Chemical Engineering Journal 331 (2018) 278–289

Contents lists available at ScienceDirect

Chemical Engineering Journal

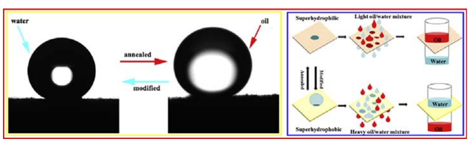
journal homepage: www.elsevier.com/locate/cej

On-demand oil/water separation of 3D Fe foam by controllable wettability

Yan Liu[a,*], Bin Zhan[a], Kaiteng Zhang[a], Cigdem Kaya[b], Thomas Stegmaier[b], Zhiwu Han[a], Luquan Ren[a]

[a] Key Laboratory of Bionic Engineering (Ministry of Education), Jilin University, Changchun 130022, PR China
[b] German Institutes of Textile and Fiber Research Denkendorf, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Fe foam
Superhydrophobic
Underwater superoleophobic
Switchable wettability
Oil-water separation

ABSTRACT

Oily pollution has become a worldwide problem due to the increasing of oil spill accidents as well as the discharge of oily wastewater. Material with superhydrophobic or underwater superoleophobic characteristic to deal with oily pollution have been reported frequently, but material with controllable wettability transition properties were still few been reported. Herein, we presented a facile, efficient, economical method to prepare a superwetting Fe foam that could achieve controllable wettability transition by modification and annealing alternately. The modified foam showed superhydrophobic and superoleophilic properties (oil-removing mode), which can be used for the filtration of heavy oil in the oil/water mixtures. With the annealing treatment, the as-prepared sample exhibited superhydrophilic/underwater superoleophobic characters (water-removing mode), which allowed water to pass through but blocked light oil. Besides, the as-prepared foam could separate various oil/water mixtures and show high separation efficiency. We are hoping that the controllable wettability filtration sample could realize on-demand oil/water separation and provide a new idea to solve the oil pollution problem.

1. Introduction

In the past few years, with the increasing of oil spill accidents and discharge of oily wastewaters, oil/water separation has become a worldwide challenge [1,2]. Frequent oil spillage and oily waste water, not only have a serious impact on environment, but also pose great threaten to the marine ecosystem. The leaked oil bring poisonous compounds into the ocean, pose a serious threaten to the marine ecosystem, and even cause serious damage to human health through the food chain, indirectly [3,4]. Therefore, efficient and environmental friendly method to deal with oil pollution has become a research hotspot. Separation technology as one method to deal with pollution, it not only reduces of secondary pollution, but also allows the collection oil be reused. Traditional separation technologies including gravity separation, filtration, chemical dispersants, flotation, in situ incineration, centrifugation, and so on [5–9]. However, most of these methods require harsh conditions, complex instruments, environmentally harmful modifier and even toxic drugs, which limits their application in industry [10]. In addition, these technologies could not separate oily wastewater completely, thus remaining oil in water or water in oil. Researchers commit to finding a new way to deal with pollution problems.

Inspired by lotus leaf [11,12], red rose petal [13], Namib desert beetle [14] and other creatures [15,16], scholars found that superwetting characteristic may provide them a new way to solve the oily wastewater pollution problem. Jiang and his team for the first time reported that a combination of hierarchic structure with some chemical constituents could lead to superhydrophobicity, and the as-prepared

* Corresponding author.
E-mail address: lyyw@jlu.edu.cn (Y. Liu).

http://dx.doi.org/10.1016/j.cej.2017.08.081
Received 30 May 2017; Received in revised form 9 August 2017; Accepted 16 August 2017
Available online 24 August 2017
1385-8947/

superwetting material used for oil/water separation. Up to now, various methods have been successfully employed for oil/water separation, including electro-spinning [17,18], sol-gel method [19], chemical vapor deposition [20,21], self-assembly [22], chemical etching [23], and so forth [24,25]. Of all the techniques mentioned above, etching process is very popular due to its simple operation. In addition, this process could obtain a rough structure without changing the surface composition, and made the as-prepared sample with better stability. Thus, etching process method shows great promise in application [26].

With the continuous development of oil and water separation technology, taking the oil density into consideration, oil-removing mode [27,28] and water-removing mode [29,30] were proposed as two efficient ways to separate oily wastewater. In oil-removing mode, the material show superhydrophobic/superlipophilic characteristics that allow heavy oil permeated rapidly while repelled water. In water-removing mode, material with superhydrophilicity/underwater superioleophobicity that can separate water from light oil wastewater. In recent years, multifunctional material that combination of oil-removing mode and water-removing mode have been reported to handle different oily pollution [31,32]. Researchers changed the material wettability by adding external stimuli. The most external stimuli were light illumination [33], electrical potential [34], pH values [35] and thermo-treatment [36]. For example, Yan et. sprayed hydrophobic ZnO nanoparticles (NPs) and waterborne polyurethane (PU) mixtures on stainless steel mesh to fabricate a multifunctional coated surface. Switchable transition between superhydrophobicity and superhydrophilicity/underwater superoleophobicity can be rapidly realized by UV illumination and heat treatment alternately [37]. Li et. via a spray coating process fabricated a diatomite coated mesh showing switchable wettability [38]. Parul Raturi et. fabricated ZnO nanowires (NWs)-coated stainless steel (SS) mesh with reversible wettability [39]. Among these external stimuli species, thermo-treatment was well-received not only for its easy operation, but also for the accurately control of the time and temperature.

Among numerous separation materials with superwetting properties, the three-dimensional porous material as a new material has aroused great concern. Compared with the traditional two-dimensional (2D) materials, the porous metal foam with three-dimensional (3D) structure has rather large specific surface area, well-developed porous structure, excellent strength, low cost and simple preparation process, made it more promising and adequate for oil/water separation [40,41]. Cheng et al. fabricated superhydrophobic nickel foam by combining electroless metal deposition ($AgNO_3$) with self-assembled monolayers (n-dodecanethiol) [42], Li et al. immersed the copper foam to KOH and $(NH_4)_2S_2O_8$ mixture solution, then dipped into stearic acid ethanol solution to fabricate a three-dimensional (3D) CuO coated superhydrophobic foam [43]. wang et al. were prepared superhydrophilic Cu foam surfaces by electrodeposition and chemical oxidation, the superhydrophilic surfaces then modified by NDM to fabricate superhydrophobic Cu foam [44]. However, to the best of our knowledge, this is the first attempt to fabricate Fe foam with controllable wettability for oil/water separation.

Herein, we presented a facile, efficient, economical method to fabricate a superwetting Fe foam and achieve controllable wettability transition by modification and annealing alternately. The superhydrophobic foam was fabricated by chemical etching and followed modified by stearic acid. This as-prepared sample allowed heavy oil passed through while repelled water, which corresponding to oil-removing mode. Considering that some oil has a lower density than water, via water-removing mode to separate the pollution would be more suitable. The as-prepared foam was heated treated with 250 °C for 2 h, the wettability would converse from superhydrophobic to superhydrophilic/underwater superoleophobic (water-removing mode), which allowed water to pass through the sample but blocked light oil. In addition, the as-prepared foam had excellent physical and chemical stability. This as-prepared foam with switchable wettability may provide a new idea to solve the oil pollution.

2. Experimental methods

2.1. Materials

Hydrochloric acid, anhydrous ethanol, chloroform, toluene, hexane, gasoline, acetone were purchased from Beijing Chemical Works. All the reagents are of analytical grade and used without further purification. Stearic acid ($C_{18}H_{36}O_2$) was purchased from Tianjin Guangfu Fine Chemical Research Reagent Institute, copper chloride ($CuCl_2$) was obtained from Tianjin Guangfu Technology Development Co., Ltd. Diesel and gasoline were products of SINOPEC. Sudan III as a coloring agent ($C_{22}H_{12}N_4O$) was purchased from Sinopharm Chemical Reagent Co., Ltd. Fe foam (average pore size of 300 μm, pore number:110 PPI) was obtained from Kunshan Electronic Technology Co., Ltd.

2.2. Sample preparation

Fe foam with size of 20 × 20 mm was ultrasonically rinsed in acetone, ethanol, 0.01 M hydrochloric acid solution for 10 min to thoroughly remove the surface impurities and native oxide. 0.5 M cupric chloride ($CuCl_2$) and 0.1 M hydrochloric acid (HCl) were added together to form a mixture solution, and then immersed the pre-treated Fe foam into the mixtures solution for different times (10 s, 30 s, 50 s, 70 s, 90 s, 110 s, 130 s). After the reaction, the foam was dried at 40 °C for 5 min. Subsequently, the dried foam was soaked into 0.1 M stearic acid ($C_{18}H_{36}O_2$) solution for 40 min and dried at 40 °C for 20 min. After annealed in heat treatment furnace at 250 °C for 2 h, the modified sample immersed in water subsequently, so that the as-prepared sample would converse from superhydrophobic to underwater superoleophobic.

2.3. Sample characterization

The water/oil contact angles were measured by contact angle meter (OCA 20 data physics, Germany) at room temperature so as to characterize the surface wettability. Water droplets (3 μL) were carefully dropped onto the surface, and the average static contact angle value was obtained by measuring five different positions of each surface. The surface morphology of sample was examined by a scanning electron microscope (SEM, EVO 18, ZEISS). The chemical composition of the sample was characterized by X-ray photoelectron spectroscopy (XPS, SPECS XR50, Japan).

2.4. Oil-Water separation apparatus

The device consists of peristaltic pump, beakers. Due to the excellent flexibility of Fe foam, the as-prepared sample folded into a box. In order to achieve continuous separation, a peristaltic pump was added as an external driving force, pipes were fixed on beaker by three binder clips. There were two beakers to collect the separate solution throughout the separation system. The beaker on the right side was used to hold oil/water mixture solution, and on the left side was used to collect the separate solution. This device could achieve continuous separation.

3. Results and discussion

3.1. Surface morphology

It is well known that morphology structure and chemical composition play an important role in the material surface wettability. The forming of surface morphology was related to the etching time. Therefore, a series of experiments were done to confirm the relationship between reaction time and surface wettability, and SEM was used to