

Investigation of CO₂ adsorption by bagasse-based activated carbon

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Abstract—Bagasse-based activated carbon (BAC) and amine-modified BAC were prepared and investigated for CO₂ adsorption capacity. Modifying BAC with amines resulted in a decrease of surface area, but the decreasing magnitude varied depending on type and loading rate of amines. At room temperature, the unmodified BAC was able to adsorb more CO₂ than the amine-modified BAC. This ability was related to the higher surface area of unmodified than that of the modified BAC. When temperature increased, CO₂ adsorption capacity of all adsorbents was decreased. However, above 323 K and a concentration of CO₂ lower than 30% v/v, the BAC modified with PEI at 5 and 25 wt% showed higher adsorption capacity. Among all adsorbents under 15% CO₂ and 348 K, BAC-PEI25 showed the highest adsorption capacity (0.20 mmol/g).

Key words: Activated Carbon, Carbon Dioxide Adsorption, Amines, Bagasse

INTRODUCTION

Carbon capture and storage technology (CCS) has the high potential to timely and effectively mitigate greenhouse gas emissions, therefore slowing down global warming [1]. It is suited to mitigate anthropogenic CO₂ emissions from a large stationary point source such as flue gas from power plant. The CCS system consists of separation, transportation and long-term isolation of captured CO₂ [2]. Currently, absorption by aqueous amine-based is the most common technology for capturing CO₂ [3-5]. Monoethanolamine (MEA) and polyethylenimine (PEI) have been in use to enhance the adsorption capability due to their high selectivity to CO₂ [6]. However, amine solution usually degrades when oxygen is present. They are also corrosive and highly volatile [7,8]. Thus, prolonged use results in lowering the adsorption efficiency. In addition, impurities gases present in the flue gas such as SO_x, NO_x can react with amine to form heat-stable salts and result in the reduction of capture performance. Reuse of amine can be achieved by reheating CO₂-rich amine to release the captured CO₂ [9], but additional energy and water are needed [10]. This is the main reason why the CO₂ capture and separation steps contribute about three-fourths of the total investment cost of CCS [11]. Alternative adsorbents with better stability and high capacity are thus desirable. Thus, activated carbon is a potential candidate for CO₂ adsorption due to its highly developed technology [3,12-16].

Typically, a fossil-fired power plant emits flue gas with relatively high temperature (243 to 423 K) and low CO₂ concentration (4-8% v/v). For the flue gas from a natural gas and coal-fired power plant, the typical CO₂ concentration is 12-15% v/v [17]. The high temperature of flue gas is the major controlling factor of adsorbent

capacity. For example, van Der Vaart et al. [18] showed that the adsorption capacity of Nortit RBI activated carbon decreased from 108 to 40 mg/g-adsorbent when the adsorption temperature increased from 295 to 348 K. To overcome this problem, CO₂ adsorption capacity of porous material at high temperature using nitrogen functionalized material has been investigated (Maroto-Valer et al. [19]). For example, amine and ammonia was used to modify the surface characteristics of adsorbent to enhance the CO₂ adsorption capacity at high temperature. It was demonstrated that activated anthracite with PEI could increase CO₂ adsorption capacity at higher adsorption temperature (348 K). Pevida [20] also demonstrated that the commercial activated carbons that were treated by ammonia have the higher CO₂ adsorption (0.076 g CO₂/g) than the untreated activated carbons (0.055 g CO₂/g) at 673 K. Zhu et al. [21] also reported that PEI modified silica gel showed better CO₂ adsorption than the non-modified silica gel.

It is well known that activated carbon can be produced from various precursors such as carbon based-materials, lignocellulose material and agricultural residues. The property of produced activated carbon, and therefore its adsorption performance, also varies due to the source precursors. This work synthesizes the activated carbon from locally available bagasse and then investigates its CO₂ adsorption capacity. The main objectives are to evaluate and to enhance the CO₂ adsorption capacity of the synthesized activated carbon at the flue gas temperature.

EXPERIMENTAL

1. Activated Carbon Synthesis

Bagasse used in this experiment was collected from the sugar factory, Mirt Phol Sugar Group, Thailand. After washing with distilled water to remove dust and other impurities, it was oven-dried at 378 K for 24 h. The production of activated carbon was modi-

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fied from Tsai et al. [22] and Önal et al. [23]. $ZnCl_2$ was used for activation of bagasse at the weight ratio of bagasse to $ZnCl_2$ of 1 : 1 at room temperature for 1 h. After drying at 378 K for 24 h, it was carbonized at heating rate of 10 K/min from room temperature up to 773 K. The temperature was held at 773 K for 1 h in a horizontal furnace under N_2 flows of 100 ml/min. The sample was then cooled to room temperature under N_2 flow and cleaned with warm distilled water until the chloride residues were not detected by using 1 M silver chloride solution. Finally, the activated carbon was dried using reduced pressure vacuum oven at 343 K, and 93.33 kPa for 24 h. The sample is hereafter called "BAC".

2. BAC Surface Modification

The surface of BAC was modified by wet impregnation using three different amines: Polyethylenimine (PEI), Monoethanolamine (MEA) and Aniline (ANL) at loading ratios of 5, 25 and 50 wt%. Analytical grade of MEA (99.5%) and ANL (99.5%) was purchased from Merck (USA) while PEI was from Sigma-Aldrich (USA). A desired amount of amine was dissolved in ethanol and stirred for 15 min. Then the parent BAC was added into amine/ethanol solution and continuously stirred for 30 min at room temperature. Finally, the impregnated sample was dried at 343 K for 24 h under reduced pressure (93.33 kPa) using a vacuum oven (Mettler, VO 500, Germany). The impregnated sample was named as parent adsorbent-amine source-amine loading; for example, BAC-PEI50 represents bagasse activated carbon impregnated with PEI at 50 wt%.

3. Sample Characterization

N_2 adsorption isotherm was studied using an automatic adsorption-desorption system (BELSORP-mini II, Osaka, BEL Japan Inc.). According to the manufacturer's recommendation, this method is based on the assumption that adsorbed nitrogen at liquid nitrogen temperature has a hexagonal cross-sectional area of 0.162 nm^2 . The surface area was calculated from the Brunauer-Emmett-Teller (BET) equation over the relative pressure (P/P_0) of 0.05-0.35. The proximate analysis and thermal stability of the modified BAC was performed by using a thermogravimetric analyzer (TGA) (Pyris 1 TGA, Perkin Elmer, Massachusetts, USA). Typically, 10 mg (particle size less than $75 \mu\text{m}$) of sample was placed into the small platinum sample holder. The sample was heated from 303 K up to 1,173 K under N_2 atmosphere. An air zero was introduced instead of N_2 and held for 10 min at the final step to obtain the ash content. The weight loss during pyrolysis was calculated to the percentage of volatile matter and fixed carbon. The elemental composition (CHNS) analysis was carried out by using an elemental analyzer (Thermo Finnigan, Flash EA 1112, Massachusetts, USA). The analytical procedure followed the protocols given by the manufacturer.

4. CO_2 Adsorption Measurement

The effects of adsorption temperature, CO_2 concentrations and CO_2 feeding rate were studied. The temperature ranges tested in this study were 303-423 K. Adsorption using different CO_2 concentrations of 15-100% v/v (balance with N_2) was also compared. A CO_2 adsorption experiment was conducted by using a tubular reactor connected to a mass spectrometer (MS; Omnistar, Pfeiffer Vacuum Inc., California, USA). Activated carbon of 0.5 g was placed into a tubular reactor supported with quartz wool. A testing cycle was composed of four steps. Firstly, the sample was pretreated with N_2 at the flow rate of 50 ml/min for 45 min. Subsequently, the baseline measurement was performed by introducing the desired CO_2

concentration directly to the MS (bypassing the sample) for 45 min. Then, CO_2 adsorption was measured by switching CO_2 gas stream passing through the sample bed. Finally, desorption was performed at the same adsorption temperature under N_2 flow (50 ml/min). The amount of ion current during adsorption experiment was recorded and converted to the amount of CO_2 using numerical integration method (trapezoidal integration) and calibration curve of standard CO_2 gases.

RESULTS AND DISCUSSION

Proximate analysis of bagasse and the synthesized activated carbon indicates that the major component of bagasse is volatile matter (83.3 wt%), fixed carbon (10.5 wt%) and ash (6.2 wt%). After activation, most of volatile fraction is lost (reduced to 13.6 wt%) and the relative content of fixed carbon increases to 84.5 wt%. The major

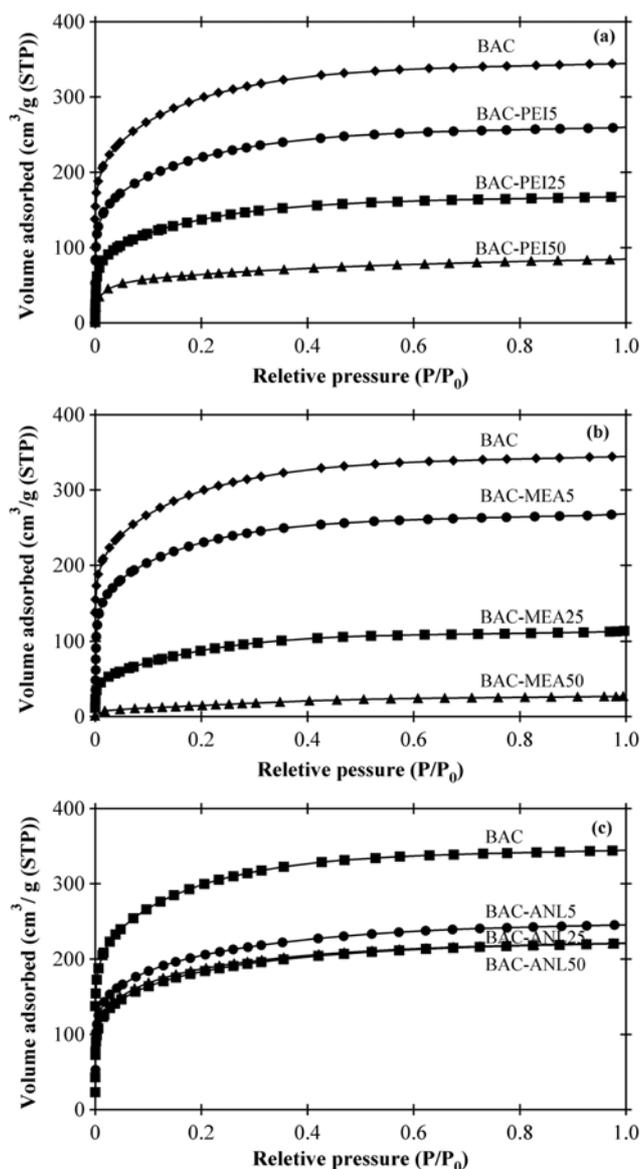


Fig. 1. N_2 adsorption isotherms of parent and modified BAC at different loadings: (a) PEI, (b) MEA and (c) ANL.

Table 1. Porosity characteristic of parent and modified BAC

| Sample | S_{BET}^a (m ² /g) | V_t^b (cm ³ /g) | V_m^c (cm ³ /g) | V_m/V_t (%) | Pore size (nm) |
|-----------|---------------------------------|------------------------------|------------------------------|---------------|----------------|
| BAC | 923.39 | 0.533 | 0.528 | 99.19 | 2.01 |
| BAC-PEI5 | 694.96 | 0.401 | 0.397 | 99.03 | 2.14 |
| BAC-PEI25 | 483.86 | 0.280 | 0.258 | 92.42 | 2.18 |
| BAC-MEA25 | 300.45 | 0.1753 | 0.1699 | 96.92 | 2.04 |
| BAC-ANL25 | 573.94 | 0.3412 | 0.3367 | 98.68 | 2.18 |
| BAC-PEI50 | 201.72 | 0.131 | 0.125 | 96.09 | 2.39 |

^aBET surface area, determined over relative pressure range from 0.05-0.35

^b V_t ; total pore volume obtaining from BET over the relative pressure of 0-0.99

^c V_m ; micropore volume calculated by t-plot method

components of volatile fraction of fiber bagasse are cellulose, hemicelluloses and lignin [24]. These results of proximate analysis are common for bagasse, but slightly varied from place to place depending on soil nutrients and growing climate [25].

1. Characteristics of Amine-modified BAC

1-1. N₂ Adsorption Isotherm and Porosity

The porosity of activated carbon was determined from the N₂ adsorption isotherm (Fig. 1). The parent BAC and modified BAC exhibit type I adsorption isotherm according to IUPAC classification [26]. This means that the adsorbents of this kind have narrow pore size distribution and thus the adsorption of N₂ is limited by micropore volume accessibility [22]. The average pore size of BAC and the amine-modified BAC was 0.8 nm, which are classified as microporous materials. The ratio of micropore to total pore volume of all samples is greater than 92% (Table 1). After being impregnated with amines, the micropore volume, BET surface area of activated carbon are decreased, and this is further decreased with the increasing amine loadings (Fig. 2). At any given loading rate, BET surface area and the total pore volume of BAC-PEI are lower than that of MEA and ANL modified materials. Thus, PEI modified BAC is affected the most by changing the loading rate when compared with MEA and ANL. This is probably due to the combination of high molecular weight and large molecular size of PEI (the average molecular weights of PEI, MEA, and ANL are 25,000, 61.08 and 93.13 g/mol). Such large molecular weight and size could result in pore blockage and surface coverage as previously reported

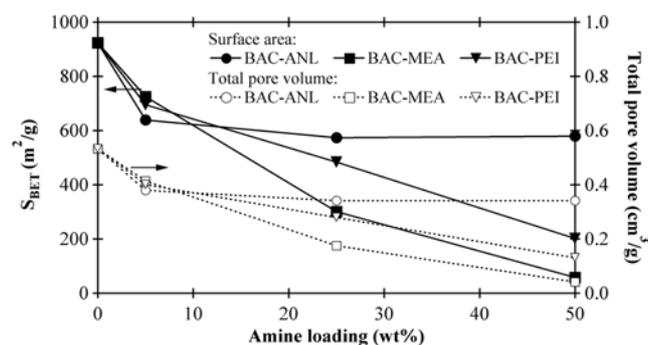


Fig. 2. BET surface area and total pore volume of parent BAC and amines modified BAC with different amines and loading. The arrows point towards the vertical axis where plotting scale is referred to.

on PEI impregnation of MCM-41 and activated anthracite [11].

1-2. Thermal Stability Test

To ensure the feasibility of using activated carbon at high temperature such as at flue gas temperature, the thermal stability of activated carbon was investigated. Fig. 3 shows the comparison of thermal weight loss and derivation thermal weight loss (DTG) of amine

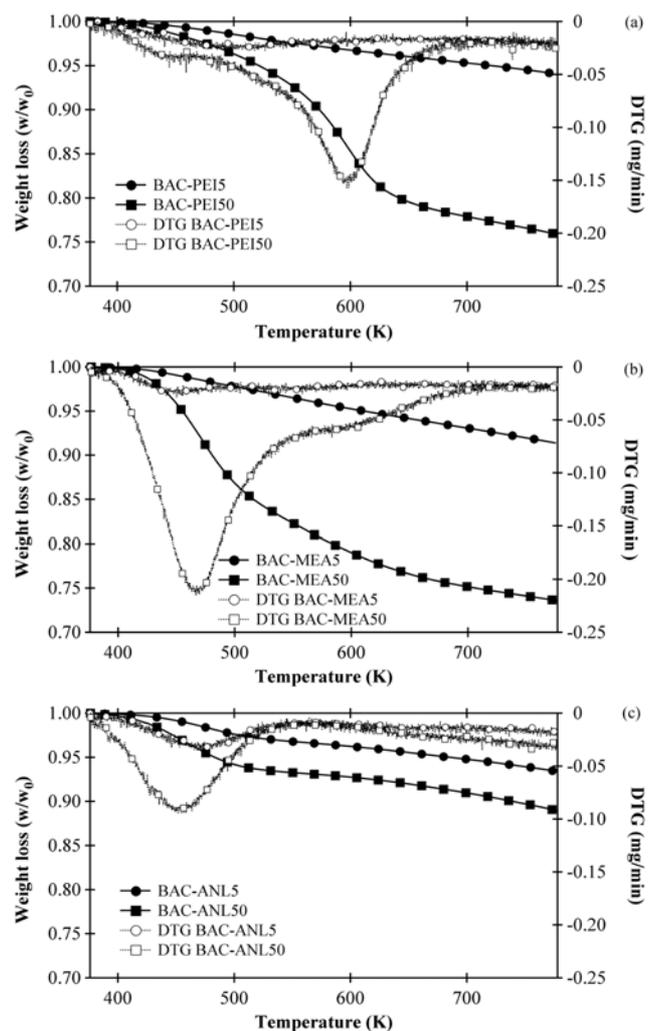


Fig. 3. Thermal weight loss and DTG of amine impregnated BAC as a function of temperature: (a) BAC-PEI, (b) BAC-MEA and (c) BAC-ANL.

impregnated samples. BAC shows high thermal stability; only about 2.3% was burned out at 773 K. When impregnated with amines, however, higher weight loss was observed. This could be due to the decomposition of organic amines. At 423 K, which is the high end of the flue gas temperature, the weight loss of 50 wt% amine-impregnated BAC was 0.56, 1.11 and 1.01%, for PEI, MEA and ANL, respectively. The major weight loss occurs at 600, 469 and 454 K for BAC-PEI50, BAC-MEA50 and BAC-ANL50, respectively. These somehow correspond to the basic properties of these amines, i.e., the boiling points of each amine which are 523, 443 and 457 K for PEI, MEA and ANL, respectively. The total net weight loss at 800 K was 25, 27 and 12%, respectively. From these results, it is concluded that loss of BAC and amine-impregnated BAC is negligible at the flue gas temperature range. Therefore, they should be able to be applied for CO₂ adsorption under such conditions.

2. CO₂ Adsorption Capacity

2-1. Effect of Amine Sources and its Relationship to Temperature

Using different sources of amines for BAC impregnation has resulted in significantly different CO₂ adsorption. Fig. 4(a) and (b) show that the adsorption capacity of all adsorbents significantly decreased with increasing of adsorption temperature, which is the behavior of the physical adsorption mechanism. However, CO₂ adsorption is also related to temperature. The relationship among sources of amines and temperature can be separated into two groups according to temperature: room and elevated temperatures.

At room temperature, CO₂ adsorption by the unmodified BAC

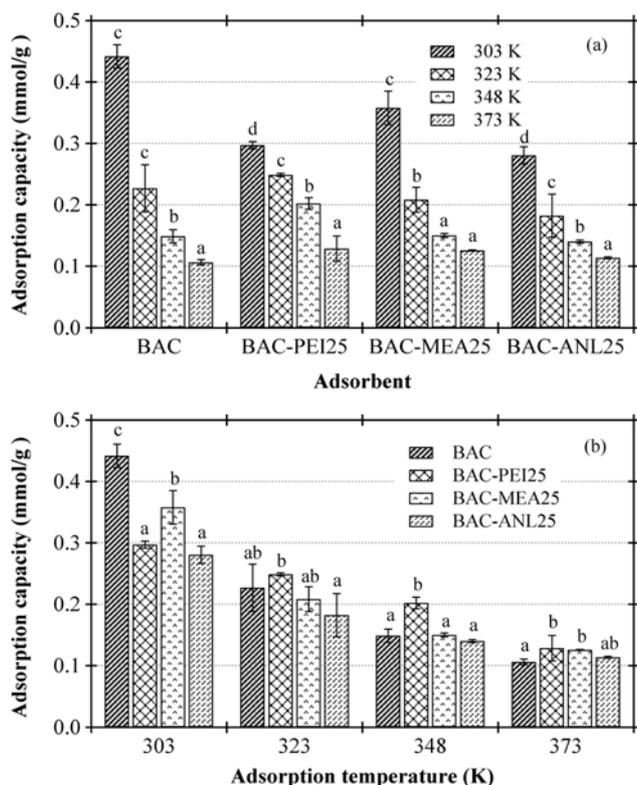


Fig. 4. CO₂ adsorption capacity of BAC modified by different amines (under the influent CO₂ concentration of 15% v/v, and the flow rate of 50 ml/min); the values followed by the same letter indicate no significant difference ($p < 0.05$); (a) among the adsorbents, and (b) adsorption temperatures.

is significantly higher than others. Among amines, MEA shows the highest CO₂ adsorption capacity and there is no difference in adsorption capacity between PEI and ANL. This is probably because BAC has highest surface area and micropore volume, which are the important characteristics for physical adsorption.

At elevated temperatures (348-373 K), CO₂ adsorption capacity by the unmodified BAC is significantly decreased. The rate of adsorption decrease is highest for the unmodified BAC, while for the amine-modified BAC the rate is lower. Gray et al. [27] studied the performance of immobilized tertiary amine solid sorbent for CO₂ capture and reported that with increasing adsorption temperature the adsorption capacity was decreased. Maroto-Valer et al. [19] studied CO₂ adsorption capacity for activated anthracite and reported that when the adsorption temperature increases, both surface adsorption energy and molecule diffusion rate increased, resulting in the adsorbed CO₂ molecules becoming more unstable and desorption process occurring. At 348 K, BAC-PEI25 shows the highest CO₂ adsorption capacity (0.20 mmol/g) while that of BAC-MEA25 and BAC-ANL25 was not different from unmodified BAC. This indicates that PEI impregnation has improved the CO₂ adsorption at elevated temperature.

Amine-modified BAC provides higher adsorption capacity than parent at high temperature, which indicates the partial roles of chemical adsorption by functional group of NH₂ and CO₂ [28]. It is possible that alkaline surface function groups can chemically adsorb CO₂ due to the acid characteristic of CO₂. Among amine-modified BAC, PEI-impregnated BAC provided the highest adsorption capacity, which may be due to its higher availability of nitrogen active sites for chemical adsorption when compared to the other amines. Because it performs the best among the amines used, PEI was selected for study of the effects of loading rate on the CO₂ adsorption capacity.

2-2. Effect of PEI Loading Rate and its Relationship to Temperatures

The amount of PEI loading rate not only affects the surface area and pore volume of BAC but also to the CO₂ adsorption capacity. In the same manner as for the effects of amine source, the effects of loading rate are also related to temperature. At room temperature, adsorption capacity decreases as loading rate increases (Fig. 5). This could be explained by the decreases in surface area and pore

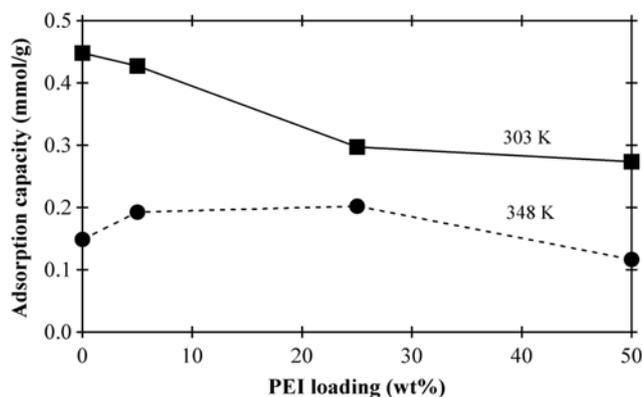


Fig. 5. CO₂ adsorption capacity of PEI modified BAC at 303 K and 348 K as a function of loading rate (under the CO₂ concentration of 15% v/v and the flow rate of 50 ml/min).

volume as mentioned above. However, at elevated temperature, the increase in loading rate between 0 to 25 wt% resulted in enhancing adsorption capacity. At 348 K the adsorption capacity of BAC-PEI5 and BAC-PEI25 (0.19 and 0.20 mmol/g, respectively) was higher than that of unmodified BAC (0.15 mmol/g). Therefore, at room temperature, the physical adsorption process seems to dominate over chemical adsorption. However, at elevated temperature, the results suggest that a chemical process may play a role in CO₂ adsorption. Xu et al. [11] proposed the chemical adsorption mechanism of CO₂ by amines that two moles of amine are needed to adsorb one mole of CO₂;

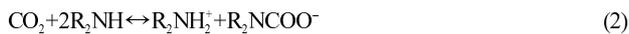


Fig. 6(a) and (b) show CO₂ adsorption capacity of BAC and PEI-modified BAC at different adsorption temperatures. At 303 K, the CO₂ adsorption capacity of BAC and BAC-PEI5 is not significantly different, but these are significantly higher ($p < 0.05$) than BAC-PEI25 and BAC-PEI50. At 348 K, the adsorption capacity of BAC-PEI5 and BAC-PEI25 is significantly higher than BAC and BAC-PEI50. The optimal loading rate for CO₂ adsorption seems to be between 5-25 wt%. As mentioned earlier, this could be explained by the fact that at 303 K amine impregnation reduces the BET surface area and porosity. Since at this temperature only physical adsorption domi-

nates, reduced surface area and porosity therefore limit the adsorption capacity as observed. However, at high temperature (343-363 K), the contribution of chemical adsorption of amino groups may be involved, resulting in the increasing adsorption capacity [29].

Using the best adsorption result (BAC-PEI5), the adsorbents were tested for regeneration performance. The adsorbents were first purged with N₂ until the CO₂ signal was negligible and constant, then CO₂ was introduced to allow the re-adsorption. The repeated eight cycles of adsorption-desorption run of BAC-PEI5 at 348 K using 15% CO₂ reveal that adsorption performance decreased slightly (from 0.19 in the first run to 0.18 mmol/g in the 8th run, data not shown). The ability to re-adsorb CO₂ was reduced because not all previously adsorbed CO₂ is released. After N₂ purging, CO₂ was still retained by the adsorbent by 1.70, 3.79, 2.16 and 1.72% for BAC, BAC-PEI5, BAC-PEI25 and BAC-PEI50, respectively. The relatively lower desorption ability of BAC-PEI5 and BAC-PEI25 than others was opposite to their relatively higher adsorption ability at this temperature (Fig. 6(a)). This may be due to strong bonding between CO₂ and PEI in BAC-PEI5 and BAC-PEI25. Nevertheless, since the re-adsorption and desorption ability of adsorbents were quite high, it can be said that the adsorbents can be effectively regenerated and reused for CO₂ adsorption.

2-3. Effect of CO₂ Concentration

The adsorption capacity as a function of influent CO₂ concentration was investigated in order to identify which ranges of influent CO₂ concentration that BAC-PEI can be applied (Fig. 7(a) and (b)).

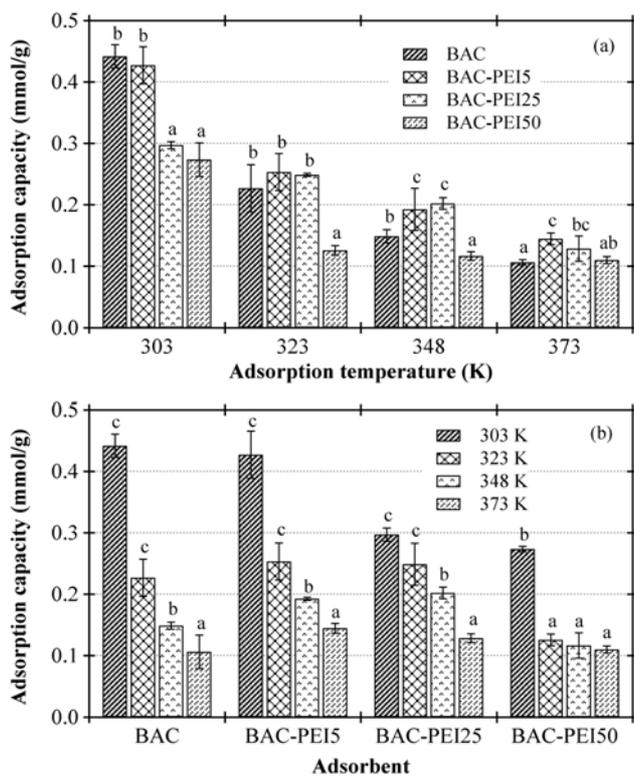


Fig. 6. CO₂ adsorption capacity of BAC and PEI modified BAC at difference adsorption temperature; the values followed by the same letter indicate no significant difference ($p < 0.05$); (a) among the adsorption temperatures and (b) among the different adsorbents.

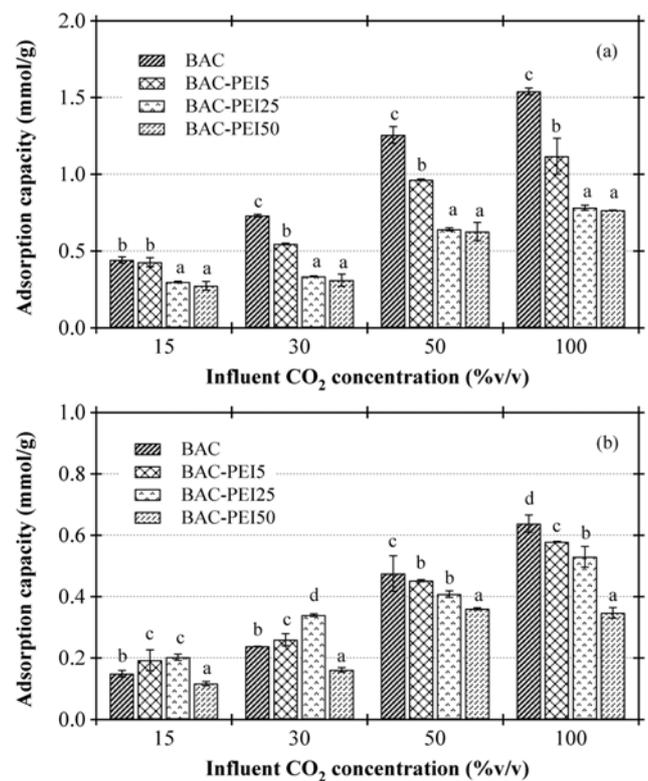


Fig. 7. Adsorption capacity of BAC at different PEI loading rate and the effects of initial CO₂ concentration at 303 K (a) and 348 K (b); the values followed by the same letter indicate no significant difference ($p < 0.05$) compared within each influent CO₂ concentration.

Adsorption capacity increases as the concentration of CO₂ increases. However, this is also affected by the adsorption temperature. At 303 K, adsorption temperature increases three-times when CO₂ concentration increases from 15 to 100% v/v. For the impregnated BAC, the effects are less obvious and only small increase is observed under the amine high loading rate. Accordingly, the maximum adsorption capacity obtained at 303 K and at 100% v/v of influent CO₂ concentration is 1.54, 1.12, 0.78 and 0.77 mmol/g for BAC, BAC-PEI5, BAC-PEI25 and BAC-PEI50, respectively. At 348 K (Fig. 7(b)), however, the adsorption capacity of the modified BAC (5-25 wt%) is higher than the unmodified, suggesting the chemical adsorption at least partly contributes to CO₂ adsorption under such conditions [30]. It can be said that under relatively high temperature, modified BAC performs better than the unmodified one. It is thus recommended for further development for fossil fuel power plant application.

CONCLUSION

The current study evaluates the CO₂ adsorption capacity of activated carbon that was synthesized from bagasse. It was found that the synthesized activated carbon has the desired characteristics to be used as CO₂ adsorbent. These include high fixed carbon content, high surface area and porosity. Testing the adsorption performance and the effects of various factors reveals that BAC modified with 5-25% PEI can adsorb more CO₂ than the unmodified BAC under the adsorption conditions of temperature higher than 323 K and the CO₂ concentration lower than 30%. Thus, the synthesized BAC may be developed further for CO₂ capture at flu gas conditions, i.e., relatively high temperature and low CO₂ concentrations.

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