

Copper (II) Uptake by Adsorption Using Palmyra Palm Nut

Joseph T. Nwabanne* and Philomena K. Igbokwe

Department of Chemical Engineering, Nnamdi Azikiwe University, P.M.B. 5025, Awka, Nigeria

ABSTRACT

The removal of copper (II) from aqueous solution using palmyra palm nut (PPN) as potential raw material for the preparation of activated carbon was investigated. Chemical activation using phosphoric acid (H_3PO_4) was employed for the preparation of activated carbon. The effect of various factors namely pH, adsorbent dosage, and adsorbent particle size was studied to identify the adsorption capacity of palmyra palm nut. The percentage of Cu^{2+} adsorbed was found to be dependent on adsorbent dosage, pH and particle size. Adsorption data were modeled using Langmuir, Freundlich and Dubinin-Radushkevich equations. The equilibrium data was best described by Freundlich model. The kinetic data were also applied to the pseudo first-order, pseudo second-order and Bhattacharya-Venkobachor models. The kinetic data followed all the three kinetic models but pseudo second-order model best described kinetics of the adsorption process. It is seen from the work that palmyra palm nut, a low-cost adsorbent, can be used for the removal of Cu^{2+} from aqueous solution.

Key words: Kinetics, adsorption, uptake, copper, palmyra palm nut.

INTRODUCTION

The progressive increase of industrialization in Nigeria has resulted in continuous increase of pollution of both surface and ground waters. With the rapid development of chemical, polymer, processing and petroleum processing industries, there is a rapid increase in the amount and the variety of chemicals that are thrown into the waters. Effort has been devoted towards minimizing these hazardous pollutants so as to avoid their dangerous effects on animals, plants and humans. Several biological and chemical methods such as filtration, coagulation, oxidation, and ion-exchange have been used for the treatment of waste water, but the continuing increase in the variety and the amount of hazardous chemicals present in our lakes, rivers and sometimes ground water reserves make these conventional methods inefficient and sometimes ineffective [1]. Consequently, the development of new and more effective technologies becomes essential. Activated carbon adsorption has been given attention in recent time by many scientists. But

commercially available activated carbons are still expensive [2,3,4]. As a result of this, many researchers have studied cheaper alternatives, which are relatively inexpensive, and equally endowed with reasonable adsorptive capacity. Among these studies are the use of rice husk [5], almond shell [6] and palm kernel shell [7].

Heavy metal ions are classified as priority pollutants [8]. These heavy metals are not biodegradable and their presence in waters leads to bioaccumulation in living organisms causing health problems in animals, plants, and human beings [9]. Copper is metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Copper is essential to life and health but, like all heavy metals, is potentially toxic as well. For example, continued inhalation of copper-containing spray is linked with an increase in lung cancer among exposed workers. For drinking water, the maximum permissible limit of copper is 1.5mg/l [10]. The maximum concentration allowed for discharge into inland water is less than 1mg/l [11].

This work was undertaken to study the removal of copper (II) from aqueous solution by adsorption using palmyra palm nut as a low cost raw material for the preparation of activated carbon.

MATERIALS AND METHODS

Preparation of activated carbon

Palmyra palm nuts were obtained from the premises of Nnamdi Azikiwe University, Awka, Nigeria. The palm nuts were washed with deionized water, dried in the sun, ground into fine particles and sieved to a particle size of 300 μ m. 200g of sample was impregnated with concentrated orthophosphoric acid at the ratio of 1:2 (wt %). The impregnated sample was dried in a Memmert oven at 120⁰C for 24hrs. The dried sample was carbonized in a Muffle furnace at 500⁰C for 2 hours. After cooling to the ambient temperature, the sample was washed several times with de-ionized water until pH 6-7, filtered with Whatman No.1 filter paper and dried in the oven at 110⁰C for 8hours. The sample was crushed and passed through different sieve sizes and then stored in a tight bottle ready for use.

Characterization of activated carbon

Determination of pH of activated carbon. The pH of the carbon was determined using standard test of ASTM D 3838-80 [12].

Determination of moisture content. Moisture content of activated carbon and raw materials was determined using ASTM D 2867-91 [13].

Determination of bulk density of activated carbon. The bulk density of the activated carbon was determined according to the tamping procedure by Ahmedna et al [14].

Determination of volatile content. 1.0g of sample was weighed and placed in a partially closed crucible of known weight. It was heated in a muffle furnace at 900⁰C for 10mins.

Determination of percentage fixed carbon. The percentage fixed carbon is given by:

$$100 - (\text{Moisture content} + \text{ash content} + \text{volatile matter}) \%$$

Determination of iodine number of activated carbon. The iodine number was determined based on ASTM D 4607-86 [15] by using the sodium thiosulphate volumetric method.

Determination of surface area: The specific surface area of the activated carbon was estimated using Sear's method [16, 17].

Adsorbate preparation and adsorption study

The reagent used was copper sulphate (CuSO₄) and de-ionized water. The reagents were of high grade. The sample (CuSO₄) was dried in an oven for 2hrs at 105⁰C to remove moisture. 2.51g of CuSO₄ was dissolved in 1000ml of de-ionized water to get the stock solution of 1000g/l. A predetermined amount of activated carbon was added to 100ml of the 100mg/l of adsorbate in a conical flask and placed on a magnetic stirrer. The stirring was done at different temperature for different times. After adsorption is complete, the solution was filtered using Whatman no.1 filter paper. The residual Cu²⁺ concentration of the effluent was determined spectrophotometrically using atomic adsorption spectrophotometer at 324.8nm wavelength. The adsorption capacity, q_e (mg/g) and percentage adsorbed were calculated from equation (1) and equation (2) respectively.

$$q_e = [(C_o - C_e) V / m] \quad 1$$

$$\% \text{ Adsorbed} = [(C_o - C_e) / C_o] \times 100 \quad 2$$

Where, C_o and C_e are the metal concentrations (mg/l) at initial and any time t, respectively, V the volume of the solution (L), and m the mass of adsorbent used (g). The effects of particle size, adsorbent dosage, pH were studied.

RESULTS AND DISCUSSION

Characteristics of activated carbon derived from palmyra palm nut:

The physico-chemical characteristics of activated carbon are shown in Table 1.

Table 1: Physico-chemical characteristics of activated carbon derived from palmyra palm nut.

Properties	Values
pH	6.8
Bulk density, g/cm ³	0.61
Iodine number, mg/g	785.78
Moisture content, %	4.10
Volatile matter, %	18.14
Ash content, %	3.40
Fixed carbon, %	78.56
Surface Area, m ² /g	820.37

Effect of adsorption dosage on the adsorption process

Adsorption dosage determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The result showed that as the adsorbent dosage increased, the percentage of

adsorption also increased but the amount adsorbed per unit mass of the adsorbent decreased considerably (Figure 1). The decrease in unit adsorption with increasing dose of adsorbent is basically due to adsorption sites remaining unsaturated during the adsorption reaction [18]. Figure 1 reveals a definite increase in the adsorption capacity of the adsorbent with dosage. This is attributed to the larger number of available adsorption sites favouring the enhanced uptake of the metal ions [19].

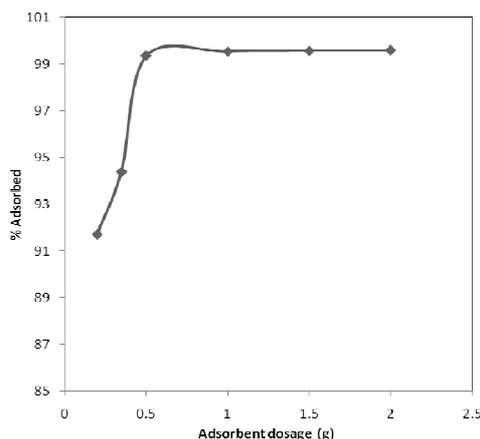


Fig. 1: Effect of adsorbent dosage on the adsorption of Cu^{2+} on PPN

Effect of particle size on the adsorption process

The removal of Cu^{2+} at different particle sizes showed that the removal rate increased better with a decrease in particle size (Figure 2). This same trend was reported by Demirbas *et al* [6]. The relatively higher adsorption with smaller adsorbate particle may be attributed to the fact that smaller particles yield large surface area. There is a tendency that a smaller particle produces shorter time to equilibrium.

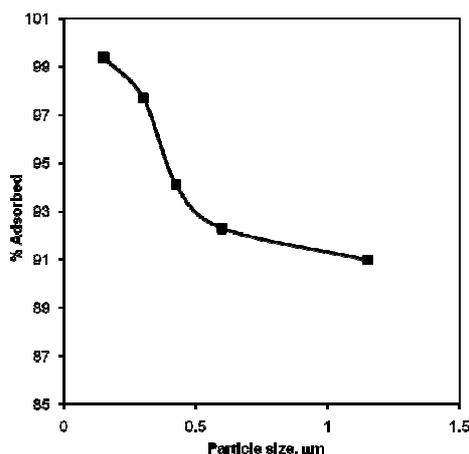


Fig. 2: Effect of particle size on the adsorption of Cu^{2+} on PPN

Effect of pH on the adsorption process

pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of heavy metal: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, and precipitation are strongly influenced by pH and on the other hand, it

strongly influences the speciation and adsorption availability of heavy metals [20]. Figure 3 presents the effect of pH on the removal of Cu^{2+} . The adsorption of the Cu^{2+} increased with increasing pH. The maximum Cu^{2+} adsorption for all the adsorbents was obtained at pH 7. Cu^{2+} adsorption decreased as pH rose beyond the optimum pH.

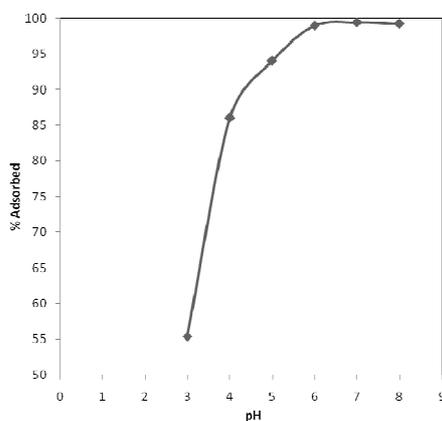


Fig. 3: Effect of pH on the adsorption of Cu^{2+} on PPN

Adsorption Isotherm

Langmuir isotherm model

The Langmuir adsorption model is given by:

$$q_e = Q \frac{b C_e}{1 + b C_e} \quad 3$$

The Langmuir equation can be described by the linearized form [20, 21].

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \left(\frac{1}{Q_0} \right) C_e \quad 4$$

Where C_e is the equilibrium concentration of the adsorbate, q_e the amount of adsorbate per unit mass of adsorbent (mg/g), and Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When C_e/q_e is plotted against C_e , straight line with slope $1/Q_0$ indicates that adsorption follows the Langmuir isotherm. The Langmuir constants, Q_0 and b were evaluated from the intercept and the slope of the linear plot of experimental data of $1/q_e$ versus $1/C_e$ and presented in Table 2. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L , defined as [22].

$$R_L = \frac{1}{1 + b C_0} \quad 5$$

where C_0 is the initial ion concentration. The R_L value implies the adsorption to be unfavourable ($R_L > 1$), Linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). R_L values for Cu^{2+} adsorption were less than 1 and greater than zero indicating favourable adsorption under

conditions used in this study (Table 2). The correlation coefficient showed that adsorption of Cu^{2+} on PPN did not followed Langmuir.

Freundlich Isotherm

The Freundlich adsorption isotherm [23] is

$$q_e = K_F C_e^{1/n} \quad 6$$

A linear form of this expression is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad 7$$

Where K_F and n are Freundlich constants, n giving an indication of how favourable the adsorption process is and K_F is the adsorption capacity of the adsorbent. K_F and n are determined from the linear plot of $\log q_e$ versus $\log C_e$. From the linear plots of $\log q_e$ versus $\log C_e$, values of Freundlich constants K_F and n were calculated from the intercept and slope, respectively, and are presented in Table 2. The magnitude of the exponent, n gives an indication of the favourability and capacity of the adsorbent/adsorbate system. Karthikeyan *et al* [19] has reported that n values between 1 and 10 represent favourable adsorption conditions. In this work, the exponent ranged from 1.6051 to 1.675 showing beneficial adsorption for the system. The correlation coefficients, R ranging from 0.978 to 0.985 indicated the Cu^{2+} adsorption followed Freundlich isotherm model. Similar results were obtained by Aksu and Tezer [24].

Dubinin-Radusherich isotherm model

The Dubinin – Radushkevich equation has the following form:

$$q_e = q_m e^{-\beta \varepsilon^2} \quad 8$$

A linear form of Dubinin – Radushkevich equation isotherm [21] is:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad 9$$

Where q_m is the Dubinin – Radushkevich monolayer capacity (mmol/g), β a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad 10$$

Where, R is the gas constant (8.31 J/mol K) and T is the absolute temperature. The constant β gives the mean free energy, E , of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using relationship [25].

$$E = \frac{1}{\sqrt{2\beta}} \quad 11$$

The Dubinin-Radushkevich constants were evaluated and given in Table 2. The correlation coefficients were determined as shown in Tables 2. R^2 indicated that the adsorption of Pb^{2+} did not follow the Dubinin-Radushkevich isotherm. If the mean free energy, E is $<8\text{KJ/mol}$, the adsorption is physisorption and if the energy of activation is $8-16\text{KJ/mol}$, the adsorption is chemisorption in nature [26]. Results of E obtained indicated that adsorption of Pb^{2+} on all the NPN is physisorption.

Table 2: Calculated isotherm parameters for the adsorption of Cu^{2+} on PPN

Isotherm model	Temperature, K		
	298	303	313
Langmuir			
Q (mg/g)	200	166.67	166.67
b (L/mg)	0.0039	0.0040	0.00351
R_L	0.7502	0.7143	0.7402
R^2	0.8744	0.9005	0.8754
Freundlich			
N	1.6051	1.6750	1.6313
K_f (L/g)	2.6669	2.9242	2.4889
R^2	0.985	0.980	0.978
Dubinin-Radushkevich			
q_D (mg/g)	52.720	52.039	50.249
β (mol^2/J^2)	6×10^{-8}	2×10^{-7}	3×10^{-7}
E (KJ/mol)	0.00003	0.0002	0.0001
R^2	0.503	0.514	0.500

Adsorption Kinetics

Pseudo first-order kinetic model

The Pseudo first-order kinetic model was proposed by Lagergren [27]. The equation is generally expressed as

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad 12$$

Where, q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mgg^{-1}), K_1 is the rate constant of pseudo first-order adsorption (L min^{-1}).

After integration and applying boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation 2.16 becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad 13$$

The values of $\log(q_e - q_t)$ are linearly correlated with t . The slope and intercept of plots of $\log(q_e - q_t)$ versus t were used to determine the pseudo-first order rate constants, K_1 and q_e at different temperatures. The results of the q_e and K_1 were evaluated and listed in Table 3. The correlation coefficients ranged from 0.970 to 0.994 indicating that Pb^{2+} adsorption fitted well to pseudo first-order kinetic equation.

Pseudo second- order model

The adsorption kinetics may also be described by a pseudo second-order equation [28, 29, 30].

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad 14$$

Integrating equation 2.19 and applying the boundary condition

$t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \quad 15$$

Equation (2.20) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad 16$$

Where, K_2 is the rate constant, t of pseudo second-order adsorption ($\text{gmg}^{-1} \text{min}^{-1}$). The slope and intercept of plot of t/q_t versus t were used to calculate the pseudo second-order rate constant, at different temperatures. Table 3 lists the results of the rate constant and q_e by pseudo second-order models. The correlation coefficient, R^2 for the pseudo second-order adsorption model has high value (> 0.984). Its calculated equilibrium adsorption capacity, q_e is consistent with experimental data. These facts suggest that the pseudo second-order adsorption mechanism is predominant. Similar phenomena have also been observed in the adsorption of direct dye on palm ash [22].

Bhattacharya – Venkobachor kinetic model

Bhattacharya – Venkobachor model [31] is expressed as

$$\ln[1 - U_{(t)}] = K_B \cdot t \quad 17$$

$$U_{(t)} = (C_o - C_t)/(C_o - C_e) \quad 18$$

The effective diffusion coefficient D_2 , is obtained from the equation:

$$D_2 = \frac{K_B \cdot r^2}{\pi^2} \quad 19$$

Where, r is particle radius. From the plot of $\ln [1 - U (t)]$ vs t , the effective diffusion coefficient D_2 and rate constant, K_B were obtained and presented in Table 3. The effective diffusion coefficients determined are in the range of 4.551×10^{-10} to $3.136 \times 10^{-10} \text{ m}^2/\text{s}$. The kinetic data also followed Bhattacharya – Venkobachor model.

Table 3: Calculated kinetic parameters for the adsorption of Cu²⁺ on PPN

Kinetic model	Temperature, K		
	303	313	323
Pseudo first-order			
K ₁ (min ⁻¹)	0.0415	0.0438	0.0484
q _e (mg/g)	12.1060	13.3660	18.9671
R ²	0.989	0.994	0.970
Pseudo second-order			
K ₂ (g/mg min)	0.0049	0.0044	0.0022
q _e (mg/g)	22.222	22.222	24.3902
R ²	0.998	0.998	0.984
Bhattacharya-Venkobachor			
K _B	0.043	0.044	0.050
D ₂ (m ² /s)	3.136x10 ⁻¹⁰	3.392x10 ⁻¹⁰	4.551x10 ⁻¹⁰
R ²	0.991	0.994	0.971

CONCLUSION

The removal of copper (II) from aqueous solution using activated carbon prepared from palmyra palm nut has been investigated in this work. The adsorption process showed that palmyra palm nut was effective in the uptake of copper (II) from aqueous solution. The amount of Cu²⁺ adsorbed was found to vary with pH, particle size and adsorbent dosage. Adsorption data were fitted to Langmuir, Freundlich and Dubinin-Radushkevich equations. The adsorption data conformed to Freundlich models. The adsorption data also fitted Bhattacharya-Venkobachor, pseudo first-order and pseudo second-order models. However, pseudo second-order best described the adsorption process.

REFERENCES

- [1] Bansal RC, Goyal M, *Activated Carbon Adsorption*, CRC Press, USA, **2005**, 1-5.
- [2] Chakraborty S, De S, DasGupta S, Basu JK, *Chemosphere*, **2005**, 58, 1079-1089.
- [3] Ambedkar G, Muniyan M, *Adv. Appl. Sci. Res.*, **2011**, 2(4), 283
- [4] Sivakumar P, Palanisamy N, *Adv. Appl. Sci. Res.*, **2010**, 1(1), 58
- [5] Malik PK, *Dyes Pigments*, **2003**, 56(3), 239-249.
- [6] Zawani Z, Luqman CA, Choong TSY, *European Journal of Scientific Research*, **2009**, 37(1), 67-76.
- [7] Demirbas E, Kobya M, Senturk E, Ozkan T, *Water SA*, **2004**, 30(4), 533-539.
- [8] Volesky B, Holan ZR, *Biotechnology Progress*, **1995**, 11(3), 235-250.
- [9] Ong S, Seng C, Lim P, *EJEA Fche.* **2007**, 6 (2), 1764-1774.
- [10] World Health Organization (WHO), *Guidelines for drinking water*, Geneva, **1971**, 88-96.
- [11] Federal Environmental Pollution Agency (FEPA), *Natural guidelines and standards for industrial effluents, gaseous emissions and hazardous waste management in Nigeria*, Lagos, Nigeria, **1991**, 33-35.
- [12] American Society for Testing and Materials, *Annual Book of ASTM Standard, Volume 15.01, Refractories, Carbon and Graphitic Products; activated Carbon*, ASTM, Philadelphia, PA. **1996**

-
- [13] American Society of Testing and Materials, *Standard test methods for moisture in activated carbon*. Philadelphia, PA: ASTM Committee on Standards, **1991**.
- [14] Ahmedna M, Johns MM, Clarke SJ, Marshall WE, Rao RM, *Journal of the Science of Food and Agriculture*, **1997**, 75, 117-124.
- [15] American Society for Testing and Materials, *Standard test method for determination of iodine number of activated carbon*. Philadelphia, PA: ASTM Committee on Standards. **1986**
- [16] Al-Qodah Z, Shawabkah R, *Braz. J. Chem. Eng.*, **2009**, 26(1), 6.
- [17] Alzaydian AS, *Am. J. Applied Sci.*, **2009**, 6(6), 1047-1058.
- [18] Bulut Y, Aydin H, *Desalination*, **2005**, 194, 259-267.
- [19] Karthikeyan G, Analagan K, Andal NM, *J. Chem. Sci.*, **2003**, 116(2), 119-127.
- [20] Sekar M, Sakthi V, Rengaraj S, *Journal of Colloid and Interface Science*, **2004**, 279(2), 307-313.
- [21] Sivakumar P, Palanisamy PN, *International Journal of Chem. Tec. Research*, **2009**, 1 (3), 502-510.
- [22] Ahmad AA, Hameed BH, Aziz N, *Journal of Hazardous Materials*, **2006**, 094, 1-10.
- [23] Ozacar M, *Adsorption*, **2003**, 9, 125-132.
- [24] Aksu Z, Tezer S, *Process Biochemistry*, **2000**, 36, 431-439.
- [25] Lin SH, Juang RS, *J. Hazard. Mater.*, **2002**, 92, 315-326.
- [26] Sarin V, Singh TS, Pant KK, *Bioresourse Technol*, **2006**, 97: 1986-1993.
- [27] Maniatis K, Nurmala M, *Biomass Energy Ind. Environ.*, **1992**, 274, 1034-1308.
- [28] Chiou MS, Li HY, *J. Hazard. Mater.*, **2002**, 93(2), 233-248.
- [29] Nwabanne JT, Igbokwe PK, *Journal of Engineering and Applied Science*, **2008**, 3(11), 829-834.
- [30] Ho YS, Chiang CC, *Adsorption*, **2001**, 7, 139-147.
- [31] Goswami S, Ghosh UC, *Water SA*, **2005**, 31(4), 597-602.