Journal of Cleaner Production 180 (2018) 307–315

Contents lists available at ScienceDirect

Journal of Cleaner Production

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

Oil removal from oily water by a low-cost and durable flexible membrane made of layered double hydroxide nanosheet on cellulose support

Xuejie Yue [a], Tao Zhang [a, b, *], Dongya Yang [b], Fengxian Qiu [a, b, **], Zhangdi Li [a], Yao Zhu [a], Hangqiang Yu [a]

[a] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, Jiangsu Province, China
[b] Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, Jiangsu Province, China

ARTICLE INFO

Article history:
Received 2 September 2017
Received in revised form
15 January 2018
Accepted 19 January 2018

Keywords:
Oil/water separation
Superhydrophobicity
In situ growth
Surface modification
Cellulose filter

ABSTRACT

Due to frequent oil spill accidents and the increase of industrial oily wastewater, the removal of oil and organic pollutants from water is highly desired. In this work, a low-cost and durable flexible membrane made of layered double hydroxides nanosheets on cellulose support is successfully fabricated by combining the *in situ* growth technique and hydrophobic modification. Firstly, the rough surface is fabricated by *in situ* growth of Zn-Al layered double hydroxide nanosheets. Then, the superhydrophobic surface is obtained by grafting the silane coupling agent. The relevant results revealed that the obtained membrane showed both superhydrophobic and superoleophilic propertied simultaneously. The samples not only show high separation efficiency (all above 94.4%), great chemical durability and good recyclability, but also display excellent separation properties for surfactant-stabilized water-in-oil emulsions with high separation efficiency (less than 25 ppm) and good flux (500 $Lm^{-2}h^{-1}$) without extra energy. Therefore, the superhydrophobic layered double hydroxide/cellulose membranes enable an efficient separation for various oil/water emulsions, showing attractive potential for practical oil/water separation.

1. Introduction

In the modern social product activity, large number of oily wastewater is daily produced because of the sharp development of oil-related industries (such as the petroleum, food, textile, leather, steel and metal-finishing industries) (Feng et al., 2017). In addition, the leakage of oil during the exploring, transportation and storing of crude oil, is also an important factor which will cause serious environmental and ecology damage (Zhang et al., 2017). For example, the 2010 Gulf of Mexico oil spill, one of the most harmful pollution accidents, released more than 210 million gallons of crude oil that greatly harmed the ecosystems of oceans, resulting in negative impacts on the fish industry, tourism, and so on (Doshi et al., 2018). Thus, separation of oils and organic solvents from oily wastewater is an important global challenge for energy conservation and environmental protection (Yue et al., 2017b).

Considerable efforts have been made for treatment of oily wastewater using various methods, including absorption (Kong et al., 2017), solvent extraction (Karatum et al., 2016), electrocoagulation (Inan et al., 2004) and coalescers (Motta et al., 2014). However, the inherent weaknesses of these techniques, such as high operational costs, low oil separation efficiency, second pollution and high energy consumption, hinder their practical applications in oily wastewater treatment (Yue et al., 2017b). Because of a fast separation efficiency, low energy consumption and facile operation, membrane separation technology is considered to be more effective and advantageous in large-scale processing for oil/water mixtures, especially for the abundant emulsions in industry. Therefore, amount of research on the design and fabrication of oil separation membranes for treatment of oily wastewater (Yue et al., 2017a).

* Corresponding author. School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, Jiangsu Province, China.
** Corresponding author. School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu Province, China.
E-mail addresses: zhangtaochem@163.com (T. Zhang), fxqiu@126.com (F. Qiu).

https://doi.org/10.1016/j.jclepro.2018.01.160
0959-6526/

It is known that the superwetting surfaces of separation membranes play a substantial role in separating oily wastewater. Most of the attention is focused on the fabrication of superhydrophobic/superoleophilic membranes based on construction of hierarchical rough structures and post hydrophobization. Various superhydrophobic/superoleophilic separation membranes, including carbon-based composite membranes (Chaudhary et al., 2014), ceramic membranes (Lu et al., 2016), foam-based membranes (Zhang et al., 2017a) and metallic mesh-based membranes (Cao et al., 2018) have been successfully fabricated prepared by utilizing the synergistic effect of surface roughness and surface hydrophobic modification. These membranes show a higher oil-water separation efficiency and wide applicability, because the superhydrophobic property of the membranes could repel water completely while the superoleophilic property makes the membranes absorb oil rapidly. For example, Chen and co-workers (2016) created superhydrophobic/superoleophilic mesh with multiscale roughness structure by spray coating, which showed that oil separation efficiency reaches up to more than 99.85%. Zhang et al. (2013) fabricated superhydrophobic $Cu(OH)_2$ nanowire-haired membranes that allow for effective separation of water-rich immiscible oil/water mixtures with extremely high separation efficiency. Although various oils separation membranes have been developed and indicated for potential applications in oily wastewater treatment, practical applications of separation membranes have been hampered by the laborious strategies, expensive raw materials, and complicated and time-consuming processes (Doshi et al., 2018). Moreover, the disadvantages of oils separation membranes, such as weak flexibility, recyclability and durability, have also affected the practical application (Šereš et al., 2016).

Cellulose filter, as a ubiquitous flexible material, is widely used for solid-liquid and solid-air separation. Compared to inorganic membrane material, the cellulose filters have proved to be more suitable candidates as oils separation membranes for treatment of oily wastewater due to its interconnected pore structures, low cost, recyclability, renewability and good flexibility (Wang et al., 2010). Layer double hydroxide (LDH), also known as anionic clays, is one of the most useful inorganic layered compounds with unique structure, which are widely used in the field of catalysts, tailor-making adsorbents, separation, precursor materials, ion exchangers, immobilization of biological compounds and metal protection (Ahmed et al., 2012). Recently, a variety of hierarchical LDH materials fabricated by *in situ* growth have received great consideration attention, because of the strong adhesion and controlled microstructures of the LDH coating on the substrate. For example, Zhang et al. (2008) reported the *in situ* fabrication of oriented Ni-Al LDH films with tuning wetting properties and high adhesion on a porous anodic PAO/Al substrate. The fabricated LDH films have potential for commercial application in the corrosion protection of aluminum. More recently, our group adopted a simple route to synthesize hierarchically LDH films by *in situ* growth of LDH platelets on the Al substrates to control the infrared radiation properties (Zhang et al., 2015). Thus, the controlled fabrication of LDH coating on the cellulose filter is important from the fundamental and application point of view of oils separation membranes.

In this work, fluorine-free hierarchical LDH coated cellulose filter with superhydrophobicity and superoleophilicity was prepared by *in situ* growth LDH on the surfaces of cellulose filter, followed by hydrophobic modification. The samples not only selectively absorb a wide range of oils from the water with high separation efficiency, but also show excellent separation properties for surfactant-stabilized water-in-oil emulsions with good flux without extra energy. More importantly, the obtained LDH/cellulose membrane shows stable recyclability and good performance in harsh environmental conditions, such as acidic and alkaline solutions. The low-cost and controlled fabrication progress, together with the high separation efficiency, make this superhydrophobic LDH/cellulose membrane for large-scale industrial production as a practical method for treating oily wastewater.

2. Experimental

2.1. Materials

Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), ammonium hydroxide (NH_4OH, 25.0–28.0%), ammonium chloride (NH_4Cl), trichloromethane ($CHCl_3$) and zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) were purchased from Sinopharm Chemical Regent Co., Ltd. Triethoxy vinyl silane (A151) was obtained from Shanghai Macklin Biochemical Co., Ltd. All above agents were of analytical grade and used without further purification. Qualitative filter paper (moderate speed, nominal pore size 15~20 μm, thickness 340 ± 20 μm) was purchased from Hang Zhou special paper Co., Ltd., China, which was thoroughly cleaned with ethanol and deionized water to remove possible impurities for further use.

2.2. Fabricating of hierarchical LDH coated cellulose membrane

The aluminum primer sol was prepared by the hydrolysis of aluminum nitrate as described in our previous work (Yue et al., 2017a). The LDH coated cellulose filter was prepared by *in situ* growth of LDH nanoplatelets on the surfaces of paper fiber. In a typical synthesis, the pretreated filter paper (7 cm in diameter) was immersed vertically into the aluminum primer sol (0.1 mol/L) for 3 min, followed by drying in a vacuum oven at 80 °C for 2 h to obtain the AlOOH/paper. The whole process was repeated 30 times to ensure the deposition of the AlOOH on the surfaces of paper fiber. Then, 1.0 mmol of zinc acetate dihydrate and 6.0 mmol of ammonium chloride were dissolved in 100 mL of deionized water under stirring for 30 min. The AlOOH/paper was immersed in the above mixed solution in a stainless-steel autoclave and treated at 115 °C for 6 h under autogenous pressure. Finally, the obtained LDH/paper membrane were taken out of the vessel, washed with distilled water and anhydrous ethanol several times, and dried in air at 60 °C for 12 h. The hierarchical LDH nanosheets coating membrane was obtained and the preparation process of hierarchical LDH coated cellulose membrane was schematic showed in Scheme 1A.

2.3. Fabricating of superhydrophobic surface

The superhydrophobic interface of LDH/cellulose membrane was fabricated by microwave hydrothermal processing. Typically, 50 mL of anhydrous ethanol, 50 mL of deionized water and 1.5 mL of A151 were mixed together, then a piece of pristine LDH/paper membrane was put into the mixture solution. The mixtures were sealed with a glass container and placed in the microwave reaction apparatus with a frequency of 2.45 GHz. The mixture was rapidly heated to 75 °C at a power of 600 W, and maintained at 75 °C for 3 h. Finally, the obtained products were washed thoroughly with distilled water and dried in vacuum oven at 80 °C for 24 h. The formation superhydrophobic surface is shown in Scheme 1C and D.

2.4. Oil–water separation experiment

The oil/water separation experiment was performed at room temperature and measured by the gravimetric method. A series of oils including toluene, edible oil, petroleum ether, heptane and chloroform were chosen to be the model oil. The superhydrophobic