

Preparation and Characterization of Adsorbents for Carbon Dioxide Adsorption

S O. Akpasi and Y M. Isa

Abstract— To reduce emissions of greenhouse gasses, there should be better control of the release of CO₂ due to human activities. In this study, an inexpensive material was developed as adsorbents for CO₂ capture. Sugarcane bagasse was used as a precursor in preparing activated carbon by chemical activation with zinc chloride (ZnCl₂) in a laboratory vacuum furnace at 500°C for 1 hour while kaolinite was obtained commercially. These adsorbents were applied for the storage of CO₂ within a range of temperatures (30°C, 50°C and 70°C) while the flow rate (30mL/min to 70mL/min) and column bed height (3cm – 5cm) were varied at constant temperature. This research also explored sample features such as surface area and porosity, functional groups, and scanning electron microscopic images. This further substantiate the conclusion that CO₂ adsorption with kaolinite and activated carbon is favoured at low temperatures, low operating CO₂ flowrates and high column bed height.

Keywords—sugarcane bagasse, activated carbon, carbonization, chemical activation, adsorption.

I. INTRODUCTION

Activated carbon is a porous material with a broad specific surface area that is suitable for the adsorption of gases and aqueous solution solutes. This is attributed to activated carbon properties that have a large active surface area that could provide high capacity for adsorption, well-developed porous structures and strong mechanical properties. [1, 2]. Therefore, it has been commonly used for gas separation, solvents recovery, removal of organic pollutants from drinking water and a catalyst support. The need for activated carbon is rising as environmental pollution is becoming a more significant problem. It is a flexible adsorbent due to its excellent adsorption properties. In addition, activated carbon is most frequently used because it is possible to design and modify most of its chemical (e.g. surface groups) and physical properties (e.g. surface area and pore size distribution) according to the appropriate requirement [3]. In addition, because of its simplicity of operation, the adsorption on activated carbon tends to be the most common techniques, because the sorbent material can be produced highly effective, simple to handle and in some cases regenerated. [4].

Activated carbons are produced from a variety of materials from carbonaceous sources. The selection of precursor is based mainly on its availability, cost, and purity, but the production process and specific purpose of the product are also critical factors [5]. Many other agricultural by-products are often used as sources of activated carbon in recent years. Due to their affordability at low costs, widely available, and sustainable resources, agricultural biomass waste has emerged to be promising raw materials for activated carbon production [5]. They have been used to produce activated carbon because of their high carbon content, high adsorption capacity, high density, and substantial good mechanical strength. They also have low ash content, which is suitable within the activated carbon system for constructing highly porous structures. Most agricultural by-products have been found to be ideal precursors for activated carbon due to their high carbon and low ash content, including sugar cane bagasse waste, coconut shell[5, 6], grain sorghum[5], coffee bean husks[5], rubber wood sawdust[5], chestnut wood[5], and fruit stones[5]. In addition, mineral clay is also one of the most available natural materials and is therefore available at a minimal cost. It is possible to substantially extend the use of clays for adsorption and separation. To our best understanding, very few studies have explored kaolinite for CO₂ capture so far and studied extensively the parameters relating to its capacity for adsorption. Most research efforts have concentrated on clay minerals from an industrial perspective. Therefore, in this study, sugarcane bagasse was chosen as a precursor to produce activated carbon. In addition, kaolinite was also selected as an adsorbent for CO₂ capture via adsorption since both materials are readily available in South Africa (sugarcane bagasse and kaolinite) but have very limited market value.

Due to its excellent natural structure and low ash content, sugarcane bagasse (SCB) is appropriate for the preparation of activated carbons. SCB is a by-product of the sugarcane industry harvested after juice extraction for the manufacture of sugar. The conversion of sugarcane bagasse into activated carbons that can be used as adsorbents, ion exchange, carbon molecular sieve, catalyst will contribute positively to these agricultural products, dramatically alleviate waste disposal costs and provide a fairly inexpensive alternative to conventional commercial carbon products. Carbonization of the precursors at high temperatures in an inert environment supported by the activation phase is the most common technique used for activated carbon preparation. The method of activation is categorized into physical and chemical processes. The Physical activation process comprises treatment of char obtained from carbonization with oxidizing gases, generally

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steam or carbon dioxide at high temperature (400 to 1000 °C) [7]. In the chemical activation process, the starting material is mixed with an activation reagent and the mixture is heated in an inert atmosphere [8, 9]. This process is usually done at lower temperature and activation time, higher producing surface area and better porosity as compared to physical activation.

The goal of this study is to prepare activated carbon from sugarcane bagasse by chemical activation using zinc chloride (ZnCl₂) to adsorb CO₂ from its source such as flue gas. To further investigate the adsorption efficiency of activated carbon and kaolinite materials. In this paper, these adsorbents were applied for the storage of CO₂ within a range of temperatures (30°C, 50°C and 70°C) while the flow rate (30mL/min to 70mL/min) and column bed height (3cm to 5cm) were varied at constant temperature. Sample characteristics such as the surface area and porosity, functional groups, and scanning electron microscopic images were also investigated in this study.

II. MATERIAL AND METHODS

2.1 Raw material

The sugarcane bagasse waste (SBW) was selected for activated carbon preparation. SBW was collected from a sugarcane mill company that is located at Kwazulu-Natal in South Africa. The materials were cleaned with distilled water several times to remove dust and impurities while the kaolinite was obtained from South Beach in Durban, South Africa. SBW samples were later dried in the oven at 110 °C for 24h to remove any surface moisture and were then grounded and sieved to particle size range of 150-250 μm. The proximate analysis of the precursor yielded, moisture 6.4%, volatile matter 31%, fixed carbon 60% and ash 2.6%.



Fig. 1. (a) Sugarcane bagasse waste (b) Grinded sugarcane bagasse (c) Kaolinite

2.2 Activation Preparation

2.2.1 Chemical activation

Chemical activation of the powdered precursor was done with ZnCl₂. 10 g of dried precursor was well mixed with 100 ml solution that contained 10 g of ZnCl₂. The chemical ratio (activating agent /precursor) was 100% in this case. The mixing was performed at 50 °C for 1 h. After mixing, the slurry was subjected to vacuum drying at 100 °C for 24 h. The resulting chemical loaded samples were then transferred into a horizontal kiln furnace as shown in Fig. 3(a). Nitrogen gas flow of 200 mL/min was used for making an inert environment inside the reactor and transporting out the volatile compounds. The reactor was heated to 500 °C and was kept at this temperature for about 1h (heating rate of 10 °C / min). The reactor was cooled down after the activation process was completed, and the char was extracted and washed repeatedly with distilled water to about 5 times to eliminate residual Zn, followed by drying at 80 °C till the solution is neutralized to achieve activated carbon. Finally, the product of ACs were ground to a fine powder (< 250 μm) as shown in Fig. 3(b) and stored for the adsorption experiment.

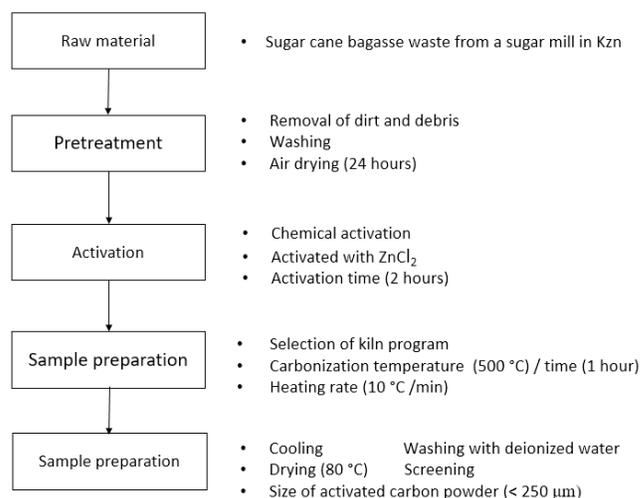


Fig. 2. Procedure for preparing Activated carbon

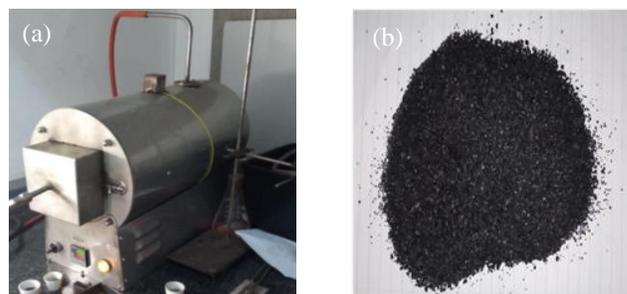


Fig. 3. (a) Horizontal kiln furnace (b) Activated carbon

2.3 CO₂ adsorption experiment

The CO₂ adsorption test was carried out using an adsorption column. For these experiments 99 % CO₂ was used. In each

experiment, the column was filled with 3.0 g of adsorbents (packing height \approx 5.0cm) and placed within a temperature control bath to maintain a constant temperature at 30 °C. The operating flow rate was varied from (30-70) mL/min at constant temperature. The temperature of the thermostatic water bath was kept constant throughout the experiment. The experiment was allowed to operate for 1200 seconds (20 minutes) at each temperature (30, 50 and 70 °C). The height of the bed was varied from 3-5cm at each run to study the behaviour of the adsorbents. This experiment was controlled and recorded; the change in the mass of the sample was measured and the amount of CO₂ adsorbed was calculated, by equation 3.3 below.

$$CO_2 \text{ adsorption capacity} = \frac{W_2 - W_1}{W_1} \times 1000 \quad (3.1)$$

Where W_2 = weight of adsorbent after adsorption
 W_1 = weight of adsorbent before adsorption

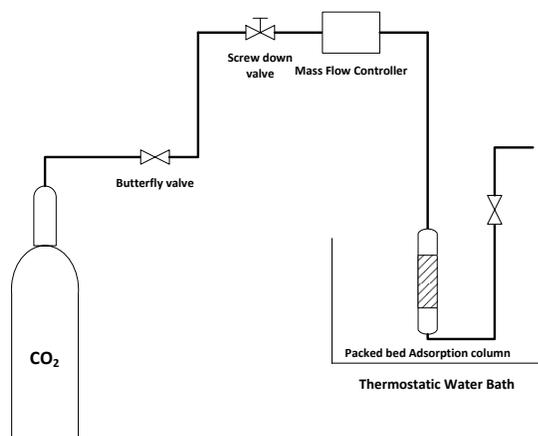


Fig. 4. Process flow diagram of the adsorption set-up

III. RESULT AND DISCUSSIONS

3.1 SEM analysis

Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the sugarcane bagasse derived activated carbon and kaolinite material. Figure 4 shows the SEM photographs of the sugarcane bagasse (before and after the carbonization at the optimum operating condition) and kaolinite material with 50 000X magnification at a resolution of 2 μ m, 5 μ m and 20 μ m. Pores of different size and shape could be observed. It can be seen from the micrographs Fig. (5b) that the external surface of the chemically activated carbon is full of caking and agglomeration occurring on the char structure and thus resulted in the formation of chars with an intact external surface. According to the micrograph, it seems that the higher aggregates resulted from the evaporation of ZnCl₂ during carbonization, leaving the space previously occupied by the ZnCl₂.

Interestingly, with the activation of the sugarcane bagasse with ZnCl₂, the carbon structure of the sample increases and begins to cohere and form sphere-shaped porous variable-size

structures. Such structures can help facilitate the movement of CO₂ gas molecules by providing abundant sites for adsorption. This demonstrates that activation removes hydrocarbons, which enhances the adsorption capacity of activated carbon. Discrete aggregation was shown in Fig. (5c) and was characterized by the presence of a few mesopores and made spherical, making the surface rough.

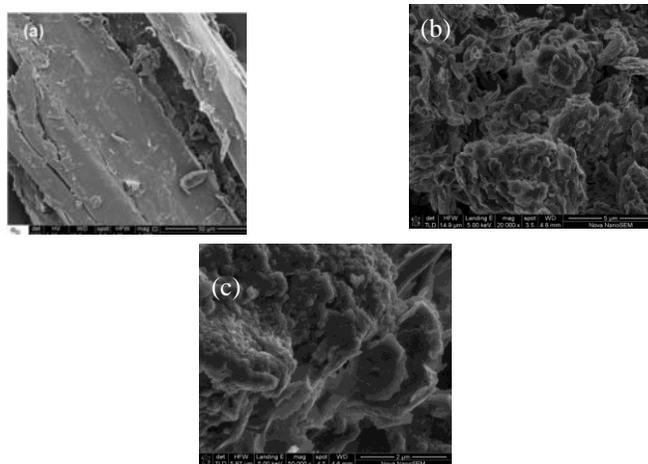


Fig. 5. Scanning electron microscopy images of sugarcane bagasse (a) before carbonization (b) after carbonization at 500 °C (c) kaolinite

3.2 BET surface area

BET surface area for sugarcane based activated carbon and kaolinite are shown in Table I. The BET surface area obtained was significantly high and it is within the acceptable range of commercial activated carbon (500-1500 m²/g). Generally, with high BET surface area, results in higher adsorption capacity because the activated carbon is capable to adsorb a number of gases under different conditions [10].

We observed that for the chemical activated sample of sugarcane bagasse, SBAC provided a larger surface area, 979 m²/g compared to kaolinite, 584 m²/g. This is because ZnCl₂ as the activating agent has contributed to create more new pores and widen the existing pores. The chemical activated SBW also exhibited the highest pore volume (0.43 cm³/g), followed by kaolinite (0.26 cm³/g) which indicated higher gas adsorption. At this moment, adsorption of CO₂ was not only related to BET surface area and pore volume, but also depended on reaction occurred between adsorbate (CO₂) and adsorbent (loaded AC) and kaolinite samples.

TABLE I. BET SURFACE AREA

Sample	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (Å)

Chemical activated carbon from SBW	712	0.43	18.77
Kaolinite	484	0.26	14.09

3.3 FTIR analysis

The FT-IR test results of sugar cane based activated carbon before and after CO₂ adsorption are presented in Fig. 6 whereas the FT-IR test results of kaolinite before and after the adsorption of CO₂ are depicted in Fig. 7. The functional group analysis was conducted at a range of 500-4000 cm⁻¹ wavelengths.

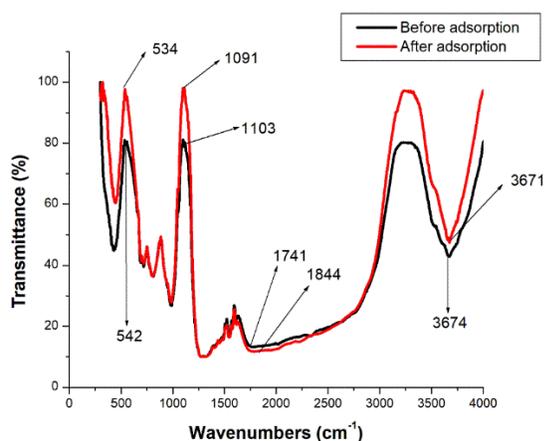


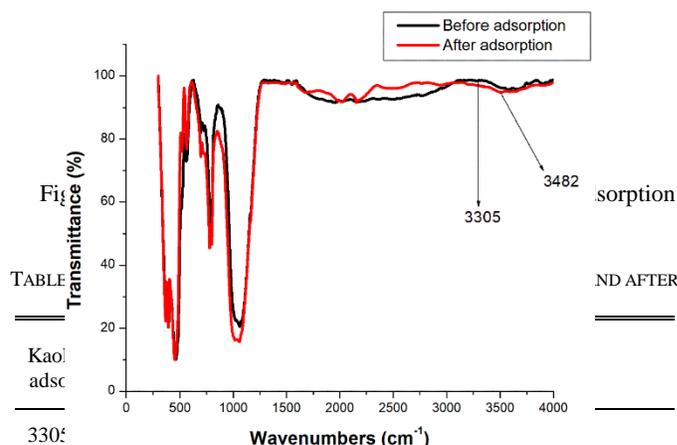
Fig. 6. The FTIR spectrum of sugar cane based activated carbon before and after adsorption

TABLE II: FTIR SPECTRAL CHARACTERISTICS OF ACTIVATED CARBON DERIVED FROM SUGAR CANE BEFORE AND AFTER ADSORPTION

Activated carbon before adsorption	Activated carbon after adsorption	Assignments
3674	3671	OH-stretch (in alcohol) C-H
542	537	bending C-O stretch (in aliphatic ether)
1103	1091	C-O stretch (in anhydride)
1741	1844	

The variations in the FTIR spectrum of activated carbon derived from sugar cane bagasse can be shown in figure 4.2 before and after CO₂ adsorption. A description of the features of the shifted bands and the existing functional groups is presented in Table II. As seen in Fig. 6, the activated carbon derived from sugar cane bagasse spectrum displaced an absorption peak of 3671 cm⁻¹ clearly indicating the presence of an O-H functional group. First, the broad peak at 3671 cm⁻¹ shifted and became

weak at 3641 cm⁻¹ due to the O-H stretch and the H-bonding of the hydroxyl group in alcohols and phenols. The asymmetry of this band indicates the presence of strong hydrogen bonds.



The peak 537 cm⁻¹ which shifted to 542 cm⁻¹ indicates the presence of C-H group. A strong band at 1844 cm⁻¹ shifted to 1741 cm⁻¹, attributed to the C=O groups of anhydride compounds. Whereas for the kaolinite spectrum before and after adsorption of CO₂ in Fig. 7, there is an absorption peak of 3305cm⁻¹ shifted to 3482 cm⁻¹ confirming the formation of O-H group that may incorporate water, alcohol, and phenol components. The comparison of the sugar cane derived activated carbon FTIR spectra before and after CO₂ adsorption indicates the change in the spectrum that occurred and it can be said that the adsorbent's functional groups were actively engaged in the adsorption process [11]. Overall, it can be concluded that the sugar cane bagasse derived activated carbon has functional groups that can help bind or trap particles including alcohols, phenols, alkanes, and alkyl halides. The hydroxyl group has a strong affinity to pollutants and heavy metal ions [12].

3.4 CO₂ adsorption

3.4.1 Effect of temperature

Fig. 8 (a) exhibits behaviour showing the effect of

temperature on the CO₂ adsorption capacity for SBAC and kaolinite. The effect of temperature was studied from 30 to 70 °C. It is expected that the temperature will influence the nature of the adsorption that occurs, i.e., physisorption or chemisorption. In other words, an increase in adsorption temperature results in a reduction in the amount of CO₂ adsorbed. Increased temperature gives more internal energy to CO₂ molecules during the gas phase. We observed that the increased energy allows the diffusion of gaseous molecules at a higher rate. However, at the same time, the possibility of CO₂ being constrained or trapped on the adsorbent surface by fixed energy adsorption sites is decreased. The highest adsorption capacity was obtained at 30 °C for SBAC and kaolinite systems at 28.97 mgCO₂/kg AC and 12.98 mgCO₂/kg kaolinite, respectively. The observed trend is that CO₂ adsorption decreased with an increase in temperature. At a constant flowrate, the kinetic energy of gases increases with temperature, resulting in lesser surface coverage of CO₂ gas. The observed trend can be attributed to the exothermic nature of the adsorption process. Le Chatelier's principle explains this, when it is applied to predict the extent of an exothermic process states that increasing the temperature will decrease the magnitude of an exothermic reaction

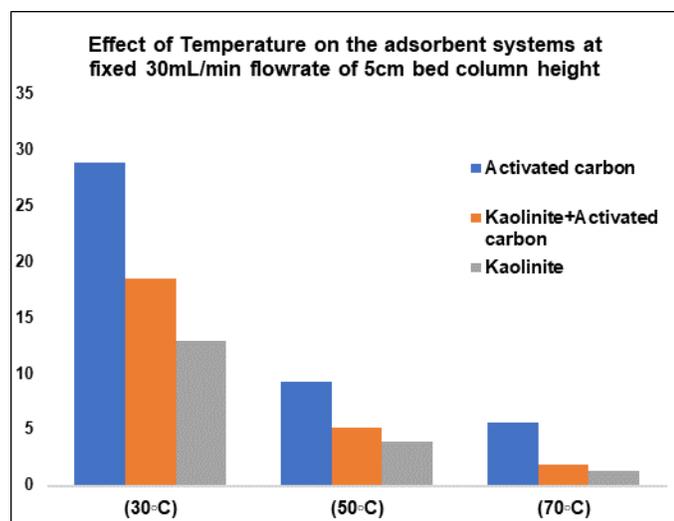


Fig. 8. Effect of temperature on CO₂ adsorption capacity of kaolinite – activated carbon

3.4.2 Effect of flowrate

Fig. 9 depicts the effect of flowrate on CO₂ adsorption capacity of SBAC and kaolinite systems. The highest CO₂ adsorbed was achieved using a flowrate of 30 mL/min. The CO₂ adsorbed with a flowrate of 40mL/min, 50mL/min, 60mL/min, and 70mL/min are lower than that achieved with a flowrate of 30 mL/min. We observed that decreasing the inlet flow rate of the gas increases the contact time and improves mass transfer between CO₂ and the adsorbents. That is, lower flow rates increase the retention time of the CO₂ molecules on the selected adsorbents within the packed bed adsorption column resulting in the high amount of CO₂ adsorbed. At lower flow rate, adsorbate (CO₂) has more time to contact with adsorbent that

resulted in higher adsorption capacity of CO₂ [13]. Longer residence times are required for a higher amount of CO₂ to be adsorbed and entrapped in the pores of the adsorbents. As a result of the aforementioned reasons, the maximum amount of CO₂ adsorbed at constant temperature of 30 °C by sugarcane based activated carbon and kaolinite systems at different flow rates of 30mL/min, 40mL/min, 50mL/min, 60mL/min and 70 mL/min CO₂ were 20.45, 19.62, 16.82, 14.70 and 12.11 mgCO₂/kg adsorbent as depicted in Fig. 9.

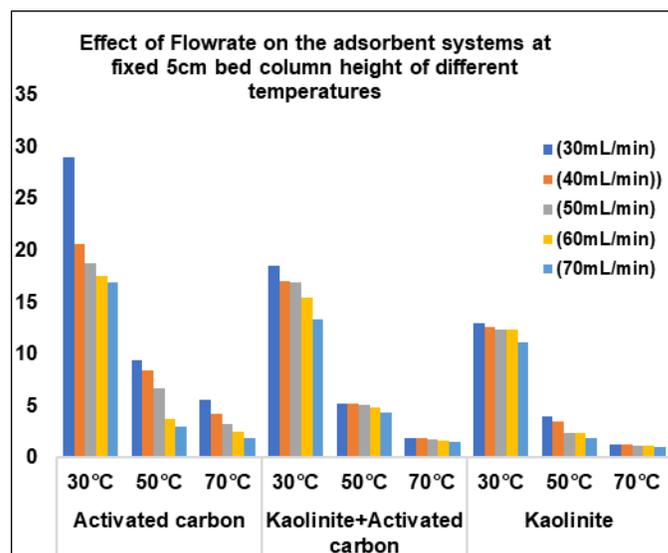


Fig. 9. Effect of flowrate on CO₂ adsorption capacity of activated carbon. Constant temperature of 70 °C

3.4.3 Effect of column height

The adsorption capacity of the packed bed increased with increasing bed height; the determined heights of bed were 3, 4 and 5cm to examine the effect on the CO₂ adsorption performance of sugarcane based activated carbon and kaolinite systems. The flow rate was kept constant at about 30 mL/min to 70mL/min. The effect of bed height for CO₂ adsorption onto SBAC and kaolinite samples at heights of 3, 4, and 5 cm is shown in Fig. 10, which indicated that CO₂ adsorption capacity for the bed heights of 3–5 cm were increasing. The highest adsorption capacity of CO₂ for SBAC and kaolinite systems was achieved at the height of 5cm. The good performance of CO₂ adsorption on sugar cane based activated carbon at a bed height of 5.0 cm could also be attributed to more contact opportunities between the CO₂ gas and adsorbent particles. However, the mass transfer zone broadened since an increase in bed height causes greater resistance to mass transfer and slower kinetics of adsorption [14]. This was attributed to an increase in the surface area and the number of binding sites available for adsorption. The time for interaction of adsorbate and adsorbent also increased with an increasing amount of adsorbent [15, 16]

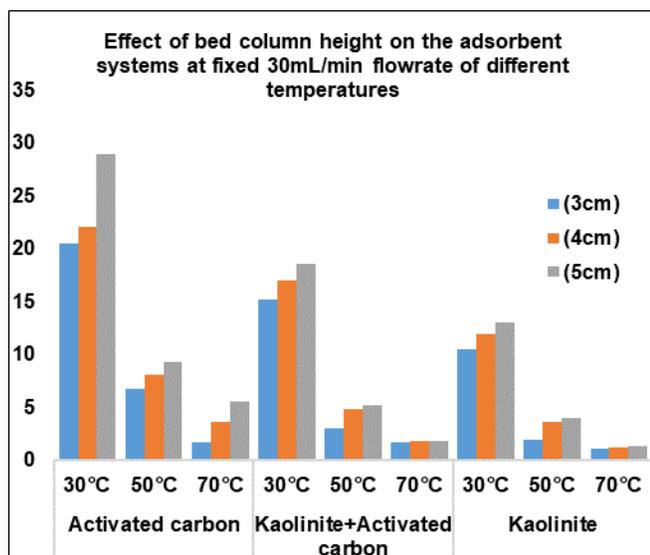


Fig. 10. Effect of height on CO₂ adsorption capacity of activated carbon. Constant temperature of 30 °C

CONCLUSIONS

This study has demonstrated that reasonably good surface area activated carbons can be prepared from the chemical activation of sugarcane bagasse waste with ZnCl₂ as activating agent. For the carbonization of the ZnCl₂ treated sample, the release of moisture and ZnCl₂ represents most of the evolution, indicating that ZnCl₂ plays an important role in increasing the surface area during carbonization. However, kaolinite, a cheap and commonly available clay mineral can also be utilized for CO₂ capture as it acts as a pollutant collector. Study of various parameters during CO₂ capture via adsorption revealed that temperature, flowrate, and column height influences the amount of CO₂ adsorbed. Under the experimental conditions investigated, the best conditions for the production of high surface area activated carbon from sugarcane bagasse waste by chemical activation are: chemical ratio (activating agent/precursor) of 100%, carbonization time of 1 h and carbonization temperature of 500 °C. At this optimal condition, the BET surface area obtained were 712 m²/g and 484 m²/g for sugarcane based activated carbon (SBAC) and kaolinite samples, respectively. The properties of SBAC and kaolinite samples were characterized in terms of FT-IR, BET surface area and SEM. FT-IR results indicated all the adsorbent's functional groups that were actively engaged in the adsorption process. According to BET, SBAC exhibited the highest pore volume (0.43 cm³/g), followed by kaolinite (0.26 cm³/g) which indicated higher gas adsorption. At higher temperature, the CO₂ adsorption capacity for each adsorbent was reduced. It appears that the sugarcane based activated carbon (SBAC) have stronger adsorption sites compare to the kaolinite samples [17]. Based on these findings, it can be concluded that the use of activated carbon derived from sugar cane bagasse and kaolinite is a promising alternative for CO₂ capture.

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