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Development and Characterization of Triethanolamine Functionalized Coconut Shell Activated Carbon for Carbon Dioxide Adsorption

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ABSTRACT

This study provide an insight into the potential of amine functionalized coconut shell activated carbon for carbon dioxide adsorption and storage. The coconut shell was carbonized (CAC) and chemically activated with KOH. The prepared CAC was further funtionalized with triethanolamine (TCAC). The activated carbons were characterized for its crystallinity, functional group and surface area using X-ray diffraction, Raman spectroscopy and Brunauer-Emmett-Teller theory, respectively before and after carbon dioxide adsorption. The effect of temperatures (40, 50 and 60 °C) on the rate of CO_2 adsorption as a function of time was also investigated. The adsorption capacity of CAC and TCAC were found to be 51 and 62 mg/g, respectively. The results characterization before and after CO_2 absorption revealed that the alteration of the structural and function group that favour formation of ammonium bicarbonate and carbonate. This study demonstrates that triethanolamine functionalized coconut activated carbon is a promising adsorbent for CO_2 sequestration and storage.

KEYWORDS

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INTRODUCTION

Environmental pollution of air, water and soil are the major problems that are faced by the world today. Air pollution pose dangerous threat to the air quality by causing climatic change, smog, acid rain and toxic air. These are responsible for severe and irreversible damage to the earth. CO_2 is the primary cause of global warming and it is released into the atmosphere from thermal power plants. Thermal power plants based on fossil fuels including coal, petroleum and gas account for over 60 % of the electricity generation worldwide. Among these fuels, coal is the most abundant and largest contributor (over 38 %) to the total word's electricity generation [1]. Consequently, coal-fired power plant is the chief culprit to the fossil-fired power plants that is fueling CO_2. Because coal-fired power plants provide energy at low cost than most other energy options, it remain an integral part of energy even in the near future.

Therefore, it is critical to reduce the CO_2 emission from fossil power plant flue gas. The three approach to reduce, control and mitigate this effect are: efficient and effective use of carbon- energy sources; switching to alternative or non-carbon energy sources and use of a post combustion capture (PCC). With the large reserve of fossil fuels, the continued dependence of international markets on this energy source and the lack of a cheaper alternative energy source, PCC technology is the optimal choice of reducing CO_2 emission in a near to middle term . This technology is attractive because it can allow coal-fired power plant to continue to be used without significant contribution to global warming.

Post combustion capture (PCC) refers to the removal of CO_2 from coal-fired plant flue gas after a complete combustion has been accomplished. The captured CO_2 is usually stored in depleted oil wells or the deep ocean. It can be used as preservative of carbonated beverages, refrigeration or for the production of value added chemicals. Presently, there are many PCC technologies used for coal-fired plant flue gas. These technologies include membrane purification, chemical absorption, cryogenic distillation and solid adsorbents. Chemical absorption and cryogenic distillation are both costly, with substantial energy required for CO_2 and phase transformation from gas to liquid respectively. Membrane purification suffers from low CO_2 selectivity and permeability. These limitations were overcome by the use of solid adsorbents [2,3].

At present, activated carbon adsorbents are recognized as the most effective and efficient technologies because of their well-developed surface area and pore size. In recent years, the search for carbon adsorbents has intensified. Among the activated carbons, amine-grafted materials is the most attractive alternative adsorbent that is used in chemical plants for CO_2 recovery. It is based on principle of neutralization reaction where amine solution is exposed to CO_2 in the flue gas to form carbonate and/or bicarbonate. The CO_2 removal system has been studied by many researchers. Amine-modified adsorbents can also be prepared by chemically grafting amine onto the porous materials, and in this case the adsorbents are stable and can be recovered. This approach involve functionalization of activated carbon source. The feedstock of activated carbons is either of inorganic matter (*e.g.* peat, lignite and all ranks of coal) or organic origin (*e.g.* wood, nut shells and coconut shells) [4,5]. Agricultural wastes are considered as good alternative feed-stock as they are abundant, easily available low-cost and renewable.

Currently, various agricultural wastes such as saw dust [6], walnut shell [7], coconut shell [8], pistachio shell [9] and wood [10] are used to produce activated carbon. It is agreed that the nature of the starting material largely influence the pore structure and pore size of activated carbon [11]. The size of the pores can be classified into micropore (less than 2 nm), mesopore (2-50 nm) and macropore (more than 50 nm) [12]. Coconut shell was selected over other raw materials due to its low-cost and availability. The shell of coconuts which account for 12 % of the total weight of the coconut, could be used more efficiently. Production of charcoal from the coconut shell offers an important export market for coconut producing areas. Carbonization of one tonne of coconut shells produces about 300 kg of charcoal, which can be further process to obtained 120 kg of activated carbon [13]. The coconut shells can be obtained in large quantity through the method of producing coconut oil (copra processing). The shell can be processed into activated carbon, which is widely used in gas and liquid phase separation, purification of various products and water treatment operation [14]. Coconut shell was selected over other raw materials due to its low-cost and availability. In a comparison between coconut shell and wood activated carbons, the coconut shell have been reported to a finer pore structure (less than 1 nm) than wood activated carbon which contained significant amounts of meso-pores and macropores [15]. Based on these properties, coconut shell activated carbon have been proven to be a good candidate for the production of activated carbon [16,17]. The sorption properties of coconut shell contain functional groups, such as hydroxyl, carboxylic and lactone, which have a high sorption capacity [17]. In this research, the surface of coconut shell was chemically modified with amine with the aim of studying CO_2 adsorption capacity and adsorbent characterization.

EXPERIMENTAL

Coconut shells used in the present study were obtained from Minna, Niger State of Nigeria. Potassium hydroxide and triethanolamine were purchased from PANLAC Chemicals, Minna, Nigeria whereas CO_2 was obtained from Nigerian Bottling Company, Kaduna State Nigeria.

X-ray diffraction (XRD) analysis were performed on non-adsorbed TCAC and adsorbed TCAC in a Bruker advance diffractometer using Cu Kα radiation at a scan rate of 2θ. The current and voltage were 40 mA and 40 kV, respectively. While the functional group of non-adsorbed TCAC and adsorbed TCAC was determined using SHIMADZU FT-IR (Fourier Transform Infrared Spectrophotometer). The surface area and porosity of adsorbent were determined using Brunauer-Emmett-Teller (BET) NOVA 1994 instruments version 11.0.

Preparation of activated carbon: Activated carbon was produced using coconut shells, which is low-cost and readily available agricultural waste as precursor. There are three stages involved in this process namely: pretreatment, carbonization and impregnation/modification stage. The precursor was washed thoroughly with water to remove all the foreign particles and dried in an oven to remove moisture. The dried coconut shells were then crushed to appropriate sizes, ready for carbonization. Dried coconut shell (300 g) was placed in a furnace for carbonization at a specified temperature. The furnace was set at 450 ℃ for a period of 1 h in order to get rid of inorganic volatile matters in the precursor leaving behind the more stable carbon and ash forming minerals. The sample was brought out of the furnace and allowed to cool to room temperature before being crushed with a mortar and sieved using a 300 mm size mesh.

Impregnation/modification stage: After carbonization, 250 mL of 1 M KOH solution was added to the sample. The treated sample was divided into two equal parts. Triethanolamine (50 mL , 1 M) was added to the second part. Both mixtures were stirred continuously and heated at 100 ℃ for 2 h. The mixtures were later heated at 100 ℃ until volatilization of ethanol was completed. It was then washed with distilled water to remove excess activating agent from the samples until pH of a mixture of water and each sample were within 6.5-7.5. The samples

were then dried in an oven, ready to be used for the adsorption process. The sample treated with KOH was designated as CAC while the sample impregnated with triethanolamine was designated as TCAC.

Carbon dioxide adsorption experiment: The experiment was performed in a cylindrical glass column. The adsorption column with known amount of adsorbent packed inside it. It is then weighed on a digital weighing balance before placing it within a temperature controlled water bath while CO_2 gas was passed through it for some time. Subsequently, the column was pulled out from the water bath and re-weighed. The amount of CO_2 captured by the adsorbent was determined by the difference in weight before and after the adsorption process. The adsorption process was studied at different adsorption time (5, 10, 15, 20 and 25 min) at constant temperature of 40 °C. To further study the effect of temperature on triethanolamine modified sample, the experiment was performed exclusively used for the adsorption process at varying times (5, 10, 15, 20 and 25 min) and temperatures (40, 50 and 60 °C), while keeping the sample mass constant. The amount of CO_2 adsorbed (q, mg/g) was determined based on the eqn 1:

$$\text{Amount of } CO_2 \text{ adsorbed} = \frac{qq_t(mg) - q_o(mg)}{q_o(mg)} \qquad (1)$$

where q_o and q_t are original mass of adsorbent and adsorbent at time t (min), respectively.

RESULTS AND DISCUSSION

Carbon dioxide adsorption: It can be observed that the isotherm curves of both CAC and TCAC follow a common pattern regardless of adsorbent type and temperature as shown in Fig. 1. This mean that the rate of CO_2 adsorption on adsorbent decrease as the time increase until the amount of CO_2 adsorbed became saturated at the maximum time of 20 min (Figs. 1 and 2). Thus, the rate of CO_2 adsorption comply with the expected physisorption trend [14]. The adsorption capacity of CAC and TCAC were found to be 51 and 62 mg/g, respectively. To further study, CO_2 adsorption on TCAC, series of temperature (*i.e.*, 40, 50 and 60 °C) were chosen in order to simulate isothermal conditions that post combustion flue gas covers [1]. The effect of temperature on CO_2 adsorption capacity behaviour was revealed based on the adsorption patterns (Fig. 2). It can be observed that the isotherm curves of both CAC and TCAC follow a common pattern regardless of adsorbent type and temperature, which mean that the rate of CO_2 adsorption on the adsorbent decrease as the temperature increase. The reduction of CO_2 adsorption with increase in adsorption temperature was in accordance with
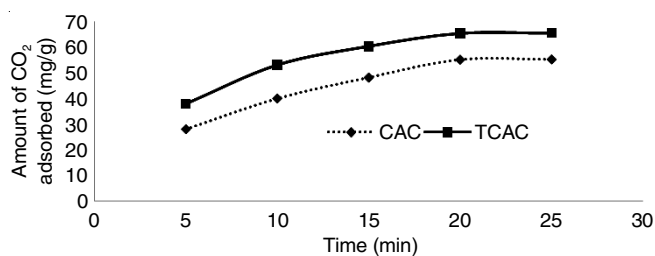
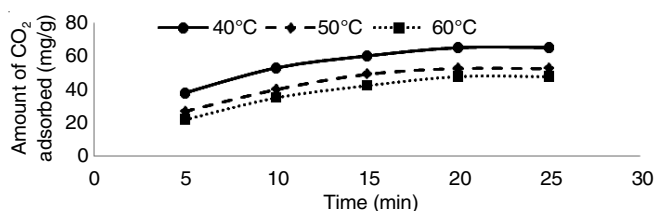Fig. 1. Isotherm curves of amount of CO_2 (g/g) against time (s)

Fig. 2. Effect of temperature on amount of CO_2 adsorbed

anticipated trend [18]. The behaviour of adsorption isotherms (Fig. 1) follows the type-I of IUPAC classification [12], which indicates adsorption of gas molecules onto microporous surface.

FTIR studies of CO_2 adsorption: The surface interactions of CO_2 with amine-modified samples were studied using FT-IR spectroscopy. A comparison of FT-IR spectra between non-adsorbed TCAC and TCAC that adsorbed CO_2 are presented in Fig. 3 (a) and (b). Different peaks were observed with intensities signifying different types of bond in the form of O-H, C-H, C-O, N-H and C-N. Strong FT-IR bands were observed in the range of 4000-400 cm^{-1} for both samples [Fig. 3(a) and (b)]. The assignment of these bands were complicated. The IR band at 1331 cm^{-1} which was found in CO_2 adsorbed TCAC can be assigned to weakly adsorbed gaseous CO_2 (Fig. 3a). The vibration band at 1382 cm^{-1} in Fig. 4 may be due to bicarbonate C-O bending [20], formed when amine adsorbed CO_2. The IR band at 1331 and 1382 cm^{-1} (Fig. 3b) are absent in non-adsorbed TCAC (Fig. 3a). The nitrogenous compounds peak at 1451 cm^{-1} in Fig. 3a become narrower after absorption due to attachment of CO_2 to amine. The IR bands at 1432 cm^{-1} are due to the asymmetric stretchings of C-O in carbamate [22]. Zelenak *et al.* [22] reported that CO_2 react with amine to form ammonium carbamate, which is subsequently transformed to ammonium bicarbonate and carbonate.

XRD studies of CO_2 adsorption: A comparison of the XRD patterns between non-adsorbed TCAC and TCAC that adsorbed CO_2 are presented in Fig. 4 (a) and (b). Characteristic peaks appear at 2θ values of 25, 33 and 28° for the activated
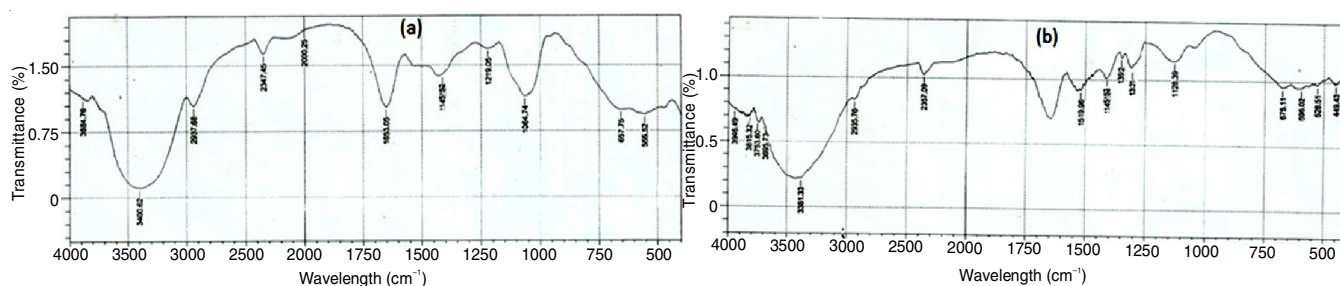
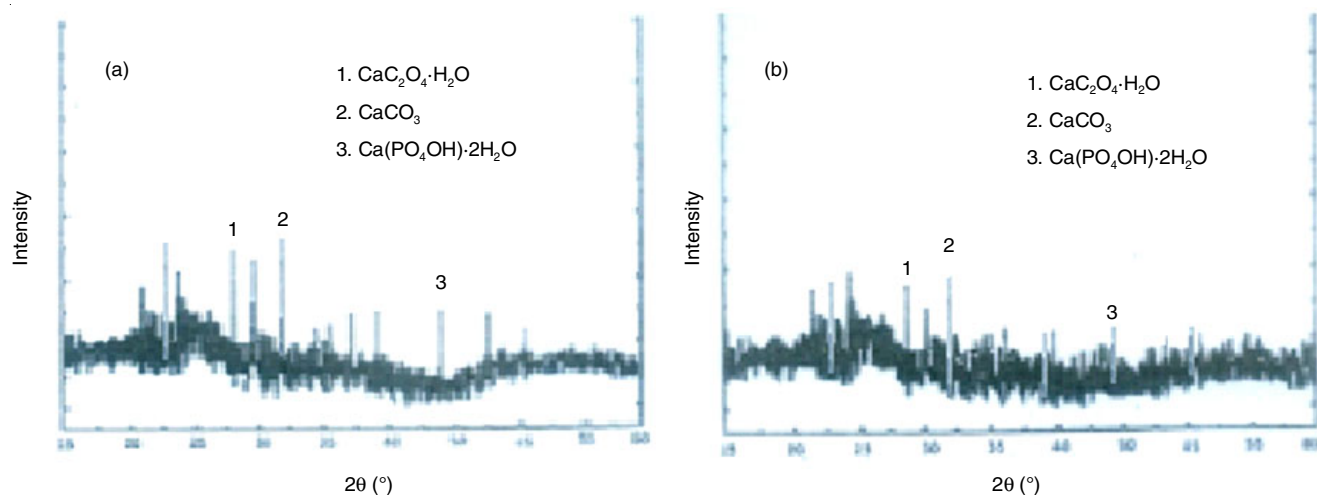Fig. 3. FT-IR spectra of TCAC (a) before CO_2 adsorption and (b) after CO_2 adsorption

Fig. 4. X-ray diffraction patterns of TCAC: (a) non-adsorbed, (b) CO_2 adsorbed

carbon correspond to $CaC_2O_4 \cdot H_2O$, $CaCO_3$ and $Ca(PO_3OH)]\cdot 2H_2O$ compounds, respectively [3]. As for case of non-adsorbed TCAC (Fig. 4a), the % peak area at $2\theta = 33°$ which was observed with high intensity confirmed the presence of $CaCO_3$ compound. This peak was found to reduce significantly after adsorption of CO_2 as shown in Fig. 4b. This reduction could be due to the presence of CO_2 on the surface of TCAC that cover its pores after adsorption which is evident in CO_2 attachment to amine to form ammonium carbonate/bicarbonate. The hydroxyl group compound of $CaC_2O_4 \cdot H_2O$ at $2\theta = 25°$ was observed to reduce. This is because basic -OH ion formed new crystals on TCAC surface covering the surface of original TCAC.

BET surface area: Analysis of BET surface area of CAC before CO_2 adsorption was found to be 687 m^2/g, with total pore volume of 0.291 cm^3/g. while that of CAC before CO_2 adsorption was found to be 709 m^2/g, with total pore volume of 0.315 cm^3/g. The pore volume of both carbon fall within the range of 0.2-0.6 m^3/g reported for activated carbons [11]. The large amount of micropores and a small amount of macropores exhibited by TCAC favours high CO_2 adsorption capacity [8].

Conclusion

Coconut shell was chemically activated with potassium hydroxide (CAC) and triethanolamine (TCAC) for CO_2 absorption studies. The amount of CO_2 absorbed by TCAC was higher when compared to that of CAC. The effect on temperature on CO_2 absorption was investigated and found that absorption of CO_2 decrease as the temperature increase. The results of carbon characterization before and after CO_2 absorption revealed the alteration of the structural and function group that favour formation of ammonium bicarbonate and carbonate. This study demonstrates that triethanolamine functionalized coconut activated carbon is found to be a promising adsorbent for CO_2 sequestration and storage.

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