CO₂ Capture Behaviors of Amine-Modified Resorcinol-Based Carbon Aerogels Adsorbents

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ABSTRACT

Activated carbon aerogel (CA)-based amine-loaded adsorbent has been successfully developed for CO₂ capture. The adsorbents were characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR), N₂ adsorption/desorption and thermogravimetric analysis (TGA). The CO₂ adsorption performance was tested by the fixed bed system at 5% CO₂ concentration. The effects of the mass ratio of KOH to CA, type of amine, amine loadings, addition of polyethylene glycol (PEG) or surfactants and adsorption temperature on the CO₂ capture performance of amine-loaded activated CA as well as the regeneration capability were examined. The results show that the adsorbents effectively remove 5% CO₂ from gas mixtures. The optimum adsorption temperature and amine loadings of polyethyleneimine (PEI)-loaded activated CA are 75°C and 55 wt.% respectively at the activation mass ratio KOH to CA of 1. Under these optimum conditions, the PEI-loaded activated CA reaches the highest adsorption capacity of 2.06 mmol g⁻¹ adsorbent. Addition of PEG facilitates the CO₂ adsorption. Suyadal’s and Yasyerli’s deactivation models both fit the experimental breakthrough curves of tetraethylenepentamine (TEPA)-loaded activated CA better than that of PEI-loaded activated CA. The adsorption kinetics nonlinear fitting results show that the adsorption process follows Bangham model.

Keywords: CO₂ adsorption; Carbon aerogel; Amine; Deactivation model; Kinetics.

INTRODUCTION

The greenhouse effect has substantially intensified owing 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 adverse impacts on the eco-environment. The Paris Agreement (United nations, 2015), which urges Parties to be dedicated to holding the increase in the global average temperature to well below 2°C above pre-industrial levels and making great efforts to limit the temperature to 1.5°C above pre-industrial levels, entered into effect on 4 November 2016. CO₂ is regarded as the significant greenhouse gas due to its huge emissions and great contribution to the greenhouse effect (Zhu et al., 2011; Luo et al., 2012). CO₂ is also believed to induce the generation or growth of particulate materials in the air environment. Consequently, technological measures for reducing CO₂ emission to retard global warming and improve air quality of the living environment of the society at large, is urgently needed.

Adsorption has appeared as one of the promising methods for CO₂ capture with its low energy consumption, cost-effectiveness, relatively simple technological process, non-corrosiveness to the equipment and extensive applicability over a relatively wide range of temperatures and pressures (Duan et al., 2014; Xu et al., 2005). The development of porous solid state adsorbents that can efficiently capture CO₂ would certainly achieve economic and environmental benefits and contribute to mitigating the greenhouse effect and global warming. Developing simple and low cost methods to synthesize highly porous materials with suitable properties for CO₂ capture has raised comprehensive concerns. On account of the unique pore structure, surface property, low cost, high thermal stability and low sensitivity to moisture, carbonaceous materials such as activated carbons (Alababi et al., 2015; Sethia and Sayari, 2015; Shahkarami et al., 2015), ordered mesoporous carbons (Liu et al., 2011; Wei et al., 2013; Yuan et al., 2013) and graphene (Zhao et al., 2012; Lee and Park, 2014; Chowdhury and Balasubramanian, 2016) have been extensively used for CO₂ capture. Zeolites with highly crystalline structure, high surface area, and 3-dimensional pore structures by altering their composition as Si/Al ratio have been widely applied as CO₂ adsorbents (Yu et al., 2012; Lee et al., 2013). Mesoporous molecular sieves (Gil et al., 2011; Wang et al., 2014) have...
2012; Xu et al., 2003) are widely used as adsorbents for gas separation because of the high surface area, large pore volume and tunable pore size. Metal-organic frameworks (MOFs) (Cho et al., 2012; Ganesh et al., 2014; Xian et al., 2015) have caused extensive concerns in the recent years due to the notably high surface area, controllable pore structure and pore surface property, and relevant researches on this field of CO2 adsorption are on the rise.

Among the porous materials, CA is attractive on account of its chemical inertness, high internal surface area and low density. CA is typically prepared by three sequential procedures which include sol-gel polymerization of molecular precursors, drying and carbonization of organic gel. CAs mostly use in the fields such as supercapacitors and lithium-sulfur batteries (Li et al., 2015; Li et al., 2016; Yu et al., 2017). Recently, only a few literatures related to CA for CO2 capture have been reported. And the researchers of the literatures focused on pure CO2 removal capacity. Mokaya’s group prepared high surface area carbon aerogels via a subcritical drying route and subsequent KOH activation. The activated CAs exhibit high CO2 adsorption capacity of 2.7–3.0 mmol g–1 at 25°C and 1 bar in pure CO2 (Robertson and Mokaya, 2013). As far as we are aware the use of amine-modified activated CA for CO2 capture has not been explored. In our study, we synthesized activated CA based on literatures of Kim’s group, Mokaya’s group and Park’s group (Robertson and Mokaya, 2013; Moon et al., 2014; Li et al., 2015) via a soft-template method, ambient drying and KOH activation, and then amine modification was applied for adsorbents’ preparation. The prepared adsorbents can efficiently adsorb 5% molar concentration of CO2 in the flow of CO2/N2. The main aim of this work is to synthesize simple, low cost and efficient adsorbents for CO2 capture at low CO2 partial pressure in the gas mixture of CO2/N2. Another distinction in our research is the investigation of experimental breakthrough curves and the kinetic of CO2 on the prepared adsorbents by deactivation models and kinetic models. A Soft-template method used in this study is to control the structure without removing the template, which simplified the synthesis procedure. The ambient drying route and KOH activation used in this work can avoid the advantages of the complicated processes and specialized equipment requirements of the common drying methods including supercritical drying and freeze-drying but without compromising porosity. The adsorbents were characterized by SEM, FT-IR, N2 adsorption/desorption and TGA. The CO2 adsorption performance was tested by the fixed bed system at 5% molar concentration of CO2, concerning the effects of the mass ratio of KOH to CA, type of amine, amine loadings, addition of PEG or surfactants and adsorption temperature on the CO2 capture performance of amine-loaded activated CAs as well as the regeneration capability. Suyadal’s and Yasyerli’s deactivation models were applied to investigate the experimental breakthrough curves of activated CA-based amine-loaded adsorbents. Also the kinetics of CO2 on the prepared adsorbents were investigated using four kinetic models, including pseudo-first-order, pseudo-second-order, intra-particle diffusion and Bangham models.

**METHODS**

**Preparation of CA**

For the synthesis of CA, resorcinol (R), formaldehyde (F), deionized water and cetyltrimethylammonium bromide (CTAB) were mixed with R/F/CTAB molar ratio of 125:250:1 under magnetic stirring for 3 hours. The reaction mixture was sealed and cured at 85°C for 48 h to induce gelation. The resulting organic aerogel was soaked in acetone at 50°C to replace the water in the gel with acetone. The resulting gel was then dried in an oven for 24 h to completely remove the acetone. The dried aerogel was heated to 900°C in a tube furnace at the speed of 5°C min–1 and kept at 900°C for 3 h under N2 atmosphere.

**Activation of CA**

KOH and CA were added to 100 mL deionized water in different mass ratios, stirred for 12 h at 80°C, and then dried at 100°C overnight. The dried substance was heated to 900°C in a tube furnace at the speed of 2 °C min–1 and kept at 900°C under N2 atmosphere for 1 h. After cooling down, the substance was washed with 0.5 mol L–1 HCl and further washed and filtered with distilled water until the filtrate became neutral, and then dried at 100°C. The activated CA was denoted as CA-K-X, where X means the mass ratio of KOH to CA.

**Amine-Modified Activated CA Adsorbents**

The amine-modified activated CA was prepared by a wet impregnation method. In a typical preparation, the desired amount of amine (PEI or TEPA), PEG or surfactants was dissolved in 30 mL of alcohol under stirring, after which activated CA was added to the solution. The resultant slurry was continuously stirred for 2 hours at 80°C, and then the solvent evaporated at the same temperature under N2 atmosphere. The sample was dried at 80°C under vacuum for experiment use. The as-prepared adsorbents are denoted as follow: CA-K-1-PEI-60 means the mass ratio of KOH to CA is 1 and the loading percentage of PEI in mass (g) of the sample is 60%. CA-K-1-KOH50-PEG-10 means the mass ratio of KOH to CA is 1 and the loading percentage of PEI and PEG in mass (g) of the sample are 50% and 10%, respectively.

**Characterization of the Adsorbents**

The surface morphologies and structures of samples were characterized by SEM (JSM-6700F, JEOL Ltd., Japan). The samples underwent conductive treatment before SEM observation. The thermal chemical and physical properties of samples were characterized by TGA (SDT Q600 V8.3 Build 101, TA Corp., America). The samples were heated at the speed of 10°C min–1 to 800°C in N2 atmosphere at a flow of 100 mL min–1. The qualitative analysis of constituents in samples was characterized by FT-IR (varia370, Thermo Electron Corp., America). KBr was used as the diluter and FT-IR spectra were recorded within a range of 400–4000 cm–1. The BET surface area, pore volume and pore size distribution of the samples were obtained by N2 adsorption/desorption (ASAP2020, Micromeritics Corp.,

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America) at liquid nitrogen temperature (77 K). Before the measurement, the activated CA was heated to 200°C and held at 200°C for more than 480 minutes under vacuum; the amine-modified activated CA was heated to 50°C and held at 50°C for more than 480 minutes under vacuum.

**Dynamic Adsorption Experiment**

The CO₂ adsorption performance was tested by the fixed bed system shown in Fig. 1. The adsorption column is made of glass with 0.85 cm in inner diameter and 25 cm in height, and the gas distribution plate (pore diameter is about 100 µm) is at the bottom of it. The gases pass the adsorption column through the side tube from the bottom to the top. The CO₂ volumetric concentrations of the adsorption column outlet and inlet were measured by the potable IR CO₂ analyzer (GXH-3010, Institute of Beijing Huayun Analytical Instrument Co., Ltd., China).

In a typical adsorption process, CO₂/N₂ gas mixture with 0.3 Mpa overall gas pressure and 5% molar fraction of CO₂ was introduced at a flow rate of 30 mL min⁻¹. The adsorbent was heated to 100°C for 150 min with N₂ at a flow rate of 100 mL min⁻¹ for regeneration.

**RESULTS AND DISCUSSION**

**Characterization of the Adsorbents**

The SEM images of CA-K-1 and CA-K-1-PEI-60 are shown in Figs. 2(a) and 2(b), respectively. It can be seen that CA-K-1 is formed as uniform nanoparticles with 20–30 nm and shows a three dimensional network structure (Fig. 2(a)). The structure of CA-K-1 is preserved after loading PEI (Fig. 2(b)).

The thermochemical and physical properties of the samples were measured by TGA. It can be seen in Fig. 3 that CA-K-1 loses 2.3% of its original mass below 110°C, which can be mainly ascribed to the desorption of moisture and gases physically adsorbed on the surface of CA-K-1. PEI begins to decompose at around 200°C, and is completely decomposed at 400°C. The mass losses for CA-K-1-PEI and CA-K-1-PEI-PEG below 110°C can be mainly put down to desorption of CO₂ and moisture. The mass losses at the temperature range of 200–400°C for CA-K-1-PEI and CA-K-1-PEI-PEG indicate that decomposition of the loaded PEI and PEG takes place. If moisture and gases adsorbed on CA-K-1-PEI and CA-K-1-PEI-PEG are excluded from the total mass, the mass losses are in line with the designed PEI and PEG loading, indicating that there was no PEI and PEG loss during the preparation process and CA-K-1-PEI and CA-K-1-PEI-PEG exhibit excellent thermal stabilities below 200°C. As shown in Fig. 3, the rate of mass loss for CA-K-1-TEPA-60 is significantly higher than that for CA-K-1 and CA-K-1-PEI-60, indicating that TEPA tends to decompose below 200°C and CA-K-1-PEI-60 has better thermal stability than CA-K-1-TEPA-60 as well. The phenomenon is attributed to the lower relative molecular mass and viscosity of TEPA compared to PEI, which makes TEPA easier volatilization.

Fig. 4 shows FT-IR spectra of CA-K-1 and the samples of amine-modified CA-K-1. There is no significant adsorption band of CA-K-1. The broad bands at around 3422 cm⁻¹ of amine-modified CA-K-1 samples in the curves of (b), (c) and (d) can be assigned to the overlap peaks of surface hydroxyl groups and N-H stretching vibration band. Moreover, the bands at 1570 cm⁻¹ can be attributed to the
Fig. 3. TGA curves of PEI and the activated CAs with different amine loadings. a. CA-K-1; b. CA-K-1-PEI-50; c. CA-K-1-PEI-60; d. CA-K-1-PEI-50-PEG-10; e. CA-K-1-PEI-70; f. PEI; g. CA-K-1-TEPA-60.

Fig. 4. FT-IR spectra of the activated CAs with different amine loadings. (a) CA-K-1; (b) CA-K-1-PEI-60; (c) CA-K-1-TEPA-60; (d) CA-K-1-PEI-50-PEG-10.

The structural parameters of activated CAs in different KOH/CA mixture activated ratios and the amine-modified samples are shown in Table 1. Figs. 5(a) and 5(b) show the nitrogen adsorption/desorption isotherms and pore size distributions of the activated CAs without and with amine loadings, respectively. The adsorption capabilities of activated CAs without amine modification increase rapidly at low relative pressure (P/Po < 0.1), which indicates the samples have micropores (Robertson and Mokaya, 2013; Moon et al., 2014). The hysteresis loops appear in the nitrogen adsorption/desorption isotherms at moderate and high relative pressure (P/Po), indicating that the samples have a certain number of mesopores (Fig. 5(a)). It can be measured by the nitrogen adsorption/desorption that CA-K-4 has the largest BET surface area of 1954 m² g⁻¹ (Table 1). Its carbon framework was etched via the redox reactions by various potassium compounds acted as chemical activating reagents, which generated a large number of micropores. The pore sizes of CA-K-1 and CA-K-2 are centered on around 0.54 nm and 50.40 nm, while the pore size of CA-K-4 is centered on around 0.54 nm, 1.18 nm and 68.50 nm (Fig. 5(a)). After loading PEI or TEPA, the BET surface areas and pore volumes of the samples decreased significantly, confirming that PEI or TEPA was successfully introduced into the channels of the activated CAs (Table 1). After loading 60 wt.% PEI or 60 wt.% TEPA, the micropores and mesopores of CA-K-1 were filled with amine and there were only some macropores left (Fig. 5(b)). 70 wt.% PEI loading led to the pores blockage of CA-K-1. The overloading PEI restricted the access of liquid nitrogen into the pores at 77 K. Therefore, the BET surface area and pore volume of CA-K-1-PEI-70 almost cannot be measured.

CO₂ Adsorption Performance
Effect of KOH/CA Activated Ratio
Fig. 6(a) shows the CO₂ adsorption performance of PEI-loaded activated CAs with different KOH/CA activated ratios. CA-K-2-PEI-60 shows the highest CO₂ adsorption capacity, whereas CA-K-4-PEI-60 shows the lowest CO₂ adsorption capacity. This may be related to the combined effects of pore size and BET surface area. In addition, pore size is the main factor that determines the CO₂ capacity. Although CA-K-4 has the largest BET surface area, the majority of the pores are micropores and macropores (Fig. 5). The micropores modified by PEI chain are prone to pore blockage and high diffusion barrier. Moreover, the low
Fig. 5. Nitrogen adsorption-desorption isotherms and pore size distributions of the activated CAs without (a) and with (b) amine loadings.

Fig. 6. CO$_2$ adsorption breakthrough curves under different synthesis conditions: (a) activated CAs in different KOH/CA ratios with 60 wt.% PEI loading; (b) CA-K-1-PEI-60 at different adsorption temperatures; (c) CA-K-1 with different PEI loadings, the PEG addition and TEPA loadings at 75°C.

BET surface area of macropores leads to the low effective PEI loadings, which has adverse influence on the CO$_2$ adsorption. Therefore, CA-K-4-PEI-60 shows the lowest CO$_2$ adsorption capacity. CA-K-1 and CA-K-2 have similar pore size distributions (Fig. 5). However, the BET surface area of CA-K-1 is higher than that of CA-K-2, which can provide more sites for amine loadings (CO$_2$ active sites). Therefore, the CO$_2$ adsorption capacity of CA-K-1-PEI-60 is higher than that of CA-K-2-PEI-60 in the same PEI loading. As a result, the breakthrough curve of CA-K-1 is in the middle.

Effect of Adsorption Temperature

Fig. 6(b) shows the adsorption breakthrough curves for CO$_2$ adsorption of CA-K-1-PEI-60 at 50, 75 and 85°C. From the perspective of the breakthrough time, with increasing temperature, the adsorption capacity of CA-K-1-PEI-60 first increases and reaches the maximum adsorption...
The CO₂ adsorption capability is determined by the adsorption kinetics and the thermodynamics (Chen et al., 2010; Wang et al., 2012). The CO₂ adsorption process mainly includes two processes. Firstly, CO₂ adsorption may occur on the PEI surface of the adsorbents. In the following process, a CO₂ diffusion process from the PEI surface to the PEI bulk restricted inside the channels of activated CAs occurs. The CO₂ adsorption on PEI surface is controlled by thermodynamics, resulting in the decreased CO₂ adsorption ability with the increasing temperature. On the other hand, the CO₂ diffusion process is controlled by kinetics. There is a positive correlation between the molecular kinetic energy of CO₂ and the temperature. The CO₂ molecules can more readily diffuse to PEI bulk in the channels of the PEI-loaded activated CAs and be adsorbed on the CO₂ active sites in PEI bulk as the temperature increases. At 50°C, though it is thermodynamically preferred for CO₂ adsorption on PEI surface, the relatively high diffusion resistance is not in favor of the CO₂ diffusion, leading to relatively low adsorption capability. As the temperature increases to 75°C, the kinetic barrier of CO₂ molecules diffusing from the PEI surface to or within the PEI bulk can be overcome due to the increasing molecular kinetic energy. Therefore, CO₂ molecules are easier to react with more CO₂ adsorption sites, leading to higher adsorption capacity. When the temperature is not above 75°C, the adsorption capacity of amine-loaded activated CA rises with the increasing temperature, which indicates that the CO₂ diffusion process is the main control factor in this adsorption process. As the temperature rises to 85°C, although CO₂ diffusion is enhanced so that more CO₂ adsorption sites become more approachable, a portion of CO₂ molecules adsorbed on the active sites of the adsorbents are more easier to desorb due to the weak bonding force between CO₂ and the PEI-loaded activated CAs. As a result, the adsorption equilibrium is rapidly reaching, leading to a drop in the adsorption capacity.

Effect of PEI Loadings

The CO₂ adsorption breakthrough curves of CA-K-1 with different PEI loadings at 75°C, are shown in Fig. 6(c). At 50%, 55% and 60% mass fraction of PEI loadings in CA-K-1-PEI, the heights of mass transfer zones are relatively short, indicating low mass transfer resistance and high utilization efficiency of adsorbent beds. On the contrary, when PEI loading increases to 70 wt.%, the height of mass transfer zone becomes longer, indicating that CO₂ diffuses to the channels of CA-K-1-PEI-70 with larger resistance.

CA-K-1 shows a low CO₂ adsorption capacity of 0.20 mmol g⁻¹ adsorbent before PEI is loaded, which is attributed to the weak interaction between CA-K-1 and CO₂. The physisorption by capillary condensation predominates in this process. With increasing loading of PEI, the CO₂ adsorption capacities of PEI-loaded activated CAs first increase then decrease. The highest CO₂ adsorption capacity of PEI-loaded CA-K-1 at 75°C is 2.06 mmol g⁻¹ sorbent when the mass fraction of PEI loading is 55%. Compared to the CA-K-1, the CO₂ adsorption capacities of PEI-loaded CA-K-1 are enhanced remarkably since the chemisorption between CO₂ and PEI predominates in this process. The CO₂ adsorption capacities of PEI-loaded activated CAs are mainly determined by the chemisorption of CO₂ molecules and the amine groups in PEI. The results shown above are because there is a synergistic effect between activated CAs and PEI on the CO₂ adsorption for PEI-loaded activated CAs. The synergistic effect may be attributed to the high surface areas and relatively large pore structures of activated CAs that can lead to a relatively uniform dispersion of PEI into the channels of activated CAs. There are numerous amine groups in PEI that can react with CO₂ through chemisorption at an appropriate temperature. When PEI is loaded on the activated CAs with high surface areas and relatively large pore structures, more amine groups (CO₂ adsorption sites) are introduced into the activated CAs. The CO₂ adsorption sites are exposed to the adsorbates and react with CO₂, which results in increased CO₂ adsorption capacities of the PEI-loaded activated CAs noticeably. On the other hand, the apparent pore sizes of the activated CAs reduce as the PEI loadings go up, which may cause channels blockage and high CO₂ diffusion barrier. The two effects may integrate together and determine the CO₂ adsorption capacities of PEI-loaded activated CAs. The highest adsorption capacity is gained when the channels of activated CA are fully filled with PEI. When PEI loadings are further raised, PEI will be coated on the external surface of activated CAs, resulting in channels blockage. Therefore, the adsorption capacities decrease (Xu et al., 2002; Xu et al., 2003; Chen et al., 2010).

The CO₂ adsorption capacities and the amine utilization ratios of the activated CAs with different amine loadings at 75°C are listed in Table S1. At 55% mass fraction of PEI loading, the PEI-loaded CA-K-1 at 75°C has highest CO₂ adsorption capacity with 2.06 mmol g⁻¹ sorbent, 3.58 mmol g⁻¹ PEI and highest amine utilization efficiency with 30.07% as well. Considering the factors of amine utilization efficiency, saturated adsorption capacity and mass transfer resistance, the optimum PEI loading of CA-K-1 is 55 wt.%. Table 2 compares the CO₂ adsorption capacities of CA-K-1-PEI-55, CA-K-1-PEI-60 and CA-K-1-TEPA-60 with the values reported in the literatures for mesoporous molecular sieves, zeolites, MOFs, activated carbons, ordered mesoporous carbons and graphite oxides. It is clear that CA-K-1-PEI-55, CA-K-1-PEI-60 and CA-K-1-TEPA-60 show relatively high CO₂ adsorption capacities.

Effect of Amine Type

The CO₂ adsorption breakthrough curves of CA-K-1-PEI-60 and CA-K-1-TEPA-60 at 75°C are shown in Fig. 6(c). The CO₂ adsorption capacity of CA-K-1-TEPA-60 with 2.84 mmol g⁻¹ sorbent is higher than that of CA-K-1-PEI-60 with 2.03 mmol g⁻¹ sorbent, which is mainly because the chemisorption between amine groups and CO₂ plays an essential role in the CO₂ capture of amine-loaded CA-K-1. The nitrogen content of TEPA with 36.98 wt.% is higher than that of PEI with 32.56 wt.%, resulting in the higher CO₂ adsorption capacity of TEPA-loaded CA-K-1 at the same amine loading. In addition, the height of mass transfer
zone in CA-K-1-TEPA-60 is shorter than that in CA-K-1-PEI-60, indicating the lower mass transfer resistance. This may be because the higher molecular weight of PEI makes it have higher viscosity than TEPA, leading to the higher CO2 diffusion resistance of CA-K-1-PEI-60. However, as can be seen from the TGA curves, the thermal stability of CA-K-1-TEPA-60 is poorer than that of CA-K-1-PEI-60, which is because the low molecular weight of TEPA leads to easy decomposition under high temperature. Therefore, CA-K-1-TEPA-60 can hardly regenerate by heat treatment.

**Effect of PEG Addition**

The adsorption breakthrough curves of CA-K-1-PEI-50 and CA-K-1-PEI-50-PEG-10 at 75°C are shown in Fig. 6(c). It can be seen that the CO2 adsorption capacity on PEI-modified CA-K-1 increases in the presence of PEG addition. PEI is a polymeric substance with plenty of amine groups (CO2 adsorption sites). Theoretically, the main reaction is that the amine groups react with CO2 to form carbamate, as shown in Eqs. (1)–(3). One mole CO2 reacts with two moles amine groups.

\[
\text{CO}_2 + 2\text{RNH}_2 \rightleftharpoons \text{NH}_4^+ + \text{R}_2\text{NCOO}^- \tag{1}
\]

\[
\text{CO}_2 + 2\text{R}_2\text{NH} \rightleftharpoons \text{R}_2\text{NH}^+ + \text{R}_2\text{NCOO}^- \tag{2}
\]

\[
\text{CO}_2 + 2\text{R}_3\text{N} \rightleftharpoons \text{R}_4\text{N}^+ + \text{R}_2\text{NCOO}^- \tag{3}
\]

In the presence of PEG, the increased CO2 adsorption capacity may be attributed to two factors: firstly, chemical reaction between CO2 and PEI may be changed in the presence of PEG. Many coexisting ether groups in PEG can act as hydrogen ion receptors owing to their strong H+ affinity. Therefore, one mole CO2 reacts with one mole amine, which increases the adsorption capacity, as shown in Eq. (4) (Yan et al., 2012); secondly, a large number of hydroxyl groups in PEG may play a synergistic contribution to the CO2 adsorption. The hydroxyl groups existing in PEG may facilitate the dispersion of PEI, which promotes the accessibility of amine groups towards CO2 molecules (Yue et al., 2008).

**Effect of Surfactants Addition**

The CO2 adsorption breakthrough curves of PEI-modified CA-K-1 with and without surfactants at 75°C are shown in Fig. S1. When the mass fraction of PEI is 55%, the 5 wt.% Span 80 additives and 5 wt.% dodecyl trimethyl ammonium bromide (DTAB) additives almost have no influence on the CO2 adsorption capacity. At 60% mass fraction of PEI, the CO2 adsorption capacities of PEI-modified CA-K-1 with 5 wt.% surfactants (Span 80 and DTAB) additives decrease, which may be ascribed to the amine and surfactants’ overloading.

**Cyclic Regeneration**

Fig. 7 shows the cyclic regeneration performance of CA-K-1-PEI-60 in 5 consecutive adsorption-desorption runs.
Fig. 7. Cyclic adsorption of CO₂ by CA-K-1-PEI-60.

The sample exhibits comparatively a high drop in adsorption capacity at the beginning of the adsorption-desorption runs. The decrease of adsorption capacity gradually slows down later and the adsorption capacity tends to be stable. This may be attributed to the incomplete desorption of CO₂ in CA-K-1-PEI-60 at 100°C. The chemical interactions between portions of CO₂ adsorbed in the pores of CA-K-1-PEI-60 and PEI are strong so that portions of CO₂ cannot desorb, leading to the decline of CO₂ adsorption capacity for CA-K-1-PEI-60.

Deactivation Models

CO₂ adsorption on the adsorbent is a process of non-catalytic gas-solid reaction. The deactivation model has been put forward to analyze the breakthrough curves of these gas-solid reactions. Considering the pore structure, the diffusion resistance caused by the formation of a dense product layer over the solid reactant, active surface area and the other factors, the deactivation model works well for the adsorption breakthrough curves of gas-solid reactions. Suyadal et al. (2000) studied adsorption properties of the trichloroethylene vapor on granular activated carbon in a packed-bed adsorber and used the deactivation model to fit the trichloroethylene breakthrough curves well. In an investigation of Yasyerli et al. (2001), the deactivation model proposed for the non-catalytic gas-solid reactions provided great predictions for the H₂S breakthrough curves of the copper oxide and Cu-V and Cu-Mo mixed oxides.

The Suyadal’s deactivation model is expressed as (Suyadal et al., 2000):

\[
\frac{C}{C_0} = \exp\left[-k_s \tau \exp(-k_d t)\right] \quad (5)
\]

where \(C_0\) and \(C\) are the inlet and outlet concentrations of gases (mol cm⁻³), \(k_s, k_d, t\) and \(\tau\) are the adsorption rate constant (cm min⁻¹), first-order deactivation rate constant (min⁻¹), time (min) and surface-time (min cm⁻³), respectively. \(\tau\) is equal to the ratio of the initial surface area of the adsorbent (\(S_o\) cm²) and the volumetric flow rate of the gases introduced to the adsorber (\(Q_o\) cm³ min⁻¹).

The Yasyerli’s deactivation model is expressed as (Yasyerli et al., 2001):

\[
\frac{C}{C_0} = \exp\left\{\frac{[1 - \exp(k_o m(1 - \exp(-k_d t))/Q_o)] \exp(-k_d t)/(1 - \exp(k_d t))}{1 - \exp(-k_d t)}\right\} \quad (6)
\]

where \(k_o\) is the initial adsorption rate constant (cm³ min⁻¹ g⁻¹).

The experimental data and nonlinear curves fitting of Suyadal’s deactivation model and Yasyerli’s deactivation model are shown in Fig. 8. The parameters of Suyadal’s deactivation model and Yasyerli’s deactivation model for CO₂ adsorption on CA-K-1-PEI-60 and CA-K-1-TEPA-60 are listed in Table 3. The CO₂ adsorption experiments were conducted in the conditions of 30 cm³ min⁻¹ volumetric flow rate, 5% molar concentration of CO₂ and 75°C. As it can be seen, both Suyadal’s deactivation model and Yasyerli’s deactivation model fit the adsorption data of CA-K-1-TEPA-60 better than that of CA-K-1-PEI-60, which the coefficients of determination (\(r^2\)) reach up to 0.995. The adsorption rate constant of CA-K-1-TEPA-60 is higher than that of CA-K-1-PEI-60, which is consistent

Table 3. Parameters of Suyadal’s and Yasyerli’s deactivation models for CO₂ adsorption on CA-K-1-PEI-60 and CA-K-1-TEPA-60.

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>CA-K-1-PEI-60</th>
<th>CA-K-1-TEPA-60</th>
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<td>Suyadal</td>
<td>(k_s)</td>
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<td>1.32 × 10⁴</td>
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<td></td>
<td>(k_d) (min⁻¹)</td>
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</tr>
<tr>
<td></td>
<td>(K_d) (min⁻¹)</td>
<td>0.435</td>
<td>0.392</td>
</tr>
<tr>
<td></td>
<td>(r^2)</td>
<td>0.974</td>
<td>0.995</td>
</tr>
</tbody>
</table>
with the experimental results that the adsorption capacity and activity of CA-K-1-TEPA-60 are higher than that of CA-K-1-PEI-60. The lower deactivation rate constant of CA-K-1-PEI-60 means the declined CO₂ desorption capacity of CA-K-1-PEI-60, which corresponds to the experimental results of the cyclic regeneration.

**Adsorption Kinetic Models**

The kinetics of adsorption give a description of the adsorption rate and determine the equilibrium time (Tan et al., 2009). The kinetic parameters are used to predict the adsorption rate, which gives valuable information in the aspects of designing and modeling the processes. The kinetics of CO₂ on CA-K-1-PEI-60 and CA-K-1-TEPA-60 were investigated using four kinetic models viz: pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Bangham models. The expressions are shown in Eqs. (7)–(10):

Pseudo-first-order (Yousef et al., 2011): \[ q_t = q_e \left[1 - \exp(-k_1 t)\right] \]  
(7)

Pseudo-second-order (Yousef et al., 2011): \[ q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \]  
(8)

Intra-particle diffusion (Yousef et al., 2011): \[ q_t = k_i d t^{0.5} + C \]  
(9)

Bangham (Liu and Wang, 2017): \[ q_t = q_e \left[1 - \exp(-k_b t^a)\right] \]  
(10)

where, \( q_t \) and \( q_e \) (mmol g⁻¹) are the amount of adsorbed CO₂ at time \( t \) (min) and at equilibrium, respectively; \( k_1 \) (min⁻¹) and \( k_2 \) (g mmol⁻¹ min⁻¹) are the adsorption rate constants of pseudo-first-order model and pseudo-second-order model, respectively; \( k_i d \) is the intra-particle diffusion constant (mmol g⁻¹ min⁻⁰.⁵); \( C \) is a constant (mmol g⁻¹) that is associated to the boundary layer thickness; \( k_b \) is Bangham constant (min⁻ᵃ), and \( a \) is a constant.

The experimental data and fitting curves of four kinetic models for CO₂ adsorption on CA-K-1-PEI-60 and CA-K-1-TEPA-60 at 75°C are shown in Figs. 9(a) and 9(b), respectively. The parameters of four kinetic models are listed in Table 4. As it can be seen, the experimental data of CA-K-1-PEI-60 and CA-K-1-TEPA-60 both give a good fit to the curves of Bangham model as shown in Fig. 9. What is more, the calculated \( q_e \) values are closer to the experimental data than the calculated values of pseudo-first-order model and pseudo-second-order model. The correlation coefficients for Bangham model listed in Table 4 are above 0.99, indicating that the CO₂ adsorption of CA-K-1-PEI-60 and CA-K-1-TEPA-60 can be more favorably approximated by the Bangham model. The results shown above demonstrate that the adsorption process of amine-loaded activated CAs is pore-diffusion-controlled (Bilgili, 2006).

**CONCLUSIONS**

Activated CA-based amine-loaded adsorbent has been prepared for CO₂ capture at 5% CO₂ concentration. The results show that the adsorbents effectively remove 5% molar fraction of CO₂ from gas mixtures. When the temperature is not above 75°C, the adsorption capacity of amine-loaded activated CA rises with the increasing temperature, which indicates that the CO₂ diffusion process is the main control factor in this adsorption process. The optimum adsorption temperature and amine loadings of PEI-loaded activated CAs are 75°C and 55 wt.% respectively at the activation mass ratio KOH/CA of 1. Under these optimum conditions, the highest adsorption capacity and amine utilization efficiency of the PEI-loaded activated CAs are obtained. The CO₂ adsorption capacity of the PEI-loading activated CA reaches a value as high as 2.06 mmol g⁻¹ adsorbent under the optimum conditions. Addition of PEG can facilitate the CO₂ adsorption. Both Suyadal’s and Yasyerli’s deactivation models fit the adsorption data of CA-K-1-TEPA-60 better than that of CA-K-1-PEI-60. The adsorption rate constants and deactivation rate constants are consistent with the experimental results of the adsorption capacities and activities. The adsorption kinetics nonlinear fitting results show that the adsorption process follows Bangham model, which further demonstrates the adsorption process of amine-loaded CAs is controlled by pore diffusion. Further work is required to optimize the carbonization and activation conditions for CAs that include the heating rate and heating time to obtain the optimized porous structure.

![Fig. 9. Adsorption kinetics of CO₂ on amine-loaded activated CAs at 75°C (a) CA-K-1-PEI-60; (b) CA-K-1-TEPA-60.](image-url)
for CO2 capture and to study the effect of moisture as well. Moreover, the regeneration performance of the PEI-loaded activated CA needs further optimization to enhance its potential for practical use in CO2 capture.

**ACKNOWLEDGMENTS**

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**SUPPLEMENTARY MATERIAL**

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

**REFERENCES**


