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New Application of Exfoliated Graphite for Environmental Pollution
-Sorption and Recovery of Heavy oil by using Exfoliated Graphite-

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Abstract

The behavior of sorption of heavy oils into exfoliated graphites was studied by using four kinds of heavy oils. The maximum sorption capacity of exfoliated graphite was found to be suprisingly high 86 g of A-grade heavy oil per 1 g of an exfoliated graphite within 1 min. Sorption capacity was found to depend strongly on bulk density of exfoliated graphite and the time to reach maximum sorption, as well as sorption capacity, for an exfoliated graphite depended strongly on grade of heavy oil. A-grade heavy oil sorbed into exfoliated graphite could be recovered by a filtration under suction with the recovery ratio of 60 - 80 %. From the present work, exfoliated graphite with low bulk density is a promising material for the sorption and recovery of heavy oil, which has been dispersed into water.

Key words heavy oil, exfoliated graphite, sorption, recovery

1. Introduction

Recent accidents of oil tankers, gave serious environmental problems, not only pollution of seawater and neighboring coasts but also serious effects on fishing, as well as a great loss of heavy oil. A preliminary experimental result was previously reported on the sorption of heavy oil onto exfoliated graphite[1)]. In our previous papers[2-4)], it was reported on the basis of the experiments in a small scale that an exfoliated graphite can sorb a large amount of heavy oil very quickly, which is suspended in water, and also about 70 % of sorbed heavy oil can be recovered by a suction filtration. Not only removing the heavy oil dispersed in water but also recovering and recycling of heavy oil. It might expect that the exfoliated graphite can be used for adsorption materials of various oils in the river or sea, and then contributed to protection for environmental disruption. In this study, the detailed experimental results on the sorption and recovery of four different grades of heavy oils are reported.

2. Experimental

In industries, residue compounds of sulfuric acid have been used as starting materials for the exfoliated graphite (EG). Using sulfuric acid used a commercially available exfoliated graphite in the present work, which was prepared from natural graphite. By using EG, different bulk densities of graphite were obtained by compressing in a beaker and used for heavy oil sorption. In Table 1, preparation conditions and their properties (bulk density, specific surface area and pore volume) are summarized together with sample codes used in the present paper.

Four grades of heavy oil were used; A-grade (specific gravity; 864 kg/m^3, viscosity at room temperature: 0.4 kg/m·s), B-grade (890 kg/m^3, 27 kg/m·s), C-grade (945 kg/m^3, 35kg/m·s) and crude oil (826 kg/m^3, 0.4 kg/m·s). In distilled water of about 0.45 dm^3 in a beaker that was kept at a room temperature, heavy oil was added and stirred in a while. But immediately after stop stirring, the oil floated on the surface of water. Onto this floating heavy oil, the exfoliated graphite was added. With the sorption of the floated oil to the exfoliated graphite, the characteristic brown color of the oil was disappeared. By changing the weight ratio of heavy oil to exfoliated graphite, the maximum sorption capacity of the exfoliated graphite was determined. As a measure of the rate for sorption of heavy oil into exfoliated graphite, the time to need for the completion of sorption of a maximum capacity was defined as the time for disappearing of the floating heavy oil on the water after the addition of exfoliated graphite to the beaker.

Porosimeter (Shimadzu, Poresizer-9320) was used to determine their properties such as bulk density, specific surface area and total pore volume.

3. Sorption of Heavy Oils by Exfoliated Graphite

3.1 Maximum sorption capacity and sorption time

By the addition of exfoliated graphite onto the heavy oil floated on the water, the characteristic brown color of heavy oil was disappeared by its sorption into exfoliated graphite. In this case brown color was completely disappeared only 1 minute after the addition of EG. After taking out of the exfoliated graphite, no contamination appeared in the water.

In Fig. 1, the maximum sorption capacity of the exfoliated graphite is compared on four grades of heavy oil. In the case of A-grade heavy oil, up to 86g

Table 1 Sample code, bulk density, specific surface area, total pore volume of exfoliated graphite used.

Sample code	Preparation condition	Bulk density (kg/m^3)	Specific surface area (m^2/kg)	Total pore volume (m^3/kg)
EG	commercial	0.006	6.2×10^{-4}	2.182×10^{4}
EG-1/3	compacted EG-1 to the volume of 1/3	1.96×10^{-5}	2.52×10^{-4}	1.6×10^{4}
EG-1/6	compacted EG-1 to the volume of 1/6	4.0×10^{-4}	1.92×10^{-4}	1.0×10^{4}
EG-S	compacted to a sheet and then pulverized	1.0×10^{-4}	—	—

was completely sorbed into 1g of the exfoliated graphite EG. In the case of use more than 100 g of oil, a small amount of oil with brown color was floating on the water surface. This sorption capacity is much higher than that of the previous paper[1] and also than the adsorbents ever used. Sorption rate of A-grade oil was so quick as to complete within 1 min. The maximum sorption capacity for a crude oil with the viscosity comparable with A-grade was similar to that for A-grade heavy oil (Fig. 1) and the sorption rate was also as high as in the case of A-grade oil; finishing within 2 min. Its capacity of EG for the crude oil was 75g.

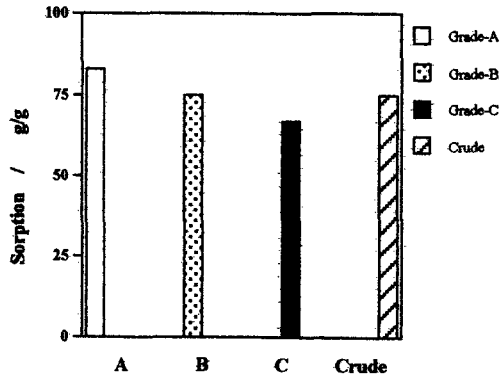

Fig.1 Maximum sorption capacity of the exfoliated graphite for different heavy oils

In the case of C-grade heavy oil with very high viscosity, sorption capacity of the exfoliated graphite EG was a little smaller than the case of A-grade oil, but still 67 g was sorbed into 1 g of exfoliated graphite (Fig. 1). Sorption proceeded very slowly, about 8 h being needed for the completion of sorption. This slow sorption is supposed to be due to high viscosity of the oil.

B-grade heavy oil showed a behavior to be sorbed into exfoliated graphite similar to that of C-grade heavy oil (Fig. 1).

3.2 Effect of bulk density of exfoliated graphite on sorption

Fig. 2 indicates the dependence of maximum sorption of various heavy oils on bulk density of exfoliated graphite EG. Maximum sorption capacity of the exfoliated graphite is found to depend strongly on its bulk density. On all heavy oils used, the capacity decreases drastically with the increase in bulk density of exfoliated graphite. The capacity of sample EG-S which was pulverized after the compression of exfoliated graphite into thin sheet, which can not be called exfoliated graphite any more and have the bulk density of about 0.10 g/cm^3, was very small, only 3～5 g for all oils. In Fig. 3, SEM micrographs of these samples are shown, certain morphology difference among four samples are recognized, though it can not be express quantitatively.

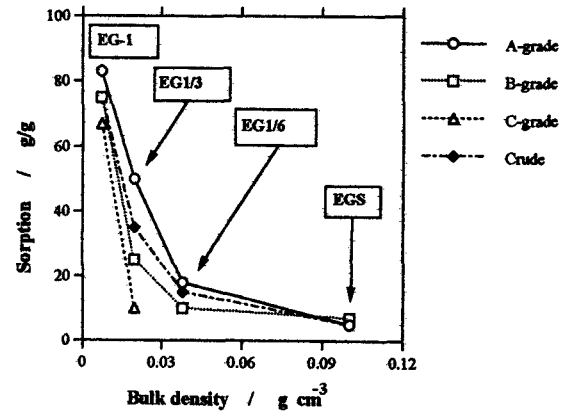

Fig.2 Maximum sorption capacity of various heavy oils for exfoliated graphite with changes the bulk density.

3.3 Recovery of heavy oil sorbed

By a filtration under suction condition of the sorbed exfoliated graphite, sorbed oils were found to be recovered. Table 2 shows the recovery ratio of sorbed oils by a filtration under suction for 120 min. The recovery ratio of A-grade and the crude oils is about 70 % and 60%, respectively. About 30～40 % of heavy oils sorbed remained probably on surface of graphite flakes and also in pores in exfoliated graphite.

4. Conclusive remarks

The behavior of sorption of heavy oils into exfoliated graphites was studied by using four kinds of heavy oils with different viscosity. The maximum sorption capacity of exfoliated graphite was found to be surprisingly high, 86 g of A-grade heavy oil per 1 g of exfoliated graphite EG and also its sorption occurs very rapidly, within 1 min. Sorption capacity was found to depend strongly on the bulk density of exfoliated

Table2 Sorption (%) after suction (120 min)

Suction time	Grade-A	Crude
120 min	72(%)	61(%)

Recovery(%)=(amount recovered by suction for 120 min./ amount sorbed)×100

graphite. The time to reach maximum sorption, as well as sorption capacity, for an exfoliated graphite depended strongly on grade of heavy oil; a large amount of A-grade heavy oil with low viscosity was sorbed in a short time, but C-grade oil with high viscosity needed a long time although sorbed amount was relatively small. A-grade heavy oil sorbed into the exfoliated graphite could be recovered by a under suction condition; its gave about 60～70 % recovery. From the present work, exfoliated graphite with low bulk density is a promising material for the sorption and recovery of heavy oil, which has been dispersed into water, particularly seawater. The mechanism of sorption of heavy oils onto the exfoliated graphite has to be clarified, in order to find out the most appropriate exfoliation conditions of graphite and the development of effective and practical techniques to recover heavy oil from sorbed graphite and also to recycle of both recovered oil and exfoliated graphite is required.

Acknowledgment
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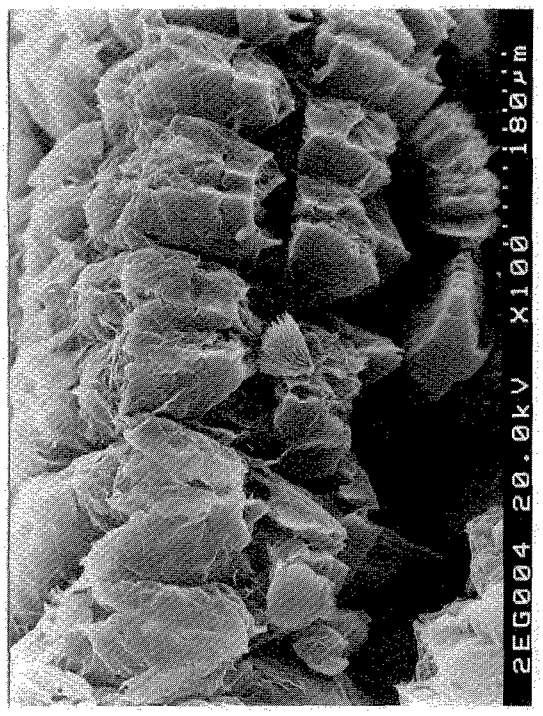
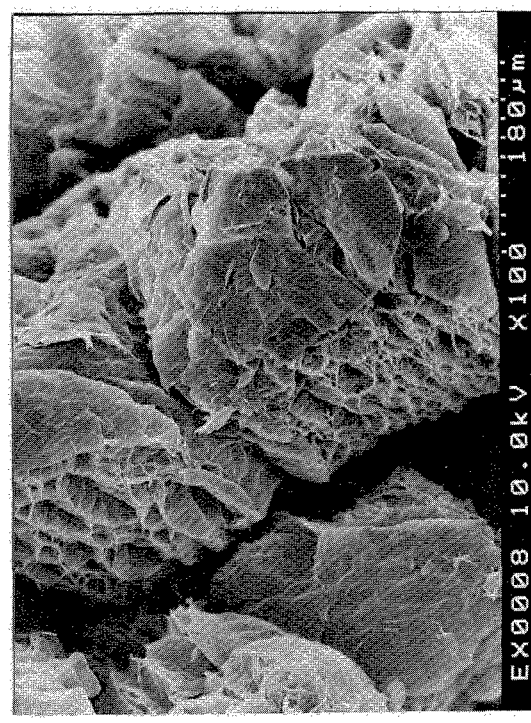
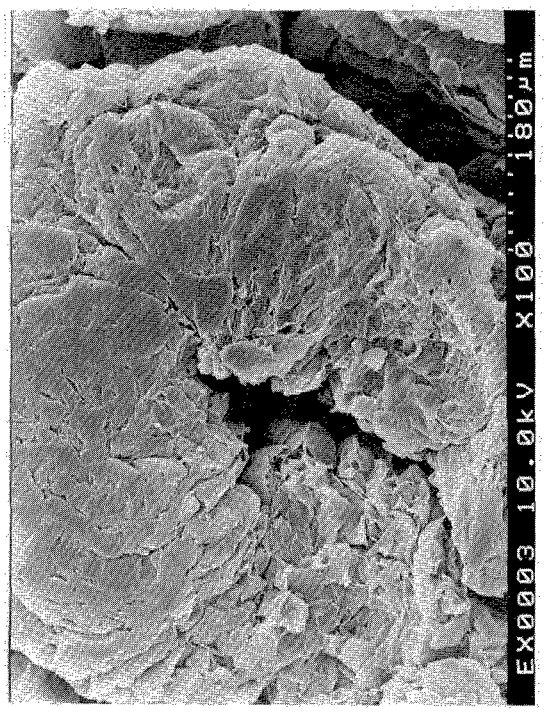


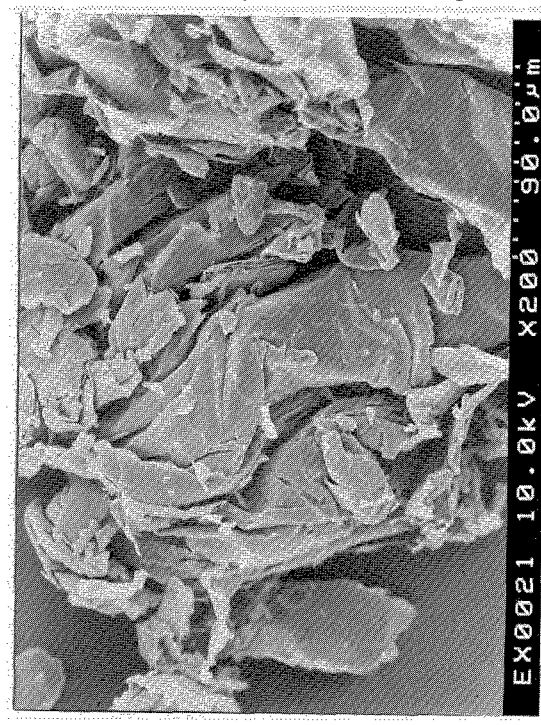
(a) as-received, bulk density of $7.2\times10^{-3}cm^3$



(b) compacted to 1/3 volume, bulk density of 1.96×10^{-2} g/cm^3



(c) compacted to 1/6 volume, bulk density of 3.78×10^{-2} g/cm^3



(d) made a thin sheet, and pulverized, by rolling, bulk density of 0.1 g/cm^3

Fig. 3 SEM micrograph of surface morphology of exfoliated graphite