NOVEL AMINO POLYMERS-MODIFIED BAMBOO CHARCOAL AS SOLID ADSORBENTS FOR CO₂ CAPTURE

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Abstract
Novel CO₂ 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 (FTIR), \( N₂ \) 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 CO₂ adsorption performance was tested by fixed bed system at low concentration CO₂ (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 CO₂ adsorption for PEPA-loaded or PEI-loaded BC. The CO₂ 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 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, CO₂ reaches the highest adsorption capacity of 35.6 mg/g-sorbent at 50°C. The CO₂ 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. CO₂ 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 CO₂ to curb global warming has caused extensive concerns around the world. CO₂ capture, sequestration and resource utilization have been considered as the key means of mitigating the greenhouse effect and global warming. Therefore, researches on CO₂ capture, sequestration and resource utilization are of great importance \[3\].

Practical methods for CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture. The PEI/HMS prepared using a HMS having complementary textural mesopores showed a CO₂ adsorption capacity as high as 184 mg/g...
sorbent with PEI loading of 60 wt.% at 75°C in pure CO₂ atmosphere. The CO₂ adsorption capacity on PEI/HMS dropped slightly after four adsorption-desorption regeneration cycles at 75°C. Shi et al. [13] prepared new CO₂ adsorbents by using SBA-16 type mesoporous silica impregnated with tetraethylene pentamine (TEPA). The highest breakthrough capacity and total adsorption capacity of about 0.625 and 0.973 mmol·g⁻¹ were achieved with 30% TEPA impregnation at 60°C and 10% volume fraction CO₂, respectively. From 60 to 80°C, the CO₂ dynamic adsorption performance of TEPA-impregnated SBA-16 is stable, which shows only a minor drop (6.45%) in total CO₂ 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 CO₂ (2%). As the same amount of amine was loading on CNTs, the CO₂ 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·g⁻¹ for TEPA-loaded CNTs and from 101.2 to 110.4 mg·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 CO₂ 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 CO₂ capture.

In this paper, novel CO₂ 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, N₂ adsorption/desorption and thermogravimetric analysis. The CO₂ adsorption performance was tested by fixed bed system, concerning the effects of different amount of PEPA or PEI loading, temperature and moisture on the CO₂ adsorption performance of BC-PEPA or BC-PEI. We believe the present work conducted should lay a theoretical foundation for the development of new CO₂ 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. Polyethyleneimine, 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 N₂ and the 10% volume fraction CO₂ balanced by N₂ 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 N₂ 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 N₂ 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 CO₂ 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: N₂ gas cylinder; 2: Mixed CO₂ 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: CO₂ monitor.](image폈)

The CO₂ volumetric concentrations of the adsorption column outlet and inlet were measured by the portable IR CO₂ 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 CO₂ at 98°C for about 1 hour in N₂ atmosphere at a flow of 500 mL/min. The temperature was then adjusted to the design temperature and CO₂/N₂ gas mixture with 0.4% volume fraction CO₂ 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 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 CO₂ 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 \([14-15, 23-24]\).
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 CO₂ and ambient pressure. Figure 6a and 6b show the adsorption breakthrough curves for CO₂ 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 CO₂ 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. CO₂ 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.](image)

The CO₂ 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 CO₂ adsorption process follows an adsorption-diffusion mechanism [15]. Firstly, CO₂ molecules may be adsorbed on the PEPA surface of BC-PEPA or the PEI surface of BC-PEI; then a CO₂ diffusion process from the PEPA (PEI) surface to the PEPA (PEI) bulk restricted inside the pores of BC occurs. The adsorption of CO₂ on the PEPA or the PEI surface is dominated by thermodynamics, while the CO₂ 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 CO₂ 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 CO₂ diffusion. Thus, only the CO₂ adsorption sites on the PEPA or PEI surface can easily react with CO₂ [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 CO₂ molecules can more readily diffuse from the PEPA (PEI) surface to or within the PEPA (PEI) bulk and the CO₂ adsorption sites inside the channels can react with CO₂, 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 CO₂ is enhanced so that more CO₂ adsorption sites are becoming easier to approach, a portion of CO₂ adsorbed on amine sites of the adsorbents become more preferential to desorb due to the weak bonding force between CO₂ 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 CO₂ and ambient pressure are shown in Figure 7a
and 7b, respectively. With increasing loading of PEPA or PEI, the CO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} adsorption for PEPA-loaded or PEI-loaded BC \cite{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\textsubscript{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\textsubscript{2} adsorption sites are exposed to the adsorbate and are easy to react with CO\textsubscript{2}, thus the CO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} will be too few, resulting in the low adsorption capacity.

![CO\textsubscript{2} adsorption breakthrough curves of BC with different amount of PEPA and PEI loading](image)

Figure 7. CO\textsubscript{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\textsubscript{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\textsubscript{2} and PEPA (PEI) jointly determine the adsorption capacity \cite{11}. As the PEPA (PEI) loading increases, the physisorption-dominated process converts to chemisorption-dominated process, thus the CO\textsubscript{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\textsubscript{2} and ambient pressure. It can be seen that the CO\textsubscript{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\textsubscript{2} and PEPA or PEI may be varied in the presence of water vapor. PEPA is a polymeric substance with plenty of amine groups (CO\textsubscript{2} adsorption sites). Theoretically, the main reaction is that the amine groups react with CO\textsubscript{2} to form carbamate without water, as shown in reaction equations (1)-(3). The adsorption capacity is restricted because one mole CO\textsubscript{2} reacts with two moles amine groups.

\[
\text{CO}_2 + 2RNH_2 \rightarrow NH_3^+ + R_2NCOO^- \quad (1)
\]

\[
\text{CO}_2 + 2R_2NH \rightarrow R_2NH_3^+ + R_2NCOO^- \quad (2)
\]

\[
\text{CO}_2 + 2R_3N \rightarrow R_3N^+ + R_2NCOO^- \quad (3)
\]
Figure 8. Comparison of the CO\textsubscript{2} adsorption breakthrough curves with and without water vapor of BC-PEPA-1. Conditions: \(T=50^\circ\text{C}\), \(p=\text{ambient pressure}\), \(C_{\text{CO}_2}=0.4\%\), amount of adsorbent=2 g, space velocity=885 \text{mL/g} \cdot \text{h}.

In the presence of water, the carbamate ion formed above will further react with CO\textsubscript{2} and water molecules to form bicarbonate in reaction equation (4). Besides, the amine groups of PEPA can also directly react with CO\textsubscript{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\textsubscript{2}, which increases the adsorption capacity of BC-PEPA adsorbents \(^{[1, 10]}\).

\[
\begin{align*}
\text{R}_2\text{NCOO} + 2\text{H}_2\text{O} + \text{CO}_2 & \rightarrow \text{R}_2\text{NH}_2^+ + 2\text{HCO}_3^- \quad (4) \\
\text{CO}_2 + \text{RNH}_2 + \text{H}_2\text{O} & \rightarrow \text{RNH}_3^+ + \text{HCO}_3^- \quad (5) \\
\text{CO}_2 + \text{RNH} + \text{H}_2\text{O} & \rightarrow \text{RNH}_2^+ + \text{HCO}_3^- \quad (6) \\
\text{CO}_2 + \text{RN} + \text{H}_2\text{O} & \rightarrow \text{RN}^+ + \text{HCO}_3^- \quad (7)
\end{align*}
\]

From the analysis above, the CO\textsubscript{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\textsubscript{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\textsubscript{2} adsorption capacities of amino polymers-modified BC in the presence of water cannot be twice than that without water.

4. Conclusions

Novel CO\textsubscript{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\textsuperscript{2}/g and 0.061 cm\textsuperscript{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\textsubscript{2} adsorption for PEPA-loaded or PEI-loaded BC. The highest CO\textsubscript{2} adsorption capacity of PEPA-loaded BC at 50\(^\circ\text{C}\) 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\textsubscript{2} reaches the highest adsorption capacity of 35.6 mg/g sorbent at 50\(^\circ\text{C}\). The CO\textsubscript{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\textsubscript{2} adsorption performance at low concentration CO\textsubscript{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\textsubscript{2} solid adsorbents based on amino polymers-modified BC have a promising prospect and research value.

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Conflicts of Interest

The authors declare no conflict of interest.

References


