

Adsorption of Copper (II) By a Nigerian Brown Coal

C Ajaero, B.N Okolue and R. N. Oze

Department of Chemistry, Federal University of Technology
P.M.B. 1526, Owerri, Nigeria

Corresponding Author: C. Ajaero

Abstract

The adsorption and desorption rates of Cu (II) by a Nigerian brown coal was investigated under various solution conditions. The adsorption of Cu (II) was found to be chemical in nature and followed first-order kinetics with respect to its concentration in solution. The adsorption isotherm exhibits Langmuir behaviour. Thermodynamic parameters for the adsorption process were determined and discussed.

Keywords: Brown Coal, Cu (II) ions, Adsorption, Desorption

INTRODUCTION

Copper, which is a heavy metal has wide application and is capable of causing haemolysis, liver and kidney damage, gastrointestinal disorder, diarrhoea, and respiratory problems Ozsoy and Kumbur (2006). The main anthropogenic pathway through which Cu (II) ions enter water bodies is via wastes from industrial processes such as dyeing, paper, petroleum, copper/brass-plating and copper-ammonium rayon (Wang et al., 2006). The concentration of Cu (II) ions from industrial activities/processes is estimated to be about 100 to 200 mg/dm³. Considering water quality standards, this value is very high and should be reduced to a value of 1.0 to 1.5 mg/dm³ (Ekmekyapar et al., 2006). Chemical oxidation and reduction, adsorption onto activated carbon, ion exchange and precipitation are the conventional methods of Cu (II) ion removal from aqueous solutions Wang and Qin (2005). High cost of operation and incomplete metal

removal (particularly at low concentrations) has been identified as factors militating against the use of these conventional processes (Cochrane et al., 2006). Recently the use of agricultural by-products, industrial wastes and raw minerals in the removal of metal ions from aqueous solutions have been considered (Bailey et al., 1999). Among the raw minerals that can be used in the removal of metal ions from aqueous solution is the Nigerian brown coal due to their extensive porosity and large area of internal surface, which contain structured groups capable of combination with other chemical species (Cullen et al., 1978). The use of coal in the extraction of metal ions from aqueous solutions have been carried out by Eskenazy (1972) and shows the use of a Nigerian brown coal in the removal of copper (II) ions from aqueous solutions

MATERIALS AND METHOD

The brown coal sample used for this study was obtained from Ihioma deposit in Imo State of Nigeria. The coal was ground and sieved to a particle size of about 75 µm before the sample were demineralized and converted to other acid form by washing with 2M HCl at room temperature for one hour. The demineralized coal sample was air dried and stored in plastic container (Eligwe and Okolue, 1994, Saha *et al.*, 1977 and Eskenazy, 1970). Adsorption experiment were performed by mechanically shaking 0.50g of demineralized coal with 100 ml of an aqueous solution of Cu(II) ions at the desired pH and concentration

at room temperature (27±2°C) in 120 ml plastic containers. The solution pH was controlled by addition of 0.1M HCl and NaOH. For kinetic studies, the coal was shaken for a predetermined time interval. After equilibration time, the coal was separated by filtration and washed with de-ionized water. The resulting supernatant was analyzed for residual Cu(II) concentration with atomic adsorption spectrophotometer (UNICAM model 919). Cu (II) adsorbed on the coal was desorbed with water by agitation for two hours. The sample was filtered and the Cu(II) concentration determined as above. The value of Cu(II) adsorbed or desorbed in each test is the average of at least three measurements.

RESULTS AND DISCUSSION

Adsorption kinetics

Typical adsorption rate curves are shown in Fig.1, which indicates that the amount of Cu (II) adsorbed is directly proportional to the solution concentration and contact time.

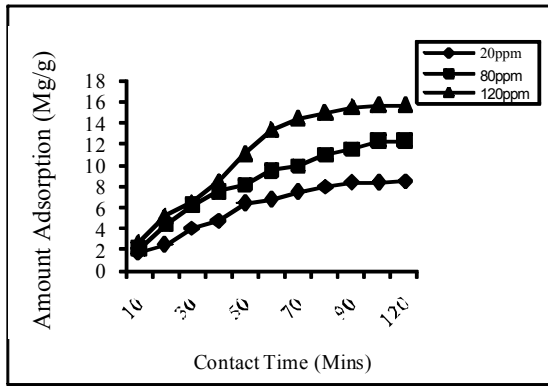


Fig. 1: Effect of contact time on Cu (II) adsorption from solutions of different concentration at pH 4.0

The initial rate of Cu (II) adsorption follows a first-order kinetics from Fig.2 and represented by the equation.

$$\ln(C_0/C_t) = kt \tag{1}$$

Where C_0 is the initial Cu (II) solution concentration, C_t is the concentration at time t and k is the rate constant

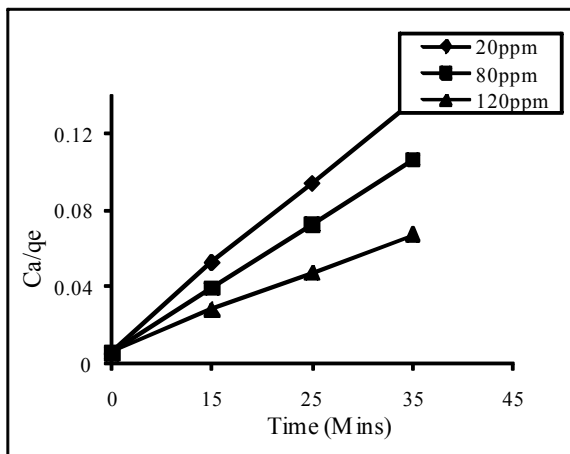


Fig. 2: First-order kinetic plot for cu (ii) adsorption onto brown coal at various concentrations

Adsorption/Thermodynamic consideration

The adsorption isotherm for Cu (II) by the coal sample is shown in Fig.3.

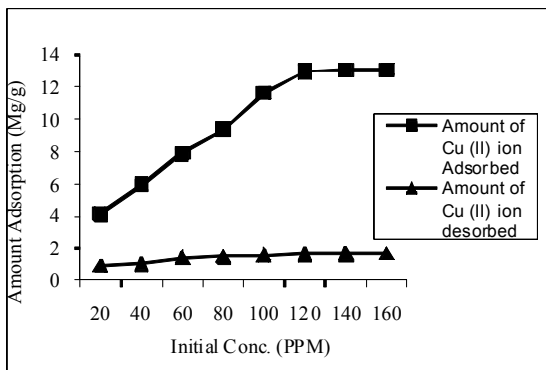


Fig. 3: Adsorption and desorption isotherms of cu (ii) onto brown coal at pH 4.0, contact time 2 hours

The isotherm belongs to type 1 in the BET classification Haworth (1990). The plot gave a typical Langmuir isotherm revealing a chemical adsorption. The isotherm is typical of a monolayer adsorption. The data for equilibrium adsorption in Fig.3 was found to follow the linearized Langmuir isotherm expression.

$$\frac{C_e}{q_e} = \frac{1}{q_0 k} + \frac{C_e}{q_0} \tag{2}$$

Where C_e is the equilibrium concentration of the adsorbates in solution, q_e is the equilibrium quantity of cu (II) adsorbed, q_0 is the amount of cu (II) adsorbed at saturation and k is equilibrium constant given by $K = \exp(-\Delta G^0/RT)$ Fig. 4 shows the plot of C_e/q_e against C_e gave a straight line from were q_0 and k could be evaluated as slope and intercept respectively.

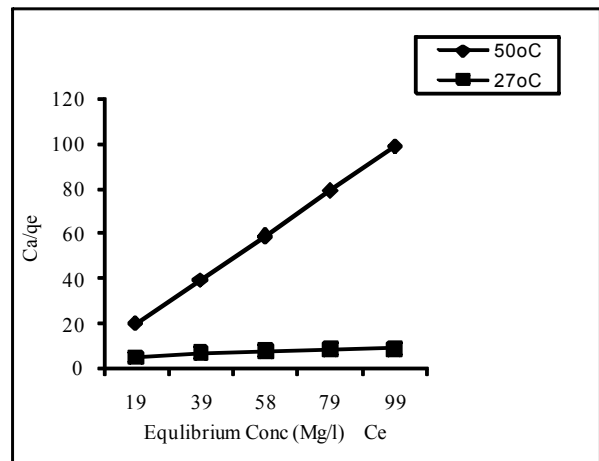


Fig. 4: Langmuir isotherms for the adsorption of Cu (ii) ions by a Nigerian brown coal

The thermodynamic parameters for the adsorption of the coal were determined from the following expressions.

$$\Delta G^0 = -RT \ln k \tag{3}$$

$$\Delta H^0 = R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \frac{k_2}{k_1} \tag{4}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{5}$$

Where ΔG^0 , ΔH^0 and ΔS^0 are free energy, enthalpy and entropy changes of the adsorption process respectively, R is the gas constant, T is Kelvin temperature and k is rate constant from Table 1,

Table1: Langmuir constants and thermodynamic parameters at 27± 2°C and pH 4.0

q_0 (mg/g)	0.066
$K(10^{-3} \text{mg}^{-1})$	3.500
$\Delta G(\text{kJ/mol})$	-3.124
$\Delta H(\text{kJ/mol})$	-63.187
$\Delta S(\text{J/mol})$	-0.2002

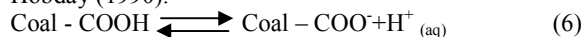
The values of free energy change (ΔG°) was negative showing the adsorption process to be spontaneous (Wang *et al.*, 2006). That is, the adsorptive forces are strong enough to overcome the potential barrier (Paday *et al.*, 1984b). The negative value of enthalpy change (ΔH°) indicates the exothermic nature of the adsorption process. The negative value of entropy change (ΔS°) of the system suggests decrease in randomness at the solid/solution interface during the adsorption process (Wang *et al.*, 2006).

Effect of Time and Concentration

Fig.1 shows the adsorption of Cu (II) by a Nigerian brown coal. Inspection of the figure shows that adsorption of Cu(II) increases with time up to 100 minutes, thereafter it becomes constant as equilibrium is attained. With the change in concentration of Cu (II) solution, the amount of Cu (II) adsorbed increases. Equilibrium was attained at 120 minutes. Optimum removal of Cu (II) was observed at higher concentration of the solution (120ppm)

Effect of pH

The experimental results obtained for the adsorption of Cu (II) ions by a Nigerian brown coal at different pH are shown in Fig.5. These indicate optimum value of adsorption of Cu(II) ion on brown coal is pH dependent since the amount of metal ion adsorbed increases with increase in pH. The adsorption of the Cu(II) ions dependence on pH was expected for carboxylic acid and phenolic exchange group on the acid washed coal and can be explained by the following equation Lafferty and Hobday (1990).



Where M represents Cu (II) ions. Equation (6) represents deprotonation of the acid washed coal and equation (7) the attachment of the metal ion. At low pH values equation (6) dominates as a result of the adsorption surface being surrounded by H^+ ions which compete for binding sites on the coal surface and whose presence would result in reduction of Cu (II) ions interaction with the binding sites because of higher repulsive force that arises (Wang *et al.*, 2006). Fig 5 shows that plots of equilibrium amounts of Cu (II) ions adsorbed versus pH have inflection points at pH 6.0.

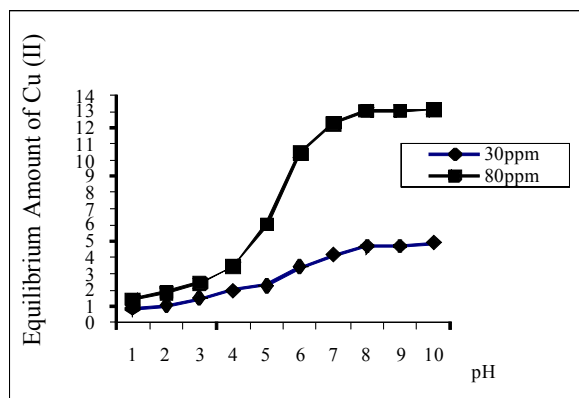


Fig. 5: Effect of pH on Cu (ii) adsorption from solution of different concentrations

The presence of the inflection point seems to suggest that at pH less than 6.0, metal ion exchange with one type of acid group is essentially complete and beyond this point exchange with another type begins. This may be responsible for the sharp increase in the adsorption capacity (Eligwe and Okolue 1994) with pH above 6.0. As the pH value is increased, the coal exchange sites is highly deprotonated with a consequent increase in adsorption for the Cu (II) ions and the hydroxide concentration is large enough for equation (8) to be significant. At such pH, both ion exchange and metal hydroxide precipitation become significant metal removal processes Lafferty and Hobday (1990).

CONCLUSION

Demineralized Nigerian brown coal was found to be an effective adsorbent for the removal of Cu(II) ions from aqueous solution. The adsorption capacity of the Nigerian brown coal was found to increase with increasing in solution concentration, contact time and pH of the system. The adsorption processes were found to be spontaneous and exothermic in nature. The result of the study shows that Cu (II) ions could irreversibly be removed from potable and wastewaters enriched in copper.

REFERENCES

- Bailey, E.S., Olin, T.J., Bricka, R.M., Adrian, D.D.1999. A review of potentially low- cost sorbents for heavy metals. *Water Res.* 33:2469-2479.
- Cochrane, E.L, Lua. s., Gibbs, S.W., and Villaescusa, I. 2006. A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media *J. Hazard.Mater.* B137:198-206.
- Cullen, G.V., Siviour N.G. and Pearson, G.M. 1978. Extracting metals from ammoniacal solution with low rank coals.*Metallurgical and Materials Transactions* 9B(4):409-413.
- Ekmekyapar, F., Ascan. A., Bayhan, Y.K and Cakici, A 2006. Biosorption of copper(II) by nonliving lichen biomass of *Cladonia rangiformis hoffm.*, *J. Hazard. Mater.* 1;137(1):293-298.
- Eligwe, C.A.and Okolue B.N.1994. Adsorption of iron(II) by a Nigerian brown coal *FUEL.* 73(4):569-572.
- Eskenazy, Gr.1972. Adsorption of titanium on peat and coals *FUEL.*51(3):221-223.
- Eskenazy, Gr. 1970. Adsorption of cobalt by lignite. *FUEL.* 49(1):61-67.
- Haworth, A. 1990. A review of the modeling of sorption from aqueous solution. *Advances in colloid and interface science.* 32:43-78.

Lafferty, C. and Hobday, M.1990. The use of low rank brown coal as an ion exchange material:Basic parameters and the ion exchange mechanism, FUEL. 69(1):78-83.

Ozsoy. H.D. and Kumbur. H. 2006. Adsorption of Cu(II) ions on cotton, J. Hazard Mater. 135:87–93.

Paday, K.K, Prasad, G., and Singh V.N.1984b Fly ash-china clay for the removal of Cr (VI) from aqueous solutions. Indian J. Chem., 23A: 514-515.

Saha A.K., Shahani, M.J., and Altekar V.A. 1977. Adsorption of cobalt by lignite. Hydrometallurgy.2(3):285-292.

Wang, X.S, Wang, J .and sun, C. 2006. Removal of Copper(II) Ions from Aqueous Solutions Using Natural Kaolinite.,Adsorption Science & Technology. 24(6): 517-530.

Wang X.S. and Qin, Y. 2005. Equilibrium sorption isotherms for Cu^{2+} on rice bran, Process. Biochemistry. 40: 677–680.