Carbon Dioxide Adsorption on Activated Carbon Hydrothermally Treated and Impregnated with Metal Oxides

(Penyerapan Karbon Dioksid pada Karbon yang Diaktifkan Secara Rawatan Hidrotermal dan Impregnasi dengan Logam Oksida)

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ABSTRACT

Activated carbon (AC) has been used widely as an agent for carbon dioxide (CO₂) adsorption due to its environmentally friendly nature, low cost, high porous structure, high surface area and good mechanical properties. Modifications have been made to AC in order to enhance its adsorptive properties. In this study, the performance of activated carbon modified by hydrothermal treatment and impregnation techniques was compared using metal oxides. The prepared samples were characterized by different techniques using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The adsorption of CO₂ was investigated using a CO₂ adsorption unit, whereby 20% of CO₂ gas was passed through the samples until a breakthrough point was achieved. During the adsorption study, it was found that AC that had been hydrothermally treated with cerium oxide (CeO₂) had the highest adsorption capacity of 0.856 mmol/g with a breakthrough time of 19.33 min.

Keywords: Activated carbon; carbon dioxide; hydrothermal; impregnation; metal oxides

INTRODUCTION

Nowadays, the climate of the earth is changing continuously due to various factors. These include anthropogenic forcing which is human induced activity that leads to increasing of the concentration of greenhouse gases (GHG) into the atmosphere as well as increasing the earth temperature that leads to global warming. (MET 2009). Increasing of carbon dioxide (CO₂) emissions has cause interest in effort to introduce efficient and cost-effective technologies for capturing or reducing CO₂ from large point sources like coal-fired power plant. One of the main technologies in reducing greenhouse gases is post-combustion capture of CO₂ because it has the potential to be retrofitted to existing coal-fired power plant without requiring substantial changes to the combustion process (Thiruvenkatachari et al. 2015).  Technologies such as membrane separation, the conventional temperature swing adsorption (TSA) or pressure swing adsorption (PSA) have been proposed to capture CO₂ from the flue gases (Zhou et al. 2012). However, these technologies have some disadvantages. For membrane separation, multiple stages of separation or recycling is needed since it cannot always give high separation degrees which makes the cost of membranes reactor is high (Olajire, 2010). The disadvantage of TSA and PSA is high energy consumption since TSA required high regeneration time while PSA need cooling and drying system for the flue gas (Pires et al. 2011).
Adsorption was considered as one of the most promising technologies in the commercial and industrial applications because of the low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures (Song 2006; Duffy et al. 2006; Thiruvenkatachari et al. 2009). Carbon capture by adsorption technology had drawn much research effort recently and had done lots of work to improve capture performance (Gibbins and Chalmers 2008; Lee and Park 2015). Activated carbon (AC) as an agent for adsorption has been used for many years in many field. Gas-phase adsorption by activated carbon is a separation process in which adsorbate molecules are transferred to the pore surface of solid activated carbon (Sumathi et al. 2010). AC is mainly amorphous material that has large surface area and pore volume.

Modification on adsorptive properties of AC can be done by using chemical and physical methods (Rashidi & Yusup 2016). AC loaded with metal oxides from salts of zinc, copper and iron has been recently reported (Hosseini et al. 2015; Kim et al. 2010; Somy et al. 2009; Yong & Mata 2001). Carbon sorbents loaded with copper oxide (CuO) can increase the adsorption capacity of the acidic gas since CuO is an electron donor as reported by Fenrong et al. (2010) and Kim et al. (2010) which show that AC modified with CuO showed higher adsorption capacity than unmodified AC. The study by Hosseini et al. (2015) shows that co-impregnation of 2 metals which are copper (Cu) and zinc (Zn) can further enhance the CO₂ adsorption by 49%. Literatures show that hydrothermal treatment can improve the chemical characteristic of carbon materials (Jain et al. 2015; Liu et al. 2010; Ma et al. 2014). Skubiszewska-Zięba et al. (2011) reported that the fractions of mesopores of carbon sorbents increase from 30 % to 60 % after hydrothermal treatment. Hence, the present study aimed on the adsorption of CO₂ on AC loaded with cerium oxide (CeO₂), CuO and mixture of CeO₂ and CuO using different modification methods; wet impregnation and hydrothermal treatment.

MATERIALS AND METHODOLOGY

A commercial AC was used as unmodified adsorbent. High purity commercial powder metal nitrates, copper nitrate (Cu(NO₃)₂·3H₂O) and cerium nitrate (Ce(NO₃)₃·6H₂O) were used as metal oxide precursor to modify AC.

HYDROTHERMAL TREATMENT

AC was impregnated with metal nitrate of 10 wt% metals loading. During the impregnation, the solutions of metal nitrate were continuously mixed with AC for 5 h. Then the samples were heated to 70°C while being constantly stirred until the liquid was totally evaporated. After that the samples were dried in an oven at 60°C for a period of 24 h. Finally, the prepared samples were heat-treated at 450°C for 1 hour in the presence of nitrogen to form the reduced sorbents (Hosseini et al. 2015; Sumathi et al. 2010b). Table 1 shows the naming of the samples prepared by both methods. Set up of hydrothermal treatment and wet impregnation were shown in Figure 1.

<table>
<thead>
<tr>
<th>Metal loaded/Method</th>
<th>Hydrothermal treatment</th>
<th>Wet impregnation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper, Cu</td>
<td>ACCu-HT</td>
<td>ACCu-WI</td>
</tr>
<tr>
<td>Cerium, Ce</td>
<td>ACCe-HT</td>
<td>ACCe-WI</td>
</tr>
<tr>
<td>Ce and Cu</td>
<td>ACCeCu-HT</td>
<td>ACCeCu-WI</td>
</tr>
</tbody>
</table>

FIGURE 1. Set up of (a) hydrothermal treatment using autoclave reactor and (b) wet impregnation using hot stirring plate of AC
ADSORBENT CHARACTERIZATION

The prepared samples were characterized by different techniques. The surface morphology of the samples is determined by Scanning Electron Microscopy (SEM). Determinations of the structure and fingerprint characterization of crystalline materials are done by using X-ray Diffraction (XRD).

CO₂ ADSORPTION TEST

The adsorption of CO₂ of the prepared sorbent was carried out in a CO₂ adsorption unit shown in Figure 2. 1 g of the sample was placed in the adsorption unit. A stream of gaseous mixture, containing CO₂ and helium (He), was passed through the prepared samples in the ration of 1:4. The reaction temperature of this process was preset to 30°C. The outlet concentrations of CO₂ were measured using a CO₂ gas analyzer after sorption activity. The concentration of CO₂ was recorded continuously for every 10 s until it reaches the breakthrough point. The activity of the sorbent towards CO₂ is expressed by adsorption capacity, which is defined by the breakthrough curves (C/C₀ versus t). C/C₀ is a dimensionless factor, where C is the outlet concentration of (ppm) from the reactor, C₀ is the initial concentration (ppm) and t is the reaction time (min). Each and every experimental run was repeated at least three times to increase the precision of the results (Sumathi et al. 2010a).

RESULTS AND DISCUSSION

CHARACTERIZATION OF MODIFIED SAMPLES

The difference surface morphology of the raw and modified samples can be seen from the result of SEM image shown in Figure 3 to 5. From Figure 3, it can be seen that the raw AC has high porosity with some impurities on it. After impregnation, from Figure 4 and 5, it can be seen that the metal particles have filled up some of the pores and covered the surface of AC. Despite that, the adsorption of CO₂ can still occur based on the reaction of the gas with metal oxides, not only on the surface and pores of the AC itself (Hidayu & Muda 2016). The metal particles can be seen more uniformly dispersed on the AC surface by hydrothermal treatment compared to wet impregnation. This may happen as hydrothermal treatment is done under a controlled system compared to wet impregnation. Based on this observation, hydrothermally treated AC samples are assumed to give better adsorption performance.
The XRD patterns for the modified AC are shown in Figure 6. The figures show the comparison of the patterns for hydrothermal treated and impregnated AC. Based on the patterns, it can be seen that ACs that undergo hydrothermal treatment produce broader and higher peaks for all samples compared to impregnated AC. A broad peak at 2θ = 20–30˚ indicates the amorphous carbon structure. The broad carbon peak can be seen clearly for samples loaded with CuO (Figure 6 (a)) and can be seen a little for CeO\(_2\) loaded AC (Figure 6 (b)) but hardy seen in AC loaded with both CeO\(_2\) and CuO (Figure 6 (c)). This results correspond SEM analysis which shown that AC was mostly covered in CeO and CuO particles for ACCeCu sample. Figure 6 (c) also indicated that most peaks belong to CeO\(_2\) particle and only a few peaks belong to CuO. This happened because the sample was first loaded with Ce, then Cu. The Ce particles may have taken up most of the area first. Based on the XRD pattern, it is found that the metal oxides particles are highly dispersed on the AC. On that account, it is expected that the adsorption efficiency can be improved due to the reaction that occurred between the metal oxides and CO\(_2\) (Hidayu & Muda 2016). Based on the following equation:

\[
\text{MO + CO}_2 \leftrightarrow \text{MCO}_3
\]  

where M is metal (Cu, Ce). It can be seen that 1 mole of metal oxide can chemically adsorb a stoichiometric equivalent of CO\(_2\) to form metal carbonate (Choi et al. 2009). Hence, the adsorption capacity is expected to be higher with the presence of metal oxides.

**TABLE 2. CO\(_2\) adsorption test**

<table>
<thead>
<tr>
<th>Sample</th>
<th>q (mmol/g)</th>
<th>Breakthrough time (min)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw AC</td>
<td>0.652</td>
<td>19.17</td>
<td>This Study</td>
</tr>
<tr>
<td>ACCu-HT</td>
<td>0.585</td>
<td>18.17</td>
<td></td>
</tr>
<tr>
<td>ACCe-HT</td>
<td>0.856</td>
<td>19.33</td>
<td></td>
</tr>
<tr>
<td>ACCeCu-HT</td>
<td>0.560</td>
<td>15.33</td>
<td></td>
</tr>
<tr>
<td>ACCu-WI</td>
<td>0.522</td>
<td>16.83</td>
<td></td>
</tr>
<tr>
<td>ACCe-WI</td>
<td>0.117</td>
<td>10.17</td>
<td></td>
</tr>
<tr>
<td>ACCeCu-WI</td>
<td>0.056</td>
<td>9.00</td>
<td></td>
</tr>
<tr>
<td>Pitch sphere</td>
<td>1.12</td>
<td>14.00</td>
<td>Plaza et al. 2010</td>
</tr>
<tr>
<td>Alumina &amp; clay impregnated with Na(_2)CO(_3)</td>
<td>0.40</td>
<td>16.00</td>
<td>Dinda 2013</td>
</tr>
<tr>
<td>AC impregnated with Na(_2)CO</td>
<td>0.09</td>
<td>-</td>
<td>Ruiz et al. 2013</td>
</tr>
<tr>
<td>Biomass AC(olive stone (OS) &amp; almond shell (AS))</td>
<td>1.1</td>
<td>-</td>
<td>González et al. 2013</td>
</tr>
<tr>
<td>Carbon fibre composite</td>
<td>2.65</td>
<td>-</td>
<td>Thiruvenkatachari et al. 2013</td>
</tr>
<tr>
<td>AC impregnated with Cu(NO(_3))(_2) &amp; ZnSO(_4)</td>
<td>2.26</td>
<td>45.1</td>
<td>Hosseini et al. 2015</td>
</tr>
</tbody>
</table>

The CO\(_2\) adsorption test was carried out using CO\(_2\) adsorption unit. The temperature was kept constant throughout the experiments at 30˚C. The samples were first flown through He to remove the CO\(_2\) present in the adsorption unit. Then, 20 % of CO\(_2\) gas was flown through the sample for adsorption study. Figure 7 shows the comparison between the breakthrough curves of raw and modified AC as well as hydrothermal treated and impregnated AC. Based on the breakthrough curves, it was found that ACCe-HT has the highest adsorption capacity which was 0.856 mmol/g. This high adsorption capacity may occur due to both physisorption and chemisorption based on the high surface area and highly dispersed metal. The breakthrough time for ACCe-HT was also high which is 19.33 min. The longer the CO\(_2\) maintain in contact with the sorbents, the better the adsorption (Sumathi et al. 2010b). ACCeCu-WI has the lowest adsorption capacity and breakthrough time which were 0.117 mmol/g and 9 min respectively. This may happened due to the low surface area of the sorbent. Since the metal oxides particles has filled up most of the pores and cover most of the AC surface, the adsorption occurred solely on chemisorption compared to other samples which both chemisorption and physisorption occur. The results of CO\(_2\) adsorption test for this study were presented in Table 2 as well as the adsorption studies by other literatures (Dinda 2013; González et al. 2013; Hosseini et al. 2015; Plaza et al. 2010; Ruiz et al. 2013; Thiruvenkatachari et al. 2013; Wang et al. 2011).
FIGURE 6. XRD patterns of modified AC (a) CuO loaded, (b) CeO$_2$ loaded and (c) CeO$_2$ and CuO loaded AC.
Based on the results from this study, it can be seen that the adsorption capacity and breakthrough time for AC hydrothermal treated are higher than the ones that are wet impregnated with metal oxides. The presence of metal on AC results in a basic surface that has strong affinity towards CO$_2$ molecules and gives high adsorption capacity (Yong & Mata 2001). However, it is important to choose the right method of introducing the metal oxide onto AC. Alvim-Ferraz and Gaspar (2005) and Moradi (2014) stated in their study that impregnation of AC will cause deposition of metal compounds and blocks some of the pores that contributes in decreasing surface area and pore volume of AC. This statement coincides with the SEM results for wet impregnated ACs that are shown in Figure 4. The metal compounds deposit can be seen on some part of the AC surface and pores. This may have result in poor physio-sorption process and more of chemisorption process since most of the surface and pores are blocked by metals compound. The modification of AC using metal oxides by hydrothermal treatment is not yet explored. However, studies on hydrothermal treatment for other application like activation of chars and carbonation of biomass are widely reported (Jain et al. 2015; Liu et al. 2010; Ma et al. 2015; Skubiszewska-Zieba et al. 2011). Jain et al. (2015) has reported that coconut shells biomass which has high content of oxygenated functional group (OFG) were pre-treated with zinc chloride (ZnCl$_2$) or hydrogen peroxide (H$_2$O$_2$) has increase the surface area and pore size of AC. It is believed that this also occurred in hydrothermal treated AC with metal oxides in this study since the pore size in SEM images appear bigger than the raw AC and impregnated AC.

CONCLUSION

The aim of the study is to determine the performance of modified AC using different techniques with metals oxides. The hydrothermal treated AC with CeO$_2$ (ACCe-HT) shows higher adsorption capacity compared to raw AC which are 0.856 and 0.652 mmol/g respectively. All the other modified AC has lower adsorption capacity than the raw. The SEM and XRD patterns show that the CeO$_2$ particles highly dispersed on the surface of AC as well as the pores. Hence, it is believed that both physisorption and chemisorbtion process involved in the adsorption of CO$_2$ using ACCe-HT. This is highly associated with the large surface area and the reaction of metal oxides with CO$_2$ molecules. The large surface area is most important in gas adsorption. Hydrothermal treatment provides better adsorption compare to wet impregnation due to the high OFG content that promotes higher surface area and pore sizes of the AC. Based on present work, it is believe that AC hydrothermally treated with metal oxides may be a promising absorbent for CO$_2$ capture.
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