

Removal of Copper(II) from Aqueous Solution by Cottonseed Carbon

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A novel adsorbent, sulphuric acid treated cottonseed carbon after soaking in sodium bicarbonate, was employed for the removal of copper(II) from aqueous solution at concentrations between 1 and 10 mg/L, in batch equilibrium experiments, in order to determine its adsorption properties. The removal of copper by the adsorbent increases with increasing adsorbent dosages. The adsorption mechanism is assumed to be an ion exchange between copper and the sodium present on the surface of cottonseed carbon. The sorption data have been analyzed and fitted to Freundlich adsorption isotherm. The batch sorption kinetics has been tested for first order kinetics reaction models. Results also showed that the intra-particle diffusion of Cu(II) on the carbon was the main-limiting step.

Key Words: Copper(II), Sorption, Cottonseed carbon, First order kinetics, Freundlich adsorption.

INTRODUCTION

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Copper and its compounds are ubiquitous in the environment and are thus found frequently in surface water. Potential sources of copper bearing waste include plating baths, fertilizer industry, paints and pigments, municipal and storm water run-off¹.

Copper is a transition metal with three common oxidation states Cu⁰ (metal), Cu⁺ (cuprous), Cu²⁺ (cupric). Toxicity of copper to living organisms is essentially exerted on enzymes, especially enzymes whose activity depends on sulphhydryl and amino group because copper like other heavy metals has a high affinity for ligands containing hydrogen and sulphur donors². The toxicity of copper in humans has been comprehensively reviewed by Aaesth and Norseth³.

Acute copper poisoning after injection may show systemic effects such as hemolysis, liver and kidney damage and fever with influenza syndrome. Therefore, it is necessary to treat copper containing wastewater before discharge into receiving bodies of water.

In the present study, it is proposed to use cottonseed carbon for the removal of copper(II) from water.

EXPERIMENTAL

Preparation of bicarbonate treated cottonseed carbon

50 g Lots of cottonseed carbon were carbonized using 20 mL of concentrated H₂SO₄ in each instance. The mixing of H₂SO₄ and cottonseed taken in the beaker was done with vigorous stirring. Charring of cottonseed occurred immediately

accompanied by evolution of fumes. When the reaction subsided, the mixture was left in an all over maintained at 140–160°C for a period of 24 h, to facilitate charring of the materials. At the end of this period, the product was washed with large volumes of water to remove free H₂SO₄ and dried at 110°C. This was soaked in 10% solution of sodium bicarbonate for a period of 24 h, until effervescence ceased. The material was then washed thoroughly with water, dried in an air oven, at the temperature of 105–110°C (CSC). Particles in the size range 20–50 mesh were considered for detailed study. The characteristics of cottonseed carbon are given in Table-1.

TABLE-1
CHARACTERISTICS OF COTTONSEED CARBON

S. No.	Description	Results	S. No.	Description	Results
1.	Bulk (or) apparent	0.53	7.	Decolorizing power (MBT) (mg/gm)	0.15
2.	Moisture (%)	12.23	8.	Phenol number	15.00
3.	Ash (%)	8.08	9.	Ion exchange capacity	0.29
4.	Matter soluble in water (%)	2.36	10.	Surface area (sq. m/g)	545.60
5.	Matter soluble in acid (%)	5.26	11.	Iron (%)	1.14
6.	pH	6.50			

Adsorbate

A stock solution of Cu(II) (1000 mg/L) was prepared by dissolving 3.930 g of CuSO₄·5H₂O in 1 L water. Suitable aliquots were diluted to get a concentration of 10 mg/L.

Batch mode studies

Batch experiments were conducted in polythene bottles of 300 mL capacity provided with screw caps; the polythene bottles were washed well with chromic acid before and after use. 100 mL of the solutions containing 10 mg/L of copper(II) ions under investigation were taken in bottles and equilibrated for specific periods of time in a rotary mechanical shaker. At the end of equilibrated period, the solutions were filtered using a G3 crucible and the concentrations of respective ions were established by spectrophotometry. Copper(II) estimation was done by Neocuproine method⁴.

RESULTS AND DISCUSSION

Effect of Equilibrium Time: In order to find out the optimum equilibrium time, experiments were carried out using 10 mg of carbon and 100 mL of Cu(II) solution of 10 mg/L at pH 4.5. The solution was analyzed and Cu(II) removal was established. The results are shown in Fig. 1, from which it is clear that 3 h equilibrium time was sufficient for maximum removal of Cu(II) by CSC. However, it was decided to maintain an equilibrium time of 4 h in all subsequent experiments for CSC.

Effect of pH Condition: In order to find out the optimum pH condition for maximum adsorption of Cu²⁺ ions experiments were carried out using 100 mg of Cu(II) solution of 10 mg/L ranging from 1–10. In each of these solutions carbon

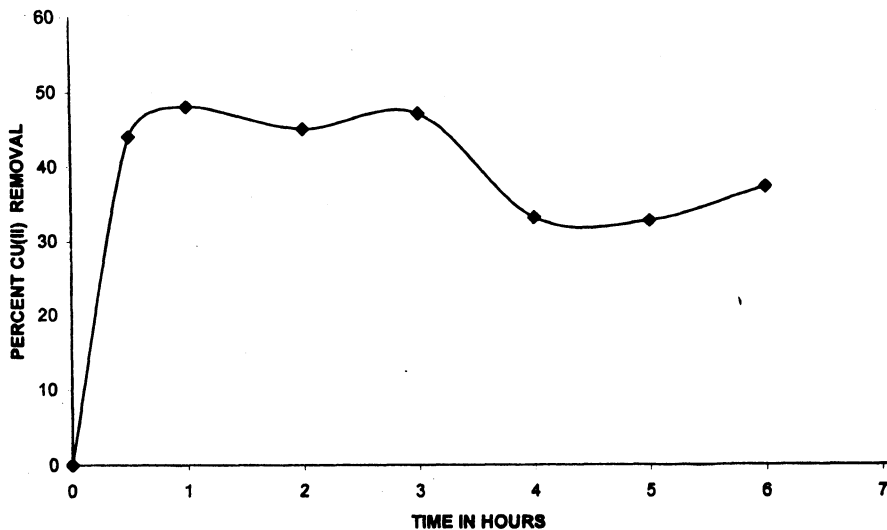


Fig. 1. Optimization of equilibration time pH 4

dosages were added in the range 100 mg/100 mL. The solutions were equilibrated for a period of 4 h and the results are given in the Figs. 2 and 2a. It has been found that under optimum pH 7.0 the maximum removal was found to be 49%.

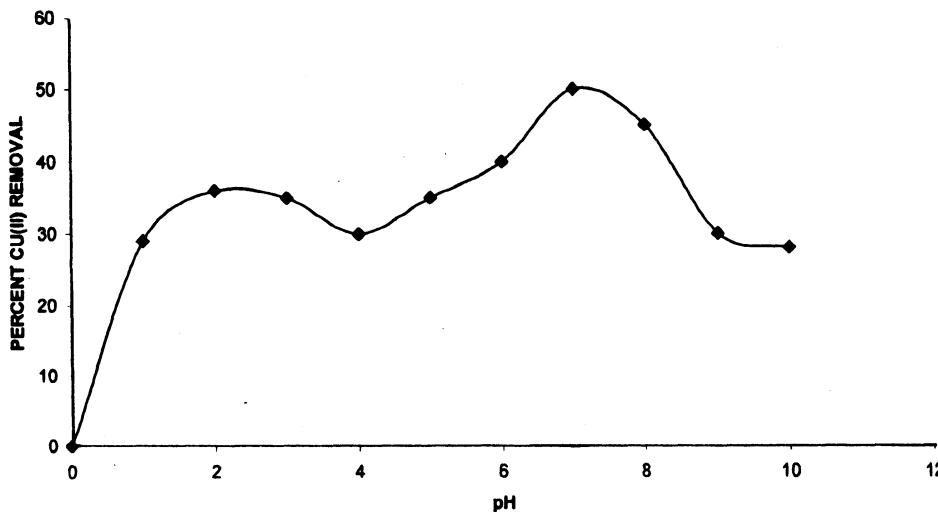


Fig. 2. Optimisation of pH

Freundlich Adsorption Isotherm

The Freundlich adsorption equation is the most widely used form in aqueous system. The equation is expressed as

$$\frac{x}{m} = K C_e^{1/n} \quad (1)$$

The Freundlich equation explains the heterogeneity of the surface and the exponential distribution of sites and their energies⁵; for liberalization of data the Freundlich equation is written in logarithmic form:

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e \quad (2)$$

Plotting $\log x/m$ vs. $\log C_e$, a straight line is obtained with a slope of $1/n$ and $\log K$ is the intercept of $\log x/m$ at $\log C_e = 0$.

The Freundlich equation can be used for calculating the amount of activated carbon required to reduce any initial concentration (C_0) to a predetermined final concentration (C_e).

By substituting $C_0 - C_e$ for x in eqn. (2).

$$\log (C_0 - C_e)/m = \log k + 1/n \log C_e$$

Experiments which were conducted in the concentration range of 10–60 mg/L of Cu(II) for both the distilled water and tap water over a wide range of pH 4.0–8.0 to understand the nature of adsorption and the nature of curves are given in Figs. 3–7.

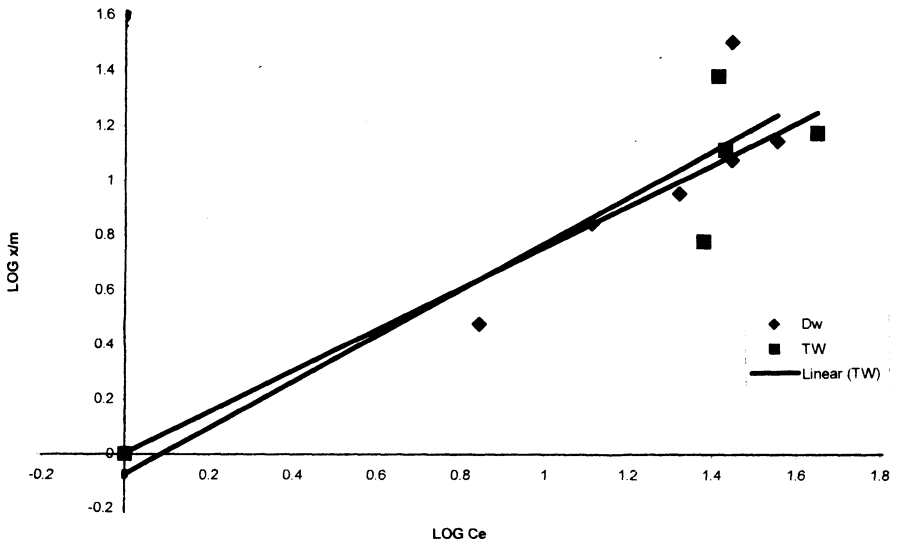


Fig. 3. Freundlich adsorption isotherm (pH 4.0)

The amount of carbon added was 1 g/L and the solutions were equilibrated for a period of 24 h. At the end of the equilibration, solutions were analyzed and Cu(II) removal was established from the data. The amount of Cu(II) removed per unit weight of carbon was calculated for all the concentration of Cu(II) under study (x/m).

The log values of these calculated quantities were plotted against the log concentrations of Cu(II) for this carbon.

The straight line nature of the plot indicates that the process follows Freundlich adsorption type. The K value of adsorption equations for all the Cu(II) concentrations under study for distilled and tap water were obtained from the intercept

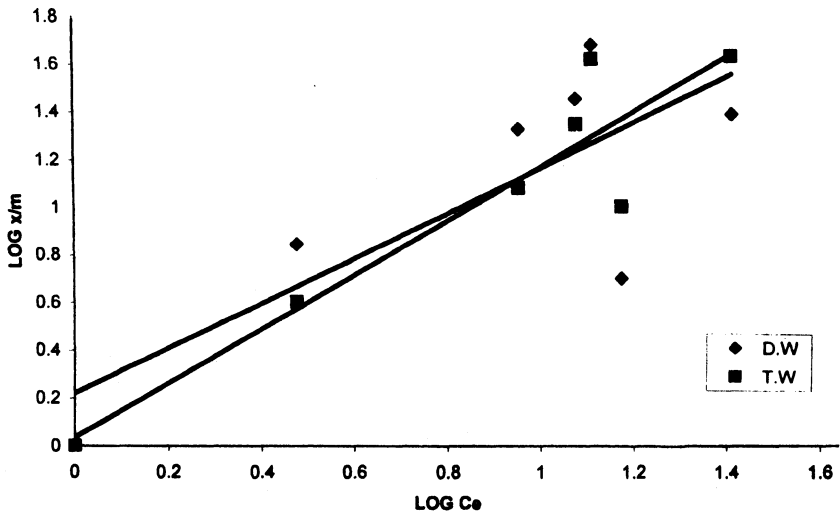


Fig. 4. Freundlich adsorption isotherm (pH 5.0)

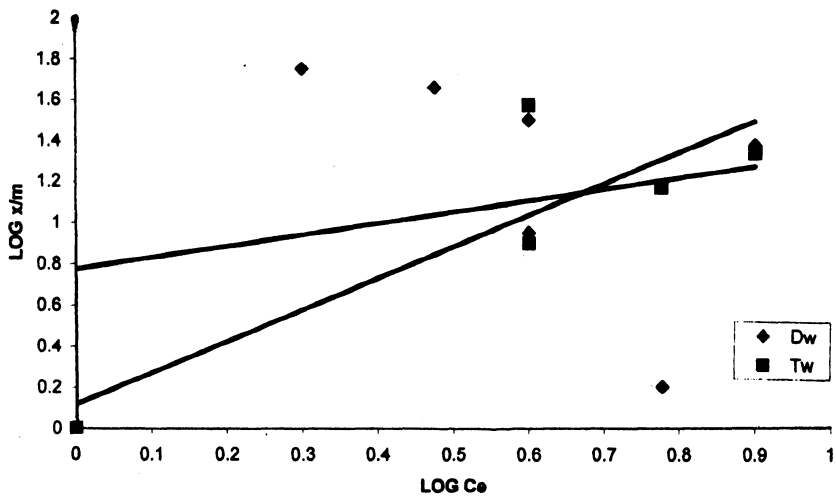


Fig. 5. Freundlich adsorption isotherm (pH 6.0)

on the x/m axis; the adsorption intensities $1/n$ were obtained from the slopes of the straight line curves. The results are given in Table-2.

It could be seen from the table that sorption capacity data of copper adsorption is slightly altered by the inorganic impurities present in the tap water.

Kinetic studies: The sorption of heavy metals such as cadmium, mercury and copper from liquid phase to solid phase can be considered as a reversible reaction

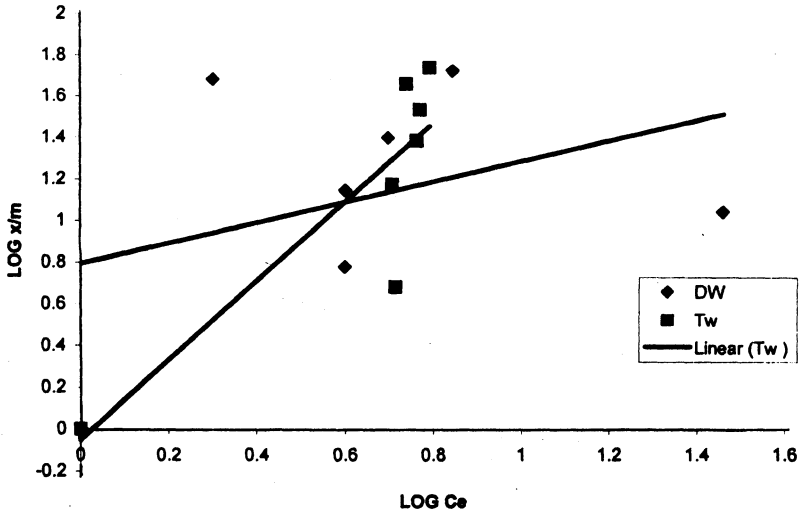


Fig. 6. Freundlich adsorption isotherm (pH 7.0)

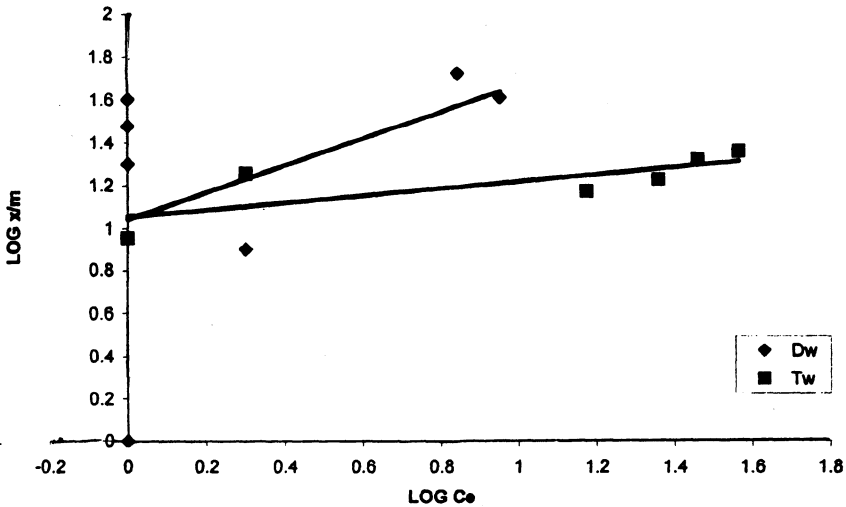
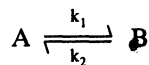


Fig. 7. Freundlich adsorption isotherm (pH 8.0)

with equilibrium being established between the two phases since one solute is generally involved in the adsorption process, a simple first order reaction kinetic model⁴ was used to establish the rate of reaction for a reversible process



where k_1 = forward reaction rate constants, and k_2 = backward reaction rate constants

TABLE-2
DATA FOR FREUNDLICH ADSORPTION ISOTHERM

pH	Distilled water		Tap water	
	K	1/n	k	1/n
4.0	1.6595	0.530	1.2589	0.7058
5.0	2.3988	1.000	1.2589	0.7143
6.0	1.9055	1.333	4.7863	0.7391
7.0	1.3803	1.500	4.5708	1.1760
8.0	3.8018	1.100	1.1096	0.9130

In order to understand the kinetics of adsorption process, experiments were carried out at pH 6.0–8.0 with cottonseed carbon using 100 mL solution containing the metal ion under study in the concentration range 5–10 mg/L; the solutions were taken in a series of 300 mL polythene containers and to each 0.1 g of cottonseed carbon was added.

The containers were equilibrated in rotary mechanical shaker for periods ranging from 1–6 h. At the end of the shaking period the solutions were analyzed for the metal content as described earlier.

The concentrations of copper content remaining in the equilibrated solution were plotted as a function of equilibration period and kinetic data were calculated and recorded in Table-3. The plots are given in Figs. 8–10.

TABLE-3
KINETIC DATA

S. No.	Concentration of ion of Cu ²⁺ in mg/L	K (hr ⁻¹) (K ₁ + K ₂)	K ₁ (hr ⁻¹)	K ₂ (hr ⁻¹)	Film diffusion D _f (sq. cm/s) (× 10 ⁻⁶)	Pore diffusion D _p (sq. cm/s) (× 10 ⁻⁵)
pH 6	5	1.3140	0.9724	0.3416	9.2780	4.7017
	7	0.7273	0.5195	0.2078	4.9573	2.6025
	10	0.6182	0.3957	0.2250	3.7755	2.2122
pH 7	5	0.6000	0.3120	0.2880	2.9770	2.1469
	7	0.5000	0.2928	0.2072	2.7943	1.7891
	10	1.4545	1.0472	0.4073	9.9937	5.2048
pH 8	5	0.5600	0.3249	0.2351	3.0990	2.0030
	7	0.8000	0.5486	0.2514	5.2345	2.8627
	10	0.7700	0.5159	0.2514	4.9226	2.7551

It could be seen from the Table-3 that overall rate constants at pH 6.0 are found to decrease as the concentration is increased. At pH 7.0 the overall rate constants are more or less increased to three times approximately, as the concentration increased. However, at pH 8.0, the rate constant remained more or less at the same value over the given concentration range. The film diffusion and pore diffusion coefficients were also calculated using the Michelson model⁶ and recorded in the same table. It could be seen that the adsorption followed film diffusion process as the coefficients are in the range 10⁻⁶ to 10⁻⁸ according to Michelson model⁶.

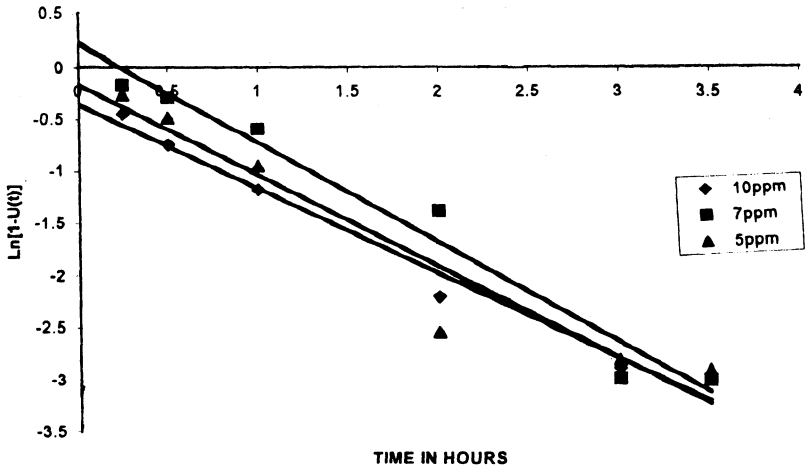


Fig. 8. Kinetic fits at pH 6.0

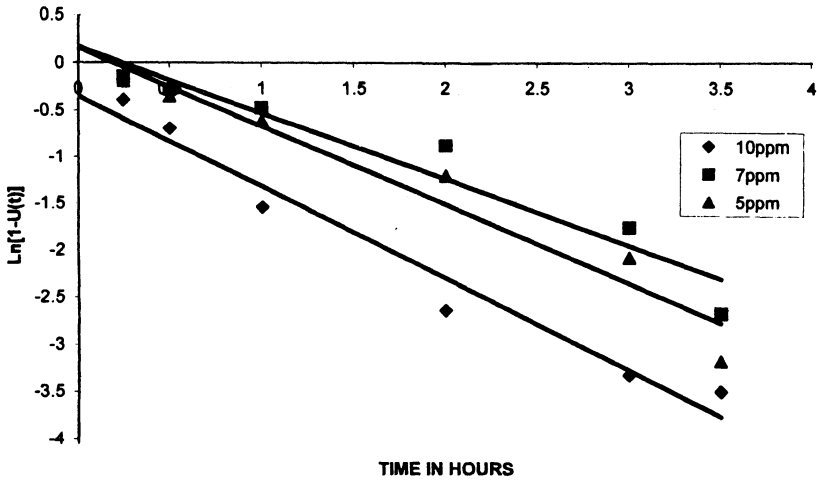


Fig. 9. Kinetic fits at pH 7.0

Conclusions

Since the carbon was prepared by mixing cottonseed with H₂SO₄ followed by sodium bicarbonate soaking, groups such as C_xONa⁺, C_xSO₃Na⁺, C_xONa₂²⁺ may be present on these surface of carbon based on Frumkin concept of formation of surface oxides. These surface oxides that are formed may undergo hydrolytic reactions and subsequent neutralization with sodium carbonate may be producing

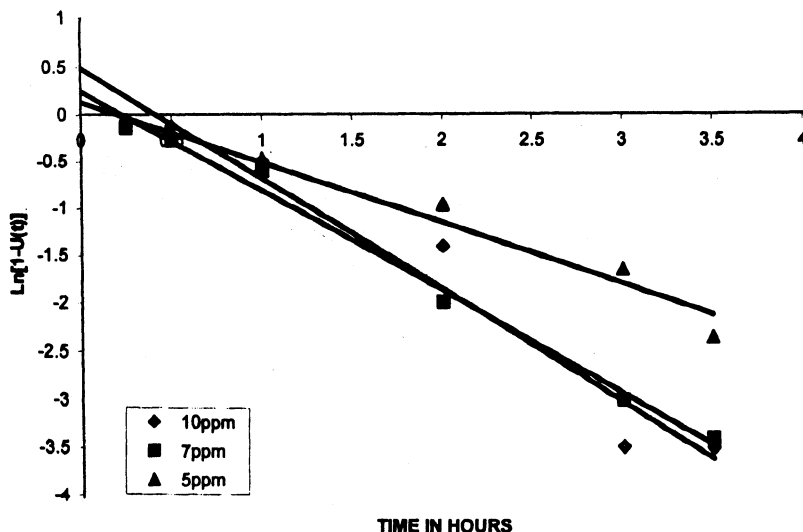
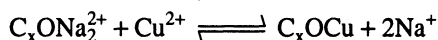
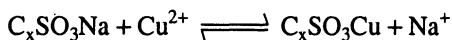
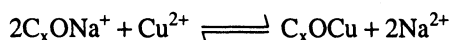


Fig. 10. Kinetic fits at pH 8.0

the above groups. It is expected that these groups participate in the process of removal of Cu^{2+} from the aqueous solution as indicated below:



Calculation of diffusion coefficient suggests that adsorption process is controlled by film diffusion process. Finally, it may be concluded that this carbon may be moderately employed to remove copper from aqueous solution. However, further details regarding cost of carbon will have to be worked out in this connection.

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