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Mutegoa, Eric

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PREPARATION OF ACTIVATED CARBON WITH DESIRED PROPERTIES THROUGH OPTIMIZATION OF IMPREGNATING AGENT

Eric Mutegoa, Isaac Onoka, and Askwar Hilonga
Department of Materials Science and Engineering, School of Materials, Energy, Water and Environmental Sciences, Nelson Mandela African Institution of Science and Technology, P.O.BOX 447-Arusha, Tanzania.
Corresponding Author: *Askwar Hilonga*

ABSTRACT
In this study, activated carbon with desired properties was prepared from peanut shell and sugarcane bagasse using chemical activation method in which potassium hydroxide (KOH) was used as a impregnating agent. The properties of the activated carbon were evaluated based on the activation temperature, yield percentage, ratio of KOH to Char impregnation, and iodine adsorption number. Based on the characterization methods employed, the desired properties for activated carbon from peanut shell were obtained at these optimum conditions: Activation temperature of 350 ^{0} C, treatment time of 1hr, and impregnation ratio of 1:2. These conditions exhibited maximum iodine number of 355 mg/g. On the other hand, sugarcane bagasse produced the superior properties (iodine number of 914.71 mg/g) at an activation temperature of 700 ^{0} C, treatment time of 1hr, and impregnation ratio of 1:1. The activated carbons with superior properties obtained in this study are suitable for the treatment of waste water associated with carboxylic acids. Our on-going project will test the performance of the final product for various innovative applications.

KEYWORDS: Peanut Shell, Sugarcane Bagasse, Activated Carbon, Iodine Number, Impregnation Ratio.

INTRODUCTION
Activated carbon is used as an adsorbent in many industrial fields. In recent years, it has been used for controlling air pollution, water pollution, odors, etc., and for environmental protection, and demand for it is increasing. Studies on activated carbons, which use organic waste sludge (Tay, Chen, Jeyaseelan, & Graham, 2001), bagasse (Mall, Srivastava, Agarwal, & Mishra, 2005), almond shell (Demirbas, Kobya, & Konukman, 2008), waste ion exchange resin (Long et al., 2008),waste phenol resin(Hameed & Rahman, 2008),etc. as raw materials, have been carried out to explore recycling options for organic waste materials. Activated carbon with desired properties is characterized by its well-developed pore structure, higher surface area, low ash content and greater adsorption capacity. Its pores are typically classified into micropores (1 nm), mesopores (1–25 nm), and macropores (25 nm) based on the pore radius (Lowell & Shields, 1991). The physical factors of these pores, such as the size, shape, distribution, specific surface area, etc., greatly affect adsorption. Because the adsorption sites for many compounds with a small molecular size are mainly located in micropores, many of the activated carbons being used at present contain well developed micropores. However, the development of mesopores and macropores is required for activated carbons used in water treatment (Fornwalt, Helbig, & Scheffler, 1963). Many researchers have worked on production of activated carbon from renewable resources, using low cost methods and materials for various applications in an environmental friendly manner. It has been reported that, agricultural and industrial waste material are good precursors for producing activated carbons used by different researchers for the removal of contaminants such as coconut husk and palm pressed fibers (Tan, Ahmad, & Hameed, 2008b), coconut shell activated carbon (Babel & Kurniawan, 2004), rice husk carbon (Gupta, Mittal, Jain, Mathur, & Sikarwar, 2006), bagasse and fly ash(Mkayula & Matumbo, 1994; Srivastava, Swamy, Mall, Prasad, & Mishra, 2006).

According to the study done on the potential of energy from sugarcane waste in Tanzania, it is reported that the three largest sugar factories in Tanzania, cultivate over 17,000 hectares of sugarcane farms and produce about 125,000 tons of sugar per annum, process over 1,300,000tons of sugar cane per year. In the process, the factories produce about 40,000 tons of molasses (a good percentage of which is exported) and about 455,000 tons of bagasse as waste (Kishimba, 2000). Also, in 2011 the groundnut yield in shells was 964.7 kg/acre in Tanzania (Katundu & Mhina). From an environ-economics point of view, the disposal of the agrowastes is not only hazardous to the environment but also it is a waste of resources. In addition, most of the activated carbons used in industries for various adsorptive purposes are imported (MDOE & MKAYULA, 2002).

In this study, four major samples were generated from two precursor; peanut shell and sugarcane bagasse. The samples prepared include peanut shell physically activated (PSPA), peanut shell chemically activated (PSCA), sugarcane bagasse physically activated

(SCBPA) and sugarcane bagasse chemically activated (SCBCA).

Thus, the objective of this study is to develop optimum conditions for activated carbon from peanut shells and sugarcane bagasse, precursors which are abundantly available. The conditions studied are activating temperature, impregnating ratio and iodine number adsorption capacity.

PROBLEM STATEMENT

Various findings have reported several low cost adsorbents such as Lakra coal, coconut shell charcoal, hydroxyapatite for adsorption of maleic acid, oxalic acid and other dicarboxylic acids (Goud, Mohanty, Rao, & Jayakumar, 2005; Ishaq, Saeed, Ahmad, Shakirullah, & Khan, 2011; Rahman et al., 2006; Vega & Colinas, 2009). Most of these adsorbents were found suitable for dilute solution but saturated easily. Some of these adsorbents showed poor adsorption capacity due to lower surface area derived from selected carbonaceous precursors. Generally, the larger the specific surface area of the adsorbent, the better its adsorption performance will be(Guo & Lua, 2003)

SIGNIFICANCE OF THE STUDY

This work is expected to give a solution towards treatment of dicarboxylic acids contaminated waters and wastewaters by using low-cost adsorbents, the pea-nutshells and sugar-cane bagasse based activated carbons. This will augment efforts to provide society with water free of pollutants. The study is also expected to produce a suitable activated carbon meeting the requirements of an effective adsorbent for wastewater treatment. In addition, the use of locally made agro-wastes based activated carbon would minimize imports of commercial activated carbons thus, contributing towards poverty eradication in developing countries especially Tanzania. Powdered form of activated carbon with high degree of mesopores is widely used for purification of drinking water. Also this work is expected to reveal various conditions such as activation temperature, activation time and impregnation agent that will optimize the ratio required for production of maximum surface area for enhancing adsorption capacity at minimal saturation level of the activated carbon that will be derived from selected carbonaceous precursors.

MATERIALS AND METHODS

Chemically Activated Carbon Preparation

Peanut shells and Sugar cane bagasse used for preparation of activated carbon was obtained locally. The precursors were first washed to remove dirt from its surface and were then dried overnight in an oven at 105 ^{0} C. The dried peanut shells and Sugarcane bagasse were cut and sieved with BS 410 mesh number 80 with aperture of 180 µm and loaded in aluminium foil and then placed in a programmable electrical furnace (Nabertherm). Carbonization of the precursor was carried out by varying the temperature from 250 ^{0} C to 700 ^{0} C and hold for 1 h. The char produced was mixed with KOH pallets with different impregnation ratio (IR); about 6.0 to 12.0g of oven dried precursor was mixed with 4.0 – 6.0g of KOH dissolved in 15.0mL of distilled water at impregnation ratio of 1:1. In this case, 12.0g of charred precursor was mixed with 6.0g of KOH, and then 6.0g of charred precursor was mixed with 6.0g of KOH dissolved in 15.0mL to make 1:2 and 1:1 impregnation ratios (KOH : charred precursor), respectively as calculated using Eq.(1):

$$IR = \frac{wKOH}{wChar} \quad (1)$$

where wKOH is the dry weight (g) of KOH pallets and wchar is the dry weight (g) of char. Deionized water was then added to dissolve all the KOH pallets and the mixture was stirred for four hours before dehydrated in an oven overnight at 105^{0}C to remove moisture and was then activated under the same condition as carbonization, but to a different final temperature. The activated product was then cooled to room temperature and then washed with hot deionized water and 0.1 molar hydrochloric acid until the pH of the washing solution reached 6–7(Tan, Ahmad, & Hameed, 2008a).

Activated carbon yield

The activated carbon yield was calculated based on Eq. (2).

$$Yield(\%) = \frac{w_c}{w_o} x\ 100 \quad (2)$$

Where wc is the dry weight (g) of final activated carbon and wo is the dry weight (g) of precursor.

Determination of Iodine Number

The adsorption of aqueous iodine is considered as a simple and quick test for evaluating the surface area of activated carbons associated with pores larger than 1 nm. The iodine number, defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration was measured according to the procedure established by the American Society for Testing and Materials (ASTM 2006)(Shrestha, Yadav, Pokharel, & Pradhananga, 2012). 0.1 g of dry activated carbon and commercial activated carbon was separately taken in dried 100 ml conical flasks. The samples were run in duplicates and added 5 ml of 5%HCl .The flasks were swirled until the carbon was wetted. 10ml of 0.1N iodine solution was added to each flask and was shaken properly for 4 minutes. 10 ml filtrate was titrated against standard (0.1N) sodium thiosulphate solution using starch as an indicator. The concentration of iodine adsorbed by activated carbon was calculated as amount of iodine adsorbed in milligrams. It is equivalent to surface area of activated carbon in m^2/g(Huruma, 2013).

Iodine number = C X Conversion factor (CF). The conversion factor can be calculated as follows:

$$CF = \frac{Mol.wt\ of\ Iodine\ x\ Normality\ of\ Iodine\ x\ 10}{Wt.\ of\ activated\ carbon\ x\ Blank\ reading} \quad (3)$$

C = Blank reading – volume of standard sodium thiosulphate consumed after the adsorption of Activated carbon.

Iodine Number is accepted as the most fundamental parameter used to characterize activated carbon

performance. It gives the measure of activity level (higher number indicates higher degree of activation)

Table 1 Percentage yield of activated carbon from peanut shell and sugarcane bagasse physically activated at different temperature.

Raw Material(Precursor)	Activation temperature (^{0} C)	Activation time (minutes)	Yield (%)
PSPA1	250	60	74.3
PSPA2	250	30	76.1
PSPA3	300	60	62.4
PSPA4	300	30	63.5
PSPA5	350	60	59.4
PSPA6	350	30	60.2
PSPA7	400	60	45.2
PSPA8	400	30	46.1
SCBPA1	600	60	32.6
SCBPA2	600	30	34.9
SCBPA3	700	60	26.5
SCBPA4	700	90	23.2

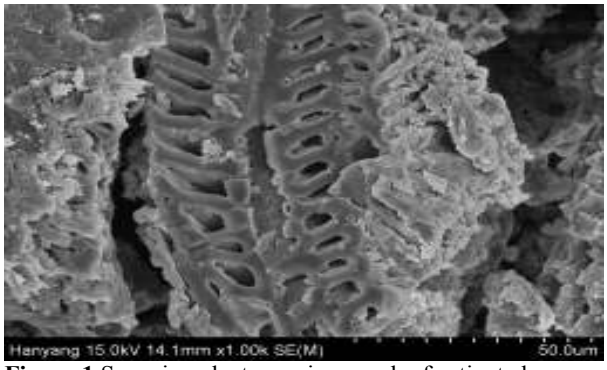

Figure 1 Scanning electron micrograph of activated carbon from peanut shell prepared under optimum conditions (activation temperature =573 K, activation time = 1hr and KOH: Char impregnation ratio = 1:2)

Table 2 Iodine number yielded at different impregnating agent ratio and activating temperature.

Raw Material(Precursor)	Activation temperature (^{0} C)	Activation time (minutes)	Impregnating agent ratio (Wt of KOH : Wt of dry Precursor)	Iodine number (mg/g)
PSCA1	250	60	1:2	140.56
PSCA2	250	60	1:1	130.72
PSCA3	300	60	1:2	128.89
PSCA4	300	60	1:1	88.55
PSCA5	350	60	1:2	355
PSCA6	350	60	1:1	224
SCBCA1	300	60	1:2	275
SCBCA2	300	60	1:1	753
SCBCA3	350	60	1:2	646.58
SCBCA4	350	60	1:1	692.96
SCBCA5	400	60	1:2	777.29
SCBCA6	400	60	1:1	819.46
SCBCA7	600	60	1:2	901..2
SCBCA8	600	60	1:1	912
SCBCA9	700	60	1:2	905.21
SCBCA10	700	60	1:1	914.71

RESULTS AND DISCUSSION

Yield of Activated Carbon

Carbonization temperature plays an important role on the yield of activated carbon. The relationship among the activation conditions and the yields of activated carbon from the carbonized material are shown in the figure 2.

As seen in the figure 2, the carbonization temperature has significant effect than carbonization time. At 250 ^{0} C for peanut shell carbonized at 1hr, the yield was 74.3% but decreased to 46.1% at 400 ^{0} C. Similar trends have been observed for sugarcane bagasse as well, the yield of 32.6% was obtained at 600 ^{0} C and decreased to 26.5% at 700 ^{0} C.

The rate of weight loss is high primarily due to the initial large amount of volatiles that can be easily released with increasing temperature as well as the loss of moisture to a lesser extent.

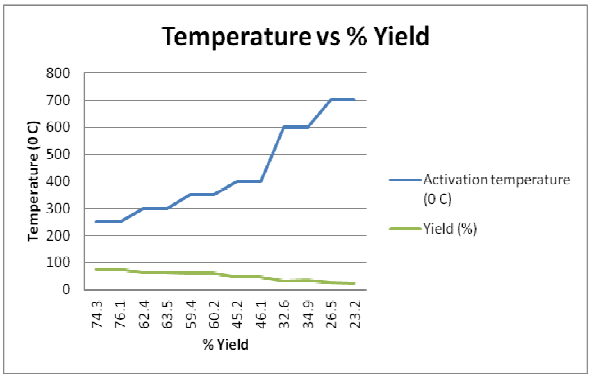

Figure 2 Relationship between temperature increase and percentage yield of activated carbon.

Effect of Temperature on Iodine Number

The Iodine number, defined as the amount of iodine adsorbed per one gram of activated carbon at an equilibrium concentration is considered as a simple and quick test for evaluating the surface area of activated carbon associated with pores larger than 1nm. From the Table2, the Iodine number generally seems to increase as the temperature increases. At a temperature range of (250 ^{0} C – 350 ^{0} C) for peanut shells, the highest number of iodine adsorbed was 224 mg/g at 350 ^{0} C and 140.56 mg/g at 250 ^{0} C which is lower than that obtained at 350 ^{0} C. The increase in iodine number as the temperature increase is much related to pore widening of the activated carbon precursors and during the process of chemical activation, a chemical applied in this case being potassium hydroxide as a strong solution at an elevated temperature penetrates the structure of the source material, swells it and opens up its cellulose structure to enhance pore widening of the material. Increase in surface area and iodine number adsorption capacity is a result of creation of more micropores and possibly the widening of the existing ones as temperature increases.

Increasing the carbonization temperature from 400 ^{0} C to 600 ^{0} C for sugarcane bagasse increases the evolution of volatile matters from the precursor leading to increase of the pore development, and creates new pores. At temperature higher than 400 ^{0} C, the reaction between potassium hydroxide and carbon occurs according to the following reaction(Ahmadpour & Do, 1997):

$$6KOH + 2C \Longrightarrow 2K + 3H_2 + 2K_2CO_3$$

The presence of metallic potassium will insert to the carbon matrix. This phenomenon results in widening of the spaces between carbon atomic layers and increases the total pore volume which increases the number of iodine adsorption per gram of activated carbon.

Effect of Chemical Ratio (impregnating agent)

The impregnation ratio has been found to be one of the important parameter in determining the surface area of activated carbon. Table 2 indicates that the iodine number adsorbed by one gram of activated carbon varies at different impregnation ratio and the type of precursor.

At the impregnation ratio of 1:2 for peanut shell activated carbon, the number of iodine adsorbed was higher than the number of iodine adsorbed at 1:1 for the same activating temperature. From table 2, the number of iodine adsorbed at 250 ^{0} C in a ratio of 1:1 and 1:2 were 130.72 and 140.56 mg/g respectively. Similar trends were also observed as the activation temperature was increasing, at 300 ^{0} C, the number of iodine adsorbed at a ratio of 1:1 and 1:2 were 88.5 and 128.89 mg/g respectively.

However, the case has been different when the number of iodine adsorbed by one gram of activated carbon from sugarcane bagasse was calculated at both 1:1 and 1:2 impregnation ratios. The activated carbon from sugarcane bagasse in this study showed to adsorb higher number of iodine at a ratio of 1:1 than that adsorbed at a ratio of 1:2 when the precursor was activated at the same temperature. From table 2, the number of iodine adsorbed at 300 ^{0} C in a ratio of 1:1 and 1:2 were 753 and 275 mg/g respectively. At 600 ^{0} C, highest number of iodine adsorbed was calculated at a ratio of 1:1, yielding 912 mg/g while at a ratio of 1:2 the number of iodine adsorbed was 901.2 mg/g.

Treating bagasse with potassium hydroxide transformed the structure and surface chemistry of the resulting activated carbons. This chemical pre-treatment was shown to increase the extent of thermal breakdown of bagasse. This in turn resulted in activated carbon exhibiting highly surface area (914.71 mg/g) determined by higher number of iodine adsorption. Intercalation of potassium hydroxide into bagasse resulting from its chemical pretreatment is found to generally develop the microporosity. The higher surface area, iodine number adsorption and micropore content of the activated carbon makes the produced activated carbon to meet with the desired properties since adsorption capacity of mostly organic contaminants are surface area phenomenon. The large number of iodine adsorbed, determined with micropore content in activated carbon; enables adsorption process without being easily saturated, the property that has been effected much by the ratio of the chemical agent in this study.

From the results above, this study shows that peanut shell produces higher surface area of activated carbon at a ratio of 1:2 while the ratio of 1:1 was observed to yield higher surface area of activated carbon derived from sugarcane bagasse precursor. Since this impregnation ratio is of weight of KOH to weight of dry precursor, the ratio used and surface area calculated signifies that the dry weight of peanut shell has lower density than that of sugarcane bagasse into which the ratio of 1:2 gives higher surface area than a ratio of 1:1. Apart from density, also these results gives out a suggestion that the percentage of cellulose in sugarcane bagasse is higher than that of peanut shell making a ratio of 1:1 suitable for yielding activated carbon with surface area desired for adsorption process.

LIMITATION OF THE STUDY

The study was limited by the type of furnace used (Nabtherm) which could not control the inert atmosphere. Thus, further carbonization of the precursor beyond 700 ^{0} C could not be achieved since the precursors were easily oxidized forming ash. On the other hand, if the tube furnace which can control the inert atmosphere would be available, the higher surface area above 914.71m^2/g could be obtained for better and sufficient adsorption.

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CONCLUSION

In this study the number of iodine adsorbed per one gram of activated carbon was determined from peanut shell and sugarcane bagasse precursors at different impregnation ratio. The peanut shell activated carbon provided higher number of iodine adsorbed at a ratio of 1:2 while sugarcane bagasse provided higher number of iodine adsorbed at a ratio of 1:1. The higher number of iodine adsorbed by one gram of activated carbon is characterized with large number of micropore due to higher carbon content, low ash content, high density and sufficient volatile content, conditions seems to suit best for sugarcane bagasse than peanut shell precursor used for this study. Treating bagasse with potassium hydroxide transformed the structure and surface chemistry of the resulting activated carbons. This chemical pre-treatment was shown to increase the extent of thermal breakdown of bagasse, the activation temperature seemed to be one of the important parameter for determining the number of iodine adsorbed by activated carbon and the increase in temperature for sugarcane bagasse favored creation of more micropores, hence higher number of iodine adsorbed. At a temperature of 300 ^{0} C, peanut shell could not develop more micropore due to burn off increase initiated by lower carbon content and hence lower number of iodine adsorbed.

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