Kinetics and thermodynamics of copper ions removal from aqueous solution by use of activated charcoal

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A study on the adsorption of copper from aqueous solutions on activated charcoal has been carried out with an aim to obtain information on treating effluents from metal finishing industries. The effects of various experimental parameters like contact time, dosage of activated charcoal, initial concentration of metal ions, pH etc. have been investigated. The percentage removal of metal ions increased with the decrease in initial concentration and increase in contact time, dosage of adsorbent and initial pH. Adsorption data were modeled with the Freundlich and Langmuir adsorption isotherms, various first order kinetic equations *viz*. Lagergren, Natarajan-Khalaf and Bhattacharya and Venkobachar equations and intra particle diffusion model. These isotherms, first order equations and models were found to be applicable. The kinetics of adsorption is found to be first order with intra particle diffusion as the rate determining step. Removal of metal ions using activated charcoal is found to be favourable and hence it could be used as an adsorbent for the treatment of effluents from metal finishing industries, especially for the removal of metal ions.

Keywords: Copper, Activated charcoal, Adsorption, Adsorption model, Kinetic model

Toxic heavy metal contamination of industrial wastewater is an important environmental problem. Many industries, such as automotive, metal finishing, electroplating, battery manufacturing, mining, electric cable manufacturing, tannery, steel and textile industries, release various concentrations of heavy metals like cadmium, nickel and copper, etc. in wastewaters. Most of the heavy metals above trace quantities are harmful to humans, animals and plants. Federal and local agencies have therefore stipulated discharge limits on the levels of these heavy metals in the effluents being discharged into the environment. In the course of tissue mineral research, copper toxicity is a common finding. By correlating thousands of tests with symptoms and diagnoses, a picture has emerged of the detrimental effects of copper toxicity on human health, both physical and emotional. Copper toxicity is a much-overlooked cause of many important health conditions like fatigue, premenstrual syndrome, anorexia, depression, anxiety, migraine headaches, allergies (food and environmental allergies) and many others. Removal of copper from effluents before they are discharged into the environment can be accomplished by processes such as chemical precipitation, cementation, solvent extraction, reverse osmosis and ion exchange[1-3]. But these techniques have disadvantages like incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal. Therefore, these processes are, sometimes, neither effective nor selective and some of them are very expensive[4].

Adsorption is a process for the removal of heavy metals, which is quite selective and effective, and is able to remove very low levels of heavy metals from the aqueous solutions/wastewater. Ion exchange resins and activated carbon[5-7] are well known materials that are used for this purpose. Adsorption of heavy metals by these materials might be attributed to their protein, carbohydrates and phenolic compounds[8] which have metal binding functional groups such as, carbonyl, hydroxyl, sulphate, phosphate, and amino groups[9].

The goals of the present work were to: (a) investigate the ability of commercial activated charcoal to remove Cu^{2+} from wastewater; (b) study the influence of specific process parameters such as, initial concentration, pH, contact time and adsorbent dose for the maximum removal of copper from its aqueous solutions/wastewater; (c) determine the kinetic equation best describing data obtained and to find the activation energy, important for the practical application of activated charcoal in wastewater treatment; and (d) determine the adsorption equation which best describes the equilibrium uptake and to calculate thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) for the practical implementation of activated carbon technology.

Experimental Procedure

Materials

Activated charcoal (supplied by Nice Chemical limited, Cohin) was used as an adsorbent without any pretreatment. All solutions were prepared using only double distilled water. All the chemicals employed for the analysis were AnalaR grade.

Methods

The adsorption experiments were carried out by batch equilibrium method. A stock solution of the adsorbate containing 1000 mg/L of copper (II) ions was prepared using $CuSO_4.5H_2O$. From the stock solution, aliquots containing different concentrations of Cu(II) ions were measured out into separate screw top flasks. A sample adsorbate of each concentration (50 mL) was mixed with 10 mg of activated charcoal and the mixtures were agitated on a mechanical shaker at 150 rpm. Samples were taken at different time intervals for the analysis of residual metal concentration in solution. The adsorbate-metal mixture was filtered for analysis of unadsorbed metal ions in the solution. Analysis was made by using Toshvin (Model-6200) atomic absorption spectrophotometer with air-acetylene flame.

Metal uptake (q_e) was calculated using the following Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{1000W} \qquad \qquad ...(1)$$

The amount adsorbed was calculated using the following Eq. (2):

$$\text{Percentage removal} = \frac{100\,(C_i - C_e)}{C_i} \qquad ...(2)$$

where q_e (mg.g^{-1}) is the amount of total adsorbed heavy metal ions, C_0 (mg.L^{-1}) the initial metal concentration, C_e (mg.g^{-1}) the equilibrium metal concentration in solution in solution at time t, V(L) the solution volume and W(g) is the adsorbent weight.

Adsorption experiments were conducted at *p*H 4. This was because of the formation of copper hydroxide at higher *p*H range with sodium hydroxide which was added to adjust the *p*H of the acidic copper solution. The experiments were repeated at three different temperatures *viz.* 293, 303 and 313 K to determine the effect of temperature on the sorptive behaviour of activated charcoal. All experiments were done in a thermostat with a shaker attached (Labline make) which maintained temperature within ± 0.1°C.

Control samples were prepared from the biomass free solution for testing metal losses due to metal precipitation and adsorption of bottle surface. All experiments were run at least in duplicate. Adsorbed metal concentrations were the averages of the duplicate experimental results.

Results and Discussions

Effect of adsorbent dosage

The results of the adsorption equilibrium experiments using different dosages *viz.* 02; 04; 0.5; 0.8; 0.9; 1; 1.5; 2.5; 5; 10 and 12.5 mg/L of activated charcoal and 63.08 mg/L of copper were carried out. Figure 1 shows the behaviour of activated charcoal with increasing adsorbent dosage. It was observed that there is a sharp increase in percentage removal with adsorbent dosage. It is apparent that the percentage removal of copper increases with increase in the dose of adsorbent due to the increased availability of the active sites/surface area for the adsorption of the copper, whereas, at lower adsorbent dosage the number of copper molecules was relatively higher, compared to availability of adsorption sites/surface[10]. Further, the rate of adsorption does not register a proportionate increase as per the experimental results. In view of this observation, it was decided to conveniently fix the dosage of activated charcoal as 10 mg for the remaining experiments. The values of log q versus log (dosage) were found to be linear and hence the q value varies with dose according to the equation.

$$q_e = (\text{dosage})^n + C \qquad \qquad ...(3)$$

The value of *n* for the copper was calculated to be 1 (r = - 0.9788). The plots of log (percentage removal) versus log (dosage) were also found to be linear with r-values close to unity. This suggests that the adsorbed copper ion may block the access to the
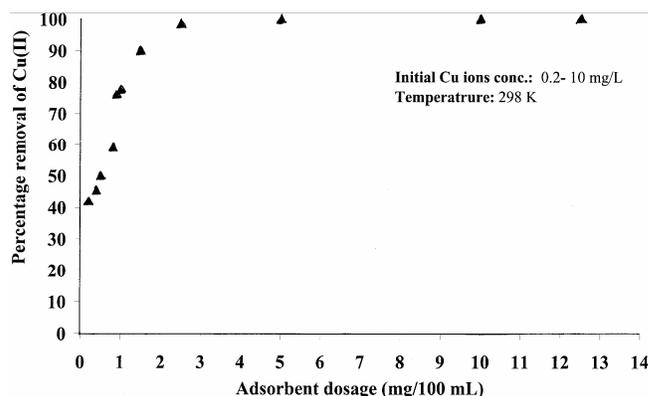

Fig. 1 — Effect of adsorbent dosages on percentage removal of copper

internal pores of adsorbent caused adsorbent particle to aggregate and thereby reducing the availability of active sites for adsorption[10,11].

Effect of contact time

Contact time required for the maximum removal of copper by activated charcoal is shown in Fig. 2. There is steep increase in the adsorption in the initial stages of the reaction as seen in the curve[12]. Maximum adsorption occurs at the 70th min after which the adsorption remains uniform, represented by attainment of equilibrium. The amount of copper adsorbed at this point is 98% under the particular operating conditions. The time variation curve is smooth and continuous and this indicates the formation of monolayer coverage on the outer interface of the adsorbent[13-15].

Effect of *p*H

The pH of the adsorption solution is one of the most important parameters controlling the uptake of copper from aqueous solutions/wastewater by adsorbent. The percentage adsorption increases with *p*H to attain maximum at *p*H 3 to 4 and thereafter, it increases with further increase in *p*H. The maximum removal of copper at *p*H 4 was found to be 84% for activated charcoal. Similar observation was reported by Kannan and Kumar[10]. The results clearly indicate that both the surface charge density of the adsorbent and charge of copper ions present depend on the *p*H. Moreover, differences in extent of adsorption are also associated with the chemical state of the copper in the adsorptive state. As observed subsequently, it determines the adsorptive species relevant to the adsorption process. The Cu^{2+} ions in aqueous solution may undergo hydration, hydrolysis and polymerization[16].
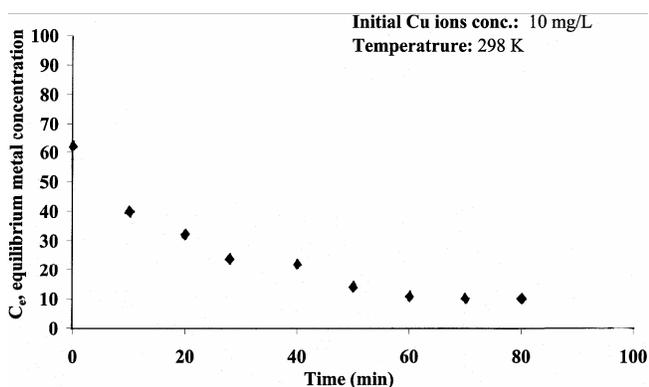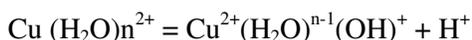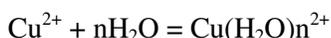
$$Cu^{2+} + nH_2O = Cu(H_2O)n^{2+}$$

$$Cu(H_2O)n^{2+} = Cu^{2+}(H_2O)^{n-1}(OH)^+ + H^+$$

Initial Cu ions conc.: 10 mg/L
Temperatrure: 298 K

Fig. 2 — Effect of contact time

$$n\,Cu^{2+} + mH_2O = Cu_n(OH)_m^{(2n-m)+} + m\,H^+$$

Lower *p*H results in the protonation of the adsorbent surface, which leads to the extensive repulsion of Cu^{2+} ions. This results in a decrease in copper adsorption. With increase in *p*H from 2 to 4.0 the surface protonation of adsorbent is minimum, leading to the enhancement of Cu^{2+} ions adsorption.

Adsorption isotherms

In order to determine the adsorption capacity and potential for selecting the adsorbent for the removal of metal ions, the study of adsorption isotherm is essential in selecting the adsorbent for the removal of metal ions. The adsorption data obtained were analyzed in the light of Langmuir and Freundlich isotherms[17].

Freundlich isotherm

Batch isotherm data fitted to the linear form of the Freundlich isotherm according to Eq. (4) as follows:

$$\log q_e = \log K + \frac{1}{n} \log C_e \qquad \ldots(4)$$

where q_e is the amount of copper sorbed per unit weight of the sorbent (mg/g) and C_e is the equilibrium concentration (mg/L) of Cu(II) in solution. The fit of the data imply that the intercept K, is roughly an indicator of the sorption capacity and the slope, $\frac{1}{n}$, of the sorption intensity, the constants incorporating all the factors affecting the adsorption process. Values of K and $\frac{1}{n}$ are calculated from the figure and the data are provided in Table 1. The linearity of the plots (r=0.9663, 0.9875 and 0.9765) at different temperatures is evident from Fig. 3. This supports the applicability of the Freundlich adsorption isotherm indicating that the adsorption by activated charcoal may be governed by physisorption. The values of *n* for this system were calculated from the slop of the curve and are found to be between 1 and 2. The present findings are in good agreement with the

Table 1 — Value of Freundlich isotherm constant for adsorption of copper for activated charcoal

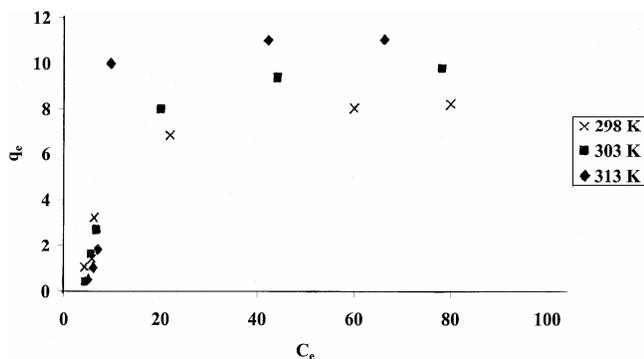| Temperature (K)	Freundlich parameter		r
	K	$\frac{1}{n}$	
298	0.8446	11.54	0.9663
303	0.3749	11.13	0.9875
313	0.3479	9.78	0.9769

Fig. 3 — Plots of C_e versus Q_e at different temperatures of copper for activated charcoal
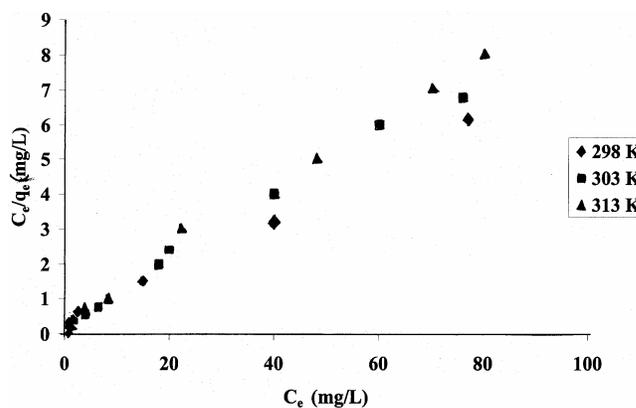
Table 2 — Values of Langmuir constants for adsorption of copper for activated charcoal

Temperature (K)	Langmuir constant			
	b (L.mg^{-1})	q_{max} (mg.g^{-1})	r	R_L
298	0.8446	11.54	0.9987	0.0452
303	0.3749	11.13	0.9939	0.0964
313	0.3479	9.78	0.9936	0.1031

findings of Treybal[18] who mathematically evaluated values of *n* for a number of mass transfer operations of systems and reported that values of *n* between 1 and 10 would represent beneficial adsorption.

Langmuir isotherm

The linear form of the Langmuir isotherm was applied in the form of Eq. (5) as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_b} + \frac{C_e}{Q} \ldots \qquad \ldots(5)$$

where Q and b are the Langmuir constants, indicating adsorption capacity and energy of adsorption respectively. C_e and q_e have their usual meaning. The values for the plot $\frac{C_e}{q_e}$ versus C_e for the adsorption by activated charcoal at different temperature were calculated and are presented in Table 2. The linear plot ($r = 0.9987, 0.9939, 0.9936$) of $\frac{C_e}{q_e}$ versus C_e at different temperature is given in Fig. 4 and that indicate the applicability of Langmuir adsorption isotherm to the adsorption process. This is due to the fact that after the formation of monoionic layer of metal ions on the surface of adsorbent at lower concentrations, any further formation of layer of metal ions is highly hindered at higher concentration

Fig. 4 — Langmuir isotherm

due to the interaction between the metal ions on the surface of the adsorbent and in the bulk of the solution[19,21]. The metal ions normally form a surface layer, which is only one molecule thick, that is monolayer on the surface of the adsorbent[21]. Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following Eq. (6)[19,20].

$$R_L = \frac{1}{1 + bC_0} \qquad \ldots(6)$$

where, C_0 is the optimum initial concentration (ppm) of metal ions and b is the Langmuir constant.

The value of R_L indicates the shape of the isotherms to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of Langmuir constants b and R_L are presented in Table 2. Since R_L values lie between 0 and 1 for all three temperature studied, it indicated that the adsorption of copper is favourable[20].

Equilibrium parameter

The plots of $\ln q_e/C_e$ versus q_e of the are given in Fig. 5. The equilibrium constant K_0 for the sorption reaction was determined from the plot $\ln q_e/C_e$ versus q_e and extrapolating to zero. An increase on K_0 value with temperature indicates that the adsorption process of copper (II) by activated charcoal is endothermic. The effect of increase in temperature on the adsorption of copper (II) at the charcoal-solution interface has been studied in the temperature range of 293-313 K. A plot of $\ln K_0$ versus $1/T$ is found to be linear as shown in Fig. 6. $\Delta H°$ and $\Delta S°$ are determined from the slops and intercepts of the plot[22]. The negative values of the standard free energy change ($\Delta G°$) for this reaction suggests that the sorptive nature is spontaneous. The positive value of $\Delta H°$ (3.32 KJ/mol) indicates that the process of adsorption
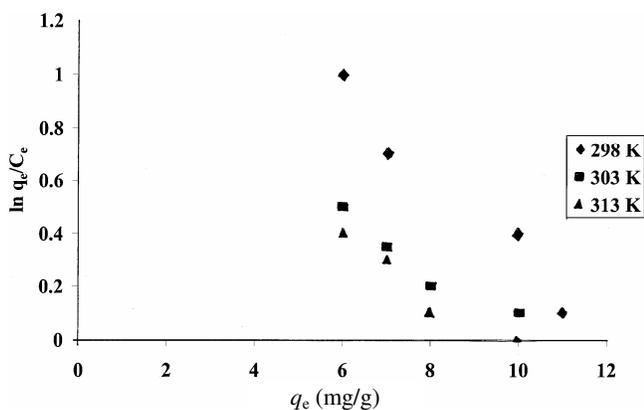
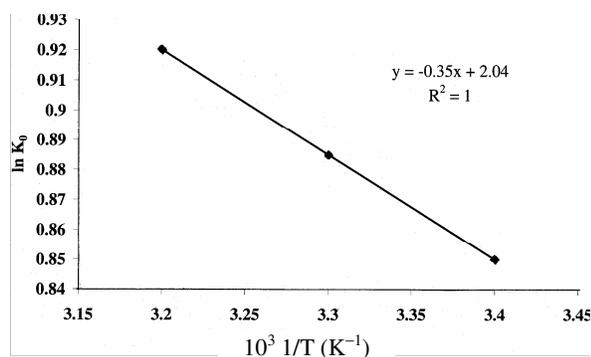Fig. 5 — Plots of In q_e/C_e versus q_e at different temperatures

Fig. 6 — Plot of In K_0 versus $1/T$

is endothermic and irreversible, probably due to nonpolar interactions[23]. The positive value of entropy change $\Delta S°$ 2.19 J/K/mol) suggests a high degree of disorderliness at the solid-solution interface during the adsorption process of copper (II) by activated charcoal. It also reflects the affinity of the adsorbent for copper (II) and suggests some structural changes in adsorbate and adsorbent. Enhancement of adsorption capacity of activated charcoal at higher temperatures may be attributed to the enlargement of the pore size and /or activation of the adsorbent surface and increase in the mobility of the metal ions.

Kinetics of adsorption

The kinetics of adsorption of metal ions has been studied by applying the following first order kinetic equations[11].

Natarajan-Khalaf equation:

$$\log\left(\frac{C_i}{C_t}\right) = \left(\frac{K}{2.303}\right)t \qquad \ldots(7)$$

Lagergren equation:

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{K}{2.303}\right)t \qquad \ldots(8)$$

Table 3 — Kinetics and dynamics of adsorption of copper by activated charcoal

Kinetic models	r	k
	(correlation coefficient)	
Natrajan-Khalaf	0.9868	0.00521
Lagergren	0.9924	0.0457
Bhattacharya and Venkobachar	0.9899	0.01025

Bhattacharya and Venkobachar equation:

$$\log\left[1 - u(t)\right] = -\left(\frac{K}{2.303}\right)t \qquad \ldots(9)$$

where u(t) = $[(C_i - C_t)/(C_i - C_e)]$; C_i, C_e and C_t are the concentration of metal ions (in ppm) at the initial time, equilibrium time and at time t, in min, K is the first-order rate constant for adsorption (min^{-1}); q_e and q_t are the amount adsorbed at equilibrium time and time t , in min. The values of (i) log (C_i/C_t) (ii) log (q_e-q_t) and (iii) log [1-u(t)] were correlated with time (in min.). The values of first order rate constant along with r-values are given in Table 3. All the linear correlations are found to be statistically significant at 95% confidence level which indicates the applicability of these first order kinetic equations. The adsorption process of metal ions on activated charcoal is found to be first order. The values of rate constant (K) calculated from Bhattacharya and Venkobachar equation for copper (II) and lead (II) ions are found to be similar to that of the K values calculated from Lagergren equation (Table 3). Therefore in future any one of these kinetic equation can be employed to calculate the rate constant for the adsorption process of metal ions.

Intra-particle diffusion model

The metal ions are most probably transferred from the bulk of the solution to the solid phase through intra-particle diffusion /transportation process, which is often the rate limiting step, in many adsorption process, especially in a rapidly stirred batch reactor[19,24]. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model[25-27].

$$q_t = K_p t^{1/2} + C \qquad \ldots(10)$$

where q_t is the amount adsorbed (in mg/g) at time t; C is the intercept and K_p is the intra-particle diffusion rate constant (in mg/g/min$^{1/2}$). The K_p values are calculated by correlation analysis and the correlations are found to be statistically significant at 95% confidence level. The results indicate the possibility

of the presence of intra-particle diffusion process[26,27] as the rate determining step. The values of intercept (C) in q_t versus $t^{1/2}$ plot give an idea about the boundary layer thickness, that is the larger the intercept, greater is the boundary layer effect[26,27]. The first, sharp portion of the curve corresponds to the external surface adsorption stage or instantaneous adsorption stage. The second, less- sloping linear portion indicates the gradual adsorption stage and final portion represents the equilibrium stage. In this model, the activated charcoal is treated as being surrounded by a boundary layer film through the metal ions must diffuse prior to adsorption on the activated charcoal. The second portion of the figures indicates the intraparticle diffusion, where diffusive transport occurs through the internal pores of the activated charcoal. As the bulk and surface metal concentrations start to decrease, the third section of the figures shows decrease in the rate of diffusion reaching a point of equilibrium[28].

Conclusions

The conclusions derived from the present studies are:

(i)   The percentage removal of metal ions increase with decrease in initial concentration and increase in contact time, dosage of adsorbent and initial *p*H of the solution.

(ii)   The adsorption data obeyed the Langmuir and Freundlich isotherms and indicate the formation of unimolecular layer of adsorbates.

(iii) The adsorption process obeys various first order kinetic equations. Therefore, it is first order with interaparticle diffusion as the rate determining step.

(iv)   Activated charcoal could be used as an adsorbent for the effluent treatment, especially for the removal of metal ions.

References

1 Kaewsarn P, *Chemosphere*, 47 (2002) 1081.
2 Kim D S, *J Hazard Mater*, B106 (2004) 67.
3 Dean J G, Bosqui F L & Lanouette K H, *Environ Sci Technol,* 6 (1972) 518.
4 Wilde E W & Benemann J R, *Biotechnol Adv,* 11 (1993) 781.
5 Dobrowalsk I R, Jaronice M & Kosmulski M, *Carbon*, 24 (1986) 15.
6 Carmen G, Marzal P & Jose J, *Water Res*, 30 (1996) 3050.
7 Netzer A & Hughes D E, *Water Res*, 18 (1984) 927.
8 Friedman M & Waiss A C, *Environ Sci Technol*, 6 (1972) 457.
9 Kuyuacak N & Valesky B, *Biotechnol Lett*, 2 (1988) 137.
10 Kannan N & Raja Kumar A, *Toxicol Environ Chem,* 84 (2003) 7.
11 Kannan N & Meenakshi Sundaram M, *Water Air Soil Pollut*, 138 (2002) 289.
12 Singh D K & Srivastava B, *Indian J Chem Technol,* 8 (2001) 133.
13 Singh D K, Gerg S K & Bharadwaj R K, *Indian J Environ Protec*, 21 (2001) 604.
14 Khatri S D & Singh M K, *Indian J Chem Technol,* 6 (1999) 112.
15 Desai M, Dogra A, Vora S, Bahadur P & Ram R N, *Indian J Chem*, 36 (1997) 938.
16 Burgess J, *Metal Ions in Solution* (Ellis Horwood, New York), 1978.
17 Adamson A W, *A Physical Chemistry of Surface* (Inter Science Publi Inc., New York), 1960, 777.
18 Treybal R, *Mass Transfer Operations* (McGraw Hill, New York), 1980.
19 Weber T W & Chakravorti, *J Am Inst Chem Eng*, 2 (1974) 228.
20 Hall K R, Eagleton L C, Acrivos A & Vermeulen T, *Ind Eng Chem Fund*, 5 (1966) 212.
21 Kannan N, *Indian J Env Portec*, 11(7) (1991) 514.
22 Manju G N, Gigi M C & Anirudhan T S, *Indian J Chem Technol*, 6 (1999) 134.
23 Stephan Inbaraj B & Sulochana N, *Indian J Chem Technol*, 9 (2002) 201.
24 McKay G, *Biochem Eng J*, 27 (1983) 187.
25 Crank G, *The Mathematics of Diffusion* (Clarendon Press, London), 1933.
26 Deo N & M Ali, *Indian J Envron Protec*, 13(7) (1993) 496.
27 Deo N & M Ali, *Indian J Envron Protec*, 13(8) (1993) 570.
28 Juang R S, Tseng R L, Wu F C & Lee H H, *J Chem Technol Biotechnol,* 70 (1997) 391.