Journal of Industrial and Engineering Chemistry 40 (2016) 47–53

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Purification of oily seawater/wastewater using superhydrophobic nano-silica coated mesh and sponge

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ARTICLE INFO

Article history:
Received 30 March 2016
Received in revised form 23 May 2016
Accepted 7 June 2016
Available online 14 June 2016

Keywords:
Superhydrophobic
Oil separation
Silica nanoparticle
Mesh
Sponge

ABSTRACT

Superhydrophobic mesh and sponge were fabricated by a simple and fast dip-coating of silica nanoparticles (SiNP). Hexadecyltrimethoxysilane (HDTMS) was used as a hydrophobic reagent to make the superhydrophobic surface, by being grated onto the SiNP-mesh or sponge. As-made HDTMS-SiNP-mesh showed a water contact angle greater than 150°, meaning the successful creation of a superhydrophobic surface, and a high separation efficiency (99%) of target oils from oily wastewater/seawater even after 20-times recycling test. In kinetic test, the higher the kinematic viscosity of the target oil, the slower the separation rate, but the higher the separation efficiency. Therefore, the present approach of simple and inexpensive fabrication of superhydrophobic HDTMS-SiNP-mesh or sponge could offer promising applications in oil–water separation and off-shore oil spills.

Introduction

With the increase in industrial oily wastewater volumes and accidental oil spills, the removal or collection of oily pollutants from water surfaces has attracted worldwide attention. As a result, the development of effective and inexpensive methods for oil–water separation has become an important issue in order to meet environmental and economic demands [1]. Despite the fact that many oil–water separation methods such as adhesion, membrane filtration, and absorbance have been developed and are widely used [2], achieving an energy- and cost-effective oil–water separator with high efficiency remains a great challenge. Since oil–water separation is governed by the interfacial features of the substrate, fabrication of preferential wettability materials toward oil or water is desirable and effective [3,4].

Recently, novel materials possessing both hydrophobic/oleophilic "oil-removing" and hydrophilic/oleophobic "water-removing" surfaces have been developed, with which oil or water phases spread and penetrate readily through the material, and the remaining water or oil phase is repelled [2–8]. For a small oil spill, oil sorbent materials are commonly used, and recent studies have focused on the preparation of superhydrophobic sponges. However, these materials have several drawbacks such as inadequate absorption capacity, low selectivity, and poor recyclability [6]. Therefore, the gravity-driven filtration method is preferred due to the high cost-efficiency and high permeability in comparison to cumbersome and expensive absorption [2,7]. The pioneering work of Fen et al., wherein a steel mesh was spray-coated with polymer composite, was one of the first reports describing the use of superhydrophobic/superoleophilic durable substrates in the selective separation of oil and water by means of pouring-type gravity-driven approaches [8]. Therefore, a water- or oil-removing membrane with a superhydrophilic or superhydrophobic surface is more effective and an ideal filter for gravity-driven filtration. Variants of this method, using various coating materials on the mesh, such as carboxylic acid [5], thiol [9], ZnO [10], silane [11], or Cu_2O film [12] have been extensively studied to achieve superhydrophobicity, and have shown effective oil–water separation. Even though the high efficient separation of different oils, from hexane to heavy mineral oil, has been achieved, the separation of oil from oily seawater or wastewater with high separation efficiency has yet to be studied [13–15]. The unusual wettability of as-made superhydrophobic substrates may render them unstable in salt solutions [9]. Therefore, the separation efficiency and stability in a complex oily seawater or wastewater environment should be evaluated for practical application.

Herein, we fabricated superhydrophobic ($\theta > 150°$) surfaces by the dip-coating of silica nanoparticles (SiNP) on stainless steel meshes (300 μm pore size). The oil-removing superhydrophobic surfaces are easily fouled and blocked by oils due to the intrinsic

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http://dx.doi.org/10.1016/j.jiec.2016.06.005
1226-086X/

oleophilic property, which critically influences the recyclability and separation efficiency. Thus, the meshes with larger pore size (300 μm) are more suitable to separate target oil from oily water, compared to smaller pore sized mesh (50 μm). The as-made SiNP-coated mesh showed excellent oil affinity and water repellency, thus, the superhydrophobic SiNP-coated mesh was used for gravity-driven separation of oils from oily water, seawater, and wastewater. For experimental comparison, the separation efficiency and recyclability of hydrophobic sponge and oil sorbent paper were also evaluated.

Experimental

Preparation of silica nanoparticles

Silica nanoparticles (SiNP) were prepared via a process based on the well-known Stöber method, using tetraethylorthosilane (TEOS) as a starting material [16]. Two milliliter of TEOS dissolved in 20 mL ethanol was added to 3.5 mL ammonia water (3.3 wt%), and the resulting solution was stirred for 4 h. The sol-type SiNP was washed three times with ethanol and deionized water (DW) by centrifugation, and the resulting SiNP was resuspended in ethanol.

SiNP coating of the mesh and sponge

The stainless steel 304L mesh, which has elemental composition (wt%) of 18.0 Cr, 8 Ni, 2 Mn, 1 Si, and 71 Fe, was selected as main substrate. The mesh with a 300 μm pore diameter was pretreated by immersion in a cleaning solution containing H_2SO_4 and saturated sodium dichromate (4 wt%) for 30 min at 60 °C [17], followed by washing with DW. The clean mesh was dipped in a mixture of 1,2,3,4-butanetetracarboxylic acid (BTCA) and NaH_2PO_2, which was used as a binding agent between the substrate and SiNP, as shown in Fig. 1, followed by drying at 50 °C. Conventional sponge (Magic Eraser, melamine foam), consisting of a formaldehyde-malamine-sodium bisulfate copolymer, was used without any pretreatment.

The mesh and sponge substrates were immersed in the SiNP-coating solution for 10 min, withdrawn vertically, and then dried at 65 °C. To enhance the hydrophobicity of the substrates, a hydrophobic silane solution was prepared with 4 wt% hexadecyltrimethoxysilane (HDTMS) and ethanol, in which the SiNP-coated substrates were immersed for 1 h, followed by heat treatment at 120 °C for a further 1 h, to make the surface more mechanically robust. The final sample is referred to as HDTMS-SiNP-mesh or sponge.

Oil separation

Artificial seawater (35%) and synthetic wastewater (460 mg/L COD and 44 mg/L TN) were prepared by previously reported methods [18,19]. Several oils including hexane, toluene, octadecane, soybean oil, and pump oil were used to evaluate the oil separation efficiency of superhydrophobic mesh and sponge. For the effective observation of oil–water separation, water and oil were dyed with methylene blue and Sudan red 3, respectively. Oil–water separation using mesh was carried out with a homemade flow tube-type oil–water separator (Fig. S1), and the oil separation efficiency of the sponge was evaluated based on the absorption capacity. Moreover, the separation efficiency and stability during recycling were evaluated for the SiNP-coated substrates, and compared with commercial oil-absorbent paper (Baiksan Lintex, Korea) consisting of polyethylene/polyethylene terphthalate.

Characterization

The particle shape and size distribution of SiNP were analyzed by transmission electron microscopy (TEM, JEM-1010, Jeol), and the surface morphology of the mesh and sponge was analyzed using field emission scanning electron microscopy (FE-SEM, S-4800). The contact angles (CA) were measured with a homemade goniometer [20] with the volume of the individual water and oil droplets being 10 μL.

Results and discussion

Superhydrophobic or superhydrophilic substrates for gravity-driven oil separation have mainly used stainless steel [5,8,10,21,22] or copper mesh [9,11,12]. In the case of copper mesh, the surface is principally modified with Cu_2O film, which is prepared by electrodeposition or thermal oxidation, to obtain hydrophobicity [12]. Stainless steel mesh is often selected by many researchers due to its high physicochemical stability, wide availability, and relatively low cost. Several methods, including spray-dry [8], electrochemical deposition [12], dip-coating [23], and immobilization of hydrophobic moieties [21], have been used to fabricate superhydrophobic stainless steel mesh, which is subsequently used to separate oil–water mixtures. Therefore, herein, the easy and simple dip-coating of SiNP on stainless steel mesh was selected as the fabrication method for the superhydrophobic oil–water separator, which is economically viable, can be implemented on a larger-scale, and is recyclable.

As illustrated in Fig. 1, SiNP was immobilized with a BTCA binder on the stainless steel mesh to change the surface properties.

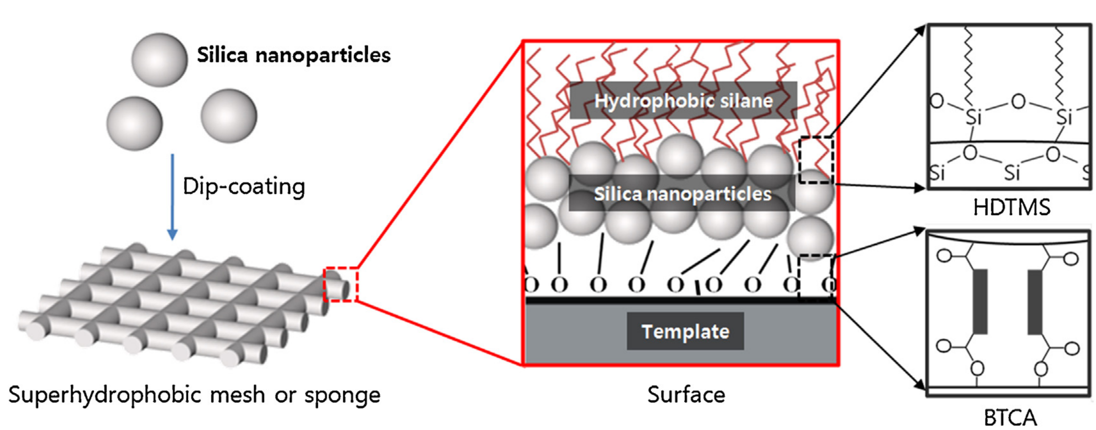

Fig. 1. Schematic diagram of the preparation of superhydrophobic mesh or sponge with hydrophobic SiNP using the dip-coating method.