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EVALUATION OF EFFECTIVENESS OF HEAVY METAL REMOVAL FROM WASTE WATER USING ACTIVATED CARBON PRODUCED FROM CORN COB AS ADSORBENT

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Abstract: Corn cob an abundant, cheap, biodegradable agricultural waste absorbs water due to its hydrophilic group. To make it useful as a sorbent for oil spill removal from land and aqueous environment, it was activated by chemical activation with concentrated H_3PO_4 acid. The adsorption of heavy metal ions such as (Pb, Cu, Cd, Fe) with corn cob as adsorbent was studied using batch adsorption method. The Physico-chemical parameters gave values of 6.13, 42 %, 23 %, 5 %, 0.5 mg/L and 55.50 mg/L for pH, attrition, ash content, moisture content, bulk density and iodine number. Atomic absorption spectrophotometer was used to monitor the adsorption of (Pb' Cu, Cd, Fe), the optimum values obtained were 84.45, 87.55, 88.45 and 89.77 % at 20 mg/L for concentration, 99.60 % at a pH of 11, 81.50,84.55,85.45 and 86.76 % at a contact time of 40 mins and 92.44 at an adsorbent dose of 5 g, signifying that corn cob is a good adsorbent for the removal of heavy metal ions from simulated waste water. The result fitted into Langmuir and Freundlich isotherm.

Key words: Activated carbon, adsorption capacity, adsorption isotherm, adsorption kinetics, batch adsorption, corn cob, equilibrium, Heavy metal ion, Langmuir

Introduction

Corn cob a biodegradable, available and abundant agricultural waste is grown widely throughout the world, it is produced annually than any other grain and it is the most important staple food in sub-Saharan Africa and Latin America. The largest African producer of corn is Nigeria with nearly 8 million tons. Corn cob is generated in large quantities in Nigeria and is hardly managed as Nigeria faces the problem of solid waste management. Corn cob is composed of cellulose, hemicelluloses and lignin; these three major chemical components of corn cob are rich in hydroxyl group, which makes it hydrophilic in nature. Water contamination by heavy metal has been a serious concern over the years due to environmental and safety reasons. Water pollutants mainly consist of heavy metals, microorganisms, fertilizers and thousands of toxic organic compounds (Chaitali *et al*., 2013). Heavy metals find their way into water as a result of the discharge of effluents from textile, chemical, dye, leather, tannery, electroplating, galvanizing, pigments, metallurgical and paint industries. Metal processing and refining operations at small and industrial scale also releases considerable amount of toxic metal ions. Their routes into the environment are natural and anthropogenic means such as natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, dumping of hospital wastes, pest and disease control agents applied to plants and air pollution (Shanmugapriya *et al*., 2013; Subba *et al*., 2003). Due to degradation problems, the presence of heavy metals in water has much effect on the micro algae which constitutes the main food source for bivalve mollusk in all their growth stages, zooplankton (rotifers, copepods, and borne shrimps) and for larval stages of some crustacean and fish species (Nazir *et al*., 2015).

Several methods have been employed in the removal of heavy metals from wastewater by agricultural industries, water treatment plants and also in medicine and these include; membrane extraction, adsorption, ion-exchange, precipitation, liquid extraction or electrolysis. Most of these techniques are extremely expensive or inefficient and take too much time. Among the techniques, adsorption using a low cost adsorbent or material such as corn cob has been employed (Lata *et al*., 2014; El-Sherif *et al*., 2013; Vieira *et al*., 2014; Manish *et al*., 2015). The choice of a suitable method for removal of heavy metals is usually influenced by different factors such as the efficiency of removing the pollutant materials, availability of used chemicals and the chemistry of the contaminated material beside the process cost. The major advantages of adsorption over conventional treatment methods are; low cost, high efficiency, no additional nutrient requirement, regeneration of adsorbent and the possibility of metal recovery (Dabrowski *et al*., 2001; Ahile *et al*., 2015).

Corn cob is an agro-waste which is produced in a large quantity by farmers. Corn cob a biodegradable, available and abundant agricultural waste is grown widely throughout the world, it is produced annually than any other grain and it is the most important staple food in sub-Saharan Africa and Latin America. The largest African producer of corn is Nigeria with nearly 8 million tons. Corn cob is generated in large quantities in Nigeria and is hardly managed as Nigeria faces the problem of solid waste management. Corn cob is composed of cellulose, hemicelluloses and lignin; these three major chemical components of corn cob are rich in hydroxyl group, which

makes it hydrophilic in nature. Apart from the three major chemical components of corn cob that are rich in hydroxyl group, the mineral composition of raw corn cob contains high quantity of Si, K, Fe, Al and P. These minerals contribute to the hydrophilic nature of the material (Ribeiro *et al*., 2000). Mineral composition of materials can be reduced when activated (Al-Qodah and Shawabkah, 2009). Conversion of materials to activated carbon yields product that is carbonaceous with large surface area and high porosity. During the activation process the precursor is converted into a hydrophobic carbonaceous material which has surface functional groups that are hydrophilic (Viswanathan *et al*., 2009).

The assessment or performance of sorting materials often needs to be assessed (Volesky, 2004). This helps in efficient application of sorbents. Efficient application of sorbents requires knowledge of data on the sorbent sorption capacity and a good understanding on the basic mechanism behind the sorption capabilities (Singh et al., 2013). In order for the comparison of two or more sorbents to be fair, it must be done under the same experimental conditions. By performance of the sorbent is usually meant its uptake (q) of a sorbet. The sorbents can be compared by their respective maximum equilibrium adsorption capacity q_m values which are calculated. A good sorbent would feature a high sorption uptake capacity q_m. Also desirable is a high affinity between the sorbent and sorbet.

This research work aim to assess the removal some heavy metal ions such as (Pb, Cu, Cd, Fe), from waste water using activated carbon produced from corn cob as an adsorbent.

Materials and Methods

Sample Collection, Activation and Carbonization of the adsorbent

Corn cob was obtained from a farmer in Wukari Taraba State-Nigeria. The corn cob was washed with distilled water to remove all dirt after which it was air dried at room temperature and later oven dried for 24 hrs at 105 °C, the dried samples was then grinded and sieved to obtain fine powder and stored in a plastic container for future use. The dried sample was activated by treating it with saturated solution of ammonium chloride with constant stirring and was steeped for 24 hours. 250 g of the adsorbent was carbonized at 650 ^oC for 25 minutes in a muffle furnace (Ney-252 model). The sample was cooled in a desiccators, washed several times with distilled water until the pH of the flushing water was between 6 and 7. The wet sample was dried and then stored in air tight bottles for further use.

Characterization of the adsorbent

The adsorbent were characterized based on bulk density, pH, ash content, moisture content, iodine number and attrition.

Determination of bulk density

5 g of the adsorbent was measured into 10 mL measuring cylinder. It was tapped on a bench until a lower volume was obtained. The density was calculated in g/mL using equation below.

$$D_{\mathbf{B}} = \frac{M_3 - M_2}{V_1}$$

Where:
D_B = Bulk density
M_2 = Mass in grams of the measuring cylinder
M_3 = Mass in grams of the measuring cylinder + sample
V_1 = volume

Determination of pH

1 g of the sample was weighed using a weighing balance. The weighed sample was steeped in 100 mL of distilled water and was place on a magnetic stirrer for 4 hrs. The sample was filtered and the pH of the filtrate was read by a pH meter and the value recorded.

Determination of ash content

2 g of the sample was weighed on a weighing balance. The sample was placed in a muffle furnace and heated till it turned to ash. The ash sample was cooled and the weight was recorded. The ash content was calculated using equation below.

$$\text{Ash content} = \frac{W_3 - W_1}{W_2 - W_1} \times 100\%$$

Where:
W_1 = Weight of the crucible
W_2 = Weight of crucible + Sample before ashing
W_3 = Weight of crucible + Sample after ashing

Determination of moisture content

3 g of the sample was weighed using weighing balance and was heated in an oven at 105 ^{0}C. This was repeated several times until a constant weight was obtained. The moisture content was calculated using below equation .

$$\text{Moisture content} = \frac{M_2 - M_3}{M_2 - M_1} \times 100\ \% = \frac{\text{Loss of weight}}{\text{Initial weight of sample}} \times 100\ \%$$

Where:
M_1 = Weight of crucible
M_2 = Weight of crucible + Sample before heating
M_3 = Weight of crucible + Sample after cooling

Iodine number

20 mL of the standard solution was titrated with sodium thiosulphate which was the blank without the adsorbent. 1 g of the adsorbent was steeped in 25 mL of the standard iodine solution and was stirred for 2 hours. The solution was filtered and the filtrate was titrated with 0.01 M solution of sodium thiosulphate using starch as the indicator. The iodine solution was calculated using equation below

$$\text{Iodine Value} = \frac{\text{Y} - \text{X}}{\text{Y} \times \text{V}} \times \frac{1}{\text{W} \times \text{M}}$$

Where:
Y = Volume of thiosulphate for blank
X = Titre value
V = Volume of the iodine solution used
W = Weight of the sample
M = Molarity of iodine solution

Attrition

1 g of the sample was steeped into 50 mL of distilled water. It was stirred with a magnetic stirrer for 2 hrs. The solution was filtered and the residue was dried and weighed. The attrition was calculated using equation below

$$\%\ \text{Loss of attrition} = \frac{\text{M}_1 - \text{M}_2}{\text{M}_1} \times 100\ \%$$

Where:
M_1 = initial mass
M_2 = final mass

Batch Adsorption Studies

The adsorption of heavy metal was studied by batch technique. 0.5 g of the adsorbent was equilibrated with 1000 mL of the heavy metal solution of known concentration of 4.0, 8.0, 12.0, 16.0 and 20.0 mg/L in stoppered borosil glass flask at a fixed temperature of 30 °C in an orbital shaker for 20-60 mins. After equilibrium, 10mL sample was collected from each flask in time interval of 20, 30, 40, 50 and 60 mins, the suspension of the adsorbent was separated from the solution by filtration using filter paper. The concentration of metal ion in the solution was measured by atomic absorption spectrophotometer.

Effect of pH

Batch adsorption experiments were used to measure the amount of heavy metal ions adsorbed by corn cob as a function of pH. The experiment was performed in an orbital shaker by using 0.5 g of the adsorbent and shaking with 50 mL of each metal solution for an hour. After the period of shaking, the amount of heavy metal adsorbed per gram of material (q_{eq}) was calculated using equation below.

$$\text{Q}_{\text{eq}} = (\text{C}_\text{o} - \text{C}_\text{e}) \times \frac{\text{V}}{\text{M}}$$

Where:
C_o and C_{eq} are the initial and equilibrium concentration of the solution respectively (mg/L)
V = is the volume of the solution (mL), M = mass of the material (g)

Contact Time

The effect of contact time was carried out at different time intervals of 10, 20, 30, 40, 50 and 60 mins at room temperature using 50 mL of the solution. 1 g of the sample was measured into a beaker and placed in a thermostat water bath at 25°C, it was filtered and the absorbance was read using an atomic absorption spectrophotometer.

Concentration

A mass of 5 g of the adsorbent was measured and contacted with 50 mL of each metal solution with concentration in the range of 4.0, 8.0, 12.0, 16.0 and 20.0 mg/L in a thermostat bath maintained at

30 °C. The solution was filtered and the absorbance was read using an atomic absorption spectrophotometer.

Adsorbent dose

1.0, 2.0, 3.0, 4.0 and 5.0 g of the adsorbent was measured and contacted with 50 mL of each metal solution on an orbital shaker for 1 hr. The solution was filtered and the residue concentration was determined using an atomic absorption spectrophotometer.

Results and Discussion

Physico–chemical characteristics were carried out on the adsorbent. The pH of the activated corn cob was found to be 6.13. For most applications, pH of 5-6 is acceptable. The bulk density of the corn cob was determined to be 0.5 mg/L. The percentage moisture content was between 4.5 - 5 %. The percentage ash content was between 22- 23 %. The percentage loss of attrition was 42 %. From the results of the physico-chemical characteristics obtained, the activated corn cob can serve as a good adsorbent for the removal of metal ions from simulated wastewater.

Effect of Concentration

The removals of heavy metals are dependent on its initial concentration. Fig 1 shows the effect of initial heavy metal concentration on the percent removal of metal ions. From Fig 1, it is observed that the percentage removal efficiency increased steadily from 75.50 % to 79.92 % with an increase in initial heavy metal concentration from 4 mg/L to 12 mg/L and takes a shorter time to reach equilibrium because of the fact that with increase in concentration, there will be increase in active adsorption sites and the process will increase. Hence, adsorption increases with increasing concentration (Amuda *et al*., 2007).

Effect of pH

The pH of the solution has been identified as the most important variable governing metal adsorption. This is partly due to the fact that hydrogen ions (H^+) themselves are strong competing ions that the solution pH influences the chemical speciation of the functional groups on to the adsorbent surfaces. From Fig 2, it can be observed that the removal of heavy metals increases with increasing solution pH and a maximum value was reached at an equilibrium pH of around 6.8 (Bernard and Jimoh, 2013).

Table 1: Physico–chemical parameters

Parameters	Value
Ash content (%)	21.10 - 23.00
Attrition (%)	40.50 - 42.00
Bulk density (mg/L)	0.45 - 0.50
Iodine number (mg/L)	50.50 - 55.50
Moisture content (%)	4.50 - 5.00
pH	6.10 - 6.13

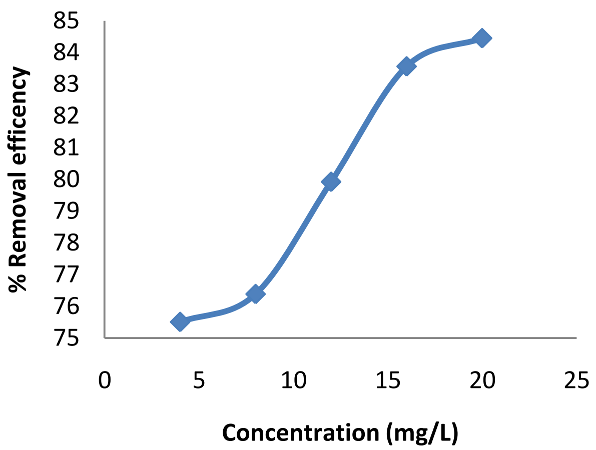

Fig. 1: Effect of Concentration of the Adsorbent.

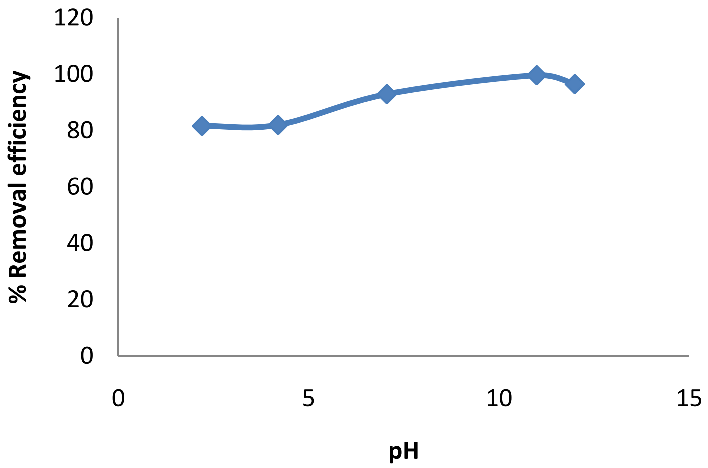

Fig. 2: Effect of pH of the adsorbent

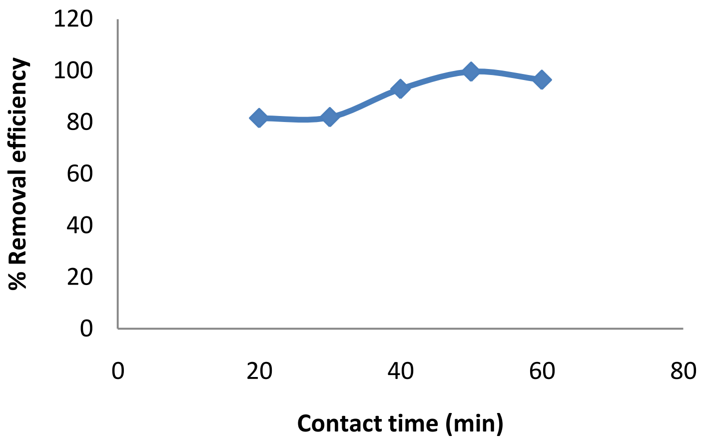

Fig. 3: Effect of Contact Time of the Adsorption.

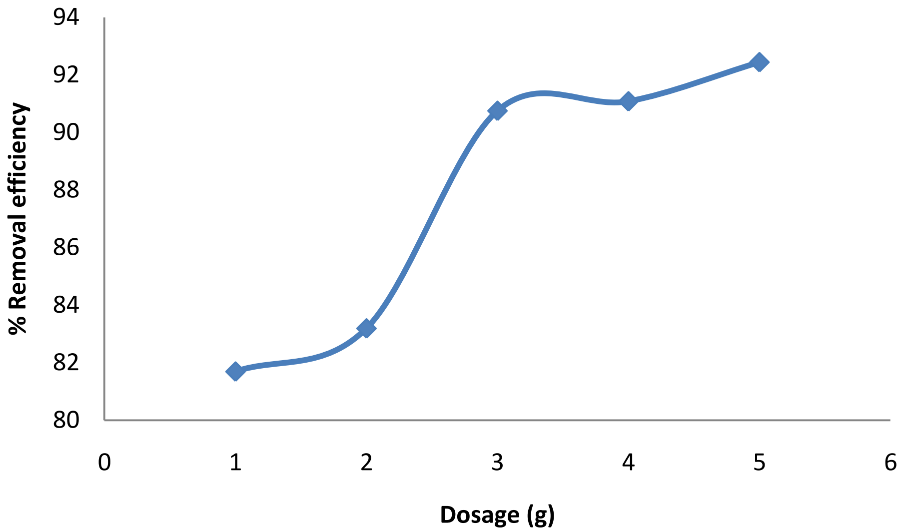

Fig. 4: Effect of Dosage of the Adsorbent.

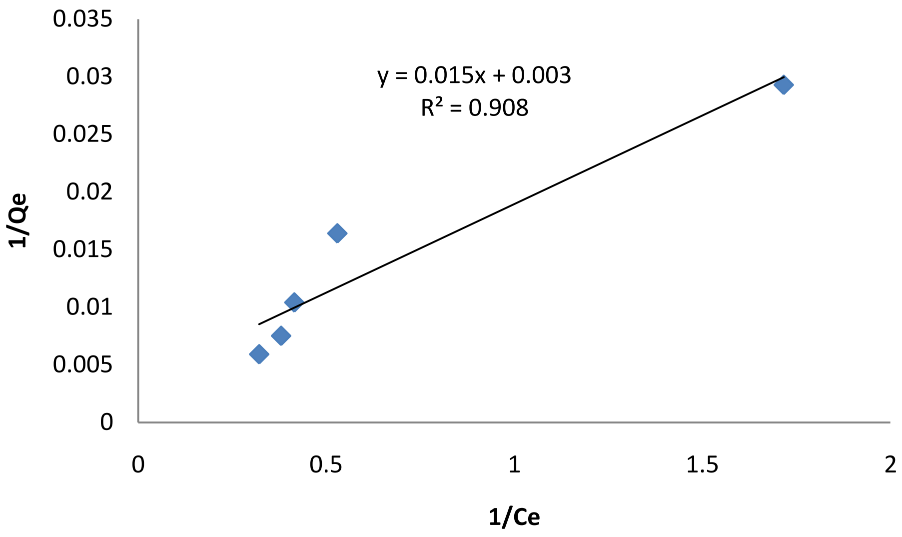

Figure 5: Langmuir Adsorption Isotherm

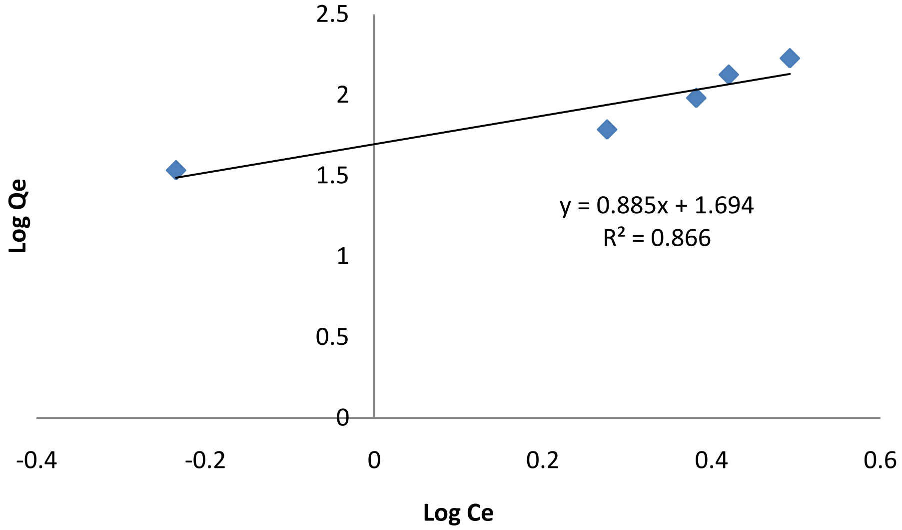

Figure 6: Freundlich Adsorption Isotherm.

Effect of contact time

The variation between adsorption efficiency in terms of percentage removal of metals and contact time is shown in Fig 3, and it was observed that the percentage removal of all the heavy metals study was least of 81.35 % at 60 mins of contact time and highest of 81.50 % at contact period of 40 mins. The adsorption of heavy metals increased with increasing contact time from 81.47 % to 81.50 % at contact period of 20-40 mins. The maximum rate of adsorption took place within a contact time of 20-40 mins. This indicates that the rate of adsorption increases with increase in time. However, the rate of adsorption was found to be fairly constant and decreased beyond 40 mins (between 50-60 mins), which is suggestive that the adsorption process was fastest within the first 40 mins as the largest amount of heavy metal ions were attached to the adsorbent within that period. Higher adsorption efficiency activated rice husks are attributed to available adsorption sites (surface functional groups) on the adsorbent surface (Vieira *et al*., 2014).

Effect of adsorbent dosage

Dosage study is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. Fig 4 illustrates the variation of adsorption efficiency with varying adsorbent dosage. The effect of adsorbent dosage on the removal of heavy metals from aqueous solution at C_o=16 mg/L was studied and the results are represented in Fig 4. The removal of heavy metals increases steadily with an increase in adsorbent dosage from 1 g to 2 g with percent removal efficiency of 81.69 % to 83.19 %. The increased adsorption with increase in adsorbent dosage is attributed to the availability of larger surface area and therefore more adsorption sites (Dabrowski, 2001).

Adsorption Isotherm

The Langmuir and Freundlich isotherms constants are illustrated in Figures 5 and 6 respectively. From Fig 5 it is observed that the regression correlation coefficient (R^2) of the Langmuir isotherm (R^2 = 0.9082), is greater than Freundlich isotherm (R^2 = 0.8664), thus the Langmuir isotherm is found to be the best fit isotherm (Oladoja *et al*., 2008)

Conclusion

In this study, batch adsorption experiment for the removal of some heavy metals from waste water have been carried out using carbonized corn cob as a low cost, readily available adsorbent. The study shows that the activated corn cob is an effective adsorbent for the removal of study heavy metals from waste water. The adsorption characteristics have been examined at different pH values, initial heavy metal concentration, contact time and adsorbent dosage governs the overall process of adsorption. The optimum percentage removal for concentration is between 82.50 - 84.45 %; pH is between 95.55 - 99.60 %, contact time at 81.50 % and adsorbent dosage at 92.44 %. Equilibrium data was represented by Langmuir and Freundlich isotherms. The adsorption studies showed that Langmuir isotherm was found to provide the best fit of the experimental data. From this study, it can be inferred that corn cob, an abundantly available agricultural waste can be used as a low cost adsorbent. The higher adsorption capacity is favored by higher number of active binding sites, improved ion exchange properties and enhancement of functional groups after chemical treatment. Overall, heavy metals are effectively adsorbed from simulated wastewater by carbonized corn cob.

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