Towards CO_2 Adsorption Enhancement via Polyethyleneimine Impregnation

Supasinee Pipatsantipong, Pramoch Rangsunvigit, Santi Kulprathipanja

***Abstract*—**To reduce the carbon dioxide emission into the atmosphere, adsorption is believed to be one of the most attractive methods for post-combustion treatment of flue gas. In this work, activated carbon (AC) was modified by polyethylenimine (PEI) via impregnation in order to enhance CO_2 adsorption capacity. The adsorbents were produced at 0.04, 0.16, 0.22, 0.25, and 0.28 wt% PEI/AC. The adsorption was carried out at a temperature range from 30 °C to 75 °C and five different gas pressures up to 1 atm. TG-DTA, FT-IR, UV-visible spectrometer, and BET were used to characterize the adsorbents. Effects of PEI loading on the AC for the CO_2 adsorption were investigated. Effectiveness of the adsorbents on the CO_2 adsorption including CO_2 adsorption capacity and adsorption temperature was also investigated. Adsorption capacities of CO_2 were enhanced with the increase in the amount of PEI from 0.04 to 0.22 wt% PEI before the capacities decreased onwards from0.25 wt% PEI at 30 °C. The 0.22 wt% PEI/AC showed higher adsorption capacity than the AC for adsorption at 50 °C to 75 °C.

***Keywords*—**Activated Carbon, Adsorption, CO_2, Polyethyleneimine

I. Introduction

GLOBAL warming isprimarily dueto therapid increase concentration of greenhouse gas like carbon dioxide (CO_2) in the atmosphere. With its impact on environmental problems, CO_2 is considered as the most important greenhouse gas for the global climate change [1]–[2]. CO_2 is produced from flue gas, separated from synthesis gas, fossil/biomass gasification gas, and reformate, or captured from atmospheric air. CO_2 in the gas product reduces significantly the energy content of the gas and decreases the efficiency in the transportation, storage, and any application of the product hydrogen [1], [3].

Capture and sequestration of CO_2 has been recognized as one of the alternatives to reduce CO_2 emission[4]–[6]. There are several techniques, such as liquid solvent absorption, cryogenic techniques, membrane separation, solid sorbents adsorption, pressure (and/or temperature) swing adsorption, and vacuum (and/or temperature) swing adsorption available for the CO_2 separation and CO_2 recovery emitted by power plants [1], [7]–[10].

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The most widely used processes in CO_2 capture plants are amine-based processes and wet scrubbing systems [11]. However, there are associated with many problems. For example, the large amount of heated water leads to the use of a lot of energy in these systems [12]. In addition, amine degradation by oxidation leads to corrosion of process equipment [13]. The cost of CO_2 sequestration process is considered because it accounts for tentatively three-fourths of the total energy cost for CO_2 separation. Therefore, the development of cost-effective techniques for CO_2 separation is essential [14].

Adsorption is recognized as one of the alternatives because of the low energy consumption, cost-effective, and the wide range of operating temperatures and pressures [15]. However, the achievement of this approach depends on the regeneration and adsorbent life with high CO_2 selectivity, adsorption capacity, and adsorption/desorption kinetics for CO_2[14].

Pichaichanlert [16]used activated carbon (AC) and AC modified with monoisopropanolamine (MIPA), n-methyethanolamine (NMEA), piperazine and K_2CO_3 by an impregnation method. XRD, BET, and TGA characterization were used to confirm the formation of amine and K_2CO_3 on the activated carbon. The activated carbon modified with different types of amine especially piperazine and MIPA showed improvement in the CO_2 adsorption at moderate temperatures over the unmodified activated carbon. The results of K_2CO_3 loading on the activated carbon showed high adsorption capacities at 30 °C but its effectiveness decreased with the increase in the temperature.

A high-capacity and high-selective CO_2 adsorbents based on a modified AC with polyethyleneimine (PEI) was reported [1]. Polyethyleneimine (PEI) is a good polymer with its affinity towards gas molecules, especially CO_2 molecule because there are many nitrogen atoms in the molecule to react with CO_2 [17].

As a part of our continuing effort in the development of the surface modification on activated carbon to increase CO_2 adsorption capacity at high temperatures, effects of using polyethyleneimine (PEI) as a modification agent were investigated.

II. Experimental

A. Preparation of Adsorbents

The AC produced from coconut shell (supporting from Carbokarn Co., Ltd.) was sieved to sizes ranging from 20 to 40 mesh and oven dried at 120 °C for 6 hrs before impregnation process. PEI with average molecular weight 600,000–1,000,000 g/mol obtained from Sigma-

Aldrich(catalog no. 03880) as a 50 wt% aqueous solution was used as the impregnation material. For the impregnation process, the AC was divided in 1 g portions and placed in vials containing 20 ml of PEI solutions with initial concentrations of 0.1–2.0g/L. The AC together with the PEI solutions wasagitated in an orbital shaker at 180rpm and 25°Cfor 3 days. Finally, adsorbents were dried at 120 °C for 3 hrs. PEI concentrations were analyzed by measuring their absorbances at 203 nm via a Shimuszu/UV-1800 UV-Vis spectrometer. The amount of PEI adsorbed was calculated using simple mass balance calculation.

B. *Characterization of Adsorbents*

Surface areas and pore volumes of the adsorbents were measured with the BET method on a Quantachrom/Autosorb1-MP instrument.Perkin-Elmer/Pyris Diamond TG-DTA instrument was used to study thermal decomposition of adsorbents in order to evaluate the actual amount of loading.The surface organic spectra were measured with the Thermo Nicolet/Nexus 670 FTIR instrument.

C. *Adsorption Measurement*

The schematic diagram of the experimental set-up is shown in Fig. 1. A pressure transmitter was installed to measure pressure of the system. One gram of the prepared adsorbent was loaded into the stainless steel adsorption chamber, which was heated by the furnace in order to reach the adsorption temperatures. He (Ultra high purity, Praxair Inc.) was used asa purge gas in this study. The adsorption processes werecarried out using high purity CO_2 gas (99.99%). Effects of adsorption temperature were investigated by varying the temperature from 30 to 75 °C within a pressure range of 0–1 atm. The temperature of the adsorption chamber was adjusted and maintained by an internal temperature sensor.

III. Result and Discussion

A. *Characterization*

Activated carbon (AC) and modified AC were characterized by thermogravimetry/different thermal analysis (TG/DTA), Brunauer-Emmett-Teller (BET) gas adsorption analysis, and Fourier transform infrared spectroscopy (FTIR). Surface area, pore volume, and pore diameter of the adsorbents are shown in Table I. AC shows a specific surface area of 1,325 m^2/g, a pore volume of 0.4757 cm^3/g, and a pore diameter of 13.40 Å. The modified AC with polyethyleneimine (PEI) has similar surface area, pore volume, and pore diameter. This result suggests that the amount of PEI on the AC does not affect the AC surface properties.

TABLE I
Surface Area, Pore Volume, and Pore Diameter Analysis of Adsorbents

Adsorbents	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore Diameter (Å)
AC	1,325	0.4757	13.40
0.04 wt% PEI/AC	1,288	0.4620	13.20
0.16 wt% PEI/AC	1,248	0.4488	13.20
0.22 wt% PEI/AC	1,225	0.4406	13.18
0.28 wt% PEI/AC	1,177	0.4226	13.16

Fig. 2 shows the nitrogen adsorption isotherms of AC, 0.04 wt% PEI/AC, 0.16 wt% PEI/AC, 0.22 wt% PEI/AC, and 0.28 wt% PEI/AC at -196 °C. These results suggest that a high volume of nitrogen is adsorbed within the relative pressures range of 0 – 0.2. And the maximum value of adsorbed nitrogen shows at the relative pressure lower than 0.3 for all three adsorbents. It can be assumed that the three adsorbents are almost 100% micropores.

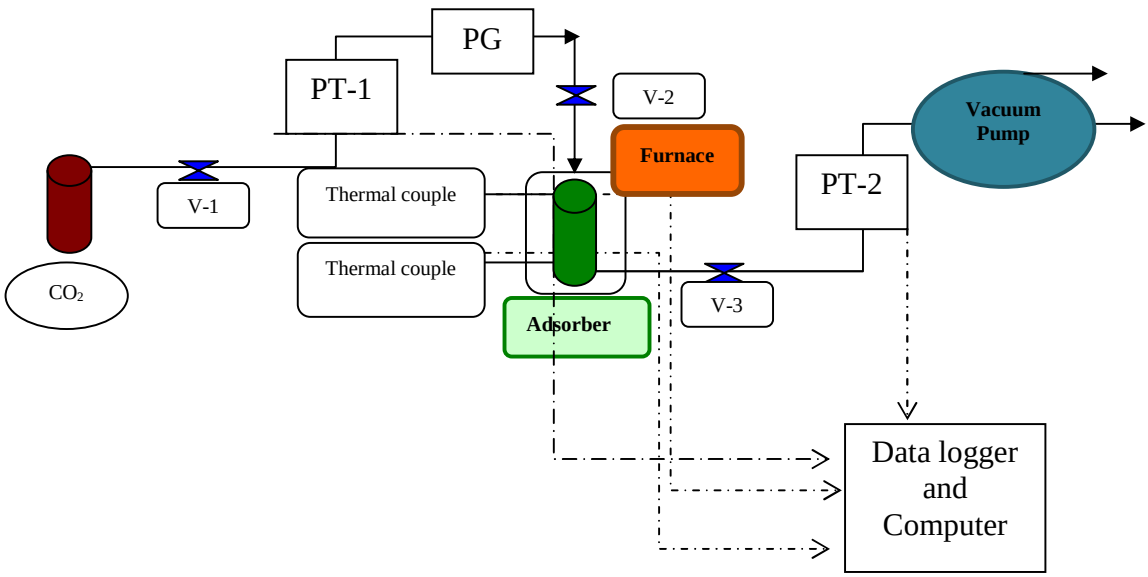

Fig. 1 Schematic of the experiment set-up

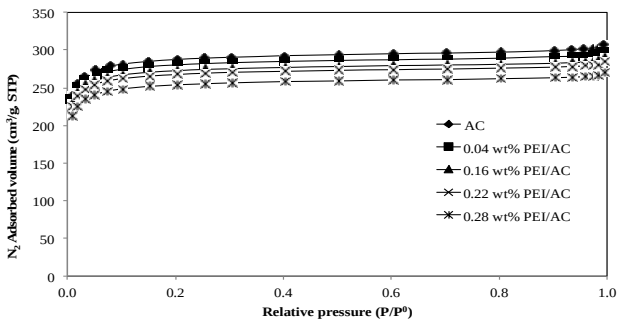

Fig. 2 Nitrogen adsorption isotherms of AC and modified AC

The FTIR transmission spectra of AC, 0.04 wt% PEI/AC, and 0.16 wt% PEI/AC are shown in Fig. 3. The band at 1,480 cm^{-1} represents the N–H bond, in which its slight increase in the transmittance for the PEI-impregnated samples compared to AC as PEI contains NH_3 group [18]. The band at 2,360 cm^{-1} is usually ascribed to the single C–H bond, which decreases in the transmittance for the PEI-impregnated samples [19]. From this observation, it can be assumed that PEI-impregnation decreases the ratio of the C–H bonds. The reduction of the C–H bond indicates the relative reduction in the presence of these generally hydrophobic bonds, which enables the more hydrophilic N–H bonds to be attached on the AC. The broad band from 2,400 to 2,900 cm^{-1} is due to the presence of aliphatic groups of the adsorbed long chained-PEI [20].The stretching vibrations from approximately 3,450 to 4,000 cm^{-1} are possibly due to the presence of surface hydroxylic groups and chemisorbed water [21]. These results confirm that PEI was successfully loaded on the AC.

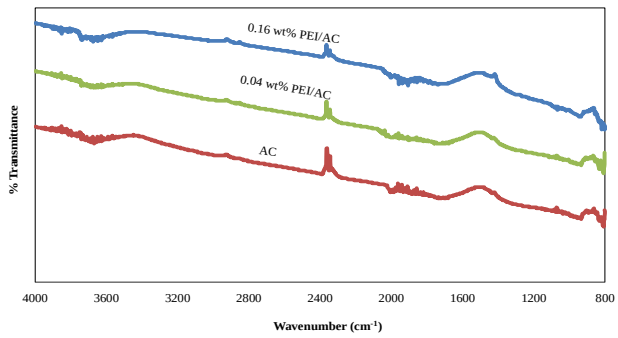

Fig. 3 FTIR transmission spectra of unmodified and modified AC

TG/DTA analysis was used to investigate the strength and amount of adsorbed water and CO_2 on the AC. In Fig. 4, the TGA profile of the AC is shown. There are two steps with distinct weight loss. The first step, the weight loss at 85.5 °C can be attributed to the desorption of moisture and volatile components. The weight loss above 250 °C can be attributed to decomposition of the AC [2].

The TGA profile of PEI (50 wt% in water) is shown in Fig. 5. There are two steps with distinct weight loss at 107.8 and 324.5 °C. The temperature at 107.8 °C indicates the maximum desorption of water. And the temperature at 324.5 °C indicates the maximum decomposition of PEI.

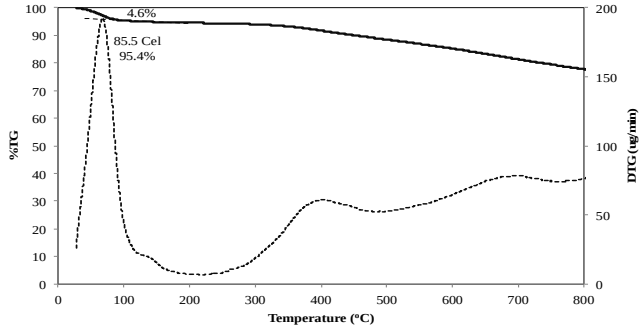

Fig. 4 TGA profile of AC; dTG(---), TG(—)

The amounts of PEI impregnated on AC were measured via the UV-visible spectrometer (203 nm.) are shown in Table II.

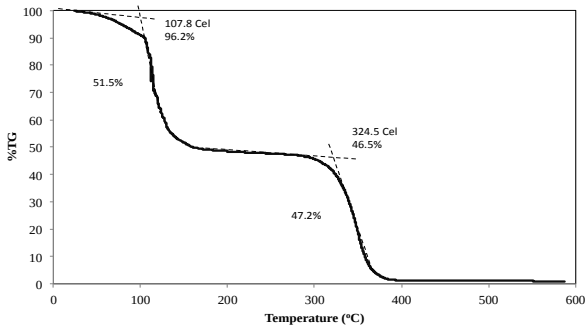

Fig. 5 TGA profile of PEI (50 wt% in water)

TABLE II
AMOUNT OF PEI IMPREGNATED ON THE AC

Initial concentration of PEI solution (g/L)	PEI impregnated on AC (wt% PEI/AC)
0.1	0.04
0.5	0.16
1.5	0.22
1.75	0.25
2.0	0.28

B. *Effects of PEI Loading on the CO_2 Adsorption*

The adsorption capacity of adsorbents strongly depends on the amount of micropores of a specific diameter present in AC as well as their volume. Fig. 6 shows separately the isotherms of CO_2 on AC and modified AC samples at 30 °C and 0 to 1 atm pressure. It can be seen that the amounts of CO_2 adsorbed on all modified AC samples increase with the increase in the amount of PEI from 0.04 to 0.22 wt% PEI. This is not unexpected as the results correspond with the increase in the nitrogen-containing group, which, in turn, increases the CO_2 adsorption. However, the adsorption capacity decreases when the amount of PEI is increased to 0.25 wt% and higher. This may be attributed to the pore filling effect that blocks the pores of adsorbent preventing CO_2 to diffuse into the pores [5], [22]. Accordingly, the adsorption process takes place only the surface of the adsorbent. More importantly, it can be

observed that the AC has higher CO_2 adsorption capacity than the AC modified with PEI. It indicates that physical adsorption dominates the CO_2 adsorption on the AC.

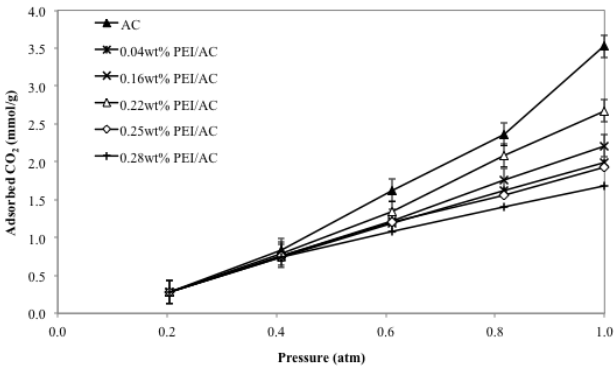

Fig. 6 CO_2 adsorption isotherms of AC and AC modified with PEI in different loadingat 30 °C

C. *Effects of Temperature on the CO_2 Adsorption*

At the elevated temperatures (50 and 75 °C), the modified AC shows higher adsorption capacities than the AC at the same temperature. In Fig. 7–8, at the beginning, the adsorption capacities of all samples are very close. When the pressures are increased, the adsorption capacities of the AC modified with 0.22 wt% PEI are significantly higher though the surface area and pore volume are lower than the AC. It implies that chemical adsorption dominates the CO_2 adsorption on the modified AC. The results confirm that the increase in the temperature facilitates the transfer of the adsorbed CO_2 molecules from the surface into the bulk of PEI by overcoming the kinetic barrier [23]. On the other hand, further increase in the temperature above 75 °C reduces the CO_2 adsorption capacity, as the control of the adsorbed shifts from the kinetic behavior to the thermodynamic behavior [24].

The adsorption capacities of AC at 75 °C have the same trend and are close to the adsorption capacities at 50 °C. On the other hand, the AC modified with 0.22 wt% PEI at 30 °C has higher CO_2adsorption capacity than that at 50 and 75 °C.

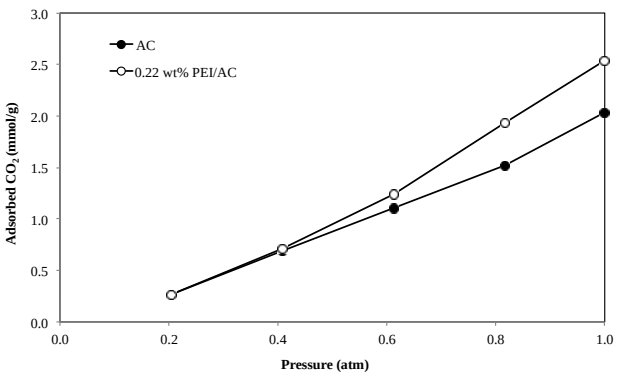

Fig. 7 CO_2 adsorption isotherms of AC and AC modified with 0.22 wt% PEI/AC and at 50 °C

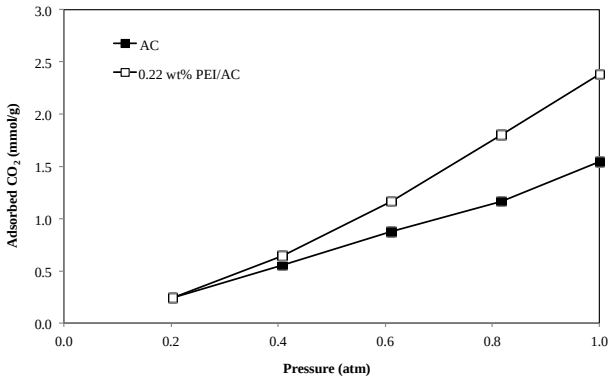

Fig. 8 CO_2 adsorption isotherms of AC and modified AC with 0.22 wt% PEI/AC and at 75 °C

IV. Conclusion

In summary, AC produced from coconut shell modified with PEI-impregnated has been developed in our laboratory for CO_2 capture. CO_2 adsorption capacity was enhanced with the increase in the amount of PEI from 0.04 to 0.22 wt% PEI before the capacity decreased onwards for 0.25 and 0.28 wt% PEI at 30 °C under 1 atm. However, the AC gives a higher adsorption capacity of CO_2 than AC modified with 0.22 wt% PEI. The AC modified with 0.22 wt% PEI showed higher CO_2 adsorption capacity than the AC at 50 and 75 °C. It can confirm that the AC modified with PEI can enhance the CO_2 adsorption capacity at the high temperatures.

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