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A low-cost mullite-titania composite ceramic hollow fiber microfiltration membrane for highly efficient separation of oil-in-water emulsion

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ABSTRACT

Oil-in-water (O/W) emulsion is considered to be difficult to treat. In this work, a low-cost multi-layer-structured mullite-titania composite ceramic hollow fiber microfiltration membrane was fabricated and utilized to efficiently remove fine oil droplets from (O/W) emulsion. In order to reduce membrane cost, coal fly ash was effectively recycled for the first time to fabricate mullite hollow fiber with finger-like and sponge-like structures, on which a much more hydrophilic TiO_2 layer was further deposited. The morphology, crystalline phase, mechanical and surface properties were characterized in details. The filtration capability of the final composite membrane was assessed by the separation of a 200 $mg \cdot L^{-1}$ synthetic (O/W) emulsion. Even with this microfiltration membrane, a TOC removal efficiency of 97% was achieved. Dilute NaOH solution backwashing was used to effectively accomplish membrane regeneration (~96% flux recovery efficiency). This study is expected to guide an effective way to recycle waste coal fly ash not only to solve its environmental problems but also to produce a high-valued mullite hollow fiber membrane for highly efficient separation application of O/W emulsion with potential simultaneous functions of pure water production and oil resource recovery.

1. Introduction

Oil-in-water (O/W) emulsion emitted into water or soil from industry and domestic sewage is a major environmental pollutant (Gao et al., 2014). Conventional O/W emulsion treatment techniques such as gravity settling (Feng et al., 2004), adsorption (Wang et al., 2012) and flotation (Al-Shamrani et al., 2002) have limitations for efficient separation of emulsions with oil droplet size less than 20 μm (Janknecht et al., 2004). With this intension, membrane separation technology (Križan Milić et al., 2013) comes into sight and is playing a very prominent role in treatment of (O/W) emulsion due to its clear advantages (Padaki et al., 2015) such as continuous membrane process operation with simultaneous production of pure water and oil resource (Chang et al., 2014). Unlike their polymeric counterparts (Janknecht et al., 2004; Salahi et al., 2010), the use of ceramic membranes (Lu et al., 2015) offers several benefits, especially in extremely aggressive environments, such as good mechanical performance, easy membrane regeneration by strong acidic or alkaline solution back-flushing (Yang et al., 2012; Deriszadeh et al., 2010). However, currently, application of ceramic membrane technology encounters several problems such as high cost and membrane fouling.

Conventionally, commercialized ceramic membranes (such as Al_2O_3, SiO_2, ZrO_2, and TiO_2) are too expensive for (O/W) emulsion treatment (DeFriend et al., 2003). As a result, the preparation and potential applications of lower-cost porous mineral-based ceramic membranes made from industrial solid waste coal fly ash have attracted more attentions due to the low cost of both abundant raw materials available and fabrication process (mainly sintering cost)

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(Marchese et al., 2000; Emani et al., 2014). Currently, large amounts of fly ash produced in China are still dumped into ponds or piled on land (Koukouzas et al., 2006) which takes up much valuable agricultural land and can be regarded as unsightly, environmentally undesirable (Iyer and Scott, 2001). Considering such reasons, environment-friendly recycling of coal fly ash is an important issue. To the best knowledge of the authors, the recycling of coal fly ash for fabricating hollow fiber membrane has not been reported in the open literature.

Moreover, in order to mitigate membrane fouling problem, one of the solutions is to develop hydrophilic modification of membrane which provides an enhanced hydrophilic character of membrane surface that can resist oil attachment and thus effectively prohibit permeation flux decline (Li et al., 2009). Coating of more hydrophilic nanoparticles, such as TiO_2 (Chang et al., 2014), Al_2O_3 (DeFriend et al., 2003) and ZrO_2 (Zhou et al., 2010) on membrane pore surface of alumina membranes has been utilized for enhancing surface hydrophilicity due to the presence of more hydroxyl groups on membrane surface (Tsuru et al., 2008). However, through moderate-temperature calcination (usually 400–600 °C), a weak adhesion between hydrophilic nano-particles and skeleton particle surface can not withstand long-term membrane operation due to a hydraulic impact especially under high pressure. To overcome this issue, dip-coating followed by higher temperature sintering of a thin porous TiO_2 membrane as hydrophilic rejection layer is proposed in our work.

In this study, waste coal fly ash was recycled not only to solve its environmental problems but also to produce a high-valued mullite hollow fiber support for the first time, then on which a TiO_2 membrane layer was dip-coated. Results from the current study may open up a facile way of using waste-fly-ash derived ceramic membrane to treat (O/W) emulsion, recycling of industrial solid waste coal fly ash for fabrication of low cost mullite-based hollow fiber membrane for economic and highly efficient treatment of oily water for potential simultaneous production of pure water and oil resource.

2. Experimental

2.1. Preparation of mullite-titania composite hollow fiber membrane

The immersion-induced phase inversion technique was applied to prepare mullite hollow fiber membrane as support using coal fly ash as raw material via a dry/wet spinning process. Preparation of hydrophilic TiO_2 top-layer membrane was carried out via dip-coating method. All those details can be found in the Supplementary Information (see SI, Section 2.1 and Fig. S1).

2.2. Characterization

The morphologies of the as-prepared mullite hollow fiber support and mullite-titania composite membranes were observed using a scanning electronic microscopy (SEM, S-4800, Hitachi Ltd., Japan) equipped with energy dispersive spectrometer (EDS) analysis. The pore size distribution was measured by a pore size distribution analyzer (Porometer 3G, Quantachrome Instruments, USA). The mechanical strength of the supports was measured by the three point bending strength method using a universal testing machine (AGS-X, Shimadzu Ltd., Japan). The crystal structure and the phase transformation were identified by X-ray diffraction (XRD, D8 advance, Bruker Corporation, Germany). Surface chemical property characterization was carried out by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250, Thermo Fisher Scientific Inc. USA) with a nonmonochromatic Al Kα radiation (150 W, 30 kV, 1486.6 eV) as an excitation source.

To probe and compare surface hydrophilic property, the water contact angles for dense disc-shaped mullite and TiO_2 samples were determined using a Kruss DSA 100 apparatus (Kruss Company, Ltd., Germany). Surface active site density was estimated by an acid-base titration of mullite hollow fiber and TiO_2 hollow fiber, the concentration of active surface hydroxyl sites was determined by considering the following equation (Stollenwerk, 1995; Tang and Johannesson, 2005).

$$\mathrm{SOH} = \frac{(\text{moles of H added}(\text{solid} + \text{system}) - \text{moles of H added}(\text{system}))}{2} \quad (1)$$

The surface sites are pH-dependent and the following protonation/deprotonation reactions are considered:

$$\mathrm{SOH} + \mathrm{H}^+ \leftrightarrow \mathrm{SOH_2}^+ \quad (2)$$

$$\mathrm{SOH} \leftrightarrow \mathrm{SO}^- + \mathrm{H}^+ \quad (3)$$

where SOH_2^+, SOH and SO^- refer to the positively charged, neutral and negatively charged sites, respectively. All these experimental details can be found in the SI.

2.3. Microfiltration experiments

2.3.1. Preparation of oil-in-water emulsion

Synthetic (O/W) emulsion with a concentration of 200 $mg \cdot L^{-1}$ was prepared using soybean oil and millipore water. The details of (O/W) emulsion preparation were shown in SI. The size of (O/W) emulsion droplets (see SI, Fig. S2), exhibiting a good stability at a storage time as long as 96 h, was measured by Malvern Mastersizer analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK).

2.3.2. Microfiltration application of (O/W) emulsion

A lab-scale cross-flow membrane separation system was employed (see SI, Fig. S3). Analysis using a total organic carbon (TOC) analyzer (TOC-Vcph, Shimadzu, Japan) gave the organic carbon content in the feed and permeate. For all the membranes the permeation flux (F, $m^3 \cdot m^{-2} \cdot s^{-1}$) was calculated by Formula 4, where the volume of permeate (V, cm^3), membrane area (A, cm^2), and time (t, s) were measured.

$$F = \frac{V}{At} \quad (4)$$

The oil removal efficiency can be evaluated according to the value of TOC removal efficiency R_{TOC}, which is defined as