Research paper

Superhydrophobic kaolinite modified graphene oxide-melamine sponge with excellent properties for oil-water separation

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A B S T R A C T

In this work, a facile and cost-effective method was reported to fabricate a novel, robust, and superhydrophobic kaolinite modified graphene oxide-melamine sponge (K-GOMS). The GO sheets were used to increase the roughness of the sponge smooth surface. The hydrophobic kaolinite adhered on GO sheets significantly enhanced the superhydrophobicity of the K-GOMS surface with a water contact angle of 152.3°. Several organic solvents and oils were selected to test the adsorption performance of the obtained adsorbents. The results revealed that the superhydrophobic K-GOMS exhibited not only superior adsorption capacity for various organic solvents and oils, from 60 to 113 times of its own weight, but also outstanding recyclability with an adsorption capacity retention higher than 94% after 30 cycles of diesel oil adsorption, and excellent environmental tolerance in wide range of pH values and temperatures. Therefore, this study provides an effective way for constructing facile, low-cost, and large-scale production of superhydrophobic adsorbents for oil-water separation.

1. Introduction

The rapid development of modern industrialization inevitably released various types of contaminants, such as dyes,(Deng et al. 2013; Gong et al. 2009) organic compounds,(Chen et al. 2015; Chen et al. 2016b; Cheng et al. 2016; Ren et al. 2017) and heavy metals,(Hu et al. 2017; Liang et al. 2017; Tang et al. 2014; Wan et al. 2017; Xu et al. 2012b; Zeng et al. 2017) even resulted in oil spill,(Tjandra et al. 2015; Wang et al. 2017; Zhang et al. 2017) which gave rise to a continuously increasing worldwide concern for water pollution.(Long et al. 2011; Tan et al. 2015; Xu et al. 2012a) Among these pollutions, oil spill, an unavoidable problem from the exploration, production, and transportation of offshore oil, has become a serious threat to environment and ecology.(Allan et al. 2012; Qiang 2013; Zhai 2014) Cleaning up oil spill and oil slick from water surface and coastline is a challenge work. (Pham and Dickerson 2014) To date, several methods such as in situ burning,(Aurell and Gullett 2010) skimming,(Broje and Keller 2007) bioremediation,(Zahed et al. 2010)chemical dispersion,(Kujawinski et al. 2011) and adsorption(Adebajo et al. 2003; Choi and Cloud 1992) have been applied to reduce the adverse influences of oil spill in environment. Among these methods, adsorption attracted great attention because of its convenient operation, low-cost and easy design.(Lü et al.

2016; Pham and Dickerson 2014) The traditional porous adsorbents such as exfoliated graphite,(Wang et al. 2010) wool,(Radetić et al. 2003) and vegetable fibers(Annunciado et al. 2005) generally have drawbacks including low adsorption capacity, poor recyclability and environmental adaption, thereby limiting their application.(Lü et al. 2016; Wu et al. 2017; Zhang et al. 2015b) Recently, sponge adsorbents have aroused considerable interest in the field of oil-water separation due to their low density, good flexibility, high porosity, and three dimensional skeleton structure.(Zhou et al. 2016; Zhu et al. 2011) However, sponge is naturally hydrophilic and oleophilic, which restricts the separation of oils and organic solvents from water.(Wang et al. 2017)

With the purpose of sponge application for oil-water separation, modifications are necessary to transform the hydrophilic-oleophilic sponge surface to hydrophobic-oleophilic surface as well as increase the surface roughness for enhancing the adsorption capacity of organic solvents and oils. For example, TiO_2 nanoparticles were used to modify the melamine sponge surface, which could significantly enhance the hydrophobicity of melamine sponge.(Cho et al. 2016) A melamine sponge incorporated with Fe_3O_4 nanoparticles and lignin not only exhibited excellent hydrophobicity and self-cleaning performance, but also could be magnetically driven to absorb the oils.(Lei et al. 2017) More recently, graphene oxide (GO), composed of two-dimensional sp^2

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carbon network, with one-atom thickness honeycomb lattice structure, can greatly enhance the pollutant removal performance due to its intriguing structure and unique physicochemical properties.(He et al. 2017; Li et al. 2010; Wang and Chen 2015; Zhang et al. 2015b) For example, (Szabó et al. 2013) prepared TiO_2-GO nanocomposites for phenol photooxidation. The presence of GO induced an accelerate sedimentation of catalyst slurry to completely separate the composites from the phenol solution in a short time as compared to pure TiO_2. Besides, GO has been reported as good adsorbent for the removal of a wide range of organic solvents. (Dékány et al. 1998) Moreover, GO coated on the skeletons of sponge could significantly increase the roughness of the sponge surface and improve the adsorption capacity of the modified sponge. Rahmani et al. (2017) immersed polyurethane (PU) sponge into GO solution to obtain GO/PU sponge. And it is confirmed that the coating process does not have a profound impact on the porous structure of the PU sponge. Even, the presence of GO gives the roughness of the surface and improved the adsorption capacity and recyclability. However, GO shows hydrophilic property due to its abundant oxygen-containing functional groups,(Lerf et al. 2006; Tamás Szabó et al. 2015) which limits its application of oil-water separation. Therefore, there is a need to explore a feasible approach to enhance the hydrophobicity of graphene oxide sponge for oil-water separation. It is well known that the chemical reduction of GO is a facile method to alter the hydrophilicity of GO. The commonly used reducing agents including N_2H_4, (Szabó et al. 2005) $NaBH_4$, hydroquinone, and so on. (Athanasios B. Bourlinos et al. 2003) Although the reduction of GO is considered to be an effective approach to enhance the hydrophobicity of the fabricated graphene oxide sponge,(Gao et al. 2009; Liu et al. 2015; Tjandra et al. 2015; Zhou et al. 2016) the reducing agents commonly used for the reduction of GO are either toxic or hazardous. Besides, the preparation methods were relatively complex. These restrict the large-scale preparation of graphene-based sponge.(Li et al. 2010) To our knowledge, various hydrophobic materials have been used for oil-water separation.(Cho et al. 2016; Lei et al. 2017) However, it is still an open question whether the combination of graphene oxide sponge with hydrophobic materials will enhance the oils removal performance. Thus, it is worthwhile to explore the potential of hydrophobic materials modified graphene oxide sponge in oil-water separation.

Clay mineral materials have received great attention due to their low-cost, easy availability, and environmental friendly.(Huang et al. 2016a) Among those materials, kaolinite, is abundant in kaolin, has been widely used for different applications because of its rich reserves, chemical stabilization, and easy modification.(Huang et al. 2016b) The modified kaolinite composites have been regarded as efficient adsorbents for the removal of dyes,(Huang et al. 2016a; Nandi et al. 2009) and heavy metals.(Huang et al. 2016b) Whereas, the application of kaolinite composites for oil-water separation is vacant. It has been reported that kaolinite can be diversely fabricated to the hydrophobic, oleophobic-hydrophilic, and amphiphobic materials, respectively.(Qu et al. 2016) Based on this property, the hydrophobic kaolinite was used to increase the hydrophobicity of graphene oxide melamine sponge for oil-water separation.

In this work, the main objective was to fabricate a superhydrophobic kaolinite modified graphene oxide-melamine sponge (K-GOMS) for oil-water separation. As a comparison, superhydrophobic kaolinite modified melamine sponge (K-MS) was prepared to test the effect of GO sheets on K-GOMS. Moreover, adsorption experiments were carried out to compare the adsorption performance of K-MS and K-GOMS for the removal of various organic solvents and oils. The results indicated that the prepared K-GOMS exhibited high adsorption capacity, outstanding recyclability and excellent environmental adaption. It is believed that this study can provide a novel and practical methodology for further constructing facile, low-cost, and high quality superhydrophobic adsorbents for oil spill treatment in environment.

2. Materials and methods

2.1. Materials

Graphite powder (C, ≥99.85) was obtained from Sinopharm Chemical Reagent Co., Ltd. Commercial melamine sponges were purchased from Chengdu Xuyang Sponge Product Co., Ltd. Kaolin, the major composition is kaolinite ($Al_2Si_2O_9H_4$), stearic acid, $K_2S_2O_8$, P_2O_5, 3-aminopropyltriethoxysilane (APTES), and all other chemicals were purchased from Shanghai First Reagent Co., China.

2.2. Preparation of GOMS

GO was synthesized from natural graphite powder via a modified Hummers Method.(Wang and Chen 2015) A commercially available melamine sponge (MS) was cut into $2.0 \times 2.0 \times 1.0 \text{ cm}^3$ cubes and cleaned by DI water and ethanol for three times, followed by drying at 60 °C for 24 h. 25 mg GO was dispersed in 50 mL DI water under ultrasonic shock for 2 h. Then, the melamine sponge was dipped into GO solution for 1.5 h and dried in a vacuum oven at 60 °C to obtain graphene oxide-melamine sponges (GOMS).

2.3. Synthesis of K-MS and K-GOMS

Kaolin was dried at 120 °C for 5 h to remove the water and treated with stearic acid firstly.(Qu et al. 2016) Briefly, stearic acid (0.5 g) was added into 24 mL of ethanol under magnetic stirring. While dissolved completely, kaolin (10 g) was added to the solution and ultrasonically dispersed for 30 min. Then, the solution was transferred into a preheated water bath (95 °C), refluxed for 2 h and finally dried at 120 °C for another 6 h to obtain hydrophobic kaolinite. Afterwards, 100 mg hydrophobic kaolinite was first dispersed in 100 mL of ethanol by probe sonication for 2 h. Then, 2 mL of APTES was added into the solution under stirring for 10 min. After that, GOMS and MS were impregnated with the solution for 1 h. Then, the sponges were raised and washed with ethanol for three times, and dried in a vacuum oven at 60 °C to obtain K-MS and K-GOMS.

2.4. Characterization

The sponge materials were characterized by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, NICOLET 5700 FT-IR Spectrometer). The elemental composition of the surface of the sponge materials was determined by X-ray photoelectron spectroscopy (XPS), performed on ESCALAB 250Xi (Thermo Fisher Scientific, USA). The surface morphology was characterized using a JSM-6700F Field Emission Scanning Electron Microscope (FE-SEM) (JEOL, Japan). X-ray analysis was done by the powder X-ray diffractometer (D8 ADVANCE, Bruker Axs). Water contact angle measurements were conducted by an OCA 15Pro goniometer (Dataphysics). Raman spectra were recorded from 200 to 4000 cm^{-1} on Raman Microprobe (Labram-010).

2.5. Adsorption experiments of K-MS and K-GOMS

The K-MS and K-GOMS were dipped into various organic solvents (*N, N*-dimethyl formamide (DMF), ethanol, methanol, and n-hexane) and oils (diesel oil, kerosene, motor oil, and liquid paraffin) for 1 min. The adsorption capacity Q_e (g/g) was calculated according to Eq. (1).

$$Qe \text{ (g/g)} = (m1 - m0)/m0 \tag{1}$$

where m_0 and m_1 are the weight of the sponge before and after adsorption, respectively.

The recyclability of sponge was evaluated by repeated adsorption−squeezing processes. The adsorption−squeezing was performed by immersing the sponge into DMF and diesel oil, until the