Composites Part B 101 (2016) 99–106

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

# A comparative study on superhydrophobic sponges and their application as fluid channel for continuous separation of oils and organic solvents from water

Shivam Gupta, Wei-Da He, Nyan-Hwa Tai*

*Department of Materials Science and Engineering, National Tsing-Hua University, Hsinchu 300, Taiwan, ROC*

ARTICLE INFO

*Article history:*
Received 18 February 2016
Received in revised form
20 May 2016
Accepted 1 June 2016
Available online 27 June 2016

*Keywords:*
Hybrid
Nano-structures
Surface properties
Wettability
Superhydrophobic

ABSTRACT

This study adopted melamine as core material to prepare porous materials possessing superhydrophobic and superoleophilic property, which is utilized to separate polar and non-polar solvents from polar/non-polar mixture. The sponges were treated by four different methods; (1) acetone treatment, (2) coating of functionalized expanded graphite (FEG), (3) coating of multi-walled carbon nanotubes (MWCNTs) and, (4) coating of reduced graphene oxide (rGO). After treatment, the functional groups on the sponge skeleton were examined and the water contact angles were also measured. Based on the experimental results, sponge treated with acetone showed the best absorption capacity, but worst hydrophobic property; while the sponges coated with FEG and MWCNTs possessed the worst absorption capacity. The sponge coated with reduced graphene oxide showed notable superhydrophobic property, as well as excellent absorption capacity. In this work, we also designed a set-up to separate organic solvents from organic-water mixture using the superhydrophobic and superoleophilic sponge. The basic idea is that, when the mixture of solvent and water was poured in the upstream of the channel, the solvent was absorbed by the treated sponge which was placed at the bottom of the channel, while water flowed down along the channel; as a result, separating the solvent from the mixture.

## 1. Introduction

Since the eighteenth century, the industrial revolution had started and the consumption of natural resources for deepening the industrial technology continued to progress, which improved human life, however, it also produced some negative impact on the environment such as oil pollution and petrochemical industry organic waste pollution. Recently, frequent water pollution, particularly oil spillage and chemical leakage accidents, have caused several ecological problems. If there will not be any special treatment or storage, it may cause long-term harm to the environment and ecological system. The subject of difficulty to deal with the industrial pollution has been existent since a long time. Generally, the treatment of industrial organic pollution mainly involves three methods, (i) bioremediation [1–3], (ii) chemical catalytic decomposition [4,5] and (iii) absorption and separation [6–8]. But, it is difficult to deal with large industrial pollution, or an oil spill by bioremediation and catalytic chemical decomposition because of their low efficiency. Among these methods for liquid organic contaminant recovery, physical sorption by porous materials is probably a simple, fast, and effective technique. Therefore, much attention has been paid to develop inexpensive, practical sorbents with potential applications in liquid organic contaminant cleanup. Water is a pure-polar solvent, and contaminants usually possess some non-polar properties. By using the material with non-polar surface properties to attract non-polar solvents, the absorbent materials can be employed for the separation of organic contaminants from water.

The separation or removal of oil and organic solvents from water can be easily performed by the naturally available porous absorbent materials such as natural fiber [9], sawdust [10] and zeolite [11] but, their inferior properties such as low absorption capacities, deficient selectivity and poor recyclability have inspired scientists across the world to develop new porous adsorbent materials possessing high absorption capacity, high porosity, large specific surface area, high selectivity, chemical inertness and excellent recyclability so that, they can perform oil-water separation effectively. To serve this purpose, superhydrophobic (water contact angle greater than 150°)

---

* Corresponding author.
*E-mail address:* nhtai@mx.nthu.edu.tw (N.-H. Tai).

http://dx.doi.org/10.1016/j.compositesb.2016.06.002
1359-8368/

and superoleophilic (oil contact angle less than 5°) materials have been developed, which can absorb oil and organic contamination while repelling water completely [12–14]. Surface treatments can alter or tune the wettability of the materials [15]. Therefore, surface treatment plays an important role on the absorption efficiency of the artificial materials with hydrophobic and oleophilic surfaces because the roughened (micro- or nanoscale asperities) surfaces combined with low surface energy materials have shown better hydrophobicity [16,17]. Many absorbent materials such as cross-linked polymers and resins [18–20], fibers [21], polymer gels [22], organic-inorganic hybrid [23], silicas [24] and nanocomposites [25–28] have been developed extensively. Natural materials such as chitosan [29], winter melon [30] and kapok wadding [31] have also been modified to prepare superhydrophobic and superoleophilic materials. Magnetic materials [32,33] have also gained much attention as it is easy to track and move these magnetic materials towards the polluted area even with small magnetic fields, thus enabling fast absorption. Moreover, magnetic materials can be easily collected safely by a magnet, if broken. However, these materials have shown low sorption capabilities along with poor selectivity and their high cost and complicated fabrication process have limited their use in the removal of oils and organic pollutants. With the demand for finding an ideal sorbent material with high absorption capacity and selectivity, lightweight, low cost, and environmental friendliness is highly imperative.

Carbon-based absorbents [34,35] such as carbon aerogels [36–38], carbon nanotube forests [39], graphene foams or sponges [40,41], carbon coatings [42], porous carbon nanoparticles [43], carbon fibers [44], exfoliated graphite [45] and hollow carbon beads [46] have been widely used because of their excellent absorption capacities, large specific surface area, high selectivity, chemical inertness, high porosity and excellent recyclability [47]. Moreover, these carbon-based absorbents are cost effective and environmentally friendly while the polymer materials take a long time in degradation, thus cause secondary pollution. Coating of hydrophobic carbon materials such as CNTs [48], activated carbon [49], graphene [50,51] or hybrid of these [52] on hydrophilic material such as polymeric sponge has also been studied to produce superhydrophobic and superoleophilic materials. The coating not only altered their nature to only absorb oils while repelling water completely, but also improved their thermal and mechanical stability.

In this study, commercially available melamine sponges were used as core material for preparing porous materials possessing superhydrophobic and superoleophilic property which was benefitted to separate polar and non-polar solvents from polar/non-polar mixture. Basically, the sponge is a three-dimensional porous polymeric material which can absorb water as well as oils and organic solvents. To alter the property from hydrophilic to hydrophobic, the sponges were treated with four different methods (i) acetone treatment, (ii) coating of functionalized expanded graphite (FEG), (iii) coating of multi-walled carbon nanotubes (MWCNT), and (iv) coating of reduced graphene oxide (rGO). The surface treatment altered its nature and introduced hydrophobic properties but it could still absorb oils and organic solvents. Based on the experimental results, the absorption capacities and hydrophobicity of treated sponges were compared. Also, a fluid channel set-up was designed for continuous removal of oils and organic solvents from water. Finally, a hexane-motor oil-water mixture was used for demonstrating the feasibility of the designed separating device. When the mixture was poured into the channel, the organic solvent was absorbed by the graphene-based sponge and flowed to a container, while the water flowed down along the channel to another container. As a result, the consecutive separation of the liquid organic contaminant with high-efficiency and high selectivity from the water mixture was achieved.

## 2. Experimental

### 2.1. Materials

The white melamine sponge, a density of 0.075–0.085 g cm$^{-3}$ and porosity of 99.44%, was purchased from the German company BASF. The natural graphite flakes (325 mesh, 99.8%) were bought from Alfa Aesar®. Sulfuric acid (95–97%), nitric acid (65%), hydrazine solution (35 wt%) and ammonium hydroxide solution (30–33%) were purchased from the Sigma-Aldrich®. Acetone, ethanol (95°) and polydimethylsiloxane (PDMS) were purchased from Uni-onward®, Echo Chemical® and Sil-more®, respectively. Carbon nanotubes (purity greater than 95 wt%, average diameter of 20 nm, length 1–25 μm) were purchased from the CNT Co. LTD. FEG and rGO were prepared through the chemical intercalation and the modified Hummer's method as described in our previous work [53,54], respectively. The oils and organic solvents used in absorption test are listed in Table 1.

### 2.2. Preparation of superhydrophobic and superoleophilic sponges

In this study, melamine sponges were treated with four different methods, (i) acetone treatment, (ii) coating of FEG, (iii) coating of MWCNT, and (iv) coating of rGO. First, the commercially available melamine sponges were cut into 2 cm$^3$ cube pieces and then washed in ethanol followed by drying in an oven at 100 °C. These cubic sponges were used in all the four different methods. In the first set of experiments, acetone was used at high temperature to produce a hydrophobic surface on the sponge. In a typical experiment, the washed sponge was saturated with acetone absorption and dried in an oven at 100 °C for 30 min. The acetone-treatment process was repeated several times to finally get a acetone hydrophobized sponge. In the second set of experiments, the sponges were coated with carbon nanomaterials i.e. FEG, MWCNT and rGO by a simple dip coating method with the weight percentage of 1.0, 3.0, 5.0 and 7.0 wt%. After coating, PDMS was used to adhere the carbon nanomaterials on the scaffold of the sponge. In a typical experiment, the solution of carbon nanomaterial and alcohol was prepared with a modulation weight ratio of 0.5:99.5, respectively, and the solution was placed in an ultrasonic vibration shaker for 30 min. The cleaned sponges were dipped in carbon nanomaterial-alcohol solution till saturated absorption and subsequently dried in an oven at 100 °C. This step was repeated several times to obtain the desired weight percentage of the coating material, i.e. 1.0, 3.0, 5.0 and 7.0 wt%. Finally, the coated sponges were dipped in the solution containing xylene, PDMS A, and PDMS B with a weight ratio of 300: 1: 0.1, respectively, followed by drying in an oven.

## 3. Absorption capacity measurement

The weights of the sponge were measured before and after absorbing the organic solvent or oil. The weight absorption capacity of the sponge is defined as

$$Weight\ absorption\ capacity = \frac{m_a - m_d}{m_d}$$

The volume absorption capacity of the sponge is defined as

$$Volume\ absorption\ capacity = \frac{Absorption\ volume}{weight\ of\ treated\ sponge} = \frac{m_a - m_d}{\rho_l \times m_u}$$

The real volume absorption capacity of the sponge is defined as