) was successfully synthesized and used for separating oil/water emulsions. Demulsification tests indicated that M-GO could separate the oil/water emulsions within a few minutes and recycle 6–7 times without losing its demulsification capability. The residual oil content in the separated water was as low as ~ 10 mg/L, corresponding to a demulsification efficiency of 99.98% at an optimal dosage. Quantum chemical calculation results indicated that the π - π/σ - π interactions between GO materials and asphaltene molecules are the major driven forces for the high demulsification performance of M-GO nanosheets. This work not only provides a promising demulsifier to demulsify the crude oil-in-water emulsion or the oily wastewater but also give a deep understanding on the intrinsic interaction between demulsifiers and asphaltenes.

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1. Introduction

In order to meet the increasing energy demand, a host of policies has been made to encourage exploiting the unconventional oil resources including the heavy oil, oil sands and oil shale [1].

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Water blending has become one of important strategies in many mining processes [2], such as the tertiary oil recovery, water-based bitumen extraction processes [3] and heavy oil viscosity reduction technology [4]. These processes generally involved the exploiting and subsequent refinery operations, and would produce large amount of oil-in-water (O/W), water-in-oil (W/O) emulsions and/or emulsified oily wastewater. The produced oil-water emulsions are highly undesirable in petroleum industry because of their high corrosion to the pipe surface and distillation equipments, high toxicity to the catalysts in refining processes, and serious pollution problems to environment. High efficiency demulsification of oil-water emulsions through various strategies is therefore of significant importance for petroleum industry. Till now, the demulsification of W/O emulsions has been considerably investigated and can be successfully realized by adding several types of chemical demulsifiers such as PAMAM-polyether [5], ethylene oxide/propylene oxide block copolymer [6], silicone surfactant [7], ethylcellulose polymer [8], alkoxyated alkyl phenol formaldehyde resin [9], and ionic liquid [10]. In contrast, the O/W emulsion has been one of worldwide challenges because of its increasing production from the oilfields and the serious contaminations resulted from oily wastewater [11]. Considerable efforts were thereby devoted to demulsify the O/W emulsions. The oil-water mixture can be classified into two types, namely, the oil-water suspension with free or dispersed oil droplet ($d > 20 \mu\text{m}$) suspended in water and O/W emulsion with oil droplet size of $d < 20 \mu\text{m}$. The former oil-water suspension, can be easily separated through the gravity separation, centrifugation, ultrasonic strategies and/or employment of superhydrophobic and superoleophilic adsorbent materials. While for the latter O/W emulsion, due to the small size of oil droplet and highly stable oil-water interface protective film, it is more difficult to separate the oil droplet from O/W emulsion. Attempts have been carried out to separate the oily wastewater by using membrane or filtration technology [12–16]. However, these techniques still have disadvantages of low separation efficiency, long separation time, and usage of special equipments with high cost and extremely large size. Moreover, these techniques would generate secondary pollutants, fouling problems, and poor regeneration/recyclability, limiting their practical application in oil/water separation [17]. Therefore, it is necessary to develop a simple but effective method for separating O/W emulsions with high separation efficiency, short separation time.

In recent study, we develop a simple but effective demulsification method for fast separating the O/W emulsions by using graphene oxide (GO) nanosheets as demulsifier [18]. The developed GO demulsifier demonstrates a demulsification efficiency of 99.9% and extremely low residual oil content (30 mg/L) in separated water at a lower dosage of 20–100 mg/L. Moreover, the whole demulsification process can be completed within several minutes. Despite the fast and high separation efficiency, after separation, the GO demulsifier stably exist in aqueous or oil phase in the form of nanosheets, which either would bring the contamination to water or oil in the subsequent refinery operation. Therefore, some measurements must be taken to recycle the GO nanosheets to minimize the contamination of GO and simultaneously reduce the demulsification cost.

Magnetic nanoparticles (MNPs) are of great interest for researchers due to their applications in most fields, such as biotechnology/biomedicine, catalysis, contrast enhancement of magnetic resonance imaging, environmental remediation and magnetic separation [19]. For example, anchoring the MNPs ($\gamma\text{-Fe}_3\text{O}_4$ and $\gamma\text{-Fe}_2\text{O}_3$) on host materials would endow them with excellent magnetism for magnetic separation. This strategy has been successfully used to separate host materials from the complex mixtures, such as the biomaterials [20] including cell, bacteria, protein, DNA, wastewater [21] and emulsions [19,22].

Inspired by the successful applications of MNPs in magnetic separation, in present study, we attempt to decorate the GO nanosheets with MNPs to recycle the GO nanosheet after the demulsification tests with the aid of external magnetic field. To prevent the self-aggregation of MNPs and increase their anti-corrosion performance in different chemical, before grafting to GO nanosheets, a thin layer of silica film was deposited on MNPs surface to stabilize them and provide a desirable surface for further amino-functionalization. Through the chemical reaction between the functional groups on GO nanosheets and amino-group on silica-stabilized MNPs, we successfully synthesize the silica-stabilized magnetic $\gamma\text{-Fe}_2\text{O}_3\text{-GO}$ composite (M-GO) for demulsifying of O/W emulsions. The developed M-GO could separate the oil/water emulsions within a few minutes and demonstrate a high demulsification efficiency of 99.98% with an extremely low residual oil content of $\sim 10 \text{ mg/L}$ in separated water. More importantly, the M-GO can be recycled within few seconds under an external magnetic field and repeated usage for 6–7 times without losing its demulsification capability, suggesting a fast a low-cost demulsification method.

2. Materials and methods

2.1. Materials

Graphite (synthetic powder, $< 20 \mu\text{m}$, Sigma-Aldrich), (3-Aminopropyl) triethoxysilane (3-APTES, Aladdin Reagent, Shanghai, China), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl, GL Biochem, Shanghai, China), and N-Hydroxy succinimide (NHS, Kefeng Chemical Reagent, Shanghai, China) were directly used without further treatment. The crude oil sample was provided by Tahe oilfield (Xingjiang Province, China). The physiochemical properties of the oil sample were reported in our previous work [18]. The iron carbonyl ($\text{Fe}(\text{CO})_5$) (Zhongke Haorong New Material Research Co., Ltd., Changchun, China) were used to prepare magnetic ferrite. The Kerosene was obtained from local gas station of Sinopec (Lanzhou, China). Ultrapure water ($18.25 \text{ M}\Omega \text{ cm}$) was used throughout the experiments.

2.2. Preparation of M-GO

The synthesis processes of M-GO by a covalent strategy were illustrated in Fig. 1(a). In the process, the iron carbonyl was used to prepare magnetic ferrite by using the oxidization/decomposition method. The magnetic ferrite was then coated with a layer of silica to improve the chemical stability and to make the surface amenable for further functionalization. The silica shell was subsequently modified with organic silane coupling agent (3-APTES) to render a surface of amine groups. Finally, the GO nanosheets (prepared by a modified Hummers method [23]) reacted with the amine groups on the amino-functionalized magnetic particles to form the magnetic GO nanosheets (the details of preparation and characterization of various magnetic nanoparticles are given in the [Supplementary Material](#)).

2.3. Preparation of the crude oil-in-water emulsion

Crude oil sample was directly used without further treatment. The crude oil-in-water emulsion was prepared by mixing crude oil with brine water (50 mmol/L NaCl). Briefly, 20 g of oil was added to 380 g brine water with pH of 5.7, 4, or 2 in a plastic bottle. The mixture was emulsified by using an ultrahigh speed homogenizer (Fluko, FA25) operated at 28,000 rpm for 5 min to form a crude oil-in-water emulsion oil content of 5.0 wt%.

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