Applied Surface Science 434 (2018) 57–62

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

A facile method to prepare dual-functional membrane for efficient oil removal and in situ reversible mercury ions adsorption from wastewater

Qingdong Zhang[a], Na Liu[a,b], Yingze Cao[c], Weifeng Zhang[a], Yen Wei[a], Lin Feng[a,*], Lei Jiang[d]

[a] Department of Chemistry, Tsinghua University, Beijing, 100084, PR China
[b] Institute of Materials for Energy and Environment, School of Materials Science and Engineering, Qingdao University, Qingdao 266071, PR China
[c] Qian Xuesen Laboratory of Space Technology, China Academy of Space Technology, Beijing, 100094, PR China
[d] Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, Beihang University, Beijing, 100191, PR China

ARTICLE INFO

Article history:
Received 6 July 2017
Received in revised form
13 September 2017
Accepted 27 September 2017
Available online 29 September 2017

Keywords:
Reversible mercury ions adsorption
Oil/water separation
Adsorption and desorption
Dual-functional membrane

ABSTRACT

In this work, a novel thiol covered polyamide (nylon 66) microfiltration membrane was fabricated by combining mussel-inspired chemistry and coupling reaction, which owns excellent dual-function that can simultaneously remove oil from water efficiently and adsorb the mercury ions contained in the wastewater reversibly. Such membrane exhibited high oil/water separation efficiency, outstanding mercury adsorption ability, and good stability. Moreover, it can be regenerated in nitric acid solution, and maintain its good adsorption performance. The as-prepared membrane showed great potentials for water purification to reduce the heavy metal ion pollution and complicated industrial oily wastewater and living wastewater.

1. Introduction

Nowadays, water pollution has been a global issue due to the rapid industrialization, unsustainable production patterns, etc. [1–3]. Oils are the important pollution in water mainly caused by frequent oil spill accidents, large quantities of oily wastewater discharged from all kinds of industries and our daily life [2,4–10]. The environmental pollution aroused by oil/water mixtures makes a lot of damage to the ecotope related to people's production and living. The treatment of wastewater has attracted great interest, and materials that can effectively separate immiscible oil/water mixtures are in great demand [11,12]. Oil/water separation materials with special wettability, representing one of the most important interface materials, have been widely developed [13–17].

Wastewater treatment not only needs to separate the oil in the effluents through the special wettability of the materials, but also to remove the water-soluble contaminants [13]. Heavy metal ions contamination is the other major aspect of water pollution, and water pollution by potential toxic metal ions has become a serious environmental problem [18–20]. Among the many heavy metals, mercury is acknowledged as one of the most harmful pollutants because of its high toxicity, volatility and bioaccumulation [21–23]. The mercury can accumulate in the human body, causing adverse effects by impairing mental and neurological functions [24–26]. Therefore, it is highly necessary to prevent contamination and efficiently remove mercury ions from the environment [27–29].

However, the reported oil/water separation materials pay little attention to simultaneously removing the water soluble contaminants. The reported oil/water separation materials can be capable of effectively separating oil/water mixture but invalid for removing the remaining water-soluble contaminants. With regard to the materials that can adsorb heavy metals, it is necessary to desorb them for regeneration through complicated procedures after adsorption. In the meanwhile, these materials are helpless for the treatment of oil/water mixtures [18,20,21]. Recently, our group has reported a novel Hg^{2+} responsive oil/water separation mesh with poly(acrylic acid) hydrogel coating and achieved wettability transition by immersion in Hg^{2+} solution, however, the mesh cannot be reversed thus severely limit its application [30]. And we also

* Corresponding author.
E-mail address: fl@mail.tsinghua.edu.cn (L. Feng).

https://doi.org/10.1016/j.apsusc.2017.09.230
0169-4332/

reported a disulfide bond coated dual functional membrane for simultaneously oil/water separation and proteins adsorption. However, the disulfide bond coated dual functional membrane cannot be reused after one time proteins adsorption [13]. Given the complexity of wastewater composition, an efficient way of wastewater treatment should not only can separate the oil from the water, but also be capable of removing the water soluble pollutants at the same time [13]. That is to say the dual-functional membranes that have the ability of separating oil/water mixtures and adsorbing soluble pollutants reversibly are in great need [13,31].

In this work, we developed a dual-functional thiol covered membrane that can remove oil efficiently and in situ reversible adsorption of the mercury ions contained in the wastewater. What is more, the dual-functional membrane can be repeated use for many times and maintain high separation and adsorption efficiency, which greatly reduces the cost of wastewater treatment and have great potential for industrial large-scale wastewater treatment. As the proof-of-concept, the as-prepared membrane exhibits special wettabilities with superhydrophilicity in air and superoleophobicity underwater. When mercury ions contained oil/water mixtures were poured onto the membrane, water could pass through the membrane by gravity while oil was blocked on the upper side. Simultaneously, the mercapto group (SH) on the membrane surface can capture mercury ions by affinity interaction. More importantly, the mercury ions are easy to be desorbed by the nitric acid immersion and the adsorption performance maintained up to about 100% even after five cycle of usage. Compared with the reported materials for the oil/water separation, the dual-functional membrane presented good chemical affinity to mercury ions, high adsorption and oil/water separation efficiency, showing great potential for practical applications in treatment of complicated industrial wastewater.

2. Experimental section

2.1. Materials

Dopamine hydrochloride (DA) (Sangon Biotech Co. Ltd., Shanghai, China), polyethylenepolyamine (PEPA) (J&K Industrial Inc., Beijing, China), 3-Mercaptopropionic acid (J&K Industrial Inc., Beijing, China), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (Aladdin Industrial Inc., Shanghai, China), Nylon membrane (Φ50 mm*0.22 μm*120 μm, XINGYA purification device factory, Shanghai, China), *N*-Hydroxysuccinimide and mercury nitrate were used as purchased. Other reagents from Sinopharm Chemical Reagent are of analytical grade and used without further purification.

2.2. Instrumentation and characterization

Concentrations of Hg^{2+} were measured by ICP-OES at 194.168 nm (Perkin Elmer ELAN DRC-e, PerkinElmer, Inc., Shelton, CT, USA) under the instrumental operating conditions recommended by producer. Scanning electron microscopy (SEM) images were obtained by field emission scanning electron microscope (SU-8010, Hitachi Limited, Japan). Contact angles were measured on an OCA 20 machine (Data-Physics, Germany) at ambient temperature. Water droplets (2 mL) were used for the WCA measurements in air. For the underwater OCA measurements, the oil droplets (1, 2-dichloroethane, *n*-hexane, etc., 2 mL) were carefully dropped onto the materials, which were immersed in water. The average value of five measurements taken at different positions on the same sample was adopted as the CA. The oil content in the filtrates was extracted by CCl_4 and then tested by infrared spectrometer oil content analyzer (OIL 480). The separation efficiency was calculated by oil rejection coefficient (R (%)) according to

$$R = (1 - C_p/C_0) * 100\%$$

in which C_0 and C_p are the oil concentration of the original oil/water mixtures and the collected water after separation, respectively. And the separation efficiency was the average value of at least three measurements with different samples.

2.3. Preparation of the PDA/PEPA films on nylon membrane

The clean nylon membrane was immersed in a beaker containing 90 mL deionized water and 0.3 g DA. After ultrasonic treatment for 5 min, a 10 mL aqueous solution containing 0.1 g PEPA was added dropwise into the solution. And then the mixture was placed at ambient temperature for 48 h. The as-prepared membrane was washed by deionized water and dried out for secondary reaction.

2.4. Preparation of dual-functional membrane

0.53 g 3-mercaptopropionic acid was first dissolved in 100 mL of the mixture solution of tetrahydrofuran and methylene chloride (1:1) to prepare the reaction solution (50 mmol/L). Second, 1.15 g of EDC was added into the mixture with ultrasonic treatment for 30 min at ambient temperature. And then 0.14 g NHS was added into the mixture with ultrasonic treatment for 10 min. Finally, the PDA/PEPA coated membrane was immersed in the reaction solution for 12 h at room temperature. The dual-functional membrane was cleaned by deionized water and ethanol twice for further characterization.

2.5. Oil/water mixtures separation and mercury ions adsorption experiments

The oil/water separation and mercury ions adsorption experiment procedure was performed as shown in Fig. S1. The dual-functional membrane was fixed between two Teflon fixtures, and both of the fixtures were attached with glass tubes, the diameter of the tube was 25 mm. The oil/water mixtures (5 mL oil mixed with 10 mL mercury ions water solution (30 ppm)) were poured onto the dual-functional membrane and the separation was achieved by the driving force of gravity.

3. Results and discussion

The polydopamine (PDA)/polyethylenepolyamine (PEPA) coated membrane was first prepared according to our previous literature reports by simple immersion in an aqueous solution of dopamine and PEPA [32–34]. Dopamine can form strong adhesive films on the surface of nylon membrane through self-polymerization in alkalescent solution, whereas, PEPA is alkalescent and rich in amino groups that can react with dopamine via Michael addition or Schiff base reaction between amine and catechol groups. The co-deposition PDA and PEPA were assembled spontaneously in solution by covalent bonds and non-covalent bonds and forming plenty of spherical nanoparticles that owned numerous amino groups on nylon membrane with the increased surface roughness (Fig. S2, SI). The hydrophilic amino groups, polar polymer and surface roughness worked together and endowed the membrane with the superhydrophilicity and thus prevented oil from permeating. In addition, the flux of PDA/PEPA coated membrane was even larger than the nylon membrane because of the superhydrophilic property (Fig. S3, SI), which also showed that the effect of coating on the inter-fibre porosity of the original membrane was very small. Meanwhile, the PDA/PEPA coated mem-