African Star Apple (*Chrysophyllum Albidium*) Seed processing into Activated Carbon for Fe and Cu removal from Wastewater

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Abstract: The quest for processing of non edible parts of agricultural produce into activated carbon for wastewater treatment is in vogue due to its addition of nothing detrimental to the treated water. This study therefore explores the potential of activated carbon produced from African star apple seeds to adsorb Fe and Cu ions from municipal wastewater. Column adsorption technique was adopted to examine the effects of packing length on the adsorption of Fe and Cu from the wastewater. The result of the Fe content of the wastewater reduced from 3.10 mg/L to 2.95 mg/L at the packing length of 10 mm and to 2.55 mg/L at the packing length of 20 mm. The Cu content also reduced from 5.95 mg/L to 4.95 mg/L at the packing length of 10 mm and to 4.55 mg/L at the packing length of 20 mm. The results obtained show that the activated carbon produced is a good adsorbent and that adsorption of the two metal ions depends on the packing length of the carbon

1. INTRODUCTION

The need to ensure wastewater disposed into our environment causes little or no harm is but a necessity. This is due to the alarming rate at which the quality of soil and fresh water system are being compromised and the health of man is being threatened. Source of wastewater has been attributed to one or combination of municipal, commercial, industrial and agricultural activities (Wan *et al.,* 2008).

Municipal wastewater are those used water from bathing, washing of domestic items (clothes, floors, dishes, cars) and from chemical substances or products (pesticides, drinks, lubricating oil, cooking oil, paint) made for domestic purposes. Though, a number of contaminants are contained in wastewater, heavy metals for their non biodegradable nature and toxicity have attracted the attention of many researchers in recent time. A number of these metals exist but few such as Iron (Fe), Chromium (Cr), Copper (Cu), and Zinc (Zn) are associated with municipal wastewater (Wan *et al*., 2008; Dinesh *et al*., 2008).

To eradicate this menace, activated carbon is used as adsorbents for the removal of harmful chemicals from contaminated water (Ao and Lee, 2005). Activated carbon is composed of black granules produced from any form of carbonaceous organic based materials such as coconut shells, palm-kernel shells, wood chip, corn cobs, rice straw, sawdust, animal bones, groundnut shell, mango seed and bamboo (Kadirvelu *et al.,* 2000).
Earlier studies by Kwaghger and Adejoh (2012) produced activated carbon from sugarcane bagasse, Barkauskas and Dervinyte (2004) and Gao *et al*. (2011) produced the carbon from corn husk and rice straw respectively. This work is aimed at removing Fe and Cu from municipal wastewater using activated carbon from African star apple seeds.

2. METHODOLOGY

African star apple (*Chrysophylum albidum*) is a plant which belongs to the family of trees known as *Sapotaceae* .Though, it is available in the Northern part of Nigeria, it is more common in the Southern part. It is commonly known as *Agbalumo* and *Udara* in Yoruba and Igbo languages respectively. Its fully ripe fruits having pale yellow with pink coloured endocarp become available from January through April. The pink-coloured pulp and the whitish cover of the brown-coloured seeds of the fruit are consumed, while the empty pale yellow pericarp and the brown-coloured seeds are discarded. It has high micronutrient content and vitamin, low in gross energy, antinutrients, carbohydrate content, calorie, sugar and it is a good source of antioxidants (Adepoju and Adeniji, 2012). The chemical used in this study is of analytical grade with percentage purity of 99.9%.

2.1 Procedure

2.1.1 Preparation of Activated carbon.

The fruit was purchased from Bosso Market, Minna Niger State in March. It was deseeded and the seeds were properly washed with distilled water to remove the surface impurities. The cleaned samples were subjected to oven drying at 80^0C for 12 hours to remove moisture as adopted by Borhan and Kamil (2012). They were then ground and sieved using 2 mm mesh sieve.

Plate 1: The seed of African star apple

The sieved sample was impregnated with 0.3 mol/dm^3 of Potassium hydroxide (KOH) for 24 hours until the mixture turned paste (Plate 2). This was done to open the pore spaces and optimize the properties of the activated carbon. It was then decanted and dried in an oven. After the retrieval from the drier, it was then introduced into the Muffle furnace and carbonized at 400^{0}C. After activation, the sample was washed with distilled water until the pH of the filtrate was ~7. The filtered solid was then dried at 80^{o}C for 6 hours to give powdered sample.

Plate 2: The impregnated Sample

Plate 3: Activated carbon produced

2.1.2 Characterization of the prepared Activated Carbon

Since the ability of activated carbon to adsorb contaminants depends on the carbon characteristics such as pore size and surface area (Dvorak, 2013), the following properties were determined:

Scanning electron microscopy (SEM): The surface morphology and microstructure of the prepared activated carbon was characterised using SEM. A small quantity of the prepared activated carbon was sprinkled on sample holder and sputter coated with Au-Pd for about 5 minutes prior to analysis. The sputter coated sample was firmly attached to the carbon adhesive tape and analysed using SEM machine equipped with In-lens standard detector at 30 kV.

Fourier Transform Infrared Spectroscopy (FTIR): The functional groups present in the prepared activated carbon were determined using the FTIR-2000, Perkin Elmer. It directed a beam of light having many frequencies of light to the activated carbon at once and measures how much of that beam is absorbed by the carbon. The spectra were recorded from 4000 to 400 cm^{-1} wave number

Brunauer-Emmett-Teller (BET) Surface Area: The surface area of the prepared activated carbon was determined using BET method in NOVA 4200e Quantachrome instruments. The sample was degassed for 4 hours for moisture and impurity removal. The degassed sample was the analysed for physisorption of the adsorbate (Nitrogen) by the adsorbent in a liquid nitrogen environment to determine the sample surface area, pore size and pore volume.

Atomic absorption spectroscopy (AAS): AAS spectrometer was used for determining Cu and Fe present in the wastewater. The spectrometer has specific lamps for each metal to be detected. The determination of the concentrations of the two metals was done before and after wastewater treatment.

2.2. Adsorption column technique

Though, there are two types of adsorption techniques (Batch and Column), column adsorption technique was adopted in this study in order to determine the effect of packing lengths of the activated carbon on adsorption of Cu and Fe. Adsorption column was packed with activated carbon with packing lengths of 10 mm.

Cr and Fe contents of municipal wastewater were determined after which 50 ml of the wastewater was measured and passed into the column from the top and was left for 20 minutes to allow for contact with the activated carbon before allowing it to run out through the bottom as show in Fig 1. This process was repeated for the packing length of 20 mm (He and Chen, 2014). The filtrates were then collected and taken to the laboratory for AAS Analysis.

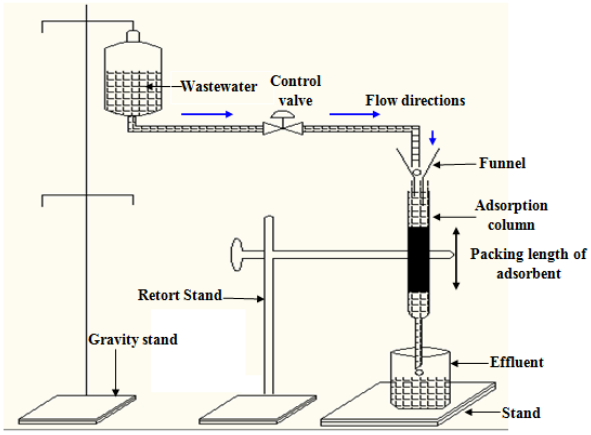

Figure 1: Experimental set-up for column adsorption

3.0 RESULT AND DISCUSSION

3.1 Characterization of the prepared activated carbon

3.1.1 SEM of the produced carbon

The particles morphology of the prepared activated carbon was studied using SEM and the results obtained at different magnifications are presented in Plate 4 and 5. The low magnification micrographs (Plate 4) revealed the presence of wide varieties of pores in the prepared activated carbon as indicated by arrows. Whereas higher magnification micrographs of x300 (Plate 5) demonstrated a more evident of large pores on the surface of the prepared activated carbon. This implies that the prepared activated carbon from African star apple seed has enough spaces for adsorption activities to take place. Hence, there is high tendency for the heavy metals adsorption since surface plays a prominent role in the adsorption process (Jambulingam *et al.*, 2007).

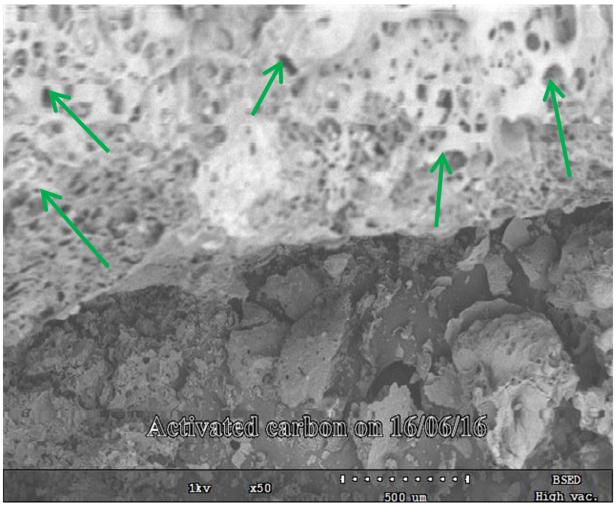

Plate 4: SEM of activated carbon from African star apple seed at x50

Plate 5: SEM of activated carbon from African star apple seed at x300

3.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of the prepared activated carbon is presented in Figure 2. The band at 3138.4cm^{-1} is conforming to O – H stretching vibrations, whiles the bands at 2370 cm^{-1}, 2113.4 cm^{-1}, 1097.2 cm^{-1}, 1543.1 cm^{-1}, 1438.8 cm^{-1}, 1384.2 cm^{-1}, were assigned to the stretching vibration of C≡C, C═C, C-CH_3 and C−O−H respectively. Band at 1114.5 cm^{-1} is characterised to the out of plane deformation of the C−H bond. Other bands at 879.7 cm^{-1}, 801.4 cm^{-1} and 700.7 cm^{-1} were due to the twist of the C−O−H. The presence of a large number of peaks in the FT-IR spectrum showed the complex nature of the prepared adsorbents. For instance the peak obtained at 3138.4 cm^{-1} signified the existence of free and intermolecular bonded hydroxyl groups (Ahmed *et al.*, 2013). This showed that the prepared activated carbon is a good adsorbent material for adsorption process. This result is in line with the findings of Ahmed *et al.* (2013)

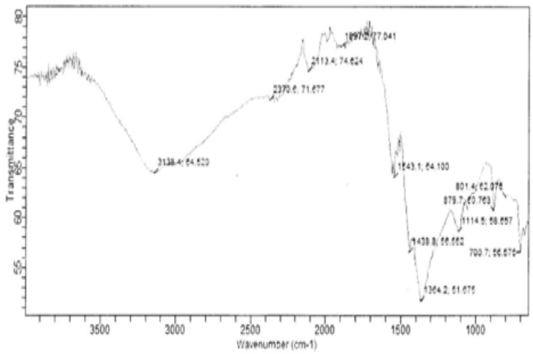

Figure 2: Fourier transforms infrared

3.1.3. Brunauer Emmett Teller Theory (BET)

The result of the BET revealed the surface area of the prepared activated carbon. BET surface area depends on the size and number of gas molecules adsorbed, Multipoint BET of the carbon was 371.4m^2/g, (Figure 3).

The Micro pore half pore width and micro pore volume of the prepared activated carbon were 26.33A and 0.1642cc/g respectively. These values also indicated that the seed of African star apple are good biomaterial for activated carbon for adsorption process.

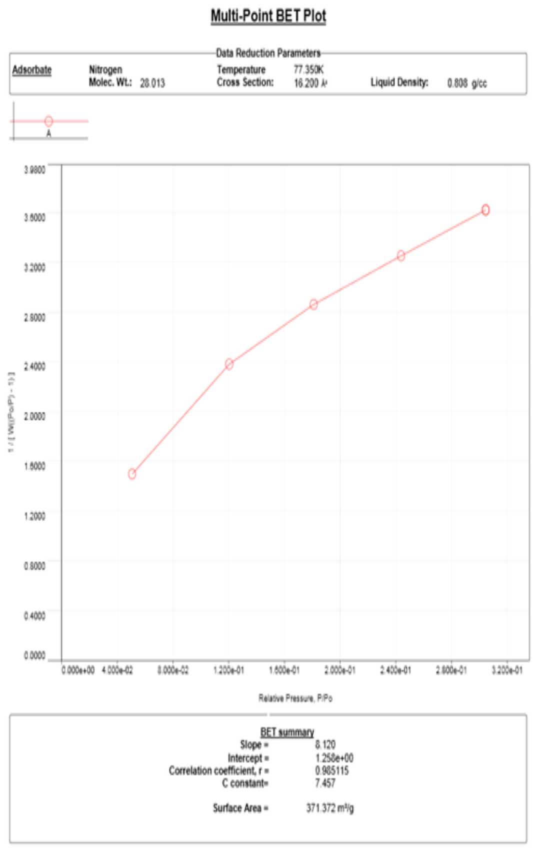

Figure 3: Brunauer Emmett Teller Theory (BET).

3.2 Wastewater analysis with AAS

The result of AAS analysis showed that the initial concentrations of Fe and Cu in the municipal wastewater were 3.10 mg/L and 5.95 mg/L respectively. After the treatment of the wastewater at the packing length of 10 mm, the wastewater showed a decrease in the concentrations of Fe from 3.10 mg/L to 2.95 and Cu from 5.95 mg/L to 4.95 mg/L. This showed that activated carbon from African star apple seed is a good adsorbent for the metals. At packing length 20 mm a higher decrease was observed as the concentration of Fe decrease from 3.10 mg/L to 2.55 mg/L and Cu from 5.95 mg/L to 4.55 mg/L. This showed high tendency of the produced carbon for more adsorption with increase in packing length. The values for Fe and Cu contents in the raw sample and the treated samples were statistically different at $p < 0.05$. This result is in line with findings of Bernard *et al.* (2013) which claimed that Cu and Fe can be removed from wastewater with activated carbon.

TABLE 1: IRON AND COPPER CONCENTRATIONS

Wastewater	Fe (mg/L)	Cu (mg/L)
Raw	3.10 ± 0.07^a	5.95 ± 0.2^a
Treatment (10 mm)	2.95 ± 0.02^b	4.95 ± 0.1^b
Treatment (20 mm)	2.55 ± 0.02^c	4.55 ± 0.2^c

Values are expressed as mean ± SD, n = 3, values with different superscript letter differ significantly at $P < 0.05$

4. CONCLUSION

This study showed the potentials of African star apple seed as a good biomaterial for activated carbon which serves as adsorbent for the removal of Fe and Cu. The study also revealed that the performance of the activated carbon in removing Fe and Cu increases with increase in packing length. This indicated that the seed of the fruit which constitute nuisance to the environment during the dry season could be converted to wealth in wastewater treatment.

REFERENCES

Adepoju, O. T. and Adeniji, P. O. (2012): Nutrient composition and micronutrient potential of three wildly grown varieties of African star apple (Chrysophyllum albidum) from Nigeria , African Journal of Food Science Vol. 6(12), pp. 344-351,

Ahamed K. R., Chandrasekaran, T. and Kumar, A. A. (2013): Characterization of Activated Carbon prepared from Albizia lebbeck by Physical Activation International Journal of Interdisciplinary Research and Innovations Vol. 1 (1) pp 26-31

Ao C. H. and Lee S. C. (2005), "Indoor air purification by photocatalyst TiO immobolized on an activated carbon filter installed in an air cleaner",Chem Eng Sci., Vol. 60, pp. 103-109

Barkauskas, J. and Dervinyte M. (2004), "An investigation of the functional groups on the surface of activated carbons", J Serb Chem Soc., Vol. 69, No. 5, pp. 363-375.

Bernard E., Jimoh A. and Odigure J.O. (2013): Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shell Research Journal of Chemical Sciences Vol. 3(8), 3-9,

Borhan, A and Kamil A. F., (2012). Preparation and Characterization of Activated Carbon from Rubber-seed Shell by Chemical Activation. Journal of Applied Sciences, 12: 1124-1129.

Dinesh Mohan P., Kunwar Singh and Vinod, Singh K., (2008) "Waste water treatment using low cost activated carbons derived from agricultural by products-a case stdy", pg 1065-1073.

Dvorak, B. I. (2013): Drinking Water Treatment: Activated Carbon Filtration, NebGuide University of Nebraska Lincoln Extension, Institution of Agriculture and Natural Resources G1489 Revised November, 2013

Gao P., Liu Z. H., Xue G., Han B. and Zhou M. H. (2011), "Preparation and characterization of activated carbon produced from rice straw by (NH)HPO activation", Bioresour Technol., Vol. 102, No. 3, pp. 3645-3648.

He J., Chen, J. P. (2014): A comprehensive review on biosorption of heavy metals by algal biomass: materials, performances, chemistry, and modeling simulation tools, Bioresour. Technol. 160 67–78.

Jambulingam, M., Karthikeyan, S., Sivakumar, P., Kiruthika, J. And Maiyalagan (2007): characteristics studies of some activated carbons from agricultural wastes Journal of Scientific & Industrial Research 66, 495-500

Kadirvelu K., Faur-Brasquet C., Le Cloirec P., (2000). Removal of Cu, Pb, and Ni by adsorption onto activated carbon, 16:8404-8409.

Kwaghger A. and Adejoh E. (2012), "Optimization of conditions for the preparation of activated carbon from mango nuts using ZnCl", Int J Eng Res Dev., Vol. 1, No. 8, pp. 1-7

Wan Ngah W. S., M. A. Hanafiah, ((2008)) Removal of heavy metal ions fromwastewater by chemically modified plant wastes as adsorbents: a review,Bioresour. Technol. 99 3935–3948.