Breakthrough CO₂ adsorption in bio-based activated carbons

Sepideh Shahkarami, Ramin Azargohar, Ajay K. Dalai⁎, Jafar Soltan

Department of Chemical and Biological Engineering, University of Saskatchewan, 57 Campus Drive, Saskatoon, SK S7N 5A9, Canada.
E-mail: ses439@mail.usask.ca

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Abstract

In this work, the effects of different methods of activation on CO₂ adsorption performance of activated carbon were studied. Activated carbons were prepared from biochar, obtained from fast pyrolysis of white wood, using three different activation methods of steam activation, CO₂ activation and Potassium hydroxide (KOH) activation. CO₂ adsorption behavior of the produced activated carbons was studied in a fixed-bed reactor set-up at atmospheric pressure, temperature range of 25–65°C and inlet CO₂ concentration range of 10–30 mol% in He to determine the effects of the surface area, porosity and surface chemistry on adsorption capacity of the samples. Characterization of the micropore and mesopore texture was carried out using N₂ and CO₂ adsorption at 77 and 273 K, respectively. Central composite design was used to evaluate the combined effects of temperature and concentration of CO₂ on the adsorption behavior of the adsorbents. The KOH activated carbon with a total micropore volume of 0.62 cm³/g and surface area of 1400 m²/g had the highest CO₂ adsorption capacity of 1.8 mol/kg due to its microporous structure and high surface area under the optimized experimental conditions of 30 mol% CO₂ and 25°C. The performance of the adsorbents in multi-cyclic adsorption process was also assessed and the adsorption capacity of KOH and CO₂ activated carbons remained remarkably stable after 50 cycles with low temperature (160°C) regeneration.

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Introduction

Climate change has become one of the most important environmental and energy policy issues in the 21st century (Nurrokhmah et al., 2013) and the rise in CO₂ emissions is considered as the main cause of the climate change. Carbon capture technologies are potential options to address this problem by providing a solution for the use of fossil fuels with reduced emissions of CO₂. Absorption with amine-based absorbents is currently the most common technology for CO₂ removal (Nurrokhmah et al., 2013). However, due to inherent problems involved in this process especially high energy penalty, corrosion and related waste disposal problems, alternative technologies are required to control CO₂ emissions from the combustion of fossil fuels (Hsu et al., 2010). Based on the Intergovernmental Panel on Climate Change (IPCC) special report in 2005, one of these alternatives is CO₂ adsorption on a solid surface (Anon, 2005; Lu et al., 2008). Porous carbon materials especially activated carbons are known to have a large adsorption capacity for CO₂ and they can be produced from low cost and abundant precursors such as bio-char (García et al., 2011). It has been shown that surface area and pore size distribution affect CO₂ capture performance of activated carbon (Heidari et al., 2014). Moreover, starting precursors have a significant effect on CO₂ adsorption behavior of activated carbons (Deng et al., 2014; Bansal and Goya, 2005).

⁎ Corresponding author. E-mail: ajay.dalai@usask.ca (Ajay K. Dalai).
However, a comparison of different methods of activation of biochar on its CO₂ adsorption performance has not been reported before. This work focused on the effect of different activation methods on porosity, surface area and adsorption capacity of the activated carbons to explain CO₂ adsorption behavior in activated carbons. Steam, CO₂ and KOH were used as activation agents for activation of biochar obtained from fast pyrolysis of whitewood.

The main challenge of post combustion carbon capture processes is operation at low concentration of CO₂ (Lu et al., 2008). In this work, the CO₂ adsorption performance of the adsorbents was investigated at atmospheric pressure, temperatures range of 25–65°C and CO₂ concentrations (C_CO₂) range of 10–30 mol% and the influence of activation method, porous structure, surface area and surface chemistry on performance of the adsorbents were studied. Adsorption capacity was analyzed using breakthrough curve in an isothermal fixed-bed reactor and the bed adsorption capacity was studied as a function of both breakthrough time and the S-shape of the breakthrough curve under the designed operating conditions. Central composite design (CCD) method was applied for the experimental design to find optimized process conditions and second-order models were developed to predict the adsorption capacity of adsorbents as functions of temperature and concentration of CO₂ in inlet stream. These models showed the significance of variables and the interactions among them on the CO₂ adsorption process.

1. Materials and methods

1.1. Biochar

The biochar used in this study was a by-product of fast pyrolysis of whitewood provided by Dynamotive Energy Systems Corporation (BC, Canada). According to the manufacturer, the operating conditions for this process were 500°C, atmospheric pressure and residence time less than 1 sec. The biochar yield of this process was 10–15 wt.%. The as-received biochar was sieved, and particle size range of 178–710 μm was collected for activation processes.

1.2. Physically activated carbon

Physically activated carbon was prepared using carbon dioxide and steam as activating agents. Before activation, sieved biochar was dried in air for 12 hr at 110°C. The process conditions of the steam and CO₂ activated carbon were chosen to obtain similar BET surface area and total pore volume in both products.

1.2.1. Steam activation

The detailed information for activation set-up was described elsewhere (Azargohar and Dalai, 2005). In each batch, 20 g of biochar was loaded into the reactor and heated to 700°C with the heating rate of 3°C/min while flowing nitrogen carrier gas at the flow rate of 140 standard mL/min. Steam was injected into the reactor with the steam-to-carbon mass ratio of 1.06 for 1.4 hr. After the injection, the reactor was cooled down to room temperature under nitrogen flow. The yield of product was 55 wt.% in steam activation process.

1.2.2. CO₂ activation

In each run, 15 g of biochar was placed in the fixed-bed reactor under an argon flow rate of 100 standard mL/min. The temperature of the reactor was increased to 890°C with the heating rate of 3°C/min. Then, the gas was switched to CO₂ with the flow rate of 130 standard mL/min. After 100 min, the reactor was cooled down to room temperature under argon gas flow. The yield of product was 52 wt.% in CO₂ activation process.

1.3. Chemically activated carbon

The physical activation set-up was also used for chemical activation of biochar. KOH was used as the activation agent. Biochar was impregnated with KOH in 100 mL of distilled water with carbon-to-KOH mass ratio of 0.81 on dry basis. After 4 hr at the room temperature, the prepared mixture was dried in oven at 110°C for 12 hr. 20 g of the dried sample was placed in the reactor under a nitrogen flow of 240 standard mL/min and was heated to 300°C with the heating rate of 3°C/min, and was held for 1 hr at 300°C (Otowa et al., 1997). Then, the temperature of the reactor was increased to 775°C with the heating rate of 3°C/min and held at this temperature for 2 hr before cooling down to room temperature. In the next step, the sample was washed with hot water, followed by 0.1 mol/L HCl, and finally by distilled water to remove the soluble salts and the potassium compounds (Lozano-Castelló et al., 2001; Lillo-Ródenas et al., 2001). Then the sample was dried in oven overnight at 110°C in air. The product yield of chemical activation was 33 wt.%.

1.4. Characterization

1.4.1. Elemental analysis and ash content

The mass fractions of carbon, hydrogen, nitrogen and sulfur in the samples were determined from elemental analysis performed on a Vario EL III elemental analyzer (Vario EL III, Elementar, Hanau, Germany). Oxygen content of samples was determined by difference. The ash contents of biochar and activated carbons were measured according to ASTM D 2896-11 method.

1.4.2. BET surface area, pore volume and pore size distribution

The nitrogen adsorption isotherms of activated carbon samples at 77 K and BET (Brunauer–Emmett–Teller) surface area and total pore volume of the samples were determined using ASAP 2020 system (ASAP 2020, Micromeritics Instruments Inc., Norcross, GA, USA). The samples were degassed at 300°C to a vacuum of 550 μm Hg prior to the analysis. The micropore size distribution was determined using the non-local Density Function Theory (NLDFT) (Landers et al., 2013; De et al., 2013) applying N₂ and CO₂ adsorption on slit-pore carbon (Carter et al., 2011) at 77 K and 273 K, respectively. Nitrogen at 77 K has a saturation pressure of 760 Torr and N₂ adsorption starts at relative pressure (P/P₀) between 10⁻² and 10⁻⁴ whereas CO₂ has a saturation pressure of 26,400 Torr and CO₂ adsorption starts at relative pressure of about 10⁻⁴. Since diffusion rates of N₂ and consequently attaining equilibrium in ultramicropores with diameter between 0.5 and 1 nm is very slow and requires very low relative pressure and high uptake of N₂, CO₂ adsorption at 273 K was used to overcome diffusion limitations (Wilcox,
The CO2 analysis results were combined with the N2 adsorption analysis for the full range characterization. IUPAC (International Union of Pure and Applied Chemistry) classification was considered for pore size distribution (Jiménez et al., 2012). Ultramicropores have pore width less than 0.7 nm, super-micropores show pore width between 0.7 and 2 nm, and mesopores have pore width between 2 and 50 nm.

1.4.3. X-ray photoelectron spectroscopy (XPS)
Surface chemistry of the activated carbon samples was studied and oxygenated functional groups on the surface were quantified using X-ray photoelectron spectroscopy. This was equipped with an omicron monochromatized Al Kα source (hν = 1486.7 eV) and SPHERA EA125 hemispherical electron energy analyzer in the Surface Science Facility at the Resonant Elastic and Inelastic X-ray Scattering (REIXS) beamline 10ID-2 of the Canadian Light Source (The Surface Science Facility, Canadian Light Source, Saskatoon, SK, Canada). The survey scan spectra were collected in the 0–1200 eV binding energy range in 0.5 eV steps with pass energy of 50 eV. High resolution scanning of the C1s region was also conducted in 0.1 eV steps with pass energy of 25 eV. An accelerating voltage of 15 kV and an emission current of 20 mA were used for the analysis. The operating pressure was less than 2 × 10⁻¹⁰ mbar. Peak deconvolutions of high-resolution C1s spectra were conducted using the Casa XPS software (version 2.3.16 PR 1.6).

1.5. Breakthrough CO2 adsorption measurements
CO2 adsorption was performed in an isothermal fixed-bed tubular reactor. A K-type thermocouple was placed inside the reactor and the reactor temperature was controlled using a heating tape and a temperature controller (2416 Temperature Controller/Programmer, Eurotherm, Ashburn, Virginia, USA). The reactor was loaded with 5 g of activated carbon and pre-heated at 160°C for 2 hr under helium (He) flow before the adsorption experiments. After cooling down the reactor to the desired operating temperature, the feed gas was switched from He to He/CO2 gas mixture. The total feed flow rate was maintained constant at 50 standard mL/min in all experiments. The feed flow rates were controlled with mass flow controllers (5850E A/B Mass Flow Controller, Brooks Instrument, Hatfield, PA, USA). For continuous monitoring, the outlet gas flow rate was recorded and the dynamic CO2 adsorption capacity was measured using a micro-gas chromatograph analyzer (CP-4900 Micro-GC, Varian Inc, Walnut Creek, CA, USA) equipped with a thermal conductivity detector (TCD). The adsorption process was continued up to the saturation point where the outlet concentration of CO2 reached the inlet concentration of CO2.

The schematic diagram of the set-up schematic is shown in Fig. 1 and the details of the set-up and calculation methods are described in supporting materials (Table S1, Figs. S1 and S2).

The CO2 adsorption process was studied using central composite design to optimize the process conditions and determine the interaction effect of parameters. For the experimental design, CCO2 and temperature (T) were selected as experimental variables and they were studied at two levels of 10–30 mol% and 25–65°C, respectively. For a 2 level study, the total number of experiments is given as 2^n - 2 + n_c where n is the number of independent process variables and n_c is the number of center points or replicates used to estimate the residual error (Azargohar and Dalai, 2005; García et al., 2013). Each center point adds one degree of freedom (df) from which the experimental error is estimated. Therefore, 14 experiments including 8 factorial and axial points as well as 6 replications at the center point were conducted for the adsorption process using each type of the activated carbons (ACs) (Table 3). The model helps to assess the responses in the variables space and to find the best region to reach the optimum response. The second-order model is used to estimate the response (Eq. (1)):

\[ y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_11 x_1^2 + \beta_22 x_2^2 + \beta_12 x_1 x_2 + \varepsilon \]  

Fig. 1 – Schematic of adsorption set-up. MFC: mass flow controller.
where $y$ is the predicted response, $\beta_0$ is the constant, $\beta_1$ and $\beta_2$ are the linear coefficients, $\beta_{11}$ and $\beta_{22}$ are the quadratic coefficients, $\beta_{12}$ is the interaction coefficients, $x_1$ and $x_2$ are the coded values of the parameters and $\epsilon$ is the residual error (García et al., 2013). The model predicts the behavior of the response as a function of the variables and their interaction. The fitness of the model is evaluated using Analysis of Variance (ANOVA) and squared-R (García et al., 2013). The response factors in this study are the CO$_2$ adsorption capacity and the breakthrough time ($t_b$). Adsorption capacities are expressed in milligrams of CO$_2$ adsorbed per gram of adsorbent and $t_b$ is defined as the time that the ratio of outlet CO$_2$ to the inlet CO$_2$ reaches 0.05. Multi-cycle adsorption/desorption performance of the adsorbents was studied to examine their durability using a temperature swing adsorption (TSA) cyclic process. For desorption, when the adsorbent was saturated, gas flow was switched to He flow and temperature was raised to 160°C and maintained at this temperature for 2 hr. The adsorbents were subjected to 50 consecutive adsorption–desorption cycles and their performance was compared.

2. Results and discussion

2.1. Characterization of adsorbents

The elemental analysis, ash content, BET surface area and total pore volume of the adsorbents are summarized in Table 1. Elemental analysis results show that KOH activation followed by acid treatment results in an increase in the hydrogen, nitrogen and oxygen content and decrease in the carbon content of the activated carbon product. Activation conditions are selected to keep the surface area of CO$_2$ activated carbon and steam activated carbon in a close range in order to study the effects of activation agent and pore volume on the adsorption behavior of the samples. Fig. 2 shows the N$_2$ adsorption isotherms of the activated carbon. The narrow hysteresis loops in isotherms of steam and CO$_2$ activated carbons indicated that both physically activated carbons were mesoporous. The micropore and mesopore size distributions of adsorbents are presented in Figs. 3 and 4. The ultra-micro pores, super-micropores and mesopores ratio of samples are also shown in Fig. 5. BET surface area of KOH activated carbon was larger than that of the physically activated carbon due to its large micropore volume. The contribution of mesopores in chemically activated carbon porous structure was negligible. The micropore volume of steam and CO$_2$ activated carbon were quite close while the total pore volume of the steam activated carbon was more than that of CO$_2$ activated carbon. KOH activated carbon had the highest ultra-micropores and super-micropores volume.

The XPS spectra and deconvolution of C1s spectra are shown in Fig. 6, and the relative content of each functional group (Zhou et al., 2007; Plaza et al., 2009; Shen et al., 2008; Shafeeyan et al., 2010) are presented in Table 2. The surface acidity was a result of oxygen functional groups such as phenolic, carboxyl, lactone, and aldehyde groups. Four peaks were detected in deconvolution of the C1s spectra of activated carbons: peak 1 (284.5 eV), –C==C–, graphitized carbon; peak 2 (286.1 eV), –C==O, –C==C==, C–O–R; peak 3 (288.7 eV), –C==O; and peak 4 (289.3 eV), –COOH. Nitrogen peak was not detected on the spectra of the samples. A comparison of the C1s spectra of the different samples showed the contributions of different oxygen groups in physically and chemically activated carbons. Table 2 shows that the identified surface functional groups on steam and CO$_2$ activated carbons are similar while chemically activated carbon has a lower content of graphitic carbon and different oxygen groups on the surface. These results suggest that KOH activation process would introduce more oxygen atoms to the surface of the activated carbon. Peak 3 which represents ketone and aldehyde groups on the surface (Bansal and Goya, 2005) was only identified in KOH activated carbon spectrum while contribution of carboxylic groups at 289.3 eV was smaller in this sample.

2.2. Adsorption of CO$_2$

The results of breakthrough adsorption measurements of KOH, CO$_2$ and steam activated carbons are summarized in Table 3. Gas adsorption begins from the bed inlet and most of the mass transfer occurs in this region. After saturation of the inlet region, the mass-transfer zone (MTZ) moves down through the bed gradually. At the $t_b$, the adsorbent between the inlet and the MTZ is fully saturated with CO$_2$. As the breakthrough continues the C$_{CO2}$ in the outlet increases gradually to the inlet concentration. At this point, no more adsorption can take place in the bed.

As can be seen in Table 3, in general, chemically activated carbon presents higher adsorption capacity than the physically activated carbon at high CO$_2$ concentration. This can be related to the higher surface area and higher micropore volume specially ultra-micropore volume of the chemically activated carbon (Jiménez et al., 2012). Although according to the literature (Shafeeyan et al., 2010), the interaction of CO$_2$–oxygen functional groups have negative impact on the CO$_2$ adsorption on the activated carbon, KOH activated carbon with higher content of oxygen groups results in a better performance which probably accounts for the larger impact of

<p>| Table 1 – Physical and chemical properties of CO$_2$, steam and KOH activated carbons (ACs). |
|-----------------------------------------------|----------|--------|--------|--------|--------|--------|</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation yield (%)</th>
<th>Elemental analysis (wt.%)</th>
<th>Ash content (%)</th>
<th>BET surface area (m$^2$/g)</th>
<th>total pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam AC</td>
<td>59</td>
<td>92.57</td>
<td>1.81</td>
<td>0.23</td>
<td>0.00</td>
</tr>
<tr>
<td>CO$_2$ AC</td>
<td>55</td>
<td>92.05</td>
<td>2.00</td>
<td>0.58</td>
<td>0.00</td>
</tr>
<tr>
<td>KOH AC</td>
<td>35</td>
<td>85.98</td>
<td>4.29</td>
<td>1.21</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Elemental analysis was on a dry ash-free basis, and oxygen content was determined by difference.
porosity of CO₂ adsorption behavior. CO₂ activated carbon and steam activated carbon present similar adsorption behavior, indicating that activating agent is not a significant parameter in CO₂ adsorption on physically activated carbons. Both temperature and C_{CO₂} affect the shape and breakthrough time of the adsorbent. As is expected, adsorption capacity of all samples decreases with increasing temperature because of the exothermic nature of CO₂ adsorption (García et al., 2011) while an increase in C_{CO₂} increases CO₂ adsorption capacity dramatically. The highest and lowest adsorption capacities are achieved at 30% C_{CO₂} 25°C and 10% C_{CO₂} 65°C, respectively. Fig. 7 shows the effects of these process conditions on the breakthrough curve and t_b for all three types of adsorbents at these conditions. At 30 mol% C_{CO₂}, 25°C (Fig. 7b), breakthrough curves of steam and CO₂ ACs coincide and chemical activated carbon presents longer breakthrough time and higher capacity but wider breakthrough curve. The wider curve can result from the mass transfer resistance or axial dispersion (García et al., 2011; Wilcox, 2012) due to smaller particle size of KOH activated carbon. Results of the experiments also show that at t > 65°C chemical activated carbon, and consequently larger pore volume and surface area, have no real advantage over physically activated carbon. The slope of breakthrough curves and t_b also vary with temperature and C_{CO₂}. At a constant CO₂ concentration, the higher the temperature is, the narrower the mass transfer zone and the shorter t_b (see Fig. 8a). On the other hand, an increase in C_{CO₂} at a constant temperature also increases the slope of the breakthrough curve, but it is less significant and it does not affect t_b (see Fig. 8b). Design Expert software version 8.0.7.1 was used to analyze the results. The CO₂ adsorption results are analyzed to develop a regression model, in order to evaluate the effect of process conditions and their interactions, and to predict the adsorption behavior of adsorbent under different conditions. For the steam and chemical activated carbons, the experimental results are fitted with the quadratic models which proved the best for the lack of fit and model statistics tests. The provisional models are tested for p-value, lack of fit and R², and the final models are obtained after the elimination of the insignificant parameters and interactions. Table 4 presents ANOVA of CO₂ adsorption models on chemical and steam activated carbons after elimination of the insignificant terms. For CO₂ activated carbon, there is a significant lack of fit indicating that the provisional model is inadequate. The ANOVA results for CO₂ adsorption capacity of CO₂ activated carbon are provided in the supporting materials (Table S2). For chemical activated carbon, interaction between two factors is insignificant (p-value > 0.05) and is omitted. The
final model of CO₂ adsorption on chemical activated carbon as a function of temperature and C₇CO₂ is as follows (Eq. (2)):

\[
\log_{10}(\text{CO}_2 \text{ adsorption capacity}) = 1.3085 - 0.0133 T + 0.0512 C_{\text{CO}_2} + 0.0001 T^2 - 0.001 C_{\text{CO}_2}^2.
\] (2)

Eq. (2) shows that adsorption capacity depends directly on C₇CO₂ and the square of temperature and inversely on temperature and the square of C₇CO₂. It also shows that C₇CO₂ has the most significant effect followed by temperature and the square of C₇CO₂. The high value of R² (0.994) confirms that most of the data variation is fitted with this model. Fig. 9a shows the response surface plot of CO₂ adsorption capacity in chemically activated carbon. For the steam activated carbon interaction of independent factors is significant:

\[
\text{CO}_2 \text{ adsorption capacity} = +10.6943 - 0.3167 T + 2.6947 C_{\text{CO}_2} - 0.0150 T C_{\text{CO}_2} + 0.0022 T^2 - 0.00157 C_{\text{CO}_2}^2.
\] (3)

As can be observed in Eq. (3), adsorption capacity of steam activated carbon increases as C₇CO₂ and the square of temperature increase and as temperature and the square of C₇CO₂ decrease but interaction of temperature and C₇CO₂ also affect the adsorption inversely. Fig. 9b shows the three-dimensional surface response plot for CO₂ adsorption capacity of steam activated carbon as well as the effect of temperature and C₇CO₂ on CO₂ adsorption capacity.

2.3. Cyclic CO₂ adsorption

The CO₂ adsorption performance of KOH activated carbon, CO₂ activated carbon and steam activated carbon in 50 cycles is presented in Fig. 10. The adsorption index (%) in this figure

<table>
<thead>
<tr>
<th>Samples</th>
<th>C 1s (%)</th>
<th>O/C</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ AC</td>
<td>0.15</td>
<td>65.9</td>
<td>17.3</td>
<td>–</td>
<td>–</td>
<td>16.9</td>
</tr>
<tr>
<td>Steam AC</td>
<td>0.17</td>
<td>56.11</td>
<td>29.58</td>
<td>–</td>
<td>–</td>
<td>14.31</td>
</tr>
<tr>
<td>KOH AC</td>
<td>0.21</td>
<td>30.41</td>
<td>49.56</td>
<td>11.16</td>
<td>8.87</td>
<td></td>
</tr>
</tbody>
</table>
is the ratio of the adsorption capacity of the regenerated adsorbent and the fresh adsorbent (Hsu et al., 2010). As can be seen in Fig. 10, chemical and CO₂ activated carbons can be fully regenerated and used in 50 cycles but adsorption capacity of the steam activated carbon starts decreasing after about 20 cycles, suggesting that steam activated carbon is not a favorable adsorbent for multi-cyclic CO₂ adsorption.

### Table 3 - Central composite design for two variables and corresponding adsorption capacity.

<table>
<thead>
<tr>
<th>Runs</th>
<th>Parameters</th>
<th>Adsorption capacity (mg CO₂/g adsorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>CO₂</td>
</tr>
<tr>
<td>1</td>
<td>45.0</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>25.0</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>45.0</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>65.0</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>45.0</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>65.0</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>25.0</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>73.3</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>45.0</td>
<td>34.2</td>
</tr>
<tr>
<td>10</td>
<td>45.0</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>45.0</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>45.0</td>
<td>5.9</td>
</tr>
<tr>
<td>13</td>
<td>45.0</td>
<td>20</td>
</tr>
<tr>
<td>14</td>
<td>16.7</td>
<td>20</td>
</tr>
</tbody>
</table>

CO₂ concentrations.

3. Conclusions

The CO₂ adsorption performances of KOH, CO₂ and steam activated carbons are tested under different temperatures and CO₂ concentrations. Adsorption results demonstrate that, in this range of parameters, the adsorption behavior of activated carbon can be mainly influenced by porosity of the adsorbent. Steam activated carbon and CO₂ activated carbon with the close range of surface area, the total porosity, micro porosity and similar surface chemistry present the same adsorption behavior, indicating the fact that activation agent is not a significant factor on performance of activated carbon for CO₂ capture under these operating conditions. Overall, KOH activated carbon with higher surface area and porosity can be considered as the best option for CO₂ capture at atmospheric pressure and low temperature of CO₂. It has been shown that the KOH activated carbon does not offer any advantages at higher temperature. The optimum adsorption capacity was achieved at 30% CO₂, 25°C. Moreover, all adsorbents were tested for durability and both CO₂ and KOH activated carbons remain active in a temperature swing process for at least 50 cycles and KOH activated carbon adsors more CO₂ under the same conditions. In this range of parameters, CO₂ is also found to be the most significant factor in the adsorption process.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2015.03.008.

Table 4 – The ANOVA (Analysis of Variance) results of the response surface models for CO2 adsorption capacity.

<table>
<thead>
<tr>
<th></th>
<th>KOH AC</th>
<th>Steam AC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sum of square</td>
<td>Mean square</td>
</tr>
<tr>
<td>Model</td>
<td>0.67</td>
<td>0.17</td>
</tr>
<tr>
<td>T</td>
<td>0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>C_\text{CO}_2</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>T^2</td>
<td>3.922E–003</td>
<td>3.922E–003</td>
</tr>
<tr>
<td>Residual</td>
<td>4.037E–003</td>
<td>5.047E–004</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>3.411E–003</td>
<td>8.527E–004</td>
</tr>
<tr>
<td>Pure error</td>
<td>6.265E–004</td>
<td>1.566E–004</td>
</tr>
<tr>
<td>Total</td>
<td>0.68</td>
<td>13</td>
</tr>
<tr>
<td>R^2</td>
<td>0.9940</td>
<td></td>
</tr>
<tr>
<td>Adjusted R^2</td>
<td>0.9910</td>
<td></td>
</tr>
<tr>
<td>Predicted R^2</td>
<td>0.9629</td>
<td></td>
</tr>
</tbody>
</table>

T: temperature; df: degree of freedom from which the experimental error is estimated.

Fig. 9 – Response surface plot of CO2 adsorption capacity of (a) KOH activated carbon and (b) steam activated carbons.

Fig. 10 – Cyclic CO2 adsorption performed at 25°C using steam, CO2 and KOH activated carbons (ACs) in 30 mol% CO2 in He.

References

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