

Study of CO₂ Adsorption Using Adsorbent Modified with Piperazine

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Adsorption of CO₂ was performed with an adsorbent impregnated with piperazine. The objective was to optimize the CO₂ adsorption capacity, via piperazine loading, moisture, adsorbent type and adsorption temperature. The surface morphology of the unmodified and impregnated activated carbon was characterized using a scanning electron microscope. There were only slight differences in the surface and pore size. A surface area analyser showed a decrease in surface area and pore volume of the micropore due to the pore blocking effect, but there was negligible change in the mesopore. A maximum piperazine loading of 3.12 wt % was impregnated on the activated carbon and was detected by a gas chromatography-flame ionization detector. The adsorption capacity of 4 % CO₂ on the unmodified activated carbon (Act.C), moisturized adsorbent, and 3.12 wt % piperazine loaded on activated carbon (Pz-Act.C) at room temperature and atmospheric pressure reached 16.47 mg/g, 6.12 mg/g, and 23.17 mg/g, respectively. It was found that moisture could deactivate the active sites of the adsorbent. The effects of temperature were also studied at 25 °C, 45 °C and 55 °C; the adsorption capacity decreased as the temperature increased due to the limitation of maximum piperazine loading of 3.12 wt %. The adsorption capacity of the adsorbents under the effect of temperature at 45 °C and 55 °C was 9.25 mg/g and 7.64 mg/g for Act.C, 3.64 mg/g and 2.95 mg/g for moisturized adsorbent, 12.63 mg/g and 8.76 mg/g for 3.12 wt % Pz-Act.C.

1. Introduction

The greenhouse gas (GHG) emission in the world has been increasing significantly, due to the energy industry and the transportation sector. It is widely accepted that carbon dioxide (CO₂) is the most important greenhouse gas with the largest impact on climate change (Shafeeyan et al., 2011). Carbon dioxide is not the gas that gives the most severe global warming impact among the greenhouse gases, but it has the highest annual emission into the atmosphere that makes it the most unavoidable anthropogenic GHG (Lee et al., 2012). In order to reduce greenhouse gas emission to the atmosphere, carbon capture and storage (CCS) strategy has been introduced. There are four main approaches to capture CO₂, including cryogenic distillation, membrane purification, absorption with liquids, and adsorption using solid. A widely developed technology to separate CO₂ from flue gas and natural gas stream is based on absorption using liquid amine. Piperazine is diamine which has been studied as promoter for amine system because it gives highest absorption rate of all alkanolamines (Cullinane and Rochelle, 2006). However, gas absorption using liquid amine has been used for CO₂ scrubbing on industrial scale for decades and with their number of shortcomings such as, severe corrosion to the equipment and regeneration of amine solution is highly energy intensive (Sayari et al., 2011). Therefore, to overcome their limitations, adsorption is considered as one of the potential options because of the low energy requirement, cost advantage, and ease of applicability over a wide range of temperature and pressures (Shafeeyan et al., 2010). There are numerous materials that can be used for CO₂ adsorption with respect to their differences in advantages and drawbacks, such as activated carbon, zeolite, mesoporous silicates, and metal oxides. Previous work studied on the synthesis and characterization of modified biopolymer with piperazine derivative for CO₂

adsorption (Saiwan et al., 2012). In this study, the adsorbent will be modified with piperazine to improve the adsorption rate and adsorption capacity.

2. Materials and methods

2.1 Materials

2.1.1 Activated palm shell based carbon, amine and based chemical

A commercial activated carbon; granular activated palm shell based carbon was supplied by Carbokarn Co., Ltd., (Thailand). Piperazine anhydrous (PZ, AR grade, $\geq 99\%$) with a molecular weight of 86.14 g/mol was obtained from Merck. Ethanol (AR grade, 99 %) with a molecular weight of 46.07 g/mol was obtained from RCI Labscan, Thailand.

2.2 Experimental setup

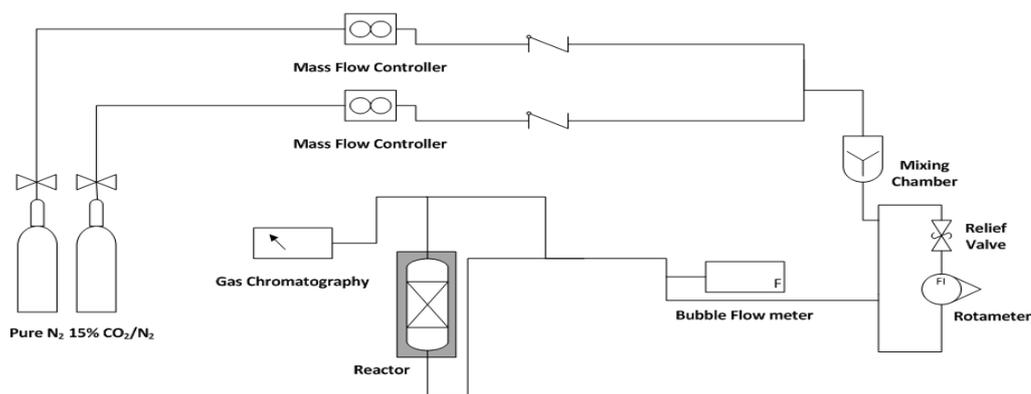


Figure 1: Schematic flow diagram for CO₂ adsorption.

In Figure 1, the outlet flow rate released from the gas cylinders is controlled by mass flow controllers before mixing premixed 15 % CO₂/N₂ with pure N₂ in the mixing chamber to obtain 4 % CO₂. The mixed gas is then controlled to a fixed pressure for ventilation and enabling a small quantity of 4 % CO₂ gas to pass through the rotameter which the flow rate will be adjusted to 5 mL/min determined by a bubble flow meter. Before testing CO₂ adsorption through the adsorption column, the 4 % CO₂ gas is analyzed by a gas chromatography-thermal conductivity detector (GC-TCD) in comparison with the calibration curve of CO₂ gas. The adsorption column is a tubular glass flow adsorber with an inner cell diameter of 4 mm, outer cell diameter of 6 mm, and 39 cm long. It is vertically oriented for the even distribution of adsorbent. The column, covered with a 40 cm long insulator wound with a heating tape, is used to maintain a stabilized temperature throughout the whole experiment. In the top 18.5 cm of the column, the adsorbent was packed and emplaced with glass wool at the top and the bottom to support the activated carbon, so the feed was running against gravity. The thermocouple was inserted at the bottom of the column to determine the temperature of internal column.

2.3 Activated carbon preparation

Granular size activated carbon was crushed and sieved to obtain a 20-40 mesh size followed by heating in a 60 °C oven for 6 h and kept in a desiccator at room temperature to avoid the moisture effect.

2.4 Impregnation process

The dry activated carbon was impregnated with 30 wt %, 40 wt % and 50 wt % piperazine. For the 30 wt % sample, 0.15 g of piperazine crystals were dissolved in 5 mL of ethanol until completely dissolved then mixed with 0.5 g of activated carbon. The mixture was mixed in a 50 mL beaker at 500 rpm using a magnetic bar on a stirring hot plate (C-MAG HS10 IKA®, USA) for 2 h. The top was sealed with parafilm. Next it was filtered using a suction pump. The impregnated piperazine was then dried in an oven at 60 °C for 1 ½ h to completely remove the ethanol. The procedure was repeated for the preparation of 40 wt % and 50 wt % with 0.2 g and 0.25 g of piperazine.

2.5 Moisturized activated carbon and impregnated activated carbon

The dry activated carbon and impregnated activated carbon were kept in the desiccators were equilibrated in a moisturized and close system for 20 h at room temperature.

2.6 Activated carbon beds and CO₂ adsorption measurement

Activated carbon beds used were unmodified activated carbon bed, impregnated activated carbon and moisturized activated carbon. The conditions for each experiment performed were 5 mL/min of 4 % CO₂ feed gas flow at room temperature (25 °C), 45 °C and 55 °C at an atmospheric pressure using 0.5 g of each prepared adsorbent in the adsorption column. Rt®-Q-BOND column with 0.53 mm id x 20 µm film thickness x 30 m length was used to operate at an isothermal temperature of 40 °C. The GC-TCD injection port was heated to 100 °C with a split flow of 8 mL/min and helium as a carrier gas. In typical CO₂ adsorption, 0.5 g of adsorbent is filled into a tubular flow glass adsorber column that was heating tape wounded around and covered with an insulator. After line cleaning-up, 0.5 g of adsorbent in the column was pre-dried at 60 °C for 1 h while purging with N₂ gas at 113 mL/min. Then, 4 % premixed CO₂ of dry gas at 5 mL/min was allowed to flow into the packed bed adsorber in order to carry out the experiment at room temperature and atmospheric pressure until the CO₂ concentrations of the feed gas at the outlet of adsorber reached equilibrium. The concentrations of CO₂ in the downstream in terms of chromatogram were continuously monitored using the WiniLab III V4.6 computer program. The dynamic adsorption capacity of the adsorbent (Q_{ads}) was calculated with Eq (1),

$$Q_{ads} = \frac{FC_0 t_q}{W} \quad (1)$$

where F (mol/min) is the total molar flow of feed gas, C₀ is the CO₂ concentration of the inlet stream, W is the mass of the solid adsorbent loaded in the column, and t_q (min) is the stoichiometric time which was determined from the breakthrough curve according to Eq (2) via MATLAB software version 7.10.0.499 (Guerreiro et al., 2010),

$$t_q = \int_0^{\infty} \left(1 - \frac{C_A}{C_0}\right) dt \quad (2)$$

where C₀ and C_A are the CO₂ concentrations of inflow and outflow gas stream of the column.

2.7 Characterization equipment

2.7.1 Surface area analysis

A surface area analyzer (Autosorb-1MP, Quantachrome, USA) was used to analyze the surface area of the adsorbent. The specific surface area, S_{BET}, was determined from the linear part of the Brunauer-Emmett-Teller (BET) equation and the calculation of pore size distribution was performed using the Barret-Joyner-Halenda (BJH) equation using the full isotherms method. These parameters were calculated to identify the effects before and after piperazine loading via the impregnation method.

2.7.2 Surface morphology

A scanning electron microscope (SEM; S-4800, Hitachi, Japan) was used to analyze the surface morphology of the adsorbent. The sample was placed on a carbon tape which was coated with platinum under vacuum. The SEM images were captured at a magnification of 2,000 and 100,000 to distinguish the pore site distribution of the activated carbon before and after piperazine loading via the impregnation method.

2.7.3 Thermal stability study

The thermal stability of the pure activated carbon and impregnated activated carbon was determined in a nitrogen atmosphere by thermogravimetric differential analysis (TG-DTA, Perkin Elmer Thailand Co., Ltd). 4–20 mg of sample was weighed on the heating pan in the chamber, then was heated at a ramping rate of 5 °C/min at room temperature with 90 mL/min of N₂ flow to 900 °C.

2.7.4 Degree of piperazine loading (wt %) on impregnated activated carbon

The impregnated activated carbon was crushed into fine particles, which was then weighed and dissolved with 5 mL of ethanol. The solution was heated to 60 °C and stirred at 250 rpm for an hour to complete the dissolution of piperazine from the activated carbon. After 1 h, the solution was cooled to room temperature then the volume was made up to 10 mL with ethanol. The fine particles of activated carbon were filtered using filter paper No. 1, then 0.04 µL of the filtrate was injected using a 0.5 µL syringe (SGC syringe) into the gas chromatography-flame ionization detector (GC-FID) via a heated injection port at 200 °C with the split flow of 10 mL/min using helium as a carrier gas. The DB® -5 column with 0.53 mm id x 1.0 µm film thickness x 30 m length was used to operate at an initial temperature of 50 °C, at a ramp rate of 10 °C/min to an isothermal temperature of 120 °C.

2.8. Characterization result

Figures 2 and 3 demonstrate the surface morphology of the non-impregnated activated carbon and 40 wt % piperazine-activated carbon (20–40 mesh size) at a magnification of 100,000 times. By comparison, there is only a slight difference in the surface and pore size. The scanning electron microscope was able to observe only the macropore (> 50 nm) and the mesopore (2–50 nm) whereas higher magnifications were needed for the micropore (<2 nm). To understand the surface morphology more precisely, surface area analysis was applied in order to distinguish the changes of the non-impregnated and impregnated activated carbon pore volume and pore size distribution. There is a decrease in the surface area and pore volume of the micropore with scarcely any change in the mesopore (Table 1). The decrease in the surface area could indicate that there was some amount of piperazine blocking in the micropore which resulted in a decrease in pore volume. The result supported the earlier SEM morphology that there was hardly change in the surface morphology for the macro and mesopore. However, from the result it can be assumed that 40 wt% piperazine did not entirely loaded into the pore site of the activated carbon because there was only a slight decrease in the pore volume of the micropore and not even in the mesopore.

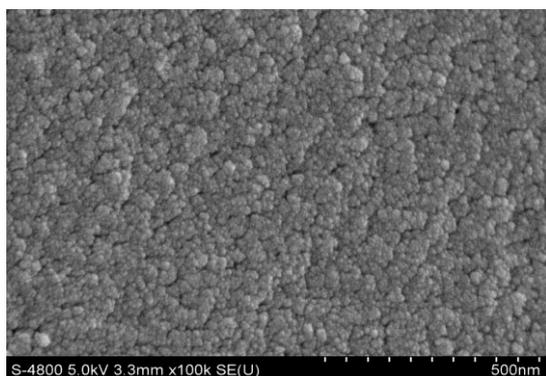


Figure 2: Non-impregnated activated carbon 20-40 mesh size magnified 100,000 times

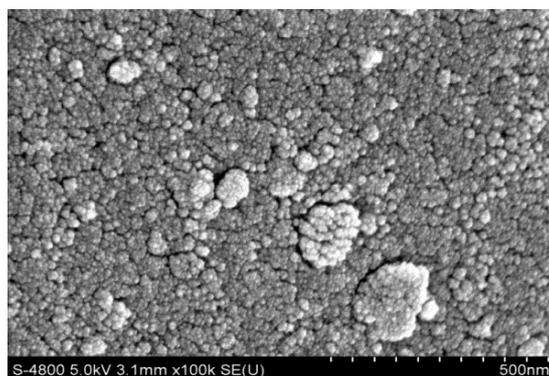


Figure 3: 40 wt % piperazine-activated carbon 20-40 mesh size magnified 100,000 times

Table 1: Surface area analysis of non-impregnated activated carbon and impregnated activated carbon

| Adsorbing bed | Surface Area (m ² /g) | | | Pore Volume (cc/g)·10 ⁻¹ | | | Average pore diameter (Å) |
|-------------------------------------|----------------------------------|----------|-----------|-------------------------------------|----------|-----------|---------------------------|
| | Total | Mesopore | Micropore | Total | Mesopore | Micropore | |
| Non-impregnated activated carbon | 801.9 | 745.2 | 764.0 | 4.43 | 2.57 | 3.79 | 22.10 |
| 40 wt % piperazine-activated carbon | 570.9 | 734.5 | 535.3 | 3.25 | 2.60 | 2.65 | 22.10 |

A calibration curve was done to determine the concentration of an unknown sample in the activated carbon by comparing with piperazine standards of known concentration. The result showed a maximum of 3.12 wt % of piperazine loaded on the activated carbon. The thermal stability of the piperazine, activated carbon, and 3.12 wt % piperazine-activated carbon were illustrated in Figure 4. Piperazine decomposes at 78.99 °C, impregnated 3.12 wt % piperazine-activated carbon decomposes at a higher temperature of 82.84 °C, and pure activated carbon decomposes at higher temperature than 900 °C.

3. Results and discussion

3.2 Breakthrough curve results

Figure 5 illustrates the breakthrough curves of pure activated carbon and impregnated 3.12 wt % piperazine activated carbon at different temperatures at an atmospheric pressure. These curves were obtained using the WiniLab III V4.6 program in the computer connecting to the GC-TCD displaying the amount of CO₂ % leaving the adsorber. The monitor displayed 0% in the beginning of the experiment as the CO₂ molecules were adsorbed by the surface and the pore sites until the saturation stage showing the S-shape and reached C/C₀ =1 at the equilibrium stage.

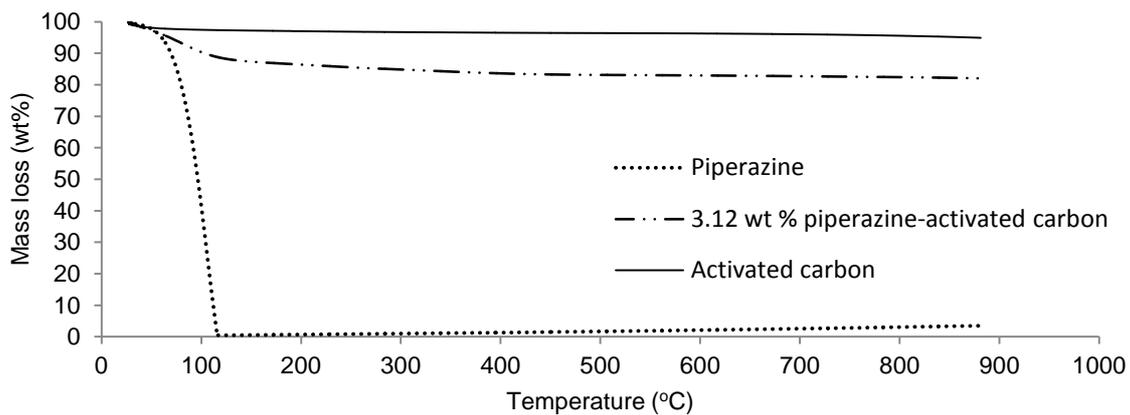


Figure 4: Thermal stability of piperazine, 3.12 wt % piperazine-activated carbon and pure activated carbon

From the result obtained, the increase of the adsorption temperature causes an early reach of the saturation stage. Carbon dioxide molecules are attached to the high surface area of the activated carbon by weak van der Waals force, which is a low heat of adsorption. Therefore, at an elevated temperature the attractive force between the surface of the activated carbon and the carbon dioxide molecules is reduced. The adsorption capacity (mmol/g) of the pure activated carbon at 25 °C, 45 °C and 55 °C is 0.3742, 0.2101 and 0.1737. The effect of the adsorption temperature on the 3.12 wt % piperazine-activated carbon indicates that the piperazine in the activated carbon in fact contributes adsorption which enhances the physisorption of the unmodified activated carbon at different temperatures. The carbon dioxide adsorption capacity drops gradually when the temperature increases. It is assumed that physisorption still dominates chemisorption at the elevated temperature due to the limitation of maximum piperazine loading of 3.12 wt %. The adsorption capacity (mmol/g) of 3.12 wt % piperazine-activated carbon at 25 °C, 45 °C and 55 °C is 0.5266, 0.2870 and 0.1990, respectively. However, the moisturized activated carbon results in a rapid saturation stage with a dramatic decrease in the carbon dioxide adsorption capacity. The adsorption capacity (mmol/g) of the moisturized activated carbon at 25 °C, 45 °C and 55 °C is 0.1390, 0.0826 and 0.0670, respectively. This indicates that the moisture could have deactivated the active sites of the activated carbon.

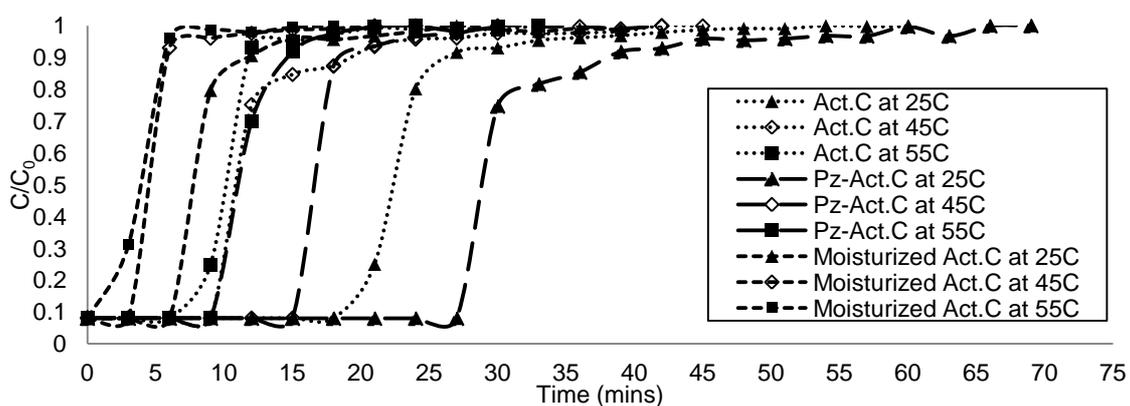


Figure 5: Breakthrough curves of activated carbon (Act.C), piperazine-activated carbon (Pz-Act.C), and moisturized activated carbon at 25 °C, 45 °C and 55 °C at an atmospheric pressure

4. Conclusion

Activated carbon beds adsorption capacity enhanced significantly after impregnation with piperazine. Although the excellence of piperazine did not reveal entirely due to the limitation of piperazine loading of 3.12 wt % as the physisorption still dominates the chemisorption. The highest CO₂ adsorption capacity improvement reaches as high as 40.73 % for Pz-Act.C in comparison with pure Act.C at room temperature. The moisturizing effect did not facilitate the adsorption but worsened the adsorption.

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