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Synthesis and characterization of a porous and hydrophobic cellulose-based composite for efficient and fast oil–water separation

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ABSTRACT

Oily wastewater is generated in diverse industrial processes, and its treatment has become crucial due to increasing environmental concerns. Herein, silanized cellulose was prepared by sol–gel reaction between microcrystalline cellulose (MCC) and hexadecyltrimethoxysilane (HDTMS) using for oil–water separation. The silanized cellulose was characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA). A higher mass ratio of HDTMS to MCC made silanized cellulose become looser, and showed lower water absorbency. The silanized cellulose exhibited specific separation performance towards vegetable oil–water mixture (not for mineral oil–water mixture) with separation efficiency of 99.93%. Moreover, the separation was fast with a water flux of 4628.5 L m^{-2} h^{-1}. The separation efficiency still remained at 99.77% even after recycling for 10 times.

1. Introduction

Every year a large volume of oily wastewater is produced from various process industries (Pagidi, Saranya, Arthanareeswaran, Ismail, & Matsuura, 2014). With the characteristics of extensive sources, complex components and poor biodegradability, oily wastewater causes great harm to ecosystems (Gao et al., 2014). Therefore, oil substances must be substantially removed from the water before discharge in order to prevent the deleterious impact on ecosystems and meet progressively more stringent environmental regulations (Barron, 2012; Dalton & Jin, 2010; Montgomery & Elimelech, 2007; Schrope, 2011; Shannon et al., 2008).

Many methods have been developed to solve the problem, but in which some traditional ones, such as dissolved air flotation (Al-Shamrani, James, & Xiao, 2002), flocculation (Yang et al., 2015) and oil skimmers (Nordvik, Simmons, Bitting, Lewis, & Strøm-Kristiansen, 1996) usually have disadvantages of low separation efficiency and high operation cost. Therefore, a variety of separation materials are further developed to overcome these disadvantages. Some meshes (An et al., 2014; La, Nguyen, Lee, Kim, & Kim, 2011; Liao, Ye, & Xu, 2014; Xu et al., 2014; Yin et al., 2014) with superhydrophilicity and superoleophobicity can permeate oil while completely repelling water, and are put effectively into use for oil–water separation. Besides, some synthetic coatings, including inorganic nanoparticles (Chen, De Leon, & Advincula, 2015), polymers (Liu et al., 2015; Xue et al., 2013) and organic/inorganic nanocomposites (Gondal et al., 2014; Li, Wang, Wang, Cheng, & Wang, 2014) were used to modify the meshes to achieve a good oil–water separation efficiency of 98–99%. Although the synthetic materials can well separate the oil–water mixture, they are environmentally unfriendly, and may further lead to secondary pollution.

Recently, some biodegradable separation materials are reported, in particular based on cellulose (Mansourizadeh & Azad, 2014; Rohrbach et al., 2014; Zhou et al., 2013). Cellulose/polyvinylidene fluoride-co-hexafluoropropylene membranes were prepared for gasoline/water separation via electro-spinning and direct coating technique (Ahmed, Lalia, Hilal, & Hashaikeh, 2014). Wang and Lin (2013) fabricated a cellulose sponge with stable wettability of superoleophobicity under water and superhydrophilicity under oil which can remove crude oil from water. Ma, Kang, and Cui (2014) reported a separator using glass microfiber as coalescence medium for diesel oil/water separation. However, only a few reports focused on the separation of different types of oil–water mixture including vegetable oil–water mixture (Liu, Ma, Zang, Gao, & Wang, 2014; Pintor, Vilar, Botelho, & Boaventura, 2014). Till now, it still remained unclear how modified cellulose could affect separation selectivity among different oil–water

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mixtures. Besides, there has been more interest in cellulose-based superfast separation materials.

In this work, we presented a simple method to fabricate hydrophobic silanized cellulose by biodegradable microcrystalline cellulose (MCC) and hexadecyltrimethoxysilane (HDTMS) with long alkyl chain. Besides of rough structure caused by SiO_2 nanoparticles via sol–gel reaction, porous network was formed by condensation reaction between MCC and HDTMS. To the best of our knowledge, no work has been reported on such hydrophobically modified porous MCC with HTDMS used for efficient and fast oil–water separation. These findings would provide a new insight to design oil–water separation materials.

2. Materials and methods

2.1. Materials

Sodium hydroxide (NaOH), thiocarbamide (CH_4N_2S), n-hexane and acetone were analytical reagents and purchased from Zhiyuan Chemical Reagent Co. Ltd. (Tianjin, China). HDTMS and Oil Red O were obtained from Aladdin Reagent Co. Ltd. (Shanghai, China). MCC (molecular weight: 36,000) was provided by Hengxin Chemical Reagent Co. Ltd. (Shanghai, China). Methylene Blue was obtained from Shengmiao Chemical Reagent Co. Ltd. (Tianjin, China). Gasoline and diesel oil were purchased from PetroChina Petrochemical Research Institute. Soybean oil used for oil–water separation experiment was obtained from local market, Urumqi, China. All chemicals were used as received without further purification.

2.2. Silanization of MCC

Three grams of MCC was added to 100 g of aqueous alkaline solution ($NaOH:CH_4N_2S:H_2O = 9.5:4.5:86$ (w/w/w)) and stirred vigorously for 100 min until a homogeneous emulsion formed. Then the above emulsion was frozen for 24 h in −20 °C refrigerator to dissolve MCC, and thawed at room temperature to obtain transparent cellulose solution. Afterwards, 0.9 g of HDTMS was added dropwise to 100 g of cellulose solution under magnetic stirring to form hydrosol. Fifteen mililiter of 4 mol/L of HCl was then added dropwise to accelerate condensation of hydrosol and form gels. Afterwards, the gel was left for 10 h at normal temperature. Finally, the silanized cellulose was obtained through washing with water until the washing water was neutral and dried at 100 °C till constant weight.

2.3. Characterization

Surface morphology of silanized cellulose was investigated by a scanning electron microscopy (SEM) (LEO1430VP, LEO, Ltd, Germany). Prior to the SEM morphology investigation, silanized cellulose after washing was freeze-dried and sprayed with gold. The chemical composition of silanized cellulose was examined by Fourier transform infrared spectroscopy (FTIR, EQUINOX-55, Bruker) in the range of 400–4000 cm^{-1}. Transmission electron microscopy (TEM) images were obtained on the transmission electron microscope (Hitachi H-600) with the accelerating voltage of 100 kV. Thermogravimetric analysis (TGA) was conducted under air atmosphere at a heating rate of 10 °C/min with a SDT-Q600 hermogravimetric analyzer (TA, America). For measurement of oil content in filtrate after separation, 10 mL n-hexane was used to extract the oil from 5 mL filtrate for three times. All extracts were collected and was adjusted to final volume of 1 L with n-hexane. UV–visible spectroscopy was taken to determine oil content in the filtrate at a wavelength of 247 nm (Zhang, Li, Ma, Wen, & Wumanjiang, 2012)

2.4. Water absorbency measurement

Water absorbency of MCC after modification was measured to evaluate silanization degree and hydrophility. One gram of dry silanized cellulose was put into 200 mL distilled water for 2 days to achieve water absorption equilibrium. The water adsorption (W, %) can be calculated by the equation:

$$W\,(\%) \quad = \quad 100\,[(m\text{-}m_0)/m_0]$$

where, m_0 and m are the weight (g) of silanized cellulose in a dry and water-saturated condition, respectively.

2.5. Oil–water separation measurement

In the process of oil–water separation, 2 g of silanized cellulose particles with 100–120 mesh were dispersed in 10 mL water under stirring, and then filled evenly into a 5 mL syringe by wet packing method. Afterwards 10 mL soybean oil–water mixture (oil:water = 1:1(v/v)) was poured into syringe at a flow speed of 1 mL/s. After the separation completed, the silanized cellulose particles were immersed in acetone to remove the oil adhered on the particle surface, and dried at 100 °C for 7 h. The dried particles were used for repeated oil–water separation according to the procedure above.

Separation efficiency (η, %) was calculated using the following equation:

$$\eta\,(\%) = 100\left[(C_{feed} - C_{filtrate})/C_{feed}\right]$$

where, C_{feed} and $C_{filtrate}$ are the oil content in the feed mixture and in the filtrate respectively.

3. Results and discussion

3.1. The sol–gel reaction

In this study, preparation of silanized cellulose via the sol–gel method includes the hydrolysis and condensation of HDTMS in MCC solution. When HDTMS was mixed in alkaline MCC solution, hydrolysis reaction took place and three methoxyl groups of HDTMS were converted into hydroxyl groups, liberating methanol as a by-product. It is believed that methanol helps the HDTMS to be fully dissolved into water (Sankaraiah et al., 2008), thus promoting the hydrolysis reaction. With HCl added, condensation reaction rate increased. Silanol groups of hydrolyzed HDTMS underwent condensation reaction with the MCC hydroxyl groups to form Si—O—C bondings, but also self-condensation to form polysiloxane network. The condensation between hydrolyzed HDTMS and MCC may lead to crosslinking of MCC, which made the silanized cellulose insoluble and hydrophobic (Fig. 1).

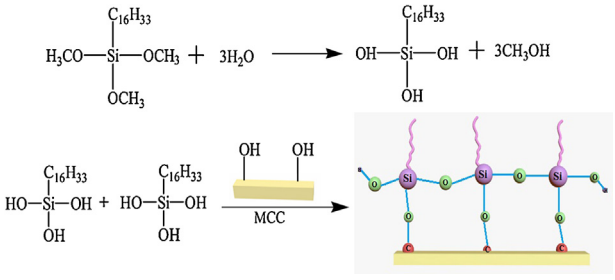

Fig. 1. Synthetic route for silanization of MCC.