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CO_2 CAPTURE ON AMINE FUNCTIONALIZED BAMBOO-BASED ACTIVATED CARBON

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Abstract

Agricultural residues were produced more than 4.9 x 10^7 ton per year. In Thailand, a huge of bamboo was used in various industries, such as food industry, furniture industry, construction, etc. A large amount of bamboo residues were overlooked. Then the utilization of bamboo residues for capturing greenhouse gases, especially carbon dioxide (CO_2), was investigated in this research. CO_2 is one of the major greenhouse gases which is emitted from conventional combustion of hydrocarbon fuels. It has been realized that CO_2 plays a crucial role in global climate change. The effect of activation the bamboo to enhance its performance of CO_2 capture were studied here. For physical activation, the bamboo was then heated under CO_2 atmosphere at various temperatures. For chemical activation, the bamboo were soaked in an acidic solution at various ratios of H_3PO_4 acid to bamboo. Moreover, the effect of tetraethylenepentamine (TEPA) functionalization on the performance of CO_2 capture was also mentioned. The bamboo samples were characterized by FT-IR, N_2 adsorption/desorption, and CHN analyzer. The experiments were done at atmospheric pressure in a temperature range of 90-110 °C. It was found from the experimental results that the maximal performance of CO_2 capture of bamboo-based activated carbon was shifted to higher temperature after TEPA functionalization.

Keywords: Bamboo, activation, CO_2 capture, tetraethylenepentamine

Introduction

Now a day, Global warming has been concerned because CO_2 emission tend to increase. CO_2 was mainly emitted from fossil fuel such as oil, coal and natural gas. After the 21st United Nations Climate Change Conference in Paris in 2015, COP21 agreement sets a new benchmark − limit the rise of global average temperature to well below 2 °C [1]. To approach the new benchmark, it is necessary to reduce the level of CO_2 content in the atmosphere. Industrially, to figure it out, liquid amine solution was used in industries to absorb CO_2 from the gaseous effluent. Despite of high efficiency up to 98 %, heavy consumption of amine-based solvent contributes toward equipment corrosion. Hence, special materials for equipment construction which can withstand corrosively of these chemicals are required [2]. Many efforts have been dedicated to develope technologies for CO_2 removal such as cryogenic separation, chemical separation, membrane separation and adsorption method. Among the various chemical and physical methods available for CO_2 removal, adsorption is one of the common methods with its cost effective [3]. At room temperature, CO_2 is strongly adsorbed on microporous solids such as zeolites and activated carbons. The activated carbons are insensitive to moisture. It shows high adsorption capacity at ambient pressure but moderate adsorption strength [4]. In Thailand, bamboo was used as a raw material in various industries, such as food industry, furniture industry, construction, etc. Then a large amount of bamboo residues was produced and overlooked. In this research, the utilization of bamboo based carbon black for capturing greenhouse gases, especially carbon dioxide (CO_2), was then investigated at atmospheric pressure in a temperature range of 90-110 °C. To enhance its performance of CO_2 adsorption, physical activation and chemical activation were carried out. For physical activation, the bamboo based carbon black were activated under CO_2-flow atmosphere at various temperatures. For chemical

activation, the carbon black were soaked in an acidic solution at various H_3PO_4 acid to bamboo ratios. The effect of tetraethylenepentamine (TEPA) functionalization on the performance of CO_2 capture was also mentioned. The bamboo samples were characterized by means of FT-IR, N_2 adsorption/desorption, and CHN analyzer.

Materials and methods

Materials

All chemical used were of analytical grade. Bamboo based carbon black (BB) was supplied from CU Research Center, Saraburi province, Chulalongkorn University. TEPA was obtained by Sigma-aldrich. Methanol (ACI Labscan) was used as solvent in TEPA solution. H_3PO_4 acid (J.T.Baker), CO_2 gas (99 %) and N_2 gas were used as activated agents. The helium with ultra-high purity grade (UHP 99.999 %) was used for pretreatment of adsorbent. The mixed gas CO_2 30 % in helium was used as gaseous influent. Distillated water was used in experiments.

Methods

Sample preparation

In case of physical activation, 6 g of BB was placed in a horizontal tube furnace under N_2 flow of 150 ml/min at 200 °C for 2 hr. After that, switching to CO_2 stream of 100 ml/min, the BB was then heated up to the desired temperature (600, 700 and 800 °C) for 30 min. The activated samples obtained were noted as BB600, BB700 and BB800, respectively. In case of chemical activation, 6 g of BB700 was soaked in 45 ml acidic solution at various BB700/H_3PO_4 ratios (1:0.5, 1:1 and 1:2). The sample was heated at 110 °C in an oven for 8 hr. to remove the excess water. After that the dried sample was placed in a horizontal tube furnace and heated up to 500 °C for 1 hr under N_2 flow of 150 ml/min. The sample was washed by 1M KOH to remove phosphate species and followed by distilled water to neutralize. Finally, the sample was dried in an oven at 100 °C for 8 hr. For TEPA functionalization, the samples were prepared by incipient wetness impregnation. 10 ml of methanol was added to the physical- and chemical- activated BB. TEPA with the desired amount loading (%wt.) was added to the samples. The sample was placed in an oven at 70 °C for 8 hr.

CO_2 procedure

CO_2 adsorption was studied by measuring the breakthrough curve with a gas–solid adsorption column as shown in Fig. 1. 0.4 g of the sample was packed in adsorption column. To remove moisture and gaseous nuisance, helium was routed to the reactor for 40 min at 100 °C. After that, cooling down to the desired operating temperature, the feed was then switched to 30% v/v CO_2 in helium balance. The operating temperature is in a range of 30 °C to 110 °C. The influent and effluent was detected by GC-2014 Shimadzu gas chromatography.

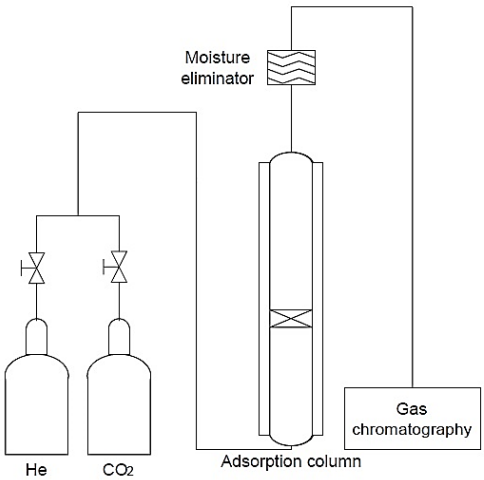

Figure 1 Experimental set-up for gas – solid adsorption column

Sample characterization

FTIR spectra of the samples were obtained in the 400–4000 cm^{-1} range by Perkin–Elmer Fourier Transform Infrared Spectrophotometer with the KBr pellet technique. The specific surface area was determined by a Micromeritics ASAP 2020 analyzer. The collected data were subjected to the Brunauer, Emmett, and Teller (BET) treatment. The C, H, and N elemental analyses were carried out using CHNS analyser EA 2400 Series II.

Results and discussion

Characterization

Fourier transform infrared transmission spectra were used to evaluate the functional group at the surface of sample as shown in Fig. 2. The IR band of 3430 cm^{-1} indicated a presence of hydroxyl group. The IR band of 1670 cm^{-1} represented to C=O carboxylic acid (conjugated, aromatics). The IR band of 1630 and 1580 cm^{-1} corresponded to C=C stretch aromatic. The IR band of 1110 cm^{-1} inferred to C-O alkoxy and The IR band 875 and 800 cm^{-1} represent to aromatic and sp2 C-H bend, respectively. In case of amine impregnation, the spectrums of 2930 cm^{-1} and 2820 cm^{-1} corresponded to aldehyde C-H stretch. The strong IR band of 1655 cm^{-1} showed characteristic of amine group such as C=N stretch and N-H bend. The IR band of 1570 cm^{-1} and 1460 cm^{-1} represented to asymmetric bending vibration of $-NH_2$ and symmetric bending vibration of $-NH_2$, respectively [5]. Likewise, the IR band of 1390 cm^{-1} presented sp3 C-H bend. The IR band of 1320 cm^{-1} also corresponded to C-O acyl and phenol. Finally, the IR band of 1170-1140 cm^{-1} reflected to C-O alkoxy. Then, it can be said that TEPA was successfully impregnated on activated carbon.

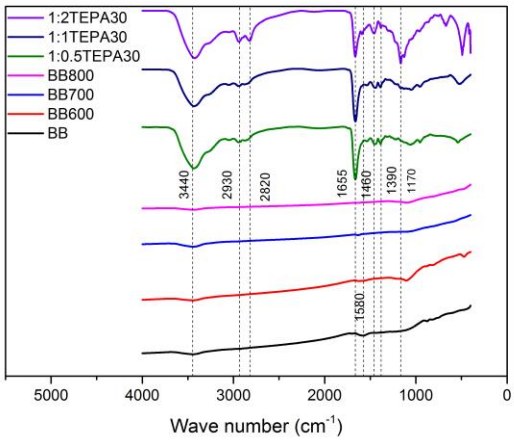

Figure 2 FT-IR spectra of the adsorbents

Textural properties of BB, BB600, BB700 and BB800 were shown in Table 1. The highest BET surface area is 526.70 m^2/g. BET surface area, total pore volume and micropore volume were increased when increasing the activation temperature. During CO_2 activation, porosity is developed by carbon gasification at elevated temperature due to the reaction "$C+CO_2 \rightarrow 2CO$". CO_2 reacts with the carbon in bamboo at elevated temperature. This process of gasification develops more porosity and higher surface area. [6]

Table 1 : Textural properties of the samples.

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore size (Å)
BB	24.92	0.051	0.0001	83.449
BB600	196.61	0.110	0.073	32.543
BB700	275.52	0.160	0.125	53.327
BB800	526.70	0.272	0.228	24.652

Element composition of samples were represented in Table 2. It can be seen that level of C content was decreased when increasing the BB700/H_3PO_4 ratio. H_3PO_4 reacts with carbon in bamboo. It creates more porosity and may also defected C atom. H_3PO_4 reacts with the char to produce volatile matters which diffuse quickly to the outer part of the particles during the chemical activation. Therefore, at higher BB700/H_3PO_4 ratio the gasification of surface carbon atoms becomes predominant and leads to a decrease of carbon yield [7]. Moreover, during H_3PO_4 chemical activation, the functional group on the surface of adsorbents and the delocalized electrons in its structure was then changed and led to the change in the surface properties especially its acidic and basic character. This has a significant effect on its adsorption capacity.

Table 2 show element composition of carbon samples.

Sample	C (%)	H (%)	N (%)	O (%)
BB	80.20	2.43	0.94	16.03
BB600	77.31	1.82	0.65	19.95
BB700	84.78	1.39	0.92	12.74
BB800	79.77	1.04	0.73	18.35
1:2TEPA30	57.38	3.02	8.17	30.92
1:1TEPA30	68.49	3.19	7.93	19.92
1:0.5TEPA30	70.51	3.07	7.66	18.31

CO_2 adsorption capacity

The effect of CO_2 activation was studied at various temperature levels, as shown in Fig 3. It can be seen that the CO_2 adsorption capacity decreased obviously when increasing in temperature. This adsorption behavior represents to the characteristic of physical adsorption. Among the adsorbents, BB800 expressed the highest CO_2 adsorption capacity of 1.9 mmol/g at 30°C on BB800. To obtain higher adsorption capacity at higher temperature, amine functionalization was then applied to BB800 (not shown here). It found that the capacity was dropped dramatically since its micropores were fulfilled and led to no diffusion of CO_2 to the active sites.

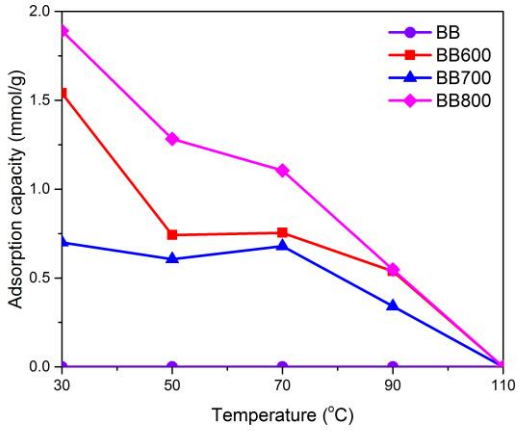

Figure 3 CO_2 adsorption capacity of BB with physical activation at different levels of adsorption temperature

To enlarger the size of the micropores and to encourage the adsorption capacity at higher temperature, combination of H_3PO_4 chemical activation and amine functionalization were then applied to BB700. Effect of H_3PO_4 acid activation was investigated, as shown in Fig.4. When the BB700/H_3PO_4 ratio decreased from 1:1 to 1:0.5, it was obvious that the CO_2 adsorption capacity decreased. The possible reason to explain is that $H_{n+2}P_nO_{3n+1}$ dehydrates and transforms into P_4O_{10} which presents various crystalline polymorphs. P_4O_{10}, which behaved as an oxidant, reacted with carbon, forming new pores, widening the existing pores and producing CO_2 [8]**.** It can be found from the results that, among the adsorbents, 1:1TEPA30 expressed the highest CO_2 adsorption capacity. When increasing operating

temperature from 30 °C to 70 °C, the capacity was then increased. Further increasing temperature, the capacity was then dropped. The maximum capacity of 0.7 mmol/g was obtained at operating temperature of 70 °C. However 1:2TEPA30 expressed the higher capacity of 0.72 mmol/g at 90 °C.

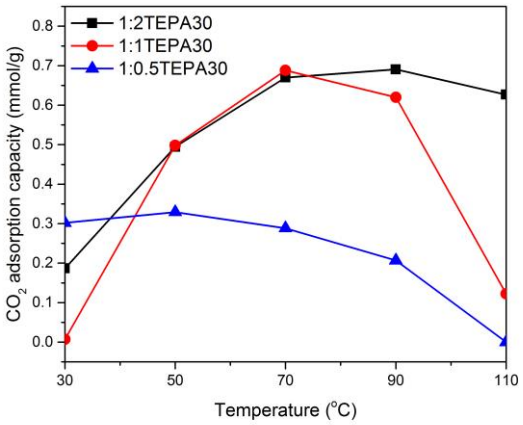

Figure 4 CO_2 adsorption capacity of 1:2TEPA30, 1:1TEPA30 and 1:0.5TEPA30 at different adsorption temperatures

Conclusion

CO_2 adsorbents were successfully prepared from bamboo-based carbon black. The highest CO_2 adsorption capacity is 1.9 mmol/g for BB800 adsorbent due to its higher BET surface area (526.70 m^2/g). However its capacity was dropped dramatically when impregnating of TEPA. It could be explained that the micropores were fulfilled and led to no diffusion of CO_2 to the active sites. To enlarger the micropores size and to encourage the adsorption capacity at higher temperature, combination of H_3PO_4 chemical activation and amine functionalization were then applied to BB700. BB700 with H_3PO_4 chemical activation at the ratio of 1:2 and loading of TEPA at 30 %wt. expressed the higher capacity of 0.72 mmol/g at 90 °C. The capacity was then increased around 2.4-folder, comparing the one without combination of H_3PO_4 chemical activation and amine functionalization

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