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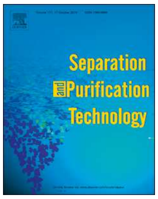

Three-dimensional attapulgite with sandwich-like architecture used for multifunctional water remediation

Mengke Cui[a], Peng Mu[a], Yongqian Shen[b,*], Guorong Zhu[a], Lan Luo[a], Jian Li[a,*]

[a] *Gansu International Scientific and Technological Cooperation Base of Water-retention Chemical Functional Materials, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China*

[b] *State Key Laboratory of Advanced Processing and Recycling of Non-ferrous Metals, Key Laboratory of Nonferrous Metal Alloys and Processing, Ministry of Education, School of Materials Science & Engineering, Lanzhou University of Technology, Lanzhou 730050, China*

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ABSTRACT

With the development of social economy, large quantities of oily wastewater discharged from our daily life and industries have already threatened human health and natural environment. Generally, during wastewater treatment, there are other pollutants including dyes and heavy metal ions in water apart from various kinds of oils. Therefore, how to remove these pollutants during the emulsion separation is of great significance. More recently, some membranes with underwater superoleophobic property have been ready to separate various oil-in-water emulsions. However, the fabrication of majority of these superwetting membranes involves complicated process control, special equipment and expensive reagents, which further restricts the multifunction of practical large-scale applications. Herein, the three-dimensional attapulgite (APT) layer with sandwich-like architecture was fabricated by a facile and universal applicable approach without any further modification of the original membranes. This method employs ordinary material with underwater superoleophobicity towards the effective and fast separation of different oil-in-water emulsions and adsorption of organic dyes and heavy metal ions. Compared with the fabrication methods of traditional coatings, the design thought of this paper is universal and brand-new that can easily be applied to a broad range of materials. This work can provide more novel ideas for the fabrication of oil/water separating materials, leading to multifunctional water purification.

1. Introduction

Water problems are predicted to deteriorate further in the future multi-decades, with water shortages occurring around the world, even in areas contemporary considered to be rich [1–8]. Besides, oil/water separation has become a pressing global problem in that the large amount of domestic sewage and the oily wastewater discharged from many industrial processes [9–16]. Generally, the oil/water mixtures involve free and emulsified oil/water mixtures (the droplet size is typically less than 20 μm) [17–20]. Inspiring from nature, various superwetting materials have been fabricated and used to separate free oil/water mixtures and surfactant-free oil/water emulsions [21–26]. Among them, the emulsified oil/water mixtures may result in serious consequences and emulsions are more difficult to be separated comparing with the immiscible oil/water mixtures [27]. Recently, such membrane materials based on special wettability have captured wide attention in separating emulsified oil/water mixtures in that they can conquer the weaknesses of the traditional filtration films to some extent [28,29]. For example, Zhu et al. fabricated the zwitterionic polyelectrolyte grafted PVDF via a surface-initiated atom transfer radical polymerization (SI-ATRP) technique for separating oil from water [30]. Zhang et al. introduced a new superhydrophilic and underwater superoleophobic poly-(acrylic acid)-grafted PVDF filtration membrane by the salt-induced phase-inversion approach [31]. However, these underwater superoleophobic membranes for oil-in-water emulsions separation always required expensive reagents, complicated preparation procedures and requirement for special equipments [32]. Furthermore, poor adhesion is often encountered by modifying the polymeric membranes with special wettability. Thus, the large-scale fabrication of these superwetting materials is still restricted. On the other hand, among the complex pollutants in water, water-soluble contaminants including heavy metal ions and dyes are also the major contaminants which are harmful to human beings and difficult to be degraded by the environment [33–35]. What's not so satisfying is that the above-mentioned membranes only could separate emulsions into oil and water phase, lacking of functions for removal of contaminants from water

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* Corresponding authors.
E-mail addresses: syqch@163.com (Y. Shen), jianli83@126.com (J. Li).

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phase [36]. It is virtually impossible to improve the versatility of membranes material due to their traditional structure. Therefore, considering the efforts undertaken so far, it is critical need to explore a lower cost, environment-friendly, and universal approach for the preparation of multifunctional separation materials with a kind of novel structure, which can not only separate surfactant-stabilized oil-in-water emulsions but also reduce the concentration of water-soluble contaminants [37]. Unfortunately, extremely rare attention has been paid to this key issue.

APT is a kind of hydrated octahedral layered magnesium aluminum silicate mineral with reactive −OH groups on the surface, which can be used as the adsorbents for removal of dyes and heavy metal ions due to its porous structure, adsorbed cations and large specific surface area [38–40]. As one of the most typical hydrophilic materials, APT shows satisfactory water-absorbing and water-retaining capacities. In this work, APT is stacked into a layer with sandwich-like architecture for effective separation of surfactant-stabilized oil-in-water emulsion and adsorption of organic dyes and heavy metal ions in aqueous solutions. This novel approach without any further modification of the original membranes is facile and universal, avoiding the complex process involving in the preparation of traditional filtering materials. Due to the outstanding water-absorbing and water-retaining abilities, the APT layer with sandwich-like architecture presents underwater superoleophobic performance and low oil adhesion. By making use of the underwater superoleophobicity and low adhesion to oils, a series of surfactant-stabilized oil-in-water emulsions could be efficiently separated by gravity with the high separation efficiency. More importantly, the unique structural features of APT provide benefits in the adsorption of dyes and heavy metal ions [41,42]. Noticeably, the unique sandwich-like structure design can improve the adsorption effect of water-soluble contaminants to some extent. Significantly, for the application of APT layer with a unique sandwich-like architecture in multifunctional water remediation, APT layer is capable of emulsions separation and contaminations adsorption in the actual application environment. We believe that the general rule using ordinary material with underwater superoleophobicity towards the separation of surfactant-stabilized oil-in-water emulsion could be also extended to develop a broad range of materials.

2. Experimental

2.1. Materials

The APT micro-powder [$Mg_5Si_8O_{20}(OH)_2(OH)_4{\cdot}4H_2O$] acquired from Jiuchuan Clay Technology Co., Jiangsu, China, was firstly activated with 4 M HCl solutions before use. Kerosene and diesel were obtained from the local store. Organic solvents (hexane, heptane and petroleum ether) were provided by Guangdong Guanghua Sci-Tech Co., Ltd. Tween-80, Methylene blue, crystal violet and orange-II were purchased from Sinopharm Chemical Reagent Co., Ltd. The other reagents were all of analytical reagent grade.

2.2. Preparation of APT layer

Firstly, the APT micro-powder was obtained through further activation treatment with 4 M HCl solution about 4 h, and then dried in an oven at 80 °C for 6 h. Subsequently, the as-prepared micro-powder was randomly accumulated to a sufficient thickness to make it form a layer onto a filter paper. Finally, the APT layer was fixed by the stainless steel mesh (300 mesh sizes) to prevent the APT micro-powder from being lost. The density (ρ_{layer}) of the APT layer can be calculated by the equation below:

$$\rho_{layer} = m_{layer}/V_{layer} \tag{1}$$

where m_{layer} and V_{layer} are the weight and volume of the APT layer, respectively. Then, the density (ρ_{layer}) of the APT layer is 0.28 g/cm^3. The porosity (ε) of APT layer can be calculated using the equation below:

$$\varepsilon_{layer} = 1 - \frac{m_{layer}/\rho_{APT}}{V_{layer}} \times 100\% \tag{2}$$

where m_{layer} and V_{layer} are the weight and volume of the APT layer, ρ_{APT} is the density of APT ($\rho_{APT} \approx 1.14$ g/cm^3). And ε_{layer} approximately is 75.75%.

2.3. Separation of surfactant-stabilized oil-in-water emulsion

Surfactant-stabilized oil-in-water emulsions were obtained by mixing water and oil (namely kerosene, diesel, hexane, heptane and petroleum ether) in a ratio of 50:1 (v/v) with 2 mg of Tween-80 per mL of emulsion and the mixtures were stirred for 6 h to obtain the milky solution. Typically, the as-prepared emulsions were stable for one month without demulsification when placed in ambient conditions (Fig. S1). Before the separation process, the APT layer was pre-wetted with water. Through synergy between the underwater superoleophobicity and the size-sieving effect of the compact APT layer, various surfactant-stabilized oil-in-water emulsions can be successfully separated. The driving force was its own gravity in the separation process. The separation efficiency was counted according to the following equation:

$$\eta = (1 - C_f/C_i) \times 100\% \tag{3}$$

where C_i and C_f are oil concentration of the feed and collected water after separation, respectively.

2.4. Adsorption studies

Adsorption experiments were carried out using the same device for the separation of oil-in-water emulsion at room temperature. The initial concentrations of methylene blue, crystal violet and orange-II solutions were 80 mg/L. The metal ions studied were Cu (II), Pb (II) and Fe (III). Similarly, the stock solutions (40 mg/L) of Cu (II), Pb (II) and Fe (III) were prepared by dissolving the appropriate amounts of $CuCl_2{\cdot}2H_2O$, $Pb(NO_3)_2$ and $FeCl_3{\cdot}6H_2O$, respectively, in distilled water. The maximum adsorption q_{max} (mg/g) was counted by the equation below [43]:

$$q_{max} = \int_0^{V_f} \frac{C_i - C(V)}{M} \mathrm{d}V = \frac{C_i V_f}{M} - \frac{1}{M}\int_0^{V_f} C(V)\mathrm{d}V \tag{4}$$

where C_i (mg/L) is the pollutant concentrations at the beginning stage, $C(V)$ is the concentrations of pollutant, V_f and M (g) are the total volume of the pollutant solution through the APT layer and the mass of the APT layer, respectively.

2.5. Characterization

The surface topography was observed by field emission scanning electron microscopy (FE-SEM, Zeiss). The size of APT was characterized by Transmission electron microscopes (TEM). The SL200KB apparatus was used to measure the contact angle (CA) and sliding angle (SA) of water/oil droplets (5 μL) at ambient temperature. Fourier transform infrared (FT-IR) spectra were recorded on a Bio-Rad FTS-165 instrument using KBr as the background. The phase structure was characterized by using an X-ray diffractometer (XRD) (Rigaku Corp., D/max-2400) equipped with graphite monochromatized Cu KαKα radiation. Droplet sizes of emulsions were measured using a Malvern Zetasizer Nano ZS (Malvern, UK). Optical microscopy images were taken on an inverted fluorescence microscope IX51 (Olympus, Japan) by dropping emulsion solution on biological counting board. The oil content in the collected filtrates was acquired by an infrared oil measurement instrument (SN-OIL480). The concentrations of dyes were tested on double beam UV visible spectrophotometer (TU-1901). The concentration of Cu (II), Pb (II) and Fe (III) ions were measured by a Z-