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Oil sorption by exfoliated graphite from dilute oil–water emulsion for practical applications in produced water treatments

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ABSTRACT

We used engine oil–water emulsion as a model produced water to evaluate the oil sorption properties of exfoliated graphite (EG) and showed that 100 mg/L of oil in emulsion can be reduced to a concentration of a 0.1-few mg/L using as-received commercially available EG and surface modified EG subjected to an additional oxidation treatment. Oil at a concentration of less than 15 mg/L, the standard of typical water treatment processes. Although EG also sorbs water, it sorbs oil preferentially and the oil concentration of the sorbed phase in EG was estimated to be about 200 times that of the initial untreated emulsion. The sorption mechanism was discussed with the aid of the ab-initio relaxation calculation and classical molecular dynamics (MD) simulation for *n*-Hexane (C_6H_{14}) adsorption on graphene. When EG was incorporated with micron-size iron particles, the oil sorbed EG was found to be effectively recovered from emulsion by using magnetic field. The oil concentration in emulsion treated with EG was able to reduce down to the level comparable to that achieved by nanofiltration (NF) or reverse osmosis (RO) membrane treatment. We concluded that EG from natural graphite can effectively remove oil component during the treatment of emulsion and exhibits high potential for practical use.

1. Introduction

The worldwide output of conventional fossil fuel resources, especially the outputs of petroleum and gas, and the production of unconventional shale gas in association with recent engineering developments are increasing. Produced water, which is defined as the residual water that remains after oil separation and removal from the water used during the extraction of crude oil, is generated as byproduct of conventional and unconventional extraction methods. The output of produced water has been reported to be approximately three to six times of crude oil or 300 million barrels per day in 2011 [1], which represents an amount of water approximately 400 times greater than the daily consumption of Tokyo. Produced water is disposed by re-injection into wells and oil layers, or is reused for enhanced oil recovery (EOR). In offshore oil fields, it is generally sent via pipelines to ground facilities, where it is treated. Produced water contains oil, gas, and various salts and inorganic and organic matter. In particular, it generally contains 10–1000 mg/L as total organic carbon (TOC) substances. As a pre-treatment for membrane process three stages of oil-removal procedures are generally performed, primary oil water separation (oil < 500 mg/L), secondary oil water separation, and tertiary oil water separation at the level of oil < 15–30 mg/L, are generally performed. If needed, advanced treatments with reverse osmosis (RO) or nanofiltration (NF) membrane separation are also performed as post-processes. Produced water is normally treated until it reaches oil concentration low enough to ensure good water quality based on the effluent standards of the site; and it is ultimately discharged to sea or injected into oil layers of the well [1]. To secure soundness of the environment of oil layers and groundwater and to minimize the environmental impact of produced water, improvements in treatment processes have been required. In such processes, the oil concentration must be reduced to a level where a RO membrane

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Table 1
Oil type, its concentrations used and amount of oil-absorbing EG added.

Oil	Oil concentration in emulsion (ppm)	Amount of EG added (mg)
Engine oil (synthetic oil)	100, 200	10, 50, 100, 150, 200
Engine oil (mineral oil)	100	100

Table 2
Properties of oil-absorbing samples used in the experiments.

Sample	Apparent density ($g\,cm^{-3}$)	Specific surface area ($m^2\,g^{-1}$)	Sample shape
T-1	0.007	49.7	Foam
C-1	0.005	29.8	Foam
C-2	0.009	28.4	Foam
C-3	0.017	24.4	Foam
TO-1	0.006	43.5	Foam
Palm shell activated carbon	2.04	1176.1	Particle
Vermiculite	0.172	6.8	Particle

is not clogged; thus the target oil content for membrane treatment is commonly less than 10 mg/L. Due to the special restrictions of platforms, offshore oil fields in particular require a more effective oil removal method. A compact and high-efficiency flocculation and magnetic separation method has been developed for this process, in order to remove oil to a concentration lower than 15 mg/L [2]. More simplified and inexpensive high-efficiency produced-water treatment technologies, including technologies for treating flow-back water, whose production volume has been increasing in association with increased shale gas extraction, are anticipated. Such technologies can help prevent environmental deterioration and enable the development of resources to achieve global sustainability.

Carbon materials have high potential for oil sorption [3–10]. Inagaki et al. reported the sorption of oil into foamed graphite or exfoliated graphite (hereafter abbreviated as EG); and their results indicated that this method is useful for oil spillage [11–17]. In order to develop an advanced water purification process based on separation membrane technology for produced water treatment, we investigated the use of foamed graphite or EG for sorption and removal of oil component in engine oil-water emulsion (a model produced water) as a primary treatment method at a stage leading to a membrane process. Because of difficulty of getting practical produced water, we used engine oil–water emulsion as a model produced water in the present investigation. In general, graphite intercalation compounds with sulfuric or nitric acid molecules inserted between graphite layers are formed by dipping natural graphite into concentrated acid [18]. EG powder with a very low density and a high specific surface area is produced by foaming, which is accompanied by the rapid release of the intercalate by subsequent water washing, drying, and rapid heating. The powder is then compressed into graphite sheets, which have been used as heat-resistant flexible sheets. Because the raw material of the foam is natural graphite, its cost is comparatively low.

In this study, we show the reduction of the oil concentration from several hundred mg/L in engine oil–water emulsion to less than several mg/L by dispersing EG within it. As noted above, Inagaki et al. found that EG is useful for the sorption of oil floating over the sea [13,15]. On the other hand, the present investigation aims at clarifying the sorption behavior of EG against oil-water emulsion. The emulsion is composed of very fine mixture of oil and water such as oil in water and water in oil [19]. Although EG is considered to be effective also for oil–water emulsion, it has not yet been practically confirmed. This paper aims at clarifying simply whether EG can be a candidate as a sorption material for oil–water emulsion in the produced water treatment. Commercially available EG was used for produced water treatment to reduce the oil concentration to a level where the treated produced water could be fed to a subsequent membrane separation process. We show that the present EG process is a simplified primary treatment for produced water. As a practical method for recovering EG after the sorption of oil, we investigated a method using a magnetic field to recover the EG as a feasible recovery method.

Because the need for the development of an effective method for treating the produced water is rising with the increasing production of petroleum and gas resources, the results of the present study are expected to lead to enhanced environmental protection in association with the extraction of such resources.

2. Experimental

The exfoliated graphite samples were characterized by scanning electron microscope (ADD SEM MODEL), powder X-ray diffraction (ADD XRD MODEL), Raman spectroscopy with a 532 nm laser excitation (Renishaw in Via Raman microscope) and by X-ray photo electron spectroscopy (Axis-Ultra, Kratos, UK apparatus).

Emulsion composed of synthetic engine oil (Castrol, Power 1 4T 10W-50) and deionized water was used; we also used a mineral engine oil (Honda, Ultra G1 10W-30) to confirm the effect of the kind of the engine oil, and found out that there is no difference in the sorption behavior of EG in both cases. Fixed amounts of engine oil and deionized water (or salt water containing 3.5 wt% NaCl in some cases) were mixed and homogenized using a magnetic stirrer (950 rpm) and a homogenizer. A prescribed amount of oil was mixed with distilled water and also salt water (3.5 wt% NaCl) using a magnetic stirrer (950 rpm) and a homogenizer to prepare engine oil–water (or -salt water) emulsion. A fresh engine oil–water emulsion was supplied for the sorption experiment. Table 1 shows the concentrations of engine oil–water emulsions used in the experiments. One litter of engine oil–water emulsion was poured into a glass beaker, and a fixed amount of EG was added under constant stirring. Additional sorption experiments using palm shell activated charcoal and vermiculite [20] were also carried out for comparing the sorption ability with that of the EG. The oil concentration in the emulsion was determined at prescribed time (5 times in 60 min) using an oil densitometer (Horiba, OCMA-505), in which oil was extracted by a solvent and the concentration was determined by the non-dispersive infrared analysis.

In each sampling, a 50 mL of emulsion was taken from the beaker and EG was removed by filtration. The amount of EG decreased during the sorption experiment due to sampling for the chemical analysis. At the final stage (60 min), the volume of emulsion and the amount of EG became about 75% of those at initial stage. However, it was confirmed from a separate experiment that there was no considerable difference in the oil concentration in the emulsion after 60 min of sorption even if the volume was kept constant during 60 min of sorption experiment. Thereby the oil-sorbing behavior of