Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 56(4) 418-427, 2014

NOVEL AMINO POLYMERS-MODIFIED BAMBOO CHARCOAL AS SOLID ADSORBENTS FOR CO_2 CAPTURE

Wenjing Xie and Rui Wang*

School of Environmental Science and Engineering, Shandong University, Jinan 250100, P. R. China; E-Mail: xiewenjing1990@126.com, * Author to whom correspondence should be addressed; E-Mail: ree_wong@hotmail.com

Received June 22, 2014, Accepted September 16, 2014

Abstract

Novel CO_2 adsorbents were developed using bamboo charcoal (BC) impregnated with polyethylene polyamine (PEPA) and polyethyleneimine (PEI), respectively. The adsorbents were characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FITR), N_2 adsorption/desorption and thermogravimetric analysis (TGA). The characterizations indicate that the structure of BC is preserved after loading PEPA, and PEPA is uniformly dispersed on the surface and into the pore channels of BC. The CO_2 adsorption performance was tested by fixed bed system at low concentration CO_2 (0.4% volume fraction) and ambient pressure. From the perspective of the breakthrough time, the adsorption capacity of BC-PEPA or BC-PEI first experiences an upward trend with the increasing temperature then declines. There is a synergetic effect between BC and PEPA or PEI on the CO_2 adsorption for PEPA-loaded or PEI-loaded BC. The CO_2 adsorption capacity of BC is 1.11 mg/g-sorbent at 50°C, and the adsorption capacity can be enhanced to varying degrees by modification. The highest adsorption capacity of PEPA-loaded BC at 50 °C is 25.7 mg/g-sorbent when the mass fraction of PEPA loading is 23.1%. At 28.6% mass fraction of PEI loading in BC-PEI, CO_2 reaches the highest adsorption capacity of 35.6 mg/g-sorbent at 50°C. The CO_2 adsorption capacities on amino polymers-modified BC increase in the presence of water vapor, however, the increased ranges depend on the experimental conditions.

Keywords: bamboo charcoal; carbon dioxide; adsorbents; polyethylene polyamine; polyethyleneimine.

1. Introduction

The greenhouse effect has aggravated due to increasing emissions of greenhouse gases from the widespread use of fossil fuels such as coal, petroleum and natural gas, which leads to global warming and has negative impacts on the ecological environment of the earth. CO_2 is considered to be the significant greenhouse gas because of its huge emissions, and its contribution to the greenhouse effect has accounted for more than 60% [1-2]. As a result, reducing and controlling the emissions of CO_2 to curb global warming has caused extensive concerns around the world. CO_2 capture, sequestration and resource utilization have been considered as the key means of mitigating the greenhouse effect and global warning. Therefore, researches on CO_2 capture, sequestration and resource utilization are of great importance [3].

Practical methods for CO_2 capture and sequestration mainly include absorption, adsorption, membrane separation and cryogenic distillation [1, 4-9]. Adsorption has appeared as one of the promising methods for CO_2 capture and sequestration with its low energy consumption, cost-effectiveness, relatively simple technological process, non-corrosive to the equipments and extensive applicability over a relatively wide range of temperatures and pressures [1, 10]. Development of new and high-efficient solid adsorbents is crucial to enhance competitiveness of this process. Researches on the development of adsorbents mostly focus on the surface modification of porous materials which include activated carbons, carbon nanotubes, zeolites, silica gels, metal oxides and mesoporous molecular sieves [1, 11-21]. Xu *et al.* [11] synthesized and modified the mesoporous molecular sieve of MCM-41 with PEI and therefore prepared new CO_2 adsorbents which were referred to as “molecular basket”. The highest adsorption capacity of MCM-41-PEI was 246 mg/g-PEI at 75°C in pure CO_2 atmosphere when PEI loading was 50 wt.%. In an investigation by Chen *et al.* [12], a series of HMS (hexagonal mesoporous silica) materials having different textural mesoporosities were synthesized and then modified with PEI for CO_2 capture. The PEI/HMS prepared using a HMS having complementary textural mesopores showed a CO_2 adsorption capacity as high as 184 mg/g

-sorbent with PEI loading of 60 wt.% at 75°C in pure CO_2 atmosphere. The CO_2 adsorption capacity on PEI/HMS dropped slightly after four adsorption-desorption regeneration cycles at 75°C. Shi *et al.* [13] prepared new CO_2 adsorbents by using SBA-16 type mesoporous silica impregnated with tetraethylenepentamine (TEPA). The highest breakthrough capacity and total adsorption capacity of about 0.625 and 0.973 $mmol\cdot g^{-1}$ were achieved with 30% TEPA impregnation at 60°C and 10% volume fraction CO_2, respectively. From 60 to 80°C, the CO_2 dynamic adsorption performance of TEPA-impregnated SBA-16 is stable, which shows only a minor drop (6.45%) in total CO_2 adsorption capacity over a ten cycles of adsorption–desorption operation. Ye *et al.* [14] introduced TEPA and triethylenetetramine (TETA) to carbon nanotubes (CNTs) to remove low concentration CO_2 (2%). As the same amount of amine was loading on CNTs, the CO_2 adsorption capacity of TEPA-loaded CNTs was higher than that of TETA-loaded CNTs. The adsorption capacity was obtained from 126.7 to 139.3 $mg\cdot g^{-1}$ for TEPA-loaded CNTs and from 101.2 to 110.4 $mg\cdot g^{-1}$ for TETA-loaded CNTs when the temperature increased from 20 to 30°C.

Bamboo charcoal is one type of porous adsorption materials with special microporous structure, abundant pore distribution, high surface area as well as extensive raw material resources and low price, which is widely used in gas and water purification as a multifunctional environmentally friendly material [22]. The carbonaceous materials selected as solid CO_2 adsorbents in current researches are mostly activated carbons and carbon nanotubes, and there has been no relevant report related to the amino polymers-modified bamboo charcoal as solid adsorbents for CO_2 capture.

In this paper, novel CO_2 adsorbents were developed using bamboo charcoal impregnated with polyethylene polyamine and polyethyleneimine, respectively. The adsorbents were characterized by scanning electron microscopy, Fourier-transform infrared spectroscopy, N_2 adsorption/desorption and thermogravimetric analysis. The CO_2 adsorption performance was tested by fixed bed system, concerning the effects of different amount of PEPA or PEI loading, temperature and moisture on the CO_2 adsorption performance of BC-PEPA or BC-PEI. We believe the present work conducted should lay a theoretical foundation for the development of new CO_2 adsorbents.

2. Experimental section

2.1 Materials

The raw material for preparing adsorbents was bamboo charcoal produced by Zhejiang Maitanwong Ecology Development Co., Ltd., China. As received, bamboo charcoal was sieved to the size range of 20-40 mesh, and then boiled in deionized water and washed several times with deionized water. It was then dried at 105°C overnight and kept in closed bottles for experiment. The sample above is referred to as BC. Analytical-grade polyethylene polyamine was supplied by Tianjin Kemiou Chemical Reagent Co., Ltd., China. Polyethylenimine, ethylenediamine branched with average Mw-800 by LS and Mn-600 by GPC was provided by Sigma-Aldrich (Shanghai) Trading Co., Ltd., China. Analytical-grade anhydrous ethanol was produced by Sinopharm Chemical Reagent CO., Ltd., China. High purity N_2 and the 10% volume fraction CO_2 balanced by N_2 were supplied by Jinan Deyang Special Gas Co., Ltd., China.

2.2 Modification of BC

The PEPA or PEI modified BC was prepared by a wet impregnation method. In a typical preparation, the desired amount of PEPA or PEI was dissolved in 50 mL of alcohol under stirring for about 30 min at 25°C, after which 5 g of BC was added to the solution. The resultant slurry was continuously stirred for about 2 hours at 80°C, and then the solvent evaporated at the same temperature. The sample was dried at 100°C for 1 hour for experiment use. The as-prepared adsorbents are denoted as BC-PEPA-X and BC-PEI-X, where X means the loading of PEPA or PEI in mass (g) in the sample.

2.3 Characterization of the Adsorbents

The surface morphologies and structures of BC before and after modification were characterized by scanning electron microscope (S-520, HITACHI Corp., Japan). The samples underwent conductive treatment before SEM observation. The thermal chemical and physical properties of BC and BC-PEPA-1 were characterized by thermal gravimetric analysis (SDT Q600 V8.3 Build 101, TA Corp., America). The samples were heated at 10°C/min to 800°C in N_2 atmosphere at a flow of 100 mL/min. The qualitative analysis of constituents in samples was characterized by Fourier Transform Infrared Spectrometer (VECTOR-70, BRUKER Corp., Germany). KBr was used as the diluter and FTIR spectra were recorded within a range of 370-4000 cm^{-1}. The BET surface area and the pore volume were obtained by N_2 adsorption/desorption (ASAP2020, MICROMERITICS Corp., America) at liquid nitrogen temperature (77K). Before the measurement, the sample was heated to 60°C at the rate of 10°C/min and held at this temperature for 20 min, then heated to 100°C at the rate of 10°C/min and held at this temperature for 450 min. The whole process mentioned above was under vacuum.

2.4 Dynamic Adsorption Experiment

The CO_2 adsorption performance was tested by fixed bed system shown in Figure 1. The adsorption column is made of glass with 1.2 cm in inner diameter, 25 cm in height and the gas distribution plate (pore diameter is about 100 μm) at the bottom of it. The gases pass the adsorption column through the side tube from the bottom to the top.

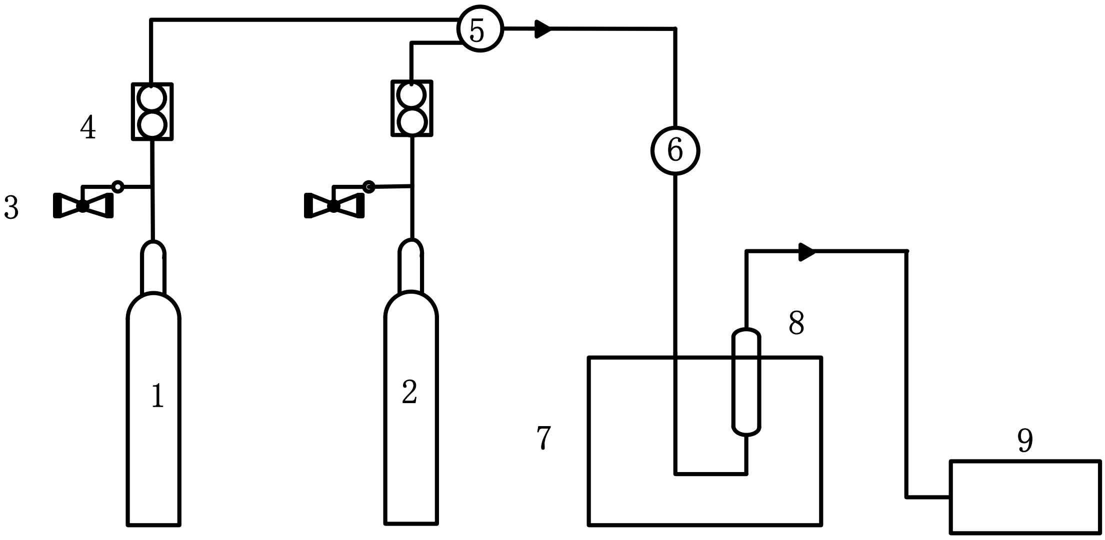

Figure 1. Schematic diagram of fixed bed adsorption system. 1: N_2 gas cylinder; 2: Mixed CO_2 gas cylinder; 3: Pressure regulator; 4: Gas mass flow controller; 5: Blender; 6: Gas moistener; 7: Quality thermostat with water-bath; 8: Adsorption column; 9: CO_2 monitor.

The CO_2 volumetric concentrations of the adsorption column outlet and inlet were measured by the potable IR CO_2 analyzer (GXH-3010, Institute of Beijing Huayun Analytical Instrument Co., Ltd., China). In a typical adsorption process, two grams of the adsorbent was placed in the adsorption column, outgassed to remove pre-absorbed CO_2 at 98°C for about 1 hour in N_2 atmosphere at a flow of 500 mL/min. The temperature was then adjusted to the design temperature and CO_2/N_2 gas mixture with 0.4% volume fraction CO_2 was introduced at a flow rate of 100 mL/min.

3. Results and Discussion

3.1 Characterization of the Adsorbents

The scanning electron microscope images of cross section and longitudinal section of bamboo charcoal are shown in Figure 2a and 2b. It can be seen that BC has high porosity. Figure 2c and 2d are SEM images of BC modified with PEPA, which indicate that the structure of BC is preserved after loading PEPA, and PEPA is uniformly dispersed on the surface and into the pore channels of BC.

The thermochemical and physical properties of BC and BC-PEPA-1 were measured by TGA which are shown in Figure 3a and 3b, respectively. The BC loses 3.94% of its original mass before 110°C, which can be mainly ascribed to the desorption of moisture by physical adsorption on the surface of BC, while there is a 6.68% mass loss for BC-PEPA-1 before 110°C and can be mainly put down to the desorption of CO2 and moisture. At the temperature range of 110-382.24°C, the BC-PEPA-1 loses 24.77% of its original mass, while there is a slight mass loss for BC, indicating that decomposition of the loading PEPA takes place. If the adsorbed moisture and CO_2 on BC-PEPA-1 are excluded from the total mass, the PEPA mass loss is in line with the designed PEPA loading and indicates that there was no PEPA loss during the preparation process.

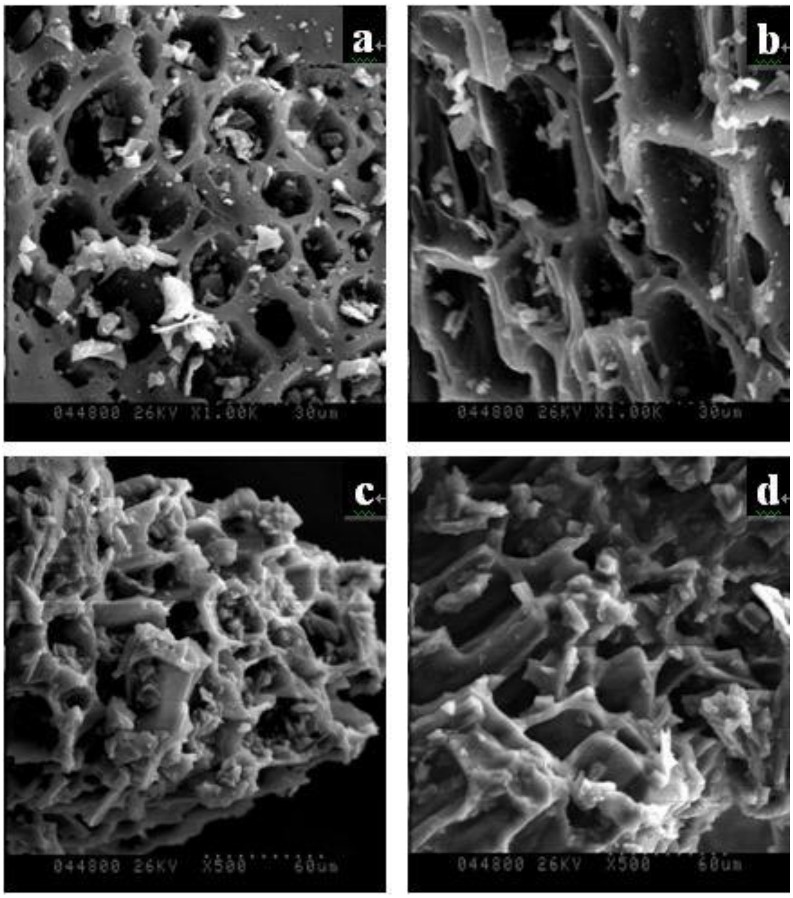

Figure 2. SEM images of BC and BC-PEPA-1: (a) (b) BC; (c) (d) BC-PEPA-1.

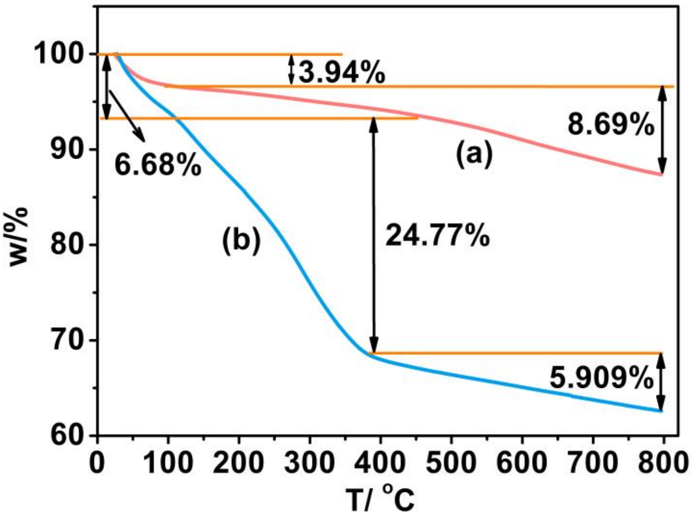

Figure 3. TGA curves of BC and BC-PEPA-1: (a) BC; (b) BC-PEPA-1.

Figure 4a and 4b show FTIR spectra of BC and BC-PEPA-1. A broad band at around 3500 cm^{-1} in Figure 4a can be assigned to the presence of surface hydroxyl groups and physisorbed water. The absorption peak of hydroxyl groups becomes significant and shows a red shift towards long wavelength after PEPA loading, which can be seen that the band shifts from 3512 cm^{-1} to 3454 cm^{-1}. Moreover, new absorption peaks at 1314 cm^{-1} and 3270 cm^{-1} appear in spectra line, which can be assigned respectively to the stretching vibration of C-N and amine N-H bonds. In the spectra of BC-PEPA-1, the bands at 1593 and 1463 cm^{-1} can be attributed to the bending vibrations of -NH_2 and N-H respectively, which indicates that the PEPA has been impregnated on BC. The bands of the BC-PEPA-1 sample at 2940 and 2828 cm^{-1} become stronger than that of the BC due to the CH_2 asymmetric and symmetric stretching modes of the PEPA chain, which further confirms that the PEPA has been impregnated on BC [14-15, 23-24].

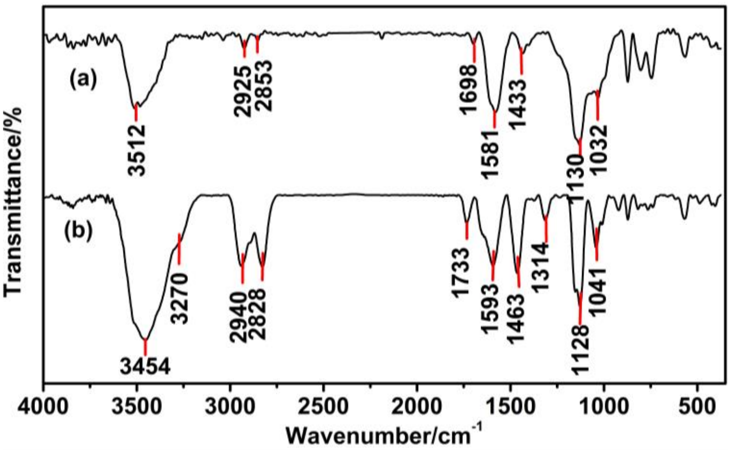

Figure 4 FTIR spectra of BC and BC-PEPA-1: (a) BC; (b) BC-PEPA-1.

Table 1 Structural parameters of bamboo charcoal

Sample	$S_{BET}/(m^2 \cdot g^{-1})$	$V_{total}/(cm^3 \cdot g^{-1})$
BC	139	0.061

S_{BET}: specific surface area calculated on the basis of the BET theory;
V_{total}: single-point adsorption total pore volume of pores less than 385.88 nm diameter at a relative pressure (p/p_0) of 0.995.

The structural parameters of BC are shown in Table 1. It can be measured by the nitrogen adsorption/desorption that the specific surface area and the pore volume of BC are 139 m^2/g and 0.061 cm^3/g, respectively. After loading the PEPA, the pores of BC were completely full of PEPA, restricting the access of liquid nitrogen into the pores at 77K, which also can be found in literature [25] in which MCM-41 were modified with PEI. Therefore, the specific surface area and pore volume of BC-PEPA cannot be measured.

3.2 CO_2 Adsorption Performance

3.2.1 Effect of the BC support

The CO_2 adsorption performance of the BC (20-40 mesh) support was tested by fixed bed system at 50°C, 0.4% volume fraction CO_2 and ambient pressure, and the adsorption breakthrough curve is shown in Figure 5. BC shows a CO_2 adsorption capacity of 1.11 mg/g -sorbent. The low adsorption capacity is due to the weak interaction between the CO_2 and the BC at relatively high temperature. To enhance the interaction between the CO_2 and the BC, the amino polymers PEPA and PEI with plenty of CO_2 affinity sites are loaded on the surface and into the channels of the BC.

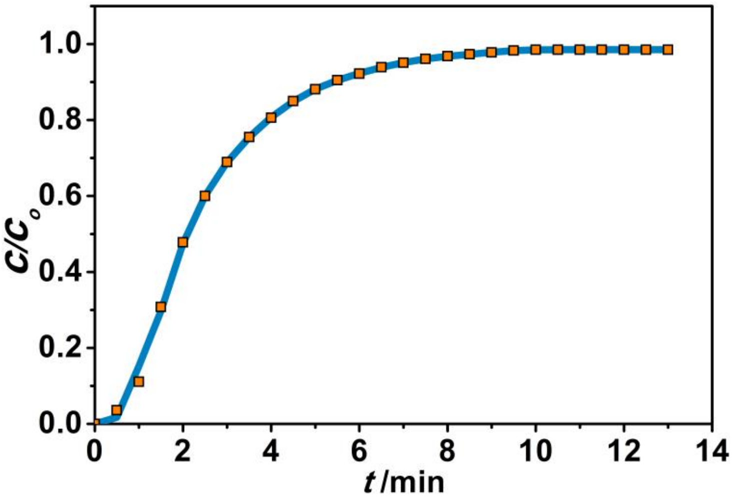

Figure 5. CO_2 adsorption breakthrough curve of BC. Conditions: T=50°C, p=ambient pressure, $\varphi CO2$ = 0.4%, amount of adsorbent=2 g, space velocity=885 /h.

3.2.2 Effect of Adsorption Temperature

Adsorption Temperature is an essential technological parameter that has a great effect on the adsorption performance of the adsorbents. The adsorbents can achieve their optimum effects when they adsorb at their best adsorption temperature. The adsorption performance of BC-PEPA-1 and BC-PEI-1 were measured at different temperatures in 0.4% volume fraction CO_2 and ambient pressure. Figure 6a and 6b show the adsorption breakthrough curves for CO_2 adsorption of BC-PEPA-1 and BC-PEI-1 at 25, 50 and 75°C. In this article, the time from the beginning of the adsorption to the CO_2 volumetric concentration of the adsorption column outlet reaching 10% of the inlet concentration is termed as the breakthrough time. From the perspective of the breakthrough time, with increasing temperatures, the adsorption capacity of BC-PEPA-1 and BC-PEI-1 both become higher and reach their maximum adsorption capacity at 50°C. When the temperature is increased to 75°C, the adsorption capacity shows a downward trend.

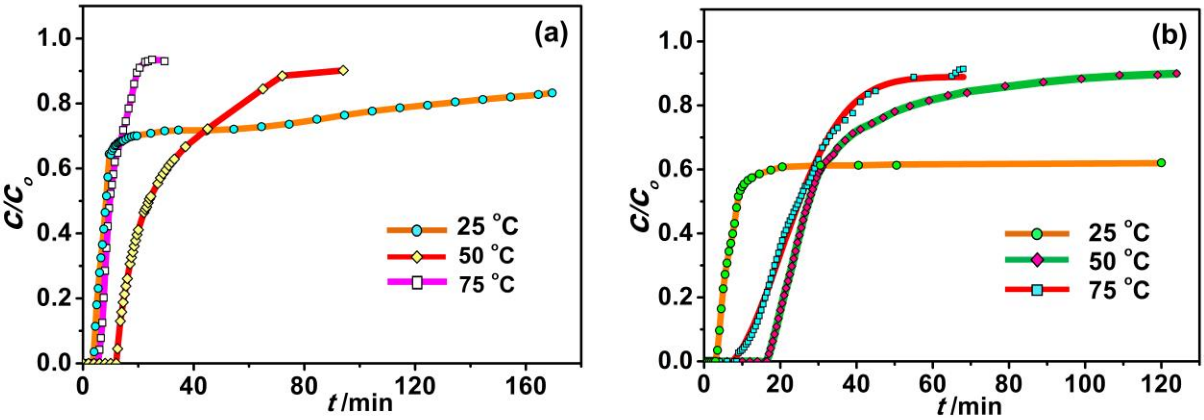

Figure 6. CO_2 adsorption breakthrough curves of BC-PEPA-1 and BC-PEI-1 at different temperatures: (a) BC-PEPA-1; (b) BC-PEI-1. Conditions: p=ambient pressure, φ_{CO2}= 0.4%, amount of adsorbent=2 g, space velocity=885 /h.

The CO_2 adsorption of BC-PEPA or BC-PEI is an exothermic process. Consequently, the adsorption capacity should decrease with the increase of temperature. However, from the perspective of the breakthrough time, the adsorption capacity of BC-PEPA or BC-PEI first experiences an upward trend with the increasing temperature then declines, which indicates it is an unusual adsorption process. The reason is that the CO_2 adsorption process follows an adsorption-diffusion mechanism [15]. Firstly, CO_2 molecules may be adsorbed on the PEPA surface of BC-PEPA or the PEI surface of BC-PEI; then a CO_2 diffusion process from the PEPA (PEI) surface to the PEPA (PEI) bulk restricted inside the pores of BC occurs. The adsorption of CO_2 on the PEPA or the PEI surface is dominated by thermodynamics, while the CO_2 diffusion process is controlled by kinetics and is the main control factor in the adsorption process. Both determine the overall adsorption performance of the BC-PEPA or BC-PEI [15,26]. At 25°C, though it is thermodynamically preferred for CO_2 adsorption on the PEPA or the PEI surface, the adsorption capacity is low because the molecular kinetic energy is low and the viscosity of PEPA or PEI is high at this temperature so that it has relatively high diffusion resistance and is not in favor of the CO_2 diffusion. Thus, only the CO_2 adsorption sites on the PEPA or PEI surface can easily react with CO_2 [15, 25-27]. As the temperature increases to 50°C, the molecular kinetic energy is increasing gradually, while the viscosity of PEPA or PEI is dropping so that the adsorbed CO_2 molecules can more readily diffuse from the PEPA (PEI) surface to or within the PEPA (PEI) bulk and the CO_2 adsorption sites inside the channels can react with CO_2, resulting in the higher adsorption capacity. In comparison, at higher temperature, such as 75 °C, although the viscosity of PEPA or PEI decreases further and the diffusion of CO_2 is enhanced so that more CO_2 adsorption sites are becoming easier to approach, a portion of CO_2 adsorbed on amine sites of the adsorbents become more preferential to desorb due to the weak bonding force between CO_2 and the amino polymers-modified BC, leading to a rapid adsorption equilibrium and a substantial drop in the adsorption capacity [15, 26-27].

3.2.3 Effect of PEPA or PEI Loading

The adsorption breakthrough curves of BC-PEPA and BC-PEI with different amount of loading at 50°C, 0.4% volume fraction CO_2 and ambient pressure are shown in Figure 7a and 7b, respectively. With increasing loading of PEPA or PEI, the CO_2 adsorption capacity of BC-PEPA or BC-PEI first increases then decreases (1.5 g PEPA>2 g PEPA>1 g PEPA>3 g PEPA>0.5 g PEPA>BC and 2 g PEI>3 g PEPA>1 g PEPA>BC). The highest CO_2 adsorption capacity of PEPA-loaded BC at 50°C is 25.7 mg/g-sorbent when the mass fraction of PEPA loading is 23.1%. At 28.6% mass fraction PEI loading in BC-PEI, the highest CO_2 adsorption capacity of 35.6 mg/g-sorbent is obtained at 50°C.

The results shown above are because there is a synergetic effect between the BC and the PEPA or the PEI on the CO_2 adsorption for PEPA-loaded or PEI-loaded BC [11, 25-26]. The synergetic effect may be attributed to the surface area and the abundant porous structures of BC which can lead to the relatively uniform dispersion of PEPA or PEI into the pore channels of BC. There are numerous amine groups in PEPA or PEI which can react with CO_2 due to the acid-alkali interaction. When the PEPA or the PEI is impregnated on the materials with relatively high surface area, more CO_2 adsorption sites are exposed to the adsorbate and are easy to react with CO_2, thus the CO_2 adsorption capacity of BC-PEPA or BC-PEI increases noticeably. The abundant porous structures of the BC may be critical to the enhancement of the CO_2 adsorption capacity. When the channels of the BC are full of the PEPA or the PEI, the apparent pore size of the BC will be reduced. In the meantime, more CO_2 adsorption sites are brought in the channels. The two effects may integrate together and lead to the further increase of the adsorption capacity. The highest computed adsorption capacity is gained when the channels of the BC are fully filled with the PEPA or the PEI. When the PEPA or the PEI loading is further raised and the PEPA or the PEI is coated on the external surface of the BC, resulting in channels blockage. The channels of BC may be destroyed by an excess of the PEPA or the PEI loading, leading to the decline of the adsorption capacity. However, in the case of low amount of PEPA or PEI loading, the active amine groups reacting with CO_2 will be too few, resulting in the low adsorption capacity.

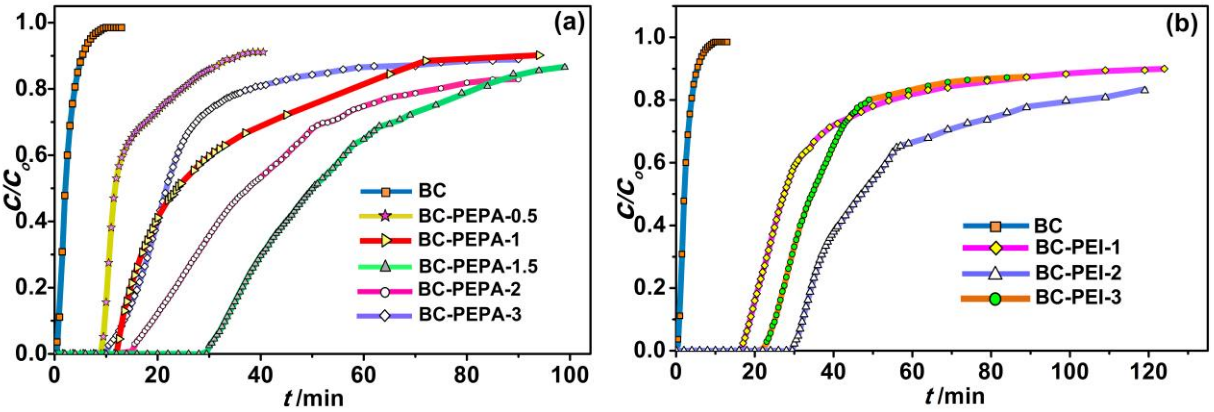

Figure 7. CO_2 adsorption breakthrough curves of BC with different amount of PEPA and PEI loading: (a) BC-PEPA; (b) BC-PEI. Conditions: T=50°C, p=ambient pressure, φ_{CO2}=0.4%, amount of adsorbent=2 g, space velocity=885 /h.

When PEPA (PEI) is loaded on BC, physisorption by capillary condensation and chemisorption between CO_2 and PEPA (PEI) jointly determine the adsorption capacity [11]. As the PEPA (PEI) loading increases, the physisorption-dominated process converts to chemisorption-dominated process, thus the CO_2 adsorption capacity is enhanced remarkably.

3.2.4 Effect of Moisture

Figure 8 shows the adsorption breakthrough curves of BC-PEPA-1 with and without moisture at 50°C, 0.4% volume fraction CO_2 and ambient pressure. It can be seen that the CO_2 adsorption capacity on PEPA-modified BC increases in the presence of water vapor.

This can be attributed to the fact that chemical reaction between CO_2 and PEPA may be varied in the presence of water vapor. PEPA is a polymeric substance with plenty of amine groups (CO_2 adsorption sites). Theoretically, the main reaction is that the amine groups react with CO_2 to form carbamate without water, as shown in reaction equations (1)-(3). The adsorption capacity is restricted because one mole CO_2 reacts with two moles amine groups.

$$CO_2 + 2RNH_2 \rightleftharpoons NH_4^+ + R_2NCOO^- \quad (1)$$

$$CO_2 + 2R_2NH \rightleftharpoons R_2NH_2^+ + R_2NCOO^- \quad (2)$$

$$CO_2 + 2R_3N \rightleftharpoons R_4N^+ + R_2NCOO^- \quad (3)$$

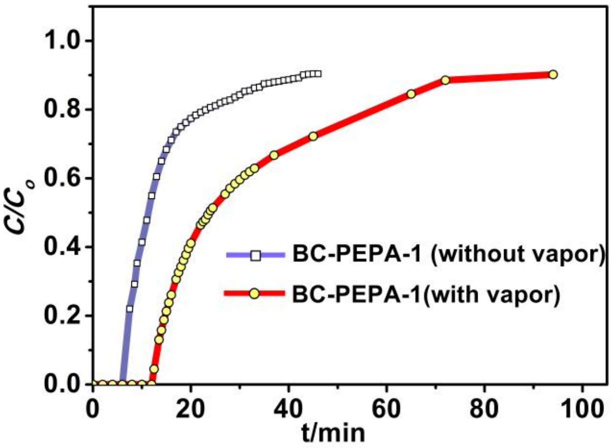

Figure 8. Comparison of the CO_2 adsorption breakthrough curves with and without water vapor of BC-PEPA-1. Conditions: T=50°C, p=ambient pressure, φ_{CO2} = 0.4%, amount of adsorbent=2 g, space velocity=885 /h.

In the presence of water, the carbamate ion formed above will further react with CO_2 and water molecules to form bicarbonate in reaction equation (4). Besides, the amine groups of PEPA can also directly react with CO_2 and water molecules to form bicarbonate, as shown in reaction equations (5)-(7). Thus, in moist condition, one mole amine group reacts with one mole CO_2, which increases the adsorption capacity of BC-PEPA adsorbents [1, 10].

$$R_2NCOO^- + 2H_2O + CO_2 \rightleftharpoons R_2NH_2^+ + 2HCO_3^- \tag{4}$$

$$CO_2 + RNH_2 + H_2O \rightleftharpoons RNH_3^+ + HCO_3^- \tag{5}$$

$$CO_2 + R_2NH + H_2O \rightleftharpoons R_2NH_2^+ + HCO_3^- \tag{6}$$

$$CO_2 + R_3N + H_2O \rightleftharpoons R_3NH^+ + HCO_3^- \tag{7}$$

From the analysis above, the CO_2 adsorption capacities on amino polymers-modified BC increase in the presence of water vapor, however, the increased range depends on the experimental conditions. Theoretically, the CO_2 adsorption capacities of amino polymers-modified BC in the presence of water will be twice than that without water. However, in practice, most of the experiments have not obtained such results. This can be ascribed to the fact that the formation of carbamate is faster than the formation of bicarbonate in the adsorption process, therefore it will take longer time to form bicarbonate. However, for the fixed bed dynamic adsorption process, the retention time of gases in the adsorption column is shorter than the equilibrium time of forming bicarbonate. Hence, the CO_2 adsorption capacities of amino polymers-modified BC in the presence of water cannot be twice than that without water.

4. Conclusions

Novel CO_2 adsorbents were developed using bamboo charcoal impregnated with polyethylene polyamine and polyethyleneimine, respectively. It can be confirmed that the PEPA have been basically loaded on BC through FT-IR and TGA. In addition, the structure of BC is preserved after loading PEPA, and PEPA is uniformly dispersed on the surface and into the pore channels of BC. It can be measured by the nitrogen adsorption/desorption that the specific surface area and the pore volume of BC are 139 m^2/g and 0.061 cm^3/g, respectively. From the perspective of the breakthrough time, the adsorption capacity of BC-PEPA or BC-PEI first experiences an upward trend with the increasing temperature then declines. There is a synergetic effect between the BC and the PEPA or PEI on the CO_2 adsorption for PEPA-loaded or PEI-loaded BC. The highest CO_2 adsorption capacity of PEPA-loaded BC at 50°C is 25.7 mg/g-sorbent when the mass fraction of PEPA loading is 23.1%. At 28.6% mass fraction PEI loading in BC-PEI, CO_2 reaches the highest adsorption capacity of 35.6 mg/g sorbent at 50°C. The CO_2 adsorption capacities on amino polymers-modified BC increase in the presence of water vapor, however, the increased range depends on the experimental conditions. The BC modified with PEPA or PEI is a new adsorbent, which has a relatively good CO_2 adsorption performance at low concentration CO_2 (0.4% volume fraction) and ambient pressure. Furthermore, the carrier BC is one type of porous adsorption materials with special microporous structure, abundant pore distribution, high surface area as well as extensive raw material resources and low price. On the whole, novel CO_2 solid adsorbents based on amino polymers-modified BC have a promising prospect and research value.

Acknowledgments

This work was supported by the "New Century Excellent Talent Project" from the Ministry of Education of China (NCET-05-0584), Municipal Scientific Research and Development Innovation Project from Jinan (201102041), and PetroChina Innovation Foundation (2013D-5006-0507).

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] Luo, Z.Y.; Fang, M.X.; Li, M.Y.; Gao, L.; Hu, J.C.; Yan, W.P.; Guo, X.Q.; Shi, Y.; Zeng, R.S. *Technology of Carbon Dioxide Capture, Storage and Utilization*, China Electric Power Press: Beijing, CHN, 2012, pp. 16-23, 74-82 (in Chinese).

[2] Zhu, Y.Z.; Liao, C.H.; Wang, C.Q.; Zhu, T.F. *Emission Reduction and Reclamation of Carbon Dioxide*, Chemical Industry Press: Beijing, CHN, 2011, p. 4 (in Chinese).

[3] Liu, Y.; Tu, N.Y.; Peng, S.H. A new way of removing and recovering CO_2 efficiently from flue gas of petrochemical industry. *Environ. Eng.* 2012, *30*, 58-62 (in Chinese).

[4] Zhang, P.; Shi, Y.; Wei, J.W.; Zhao, W.; Ye, Q. Regeneration of 2-amino-2-methyl-1-propanol used for carbon dioxide absorption. *J. Environ. Sci.-China* 2008, *20*, 39-44.

[5] Oyenekan, B.A.; Rochelle, G.T. Alternative stripper configurations for CO_2 capture by aqueous amines. *AIChE J.* 2007, *53*, 3144-3154.

[6] Hwang, H.T.; Harale, A.; Liu, P.K.T.; Sahimi, M.; Tsotsis, T.T. A membrane-based reactive separation system for CO_2 removal in a life support system. *J. Membrane Sci.* 2008, *315*, 116-124.

[7] Aaron, D.; Tsouris, C. Separation of CO_2 from flue gas: A review. *Separ. Sci. Technol.* 2005, *40*, 321-348.

[8] Serna-Guerrero, R.; Sayari, A. Modeling adsorption of CO_2 on amine-functionalized mesoporous silica. 2: Kinetics and breakthrough curves. *Chem. Eng. J.* 2010, *161*, 182-190.

[9] Veawab, A.; Tontiwachwuthikul, P.; Chakma, A. Corrosion behavior of carbon steel in the CO_2 absorption process using aqueous amine solutions. *Ind. Eng. Chem. Res.* 1999, 38, 3917-3924.

[10] Xu, X.C.; Song, C.S.; Miller, B.G.; Scaroni, A.W. Influence of moisture on CO_2 separation from gas mixture by a nanoporous adsorbent based on polyethylenimine-modified molecular sieve MCM-41. *Ind. Eng. Chem. Res.* 2005, *44*, 8113-8119.

[11] Xu, X.C; Song, C.S.; Andrésen, J.M.; Miller, B.G.; Scaroni, A.W. Preparation and characterization of novel CO_2 "molecular basket" adsorbents based on polymer-modified mesoporous molecular sieve MCM-41. *Micropor. Mesopor. Mat.* 2003, *62*, 29-45.

[12] Chen, C.; Son, W.J.; You, K.S.; Ahn, J.W.; Ahn, W.S. Carbon dioxide capture using amine-impregnated HMS having textural mesoporosity. *Chem. Eng. J.* 2010, *161*, 46-52.

[13] Shi, J.J.; Liu, Y.M.; Chen, J.; Zhang, Y.; Shi, Y. Dynamic performance of CO_2 adsorption with amine-modified SBA-16. *Acta Phys. -Chim. Sin.* 2010, *26*, 3023-3029 (in Chinese).

[14] Ye, Q.; Zhang, Y.; Li, M.; Shi, Y. Adsorption of low concentration CO_2 by modified carbon nanotubes under ambient temperature. *Acta Phys. -Chim. Sin.* 2012, *28*, 1223-1229 (in Chinese).

[15] Wang, X.X.; Ma, X.L.; Schwartz, V.; Clark, J.C.; Overbury, S.H.; Zhao, S.Q.; Xu, X.C.; Song, C. S. A solid molecular basket sorbent for CO_2 capture from gas streams with low CO_2 concentration under ambient conditions. *Phys. Chem. Chem. Phys.* 2012, *14*, 1485-1492.

[16] Zhao, H.M.; Lin, D.; Yang, G.; Chun, Y.; Xu, Q.H. Adsorption capacity of carbon dioxide on amine modified mesoporous materials with larger pore sizes. *Acta Phys. -Chim. Sin.* 2012, *28*, 985-992 (in Chinese).

[17] Bezerra, D.P.; Oliveira, R.S.; Vieira, R.S.; Cavalcante, C.L., Jr.; Azevedo, D.C.S. Adsorption of CO_2 on nitrogen-enriched activated carbon and zeolite 13X. *Adsorption* 2011, *17*, 235-246.

[18] Plaza, M.G.; Pevida, C.; Arenillas, A.; Rubiera, F.; Pis, J.J. CO_2 capture by adsorption with nitrogen enriched carbons. *Fuel* 2007, *86*, 2204-2212.

[19] Son, W.J.; Choi, J.S.; Ahn, W.S. Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials. *Micropor. Mesopor. Mat.* 2008, *113*, 31-40.

[20] Xu, X.C.; Song, C.S.; Miller, B.G.; Scaroni, A.W. Adsorption separation of carbon dioxide from flue gas of natural gas-fired boiler by a novel nanoporous "molecular basket" adsorbent. *Fuel Process. Technol.* 2005, *86*, 1457-1472.

[21] Shao, Y.; Ma, Y. Amino group surface-functionalized ordered mesoporous materials: one-pot synthesis, heavy-metal ion and CO_2 adsorption. *Acta Chim. Sinica* 2012, *70*, 1957-1962 (in Chinese).

[22] Hu, Y.J.; Huang, X.H. Study on the bamboo charcoal-foam adsorption properties for formaldehyde vapour. *Chin. J. Synth. Chem.* 2005, *13*, 603-606 (in Chinese).

[23] Wang, X.X.; Schwartz, V.; Clark, J.C.; Ma, X.L.; Overbury, S.H.; Xu, X.C.; Song, C.S. Infrared study of CO_2 sorption over "molecular basket" sorbent consisting of polyethylenimine-modified mesoporous molecular sieve. *J. Phys. Chem. C* 2009, *113*, 7260-7268.

[24] Dong, H.R. *Instrumental Analysis*, Chemical Industry Press: Beijing, CHN, 2010, pp. 197-199, 204 (in Chinese).

[25] Xu, X.C.; Song, C.S.; Andrésen, J.M.; Miller, B.G.; Scaroni, A.W. Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO_2 capture. *Energ. Fuel.* 2002, *16*, 1463-1469.

[26] Ai, Y.Y. Research on efficient adsorbents for low concentration CO_2 capture. Master Thesis, Dalian University of Technology, Dalian, CHN, 2010 (in Chinese).

[27] Wei, L.; Lan, R.K.; Jing, Y.; Gao, Z.M.; Wang, Y.D. Modification of MCM-41 with pentaethylenehexamine (PEHA) and its performance of adsorption for CO_2. *Chem. Ind. Eng. Prog.* 2011, *30*, 143-148 (in Chinese).