Journal of Environmental Management 168 (2016) 142–148

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Preparation and characterization of amine-functionalized sugarcane bagasse for CO_2 capture

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ARTICLE INFO

Article history:
Received 25 June 2015
Received in revised form
21 September 2015
Accepted 23 September 2015
Available online 17 December 2015

Keywords:
Sugarcane bagasse
Solid amine
Adsorbent
CO_2 capture

ABSTRACT

A low-cost solid amine adsorbent for CO_2 capture was prepared by using sugarcane bagasse (SB), a dominant agro-industrial residue in the sugar and alcohol industry as raw materials. In this preparation process, acrylamide was grafted on SB, and the grafted fiber was then aminated with different type of amine reagents to introduce primary and secondary amine groups onto the surface of SB fibers. The graft and amination conditions were optimized. The prepared solid amine adsorbent showed remarkable CO_2 adsorption capacity and the adsorption capacity of the solid amine adsorbent could reach 5.01 mmol CO_2/g at room temperature. The comparison of adsorption capacities of amine fibers aminated with various amination agents demonstrated that fibers aminated with triethylenetetramine would obtain higher adsorption capacities and higher amine efficiency. These adsorbents also showed good regeneration performance, the regenerated adsorbent could maintain almost the same adsorption capacity for CO_2 after 10 recycles.

1. Introduction

Global warming mainly caused by greenhouse gas emissions is seriously threatening human's survival and development. The separation and storage of CO_2, has become the hot research spot (D'Alessandro et al., 2010; MacDowell et al., 2010). The conventional carbon capture and storage process (CCS) includes CO_2 separation and enrichment, transport, and storage. Among them, the cost of separation and enrichment accounts for about 75% of the whole CCS cost (Feron and Hendriks, 2005; Rubin, 2012). To drastically reduce the cost of CO_2 separation and capture, and make CCS available for practical application, adsorbents with high selectivity, high adsorption capacity, and stable adsorption and desorption performance should be developed (Filburn et al., 2005; Khatri et al., 2005). Solid amine adsorbents are considered to be promising adsorbents for CO_2 capture. They can be prepared through immobilizing amines onto the solid supports like active carbon (Keramati and Ghoreyshi, 2014; Lin et al., 2013a), zeolite (Bezerra et al., 2011; Su et al., 2010), and porous silica via physical or chemical methods (Du et al., 2013; Klinthong et al., 2013; Le et al., 2013; Tanthana and Chuang, 2010; Zhang et al., 2013a), and have been proved to be good CO_2 adsorbents. In our previous works, various fibrous solid amine adsorbents have been successfully prepared, in which amine were coated or grafted onto fibers including glass fiber (Li et al., 2008a, 2008b), polyacrylonitrile fiber (Yang et al., 2010), viscose fiber (Lin et al., 2013b) and polypropylene fiber (Zhuang et al., 2013; Wu et al., 2014; Xu et al., 2015). Compared to granular supports, the fibrous adsorbents enjoy many advantages, such as large external surface, short transit distance, low pressure drops (Zhang et al., 2008; Yang et al., 2010; Lin et al., 2013b), high chemical stability and desirable flexibility, which make them efficient adsorbents for CO_2.

Sugarcane bagasse (SB) is one of the largest agro-industrial residues in the sugar and alcohol industry (Velazquez-Jimenez et al., 2013) and an abundant natural fiber resource with high cellulose content (Huang et al., 2012; Kaushik et al., 2009). Thousands of tons of SB can be produced daily by the sugarcane processing industry and thus become a menace of environment (Khosravi-Darani and Zoghi, 2008; Liang et al., 2013; Sun et al., 2004). One of the potential application of this biomass is to be used as bio-

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http://dx.doi.org/10.1016/j.jenvman.2015.09.033
0301-4797/

adsorbent for the removal of environmental pollutants, such as dye (Adebayo et al., 2014; Cheng et al., 2012; Kadam et al., 2013), and heavy metal ions (Homagai et al., 2010; Karnitz et al., 2010; Liu et al., 2012a) and so on (Brandao et al., 2010; Carvalho et al., 2011; Zhang et al., 2012). Meanwhile it is also a good alternative adsorbent for CO_2 capture. Toochinda group (Bachelor and Toochinda, 2012) has prepared a solid amine adsorbent by impregnating organic amine on SB, and found that SB would enhance the CO_2 adsorption ability due to its light weight and various forms. However, excessive regeneration temperature would lead to the amine volatilization or emission from fibers that prepared by impregnation, which limits its application.

In order to make effective use of agro-industrial residues, in this study, a solid amine adsorbent was prepared by using SB as the matrix fiber, in which amine was covalently bound onto SB fiber by grafting copolymerization, as shown in Fig. S1. The preparation conditions and physicochemical properties of the SB based solid amine fiber were studied. The CO_2 adsorption properties of the obtained fibers were evaluated.

2. Experimental section

2.1. Preparation of solid amine adsorbent

Sugarcane bagasse (SB) was provided by Guangzhou Sugarcane Industry Research Institute (China) and was ground to 20–30 mesh size before being used. In order to break the lignin seal and disrupt the crystalline structure of cellulose, SB was treated by sodium hydroxide (NaOH) before graft polymerization. 1 g alkali-treated bagasse (NaOH-treated SB) was immersed in 10 wt% Acrylamide (AM) aqueous solution. The mixture was stirred for 15 min, and N_2 was bubbled for another 10 min to remove oxygen in the mixture. After addition of the initiator ferrous ammonium sulfate (FAS) and hydrogen peroxide (H_2O_2, 30%), the graft polymerization was performed at a preset temperature under nitrogen atmosphere for a preset time period. The resulting fiber, polyacrylamide-grafted sugarcane bagasse (SB-AM), was washed with deionized water at 80 °dried at 60 °C under vacuum. Graft yield (G) and Graft efficiency (E) were calculated according to the following eqs. (1) and (2).

$$G = \frac{W_g - W_0}{W_0} \times 100\% \quad (1)$$

$$E = \frac{W_g - W_0}{\mathrm{m}} \times 100\% \quad (2)$$

Where W_0 and W_g are the weights of NaOH-treated SB and SB-AM, respectively, and m is the mass of AM.

With aluminum chloride, hexahydrate ($AlCl_3 \cdot 6H_2O$) as catalyst, 1 g SB-AM was aminated with 80% triethylenetetramine (TETA) aqueous solution in a round bottomed flask at 110 °C for 8 h. Then, the obtained solid amine fiber named SB-AM-TETA was washed thoroughly with deionized water and dried at 60 °C under vacuum. Amination rate Da (%) of the resulting solid amine adsorbent SB-AM-TETA was calculated according to the following eq. (3).

$$Da = \frac{71 \times (Wa - Wg) \times (1 + G)}{(146.2 - 17) \times Wg \times G} \times 100\% \quad (3)$$

Where W_g and W_a are weights of the SB-AM and SB-AM-TETA, respectively. And G is the grafting degree of SB-AM. 71, 146.2 and 17 are the molecular weights (g/mol) of AM, TETA and NH_3, respectively. 4 is the number of amino groups per TETA molecule.

To investigate the relationship between the type of amine and CO_2 adsorption performance, a series of solid amine fibers were fabricated by grafting AM and then subsequently aminating with different type of amines: ethylenediamine (EDA), diethylenetriamine (DETA), TETA, tetrathylenepentamine (TEPA); Their ratios of 1°:2° alkyl amines in SB-AM-X (X represents different type of amines) are 1:0, 1:1, 1:2, and 1:3, respectively.

2.2. Structure characterization

Nitrogen, hydrogen, and carbon content of the fiber samples were determined by Perker-Elmer Elemental Analyzer Vario EL (Germany). FT-IR spectra were collected on a Nicolet/Avatar 330 FT-IR spectrometer. Each spectrum was recorded from 4000 to 400 cm^{-1}. TGA analyzer (Netzsch TG-20) was used to determine the thermal stability of all samples. The tests were carried out under a nitrogen atmosphere from ambient temperature to 600 °C with a heating rate of 10 °C/min. SEM micrographs were obtained with a field emission scanning electron microscope (Hitachi S-4800, Japan). All samples were sputter coated with Au.

2.3. CO_2 adsorption procedures

Fiber samples (1.0 g) were placed in an adsorption column. Air in the column and pre-adsorbed species were removed by a dry N_2 flow with a flow rate of 30 mL/min. Then the CO_2/N_2 mixture gas was introduced. The inlet and outlet concentration of CO_2 was determined by a gas chromatograph (D7900, Techcomp, China) with a thermal-conductivity detector (TCD). The adsorption temperature was adjusted by a water bath. The inlet concentration of CO_2 was adjusted to 10% in volume ratio.

The adsorption amount was calculated as follows:

$$Q = \int_0^t \left(C_{in} - C_{eff}\right) \cdot V \cdot dt / 22.4W \quad (4)$$

Where Q is the adsorption capacity of SB-AM-TETA (mmol CO_2/g), t is the adsorption time (min), and C_{in} and C_{eff} were the influent and effluent flow rate of CO_2 (mL/min), respectively. V is the total flow rate, 30 mL/min; W and 22.4 are the weight of SB-AM-TETA (g) and molar volume of gas (mmol/mL), respectively. After adsorption, SB-AM-TETA was regenerated by heating in boiling water for 15 or 30 min.

3. Result and discussion

3.1. Characterization of solid amine adsorbent

The chemical composition and the chemical group content of the fibers were determined using elemental analysis. The elemental analysis results are shown in Table 1. After grafting polymerization with AM, the nitrogen content of SB-AM reached to 10.60 wt%, and the amide group content of SB-AM was 7.57 mmol/g, assuming all nitrogen were derived from grafted AM. Total nitrogen content of the solid amine fiber aminated with TETA had further increased to 15.75 wt%. Since the increment of nitrogen content of SB-AM-TETA was stemmed from alkyl amino groups of TETA, the acquired alkyl

Table 1
Elemental analysis of SB, SB-AM and SB-AM-TETA.

Fibers	Element content (wt %)			Group content (mmol/g)	
	C	H	N	Amide	Alkyl amino
SB	44.17	7.02	0.21		
SB-AM	46.52	7.02	10.60	7.57	–
SB-AM-TETA	41.83	8.05	15.75	5.77	5.50