Potential of Activated Carbon Prepared from Rice Husk at Different Activation Temperature in CO_2 Capture

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Abstract CO_2 capture from exhaust gas with rice husk (RH) as a potential raw material for preparation of activated carbon (AC) was studied. Physical activation was employed using water vapour at 700 and 750 ^{o}C for preparation of the AC. Physicochemical properties were determined using standard methods, while FTIR was used to determine the functional group in the prepared AC. The effects of particle size, contact time, and adsorbent dosage were studied to evaluate the adsorption capacity of the activated carbons. The values of the physicochemical properties evaluated for RH activated carbon prepared at activation temperature of 750 and 700 ^{o}C were respectively: moisture (2.10, 3.40%), ash (6.40, 4.90%), volatile matter (13.40, 24.50%), fixed carbon (78.10, 78.10%), bulk density (0.68, 0.56 g/cm^3), surface area (850.00, 730.00 m^{2}g), and iodine number (814.40, 679.40 mg/g). The results of FTIR spectra of the activated carbons revealed the presence of hydroxyl, phenols, carboxyl, carbonyl, lactones, pyrones, and anhydride groups. Particle size, contact time, and adsorbent dosage were found to have effect in the percentage of CO_2 adsorbed and more than 55% of CO_2 was captured within the range of parameter studied. Both activated carbons were effective in the capturing of CO_2 from the exhaust gas.

Keywords CO_2, capture, adsorption, activated carbon, environment

Introduction

Adverse climate warming and weather changes with increasing concentration of carbon dioxide in the atmosphere strengthened the scientific consensus that higher concentration of CO_2 in the atmosphere, combines with incoming solar radiation, trapping energy from the sun in form of heat, therefore, influencing the temperature of the earth's surface. CO_2 concentration have increased from preindustrial levels of 280 ppm to 372 ppm currently, due to anthropogenic CO_2 emissions into the atmosphere mainly as a result of fossil-fuel combustion for energy production, that enhances the natural greenhouse effect, which have led to climate warming and weather changes [1,2].

Increase in concentration of greenhouse gases contributed majorly by increase in emission of anthropogenic CO_2 gas into the atmosphere has led to irreversible climate change such as atmospheric or global warming, consistent rise in sea level, occurrence of more harsh weather due to imbalance caused by overconcentration of the greenhouse gases especially CO_2, which affect the heat flux between the earth and atmosphere. The most practicable and immediate option to decrease huge quantity of CO_2 emission and thereby prevent global-scale warming is through artificial

capturing of CO_2 contained in flue gas from thermal power plants, steel works, factories, and other facilities in the course of industrial activity, followed by fixation and effective utilization [3], and long term CO_2 sequestration [4]. Generally, technologies available or being considered or used for CO_2 capture are chemical absorption using an amine (solution, solvent absorption), physical adsorption using an adsorbent, membrane systems, cryogenic fractionation, chemical looping, and fuel cell technology [5]. One major challenges faced by all these CO_2 sequestration technologies is high cost of CO_2 separation and capture. Therefore, for realization of these technologies in practice, cost of CO_2 capture and separation must be significantly reduced by any means possible. Amongst the technologies under development and consideration for CO_2 capture, the adsorption technology employing activated carbon from local and low-cost materials seems promising and realizable in practice considering low energy consumption involved [6].

Activated carbons available for sale in Nigeria are imported, and expensive. This has prompted researches toward formulation and development of activated carbon from local sources such as rice husk, coconut shell, oil palm shell, oil palm fiber and other waste from plants; converting these wastes to wealth, as well as reducing the overall cost of AC.

Rice husks also known as rice hulls are the hard outer part that cover and protect the grains or the rice seed which mostly cannot be digested by humans. One of the ways in which this wastes can be converted into useful product (wealth) is by carbonization of the materials. Carbon that has been processed to become extremely porous and to have a very large surface area available for adsorption is called activated carbon, activate charcoal or activated coal [7]. This work studied the potentials of activated carbon produced from rice husk (RH) at different activation temperature of 700 and 750 ^{o}C in CO_2 capture.

Experimental

Rice husk was collected from a rice husk dump in a rice mill in Omor, Anambra State, Nigeria. The sample was thoroughly washed to remove any adhering impurities with distilled water and then air-dried at room temperature. The washed and air-dried sample was separately burned in a muffle furnace at 974K for 3 hours under inert atmosphere (absence of oxygen). The burnt sample namely (rice husk) was washed again with distilled water to neutralize the pH and to remove from the surface of the burnt material any remaining adhering impurities such as light empty grains, dust, fine dirt, and sand. In order to remove metallic impurities and to aid in separation of SiO_2 the washed and neutralized material (RHA) was reflux with 6N HCl (Merck GR) for 1 hour 30 minutes (1.5 h) and then filtered to obtain filtered rice husk ash (FRHA). The filtered material was thoroughly and repeatedly rinsed with hot water and then boiled with 2.5N NaOH (Merck GR) solution for 1h 30m at 354K while being stirred magnetically, producing sodium silicates (Na_2SiO_3) and solid residue (pure carbon) after the reaction in each case. Then, the product of reactions in each case were filtered to obtain the solid residue (carbon) which were dried at room temperature and later activated by physical method with water vapour in a reactor with external electric heating at temperature of about 700 and 750 ^{o}C without access of air in order to reduce loss of the loaded carbon material.

The activated carbon obtained at activation temperature of 700 ^{o}C designated (RH700) and that obtained at activation temperature of 750 ^{o}C designated (RH750) were then pulverized and sieved with different sieve sizes and then stored in air tight well labelled bottles for further analysis and utilization. The activated carbons (AC) yields in percentage were calculated from samples weight after activation to its initial weight using Equation 1.

$$\%AC = \frac{Weight\ Obtained\ after\ activation}{Weight\ of\ the\ sample} \times \frac{100}{1} \qquad (1)$$

Characterization of Activated Carbon
Determination of pH of Activated Carbon
The pH of the carbon samples was determined according to ASTM [8].

Determination of Moisture Content of the Raw Materials and Activated Carbon
The moisture content of the samples was determined according to ASTM [9].

Determination of Ash content
The ash content of the samples was determined according to ASTM [10].

Determination of Bulk Density of Activated Carbon
Tapping procedure was used to determine the bulk densities of the activated carbon [11].

Determination of Iodine Number of Activated Carbon
The iodine number of the samples was determined using the sodium thiosulphate volumetric method [12].

Determination of volatile Content of the Samples
1.0g each of sample was weighed into a partially closed crucible of known weight. The crucible with the sample was heated in a muffle furnace at 900 ^{o}C for 10min. Then the crucible and its content was allowed to cool and reweighed [13].

Determination of Percentage Fixed Carbon (FC)
FC is the solid residue other than the ash resulting from the volatile matter test. The percentage fixed carbon (%FC) for the samples were obtained by subtracting the sum of moisture content, volatile matter, and ash content from 100% for each sample as given in Equation 2.
%FC = 100 – (Moisture content + ash content + volatile matter) %   (2)

Determination of Surface Area
The specific surface area of the activated carbons was estimated by agitating 1.5g of the activated carbon samples in 100ml of diluted hydrochloric acid at a pH = 3 [14,15].

Fourier Transform Infrared (FTIR) Spectrometer
The chemical groups present in activated carbon samples were identified by FTIR spectroscopy. KBr was used as background material in the analysis. FTIR spectra of the samples were examined and recorded using FTIR spectrophotometer with range 400-4000cm^{-1}.

Evaluation of CO_2 Capture by Adsorption Process using AC adsorbents
The exhaust gas stream of diesel generator was the source of CO_2 in this study.
An empty glass tube was fixed firmly to an exhaust pipe of a diesel generator to collect the exhaust (flue) gas and then connected to a gas analyzer and the generator was switched on for 10 minutes to determine the compositions of the exhaust gas before adsorption. Then, 15g of activated carbon samples was packed in another glass tube which was fastened firmly at one end to a glass tube connected firmly to the exhaust pipe of the petrol generator, while the other end of the packed glass tube was fixed firmly to gas analyzer to determine the composition of the exit exhaust (flue) gas from the packed glass tube after adsorption must have taken place. This procedure was repeated for different adsorbents, contact time, particles sizes and adsorbent dosage. The percentage CO_2 adsorbed in each case was calculated using Equations 3.

$$CO_2 \ Adsorbed \ (\%) \ = \ \frac{C_o - C_e}{C_o} \ x \ \frac{100}{1}$$ (3)

Where, C_o and C_e are respectively the percentage composition of CO_2 in the flue gas at initial and any time t of adsorption.

Results and Discussion

Yield and Physicochemical Properties of Activated Carbons

RH700 and RH750 were respectively calculated to be 37.99% and 38.03%. This implies that RH700 and RH750 contain nearly the same amount of fixed carbon as further showed by the result of physicochemical properties of the produced activated carbons in Table 1, thus, making rice husk good potential source of carbon.

Iodine number is usually used to roughly estimate the surface area of activated carbon at room temperature condition. It is used as an indicator for the porosity and adsorbent capacity of the activated carbon [16,17,18]. From Table 1, the iodine number of RH750 (814.40 mg/g) is higher than that of iodine number of RH700 (679.40. mg/g).

Table 1: Physicochemical Properties of Activated Carbon Obtained from RH activated at 700 and 750 ^{o}C

Parameters	RH 700	RH 750
Moisture content (%)	3.4	2.1
Volatile matter (%)	24.5	13.4
Ash content (%)	4.9	6.4
Fixed carbon (%)	78.1	78.1
pH	6.8	6.8
Surface area (m^2g)	730	850
Iodine number (mg/g)	679.4	814.4
Bulk density (g/cm^3)	0.56	0.68

It has been emphasized that the higher the bulk density of adsorbing material, the higher the volumetric adsorption capacity of the material [19]. Also, the larger the surface area of adsorbent, the higher the adsorption capacity of that adsorbent due to increased porosity. From Table 1, RH750 has higher bulk density (0.68 g/cm ^{3}), and higher surface area (850.00 m^2g) than RH700 with bulk density (0.56 g/cm^3) and surface area (730.00 m^2g)), making 750 ^{o}C activation temperature a better temperature for preparation of activated carbon.
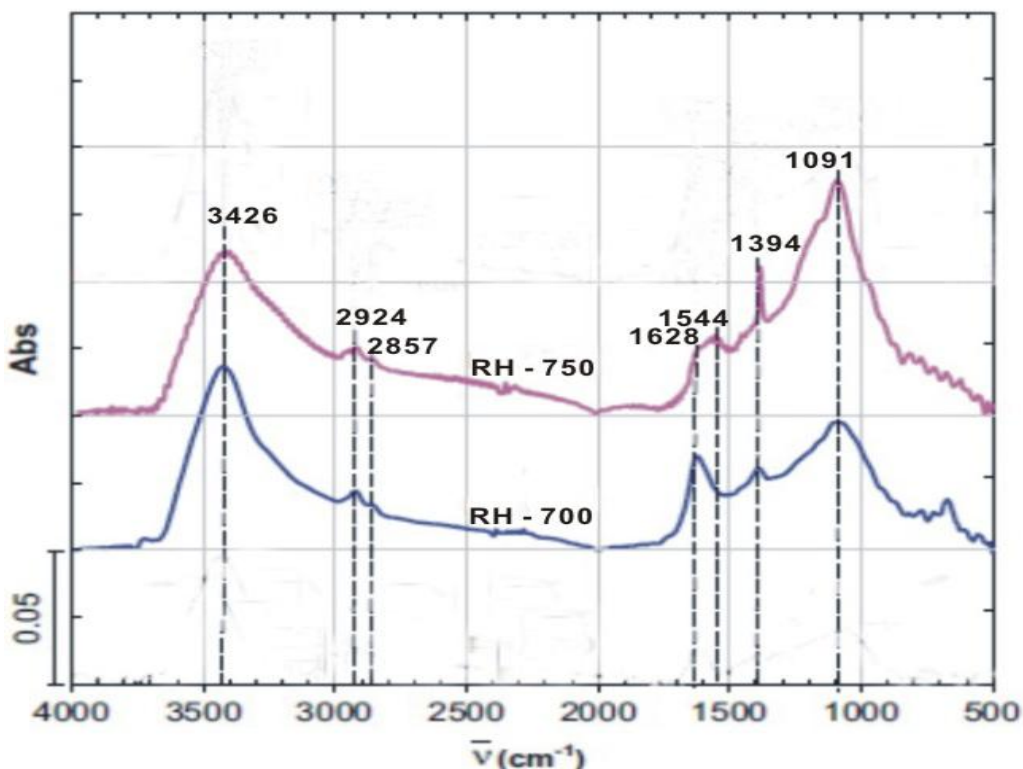

Figure 1: FTIR spectrum for the Activated carbons from RH at Activation Temperature of 700 and 750 ^{o}C

FTIR of the Activated Carbons

The results of the qualitative characterization of surface functional groups of AC samples performed by the FTIR technique are presented in Figure 1 for RH700 and RH750. From the result of FTIR of RH samples in Figure 1, the band at 3425 cm^{-1} can be assigned to O–H stretching of hydroxyl groups or adsorbed water [20]. The bands at 2924 and 1393 cm^{-1} are attributed to C–H stretching of aliphatic carbon or due to CH_2 of CH_3 deformation. The band at 2858 cm^{-1} indicates the vibration of CH_3–O group. The band appearing at 1627 cm^{-1} corresponds to the C=O vibration of lactonic, carboxyl or anhydride groups [21]. The bands around 1545 and 1096 cm^{-1} are assigned to ring vibration in a large aromatic skeleton generally found in carbonaceous material, such as activated carbon [22]. The region between 700 and 1200 cm^{-1} contains various bands related to aromatic, out of plane C–H bending with different degrees of substitution [23]. The result of FTIR implies that the RH activated carbons have no silica since there are no SiO_2 absorption peaks at 1101, 944, 789 and 470 cm^{-1} according to [24].

Adsorption Process

Effect of Particle Size on the Adsorption Process

Activated carbon adsorption capacity increases with decrease in particle size. From the CO_2 removal at different particle sizes in Figure 2, it can be seen that the removal rate increased with a decrease in particle, implying that CO_2 removal rate was higher (better) at smaller particle size. The relatively higher adsorption with smaller adsorbate particle may be attributed to the fact that smaller particle yield large surface area. There is a possibility that shorter time to equilibrium is produced by a smaller particle. The breaking of larger particles tends to open tiny cracks and channels on the particle surface of the material resulting in more accessibility to better diffusion, due to the smaller particle size [25].
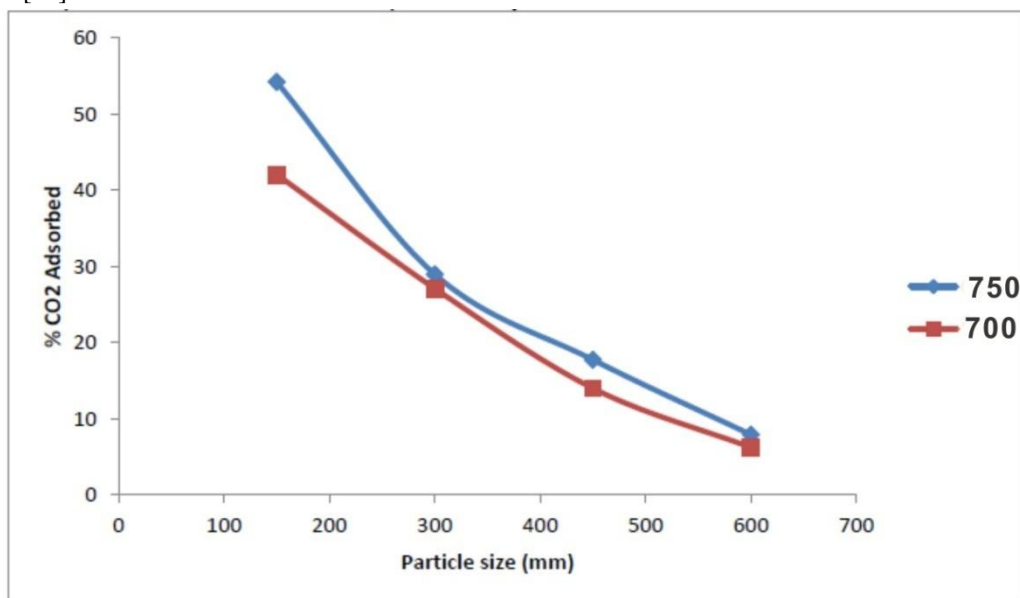

Figure 2: CO$_2$ Adsorption with Different Particle Sizes of RH700 and RH750 Adsorbents Dosage of 30g for a Period of 30mins

Effect of Contact Time on the Adsorption Process

It was observed from Figure 3 that the CO_2 adsorption percentage increased with increasing contact time. In the first 15 to 30 mins, above 30% of CO_2 adsorption occurred and thereafter, there was observed reduction in the rate of adsorption of the adsorbate species unto the adsorbent. This implies that 30 mins was the time required to reach equilibrium on CO_2 adsorption in this study for RH750, while it took a little longer about 45 mins for RH700 to reach equilibrium, meaning that rice husk activated at 750 ^{o}C (RH750) has higher adsorption rate.

The rapid adsorption at the initial stage could be attributed to availability of the large surface area of the adsorbents for adsorption. The later slow adsorption is probably due to deactivation of the surface area of the activated carbons as a result the pores been filled up, and the slow pore diffusion of the solute CO_2 into the bulk of the adsorbent [26]. Furthermore, the rapid adsorption at the beginning of the process is due to external surface of the adsorbent, and is followed by slower internal diffusion process [19].
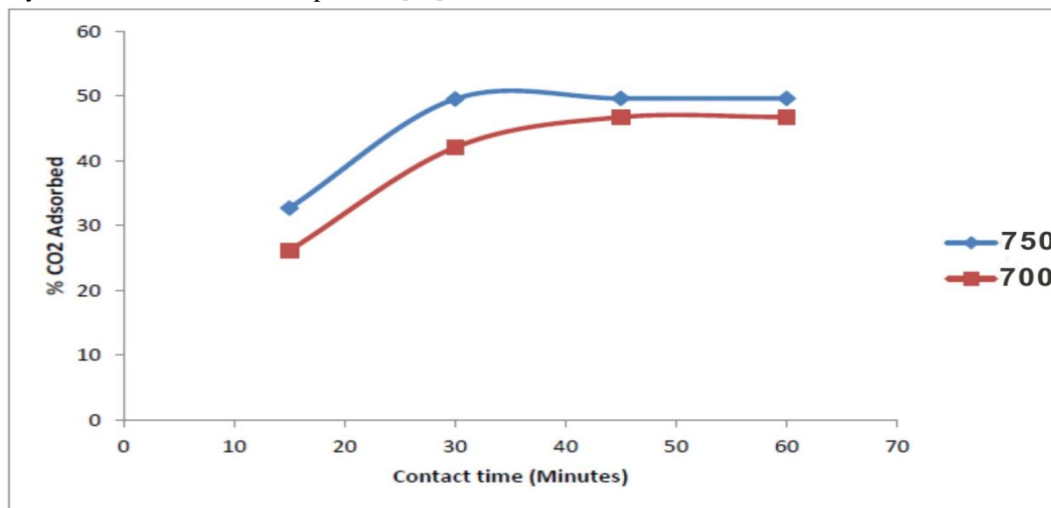

Figure 3: CO_2 Adsorption at Different Time for RH700 and RH750 of Adsorbents Dosage of 30g and 150 mm of Particle Size

Effect of Adsorption Dosage on Adsorption Process

Adsorption dosage determines the capacity of an adsorbent for a given initial concentration of the adsorbate. Thus, it is an important parameter. From Figure 4, it was observed that as the adsorbent dosage increased, the percentage of adsorption also increased but the amount of CO_2 adsorbed per unit mass of the adsorbent decreased significantly. The decrease in unit adsorption with increasing dose of adsorbent is basically due to adsorption sites remaining unsaturated during the adsorption reaction [27]. The definite increase in the adsorption capacity of the adsorbents with dosage revealed in Figure 4, according to [28] and [29], is due to the larger number of available adsorption sites which favour the enhanced uptake of the amount of solute absorbed per unit mass of adsorbent.
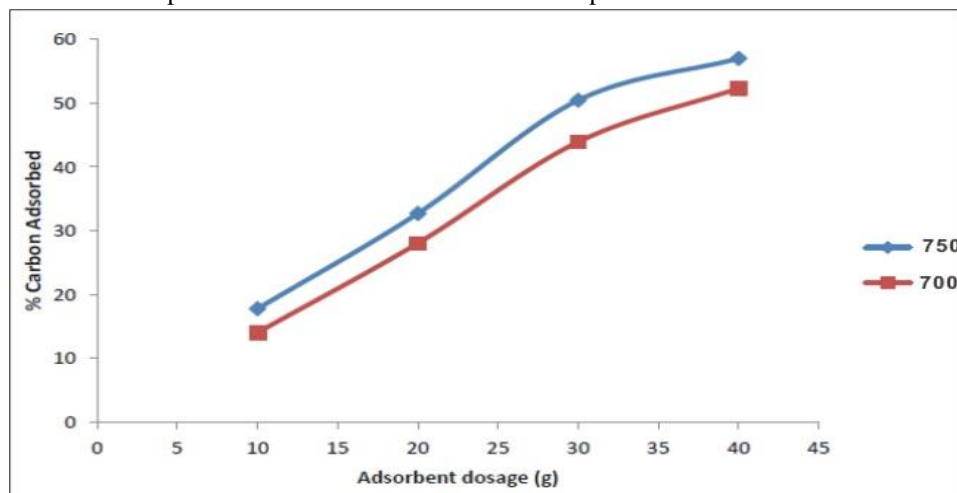

Figure 4: CO_2 Adsorption at Different RH700 and RH750 Adsorbent Dosage at Condition of 150 mm of Particle size and 30 mins Adsorption Time

Conclusion

The produced activated carbons from rice husk activated at 700 ^{o}C (RH700) and rice husk activated at 750 ^{o}C (RH75)) have excellent properties required of good adsorbents. Both activated carbons were effective in the capturing of CO_2 from the exhaust gas stream. Factors such as particle size, adsorbent dosage, and contact time had significant effect on the amount of CO_2 adsorbed and more than 55% of CO_2 initially present in the exhaust gas stream was captured within the range of parameter investigated.

Acknowledgement

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