Potential of Activated Carbon Prepared from Rice Husk Waste and Oil Palm Fibre in Carbon Dioxide Capture

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Abstract

 CO_2 capture from exhaust gas using rice husk (RH) and oil palm fiber (OPF) as potential raw materials for the preparation of activated carbon (AC) was studied. Physical activation was employed using water vapour at 800 °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 and OPF activated carbons were respectively: moisture (2.100, 3.400%), ash (6.40, 4.90%), volatile matter (13.40, 24.50%), fixed carbon (78.10, 67.20%), bulk density (0.68, 0.56 g/cm³), surface area (850.00, 730.00 m²g), 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 CO₂ adsorbed and more than 55% of CO₂ was captured within the range of parameter studied. Both activated carbons were effective in the capturing of CO₂ from the exhaust gas.

Keywords: CO₂-capture, adsorption, activated carbon, environment

Introduction

Adverse climate warming and weather changes with increasing concentration of carbon dioxide atmosphere in the 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. CO₂ 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 (Wilson and Gerard 2007; Bachu and Shaw, 2003).

Increase in concentration of greenhouse gases contributed majorly by increase in emission of anthropogenic CO₂ 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 globalscale 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 Ida et al. (2012), and long term CO_2 sequestration (Jahangiri and Zhang, 2011).

sequestration (Jahangiri and Zhang, 2011). Generally, technologies available or being considered or used for CO_2 capture are absorption using chemical an amine solvent absorption), physical (solution, adsorption using an adsorbent, membrane systems, cryogenic fractionation, chemical looping, and fuel cell technology (Forbes *et al.*, 2008).One major challenges faced by all these CO_2 sequestration technologies is high cost of CO_2 separation and capture. realization Therefore. for of these technologies in practice, cost of CO₂ capture and separation must be significantly reduced by any means possible. Amongst the development technologies under and consideration for CO₂ capture, the adsorption technology employing activated carbon from local and low-cost materials seems promising and realizable in practice considering low energy consumption involved (Siriwardane et al., 2001).

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, while oil palm fiber (OPF) is non-hazardous biodegradable fibrous residue obtained after the oil have been separated from the sterilized fruit. One of the ways in which these 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 (Hariprasad et al., 2016). This work studied the potentials of activated carbon produced from rice husk (RH) and oil palm fiber (OPF) in CO₂ capture.

Experimental

Rice husk and the oil palm fibre were respectively collected from a rice husk dump in a rice mill and a palm oil processing plant both in Omor, Anambra State, Nigeria. The samples were thoroughly washed separately to remove any adhering impurities with distilled water and then air-dried at room temperature. The washed and air-dried samples were separately burned in a muffle furnace at 974K for 3 hours under inert atmosphere (absence of oxygen). The burnt samples namely: burnt rice husk (BRH) and burnt oil palm fibre (BOPF) were separately washed again with distilled water to neutralize the pH and to remove from the surface of the burnt materials any remaining adhering impurities such as light empty grains, dust, fine dirt, and sand. In order to remove metallic impurities and to aid in of SiO₂ the washed and separation neutralized materials (RHA and BOPF) were reflux separately with 6N HCl (Merck GR) for 1 hour 30 minutes (1.5 h) and then filtered to obtain filtered rice husk ash (FRHA) and filtered oil palm fiber ash (FOPFA).The

filtered materials were thoroughly and repeatedly rinsed separately 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 (Na₂SiO₃) 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 at temperature of about 800 °C heating without access of air in order to reduce loss of the loaded carbon material.

The activated carbon 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.

 $%AC = \frac{WeightObtainedafteractivation}{Weightofthesample} \times \frac{100}{1}$ (1)

Characterization of Activated Carbon

Determination of pH of Activated Carbon ASTM D 3838-80 (1996) was used to determine the pH of the carbon samples.

Determination of Moisture Content of the Raw Materials and Activated Carbon

ASTM D 2867-91 (1991) was used to determine the moisture contents of the samples.

Determination of Ash content

ASTM D 2866- 94 (2018) was used to determine the ash contents of the samples.

Determination of Bulk Density of Activated Carbon

Tapping procedure by Ahmedna et al. (1997) was used to determine the bulk densities of the activated carbon.

Determination of Iodine Number of Activated Carbon

The iodine number of the samples was determined using the sodium thiosulphate volumetric method according to ASTM D 4607-86 (1986).

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 9000C for 10min. Then the crucible and its content was allowed to cool and reweighed (ASTM D 5832-98, 1998).

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 according to Sear's method employed by Al-Qodah and Shawabkah (2009) and Alzaydian (2009).

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 CO₂ 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 10minutes 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.

$$= \frac{CO_2Adsorbed(\%)}{C_o - C_e} \frac{100}{1}$$

Where, C_o and C_e are respectively the percentage composition of CO₂ in the flue gas at initial and any time t of adsorption.

Results and Discussion

Yield and Physicochemical Properties of Activated Carbons

The yield of activated carbons in percentage for OPF and RH were respectively calculated to be 37% and 38.3%. This implies that rice husk contain more fixed carbon than oil palm fiber as further proved by the result of physicochemical properties of the produced activated carbons in Table 1, thus, making RH more potential source of carbon.

Parameters	Values	
	RH	OPF
Moisture content (%)	2.10	3.40
Volatile matter (%)	13.40	24.50
Ash content (%)	6.40	4.90
Fixed carbon (%)	78.10	67.20
pH	6.80	6.70
Surface area (m^2/g)	850.00	730.00
Iodine number (mg/g)	814.40	679.40
Bulk density (g/cm ³)	0.68	0.56

Table 1: Physicochemical properties of activated carbon obtained from RH and OPF

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 (Sugumaran et al., 2012; Sahira et al., 2013; Ekpete et al., 2017). From Table 1, the iodine number of RH activate carbon (814.40 mg/g) is higher than that of iodine number of OPF activated carbon (679.40. mg/g).

Lui et al. (2018) opined that the higher the bulk density of adsorbing material, the higher the volumetric adsorption capacity of the material. Also, the larger the surface area of adsorbent, the higher the adsorption capacity of that adsorbent due to increased porosity. From Table 1, RH has higher bulk density (0.68g/cm³), and higher surface area (850.00m²g) than OPF activated carbon with bulk density (0.56 g/cm³) and surface area (730.00m²g)), making RH a superior precursor for preparation of activated carbon.

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 RH and Figure 2 for OPF. From the result of FTIR of RH sample in Figure 1, the band at 3425 cm⁻¹ can be

assigned to O-H stretching of hydroxyl groups or adsorbed water (Guo and Rockstraw, 2007). 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 CH₃–O group. The band appearing at 1627 cm⁻¹ corresponds to the C=O vibration of lactonic, carboxyl or anhydride groups (Kennedy et al., 2005). 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 (Sun and Tomkinson, 2001). 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 (Mastalerz and Bustin, 1995).

The result of FTIR implies that the RH activated carbon has no silica since there are no SiO₂ absorption peaks at 1101, 944, 789 and 470 cm⁻¹ according to Ambedkar and Muniyan (2011). Also, the FTIR spectra of the produced OPF activated carbon shown in Figure 2 indicated the presence of hydroxyl, phenols, carboxyl, carbonyl, lactones, pyrones, and anhydride groups, which are important sorption sites according to Karthikeyan et al. (2007).



Fig 1: FTIR spectrum for activated carbon from RH



Fig 2: FTIR spectrum for activated carbon from OPF

Adsorption Process

Effect of Particle Size on the Adsorption Process

Activate carbon adsorption capacity increases with decrease in particle size. From the CO₂ removal at different particle sizes in Figure 3, 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 (Weber and Morris, 1963).

Effect of Contact Time on the Adsorption Process

It was observed from Figure 4 that the CO_2 adsorption percentage increased with

increasing contact time. In the first 15 to 30 mins, above 30% of CO₂ adsorption occurred and thereafter, 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 CO₂ adsorption in this study for RH activated carbon, while it took a little longer about 45 mins for OPF activated carbon to reach equilibrium, meaning that RH activated carbon 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 (Goswami and Ghosh, 2005). 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 (Li et al., 2008).



Fig 3: CO₂ adsorption with different particle sizes of rh and OPF adsorbents dosage of 30g for a period of 30mins



Fig 4: CO₂adsorption at different time for RH and OPF adsorbents dosage of 30g and 150 mm of particle size

Effect of Adsorbent 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 5, 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. According to Bulut and Aydin (2006), the decrease in unit adsorption with increasing dosage of adsorbent is basically due to adsorption sites remaining unsaturated during the adsorption reaction. The definite increase in the adsorption capacity of the adsorbents with dosage revealed in Figure 5, according to Sricharoenchaikul et al. (2008) and Ambedkar and Muniyan (2011), 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.



Fig 5: CO₂ adsorption at different RH and OPF adsorbent dosage at condition of 150 mm of particle size and 30 mins adsorption time

Conclusion

The produced activated carbons from rice husk (RH) and oil palm fiber (OPF) 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.

References

- Ahmedna, M., Johns, M.M., Clarke, S.J., Marshall, W.E., Rao, R.M. (1997) Potential of agricultural by-product-based activated carbons for use in raw sugar decolouration. *Journal of the Science of Food and Agriculture*, 75, 117-124.
- Al-Qodah, Z. & Shawabkah, R. (2009). Braz. J. Chem. Eng, 26(1), 6.
- Alzaydian, A.S. (2009). Adsorption of methylene blue from aqueous solution onto a low cost natural Jordanian Tripoli. *Am. J. Applied Sci.*, 6(6), 1047-1058.

Ambedkar, G. & Muniyan, M. (2011). <u>Bioaccumulation of some heavy metals in the selected five</u> <u>freshwater fish from Kollidam River, Tamilnadu, India. Adv. Appl. Sci. Res.</u>, 2(4), 283.

- ASTM D 4607-86 .(1986). American Society for Testing and Materials, Standard test method for determination of iodine number of activated carbon; ASTM Committee on Standards. Philadelphia, PA.
- ASTM D 2867-91. (1991). American Society of Testing and Materials, Standard test methods for moisture in activated carbon; ASTM Committee on Standards, Philadelphia, PA.
- ASTM D 3838-80. (1996). American Society for Testing and Materials, Annual Book of ASTM Standard, Volume 15.01, Refractories, Carbon and Graphic Products; activated Carbon, ASTM, Philadelphia, PA.
- ASTM D5832-98 (1998), Standard Test Method for Volatile Matter Content of Activated Carbon Samples, ASTM International, West Conshohocken, PA. DOI: 10.1520/D5832-98.
- ASTM D2866-11 (2018), Standard Test Method for Total Ash Content of Activated Carbon, ASTM International, West Conshohocken, PA, 2018. https://doi.org/10.1520/D2866-11R18.
- Bachu, S. & Shaw, J. (2003). Evaluation of the CO₂ sequestration capacity in Alberta's oil and gas reservoirs at depletion and the effect of underlying aquifers. *Journal of Canadian Petroleum Technology*, 42(9), 51-61.
- Bulut, Y. and Aydin, H. (2006). A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 194(1-3), 259-26. https://doi.org/10.1016/j.desal.2005.10.032.
- Ekpete, O.A., Marcus, A.C., and Osi, V. (2017). Preparation and Characterization of Activated Carbon Obtained from Plantain (Musa paradisiaca) Fruit Stem. *Journal of Chemistry*, 2017, 1-6.
- Forbes, S.M., Verma, P., Curry, T.E., Bradley, M.J., Friedmann, S.J., and Wade, S.M. (2008).*Guidelines for carbon dioxide capture, transport, and storage*.Washington, DC: World Resources Institute.
- Goswami, S. and Ghosh, U.C. (2005). Studies on Adsorption Behavior of Cr (VI) onto Synthetic Hydrous Stanniz Oxide. *Water SA*, 31, 597-602.
- Guo, Y. and Rockstraw, D.A. (2007). Activated carbons prepared from rice hull by one-step phosphoric acid activation. *MicroporousandMesoporousMaterials*. 100(1-3), 12–19.
- Hariprasad, P., Rajeshwari, S., & Aniz, C. (2016). Preparation and characterization of activated carbon from rice husk. *International Research Journal of Engineering and Technology* (*IRJET*), 3(4), 551 558.
- Ida, H., Ono, N., Takasu, N., Ebinuma, T. (2012). CO₂ capture technology by using semiclathratehydrates. *Carbon Management Technology Conference held in Orlando*, Florida, USA, 7-9, February, 2012.

- Jahangiri, H.R. and Zhang, D. (2011).Optimization of the net present value of carbon dioxide sequestration and enhanced oil recovery. *Offshore Technology Conference* Houston, Texas, USA, 2-5 May.
- Karthikeyan, S., Balasubramanian, R., Iyer, C.S.P. (2007).Evaluation of the marine algae Ulvafasciata and Sargassum sp. for the biosorption of Cu (II) from aqueous solutions.*Bioresource Technology*, 98 (2), 452-455.
- Kennedy, L.J., Vijaya, J.J., Sekaran, G. (2005). Electrical conductivity study of porous carbon composite derived from rice husk.*MaterialChemistryandPhysics*, 91, 471–476.
- Mastalerz, M. and Bustin, R.M. (1995). Application of reflectance micro-Fourier transform infrared spectrometry in studying coal macerals: comparison with other Fourier transform infrared techniques. *Fuel*, 74, 536–542.
- Li, W., Zhang, L., Peng, J., Li, N., Zhang, S., Guo, S. (2008). Tobacco stems as a low cost adsorbent for the removal of Pb(II) from wastewater: Equilibrium and kinetic studies. *Industrial Crops and Products*, 28, 294-302.
- Liu, J., Liu, X., Sun, Y., Sun, C., Liu, H., Lee, A.S., Li, K., and Snape, C.E. (2018). High density and super ultra-microporous-activated carbon macrospheres with high volumetric capacity for CO2 capture. *Adv. Sustainable Syst.*, 2, 1-8.
- Sahira, J., Mandira, A., Prasad, B.P., and Ram, R.P. (2013).EEffect of activating agents on the activated carbons prepared from lapsi seed stone. *Research Journal of Chemical Science*, 3(5), 19–24.
- Sricharoenchaikul, V., Chiravoot, P., Duangdao, A., Duangduen, A.T. (2008). Preparation and characterization of activated carbon from the pyrolysis of physic nut (Jatrophacurcas L.) waste. *Energy Fuels*, 22, 31-37.
- Siriwardane, R.V., Ming-Shing, S., Fisher, E.P., and Poston, J.A. (2001). Adsorption of CO₂ on molecular sieves and activated carbon. *Energy and Fuels*, 15, 279-284.
- Sugumaran, P., Priya, S.V., Rauichandran, P., and Seshadri, S. (2012). Production and characterization of activated carbon from banana empty fruit bunch and delonixregia fruit pod. Journal of Sustainable Energy and Environment, 3(1), 125–132.
- Sun, R.C. and Tomkinson, J. (2001).Fractional separation and physico-chemical analysis of lignins from the black liquor of oil palm trunk fibre pulping. *Separation andPurificationTechnology*, 24(3), 529–539.
- Weber, W.J. & Morris, J.C. (1963). Kinetics of adsorption on carbon from solution. J. Saint. Eng. Div. Am. Soc. Civ. Eng., 89 (1963), pp. 31-60.
- Wilson, E. J. & Gerard, D. (2007) Carbon capture and sequestration: Integrating technology, monitoring and Regulation. Blackwell Publishing.