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Sorption and decomposition of crude oil using exfoliated graphite/ZnO composites

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ABSTRACT

Exfoliated graphite/ZnO composites (EG/ZnO) were prepared by impregnating expandable graphite with $Zn(OH)_2$, abruptly expanding at 700 °C for 40 s, and heating at 500 °C for 3 h. The composites were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), nitrogen adsorption and mercury porosimetry. The sorption capacity of the composites for spilled crude oil was measured and under UV irradiation the decomposition of the absorbed crude oil was investigated. The results showed that the composites provided with the adsorption and photocatalysis capacity for crude oil at the same time. The sorption capacity of the composites decreased gradually on increasing the ZnO content of the composites. Moreover, the decomposition ratio of the absorbed crude oil increased on increasing the ZnO content or decreasing the weight ratio of crude oil to composites.

1. Introduction

In recent years the ecological problems arising from the oil spills in the world have been observed frequently. Exfoliated graphite (EG) is an excellent inorganic carbon material with a porous structure, which has many characteristics such as low density, non-toxicity, non-pollution and easy disposal. This material has been used as an absorbent for removing spilled oils due to its large pore structure. It is reported that the sorption capacity of EG for heavy oil reached 83 g/g, and the sorption could occur very rapidly [1–5]. However, the reproducibility of the EG is unsatisfactory, which has become one of the main factors obstructing its practical application. By a simple compression on the absorbed EG, about 80% of the absorbed heavy oil could be squeezed out [6]. However, the characteristic pore structure of the EG was seriously destroyed by the compression, and consequently the EG hardly had the ability to absorb heavy oil again. About 70% of the absorbed heavy oil also could be recovered by a filtration with suction, but the oil sorption capacity of EG decreased markedly with its recycling [7]. In 2002, Toyoda [8] and Tsumura [9] reported that loading TiO_2 photocatalyst on EG could accelerate markedly the decomposition of the absorbed heavy oil. Our recent results additionally argued that the decomposition rate of the absorbed oil was greatly related to the TiO_2 loading technique [10].

As a direct wide-band-gap (~3.27 eV at room temperature) semiconductor with a large exciton binding energy of 60 eV, ZnO has been used as an environmental photocatalyst for organic pollutants' degradation and exhibited superior photocatalytic decomposing ability [11–13]. In the present work, we tried to load ZnO photocatalyst on EG to form EG/ZnO composites, and investigate the sorption of the composites for spilled crude oil and under UV irradiation the decomposition of the absorbed crude oil.

2. Experimental

2.1. Materials

Natural flake graphite (35 mesh, 99% purity) was purchased from Qingdao Tianhe Graphite Company, China. Zn $(NO_3)_2 \cdot 6H_2O$, sulphuric acid (98%), hydrogen peroxide (30%), $CO(NH_2)_2$, ethanol and distilled water were of laboratory reagent grade and used without further purification.

2.2. Preparation of the composites

Natural flake graphite (6 g) was mixed with sulphuric acid (10 mL) and hydrogen peroxide (1.0 mL), placed at 50 °C for 90 min, washed to pH 5–7 and dried at 70 °C for 24 h, forming expandable graphite. EG could be obtained by abruptly heating the expandable graphite at 700 °C for 40 s.

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The reaction equations for the preparation of ZnO could be described as follows:

$$CO(NH_2)_2 + 3H_2O \xrightarrow{\Delta} CO_2\uparrow + 2NH_3 \cdot H_2O \tag{1}$$

$$Zn^{2+} + NH_3 \cdot H_2O \rightarrow Zn(OH)_2\downarrow + 2NH_4^+ \tag{2}$$

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O\uparrow \tag{3}$$

According to Eqs. (1) and (2), $Zn(OH)_2$ was prepared as follows: in a 1000 mL conical flask, Zn $(NO_3)_2 \cdots 6H_2O$ (0.1 mol/L) and $CO(NH_2)_2$ (0.3 mol/L) were dissolved in 500 mL distilled water under vigorous stirring at room temperature, dispersed by ultrasonication for 10 min, forming a transparent solution. The transparent solution was stirred at 90 °C for 3 h, forming a milk-like liquid. After that, the milk-like liquid was cooled to room temperature, forming some white precipitates at the bottom of the conical flask. To obtain $Zn(OH)_2$, the white precipitates were collected by centrifugation and washed successively by distilled water and ethanol. According to Eq. (3), ZnO could be obtained by heating the $Zn(OH)_2$ at 700 °C for 40 s and 500 °C for 3 h. TEM observation showed that the ZnO as-prepared was of spherical particles with size 60–110 nm and XRD measurement revealed that it belonged to the hexagonal wurtzite ZnO (the corresponding figures were not presented here). Therefore, EG/ZnO composites could be prepared as follows: the expandable graphite was mixed with $Zn(OH)_2$ solution, placed at 30–40 °C for 3 days and dried at 70 °C for 24 h, and then finally heated at 700 °C for 40 s and 500 °C for 3 h.

2.3. Characterization of the composites

Complex titration analysis method was used to measure the ZnO content in the composites (wt%), which was found to be 1–35%. The phase composition was determined by X-ray diffraction (D/max-rB, Rigaku, Japan) and the morphology was observed by a scanning electron microscope (SEM, KY2828). The pore structure was characterized using physical nitrogen-adsorption measurement at 77 K (ASAP 2010), which was applied to access micropores and mercury porosimeter measurement (Autopore IV 9500, quantach), which in turn was applied to access both mesopores and macropores. The specific surface areas (S_{BET}) were calculated by the BET equation and the total pore volumes were obtained from the nitrogen gas adsorption capacity at a relative pressure of 0.925.

2.4. Sorption and decomposition of crude oil by the composites

To seawater (from Qinhuangdao sea area), about 500 mL in a 1000 mL beaker, crude oil (density of 837 kg/m^3, viscosity of 0.602 Pa s, provided by Qinhuangdao Port Office) was added and stirred for a while. Immediately after stirring, however, the crude oil floated onto the surface of the seawater. Onto the floated crude oil, the composites were added. The sorption process of the floated crude oil is shown in Fig. 1. It could be seen that with the sorption of the floated crude oil to the composites, the characteristic brown colour of crude oil disappeared (Fig. 1a, b). When the amount of crude oil was slightly larger than the maximum sorption capacity of the composites, a small amount of brown oil still floated around the composites due to the saturating sorption (Fig. 1c). Based on

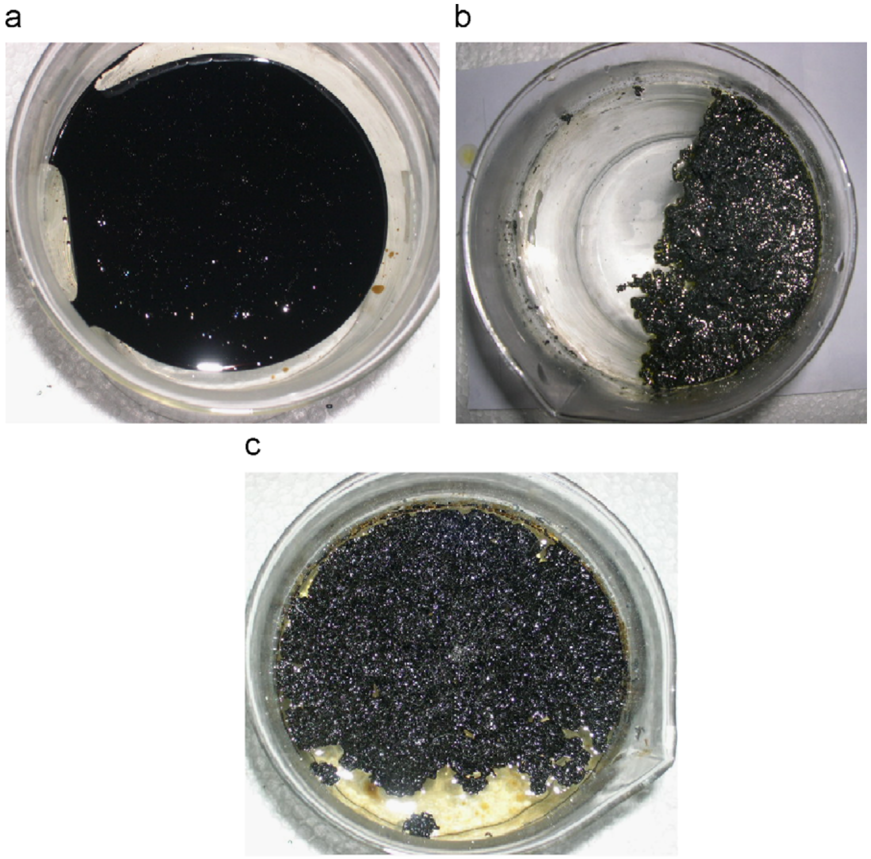

Fig. 1. Appearance of sorption of floated crude oil by the composites: (a) crude oil floating on seawater; (b) 2 min after adding the composites and (c) after saturated sorption.