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Biogas improving by adsorption of CO_2 on modified waste tea activated carbon

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A B S T R A C T

Activated carbon (AC) was prepared from waste tea (WT) and the obtained product, WTAC, was modified with ethylenediamine (MWTAC). Unmodified and modified WTAC samples were characterized in terms of structural, morphological and chemical properties. Carbon dioxide (CO_2) adsorptions from pure CO_2 and swine farm biogas of WT, WTAC and MWTAC were investigated to determine the effect of activation and modification as well as the effect of methane in real swine farm biogas on the CO_2 adsorption performances. The adsorption capacities of pure CO_2 on the WT, WTAC and MWTAC were 15.39, 87.42 and 108.97 mg/g, respectively, while the adsorption capacities of 40% CO_2 from swine farm biogas were 4.22, 60.64 and 78.98 mg/g, respectively, indicating that modified AC leads to a higher CO_2 adsorption capacity. In addition, density functional theory (DFT) calculations revealed that the adsorption energies for graphene + CO_2, unmodified AC + CO_2 and modified AC + CO_2 models were −7.53, −50.74 and −65.21 kJ/mol, respectively, indicating the modified AC model led to a higher adsorption than that of the unmodified AC and graphene models, owning to hydrogen bond and dispersion interactions between the CO_2 molecule and more active atoms on the surface of the modified AC model.

1. Introduction

Nowadays, high energy demand has led to an increasing interest in finding alternative energy sources. Biogas is an interesting alternative energy because it can be produced from anaerobic digestion of different types of sources of waste such as farm/manure waste, industrial waste, municipal solid waste, and household. The composition of biogas is a mixture of different gases, including methane (CH_4 of 55–80%), carbon dioxide (CO_2 of 20–45%), moisture and other impurities [1–3]. Methane has a high colorific value (37.78 MJ/m^3), making biogas a good renewable energy source [4]. Nevertheless, in the case of biogas, the main drawback is its high content of carbon dioxide (it might be as high as 40% or more) which significantly reduces its heating capacity [5]. Therefore, for biogas to be used, an intensive study on how to reduce the CO_2 content is needed [3–6].

To remove CO_2 in biogas, several techniques have been proposed to capture CO_2 [7–9]. Adsorption is a widely used technology for gas treatment due to its versatility, efficiency, minimal environmental impact and low cost [10–12]. Among all adsorbents, activated carbons (AC) have been proposed as a suitable alternative for CO_2 capture because activated carbons are inexpensive, less sensitive to moisture, present a high CO_2 adsorption capacity at ambient pressure and have a large surface area [13–15].

3. ACs are commonly prepared from agricultural wastes [16–18] because they are low cost, easily available and added value of wastes. Waste tea is one of the best alternative low-cost materials for AC preparation since it has a high amount of organic content [19–21], is locally available, there is a high amount of waste material from coffee shops and small sample sizes that are easily prepared. The surface of the activated carbon can be modified to increase the specific adsorption capacity. Increasing basic functionality of adsorbents can be carried out through: modification of surface oxygen functionalities, adsorbent basal planes, functionalization with nitrogen containing compounds (NH_3, amines etc.), and decomposition of surface acidic functional groups through calcinations [22–24]. Recently, there are several excellent

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researches about the removal of CO_2 by modified activated carbon as an adsorbent [25,26], while the amine modification of adsorbents for capturing CO_2 is a promising way of evacuating it from flue gases [26–28]. In addition, amine modified adsorbents have high selective adsorption and high rate of diffusion of the CO_2 molecule [29,30]. Ethylenediamine, a nitrogen containing compounds, modification on AC for capturing CO_2 is used in the present study.

In this research work, waste tea (WT) was chemically activated by KOH and combusted at 500 °C to obtained activated carbon (WTAC) and the WTAC was modified with ethylenediamine to obtained modified activated carbon (MWTAC). WTAC and MWTAC samples were characterized in terms of structural, morphological and chemical properties. Carbon dioxide (CO_2) adsorptions from pure CO_2 and swine farm biogas of WT, WTAC and MWTAC were investigated to determine the effect of activation and modification as well as the effect of methane in real swine farm biogas on the CO_2 adsorption performances. In order to compare and understand the interactions of the chemical structure of one pristine graphene sheet (GP), the pore structure of pristine graphene which represents activated carbon (WTAC_P), the effect of C–OH functional group on the surface of pore AC (WTAC_F) as well as the influence of EDA modified AC (MWTAC) between before and after interacting with CO_2 and CH_4 molecules were examined. Note that theoretical investigations on the adsorption of CO_2 on graphene sheets using density functional theory (DFT) calculations have been previously reported [31–33]. High adsorption energies were achieved by chemical doping and substituting impurities into graphene [32].

2. Material and methods

2.1. Materials

KOH (Ajax, Australia) was used as a chemical activation agent for the activation process. Ethylene diamine (EDA) (Merck, Germany) was used as a chemical agent for the AC surface modification process. Purified carbon dioxide (99.99%) and nitrogen (99.999%) were purchased from Linde Co. Ltd (Thailand). Swine farm biogas was collected from the local swine farm in Phapayom District, Phattalung Province, Thailand. This farm has a process to trap H_2S gas. Before studying the CO_2 adsorption ability of WTAC and MWTAC, swine farm biogas was first measured the composition by gas chromatography (GC) (shimazu, 8A). The compositions of swine farm biogas of each collecting time were not equal, but the values were not significantly different (Table 1). The value used to calculate the CO_2 absorption efficiency of adsorbents is the actual value collected at that time. The composition of swine farm biogas contained 40% CO_2 (v/v) and 60% CH_4 (v/v).

2.2. Preparation of activated carbon from waste tea

Waste tea (WT) was taken from a tea shop at Thaksin University, Phatthalung, Thailand. Before producing activated carbon, WT was first dried in a drying oven at 105 °C for 24 h and then crushed and sieved with mesh No. 200 to a particle size of 0.25 mm. Generally, from an energy point of view, the single-step process is preferable. Since many authors are using either the single-step or two-step carbonization process, both techniques were compared in this research work. Each step of carbonization was impregnated with KOH at room temperature for 24 h and compared to impregnation with KOH at 85 °C for 3 h by reflux technique of AC synthesis. The single-step synthesis was carried out as following: the WT was mixed with KOH solution in a 1:1 mass ratio (5 g deionized water per gram of KOH) at room temperature for 24 h. Then, the sample was dried at 85 °C for 12 h. After removing excess solution, the sample was put into a crucible and then it was placed into a high temperature furnace (Carbolite CWF 13/23, England). The mixture inside the furnace was combusted in air atmosphere at 500 °C for 2 h. After cooling to room temperature, the activated carbon was washed with HCl (0.1 mol/L) to remove excess of basic and rinsed again with deionized water until a neutral pH was achieved. Then the activated carbon was dried in an oven at 105 °C for 24 h, crushed and sieved to a size of 0.15 mm. The obtained final product was labeled as WTAC. For the sample that was impregnated at 85 °C for 3 h by the reflux technique, the sample was combusted at the same conditions as in the WTAC sample. The obtained final product was labeled as WTRAC.

The two-stage carbonization process was performed as following: the WT was firstly combusted at 600 °C for 2 h (heating rate 10 °C/min). After the first carbonization step, the obtained product was labeled as WTC. The chemical activation of the waste tea char (WTC) with KOH solution was performed at the same conditions as in the first stage. Then the two obtained final products were labeled as WTCAC and WTCRAC for KOH impregnation at room temperature for 24 h and at 85 °C for 3 h by the reflux technique of synthesis of AC, respectively.

Production conditions of the activated carbon samples such as impregnation ratio and carbonization temperature, which produced the optimum BET specific surface area value, the percent yield and pore volume of adsorbents, were chosen from the literature [20,34,35]. The schematic illustration of the production process is given in Fig. 1.

2.3. Surface modification of activated carbon sample

An ethylenediamine (EDA) modified WTAC sample was prepared. First, 1 g of WTAC was immersed in 5 mL of 3%W/V of EDA in methanol. The mixed sample was agitated at room temperature (30–34 °C) for a period of 3 h. Then the obtained sample was placed in a water bath and agitated at 70 °C to allow slow evaporation of the solvent. Finally, the modified WTAC with EDA was dried overnight in a vacuum desiccator. The modified AC sample was labeled as MWTAC.

2.4. Characterization of adsorbents

The obtained adsorbents were characterized by several techniques. For surface analyses, about 0.2 g of samples were measured on a surface characterization instrument by N_2 adsorption at 77 K. The BET surface area (S_{BET}) was calculated by the Brunauer-Emmett–Teller equation. The surface morphology of the samples was viewed by using a scanning electron microscope (Oxford,

Table 1
The composition of biogas from swine farm used in this research.

Compositions of swine farm biogas	Concentrations (%v/v) in swine farm biogas	Average concentrations (%v/v) in swine farm biogas
CH_4	58.30–62.33	60
CO_2	36.38–44.29	40
N_2	1.29–2.01	–