Synthesis of char adsorbent made from Pistachio skin for carbon dioxide capture

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Abstract

Adsorption-based CO_2 capture has enjoyed considerable research attention in recent years. Several effective post-combustion CO_2 capture technology has been reported, and one of the approaches is through the adsorption process. This study focused on the adsorption onto low-cost adsorbents that can be produced from waste biomass through the carbonization method. Pistachio skin was used as a precursor and carbonized at 320 and 720 °C under ambient conditions. The chemical and physical properties showed that chars' surface area, pore-volume, ash, moisture, and carbon content increased, while the yield decreased with increasing carbonization temperatures. The char adsorbent carbonized at higher temperature (720) showed better performance with a CO_2 adsorption capacity of 10.20 mmol/g at 25 °C. It was revealed that carbonization temperature dramatically affects the properties of Pistachio skin, hence influencing the ability of the adsorbent to capture CO_2. Therefore, these unique properties and adsorption performance showed that char adsorbents enable to be used as an effective adsorbent for CO_2 capture and thus improving environmental quality and sustainability.

Keywords: Pistachio skin, Carbon dioxide, Char, adsorption, adsorbent

Introduction

Public concerns over the global warming and climate change have been widely reported due to the increasing of CO_2 concentration in the atmosphere. Major anthropogenic sources of CO_2 emission to environment are conventional fossil fuels such as coal, oil, and natural gas combustion [1] for the purpose of electricity generation, transportation and industrial sector [2]. Due to these global concerns, strict regulations of CO_2 emission to the atmosphere have been imposed. Currently several available technologies for post-combustion capture of CO_2 were developed including wet absorption [3], membrane- based technologies [4], cryogenics [5], and dry adsorption [6] that are currently used in many industries. However, some of the methods need high operation cost and poor performance. Therefore, their application becomes limited in a wide range of industries. Adsorption is considered the most economic method for CO_2 removal using various types of adsorbents such as activated carbon, zeolites, hollow fibers, alumina, silica materials, metal organic frameworks (MOFs), and metal oxide-based adsorbents [7, 8]. Extensive studies are still being carried out to produce low-cost, effective, and environment-friendly adsorbents. The research has been directed towards the use of cheap adsorbent precursors such as agriculture wastes. In the past few decades, the removal of organic and inorganic pollutants using carbon/char prepared from inexpensive and renewable sources such as from agricultural biomass residues [2, 9, 10], woody biomass [11, 12], and industrial wastes [11] have gained considerable interests by many researches. The mutable properties of the chars depend upon several factors like biomass properties (e.g. type of biomass, moisture content, and particle size), reaction conditions (e.g. reaction temperature, reaction time, and heating rate), surrounding environment (e.g. types of carrier gas and flow rate), and other factors (e.g. catalyst and reactor type) [13, 14]. The chars and activated carbons prepared from various precursors and conditions have been studied for the post combustion CO_2 capture [2]. The use of chars from a Pistachio skin for CO_2 adsorption has not been reported so far. The Pistachio skin was selected as a char precursor since it has high carbon and oxygen contents [15]. It is also abundantly available in tropical countries and cheap. Thus, this study was focusing on the effect of carbonization temperature on Pistachio skin towards physical and chemical properties of derived chars and their effect towards CO_2 adsorption performance and mechanism.

EXPERIMENTAL

Pistachio skin was collected and was used as received. The preparation of char adsorbent was conducted similar to the method previously employed by Johari et al. [16]. The product was then dried in an oven at 105 ± 1 °C. The resulting char samples were denoted as Pistachio skin 'T' in which 'T' represents the pyrolysis temperature. The chemical and physical properties of char adsorbents were characterized and analyzed using proximate analysis (modified ASTM method [17]), CHNS/O analyzer (model FLASH, 2000; Thermo Scientific, USA), surface analyzer by nitrogen adsorption/desorption method (model NOVA-2000e; Quantachrome Corp., USA), and Fourier transform infrared (FTIR) spectroscopy (model PerkinElmer, 2000; USA). The evaluation of CO_2 adsorption capacity towards char adsorbent was carried out using the standard procedure of mini BELSORP volumetric adsorption measurement.

RESULTS AND DISCUSSION

The surface morphology of Pistachio skin chars showed different pore openings. It was found that the pores of Pistachio skin at 700°C had wider opening compared to Pistachio skin at 300°C. Carbonization at higher temperature shows the degree of roughness of the char surface due to the breaking down of biomass structures such as cellulose, hemicellulose, and lignin. Table 1 shows the results of the yield and proximate analysis for Pistachio skin carbonized at temperature of 300 °C and 700°C. It is apparent that increasing the carbonization temperature decreases the yield from 61 wt% to 31 wt%. In addition, the results obtained for moisture, ash, and fixed carbon increase with increasing of carbonization temperature while yields and volatile matter decreased. The major elements present in Pistachio skin char adsorbents are carbon (C), oxygen (O_2), nitrogen (N_2), and sulphur (S). It can be observed that at high carbonization temperature, the percentage of carbon increases whereas the amount of hydrogen, nitrogen, sulphur, and oxygen decreases.

Table 1. Pyrolysis yields and properties of Pistachio skin at 300 °C and Pistachio skin at 700 °C adsorbents.

	300 °C	700 °C
Yields (wt. %)	61.17 ± 1.34	31.42 ± 1.39
Moisture (wt.%, dry basis)	1.37 ± 0.02	7.28 ± 0.15
Volatile matter (wt.%, dry basis)	54.69 ± 0.81	22.68 ± 0.96
Ash (wt.%, dry basis)	3.71 ± 0.39	4.42 ± 0.17
Fixed carbon (wt. %, dry basis)	40.23 ± 0.43	65.62 ± 0.98
Elemental analysis (wt.%, ash-free basis)		
Carbon (C)	59.74 ± 1.41	76.24 ± 0.40
Nitrogen (N)	4.46 ± 0.01	3.37 ± 0.09
Hydrogen (H)	3.72 ± 0.01	1.67 ± 0.04
Sulfur (S)	0.16 ± 0.03	0.15 ± 0.01
Oxygen (Oa)	32.91 ± 1.40	18.57 ± 0.04
Surface area (m^2/g)	3.98	315.06
Pore volume (cm^3/g) x10^3	4.39	2.40
Pore diameter (nm)	1.34	1.90

Surface functional groups over the Pistachio skin at 300°C and Pistachio skin at 700°C can be observed in the FTIR spectra within the range of 4000–400 cm^{-1} (Fig. 1). It can be seen that the major peaks of O-H (~3420 cm^{-1}), C=O (~1620 cm^{-1}), and C-H (~1400 cm^{-1}) groups confirm the presence of cellulose, hemicelluloses, and lignin which are the typical characteristics of natural fiber [18]. The strong absorption peaks at 3416 and 3426 cm^{-1} are attributed to the presence of hydroxyl group (O-H) and amine (N-H) groups. The weak peak at ~2930 cm^{-1} shows the presence of C-H stretching from CH_2 groups. This is derived from the hemicellulose and lignin structures [16]. The peaks at ~1624 and 1634 cm^{-1} are assigned to the O-H bending while the peak at 1401 cm^{-1} is attributed to C-O-H bending. Similar peak intensities around 3416–3426 cm^{-1} indicating the constant moisture contents (1.37–7.28 wt.%) of Pistachio skin at 300°C and Pistachio skin at 700°C adsorbents. The decrease of intensities at peaks 1624 cm^{-1} (Pistachio skin at 300°C) to 1634 cm^{-1} (Pistachio skin at 700°C) mean that with the increase of pyrolysis temperatures, nearly all hemicellulose and cellulose decompose at temperatures of 300°C and higher [20].

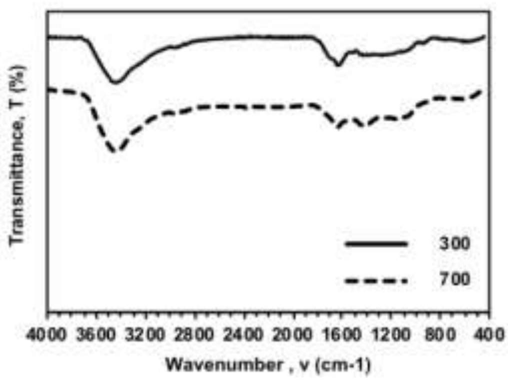

Fig. 1 FTIR spectra of Pistachio skin at 300 °C and Pistachio skin at 700 °C adsorbents.

The variation of CO_2 adsorption capacity of char adsorbents is illustrated in Fig. 2. It was found that Pistachio skin at 700°C (10.00 mmol/g) performed better adsorption capacity compared to Pistachio skin at 300°C adsorbent (0.18 mmol/g). The highest CO_2 adsorption of Pistachio skin at 700°C adsorbent was relatively high compared to previous literature, e specially on CO_2 removal by Pistachio-based adsorbent [20, 21]. In addition, the adsorption rate increased rapidly at the beginning of relative pressure due to the presence of vacant pores being available for adsorption. As relative pressure increased, the rate of adsorption started to decrease. It means that the adsorption process is exothermic in nature, which corresponds to the CO_2 gas adsorbed on the surface of char adsorbent by intermolecules (van der Waals) forces [22]. In this study, high CO_2 adsorption capacity by Pistachio skin at 700°C adsorbent was attributed by high carbon content and large surface area (315.06 cm^2/g), even without activation. The high surface area of the char helped in enhancing the CO_2 adsorption capacity. This is consistent with the finding of previous studies using chars from carbonization or pyrolysis of raw biomass [20, 23].

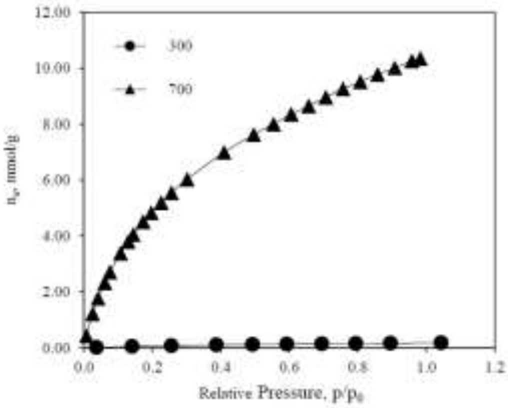

Fig. 2. CO_2 adsorption of Pistachio skin at 300°C and Pistachio skin at 700°C adsorbents.

CONCLUSION

The Pistachio skin chars were successfully synthesized and characterized to be used as an adsorbent for CO_2 gas removal. It can be observed that as the carbonization temperature becomes higher (700ºC), the properties of char such as surface area, moisture, ash, and carbon content of chars increased, while the yield content decreased. The carbonization temperature has a significant effect on the structural changes in Pistachio skin char which resulted in different pore texture and chemical reactivity, as well as the CO_2 ad sorption performances. The Pistachio skin char carbonized at higher temperature (700) showed the better performance with CO_2 removal capacity of 10.00 mmol/g. Thus, with the unique properties and high adsorption performances, Pistachio skin char adsorbent could be a cost-effective and environmental-friendly adsorbent for CO_2 capture.

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