Effects of Activating Agent on the Activated Carbons Prepared from Pandanus Sanderi stem

ILOKA, A. U., DIM, P. E. and OKAFOR, J. O.

Department of Chemical Engineering, Federal University of Science and Technology, Minna.
*Corresponding author email and phone number: uwejesus4life@yahoo.com, +2347030616338

Abstract:

Activating agent have a great influence on the pore development and surface characteristics of the activated carbon produced. In this study a low cost activated carbon was prepared from Pandanus Sanderi stem by chemical activation using Sodium Hydroxide (NaOH). The precursor was carbonized at 600 °C at 3 hrs. before and after treatment. The characterization results of Bulk Density, Ash Content, pH, Moisture Content and Pore Volume were compared with literature and it was found to be consistent. The Iodine Number and maximum adsorption capacity (qm) for methylene blue were determined. The Iodine Adsorption Number was found to decrease after activation from 118.36 to 69.36 mg/g and the Surface Area increased from 49.22528 to 112.9904 ($10^{3}km^{2}kg^{-1}$). Surface functional groups were analyzed by Fourier Transform Infra-Red Spectroscopy (FT-IR). The spectra analysis identified the present of hydroxyl, carbonyl, carboxyl and lactones.

Key words: Pandanus Stem, Sodium hydroxide, activated carbon, chemical activation, methylene blue, Iodine number.

1. Introduction

The problem of protecting the environment from pollution and contamination by various types of effluent discharges is now focus attention all over the world. This effluent may contain spent grains, waste yeast and total suspended dissolve particles (TSDP), these maybe non-degradable and toxic and their concentration must be reduced before discharging the wastewater into the environment. Many methods can be used; such as coagulation and flocculation, adsorption, chemical oxidation, anaerobic decolourization and reverse osmosis. Adsorption is preferred because of its efficiency and the most widely used is activated carbon. (Menkiti et al., 2014). Activated carbon are made from materials rich in carbon through carbonization and an activation process, and the properties of carbonaceous materials can be determined through either physical or chemical activation using chemical activating agents like Zinc chloride ($ZnCl_2$), Potassium oxide (KOH) and Phosphoric acid (H_3PO_4). (Shamsuddin et al., 2015). The ability of activated carbon to remove a large variety of compounds in contaminated water led to its use, and the low cost, its availability, its carbon rich and low ash content makes it easy for designing in more economic ways. (Odubiyi et al., 2012). According to Onwa et al. (2014), The heavy metal ions in industrial wastewater which maybe toxic to aquatic flora, animals and human beings even at relatively low concentration, can cause harm. This must be removed before being discharged to the environment. The selection of the treatment process depends on the nature of the effluent. (Oboh et al., 2009). Pandanus Sanderi originated from Pandanus plant (Screw-pine) which can be found in the wide cultivated area (Mario et al., 2019). It belongs to the family of Pandanaceae which comprises about 700 species (Fillaeli et al., 2019). It can be used as a flavor in Southeast Asian cooking and the pleasant smell comes from aroma compound of 2 acetyl-1-pyrroline (Kantilal et al., 2009). Shigeyuki et al. (2016) carried out a study that found Pandanus leaves as useful in medicinal area such as antispasmodic, diuretic, although no much work had done with Pandanus plant on activated carbon. In this study, activated carbon was prepared from locally Pandanus Sanderi stem using Sodium hydroxide (NaOH) as activating agent. The use of this raw material in carbon production is because of its availability at low cost, its high carbon content, act as a local replacement for existing commercial materials and can be effective in the removal of heavy metals. (Sudha et al., 2007).

2. Materials and Methods

Pandanus plant stem was used as a precursor for the preparation of activated carbon. The Pandanus stems were purchased from local market of Anambra State, Nigeria. They were washed and dried for seven days and then crushed into powder. The Pandanus stem powder was then sieved to obtain the fraction of size between 1.00 – 1.70 mm. The dried powdered Pandanus stem were processed to obtain the activated carbon as described below. The analytical grade chemical Sodium Hydroxide (Merck,Germany). **Carbonization without Chemical Activation:** 15 g of dried Pandanus stem powder was subject to carbonization in electric furnace at 600 °C for 3 h. After carbonization, the carbonized product was repeatedly washed with distilled water. The sample was then oven dried at105 °C for 4 h, sieved to get the particles size 1.70 mm. Then the unmodified Activated Carbon was labelled as Control Activated Carbon (CAC) when storing in an air tight container for further used. **Carbonization with chemical activation:** 15 g of the crushed pandanus was impregnated with activating agent of Sodium Hydroxide (NaOH) in ratio of 1:1 by weight for 12 h. The impregnation was carried out at 80 °C in a hot air oven to achieve well penetration of chemical into the interior of the precursors. After impregnation, the mixture was introduced into the hot zone of a muffle furnace for carbonization at temperature of 600 °C for 3 h in order to establish the optimum conditions for the process. The content was then removed from the muffle furnace after the set period and cooled in an open air for one hour. The resulting carbon was washed with distilled water. They were then dried in an oven at105 °C for 4 h, sieved to get the particles size 1.70mm. then the modified Activated Carbon was labelled as Sodium Hydroxide Powdered Activated Carbon (NaOH-PAC) when storing in an tight container for further used.

2.1 Characterization of Activated Carbon

2.2 FTIR analysis

The surface functional group of the activated carbon was determined at room temperature using Thermo Electron Nicolet 4700 FT-IR Spectra which has transmission percentage (%) recorded 500 – 4000 cm^{-1}.

2.3 Iodine Adsorption Number (IAN):

The Iodine Number was determined to access the absorptive capacity of prepared activated carbon. 1-gram sample mixed with 25 ml of Iodine Solution (0.023M) in a beaker were swirled vigorously for 10 minutes and then filtered. 20 ml of the filtrate was titrated with the (01095M) Thiosulphate Solution to observe a pale yellow colour. 5 ml of freshly prepared starch indicator was added and titrated slowly until a colourless solution appeared. The procedure was carried out two more times. Another titration was performed with 20 ml of the Iodine Solution not treated with sample to serve as blank titration.

The Iodine Number (IAN) was calculated from the relationship:

$$IAN = [12.69 \times M \times (V_2 - V_1)]/D \text{ mole iodine/g sample} \quad (1)$$

V_1 = average titer ≡ volume of thiosulphate need to titrate against residual iodine after treatment with carbon;

V_2 = blank titer ≡ volume of thiosulphate need to titrate against iodine that is not treated with carbon;

D = adsorbent dosage i.e. mass of carbon used;

M is the molarity of standard sodium thiosulphate used ($Na_2S_2O_3.5H_2O$).

Percentage (%) Yield and Burn Off

Percentage yield and burn off were calculated by the following equations;

Percentage (%) Yield and Burn Off

Percentage yield and burn off were calculated by the following equations;

$$\%RE = \frac{W_1}{W_0} \times \frac{100}{1} \quad (2)$$

$$\%LI = \frac{W_0 - W_1}{W_0} \times \frac{100}{1} \quad (3)$$

W_0 = weight of sample, W_1 = weight of char after carbonization, % RE = percentage recovery or Yield, % Li = loss on ignition or % burn off

W_0 = weight of sample, W_1 = weight of char after carbonization, % RE = percentage recovery or Yield, % Li = loss on ignition or % burn off..

2.4 Methylene blue number

Surface Area was determined using Langmuir Isotherm of methylene blue adsorption according to Itodo, *et al.* (2010), in which different concentration of methylene blue was prepared ranging from 5 mg/l - 50 mg/l. 0.5 g of adsorbent was weighed into 250 ml Erlenmeyer flask, 20ml of each methylene blue concentration was measured into the flask and it was corked. The mixtures were equilibrated for 24 hours and the amount of methylene blue adsorbed per gram of the adsorbent (Q_e) was calculated with the following equation:

$$q_e = \frac{v(Co - Ce)}{m} \quad (4)$$

Where qe is metal concentrated on the adsorbent (mg/g) at equilibrium, Ce is metal concentrated in solution (mg/L) at equilibrium, Co is Initial metal concentrated in solution (mg/L), V is volume of initial metal solution used (L) and M is Mass of adsorbent used (g). And the result adsorption results were analyzed with Langmuir Isotherm; such as

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_M} \quad (5)$$

The plot of Ce/qe vs. Ce gives a straight line with slope equal to 1/*q*m, and intercept equal to 1/*Kq*m. Therefore, the Langmuir isotherm is an adequate description of the adsorption of the methylene blue onto adsorbent and The specific surface area was calculated by the following equation;

$$S_{MB} = (q_m \times a_{MB} \times N_A \times 10^{-20})/M \quad (6)$$

Where S_{MB} is the specific surface area; q_m is the number of molecules of methylene blue adsorbed at the monolayer of fibers in $mg g^{-1}$.

a_{MB} is the occupied surface area of one molecule of methylene blue = 197.2 Å²

N_A is Avogadro's number, 6.02 x 1023 mol^{-1}; and M is the molecular weight of methylene blue, 373.9 g mol^{-1}.

2.5 Pore Volume

1 gram of the sample in a 10 ml measuring cylinder was transferred into a beaker containing 20 ml of deionized water and was boiled for 5 minutes. It was filtered, dried and weighed. The pore volume was determined by dividing the weight of sample by density of water, and the bulk density of all samples were calculated as the ratio of weight and volume of packed dry material.

1. Results and Discussion

1.1 Characteristics of Activated Carbon

The characteristics of activated carbon made from Pandanus plant are Bulk density, ash content, pH, moisture content and pore volume are given in Table 1, from the table it can be observed that Activated carbon produced from Pandanus has properties within the limit of the reference activated carbon. The activated carbon produced in this work had acceptable properties and compared favorably with reference activated carbon which is an indication of quality of adsorbent that can be used for both liquid and gaseous purification on operations. Table 1 also showed that the IAN of unmodified activated carbon is 118.364mg/g, which was found to decease to 69.359mg/g after the modification process with NaOH. Nevertheless, the activated carbon has the percentage recovery and percentage burn off 50.66905 and 49.33095 respectively in Table 2.

Table 1: characteristics of activated carbon

Table 1: characteristics of activated carbon

Parameters	Unmodified AC (CAC)	Modified AC (NaOH-PAC)
Bulk density (g/cm^3)	0.354	0.444
% Ash Content	11.663	17.622
pH	6.460	6.550
% Moisture Content	7.784	4.382
Pore Volume (cm^3)	1.346	1.148
Surface Area ($10^{-3}km^2kg^{-1}$)	49.22528	112.9904
IAN (mg/g)	118.364	69.359

Table 2: Percentage recovery and burn off

% RE	% LI
50.66905	49.33095

Table 3: characteristics of activated carbon compared with the literature reviewed.

Parameters	Unmodified AC (CAC)	Modified AC (NaOH-PAC)	Reference activated carbon modified between 400^0C to 800^0C
Bulk density (g/cm^3)	0.354	0.444	0.458 (Ademiluyi, F. T. et al., 2016).
% Ash Content	11.663	17.622	4.67-6.17 (Musah M. 2011)
pH	6.460	6.550	6.85 (Shanmugam A. et al., 2009)
% Moisture Content	7.784	4.382	1.85 (Shanmugam A. et al., 2009)
Pore Volume (cm^3)	1.346	1.148	1.031 (Ademiluyi, F. T. et al., 2009).
Surface Area ($10^{-3}km^2kg^{-1}$)	49.22528	112.9904	13.579-18.170 (Itodo A. U. et al., 2010)
IAN (mg/g)	118.364	69.359	1160 (Madu P. C. et al., 2013)

49.22528 and 112.9904 ($10^{-3}km^2kg^{-1}$) in Table 1 are the results of surface area which was determined using methylene blue adsorption by Langmuir Isotherm method. The Langmuir Isotherm showed that the amount of Methylene blue adsorbed increases as the concentration increase. Adsorption will increase with increasing methylene blue concentration. The modified activated carbon (NaOH-PAC) proves to have a higher surface area (S_{MB} = 112.9904 (10^{-3} km^2/kg)) which compared more to that of the unmodified activated carbon (CAC), (S_{MB} = 49.22528($10^{-3}km^2/kg$). The trends therefore, imply that the level of accessible area of solid surface (Pandanus carbon) per unit mass of material (methylene blue dye) follows the order of: NaOH-PAC > CAC.

Sorbents with high Iodine Adsorption Number performs better in removing small sized contaminants and high value indicate high degree of activation (Itodo *et al.*, 2010).

Fourier Transform Infrared (FTIR) Spectra: Oxygen containing surface functional groups plays important role in influencing the surface properties and adsorption behavior of activated carbons. These groups can be formed during activation process or can be introduced by oxidation after preparation of activated carbon. The FTIR spectra obtained for the prepared activated carbon are given in Figure 1 and 2. The spectra show that the surface functional groups of the activated carbon exhibit significant differences on the intensity of the bands detected.

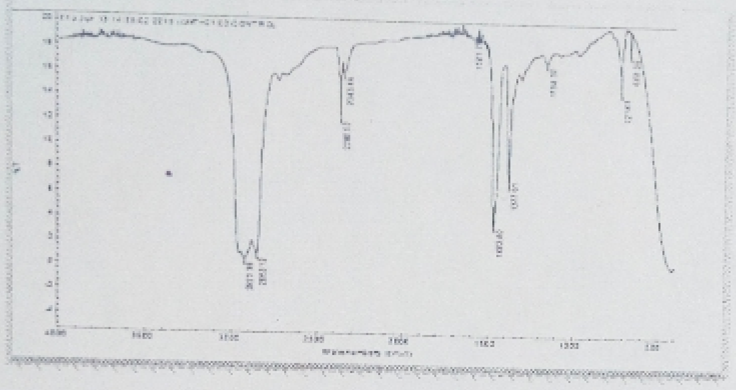

Figure 1: FTIR spectrum of Unmodified Activated Carbon (CAC)

A strong and broad adsorption peak appeared at 2923.39 – 2853.12 cm^{-1}, which corresponds to the C-H functional group and this shows the presence of methyl group sp^3 in the raw sample. There was another weak peak observed around 2360.52 – 2343.44 cm^{-1}, corresponding to the O-H showing the presence of phenol group. the band located at 1561.79cm^{-1} corresponds the presence of C=C showing the presence of aromatic carbon. Another peak were observed around 1462.40 and 1377.01cm^{-1}, corresponding the presence of (= - Ch3).

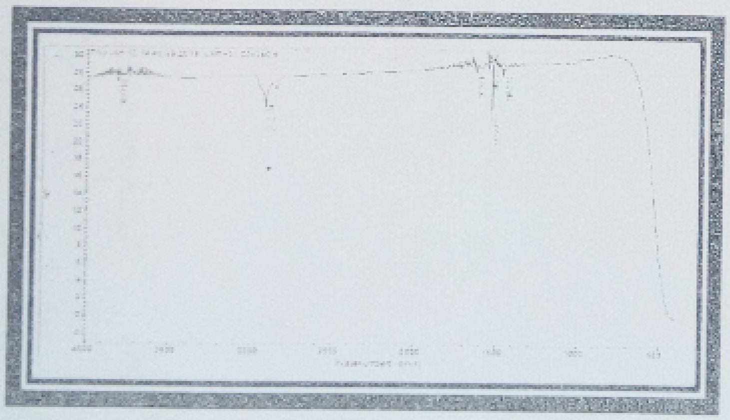

Figure 2: FTIR Spectrum of Modified Activated Carbon

A subsequent small rise at 1154.30 cm^{-1} could be assigned to the stretching of C-O in esters. The peak at 721.61 cm^{-1} indicate the presence of (-C-H). It can be suggested from the spectrum that the main oxygen groups present in the AC1 are methyl, aromatic and esters group. Furthermore, the AC1 samples contain a lot of elements and impurities before undergoing the activation process. Unlike spectrum showed by AC1, spectrum of AC2 in Figure 2, indicates the reduction in absorption peaks of functional groups. The band indicates the presence of O-H alcoholic group which was observed at the absorption around 3813.98 cm^{-1}. The presence of weak peak at 2922.64 indicates the presence of C-H methyl group sp^3. The band at 1630.43-1462.12 cm^{-1} corresponding to C=C aromatic group. This absorption illustrates the presence of active carbon in the prepared samples. This further proves that the presence of active carbon might be obtained during carbonization were successfully removed, as the volatile compounds.

1. Conclusion

The effect of NaOH as an activating agent on the properties of activated carbon prepared from Pandnus Sanderi stem by chemical activation has been investigated. The FTIR result shows that activating agent had a significant effect on the nature of surface functional group. It indicates that the activated carbon prepared contains hydroxyl, carbonyl, carboxyl and lactones as oxygenated surface functional groups. Iodine Number decreased and methylene blue adsorption capacityincreased after activation. Hence this study shows that Pandnus Sanderi stem can be used as a source of agricultural waste material for the preparation of low cost, high surface area activated carbon with well-developed porosity using NaOH as an activating agent.

References

Menkiti M. C., Aneke M. C., Ejikeme P. M., Onukwuli D. O. and Menkiti N. U., (2014). Adsorptive Treatment of Brewery Effluent using activated Chrysophyllum Albidium seed shell carbon. International Journal of Chemistry and Material Science., Vol.3(1) pp1. https://doi.org/10.1186/2193-1801-3-213

Shamsuddin M.S., Yusoff N. R. N. and Sulaiman M. A., (2015). Synthesis and Characterization of Activated Carbon Produced from Kenaf Core Fibre using H_3PO_4 Activation. 5th International Conference on Recent Advances in Materials and Environment (RAMM) & 2nd International Postgraduate Conference on Material, Mineral and Polymer (MAMIP)., vol. 19 pp558-565.

Odubiyi O. A., Awoyale A. A. and Eloka-Eboka A. C., (2012). Wastewater Treatment with Activated Charcoal produced from Cocoa Pod Husk. International Journal of Environmental and Biology,vol:4(3), pp162-175.

Onwu F. K., Sonde C. U. and Igwe J. C., (2014), Adsorption of Hg(II) and Ni(II) ions from Aqueous Solutions using Unmodified and Carboxymethylated Granular Activated Carbon (GAC). American Journal of Physical Chemistry, vol.3(6), pp89-95.

Oboh I. O., Aluyor E. O. and Audu O. K., (2009) Use of Chrysophyllum Albidum for the removal of metal ions from aqueous solution. Academic Journals of Scientific Research and Essay,vol.4(6), pp632-635.

Mario A. T. and Hiromitsu T., (2018) Chemistry of Pandanus Alkaloids. International Journal of Chemistry and Biology, vol. 82, pp.1-28.

Kantilal V. W., Altafhusain B. N., Ratnakar J. T. and Narendra J. (2009). In-vitro Regeneration Plantlets in Pandanus Amarylifolius Roxb as a model system to study the development of Lower Epidermal Papillae. Society for In-vitro biology, vol.45, No.6, pp.701-707.

Fillaeli A., Kristianingrum S., Siswani E. D., Sulistyani and Fatimah S. D, (2019), Synthesis Activated Carbon of Screw-pine leaves by HNO_3 and its properties. Journal of Physics: Conf. Series 1156 (2019) 01200. Doi:10.1088/1742-6596/1156/1/012001.

Baba S., Hung T. C., Mio K., Tomomi I., Eric W. C.C., (2016), Artocarpus Altilis and Pandanus Tectorius: Two important fruits of Oceania with medicinal values. Journal of Food and Agriculture, vol.28(8), pp.531-539, doi:10.9755/ejfa.2016-02-207.

Sudha R. and Premkumar P. (2016). Lead Removal by Waste Organic Plant Source Materials Review. International Journal of Chem. Tech. Research, vol.9, No.01. pp.47-57.

Itodo, A. U; Itodo, H. U and Gafar, M. K., (2010). Estimation of Surface Area using Langmuir Isotherm method. Journal of Applied Science, Environmental Management, vol.14(4), pp.141-145.www.bioline.org.br/ja.

Ademiluyi F. T and Nze J. C., (2016) Multiple Adsorption of Heavy Metal ions in Aqueous Solution using activated carbon from Nigerian Bamboo. International Journal of Research in Engineering and

Technology.

Musha M. (2011) Kinetic Study of the Adsorption of Pb2+ and Cr2+ ions on Palm Kernel Shell Activated Carbon. Vol.3(10). http://www.sciencepub.net/researcher.

Shanmugam A., Thenkuzhali M. and Martin P. D. P. (2009). Adsorption of Rhodamine-B by Acid Activated Carbon Kinetic, Thermodynamic and Equilibrium Studies. Vol.1(2).pp.138-155.

Itodo, A. U., Abdulrahman, F. W., Hassan, L. G., Maigandi, S. A. and Itodo, H. U. (2010). Application of Methylene Blue and Iodine Number in the Measurement of Specific Surface Area by four Acid and Salt Treated Activated Carbon. Vol.3(5).

Madu, P. C and Lajide L. (2013). Physicochemical Characteristics of Activated Charcoal derived from Melon Seed Husk. Journal of Chemical and Pharmaceutical Research. vol.5(5). pp.94-98

Ademiluyi F. T., Amadi, S. A. and Amakama, N. J., (2009) Adsorption and Treatment of Organic Contaminants using Activated Carbon from Waste Nigerian Bamboo. J. Appl. Sci. Manage. Vol.13(3). Pp.39-47.

M. M. Aji, B. Gutti and B. K. Highina (2017). Production and Characterization of Activated Carbon (AC) from Groundnut Shell and its Application in Water Treatment. University of Maiduguri, Faculty of Engineering Seminar Series, vol.8.

Adebayo, G. B.; Mohammed, A. A; Sokoya, S. O.,(2016). Bio-sorption of Fe (II) and Cd (II) ions from aqueous solution using a low cost Adsorbent from Orange Peels. International Journal of Applied Sciences and Environmental Management, vol.20(3). Pp.702-714. http://dx.doi.org/10.4314/jasem.v20i3.25

Hesas R. H., Arash A. N., Wan Mohd A. W. D. and Sahu J. N., (2013) Preparation and Characterization of activated carbon from apple waste by microwave-assisted phosphoric acid activation: application in methylene blue adsorption. Vol. 8(2), pp. 2950-2966. Bioresources.com

Okoroigwe, E. C., Ofomatah, A. C., Oparaku, N. F. and Unachukwu, G. O. (2013). Production and evaluation of activated carbon from palm kernel shells (PKS) for economic and environmental sustainability. International Journal of Physical Sciences, vol.8(19), pp.1036-1041.,www.academicjournals.org/IJPS.

Mohamed S., Jacek N. and Andrzej G. (2017). Low-cost Adsorbents Derived from Agricultural By-products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review. Pol. J. Environmental Studies., vol.26 (2), pp.479-510. DOI: 10.15244/pjoes/66769