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Kinetic studies of adsorption of Cu^{2+} from aqueous solution using coconut shell activated carbon

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Abstract

Carbonized coconut Shell was used for the adsorption of Cu^{2+} from aqueous solutions using Batch adsorption method. The result for physico-chemical characterization give the ash content to be 3%, moisture content as 11%, 45% for attrition, the tap density was 0.3 g/mL, pH as 6.24 while the iodine number was found to be 46.90%. The equilibrium adsorption was studied and the result fitted into the Temkin model. From the results obtained, the adsorbent proved to be an effective adsorbent for the removal of Cu^{2+} from aqueous solutions. Atomic absorption spectrophotometer was used to monitor the adsorption of Cu^{2+}, the optimum values obtained were 50.2 % at 20 mg/L for concentration, 99.60 % at a pH of 99.6%, 59.9 % at a contact time of 40 minutes and 50.9 at an adsorbent dose of 5 g, from the results, coconut shell is a good adsorbent for the removal of Cu^{2+} from aqueous solution.

Keywords: Coconut shell; copper; heavy metals; adsorption isotherm; Temkin.

1.0 Introduction

Heavy metals are any metals or metalloids of environmental concern with specific gravity of 5.0 grams per cubic centimeter and above (Tasrina *et al.*, 2014). The term originated with reference to the harmful effect of Cadmium, Mercury, Lead and Nickel etc. all of which are denser than Iron. It has since been applied to any other similar toxic metals such as Arsenic (Tangjiuank *et al.*, 2009).

Heavy metals in the ecosystem are a wellspring of some concern due to their potential toxicity, mobility and reactivity in soil. Some heavy metals like zinc and copper are very important for plants and animals health. Nevertheless, at environmental concentrations above permissible limit, it may cause harm (Shahmonammadi *et al.*, 2011). Metals and their compounds are absolutely necessary to the agricultural, industrial and technological development of any nation. With quick growth of industrial activities, pollution derived from heavy metals have been in waste streams from tanneries, mining activities, electroplating, electronics and petrochemical industries (Musah, 2011). Other heavy metals like Cd and Pb are not known to be important to animal and plants. Removal of heavy metals from water is of primary importance as water of high quality is essential to human life and water of acceptable quality is essential for domestic, industrial, agricultural, and commercial uses (Abdel – Ghani and Mahmoud, 2007). In agreement with World Health Organization (WHO), the metals of most crucial interest are copper, chromium, zinc, iron, lead and cadmium. In order to solve problems relating to heavy metal pollution in our environment, it is crucial to bring practical solutions to the issue (Shahmonammadi *et al.*, 2011).

Contamination of drinking water with high level of copper may lead to chronic anemia. It accumulates in liver and brain, while its toxicity is a fundamental cause of Wilson's disease. Copper particles are released into the atmosphere by windblown dust, volcanic eruptions, and anthropogenic sources, primarily copper smelters and ore processing facilities the fate of elemental copper in water is complex and influenced by pH, dissolved oxygen and the presence of oxidizing agents and chelating compounds or ions (Ruqia *et al.*, 2015). A number of technologies are available to purify water or remove metal ions from water with varying degrees of success nowadays. These techniques are filtration, coagulation, electrolysis, solvent extraction, electron analysis, chemical precipitation, ion exchange, aerobic and anaerobic treatment, adsorption, ultrafiltration, reverse osmosis etc. (Adejo *et al.,* 2008).

Among these techniques for the removal of toxic metal ions from water, adsorption method is mostly preferred due to its high efficiency, easy handling and availability of different adsorbents. Those other techniques have the disadvantages of high cost, they are ineffective, for the removal of metals of low concentration, time consuming, required trained personnel, complicated and may generate toxic slurry which are difficult to dispose (Onundi *et al.*, 2010). We report here the preparation of low cost absorbent from coconut shell and to apply it in the removal of Cu(II) from simulated wastewater.

Materials and methods

2.1 Sample collection and pretreatment

The adsorbent (coconut shell) was gotten from Wurukum market in Makurdi, Benue State-Nigeria. The shell was washed with a large quantity of water to remove dirts and then dried under the sun for three days. The dried shell was pound with mortar and pestle, sieved, stored in a desiccator (Najua *et al.,* 2008).

2.2 Preparation of activated carbon

Coconut shell weighing 50 g was activated using ammonium chloride for twenty-four hours. It was fully rinsed with distilled water and dried at room temperature. The husk was carbonized at 400ºC by using a muffle furnace (Ney M-252 model) in porcelain crucibles for twenty minutes. The sample was then dried in the laboratory and kept for further use (Ahile *et al.,* 2015).

2.3 Preparation of stock and working solutions

About 4 g of $CuSO_4.5H_2O$ was measured and dissolved in 1 L of distilled water in a volumetric flask to produce the solution of synthetic effluent. To prepare working solutions, the stock solution was diluted working solutions of desired concentration. The stock solution was shaken for about two hours using a shaker at 30ºC and 100 rpm to make sure that it was thoroughly homogenous each time the standard solution is prepared. The stock solution was then kept for serial dilution (Kamphake *et al.,* 1967).

2.4 Preparation of starch indicator

1 g of the starch solution was added to 100 mL of boiling water and was constantly agitated for some minutes for complete homogeneity. Then it was allowed to cool (Beebe, 2005).

2.5 Preparation of 0.1 M sodium thiosulphate solution

To prepare sodium thiosulfate solution, 2.4 g pellets were weighed into 70 mL of distilled water and transferred into a 100 mL volumetric flask. It was shaken to homogenize the solution and the volume made up to mark. 20 mL of iodine solution was measured and transferred into an erlenmayer conical flask, it ws titrated with the sodium thiosulfate with continued swirling until a pale yellow colour appeared after which 5 mL of starch solution was added as an indicator. The titration continued with continuous swirling of the flask until the blue colour disappeared.

2.6 Characterization of the adsorbent

2.6.1 Ash content

The crucibles used were washed very well, dried in an oven and cooled in a desiccator. The weight of each crucible was recorded as W_1. Then 2 g of the sample was measured into the pre-weighed crucible and the weight of both the sample and the crucible were recorded as W_2. The sample was then heated at a temperature of about 750ºC in a muffle furnace with the crucible left opened for 58 minutes. It was then removed from the furnace, allowed to cool and the weight of the sample and the crucible after ashing was recorded as W_3. The ash content for the sample was calculated according to the following equation (Smrutirekha, 2014).

$$\text{Ash content} = \left[\frac{W_3 - W_1}{W_2 - W_1}\right] \text{x}100 \quad 1$$

Where: W_1 = weight of the empty crucible, W_2 = weight of crucible + sample before heating, W_3 = weight of crucible + sample after heating

2.6.2 Moisture content

The weights of a dried crucible were recorded as W_1. Then 3 g of the sample was weighed into a pre – weighed crucible and the weight of both of the sample and the crucible was also recorded as W_2. The sample was dried at 115ºC in an electric oven with the crucible left opened in the oven for 2 hrs, 2 mins and the weights were recorded after the samples were allowed to until a constant weight was obtained by following the equation below (Smrutirekha, 2014).

$$\text{Moisture content} = \left[\frac{M_2 - M_3}{M_2 - M_1}\right] \text{x}100 \quad 2$$

2.6.3 Bulk density

The bulk density was determined by steeping 3.0 g of the uncarbonised groundnut shells into a 10 mL measuring cylinder, it was tapped on a table until it occupied a minimum volume, the apparent volume was taken at the nearest graduated unit. The bulk density was calculated in g/mL using the formula below.

$$D_B = \frac{(M_2 - M_1)}{v} \quad 3$$

Where: M_1 = mass of the empty measuring cylinder in grams, M_2 = mass of measuring cylinder + its contents, V = volume of the measuring cylinder in litres

2.6.4 pH determination

1 g o f the carbonized carbon of the shell sample was measured into a conical flask and 100 mL distilled water was mixed with it. The mixture was vigorously agitated for an hour and then filtered. The pH of the filtrate was recorded using a pH meter (Yusufu *et al.,* 2012).

2.6.5 Iodine number determination

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 2hrs. The solution was then filtered and the filtrate was titrated with 0.01 M solution of sodium thiosulphate using starch as the

indicator. The iodine number was calculated using the equation below (Yusufu *et al.*, 2012).

Iodine value (mg/g) = Y – X / Y x V / W x M 4

Where: Y = volume of thiosulphate for blank, X = titre value, V = volume of iodine solution used, W = weight of the sample, M = molarity of iodine solution

2.6.6 Attrition

1 g of the carbonized carbon was steeped into a 50 mL distilled water and agitated with a magnetic stirrer for two hours, the solution was then filtered and the residue was dried and weighed. The loss on attrition was calculated using the following formula (Madakson *et al.*, 2012).

$$\text{Loss on attrition} = \frac{M_1 - M_2}{M_1} \text{ x } 100 \qquad 5$$

Where: M_1 = initial mass, M_2 = final mass

2.7 Batch adsorption experiment

Batch adsorption experiments were carried out at room temperature of 32 ^oC to determine the rate of adsorption and equilibrium data. This was achieved by varying the contact time, pH, adsorbent dosage and concentration.

The adsorption study was done by measuring 50 mL of the simulated effluent and poured into a 100 mL conical flask. 0.2 g of the already prepared activated carbon was placed on a rotary shaker and shook at 150 rpm at a room temperature of 32 ^oC for a period 2 hours to ensure homogeneity. The suspension was then filtered using filter paper. Atomic adsorption spectrometer (AAS) was used to analyze the concentration of the metal ion present in the filtrate. The amount of metal ions adsorbed by the adsorbent was evaluated using equation (Okieien *et al.*, 1991).

$$q_t = \frac{(C_o - C_t)\, V}{W} \qquad 6$$

The mass balance equation was used to determine the adsorption capacity (q_e) from equation (2)

$$q_e = \frac{(C_o - C_e)\, V}{W} \qquad 7$$

Where C_o and C_t are the initial and final concentration of the heavy metal present in the wastewater before and after adsorption for a period of time t (mg/L) respectively Ce represent the concentration of the heavy metal in effluent (mg / L) when equilibrium was attained. The volume of the simulated effluent used is represented by v(ml).

W represents the mass (g) of the adsorbent used.

The percentage of the metal ion removed was obtained from equation (3)

$$R\ (\%) = \frac{(C_o - C_t)}{C_o} \text{ x } 100 \qquad 8$$

Where (R%) is the ratio of difference in metal concentration before and after adsorption.

2.7.1 Determination of pH

50 mL simulated effluent was measured into 250mL conical flasks labeled A – E. The pH in of the solution was varied from 3 to 7 then 1 g of the activated carbon was added to each of the flask. The mixture was agitated for 1 hour at a speed of 150 rpm. The pH was adjusted from 3 – 7 using HCl and then filtered using filter paper. The filtrate was then taken for analysis of the concentration of the metal ions present (Oladoja *et al.* 2008*)*.

2.7.2 Determination of contact time

The removal of metal ions was studied for a period of one hour. 1.0 g of the activated carbon was added to different conical flask containing 50 mL of wastewater, the conical flask was closed and placed in a rotary shaker and agitated at 150 rpm, for each of the different contact times chosen (10, 20, 30, 40, 50 & 60 minutes). The sample at each contact time filtered and analyzed after each agitation time (Okieien *et al.*, 1991).

2.7.3 Determination of the adsorbent dosage

Several dosages of the adsorbent of 1, 2, 3, 4, and 5 g were added into different conical flasks containing 50 mL of the stock solution. It was then corked and agitated in a shaker for 1 hour at a speed of 150 rpm at a room temperature of 32^{o}C. The content of each flask was then filtered and the concentration determined after each agitation time (Okieien *et al.*, 1991).

2.7.4 Determination of concentration

5 g of the activated carbon was mixed with 50 mL of the Copper Sulphate solution in the beakers at the concentration of 4, 8, 12, 16, 20 (mgL^{-1}) using a thermostat water bath at the temperature of 25 ^oC with a speed of 250 rpm for 2 hours. The contents where then filtered and the filtrate was taken for analysis (Hutchin, 1988).

Results

Table 1: Physico-Chemical Characteristics of Carbonized Coconut Shell

Parameters	Values
Ash content (%)	3
Moisture content (%)	11
Attrition (%)	45
pH	6.24
Iodine number(mg/L)	46.9
Tap density (mg/L)	0.3

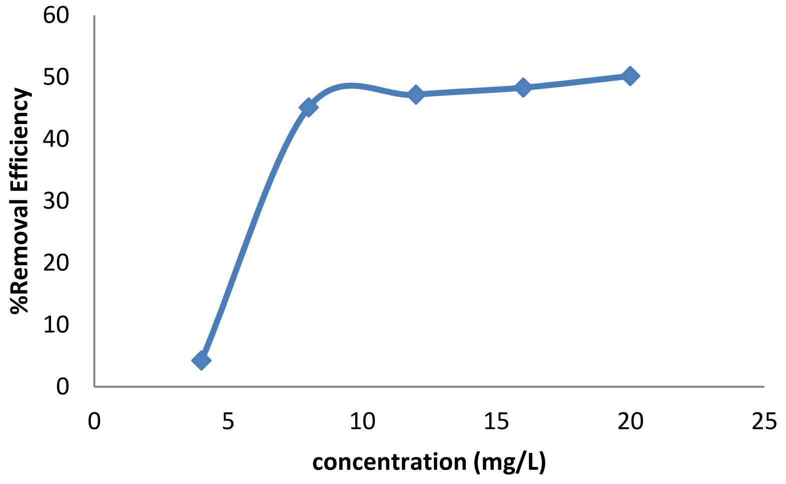

Figure 1: Effect of concentration of adsorbent.

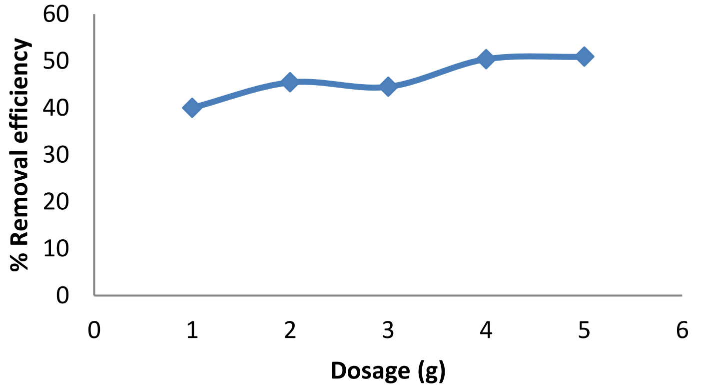

Figure 2: Effect of adsorbent dose.

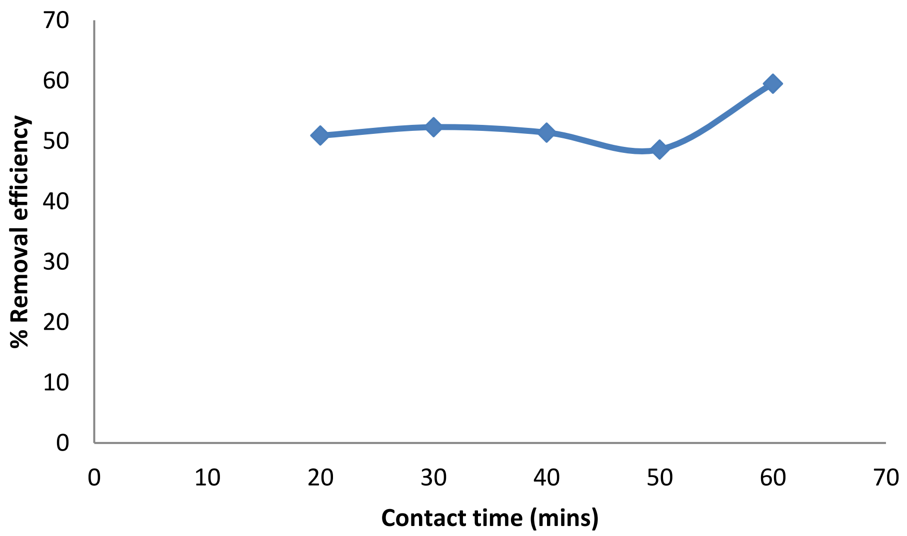

Figure 3: Effect of Contact time (mins)

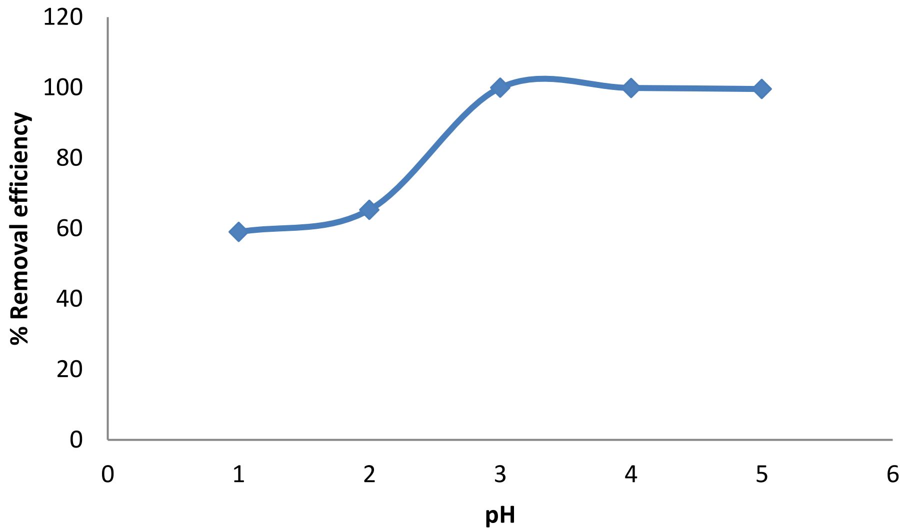

Figure 4: Effect of pH on the adsorption of Cu^{2+} on coconut shell

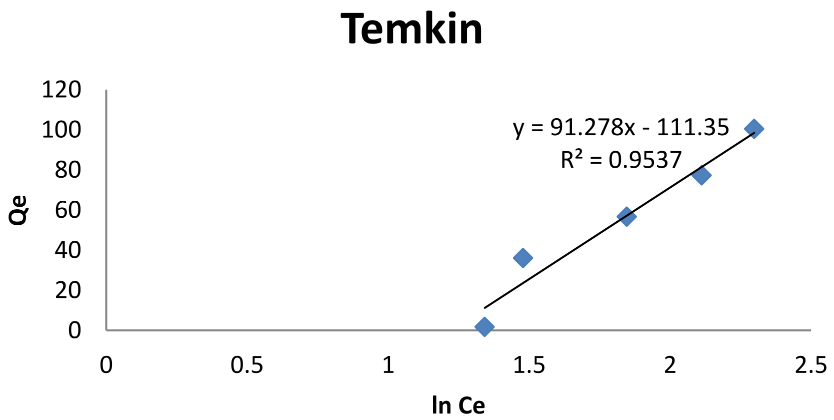

Figure 5: Temkin Isotherm

Discussion

3.1 Physio-chemical parameters

The results of the physico-chemical characterization of carbonized coconut shell is presented in Table 1. The results give the ash content to be 3%, moisture content 11%, attrition 45%, the tap density was 0.3 g/ml, pH 6.24 while the iodine number was found to be 46.90%. these results agreed with the works of other researchers, therefore, it was concluded carbonized coconut shell can serve as a good adsorbent for the removal of Cu (II) from wastewater (Smrutirekha, 2014; Yusufu *et al.*, 2012; Madakson *et al.*, 2012; Temkin and Pzyhev, 1940).

3.2 Adsorption isotherms

The adsorption of Cu (II) on coconut shell fitted only into Temkin isotherm as shown in Fig 4.5 giving regression correlation coefficient (R^2) of 0.9537. From the result, it can be suggested that Temkin adsorption isotherm follows physical adsorption isotherm (Agbozu and Emoruwa, 2004; Okieimen *et al.,* 2004).

3.3 Effect of contact time.

The effect of contact time on the adsorption efficiency was shown in Fig 4.3. Adsorption experiments were carried out at different time interval: 20, 30, 40, 50 and 60 min. It was observed that the removal of the tested metal increases due to the increase in contact time. Adsorption of Cu(II) ion attained maximum within 60 min with the value of 59.5. This indicates that the rate of adsorption increases with increase in time which is attributable to available adsorption sites on the adsorbent surface (Abdel – Ghani and Mahmoud, 2007; Kailas, 2010).

3.4 Effect of concentration

Sorption of the metal ion in solution is influenced by the concentration of the metal ion in solution. The effect of metal ion concentration on the adsorption efficiency of coconut shell was shown in Fig 4.1. Adsorption experiments were carried out at different metal ion concentrations of 4, 8, 12, 16 and 20 mg/L in metal ion solution. The adsorption efficiency increased with increasing initial metal ion concentration. This result is in accordance with the work of other authors (Ahile *et al.,* 2015). It is generally expected that as the concentration of the adsorbate increases, the metal ions removed should increase. It is believed that increase in concentration of the adsorbate brings about increase competition of adsorbate molecule for few available binding sites on the surface of the adsorbent; hence increase in the amount of metal ions removed. As the concentration increases from 4 to 20 mg/L, the amount of the Cu (II) ion adsorbed also increases steadily from 4.25 to 50.2 (Agbozu and Emoruwa, 2004; Kailas, 2010).

3.5 Effect of pH

The uptake and percentage removal of Cu(II) ion from aqueous solution are strongly affected by the pH of the solution. Fig 4.4 shows the effect of pH variation on Cu(II) ion on adsorbent surface. The minimum adsorption observed at low pH of 3 was due to the high solubility and ionization of metal salt in the acidic medium plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydrogen ions (H^+) thereby preventing metal ions from approaching the binding sites of the adsorbents. As the pH increases, more positively charged surface becomes available thus, facilitating greater removal of Cu(II) ion. The maximum adsorption observed in the pH of 9 with the value of 99.9 might be due to partial hydrolysis of metal ions. Also, the low solubility of hydrolyzed metal species may be another reason for maximum adsorption in this pH (Onundi *et al.,* 2010; Mohammed, 2011).

3.6 Effect of adsorbent dosage

The availability and accessibility of adsorption site is controlled by adsorbent dosage. The effect of mass of adsorbent on Cu(II) ion removal using coconut shell was determined by varying the weight of the adsorbent from

1 to 5 g for 50 ml of the stock solution. The effect of the adsorbent dosage was shown in Fig 4.2 which can easily be stated that the percentage removal of the metal ion increased by increasing the weight of the adsorbent. This is as result of greater availability of the exchangeable sites at higher dose of the adsorbent. This result is in agreement with previous studies (Abdel – Ghani and Mahmoud, 2007; Kailas, 2010). The observed trend of the percentage removal of the metal ion was at 1 g, the percentage removal was 40.02 and at 5 g was 50.9 respectively.

4.0 Conclusion

On optimizing all conditions studied in this research, it was discovered that coconut shell is an effective adsorbent for the removal of wastewater and can compete favorably with known commercial adsorbents such as zeolite. The various operational parameters observed during the work revealed that contact time, concentration, pH and adsorbent dose governs the overall process of adsorption. The optimum percentage removal for concentration was 50.20, pH was 99.9, contact time was 52.3 and dosage was 50.9. Equilibrium adsorption data was best represented by Temkin isotherm and from the results obtained at the end of the study, Cu(II) ion is excellently absorbed by carbonized coconut shell from wastewater.

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