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Kinetics and thermodynamics of copper ions removal from waste water by use of bentonite

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ABSTRACT

A study on the adsorption of copper from aqueous solutions on bentonite has been carried out with an aim to obtain information on treating effluents from metal finishing industries. The effect of various experimental parameters like contact time; dosage of bentonite; initial concentration of metal ions; pH etc. 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 bentonite is found to be favorable 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.

Key words: Copper removal, Kinetics, Bentonite

INTRODUCTION

Pollution by heavy metals is one of the most serious environmental problems facing life of earth. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. For example, sludge contamination by heavy metals is one of the serious problems encountered in the use of sewage sludge as a natural fertilizer. Excessive levels of metals in the marine environment can affect marine bio-systems and pose a risk to human consumers' seafood. For this reason, the concentration of heavy metals in waste water and drinking water as water used for agriculture must be reduced to the maximum permissible concentration [1]. Current technologies for the removal of heavy metal ions include adsorption onto activated carbons and biosorbents, chemical precipitation, ion exchange, electrochemical re- moval, and membrane techniques carried out in several studies [2–6]. Adsorption is the method most often applied using activated carbon or ion-exchange resin. However, as shown in the study presented by Pollard et al. [7], the relatively high-cost preparation and regeneration of activated carbons has encouraged many researchers to examine the feasibility of using other low-cost adsorbents such as local clays.

Natural clays were tested for the removal of heavy metal ions by several researchers because of their low cost and availability [8–11]. One such clay is bentonite, which exists in most continents of the world. Bentonite exhibits an enormous surface area when it is hydrated in water. It consists of numerous microscopic platelets, each with negative charges on flat surfaces and positive charges on edges. Hydration causes these platelets to separate into a porous structure containing both positive and negative charges. It is known that the ionic charge and the porous structure give bentonite the ability to adsorb the toxins [9]. Numerous researches have been conducted on natural bentonite to examine its potential for the removal of heavy metal ions. The use of untreated bentonite for the removal of various heavy metals from their aqueous solutions was examined and it was found that all the metals tested exhibited maximum adsorption at 20^0 C [10]. It is found that natural bentonite could be used effectively for the removal of zinc ions from aqueous solutions [11]. The adsorption of toxic heavy metal cations, such as Cu(II), Cd(II), and Pb(II), on red mud was investigated by Apak et al. [12]. They calculated the related adsorption parameters at fixed pHs of 5.0 and 5.5 and found that the adsorption intensity and surface binding constant of Cu(II) were the highest among the studied materials. A proportion of 85% of Cu(II) ions could be removed from aqueous solutions by adsorption onto natural bentonite at pH 3.8 in a study by Rauf et al.[13].

In the adsorption process, an important problem is regeneration of adsorbent. Generally, thermal and chemical methods are commonly used for regeneration of adsorbent, but even Breitbach and Bathen [14] presented disadvantages for these methods. The objective of the present study was to investigate theefficiency of locally available silica/alumina-based bentonite as an adsorbent for the removal of cadmium and zinc from different aqueous–acidic solutions. In addition the effect of ultrasound power on desorption was investigated.

The goals of the present work were to: (a) investigate the ability of bentonite 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 were optimized ; (c) determine the kinetic equation best describing data obtained and to find the activation energy, important for the practical application of bentonite 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 bentonite technology.

MATERIALS AND METHODS

Materials

The bentonite used as the adsorbent in the present study was supplied from Nice Chemical limited, Cohin. It was crushed, ground, and washed with distilled water to remove dirt and other water-soluble impurities. The grain size was mostly (>94%) less than 200 mesh (75 µm). The chemical analysis of bentonite was carried out by X-ray fluorescence, XRF (ARL 9800 XP), and the results are given in Table 1.

All experimental solutions were prepared using only double distilled water. All the chemicals employed for the analysis were AnalaR grade.

Procedure:

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 flask. A sample adsorbate of each concentration (50 mL) was mixed with 10 mg of bentonite and the mixtures were agitated on a mechanical shaker at 150 rpm. Samples were taken at 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 mixture. Analysis was made by using Toshvin (Model-6200) atomic absorption spectrophotometer with air-acetylene flame.

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

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

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

$$Percentage\ removal = \frac{100\,(C_0 - C_t e)}{W} \qquad (2)$$

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 pH 4. This was because of the formation of copper hydroxide at higher pH range with sodium hydroxide which was added to adjust the pH of the acidic copper solution. The experiments were repeated at four different temperature viz. 293, 303, 313 and 323 K to determine the effect of temperature on the sorptive behavior of bentonite. 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 means of the duplicate experimental results.

RESULTS AND DISCUSSION

Effect of adsorbent dosage

The results of the adsorption 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 bentonite and 63.08 mg/l of copper were carried out. Figure 1 shows the behavior 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 [15].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 bentonite as 10 mg for the remaining experiments. The values of log *q* vs log (dosage) were found to be linear and hence the q value varies with dose according to the equation.

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

The value of n for the copper was calculated to be 169 (r = - 0.9788). The plot of log (percentage removal) vs log (dosage) were also found to be linear with r-values close to unity. This suggests that the adsorbed copper ion may either block the access to the internal pores of caused adsorbent particle to be aggregate and thereby reducing the availability of active sites for adsorption [15-16].

Effect of contact time

Contact time required for the maximum removal of copper by bentonite is shown in Figure 2.There is steep increase in the adsorption in the initial stages of the reaction as seen in the curve [17]. Maximum adsorption occurs at the 70th minute after which the adsorption remains uniform, represented by attainment of equilibrium. The amount of copper adsorbed at this point is the maximum 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 [18-20].

Effect of pH

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 pH to attain maximum at pH 3 to 4 and thereafter, it increases with further increase in pH. The maximum removal of copper at pH- 4 was found to be 84% for activated charcoal. Similar observation was reported by Kannan et al. [15].The results clearly indicate both the surface charge density of the adsorbent and charge of copper ions present depends on the pH. 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 [21].

$Cu^{+2} + nH_2O = Cu\ (H_2O_)n^{+2}$
$Cu\ (H_2O_)n^{+2} = Cu^{+2}\ (H_2O)^{n-1}(OH)^{+} + H^{+}$
$n\ Cu^{+2} + mH_2O = Cu_n(OH)_m^{(2n-m)\,+} + m\ H^{+}$

Lower pH 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 pH from 2 to 4.0 the Cu exists as $Cu(OH)_2$ in the medium and 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 [21].

Freundlich isotherm

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

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

Where q_e is the maount 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 graph and the data are provided in Table 2.The linearity of the plots (r=0.9663,0.9875 and 0.9765) at different temperatures is evident from Figure 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. Our findings are in good agreement with the findings of Treybal [22] 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 equation of the Langmuir isotherm was applied in the form of equation (5) as follows:

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

where Q and b are the Langmuir constants, indicating adsorption capacity and energy of adsorption respectively. C_e and q_e have their usual significance. 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 presented in Table 3.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 Figure 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 due to the interaction between the metal ions on the surface of the adsorbent and in the bulk of the solution [23, 24].The metal ions normally forms a surface layer, which is only one molecule thick, that is monolayer on the surface of the adsorbent [28]. Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation (6) [23-25].

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

where, C_0 is the optimum initial concentration (ppm) of metal ions and *b* is the Langmuir constant. The value of separation factor R_L indicates the shape of the isotherms and nature of adsorption i.e. the adsorption is favorable or not, as per the criteria given subsequently [23].

R_L value	Nature of the process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of Langmuir constants *b* and R_L are presented in Table 3.Since R_L values lie between 0 and 1 for all three temperature studied, it is seen that the adsorption of copper is favorable [25].

Equilibrium parameter

The plots of ln q_e/C_e versus q_e of the reactions are given in Figure 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 lnK_0 vs 1/T is found to be linear as shown in Figure 6. ΔH° and ΔS° are determined from the slops and intercepts of the plot [26].The negative values of the standard free energy change (ΔG°) for this reaction suggests that the sorptive nature is spontaneous. The positive value of ΔH° (3.32 KJ/mol) indicates that the process of adsorption is endothermic and irreversible, probably due to nonpolar interactions [27] the positive value of entropy change (ΔS° = 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 [10].

Natarajan-Khalaf equation:

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

Lagergren equation;

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

Bhattacharya and Venkobachar equation:

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

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 4. 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 4). 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 [27-32]. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [23-28].

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

where q_t is the amount adsorbed (in mg/gm) at time ,t; C is the intercept and K_p is the intra-particle diffusion rate constant (in mg/gm/min$^{0.5}$). 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 [29-30] as the rate determining step. The intra-particle diffusion plots are shown in Figure 10.the values of intercept (C) give an idea about the boundary layer thickness, that is the larger the intercept , greater is the boundary layer effect [29-30].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, which is predominant in the rate-controlling step 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 [31].

Table 1 XRF Chemical Analysis of Bentonite

Constituent	Weight Percentage	Constituent	Weight Percentage
SiO_2	45.47	CaO	6.00
Fe_2O_3	8.23	MgO	4.06
K_2O	2.50	Al_2O_3	17.50
Loss on ignition	11.96	Na_2O	4.04

Table 2 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

Table 3 Values of Langmuir constants for adsorption of copper for activated charcoal

Temperature (K)	Langmuir constant		r	R_L
	b (L.mg$^{-1-)}$	q_{max} (mg.g^{-1})		
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

Table 4 Kinetics and Dynamics of adsorption of Copper by activated Charcoal:

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

Figure 1 Effect of adsorbent dosage on percentage removal of copper

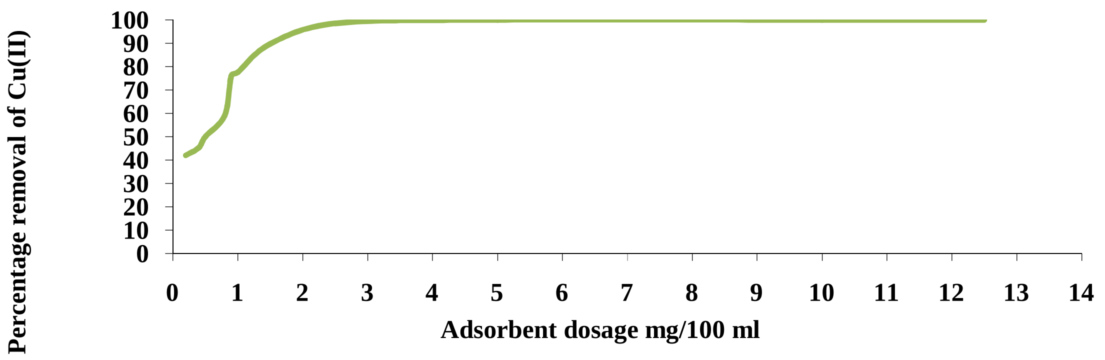


Figure 2 Effect of Contact Time

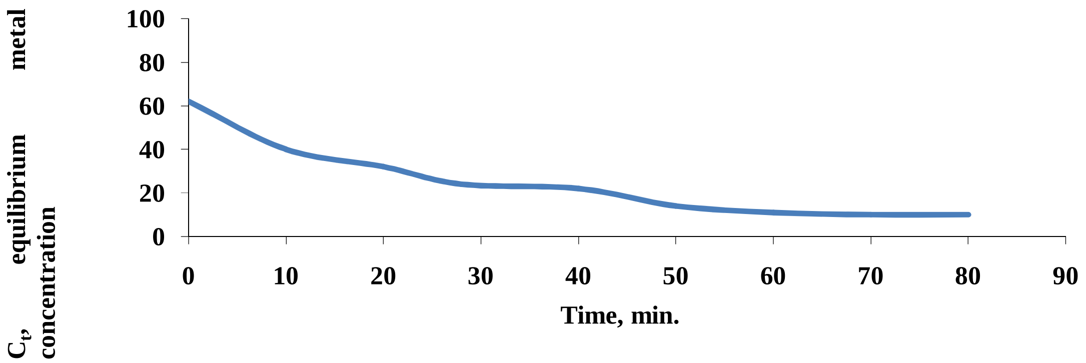


Figure 3 Plot of C_e vs q_e at different temperatues of copper for bentonite

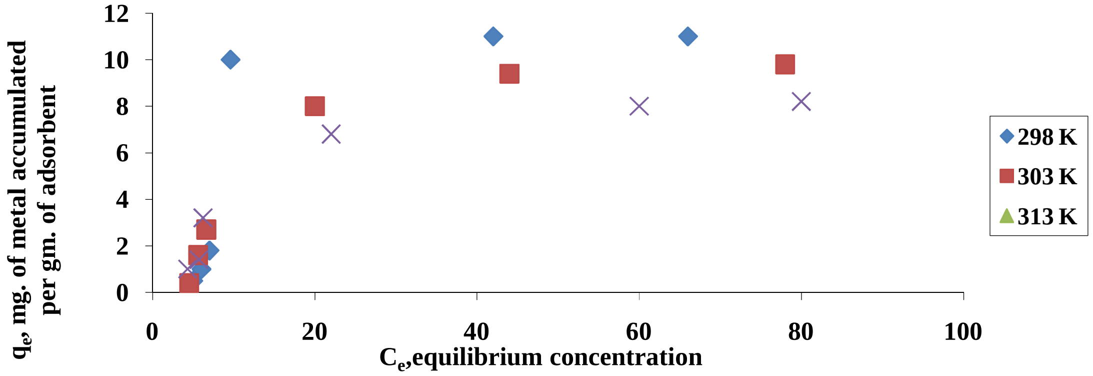


Figure 4 Langmuir isotherm

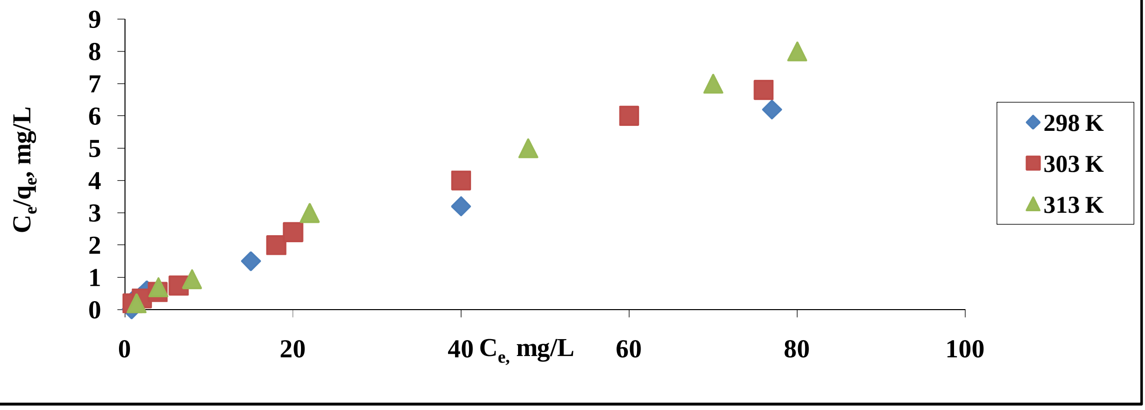


Figure 5 Plot of ln q_e/Ce vs q_e

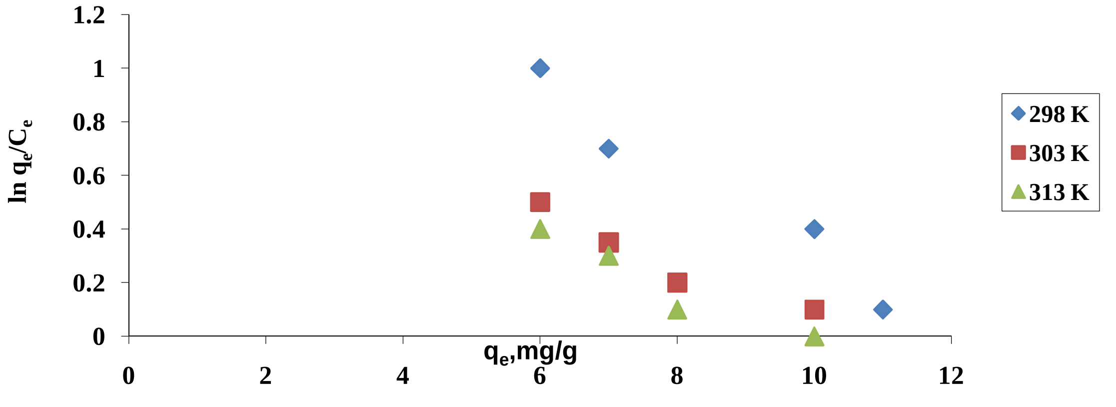


Figure 6 Plot of $\ln K_0$ vs 1/T

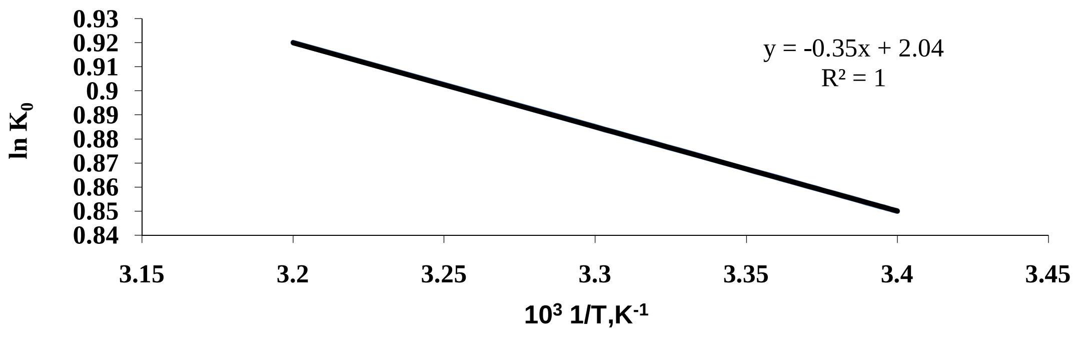


Figure 7 Natrajan-Khalaf kinetic model of copper for bentonite

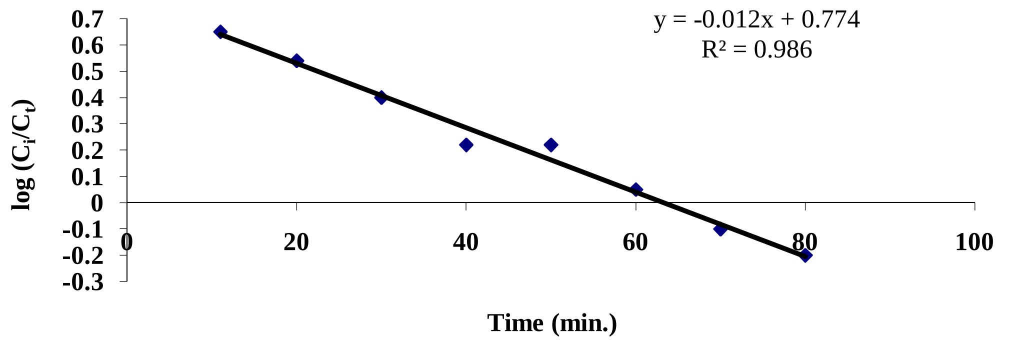


Figure 8 Lagergren kinetic model of copper for bentonite

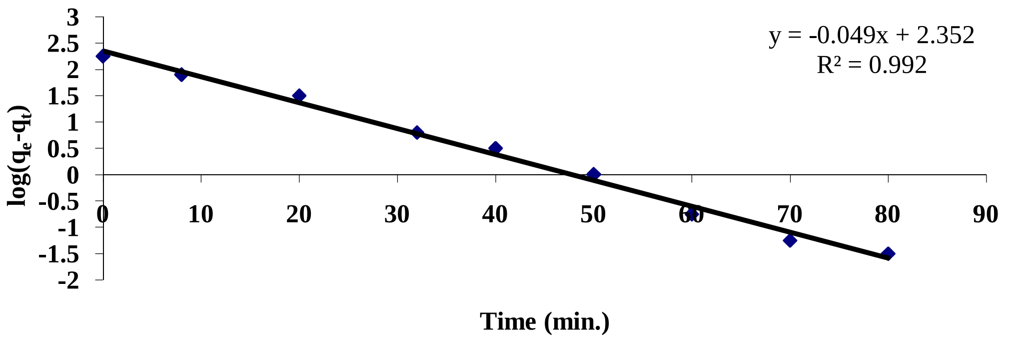


Figure 9 Bhattacharya and Venkobachar kinetic model of copper for bentonite

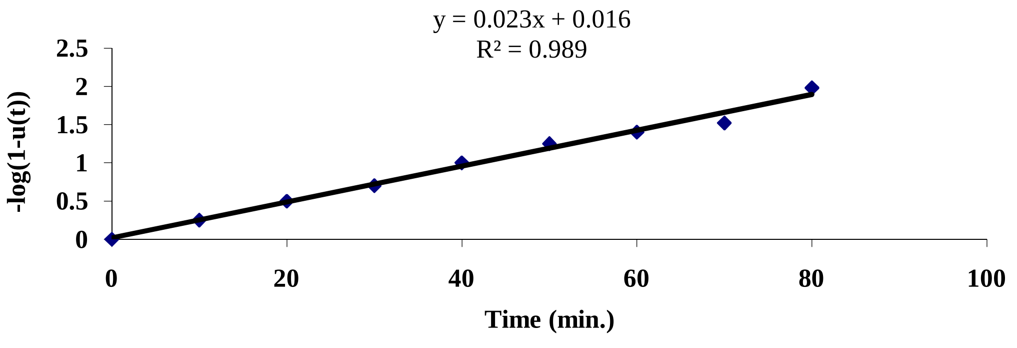
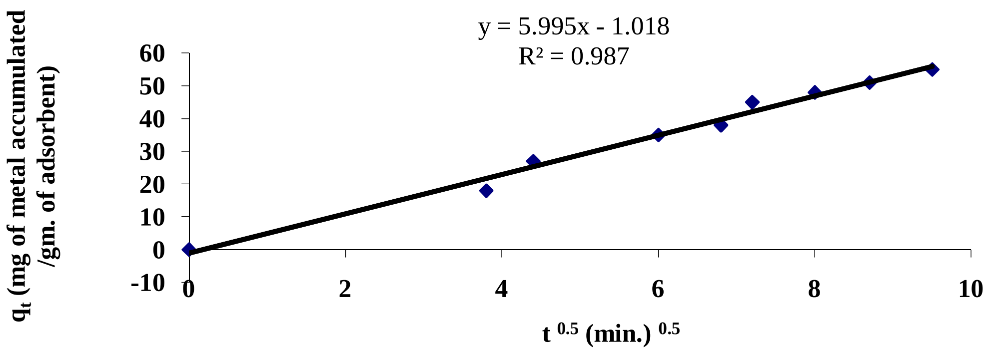


Figure 10 Plot of intra particle diffusion model of copper for bentonite



CONCLUSION

The conclusions derived from the present studies are:

1. The percentage removal of metal ions increase with decrease in initial concentration and increase in contact time, dosage of adsorbent and initial pH of the solution.
2. The adsorption data obeyed the Langmuir and Freundlich isotherms and indicate the formation of unimolecular layer of adsorbates.
3. The adsorption process obeys various first order kinetic equations. Therefore, it is first order with interaparticle diffusion as the rate determining step.
4. Bentonite could be used as and adsorbent for the effluent treatment, especially for the removal of metal ions.

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