Optimization Synthesis Conditions and Characterization of Oil Biosorbent: Sugarcane Bagasse Cellulose-Graft-Polystearylmethacrylate Copolymer

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In this research, sugarcane bagasse cellulose, an abundant non-wood plant fibrous raw material from Guangxi, was the substrate, stearyl methacrylate was the monomer, and ammonium persulfate was the initiator used to prepare an economical environmental oil biosorbent named sugarcane bagasse cellulose-graft-polystearylmethacrylate (SBC-g-PSMA), which can be obtained through homogeneous graft copolymerization in the ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl). Confirmation of successful synthesis was rendered using various analytical tools, including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-Ray Diffraction (XRD). Furthermore, the effects of various reaction parameters on the sorption capacity were all evaluated. Optimum conditions for the synthesis process were obtained as follows: the mass ratio of the monomer to sugarcane bagasse cellulose was 4:1, and the initiator to sugarcane bagasse cellulose ratio was 1:10, with a reaction time of 2 h. Under the optimum conditions, the maximum sorption capacities of the SBC-g-PSMA for 0.2 wt% hydrocarbon (benzene, kerosene, and diesel) were 10.24 g/g, 9.76 g/g, and 9.74 g/g, respectively. The SBC-g-PSMA was light and hydrophobic. It is a selective oil absorption material, so it holds promise to be applied in the treatment of low concentration oily wastewater.

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INTRODUCTION

Oil is an important resource that is widely used in the energy, food, and chemical industries. However, the unregulated application of oil has led to serious pollution and environmental problems, which in turn cause great harm to human health. The severity of the oil pollution problem coincides with the expansion of oil exploration and production activities, as well as industrial growth around the world (Abdullah *et al.* 2010). Oil pollution is one of the foremost environmental issues facing the public today (Ibrahim *et al.* 2010). Although some advanced technology has been developed and used in oil pollution treatment, (such as chemical coagulation, microfiltration, and ultrafiltration), the expensive initial and operating costs inhibit the application of these methods (Hu *et al.* 2004; Banerjee *et al.* 2006). Therefore, an efficient, cost-effective, and environmentally sound method of removing oil pollutants from water has become extremely desirable.

Emerging as a promising material, biosorbents are beginning to be used for oil removal from polluted water. These materials are usually cost-effective, environmentally friendly, and sustainable biomaterials such as diatomite, vermiculites, horticultural peat, cotton, and wood fiber (Rajakovic *et al.* 2007; Moriwaki *et al.* 2009). One of the newest biomaterials, modified cellulose adsorbent, is becoming increasingly popular. Modified cellulose absorbent has some advantages over traditional absorbents (Ali *et al.* 2011; Meng *et al.* 2014). Firstly, modified cellulose absorbent is based on cellulose as a raw material and is a kind of environmentally friendly, biodegradable absorbent that does not cause secondary pollution. Secondly, cellulose resources are the most abundant and cheapest reproducible resources. Finally, cellulose can be combined with high oil-absorbing materials *via* modification, due to the existence of massive hydroxyl groups.

In the past few years, researchers have focused on using sugarcane bagasse cellulose to produce an oil biosorbent for treating low concentrate oily wastewater, and a synthesis method using a homogeneous system has been reported (Zhu *et al.* 2011). Cellulose graft copolymerization has been carried out in a homogeneous system, which improves the uniformity of the reaction speed and the properties of the product, so as to enlarge its range of application (Duan *et al.* 2011; Wang *et al.* 2011; Li *et al.* 2013). Based on the cellulose graft copolymerization, the synthesis method has been improved and implemented in this study. Because the dissolution of sugarcane bagasse cellulose and the grafting reaction could potentially occur at the same time, the predissolution time was shortened to 1 h, the temperature set to 80 °C, and no crosslinking agent was used during the process. Also stearyl methacrylate was introduced onto the cellulose chains, so the material with both hydrophobic and oleophilic properties had high selectivity to oil and water, which have the potential of treating low concentrate oily wastewater. The effects of various reaction parameters on the sorption capacity were considered. This approach simplifies the synthesis process and decreases the energy consumption.

EXPERIMENTAL

Materials

Sugarcane bagasse pulp (60.8% cellulose content) obtained from Nanning Sugar Manufacturing Co., Ltd. (China) was used as the substrate material in this study. It was dried in a vacuum at 80 °C for 2 h prior to use. The ionic liquid 1-butyl-3-methyl-imidazolium chloride ([BMIM]Cl) was purchased from Henan Lihua Pharmaceutical Co., Ltd. (China). Stearyl methacrylate, of technical purity, was purchased from Zhejiang Juhua Group Technology Center (China). Ammonium persulfate, analytical pure, and benzene, technical pure, was purchased from Chengdu jinshan Chemical Reagent Factory (China). Kerosene oil and diesel oil was obtained from Nanning Branch of China National Petroleum Company (China). All components were used without further purification.

Methods

Dissolution of cellulose in ionic liquids and preparation of SBC-g-PSMA

According to the typical preparation of cellulose solution in ionic liquids (Holbrey *et al.* 2003), 1.5 g of dried cellulose was added to a three-neck flask containing 45 g of preheated molten [BMIM]Cl.

The mixture of cellulose and [BMIM]Cl was stirred at 80 °C for 1 h in an oil bath; then, the ammonium persulfate initiator agent was added to the cellulose/[BMIM]Cl, and the resulting mixture was stirred under N_2 atmosphere. After five minutes, the stearyl methacrylate monomer agent was added to the mixture before the reaction reached the required time, and the resulting mixture was slowly poured into ethanol (99.7%, AR) with agitation. To remove the ionic liquid, un-reacted initiator, and homopolymer, the products were filtered out and washed thoroughly with methanol. The final solid samples were dried under a vacuum at 50 °C.

Oil absorbency test

The oil absorbency of SBC-g-PSMA was determined by placing 0.1 g of the sample on a stainless steel mesh (4 cm × 4 cm × 2 cm) and immersing in each in 0.2 wt% hydrocarbon (*i.e.,* benzene, kerosene, or diesel fuel) at room temperature to reach swelling equilibrium according to ASTM F726-81 (1993). The sample and the mesh were picked up together from the oil, drained for 20 sec, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighed on a balance. The oil absorbency (*Q*, g/g) was calculated according to Eq. 1,

$$Q = (m_t - m_0)/m_0 \tag{1}$$

where m_t (g) and m_0 (g) are the weight of gel after and before oil absorption.

Water absorbency test

The test also conducted by ASTM F726-81 (1993).

Measurements

X-ray powder diffraction (XRD) was performed in the 2θ range from 10° to 70° on a Rigaku D/Max 2500-PC diffractometer (Japan) with Cu Kα radiation (λ= 0.15418 nm) and a graphite monochromator at ambient temperature. Fourier transform infrared spectroscopy (FTIR) was carried out on a FTIR spectrophotometer (HP Nicolet 510, USA) using the KBr disk method. Scanning electron microscopy (SEM) images were recorded with a Hitachi S-3400 N scanning electron microscope (Japan) operating at an accelerating voltage of 20 kV. All samples were coated with Au prior to SEM examination.

RESULTS AND DISCUSSION

Characterization

To investigate the microscopic structures of the untreated sugarcane bagasse cellulose and SBC-g-PSMA, SEM analysis was conducted (Fig. 1). It was found that the surface of untreated sugarcane bagasse cellulose was a smooth and homogeneously columnar structure (Figs. 1a and 1b), but the surface of SBC-g-PSMA had obviously become coarse and split (Figs. 1c and 1d), which indicated that the cellulose participated in the reaction.
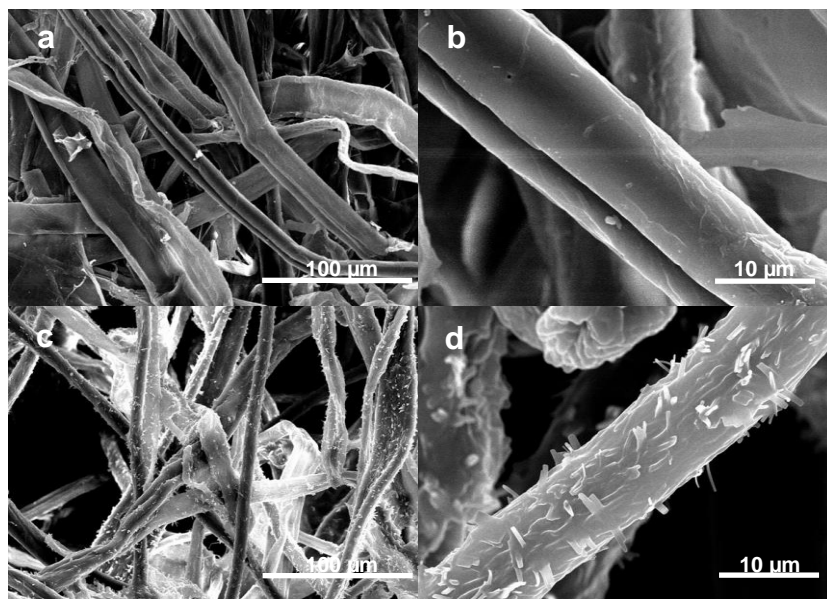
Fig. 1. SEM images of (a, b) untreated sugarcane bagasse cellulose and (c, d) SBC-g-PSMA

Untreated sugarcane bagasse cellulose and SBC-g-PSMA were further examined using FTIR. As shown in Fig. 2, the graft copolymerization kept the characteristics of cellulose intact. The characteristic absorption bands appeared at 2854 cm^{-1} and 2921 cm^{-1} (stretching vibration of aliphatic C-H bond), 1722 cm^{-1} (stretching vibration of C=O bond), and 1316 cm^{-1} (flexure of C-H bond), which indicated that the stearyl methacrylate had been introduced onto the cellulose chains.
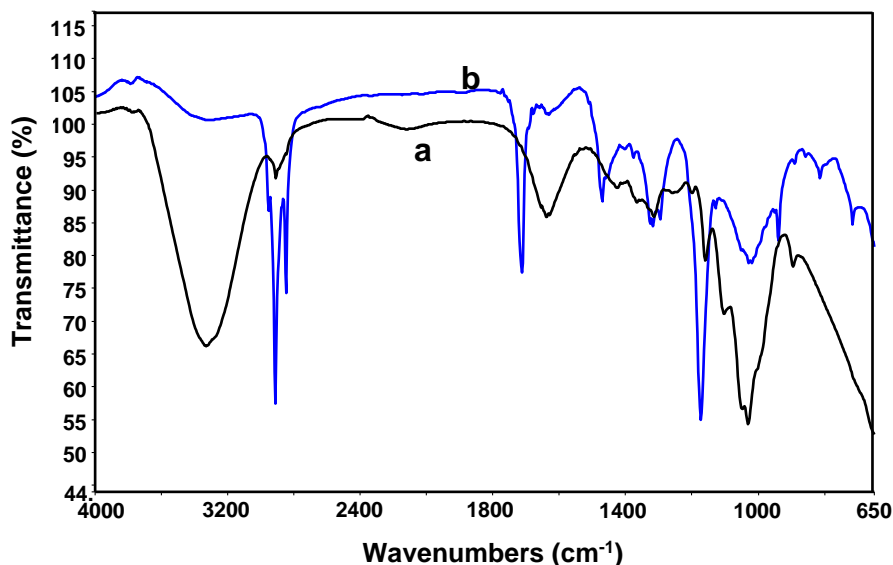
Fig. 2. FTIR spectra of (a) untreated sugarcane bagasse cellulose and (b) SBC-g-PSMA

The X-ray diffraction patterns of untreated sugarcane bagasse cellulose and SBC-g-PSMA at room temperature from $2\theta = 10^{\circ}$ to 70° are shown in Fig. 3. In the XRD pattern of the untreated cellulose, diffraction peaks appear at $2\theta = 15.5^{\circ}$, 22.3°, and 34.6°, which are consistent with the typical diffraction peaks of cellulose in the I crystalline

form (Lin *et al.* 2009; Liu *et al.* 2010). However, in the XRD pattern of SBC-g-PSMA, the typically intense diffraction peak at $2\theta = 34.6°$ belonging to cellulose disappeared, and only weak peaks at 15.5° and 22.3° are seen. The disappearance of the peaks indicates that the crystalline structure of cellulose was partially damaged after grafting in ionic liquid and the spatial structure was maintained, which benefited the sorption capacity of SBC-g-PSMA. Liu *et al*. (2007; 2009) also found that the crystalline structure of cellulose that regenerated from ionic liquids was severely damaged, and only amorphous cellulose could be obtained.
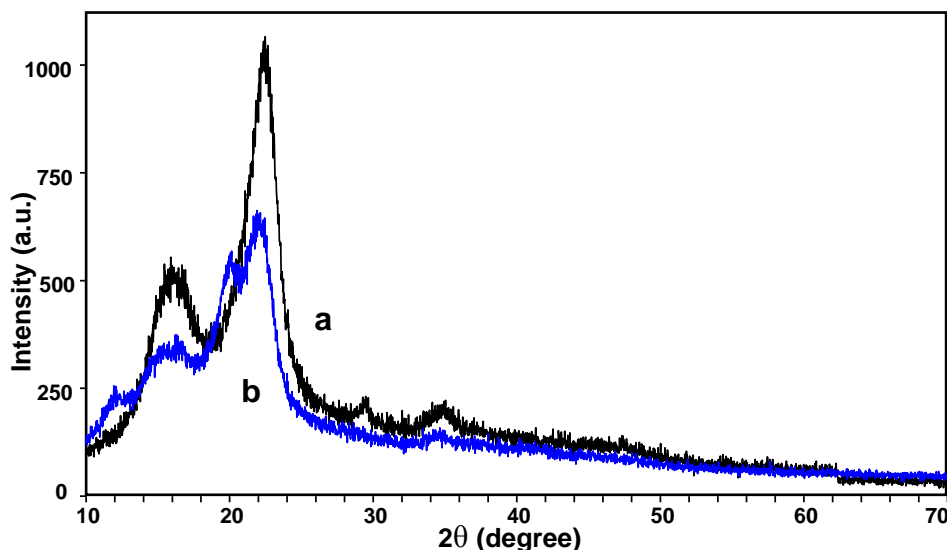

Fig. 3. XRD patterns of (a) untreated sugarcane bagasse cellulose and (b) SBC-g-PSMA

Effects of Monomer Amount on the Sorption Capacity of SBC-g-PSMA

Figure 4 shows the effects of the monomer amount on the sorption capacity of SBC-g-PSMA.
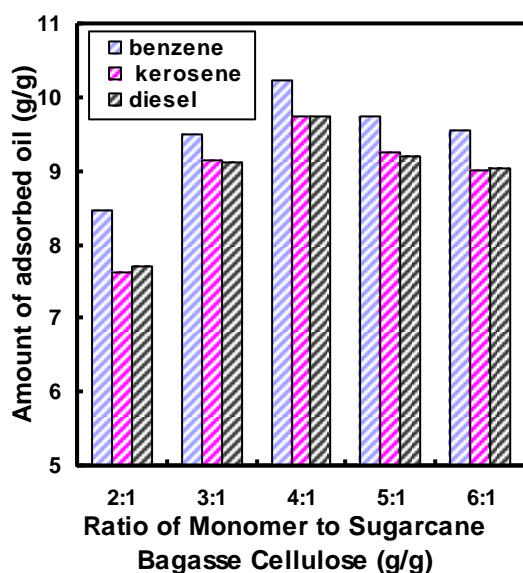

Fig. 4. Effect of monomer amount on the sorption capacity of SBC-g-PSMA
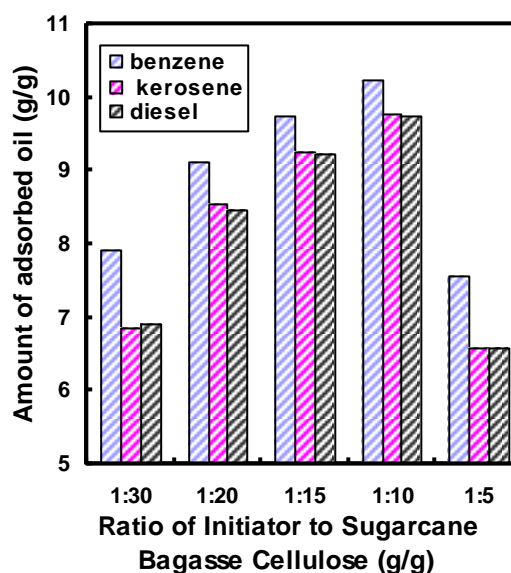
Fig. 5. Effect of initiator amount on the sorption capacity of SBC-g-PSMA

The reactions were performed with an initiator to sugarcane bagasse cellulose ratio of 1:10, reaction temperature of 80 °C, and reaction time of 2 h. As Fig. 4 shows, the sorption capacity increased initially, but eventually decreased with increasing ratio of monomer to sugarcane bagasse cellulose. It is known that with increasing monomer, the number of lipophilic groups on the surface of SBC-g-PSMA and the sorption capacity also increase. However, if too much of a highly concentrated monomer is present, the opportunity for homopolymerization among monomers would increase, which consequently restrains the copolymerization reaction (Ren *et al.* 2003), decreasing the sorption capacity.

Effects of Initiator Amount on the Sorption Capacity of SBC-g-PSMA

Figure 5 shows the effect the initiator amount has on the sorption capacity of SBC-g-PSMA. The grafting efficiency and sorption capacity depends on the number of active sites available. The increase in initiator amount is expected to increase the sorption capacity. With increasing ratios of monomer to sugarcane bagasse cellulose, however, the rate of homopolymerization or copolymerization increases faster than the rate of grafted terpolymer. Furthermore, the decomposition rate of the initiator also increases and eventually descended the trigger efficiency after excessive amounts of initiator. A similar observation was made in the work of (Zhou *et al*. 2002). As a result, the sorption capacity increases initially, but after further increasing the initiator amount, the sorption capacity decreases.

Effects of Reaction Time on the Sorption Capacity of SBC-g-PSMA

The effects of reaction time on the sorption capacity of SBC-g-PSMA are shown in Fig. 6. As the reaction time increased, the sorption capacity also increased, until a maximum was reached at 2 h, after which the capacity leveled off and slightly decreased. The explanation for the decrease in sorption capacity lies in the formation of homopolymers or copolymers, as well as the increase in viscosity of the reaction mass along the reaction path (Zhou *et al.* 2002).
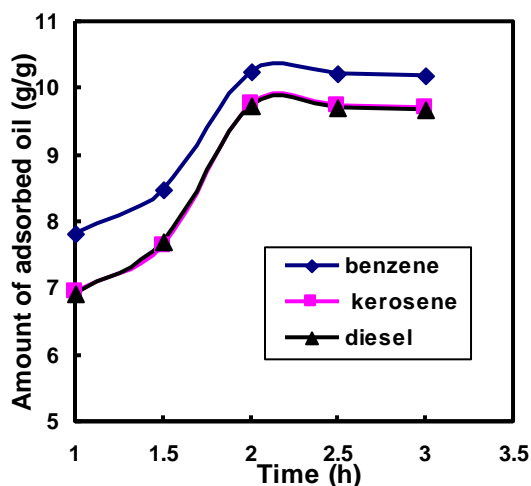

Fig. 6. Effects of reaction time on the sorption capacity of SBC-g-PSMA

Water Sorption Capacity of SBC and SBC-g-PSMA

The water sorption capacity of SBC is 6.52 g/g and the SBC-g-PSMA is 0.04 at room temperature. The result indicates that the surface of the sugarcane bagasse cellulose

could be changed from hydrophilic to hydrophobic by surface modification. The sugarcane bagasse cellulose was modified by grafted copolymerization of hydrophobic SMA monomer, creating a rough surface structure. It was also shown that the SBC-g-PSMA with both hydrophobic and oleophilic properties have the potential of treating low concentrate industrial oily wastewater.

CONCLUSIONS

1. A green and economical oil biosorbent (SBC-g-PSMA) was readily synthesized with sugarcane bagasse cellulose in a homogenous [BMIM]Cl medium, as shown in the SEM, FTIR, and XRD analyses. Some favorable aspects were as follows:

   (a) The substrate was sugarcane bagasse cellulose, a rich, non-wood, plant fibrous raw material from Guangxi.

   (b) The process of synthesis and use of product didn't produce pollution.

   (c) The product was biodegradable and reusable.

   (d) The oil biosorbent had a sorption capacity of 0.2 wt% hydrocarbon (benzene 10.24 g/g, kerosene 9.76 g/g, and diesel 9.74 g/g) that were about four times those of untreated sugarcane bagasse.

   (e) The product was so light that it could float on the water and easily absorb oil spill. Meanwhile, it was a hydrophobic and oleophilic absorbent. A possible use is in oil/water separation such as low concentrate industrial oily wastewater and oil-spill pollution, as well as environmental protection.

2. The optimum reaction conditions for the maximum sorption capacity of SBC-g-PSMA were obtained as follows: the mass ratio of monomer to sugarcane bagasse cellulose was 4:1, initiator to sugarcane bagasse cellulose ratio was 1:10, and reaction time was 2 h.

3. The synthetic strategy reported in this study develops a new method to the manufacturers of oil biosorbent, as well as increasing the high number of value-added applications of sugarcane bagasse.

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