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Studies on the Adsorption of Copper (II) by Activated Charcoal and its Application in the Treatment of Textile Industry Effluents

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Abstract. The adsorption of divalent copper ions on activated charcoal was studied as a function of pH, amount of charcoal and the concentration of copper ions to optimize the operational conditions for the removal of copper ions using activated charcoal. The cross-interferences with other ions or matrix components of the textile industries effluents were also investigated. The applicability of Freundlich and Dubinin-Radushkevich equations for the said system was tested. Thermodynamic parameters, such as free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) during the adsorption were computed. The treatment of textile industries wastes, containing higher concentrations of copper ions, has been evaluated using activated charcoal based on adsorption technique. The overall performance of the treatment system indicated that activated charcoal can be utilized as a potential decontaminate for the removal of copper ions from textile effluents before discharge into the hydrosphere.

Keywords: adsorption isotherms, activated charcoal, textile industries waste, copper ions removal, industrial effluents, wastewater treatment

Introduction

Copper is an essential mineral, which is a component of several important enzymes in the body and is thus essential for good health. It is found in all the body tissues. Copper deficiency leads to a variety of abnormalities, including anaemia, skeletal defects, degeneration of the nervous system, reproductive failure, pronounced cardiovascular lesions, and elevated blood cholesterol. However, high copper intake can be toxic and may cause headaches, hypoglycemia, increased heart rate, nausea, damage to the kidney and liver, and hair loss in women. It may also cause psychological problems, such as brain dysfunction (Nolan, 1983), and depression and schizophrenia (Pfeiffer and Iliev, 1972).

Trace metals are natural elements in the aquatic ecosystems. However, deposits of anthropogenic origin have caused a progressive increase in their concentration, thus creating environmental problems in coastal zones, lakes and rivers. In most cases, the source is traceable to untreated industrial and sewage deposits. The concentration of these elements above tolerable levels is a disturbance factor for the survival of species and stability of the ecosystem. Hussain *et al.* (2000) have reported high level of trace metal pollution in sediments and liquid wastes from textile industries of Pakistan. It is, therefore, particularly necessary to treat textile effluents prior to their discharge into the receiving waterbodies (Manju *et al.,* 1998; Choi and Cho, 1996; Sapari, 1996). The most common methods used for the removal of trace metals from industrial wastewaters include, chemical precipitation, sedimentation, flotation, coagulation, and ion exchange. Adsorption, however, has an edge over other methods, mainly due to its simplicity and the sludge-free clean operation. Several adsorbents have been used for the treatment of effluents rich in Cu (II) at the solid-solution interface (Sameer and Banat, 2002; Samra, 2002; Ajmal *et al.,* 1998; Giles *et al.,* 1960). During recent years, carbon as an adsorbent has become the more accepted medium for the physicochemical treatment of wastewaters (Malik and Stelko, 2002; Sameer and Duvnjak, 1999). Activated charcoal has found many applications in several industries because of its large surface area, high adsorption capacity, microporous structure, selective adsorption, radiation stability, and high purity in removing the toxic and health hazardous particles and ions from gases and solutions. Activated charcoal is evaluated in the present study for the removal of copper from aqueous solutions under optimized conditions. The adsorbent was successfully applied for the removal of Cu (II) from the textile industry wastewaters.

Materials and Methods

Instrumentation. All analyses for Cu determination were done on atomic absorption spectrometer (Perkin-Elmer 3100, flame atomic absorption spectrometer), equipped with a hollow cathode lamp. An Orion 710 pH meter attached with a combined electrode was used for adjusting the pH of the solutions. Shaker-incubator (1000 - Heidolph) was used for sha-

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king, and Eppendorf 5417 microcentrifuge was used to centrifuge the solution.

Activated charcoal and reagents. Activated charcoal (Merck) with an average particle size 0.02-0.08 mm and the diameter of micropores in the range of 30-90 Å was used as the adsorbent. The stock solution of Cu (II) was prepared (0.01 mol/l) by dissolving $CuCl_2.2H_2O$ (BDH, Analar) in distilled water. All other reagents used were of AR grade.

General procedure. Copper sample solutions were transferred to 250 ml Erlenmeyer flasks, adjusted to pH 2.0 by using appropriate buffer system. 0.05 g of activated charcoal was added and the mixture was agitated in shaker incubator for 60 min and subsequently centrifuged at 4000 rpm for 10 min. The concentrations of metal ions remaining in the solution were assayed by standard atomic absorption spectrometry procedures and corrected for the adsorption loss of copper ions on the walls of flasks by running a blank experiment (without adding activated charcoal). The distribution coefficients (K_D in ml/g) were computed as follows:

$$K_D = \frac{C_1}{C_2} \times \frac{\text{volume of solution (ml)}}{\text{mass of solute (g)}} \qquad (1)$$

where:

C_1 = the amount of adsorbed copper ions per gram of the activated charcoal

C_2 = the concentration of copper ions per ml of the aqueous solution at equilibrium

The percentage removal was calculated using the following expression:

$$\text{Cu removal (\%)} = \frac{100\,K_D}{K_D + \frac{V}{m}} \qquad (2)$$

where:

K_D = distribution coefficient
V = volume of solution
m = amount of activated charcoal used

Results and Discussion

Effect of the amount of activated charcoal. The dependence of copper ion adsorption on the amount of activated charcoal was investigated by varying the amount of activated charcoal from 0.01 to 0.50 g. The effect of these variations is presented in Fig. 1. The observations obtained indicate that the values of distribution coefficient (K_D) and percentage removal increased with the increase in the quantity of activated charcoal and attained maximum values at 0.05 g, which then started decreasing with further increase in the amount of activated charcoal. This behaviour reflects the decrease in the effective surface area resulting in the conglomeration of the adsorbent particles, especially at the higher quantities. Therefore, for all further studies 0.05 g of activated charcoal was used as the optimum quantity.

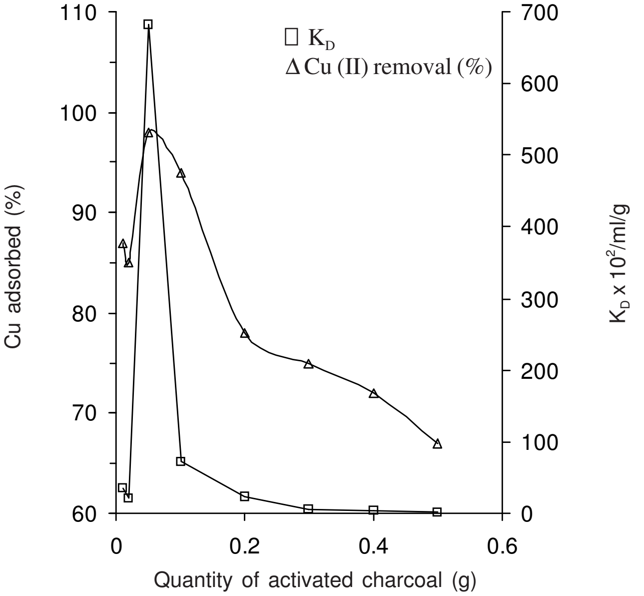

Fig. 1. Effect of the quantity of activated charcoal on the adsorption of Cu (II).

Effect of pH. The influence of pH on copper ion adsorption by activated charcoal was studied by keeping the other parameters constant. The dependence of copper (II) adsorption by activated charcoal, as a function of pH varied from 1 to 6, was evident from the variation of distribution coefficients (K_D) and percentage adsorption values, which were the maximum at pH 2.0 (Fig. 2). Therefore, for all subsequent studies pH 2.0 was used.

Effect of concentration of copper (II) ions. The effect of copper ion concentration on its adsorption by activated charcoal was studied in the metal concentration range of 5 to 50 mg/l. The variation in the distribution coefficients (K_D) and percentage adsorption at different metal concentrations at temperatures 303 through 318 K are shown in Fig. 3(a) and 3(b). The comparison of distribution coefficients (K_D) and percentage adsorption values for the activated charcoal range from 3.52 to 19.74 x 10^2 ml/g and from 58.2 to 90.8%, respectively, at concentrations ranging from 5 to 50 mg/l, indicate the quantitative recovery of copper ions at relatively higher temperatures.

Adsorption isotherms. The adsorption isotherms measured at temperatures ranging from 303 to 318 K are shown in Fig. 4.

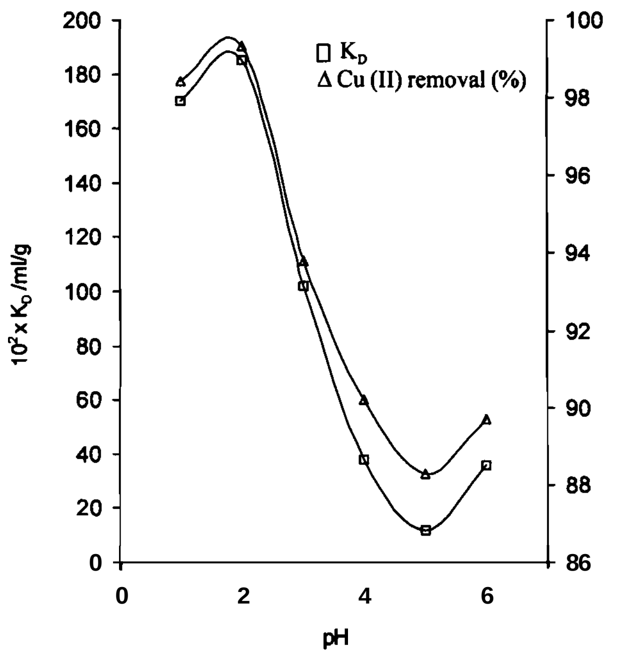

Fig. 2. Effect of pH on the adsorption of Cu (II) by activated charcoal.

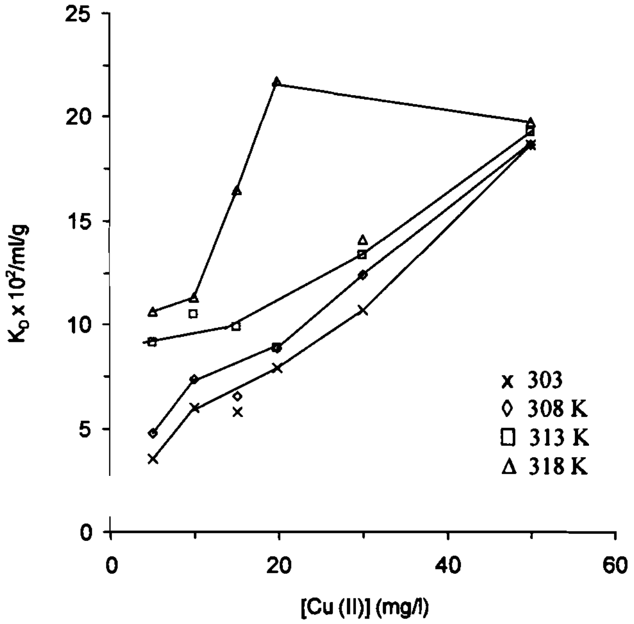

Fig. 3(a). Effect of [Cu (II)] on the K_D values of adsorption by activated charcoal at different temperatures.

The data have been plotted in terms of the amount of Cu ions adsorbed (x) per gram activated charcoal (g) versus the equilibrium concentration (C,) expressed in **mol/l.** The **x/m** expres-sed in **g/g** was calculated from the formula:

$$x/m = (C_0 - C,)\, V/m \quad (3)$$

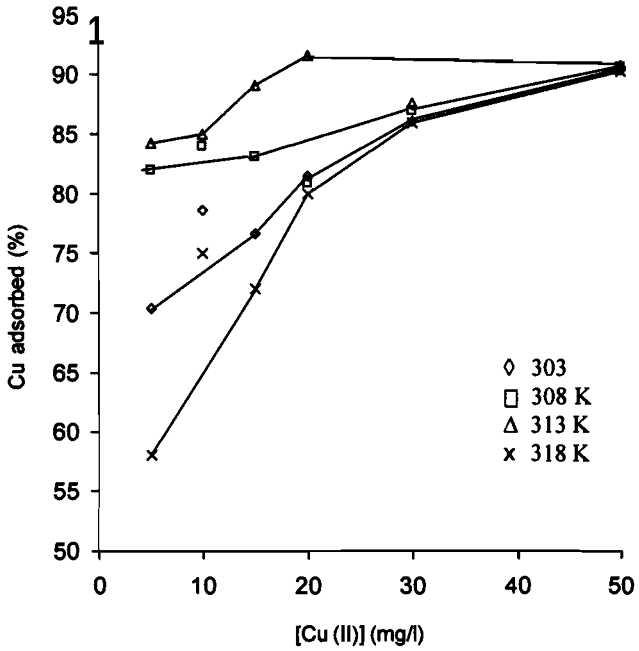

Fig. 3(b). Effect of [Cu (11)] on its percentage adsorption by activated charcoal at different temperatures.

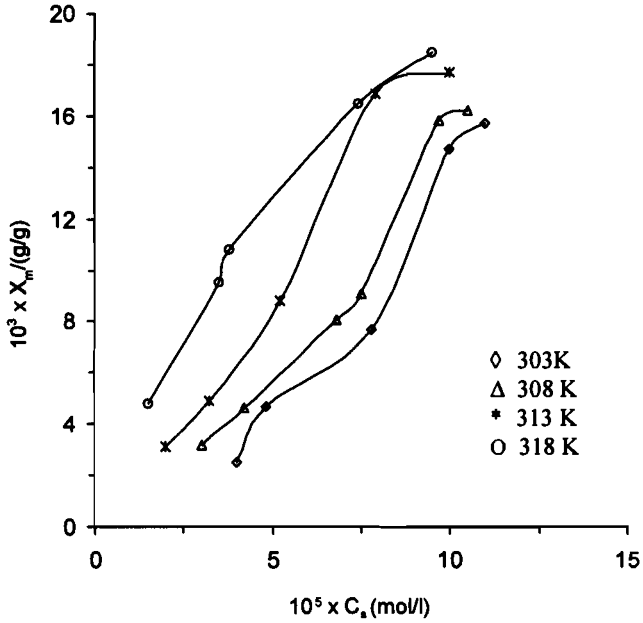

Fig. 4. Adsorption **isotherms** of charcoal for the adsorption of copper ions at different temperatures.

where:

x/m = amount of Cu (II) adsorbed per g activated charcoal
C, = initial concentration of copper ions in the system
C, = equilibrium concentration
V = volume of solution
m = amount of activated charcoal used

All the isotherms were of L_3-type according to the classification of Giles *et al.* (1960). The initial portion of isotherms provides information about the availability of the active sites for an adsorbate, while the plateau signifies the monolayer formation. The increase in adsorption with temperature indicates that adsorption of copper ions is an endothermic process. The data were also put to the Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms equations. The Freundlich isotherms have been expressed in the form of:

$$x/m = A\, C_s^{1/n} \qquad (4)$$

where:

A and 1/n = empirical constants

x/m and C_s have their usual meanings as detailed for equa-tion (3)

Fig. 5 depicts the Freundlich plots obtained at the various temperatures studied for the present system. Values of A and n computed from the respective slopes and intercepts of these plots are listed in Table 1. The values of n relate to the nature and strength of the adsorptive forces involved. The higher values of 1/n signify that strong adsorption forces were operating on activated charcoal (Ajmal *et al.,* 1998). However, the values of log A decreased with increasing temperature, which shows that the adsorption was more favourable at higher temperatures.

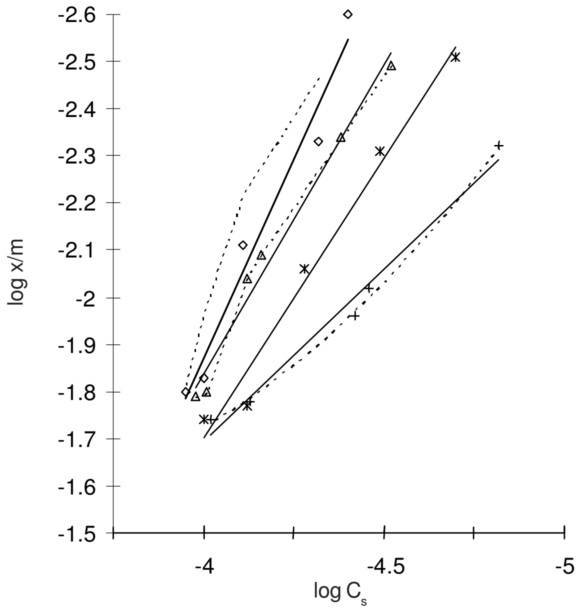

Fig. 5. Freundlich plots for the adsorption of Cu (II) by activated charcoal at different temperatures.

Table 1. Freundlich and Dubinin-Radushkevich (D-R) isotherms parameters of adsorption of Cu (II) ions by activated charcoal

Temperature	Freundlich parameters		D-R parameters		
(K)	n	A	x_m x 10^4 /mol/g	-K x 10^3 /mol^2 kJ^2	Es/kJ/mol
303	0.584	145.5	17.1	7.87	7.97
308	0.770	28.5	7.90	6.50	8.77
313	0.852	19.91	1.48	3.57	11.83
318	1.365	10.09	1.36	2.64	13.76

K= absolute temperature on the Kelvin scale; 0 °C= 273K, 100 °C= 373K

The Langmuir adsorption isotherms is the best known model and most frequently utilized to determine the adsorption parameters. The Langmuir expression can be represented as:

$$\frac{1}{X} = \frac{1}{x_m K}\,\frac{1}{C_s} + \frac{1}{x_m} \qquad (5)$$

where:

$X = \frac{x}{m}$ having the same meaning as described for equation (3)

K = Langmuir adsorption constant

x_m = the limited amount of the adsorbate that can be taken up per mass of the adsorbent

C_s = the same meanings as in the Freundlich isotherms as described for equation (3)

Thus, a plot of 1/X against $1/C_s$ is linear with a gradient of $1/x_m$, K and intercept of $1/x_m$ (Fig. 6).The dotted and solid lines represent linear and non-linear regression fits for both the isotherms. Their correlation coefficient values are summarized in Table 2, which indicates that the data fit the Langmuir isotherms better than the Freundlich isotherms, both in the case of linear and non-linear regressions.

The Freundlich type adsorption isotherms is an indication of surface heterogeneity of the adsorbent, whereas Langmuir type isotherms hint towards surface homogeneity of the adsorbent. This leads to the conclusion that the surface of activated charcoal is made up of small homogeneous adsorption patches, which are very much similar to each other in respect of adsorption phenomenon. The good correlation coefficient values for Langmuir isotherms also explain a strictly localized monolayer adsorption phenomenon.

The data were put to the Dubinin-Radushkevich (D-R) equation in the linearized form as:

$$\ln \frac{x}{m} = \ln x_m - K' \varepsilon^2 \qquad (6)$$

where:

$$\varepsilon = RT \ln (1 + 1/C_s) \qquad (7)$$

x_m = monolayer capacity of adsorbent

K' = constant related to adsorption energy

ε = adsorption potential
R = gas constant
T = absolute temperature
x/m and C, = usual meanings as described for equation (3)

The D-R plots of ln (x/m) versus ε^2 obtained at various temperatures are shown in Fig. 7. Values of x_m and K′ were calculated fiom the intercept and slope of these plots, and the values of mean free energy of sorption (E,) were calculated fiom K′ according to the following eqation:

$$E_s = (-2K')^{-1/2} \qquad (8)$$

All these values are listed in Table 1, which show that the value of E_s increases with temperature, indicating an increase in copper ion sorption with increasing temperature.

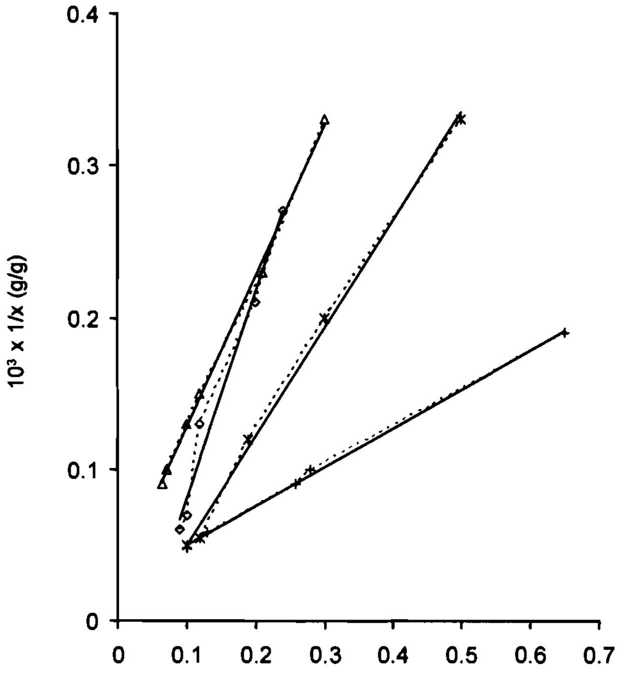

Fig. 6. Langmuir isotherms plots for the adsorption of Cu (II) ions by activated charcoal at different temperatures.

Table 2. Correlation coefficients for linear and non-linear regression fits of different adsorption isotherms

Temperature (K)	Correlation coefficients			
	Linear regression		Non-linear regression	
	Freundlich isotherms	Langmuir isotherms	Freundlich isotherms	Langmuir isotherms
303	0.9715	0.9893	0.9868	0.9953
308	0.9777	0.9974	0.9953	0.9988
313	0.9827	0.9964	0.9827	0.9969
318	0.9882	0.9981	0.9974	0.9983

The thermodynamic quantities, such as free energy change (AG), enthalpy change (AH), and entropy change (AS) for copper adsorption were calculated using the following equations:

$$\Delta G = -RT \ln K_D \qquad (9)$$

$$\Delta G = \Delta H - T\Delta S \qquad (10)$$

The values of thermodynamic parameters are given in Table 3. The positive values of AH and AS, and the decrease in AG values with increasing temperature, show that the adsorption of copper ions on activated charcoal was favoured at higher temperatures. This may be due to desorption of the copper ions at higher temperatures leading to an endothermic adsorption process, which may be chemical in nature.

Study of interferences. A study of the interferences of Co, Cd, Zn, Ni, Cr (VI), Mn, Ag, Mg and Pb on the Cu ion adsorption by activated charcoal was also done. Solutions of 50 mg/l Cu (II) were treated with 0.05 g of the adsorbent in the presence of increasing concentrations of interfering ions fiom

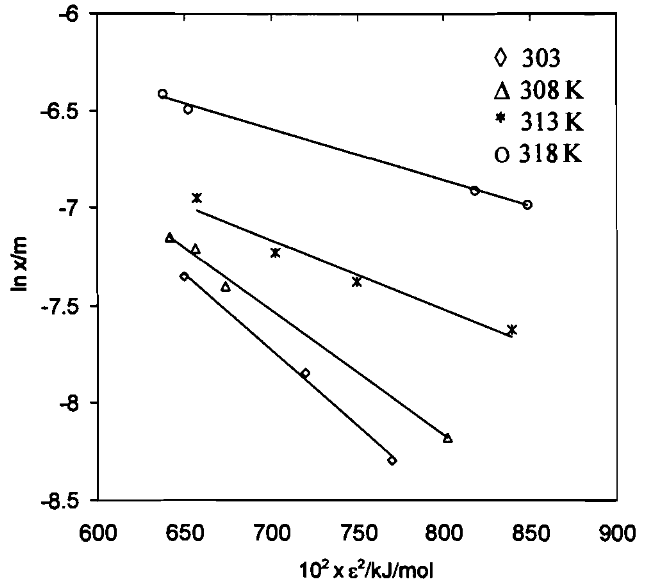

Fig. 7. D-R isotherms for the adsorption of copper ions by activated charcoal at different temperatures.

Table 3. Thermodynamic parameters of activated charcoal for the adsorption of Cu (II) ions at different temperatures

Concentration/mg/l	ΔH/kJ/mol	ΔS/kJ/K/mol	ΔG/kJ/mol			
			303 K	308 K	313 K	318 K
5.000	52.49	0.184	-14.77	-15.77	-17.45	-18.43
15.00	45.14	0.163	-16.02	-16.60	-17.94	-19.58
20.00	37.17	0.139	-16.81	-16.99	-17.66	-20.31
30.00	12.00	0.060	-17.58	-18.24	-18.73	-19.17
50.00	2.47	0.032	-18.97	-19.29	-19.68	-20.06

0 to 200 mg/l and the results obtained were evaluated in terms of Cu removal from the solution. No significant influence of these ions was noted under optimized conditions indicating selective Cu (II) adsorption.

Adsorption of copper ions from textile waste. A 25 ml textile effluent sample TXS_3 containing the maximum copper concentration of 339 mg/kg was diluted seven times and treated against 0.05 g activated charcoal at 318 K under optimized conditions. A removal percentage of total copper in the order of 80±5% was obtained. This comparativly low percentage removal, 90.8% as mentioned in Fig. 3(b), was probably due to the influence of the textile waste matrix components on the adsorption of copper by activated charcoal.

Conclusion

Activated charcoal was noted to be a good adsorbent for the adsorption of Cu (II) from aqueous solutions, the process being influenced by pH, temperature, mass of adsorbent and copper concentration. The equilibrium data fit well in the Langmuir, Freundlich and D-R models of adsorption isotherms. pH 2.0 and 0.05 g of activated charcoal were most appropriate for the quantitative removal of copper (II) in the presence of other ions or other matrices of textile industry effluents.

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