Soil with high porosity as an excellent carbon dioxide adsorbent carbon-rich soil as an effective adsorbent for carbon dioxide

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Abstract. Carbon dioxide, a type of greenhouse gases has drawn world wide's attention as major contributors to global warming and climate change. Thus, several methods have been developed to mitigate this problem such as through adsorption. There are numerous types of adsorbents available, for instance is carbon-based adsorbent that can be synthesised from various type of biomass as reported in previous studies. However, there are very few studies used soil as an adsorbent for gases. Soils are porous medium developed in the uppermost layer of Earth's crust which are available in several forms, abundance and cheap. In this study, three types of carbonised soils were used as carbon-based adsorbent to investigate its adsorption capacity for carbon dioxide. Influence of moisture content in this study is negligible as it is too low. Due to the nature of raw materials used, ash content for all sample was incredibly high which almost all exceeded 90%. Determination of densities by pycnometer showed that carbonised soil 2 has the lowest particle and bulk density of 2.4802 g/cm^3 and 0.5248 g/cm^3 respectively. Then the adsorption capacity of each sample was determined by sorption measuring instrument with magnetic suspension balance. Results showed that carbonised soil 2 with high surface area, pore volume, and small pore size has the highest adsorption capacity of 6.4 mg/g at 25 ˚C under atmospheric pressure. Therefore, soils exhibit prominent potential to be developed as carbon dioxide adsorbent with desirable properties.

1. Introduction

Carbon dioxide is known as the major type of greenhouse gases (GHGs) emitted to the atmosphere. Excessive emission and accumulation of carbon dioxide have long associated with adverse environmental effects such as global warming and climate change. Therefore, many methods have been established to mitigate this global issue. Absorption by using amine-based solvent is the most utilised method to capture carbon dioxide. However, this method has several significant drawbacks such as emission of dangerous by-products and high energy consumption while other methods such as cryogenic distillation and membrane separation are limited as they are costly. Therefore, establishment of carbon dioxide capture through adsorption has captured attention of many researchers.

Adsorption is a process where the gas molecules, also known as adsorbate adhere to the solid surface of an adsorbent. Figure 1 illustrates the adsorption mechanism where adsorbate fills the pores of an

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adsorbent [1]. There are numerous types of adsorbents available such as carbon-based adsorbents which can be developed from renewable and non-renewable sources. The utilisation of renewable sources is preferred as it promotes sustainable development process. Examples of renewable sources that have been used as precursors in the development of carbon dioxide adsorbents are coconut shell, peanut shell, sugarcane bagasse, olive stone, kenaf, wood and many more.

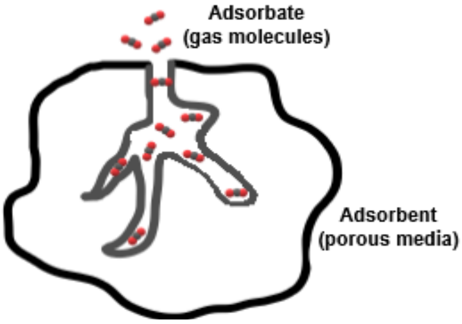

Figure 1. Mechanism of carbon dioxide adsorption in porous media.

In this study, three carbonised soils were characterised to determine its ability to adsorb carbon dioxide. Thus far, previous studies have only utilised the dried soil to adsorb carbon dioxide and the reported adsorption capacity are low. A study conducted by Quiroz-Estrada investigated adsorption of carbon dioxide using sun-dried soil and the highest adsorption capacity recorded was about 4.6 mg/g at elevated temperatures and pressure [2]. Therefore, in current study, the soil was further carbonised after drying process and expected to have better properties and performance. Primarily in adsorption studies, the characteristics of an adsorbent's surface such as its surface area, pore-volume, and pore size are mostly investigated. Several previous studies agreed that high surface area and pore volume would lead to high adsorption capacity [3-5]. A study conducted by Deng et al. reported a high adsorption capacity for carbon-based adsorbents prepared from peanut shell and sunflower seed shell which have high surface area of 956 m^2/g and 1790 m^2/g and high pore volume of 0.43 cm^3/g and 0.77 cm^3/g respectively [6]. Influence of pore size which can be classified into three categories; micropore (< 2 nm), mesopore (2-50 nm), and macropore (> 50 nm) is also investigated. Small pore size is great for carbon dioxide adsorption due to the small size of the gas molecules.

Besides that, the selection of suitable adsorbents is usually determined by its low moisture and ash content. Other than that, neutral pH adsorbents are usually utilised in accessing the ability of an adsorbent to adsorb carbon dioxide. Meanwhile, densities of the adsorbents influenced the adsorption process indirectly as readings of densities always inferred to the elemental composition of a sample. For instance, a study conducted by Abiko revealed that high true density is mainly because of high content of oxygen [7]. Conjointly, a study done by Hao concluded that coal-based adsorbent with higher oxygen surface groups has lower methane adsorption capacity [8].

2. Experimental design

2.1. Sample preparation

In this study, three different types of soils were used as tabulated in Table 1. Samples included in the study were prepared through direct carbonisation. Initially, about 20 g of each raw material was dried in an oven at 105°C for 24 hours following the standard test procedure of ASTM D2974-14 to remove moisture. Then, carbonised samples were prepared by carbonising the dried samples in a muffle furnace at 300°C for 3 hours. The carbonised samples were sieved to the size of 300-100 μm, stored in an airtight bottle and labelled. The prepared samples were labelled as CSX for carbonised soils respectively, where X= 1, 2 and 3.

Table 1. List of raw material and prepared samples.

No	Raw material	Carbonised sample at 300°C
1	Soil 1	CS1
2	Soil 2	CS2
3	Soil 3	CS3

2.2. *Determination of moisture and ash content*

Moisture and ash content of the prepared samples were determined based on the standard test method of ASTM D2974-14. About 2 g of sample was placed in a pre-weighed crucible and dried in an oven at 105°C for 24 hours. Then, the moisture content was calculated by using equation (1). In order to calculate the ash content of the prepared samples, about 2 g of dried sample was burned in a muffle furnace at 440°C for 3 hours and the ash content was calculated using equation (2).

$$\text{Moisture content, } \% = [(A-B) \times 100]/A \tag{1}$$

$$\text{Ash content, } \% = (C \times 100)/B \tag{2}$$

where; A is the initial mass of the soil (g), B is the mass of the oven-dried soil (g) and C is the mass of ash (g).

2.3. *Determination of pH*

The pH for each carbonised soil was taken by using pH meter. About 2.0 g of carbonised soil was weighed and transferred into a beaker. Then, the sample was mixed with about 40 ml of distilled water. The mixture was thoroughly mixed before the reading of pH was taken.

2.4. *Determination of true density and bulk density*

True densities of the prepared samples were determined through a non-destructive method by using pycnometer (ULTRAPYC 1200e Automatic Density Analyser, USA). During the analysis, each sample was filled and sealed in a known volume of the instrument compartment. An inert gas of helium is then filled up the pores, and the sample weight is divided by the volume to determine the gas displacement density, which is denoted as particle density. This technique was repeated for five cycles for each sample before obtaining the average density.

Determination of bulk density of the prepared samples was done by filling up the sample in the pre-weighed 10 mL measuring cylinder. Then, the bulk density was determined by using equation (3) [9].

$$\text{Bulk density, } g/cm^3 = W_s/V_c \tag{3}$$

where; W_s is the recorded weight of the sample (g), and V_c is the volume of the cylinder (cm^3).

2.5. *Nitrogen adsorption and desorption isotherm*

Nitrogen adsorption and desorption isotherm was conducted to analyse the physical properties of the prepared samples with the means of a volumetric adsorption instrument (NOVAtouch^{TM} LX^3 Surface area & pore size analyzer, USA) with accompanying software (Quantachrome TouchWin^{TM}). Initially, all samples were degassed at 300°C for 3 hours to remove all gaseous and vapours. Then, the sample was cooled down at room temperature and moved to the analysis port of the instrument for nitrogen adsorption measurement.

The instrument records various pressures of gas in the sample cell due to adsorption and desorption. Series of data obtained was used to calculate Brunauer-Emmett-Teller (BET) surface area, total pore volume and average pore size of the prepared samples.

2.6. Adsorption of carbon dioxide

Adsorption test of carbon dioxide was carried out by using a sorption measuring instrument with magnetic suspension balance (Rubotherm, Germany). Each sample went through three configuration steps; pre-treatment, buoyancy, and adsorption. Initially, each sample underwent pre-treatment and buoyancy configuration to remove moisture from the sample and to measure its actual mass respectively. Then, adsorption test for all carbonised samples was carried out at 25°C and pressure up to 30 bar.

3. Results and discussion

3.1. Moisture content, ash content, pH, and densities

Physical properties of the carbonised soils are presented in Table 2. Observed moisture content for all carbonised soils is relatively low which less than 1%. An adsorbent with low moisture content is good as recent studies [10, 11] reported that when the moisture content is high, the adsorption capacity of an adsorbent for gas molecules will be reduced. This negative relationship is because when gas and water molecules co-exist, there will be competition among them for hydrophilic sites available in the adsorbent. Other than that, the existence of water molecules may block the adsorption sites and inhibits adsorption of gas molecules to take place. Therefore, in this study, the effect of moisture content on adsorption capacity is negligible.

In term of ash content, all samples have incredibly high ash content that implies a high presence of inorganic matter and minerals which is common in soil [12]. Whereas, a study by Ekpete stated that sample with lower ash content is more suitable to be used as adsorbent [13]. A contrary argument was reported in a study conducted by Feng who investigated the effect of ash content on methane adsorption by coals. In his study, when ash content increased to certain threshold limit, the adsorption capacities increased. However, the performance of coals was reduced drastically if the ash content were beyond the threshold [14].

Recorded pH values are different for CS1, CS2, and CS3 with being basic, neutral and acidic respectively. Different pH values were observed for all carbonised soils prepared from different raw materials. A basic surface is assumed to adsorb carbon dioxide better as the gas is slightly acidic. Particle density and bulk density observed for all samples are comparable with other related studies [7, 15, 16]. Observed in this study, CS2, which has the lowest particle density and bulk density exhibits the highest gravimetric adsorption capacity under atmospheric condition. For gravimetric adsorption capacity like in this study, there is a good relation between BET surface area and adsorption capacity rather than the density [17]. Meanwhile, for volumetric adsorption capacity, which is not conducted in this study, a good relation between bulk density and adsorption capacity was reported in several studies [17, 18]. They stated that the higher the bulk density, the better is the adsorption.

Table 2. Physical properties of the carbonised soils.

Samples/Properties	CS1	CS2	CS3
Moisture content (%)	0.01	0.79	0.32
Ash content (%)	96.45	88.55	97.44
pH	8.62	6.92	4.82
Particle density (g/cm^3)	2.6770	2.4802	2.6379
Bulk density (g/cm^3)	0.9270	0.5248	0.7365

3.2. Nitrogen adsorption and desorption isotherm

The isotherm of the carbonised samples CS1, CS2, and CS3 as shown in Figure 2 are typically type II isotherms which implies that the sample is almost non-porous. BET surface area, total pore volume, and average pore size of carbonised soils are presented in Table 3.

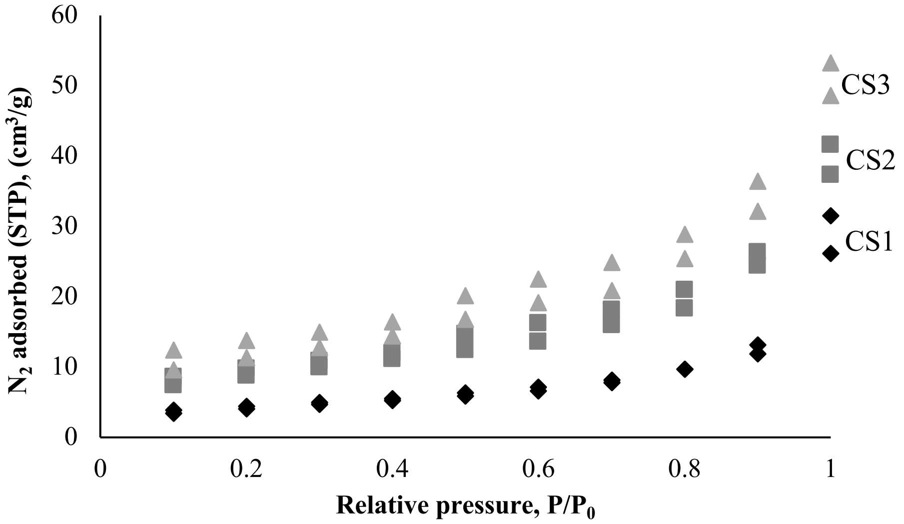

Figure 2. N_2 adsorption and desorption isotherms at 77 K of carbonised soils.

Among all the prepared samples, CS3 has the highest surface area and total pore volume of 40.99 m^2/g and 0.08 cm^3/g respectively. Although the recorded surface area and pore volume are low compared to previous literature, other processes such as carbonisation at higher temperature or activation can be implied in the future to modify these properties. A study by Sevilla investigated the performance of biochar produced from sugarcane bagasse and hickory wood in carbon dioxide adsorption reported that carbonisation temperature plays a crucial role [17]. Biochar produced at a higher temperature has a higher surface area. In comparison, biochar of hickory wood produced at 300˚C and 600˚C have surface area of 0.10 m^2/g and 401.00 m^2/g respectively.

Similarly, study by Evbuomwan also reported that increase in carbonisation temperature would cause increase in specific surface area, pore volumes, ash content, and density and reverse effect with yield, moisture content and porosity [18]. Hence, carbonisation temperature must be adequate to volatilise all non-carbon substances as partially burnt off carbon changes the arrangement of electron cloud and causes unpaired electrons to appear, and this will interfere with the adsorption capacity of an adsorbent [13].

Pore size as close as to the size of gas molecules is usually preferred. Micropore is usually associated with high adsorption capacity as narrow micropores have strong adsorption potential for carbon dioxide molecules compared to bigger pore size [17]. Average pore size for all carbonised samples in this study, as shown in Table 3. falls into mesopore category.

Table 3. BET surface area, total pore volume and average pore size of carbonised soils.

Samples/Properties	CS1	CS2	CS3
BET Surface area (m^2/g)	14.8747	31.7831	40.9829
Total pore volume (cm^3/g)	0.0489	0.0645	0.0826
Average pore size (m)	6.57×10^{-9}	4.06×10^{-9}	4.03×10^{-9}

3.3. Adsorption of carbon dioxide

The adsorption of carbon dioxide by the carbonised samples at 25˚C and pressure up until 30 bar showed similar kinetic behaviours as presented in Figure 3. Adsorption was considerably fast at low pressure; however, it slowed down after about 15 bar, indicating it was approaching equilibrium. From previous studies conducted, a trend for carbon dioxide adsorption was concluded to be higher at high pressure and poorer at low pressure as what is observed in this study. Although CS1 has a basic surface, it has the lowest adsorption capacity at 1 bar and 30 bar with only 2.2 mg/g and 7.4 mg/g, respectively since the surface area and total pore volume was the smallest as well as bigger pore size. Meanwhile, the adsorption capacity of CS2 and CS3 were quite similar since they have a comparable surface area, total pore volume, and pore size.

At low pressure of 1 bar CS2 has slightly higher adsorption capacity of 6.4 mg/g than CS3 with an adsorption capacity of 5.4 mg/g. Here, adsorbent around neutral pH is better in adsorption of carbon dioxide, a slightly acidic gas under atmospheric pressure. However, at higher pressure CS3, with acidic pH value recorded a higher adsorption capacity of 18.7 mg/g compared to CS2 with adsorption capacity of 16.4 mg/g. This proved that adsorption of carbon dioxide depends on the samples properties as well as the experimental condition. Adsorption capacities obtained by carbonised soils in this study were higher compared to previously reported literature. For instance, a study conducted by Quiroz-Estrada recorded the highest carbon dioxide adsorption capacity of only 4.6 mg/g by sun-dried soil at elevated temperature and pressure [2].

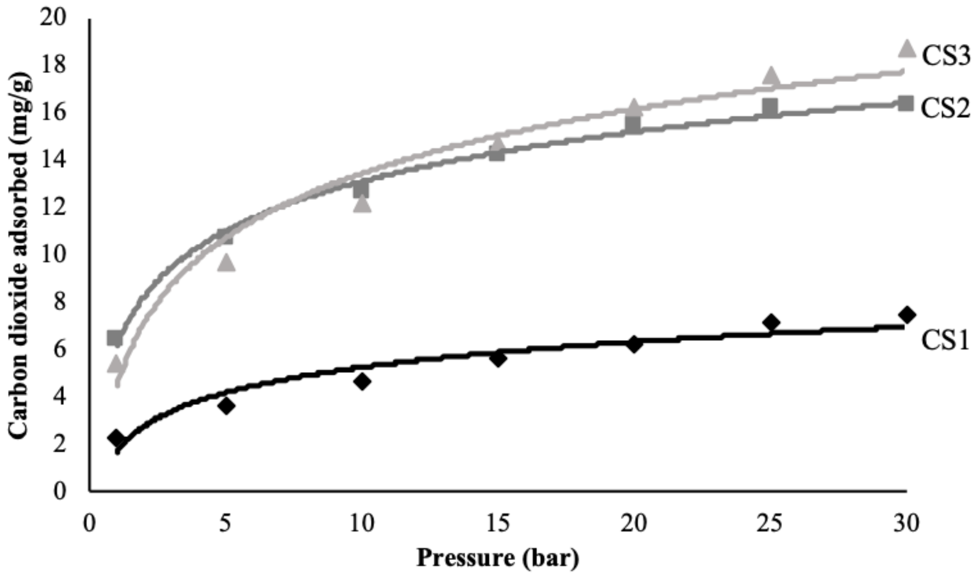

Figure 3. Adsorption of carbon dioxide by carbonised soils.

4. Conclusion

The carbon-based adsorbents are not only cost-effective, but it is also environmentally friendly, abundant, and easy to operate with a high energy efficiency where these renewable sources can be obtained as raw biomass or waste biomass. The highest adsorption capacity at 25˚C under atmospheric and elevated pressure recorded in this study was 6.4 mg/g and 18.7 mg/g for CS2 and CS3 respectively. In this work, enhanced adsorption capacity was influenced by the properties of the carbonised soils as well as the experimental condition.

Therefore, soils have distinguished potential to be developed as carbon dioxide adsorbent if it undergoes further preparation process. In future research, other preparation methods such as chemical activation and amine functionalization can be applied to enhance the adsorbent properties and adsorption capacity. Thus, potential for sustainable development of carbon dioxide adsorbent will proliferate.

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