BIOPOLYMER BASED ADSORBENTS FOR THE POST COMBUSTION CO$_2$ CAPTURE

ARTI VALECHHA, JAYSHRI THOTE, NITIN LABHSETWAR AND SADHANA RAYALU

CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur, MS, India.
*Corresponding Author: Email- s_rayalu@neeri.res.in

Abstract- CO$_2$ emissions due to the extensive use of fossil fuels from different industrial sources such as coal-fired thermal power plants, iron & steel industries, cement and other industries has led to the phenomenon of global warming in the recent years. Carbon dioxide is considered to be one of the major contributors to the global warming. Selective adsorption is seen as one of the viable options to capture and pre-concentrate CO$_2$ before it can be processed for sequestration. Array of adsorbents have been attempted with high adsorption capacity and selectivity for CO$_2$ at high temperature and varying moisture content by many researchers. A series of chitosan based adsorbents has been synthesized to investigate the free available amine interaction with carbon dioxide molecules. The effect of crosslinking and functionalization has also been investigated in the present application. Experimental studies show that the adsorption capacity of chitosan glutaraldehyde was superior then that of Chitosan which can be attributed to the formation of imine functionality.
Keywords- Chitosan, carbon dioxide, adsorption, functionalization

Introduction

The global warming caused due to increase in the greenhouse gas emissions is a serious concern all over the world. Carbon dioxide is generated in large quantities by various industries like fossil fuel based power plants, chemical and petrochemical manufacturing, cement and steel production etc. The capture and separation of CO$_2$ from large point source is a crucial step with respect to technical and economic feasibility of overall sequestration process [1]. Presently most of the CO$_2$ capture plants exploit technologies based on chemical absorption using amine based absorbents. However, the process has several limitations for treating flue gases which are mainly associated with high energy consumption and investment cost. The development of low cost means of capturing CO$_2$ is a key to curtail the increasing concentration of carbon dioxide in the atmosphere. Adsorption is considered to be one of the most potential options for the capture of CO$_2$ from the point sources and the flue gas stream where the amount of CO$_2$ varies from 4% to 15% by volume [2]. Efforts are being made in the direction of development of low cost adsorbents with high CO$_2$ selectivity at high temperature and which can execute well in presence of moisture. Zeolite, molecular sieve and activated carbon are typically used in this regard. However the deteriorating effect in presence of moisture and low adsorption capacity at higher temperatures needs to be substantiated for these conventional adsorbents. In this context, low cost chitosan based adsorbents were considered as a viable option for the post combustion CO$_2$ capture because of its non-toxic, hydrophilic and bio-degradable properties. Chitosan, is a natural biomaterial, an N-deacetylated product of chitin, which is the second most abundant natural polymer after cellulose and has a structure similar to cellulose. The presence of large number of amine groups on the Chitosan chain facilitates the acidic CO$_2$ molecule to get adsorbed on the surface of the adsorbent molecule. Presence of hydroxyl and amine group in the repeating hexosaminide residue in chitosan makes it a very suitable adsorbent for CO$_2$, however it is reported these functional groups can be chemically modified to undergo intermolecular hydrogen bonding to overcome these problems for the high uptake of CO$_2$ [3-5]. The cross-linking of glutaraldehyde

with the Chitosan increases the stability of Chitosan in acid solutions and the reaction leads to the formation of imine functional groups >C=N- between the amine group of the biopolymer and the cross-linking agent. Imine functionality in this adsorbent facilitates the CO$_2$ adsorption.

In the present work, a series of chitosan based adsorbents were synthesized, effect of crosslinking and functionalization were also observed for CO$_2$ uptake capacity. The presence of higher content of amino functional groups in chitosan can be effectively used for adsorption of acidic gases like CO$_2$. Characterizations like FT-IR, powder XRD and SEM were also performed. Dynamic adsorption studies were carried out in a simulated multi component gas stream containing 15% CO$_2$ and balance N$_2$ in evaluation system as reported previously [6].

Materials and Methods

Biopolymer Chitosan was procured from M/s.Chemchito Ltd.,Chennai. A.R. grade acetic acid and ammonia solution were purchased from Qualigens, India, whereas A.R. grade glutaraldehyde and AMP (2-Amino-2-methyl-1-propanol) were procured from E-Merck, India respectively. Double distilled water was used in the entire synthesis.

Synthesis of Chitosan beads

Chitosan solution was prepared by dissolving 3g of Chitosan flakes in 100ml of 5% (v/v) acetic acid solution. This slurry was stirred in the laboratory stirrer for about 1hr and then it was added to 1M NH$_4$OH solution for neutralizing the acetic acid within the Chitosan gel resulting in the spherically uniform Chitosan beads. These beads were then thoroughly rinsed with distilled water in order to remove any residual NH$_4$OH and finally it was dried at ambient temperature..

Synthesis of cross linked glutaraldehyde Chitosan beads

Chitosan glutaraldehyde beads were synthesized in a similar way described by Guibal et al. Recently prepared wet Chitosan beads (as described before) were suspended in 1 M glutaraldehyde solution to obtain crosslinked chitosan beads. These beads were then left for 24 hrs at room temperature. After 24 hrs these cross linked Chitosan beads were thoroughly washed with distilled water, filtered and dried at ambient temperature.

Synthesis of Chitosan glutaraldehyde AMP beads

Chitosan beads were synthesized as described in section 2.1.1. Synthesized beads were precipitated in 25% AMP solution. These wet beads were then suspended in 1 M glutaraldehyde solution to obtain crosslinked chitosan glutaraldehyde AMP beads. These beads were then left for 24 hrs, washed thoroughly with distilled water and dried at ambient conditions.

Characterization

X ray diffraction patterns of synthesized adsorbents were collected using Rigaku Miniflex II with Cu Kα1 radiation with monochromator operated at 30kV and 15 mA. The samples were scanned for 2θ ranges from 10 - 80º with scanning speed 5O/ min. Diffraction peaks were compared with standard database reported in the Joint Committee on Powder Diffraction Standards (JCPDS) cards. The Fourier transform infrared (FTIR) spectrum of the synthesized adsorbents was recorded on a Bruker Vertex-70 instrument in the range of 3500-400 cm-1. The surface morphology of the material was studied by performing the Scanning electron microscopy (SEM) of the materials using a JEOL6380A instrument.

Evaluation of adsorbents

CO2 adsorption studies were performed in a dynamic adsorption flow system wherein a fixed mass of adsorbent (3g) was placed in a packed bed column. As reported in our previous studies [2,8], a fixed mass of the moisture free adsorbent (subjected to drying in oven at 110°C for 3 hours) was packed in glass column. The adsorbent bed was supported by a layer of ceramic wool and the temperature was maintained with the aid of a PID temperature controlled furnace. The experimental set up used, was similar as reported in our previous studies [7], and consisted of mass flow controllers (Aalborg, USA) and a mixing chamber for preparation of a simulated flue gas. The moisture free adsorbent was then pre-treated in helium flow (25ml/min) for 6 hours at 110°C, so as to remove any volatile contaminants and any pre-adsorbed gases present in the pores of adsorbent. The adsorbent bed was allowed to cool to the desired adsorption temperature and then a flow of 15% by volume of CO$_2$ and balance N2 was provided to the adsorbent in the glass column. During the entire course of the experiment, the total feed flow rate was maintained at 20ml/min (CO$_2$ = 3 ml/min; N2 = 17ml/min). The effluent stream was continuously analyzed by using a Perkin Elmer gas chromatograph equipped with a thermal conductivity detector (TCD) and Porapak-Q packed column. Analysis was continued till the saturation of the adsorbent bed.

Result and discussion
Characterization of chitosan

Fig 2 shows the FT-IR spectrum of chitosan flakes and beads. Chitosan is a heteropolymer made up of glucosamine and acetyl glucosamine units. The functional groups of chitosan are amino group and hydroxyl group which are very important for immobilization of enzyme. The band at 3694 cm^{-1} in chitosan flakes is attributed to stretching vibration of N-H group, which shifted to 3653 cm^{-1} in chitosan beads. The hydroxyl group in chitosan flakes detected at 3298cm^{-1} is shifted to 3308 cm^{-1} in chitosan beads. This shift of band may be due to the formation of weak intermolecular hydrogen bonding between amino and hydroxyl groups of chitosan.
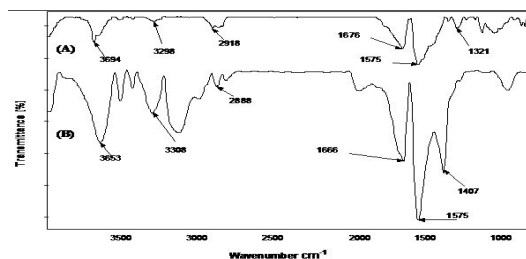

Fig. 2- FT-IR spectrum of (A) Chitosan flakes (B) chitosan-NH$_4$OH beads

The scanning electron micrographs (SEMs) of chitosan flakes and beads are shown in fig 3. It is clear from the figure that chitosan flakes consist of amorphous particles which are irregular in size and shape while chitosan beads have spongy surface morphology.
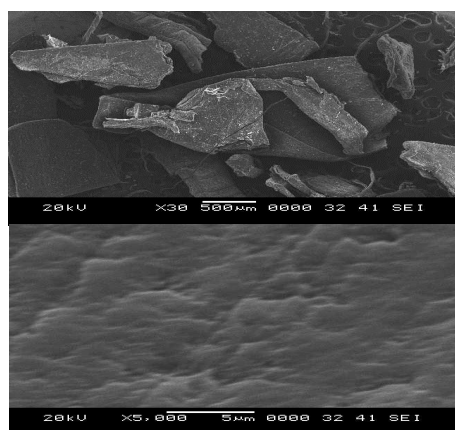
Fig. 3- SEM images of chitosan flakes and beads

Fig.4 shows the XRD spectra of chitosan-NH4OH beads. From the figure, two major peaks i.e. 2Θ of 100 and 200 have been observed for chitosan flakes, while in chitosan beads major peak is observed at $2\Theta = 200$ indicating that the degree of crystallinity decreases in chitosan beads as compared to chitosan flakes.
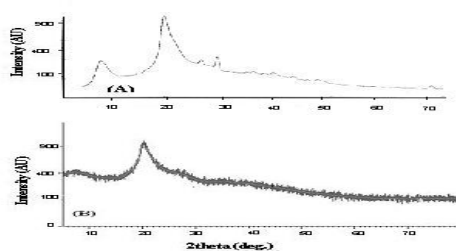

Fig. 4- XRD spectra of (A) Chitosan flakes, (B) Chitosan-NH4OH beads

Evaluation of adsorbents for CO_2 adsorption
Effect of crosslinking and functionalization on chitosan beads

Synthesized chitosan beads, crosslinked chitosan beads and functionalized beads were evaluated for adsorption of CO_2 from a CO_2/N_2 gas mixture comprising of 15% by volume of CO_2 and balance N2. The evaluation was carried out at 55 °C using the experimental setup described as in section 2.3. The breakthrough curves were then plotted (Figure 5) and the adsorption capacities were calculated and are reported in Table 1. It is observed from Table 1, there is no significant change in adsorption capacity after crosslinking chitosan with gluteraldehyde, however the capacity increases by a factor of 2 when this crosslinked gluteraldehyde is functionalized with AMP.
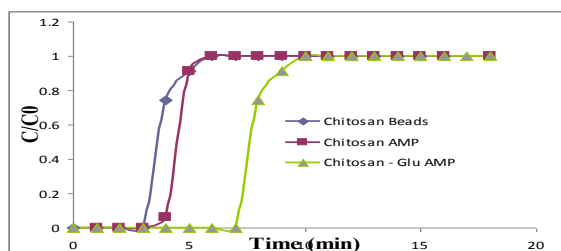

Fig. 5- Breakthrough curves for chitosan, chitosan AMP & chitosan gluteraldehyde AMP

Table 1- Breakthrough adsorption capacities of chitosan, chitosan AMP & chitosan gluteraldehyde AMP

Adsorbent	Adsorption temperature (° C)	Adsorption capacity (mg/g)
Chitosan beads	55	2.5
Chitosan glu beads	55	2.1
Chitosan glu AMP beads	55	5.02

Effect of moisture on chitosan and chitosan gluteraldehyde AMP beads

Chitosan beads and chitosan glutaraldehyde AMP were further evaluated for adsorption of CO_2 from a CO_2/N_2 in presence of moisture comprising of 15% by volume of CO_2, 10% H_2O and balance N_2. The evaluation was carried out at 55 °C with a pretreatment temperature of 110 °C The adsorption capacities is tabulated in table 2. It is observed from table 2, moisture favours the adsorption of CO_2 in case of chitosan while the capacity decreases in case of crosslinked glutaraldehyde AMP beads.

Table 2- Breakthrough adsorption capacities of chitosan & chitosan gluteraldehyde AMP in presence of moisture

Adsorbent	Adsorption Temp. (°C)	Condition	Adsorption Capacity (mg/g)
Chitosan beads	55	CO_2/N_2	2.5
Chitosan beads	55	$CO_2/N_2/H_2O$	6.62
Chitosan glu AMP beads	55	CO_2/N_2	5.02
Chitosan glu AMP beads	55	$CO_2/N_2/H_2O$	1.82

Conclusion

Chitosan beads were chosen owing to high diffusion properties of beads rather than flaked material. The adsorption capacity of Chitosan beads increases by a factor of 2 and this may be attributed to the reported reaction of 1 mole of CO_2, a mole of H_2O and 1 mole of amine when react forms bicarbonate. However when Chitosan precipitated in AMP was crosslinked with glutaraldehyde, the amino groups of Chitosan and AMP react with aldehydic group of glutaraldehyde to form imine functionality. In this case CO_2 was adsorbed at imine functional site and therefore the above referred reaction enhancing the adsorption capacity in presence of water was not observed when Chitosan-AMP-Glutaraldehyde was tested in presence of water. Efforts are now being made to break the intermolecular hydrogen bonding to increase the adsorption capacity of chitosan and some encouraging results have already been obtained.

Acknowledgement

References
[1] Li W.B., Zhuang M., Xiao T.C., Green M.L.H. (2006) *Journal of Physical Chemistru.* B 110 215682.

[2] Olivier J.G.J., Van Aardenne J.A., Dentener F., Pagliari V., Ganzeveld L.N., Peters J.A.H.W. (2005) *Environmental Science.* 2 81.

[3] Garg A., Shukla P.R., Kapshe M. (2006) *Atmospheric Environment* 40 4608.

[4] Thambimuthu K., (1993) *IEA Coal Research.*

[5] Klara M.S., Srivasta R.D. (2002) *Environmental Progress.* 21247.

[6] Xu X.C., Song C.S., Andresen J.M., Miller B.G. Scaroni A.W. (2003) *Microporous and Mesoporous Materials* 62, 29.

[7] Dong Q., Su H., Zhang D., Liu Z., Lai Y. (2007) *Microporous and Mesoporous Materials.* 98 344-351

[8] Jadhav P.D., Chatti R.V., Biniwale R.B., Labshetwar N.K., Devotta S., Rayalu S.S., *Energy & Fuels.*, 21(6), 3555-3559.