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Removal of Copper from Aqueous Solutions Using Sawdust, Zeolite and Activated Carbon: Equilibrium Time Convergence

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Abstract. In this study, adsorption of copper(II) ions from aqueous solutions on sawdust, zeolite and activated carbon was studied using batch experiment techniques. The effect of different parameters such as pH of solution, adsorption time and amount of adsorbents were evaluated. Favourable pH for maximum copper adsorption was 6, 6 and 4 for sawdust, zeolite and activated carbon, respectively. The equilibrium of copper adsorption has been described by the Langmuir, Freundlich and Temkin isotherms and their fitness for adsorption was compared. The Temkin model had a better fitness than the other models. Maximum adsorption capacity of sawdust, zeolite and activated carbon were 96.11%, 96.2% and 97.02% (mg/g), respectively. The study of applicability of kinetic models of Lagergren (1898) and Ho *et al.* (1996) showed the latter model to be better fit than the former. The rates of adsorption obey the rules of A-order model with good correlation.

Keywords: adsorption efficiency, sawdust; zeolite, activated carbon, equilibrium time, copper

Introduction

Presence of heavy metals in water and wastewater beyond a certain limit motives toxicity in natural sources. Several methods are used to decrease heavy metal concentration in water and wastewater (Esteves *et al.*,2000). Among heavy metals, Pb, Zn, Cu and Cd head the list of environmental threats because even at extremely low concentrations they can cause brain damage in children (Ahmedna *et al.*, 2004). Treatment of aqueous wastes containing soluble heavy metals involves decreasing concentration of metals followed by their recovery or secure disposal of the waste (Ertugay and Bayhan 2010).

Copper is among the common toxic pollutants found in industrial effluents. Efficient removal of copper from wastewater by appropriate treatments has long been a crucial issue (Da'na *et al.*, 2010). There is wide usage of copper in industry such as relating to electroplating, electrical appliances, machinery, transportation and military supply sites etc. Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage and stomach and intestinal irritation (Kabra *et al.*, 2008). The accumulation of Cu^{2+} in human body also causes brain, skin, pancreas and heart diseases (Veli and Aly¨uz, 2007).

Several adsorbents are suggested for removing heavy metals from aqueous media. Zeolite exhibited high selectivity for certain heavy metal ions such as Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} (Sljivic *et al.*, 2009; Sreejalekshmi *et al.*, 2009; Camilo *et al.*, 2005; Babel and Karniawan, 2003). Sawdust is one of the cheapest and abundantly available adsorbents and has the capacity of adsorbing heavy metals from water and wastewater. Metal ions connect to functional groups of sawdust such as COOH and OH and release H^+ ions (Asadi *et al.*, 2008). Several studies are available relating to the preparation of activated carbon from agricultural wastes such as *Phaseolus aureus* hulls (Rao *et al.*, 2009), walnut, hazelnut, almond, pistachio shell and apricot stone (Kazemipour *et al.*, 2008), maize cob husk (Igwe *et al.*, 2005), nut shells (Ahmedna *et al.*, 2004), black gram husk (Saeed and Iqbal, 2003), peanut husks (Ricordel *et al.*, 2001), sugarcane bagasse pith (Krishnan

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*Author for correspondence; E-mail: hirmandriver@gmail.com and Anirudhan, 2002 a;b) and their application for the removal of copper from water and wastewater. Still, there exists the need to develop suitable low-cost indigenous adsorbents for the removal of metal ions from aqueous solutions (Rao *et al.,* 2009). Also there are a few studies available on removal of Cu(II) from water and wastewater such as zeolite, clay and a diatomite (Sljivic *et al.,* 2009), three species of dead fungal biomasses (Li *et al.,* 2009) and sawdust (Asadi *et al.,* 2008; Meena *et al.,* 2007).

For treating water and wastewaters, adsorption was found to be a promising technique for removal of trace amount of adsorbates from aqueous solutions. Moreover, waste materials and their value added products used as adsorbent for treating heavy metals can improve the economic viability of the adsorption process (Sreejalekshmi *et al.,* 2009). At low concentrations, pollutants can be more effectively removed by ion-exchange or adsorption on solid sorbents such as activated carbon (Nelson *et al.,* 1974; Sigworth and Smith,1972), activated carbon from rice hulls and coal fly ash (Sen and De, 1987; Prabhu *et al.,* 1981). Presently, household water purification systems in south of Iran (Heidari and Moazed, 2008; Heidari *et al.,* 2008) use activated carbon which is very expensive. The aim of this study is checking the feasibility of using zeolite and sawdust for removal of copper (II) in low concentrations in order to choose the optimal economical adsorbent. In this paper, the sorption kinetics and the convergence of equilibrium time for removal of Cu(II) from aqueous solutions using sawdust, zeolite and activated carbon in low concentrations are reported.

Materials and Methods

Preparation of adsorbents. Sawdust was obtained from a local factory near Zabol, Iran. It was passed through 1.5 mm mesh sieve, washed with hot distilled water and finally dried in oven at 90 °C for 3 h. Zeolite was collected from Firoozkouh village in the city of Tehran, Iran. Sawdust, zeolite and activated carbon particles of 1.5 mm diameter were used. The activated carbon used was a commercial product of the Merck Chemicals Company prepared from wood.

Adsorbate solution supply. Copper (II) stock solution was prepared from analytical grade copper nitrate $Cu(NO_3)_2$ in concentration of 1000 mg/L. For aqueous solution of copper nitrate, double distilled water was used. Test samples of various concentrations were prepared from this stock solution (APHA, AWWA, WPCF, 1989).

Instrumentation. The measurements were made with a Spectrophotometer (model AA220 made by Varian Co., Australia). pH was determined with model 630 metrohm pH meter with combined glass calomel electrode.

Batch mode adsorption studies. For determining the optimum adsorption pH for all the 3 adsorbents, separate 250 mL Erlenmeyer flasks were used which were washed with dishwashing liquid and then with acid and deionized water. For each experiment, 100 mL of copper solution of 10 mg/L concentration and 1 g of adsorbent were placed in each flask. The pH of solution was adjusted, at 2, 3, 4, 5, 6, 7, 8 and 9. The samples were agitated at room temperature (30±1 °C) using a mechanical shaker at a constant rate of 150 rpm for 12 h to attain equilibrium (Heidari *et al.,* 2008). Then solutions were passed through Whatman filter paper No. 45. The pH of solutions was adjusted at 2 using nitric acid and the adsorption experiments were performed immediately. As pH of the solution approaches 2, cations remaining in the solution will have a lower chance of being adsorbed by the glass surface because the competition between cations and H^+ ions increases. Thus, by reducing the pH to 2, experimental errors will be lowered to minimum. While running kinetic adsorption experiment, 1 mg of sawdust adsorbent and 100 mL of copper solution at 1 mg/L concentration were added to each flask and their pH was adjusted at 6. The kinetics and adsorption contact time were determined for 5-150 min then the samples were removed from the shaker and the concentration of solution was measured. The experiments were repeated, varying the initial metal ion concentration from 10 to 300 mg/L. The experiments were performed similarly with zeolite and activated carbon. It is notable that in all the experiments, pH adjustments were made using dilute aqueous solutions of HCl and NaOH. pH of solution was measured at each stage of the experiment with pH meter (Model: PTR 79).

Kinetic models. The two adsorption kinetic models used in this study are pseudo-first-order and pseudo-second-order equations developed by Lagergren (1898) and Ho *et al.* (1996), respectively. The Lagergren pseudo-first-order equation is as below:

$$\log(q_e \quad q_t) = \log q_e - \frac{\mathbf{k}_1}{2.303} \tag{1}$$

Where k_1 is the rate constant of pseudo-first-order adsorption and q_e and q_t denote the amount of adsorption at equilibrium and at time t, respectively. The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

Where q_e and q_t are the amount of metal ion adsorbed (mg/g) at equilibrium and at time t, respectively. k_2 is the adsorption constant (g/mg/min). The product $k_2 q_e^2$ is the initial sorption rate represented as $h = k_2 q_e^2$. Kinetic parameters of these models were calculated from the slope and intercept of the linear plots of log $(q_e - q_t)$ *vs* t and t/q_t *vs* t (Asano, 1998).

Adsorption isotherm models. The sorption equilibrium data of copper ion onto activated carbon, zeolite and sawdust, were analyzed in terms of Langmuir, Freundlich and Temkin isotherm models (Pehlivan *et al.*, 2008). For performing the isotherm experiments, the flasks were washed with dish washing liquid, abundant water and finally with deionized water. The experiments were conducted at the optimum pH and room temperature. Adsorption isotherms were studied at different initial metal ion concentrations over a range of 10-120 g/L in 100 mL metal solution of 50 mg/L concentration and the samples were placed on mechanical shaker at a constant rate of 150 rpm for 2 h. Afterwards, the samples were filtered and amount of copper ions was measured; this process was repeated for all the adsorbents. All the experiments were carried out in duplicate and the values were reported as average of two readings.

Langmuir isotherm. The Langmuir adsorption isotherm is probably the most widely applied one. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites of the adsorbent. The saturated monolayer isotherm can be represented by the below given equation (Runping *et al.*, 2005).

$$q_e = \frac{abC_e}{1 + a\,C_e} \tag{3}$$

Where q_e is the amount of metal ions adsorbed (mg/g), C_e the equilibrium concentration (mg/ L), b is the monolayer adsorption capacity of the adsorbent (mg/g) and a is the Langmuir adsorption constant (L/mg) related to the free energy of adsorption.

Freundlich isotherm. The Freundlich isotherm equation $q_e = kC_e^{1/n}$ can be written in the linear from as given below:

$$\log q_e = \log k + \frac{1}{n} \log C_e \tag{4}$$

Where q_e and C_e are the equilibrium concentrations of metal ions in the adsorbed and liquid phases in mmol/g and mmol/L, respectively, k and n are the Freundlich constants which are related to the sorption capacity and intensity, respectively. The Freundlich constants k and n can be calculated from the intercept and slope of the linear plot of log q_e *vs* log C_e.

Temkin isotherm. Temkin isotherm was derived assuming that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. It is expressed as:

$$q_e = \frac{RT}{b}\ \mathrm{In}(k_T C_e) = B_1 \mathrm{In}(k_T C_e) \tag{5}$$

Where q_e and C_e are the equilibrium concentrations of metal ions in the adsorbed and liquid phases in mmol/g and mmol/L, respectively, and constant $B_1 = RT/b$ is related to the heat of adsorption, R the universal gas constant (J/mol/K), T the temperature (K), b the variation of adsorption energy (J/mol) and k_T is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy.

Adsorbent characterization. Activated carbon is a form of carbon that has been processed to make it extremely porous and thus having a very large surface area available for adsorption or chemical reactions. Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 500 m². Activated carbon does not bind well to certain chemicals, including alcohols, glycols, ammonia, strong acids and bases, metals and most inorganics, such as lithium, sodium, iron, lead, arsenic, fluorine and boric acid. Therefore, it has been used in adsorption processes as an efficient adsorbent. Zeolite has received much attention due to the fact that it has a wide range of structure having different chemical composition and physicochemical properties. In general, zeolite structure consists of alumino-silicate crystalline material. The zeolite crystal is made up of the interlocking tetrahedrons of SiO^4 and AlO^{4-}. Due to these properties, zeolite has been used for heavy metal adsorption. Sawdust is one of the low-cost adsorbents which consists of lignin, cellulose and hemicellulose, with polyphenolic groups playing important role for binding dyes through different mechanisms (Gupta and Suhas, 2009). In order to characterize the adsorbents, their surface area was determined using the methylene blue adsorption method described by Viladkar *et al.* (1996). Other properties of the adsorbents are shown in Table 1.

Table 1 Characteristics of adsorbents

Parameter	Sawdust	Zeolite	Activated carbon
Surface area (m^2/g)	600 - 750	640 - 800	850 - 1000
Bulk density (kg/ m^3)	1020	2100	763.5
Moisture (%)	8.50	7-8	1-2

Results and Discussion

Studies on pH. pH is one of the most important parameters controlling the adsorption. The effect of pH on the adsorption of copper ions from water samples was investigated in the pH range of 2 to 8. The pH of the solution sample was adjusted to the required value by addition of sodium hydroxide and hydrochloric acid. The results showed (Fig. 1) that the extraction percentage was almost constant and quantitative at pH 6, 6 and 4 for sawdust, zeolite and activated carbon, respectively. Since adsorption process is pH sensitive and also due to different binding conditions of the adsorbent groups, the maximum adsorption efficiency for activated carbon occurred at pH 4. Results obtained by others are the same as the study of Sreejalekshmi *et al.* (2009) which revealed that this difference may be due to the utilization of new adsorption sites offered by –COOH groups on the adsorbed citric acid. At higher pH, the adsorption efficiency decreased a little. The adsorption capacity of copper for sawdust and zeolite increased from pH 2-5 but it decreased above pH 6, whereas for activated carbon, it increased from 2-4 and decreased above pH 4. Fan *et al.* (2009) stated that the removal of Ni(II) in 0.01M $NaNO_3$ solutions was more at pH 2-8 than at other pH. The rapid increase in adsorption efficiency is due to two reasons; first at low pH, H^+ ions existed in solution which competed with copper ion for surface adsorption, second is that there is a critical pH range for each hydrolysable metal ion; at which the metal adsorption efficiency reaches from low level to maximum level. This pH range is called surface adsorption edge (Kumar and Bandypadhyay, 2006). Decrease in adsorption of copper ions is due to formation of soluble carboxylic groups (Krishnan and Anirudhan, 2002 a; Raji *et al.*, 1997). The little decrease in adsorption in this study, at pH levels higher than optimum pH, agrees with other studies (Pehlivan *et al.*, 2008; Gupta *et al.*, 2003; Krishnan and Anirudhan, 2002 b; Mathialagan *et al.*, 2003).

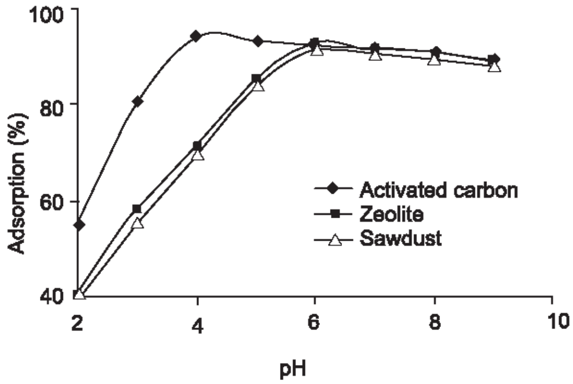

Fig. 1. Entrance pH effect on copper adsorption efficiency of sawdust, zeolite and activated carbon.

Kinetic adsorption studies. ***Effect of contact time and initial concentration.*** Figures 2-4 show the effects of contact time and initial concentration on copper

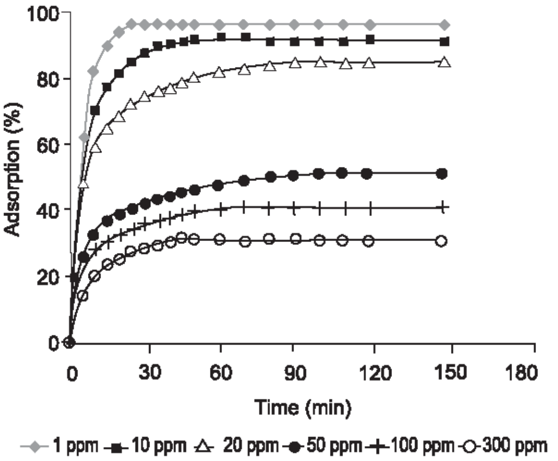

Fig. 2. Effect of contact time and copper initial concentration on sawdust adsorption efficiency.

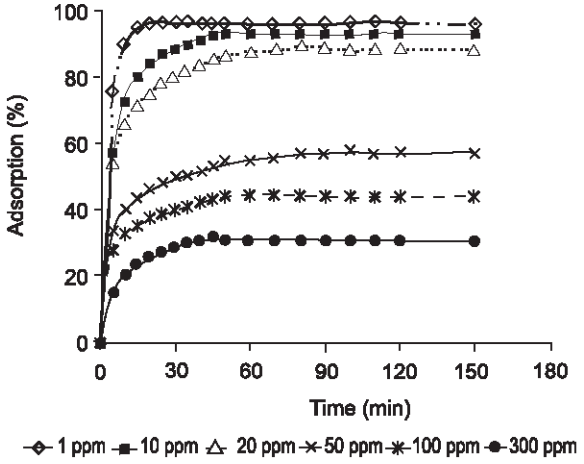

Fig. 3. Effect of contact time and copper initial concentration on zeolite adsorption efficiency.

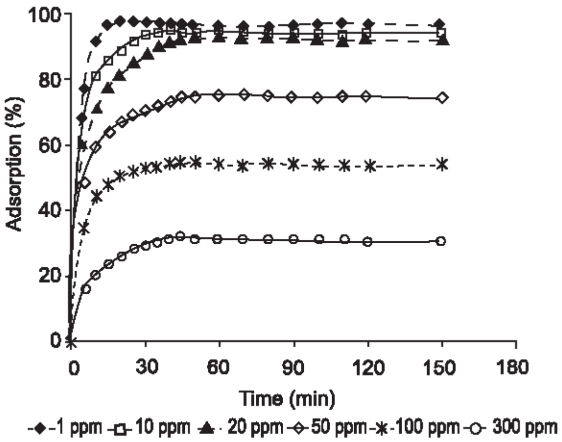

Fig. 4. Effect of contact time and copper initial concentration on activated carbon adsorption efficiency.

adsorption efficiency for sawdust, zeolite and activated carbon. It can be seen that with increase in the contact time, adsorption efficiency of all the 3 adsorbents increased. Therefore, for each of the 3 adsorbents, minimum equilibrium time was for concentration 1 mg/L and maximum equilibrium time for concentration 50 mg/L. In other words, the adsorption speed was maximum in concentration of 1 mg/L. Li *et al.* (2009) found that copper biosorption increased with the rise of initial Cu(II) ion concentration at un-perceptible pH. Under these conditions since more copper ions were available for adsorption at higher concentration, adsorption efficiency increased. The adsorption kept constant because the adsorbent became saturated after 50 mg/L metal ion concentration.

Effect of initial concentration on equilibrium time. Figure 5 shows the variation in equilibrium time of adsorption of copper in different concentrations by sawdust, zeolite and activated carbon. The maximum equilibrium time for sawdust, zeolite and activated carbon was 110, 100 and 70 min, respectively, in 50 mg/L concentration. With the increase in the concentration of solution from 50 to 300 mg/L, the equilibrium time of adsorption decreased. At higher concentrations, due to accumulation of metal ions around the adsorbent and there being more chances of metal contact with the adsorbent, the adsorbance is completed in less time and the process attains equilibrium, sooner. Also it was observed that by decreasing the concentration of solution from 50 to 1 mg/L, the equilibrium time for sawdust, zeolite and activated carbon decreased to 25, 20 and 20 min, respectively. With decreasing the initial concentration, the equilibrium time is expected to increase due to less chances of metal contact with the adsorbent. But due to the low quantity of metal ions in solution at low concentrations, this small number of ions is adsorbed in less time; thus with the decrease in the initial concentration of copper, the equilibrium time also decreased. Hence, the concentration of solution is the determining factor of equilibrium time and not the adsorbent capacity. Also with decreasing the concentration of solution from 50 to 1 mg/L, the difference between the equilibria of all the 3 adsorbents gradually decreased and then converged (Fig. 5). Convergence of equilibrium time at higher concentrations was also observed. It is evident from Fig. 5 that at median concentrations, the difference between the equilibrium time reached its maximum level, hence the effect of adsorbent capacity then was more obvious.

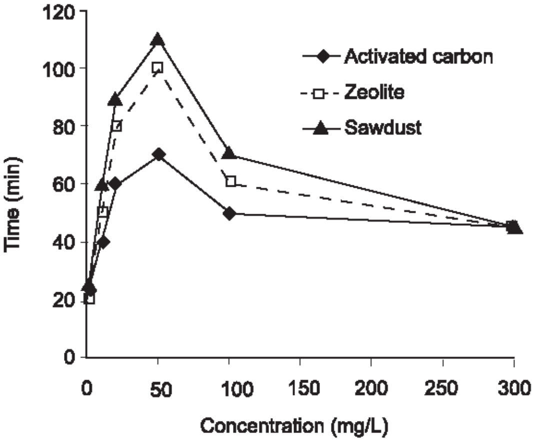

Fig. 5. Effect of initial concentration of copper on equilibrium time.

Effect of initial concentration on adsorption efficiency. Variation in adsorption efficiency (adsorption efficiency in equilibrium time) of sawdust, zeolite and activated carbon for copper in different concentrations is shown in Fig. 6. It is obvious that with decreasing the concentration of copper solution from 300 mg/L to 1 mg/L, the adsorption efficiency of sawdust, zeolite and activated carbon increased. Thus the maximum adsorption efficiency in 1 mg/L concentration was 97.02% for activated carbon, 96.2% for zeolite and 96.11% for sawdust. With the decrease in the initial concentration of solution (and thus the number of metal ions in the solution) from 100 to 50 mg/L, the difference in the adsorption efficiency of all the adsorbents increased; with further decrease of the concentration from 50 mg/L to 1 mg/L, the difference between the adsorption efficiency of all the adsorbents decreased and became closer and closer

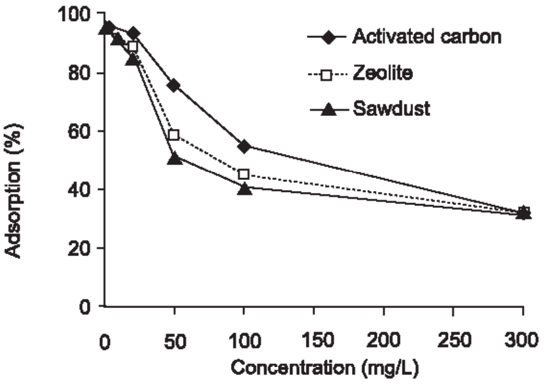

Fig. 6. Variation of adsorption efficiency with copper initial concentration in equilibrium time.

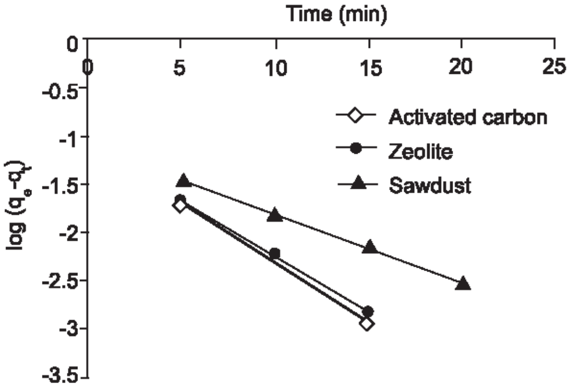

Fig. 7. Fitting Lagergren model for sawdust, zeolite and activated carbon adsorbents.

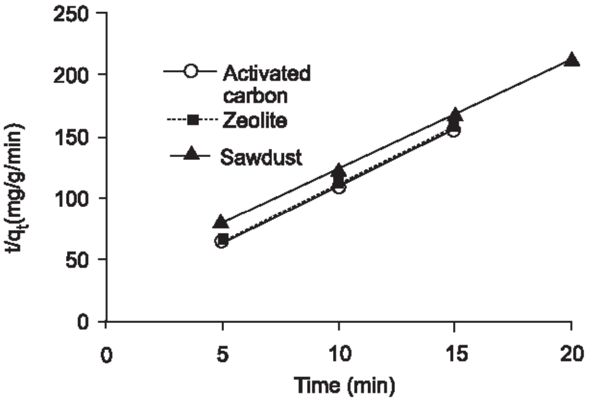

Fig. 8. Fitting Ho *et al.* (1996) model for sawdust, zeolite and activated carbon adsorbents.

to each other till they converged at the concentration of 1 mg/L. This conforms with the other studies. Mukherjee *et al.* (2007) showed that phenol removal efficiency decreased with the increase of the initial phenol concentration. At low concentrations, the limiting parameter of adsorption efficiency is the concentration of solution and adsorbent capacity does not have an effective role (Heidari *et al.,* 2008). Thus with decreasing the initial concentration of metal ions, the difference of the adsorption efficiency between the adsorbents decreases and ultimately they converge with each other. With increasing the concentration of solution from 50 to 300 mg/L, the difference of the adsorption efficiency between the adsorbents decreases as the adsorption efficiencies of all the sdsorbents become almost equal.

Kinetic adsorption studies. The models of Lagergren (1898) and Ho *et al.* (1996) fitted with the data obtained from the kinetic adsorption experiments for initial concentration. For determining the Lagergren coefficients, log (q_e-q_t) was plotted *vs* t (Fig. 7).

Ho *et al.* (1996) model correlation coefficients for sawdust, zeolite and activated carbon resulting from plotting t/q_t *vs* t are shown in Fig. 8.

As shown in Table 2, correlation coefficient of Ho *et al.* (1996) model is greater than the correlation coefficients obtained for Lagergren model for all the adsorbents. It, therefore, follows that Ho *et al.* (1996) model describes the data better than Lagergren model. Also the former model has a good compatibility with the present results. Its application to all the adsorbents showed that the speed of surface adsorption of copper by activated carbon is more than by zeolite and sawdust adsorbents. Kurniawan *et al.* (2006), in their study on different adsorbents, stated that among the adsorbents

Table 2. Constant coefficient of kinetic adsorption models for copper by sawdust, zeolite and activated carbon adsorbents

	Ho *et al.* model			Lagergren model			
Absorbent	R^2	K_2	$q_{e\ cal}$	R_2	K_1	$q_{e\ cal}$	$q_{e\ cal}$
Sawdust	0.9997	2.24580	0.11288	0.9982	0.16074	0.07785	0.09611
Zeolite	0.9991	4.278184	0.10761	0.9975	0.25885	0.06989	0.0962
Activated carbon	0.9996	4.471541	0.10931	0.9971	0.28764	0.08824	0.09702

derived from agricultural waste, hazelnut shell activated carbon (Cr(VI): 170 mg/g), orange peel (NiII): 158 mg/g and chemically modified soybean hull (CuII): 154.9 mg/g) had significantly higher metal adsorption capacities, compared to those from natural materials such as clay Ni(II): 81 mg/g; Cu(II): 83 mg/g; Zn (II): 63 mg/g). The kinetic studies of Lu *et al.* (2009) showed that correlation coefficients of the pseudo-first-order model were in the range 0.8507-0.9990 and for the pseudo-second-order model were in the range 0.9446-0.9988.

Figure 9 shows the variation of Ho *et al.* (1996) model coefficients with change in concentration of activated carbon; maximum value of k_1 was attained at the concentration of 1 mg/L and equals 0.287/min. With increasing the concentration of solution from 1 to 10 mg/L, the value of k_1 decreased down to 0.115. At concentration of 20-300 mg/L, the value of k_1 becomes very low and approximately constant. This proves that with the decrease in concentration, the speed of adsorption increases, hence the equilibrium time will decrease. Sreejalekshmi *et al.* (2009) in their studies showed that between the pseudo-first-order and the pseudo-second-order kinetic models, the former one was found to be the best-fit kinetic model for adsorption.

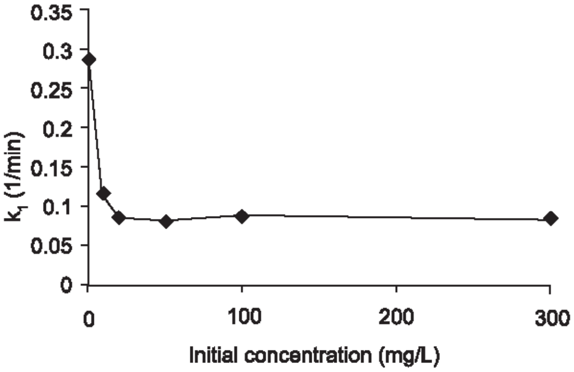

Fig. 9 . Variation of Ho *et al.* (1996) model with initial concentration of copper for activated carbon adsorbent.

Adsorption isotherm studies. The results of adsorption isotherm were analyzed using correlation method by SPSS (version 14). Model parameters and their statistical characteristics were accomplished using the nonlinear correlation for Langmuir, Freundlich and Temkin isotherm models. The results were calculated under 95% level of significance (Table 3). Regression coefficients showed that Temkin model had better fitness than the Langmuir and the Freundlich ones.

Dimeionless separation factor R_L can be calculated from the Langmuir constant using the equation as below:

$$R_L = 1/(1 - a.\ C_0) \qquad (6)$$

R_L is related to the nature of the interaction between adsorbent and adsorbate and also isotherm type: unfavourable ($R_L>1$), linear ($R_L=1$), favourable ($0<R_L<1$), or irreversible ($R_L= 0$) (Sljivic *et al.*, 2009). The calculated R_L values for various initial Cu(II) concentrations were 0.0340 (activated carbon), 0.0340 (zeolite) and 0.0769 (sawdust). Thus, the adsorption process in all the investigated systems was favourable. These results correspond with those of Madhava *et al.* (2009) and Sljivic *et al.* (2009) relating to copper removal studies. Freundlich coefficient value (n), less than 1 also matches with the values of Mukherjee *et al.* (2007) and Mathialagan *et al.* (2003). The value of $1/n > 1$, shows that the adsorbent has suitable capacity for metal ion adsorption because curve gradient is intensive. The copper adsorption efficiency for activated carbon was more than that of other adsorbents; coefficient *k* was 7.42, 5.53 and 5.32 for activated carbon, zeolite and sawdust, respectively.

Table 3. Copper adsorption parameters calculated by Langmuir Freundlich and Temkin equations

Model	Parameters	Activated carbon	Zeolite	Sawdust
Langmuir	R^2	0.902	0.932	0.880
	a (L/mg)	0.57	1.20	0.24
	b (mg/g)	23.72	13.55	11.07
Freundlich	R^2	0.832	0.786	0.772
	k	7.42	5.53	5.32
	n	0.67	0.79	0.696
Temkin	R^2	0.977	0.965	0.993
	b (J/mol)	10.73	9.26	7.39
	K_T (L/mg)	4.66	5.71	3.79

The Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interaction (Mathialagan *et al.,* 2003). With respect to the experimental values, the adsorption capacities predicted by Temkin model were higher (Table 3). The adsorption energy (b), obtained from Temkin isotherm was the highest for activated carbon and the lowest, for sawdust. The positive values of parameter b indicated that the processes were exothermic (Rao *et al.,* 2009; Sljivic *et al.,* 2009).

Optimum adsorption occured at about pH 6 for all the adsorbents. In the range of 25-55 the adsorption efficiency of all the adsorbents was high. Obviously, at lower concentrations, the adsorption was higher. At concentration of 50, the equilibrium time was the highest; showing that at concentrations higher and lower than 50, there were some conditions at which the adsorption occured more rapidly. At extreme concentrations, the adsorption rate of each of the 3 adsorbents was the same indicating that there is not any difference between the adsorbents at these concentration ranges.

Conclusion

With decreasing the initial concentration of solution from 50 to 1 mg/L, the equilibrium time for sawdust, zeolite and activated carbon decreases and ultimately become closer to each other. Also with decreasing the initial concentration of copper in solution, the adsorption efficiency of all the adsorbents increases. Thus the less the copper concentration is, the less becomes the adsorbent capacity and *vice versa.*

References

Ahmedna, M., Marshall, W.E., Husseiny, A.A., Rao, R.M., Goktepe, I. 2004. The use of nutshell carbons in drinking water filters for removal of trace metals. *Water Research,* **38:** 1062-1068.

APHA, AWWA,WPCF 1989. *Standard Methods for the Examination of Water and Wastewater,* 17th edition, American Public Health Association, Washington, DC., USA.

Asadi, F., Shariatmadari, H., Mirghaffari, N. 2008. Modification of rice hull and sawdust sorptive characteristics for removal of heavy metals from synthetic solutions and wastewater. *Journal of Hazardous Materials,* **154:** 451-458.

Asano, T. 1998. *Wastewater Reclamation and Reuse,* 1528 pp., Technomic Publishing Co. Inc., Lancaster, Pennsylvania, USA.

Babel, S., Kurniawan, T. A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials* **B97:** 219-243.

Camilo, C., Carmen, G., Paula, M. 2005. Sorption characteristics of heavy metal ions by a natural zeolite. *Journal of Chemical Technology and Biotechnology,* **80:** 477-481.

Da'na, E., De Silva, N., Sayari, A. 2010. Adsorption of copper on amine-functionalized SBA-15 prepared by co-condensation: kinetic properties. *Chemical Engineering Journal,* **166:** 454-459.

Ertugay, N., Bayhan, Y.K. 2010. The removal of Copper (II) ions by using mushroom biomass *Agaricus bisporus* and kinetic modeling. *Desalination,* **255:** 137-142.

Esteves, A.J.P., Valdman, E., Leite, S.G.F. 2000. Repeated removal of cadmium and zinc from an industrial effluent by waste biomass *Sargassum* sp. *Biotechnology Letters,* **22:** 499-502.

Fan, Q.H., Shao, D.D., Wu, W.S., Wang, X.K. 2009. Effect of pH, ionic strength, temperature and humic substances on the sorption of Ni(II) to Na-attapulgite. *Chemical Engineering Journal,* **150:** 188-195.

Gupta, V.K., Jain, C.K., Ali, I., Shahram, M., Saini, V.K. 2003. Removal of cadmium and nickel from wastewater using bagasse fly ash a sugar industry waste. *Water Research,* **37:** 4038-4044.

Gupta, V., Suhas, K. 2009. Application of low-cost adsorbents for dye removal - A review. *Journal of Environmental Management,* **90:** 2313-2342.

Heidari, Z.S., Moazed, H. 2008. Convergence of adsorption efficiency of cadmium by rice husk. *Journal of Sciences Shahid Chamran University,* **20:** 126-136.

Heidari, Z., Moazed, H., Jaafarzade, N., Jou, P.H. 2008. Removal of low concentrations of cadmium from water using improved rice husk. *Journal of Water and Wastewater,* **19:** 1024-5936.

Ho, Y.S., Wase, D.A.J., Forster, C.F. 1996. Kinetic studies of competitive heavy metal adsorption by *Sphagnum* moss peat. *Environmental Technology,* **17:** 71-77.

Igwe, J.C., Ogunewe, D.N., Abia, A.A. 2005. Competitive adsorption of Zn(II), Cd(II) and Pb(II), ions from aqueous and non-aqueous solutions by maize cob and husk. *African Journal of Biotechnology,* **4:** 1113-1116.

Kabra, K., Chaudhary, R., Sawhney, R.L. 2008. Solar photocatalytic removal of Cu(II), Ni(II), Zn(II) and Pb(II): Speciation modeling of metal-citric acid complexes. *Journal of Hazardous Materials,* **55:** 424-432.

Kazemipour, M., Ansari, M., Tajrobehkar, S., Majdzadeh, M., Kermani, H.R. 2008. Removal of lead, cadmium, zinc and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell and apricot stone. *Journal of Hazardous Materials,* **150:** 322-327.

Krishnan, K.A., Anirudhan, T.S. 2002 a. A preliminary examination of the adsorption characteristics of Pb(II) ions using sulphurised activated carbon prepared from bagasse pith. *Indian Journal of Chemical Technology,* **9:** 32-40.

Krishnan, K.A., Anirudhan, T.S. 2002 b. Uptake of heavy metals in batch systems by sulfurized steam activated carbon prepared from sugarcane bagasse pith. *Industrial and Engineering Chemical Research,* **4:** 5085-5093.

Kumar, U., Bandyopadhyay, M. 2006. Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource Technology,* **97:** 104-109.

Kurniawan, T.A., Chan, G.Y.S., Lo, W.H., Babel, S. 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment,* **366:** 409-426.

Lagergren, S. 1898. About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakad Emiens Handlingar,* **24:** 1-39.

Li, X.N, Xu, Q.Y., Han, G.M., Zhu, W.Q., Chen, Z.H., He, X.B., Tian, X. 2009. Equilibrium and kinetic studies of copper(II) removal by three species of dead fungal biomasses. *Journal of Hazardous Materials,* **165:** 469-474.

Lu, D., Cao, Q., Li, X., Cao, X., Luo, F., Shao, W. 2009. Kinetics and equilibrium of Cu(II) adsorption onto chemically modified orange peel cellulose biosorbents. *Hydrometallurgy,* **95:** 145-152.

Mathialagan, T., Viraraghavan, T., Cullimore, D.R. 2003. Adsorption of cadmium from aqueous solutions by edible mushrooms. *Water Quality Research Journal of Canada,* **38:** 499-514.

Meena, A.K., Kadirvelu, K., Mishra, G.K., Rajgoapal, C., Nagar, P.N. 2007. Adsorptive removal of heavy metals from aqueous solution by treated sawdust *(Acacia arabica). Journal of Hazardous Materials,* **150:** 604-611.

Mukherjee, S., Kumar, S., Misra, A.K., Fan, M. 2007. Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal. *Chemical Engineering Journal,* **129:** 133-142.

Nelson, F., Phillips, H.O., Kraus, K.A. 1974. Adsorption of inorganic materisls on activated carbon. *Engineering Bulletin Extension Service Purdue University,* **145:** 1076-1090.

Pehlivan, E., Yanik, B.H., Ahmetli, G., Pehlivan, M. 2008. Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. *Bioresource Technology,* **99:** 3520-3527 .

Prabhu, P.V.S.S., Narayan Swamy, M.S., Narosaraiu, 1981. Adsorption of Zinc from aqueous solutions by fly ash. *IAWPC (Indian Association for Water Pollution Control) Technical Annual,* **8:** 46-52.

Raji, C., Manju, G.N., Anirudhan, T.S . 1997. Removal of heavy metal ions from water using sawdust-based activated carbon. *Indian Journal of Engineering and Material Sciences,* **4:** 254-260.

Rao, M.M., Ramana, D.K., Seshaiah, K., Wang, M.C., Chien, S.W.C. 2009. Removal of some metal ions by activated carbon prepared from *Phaseolus aureus* hulls. *Journal of Hazardous Materials,* **166:** 1006-1013.

Ricordel, S., Taha, S., Cisse, I., Dorange, G. 2001. Heavy metals removal by adsorption onto peanut husk carbon: Characterization, kinetic study and modeling. *Separation and Purification Technology,* **24:** 389-401.

Runping, H., Zhang, J., Zou, W., Shi, J., Liu, H. 2005. Equilibrium biosorption isotherm for lead ion on chaff. *Journal of Hazardous Materials,* **B125:** 266-271.

Saeed, A., Iqbal, M. 2003. Bioremoval of cadmium from aqueous solution by black gram husk *(Cicer arientinum). Water Research,* **37:** 3472-3480.

Sen, A.K., De, A.K. 1987. Adsorption of mercury (II) by coal fly ash. *Water Research,* **21:** 885-888.

Sigworth, E. A., Smith, S. B. 1972. Adsorption of inorganic compounds by activated carbon. *Journal of American Water Works Association,* **64:** 386-391.

Sljivic, M., Smiciklas, I., Pejanovic, S., Plecas, I. 2009. Comparative study of Cu^{2+} adsorption on a zeolite, a clay and a diatomite from Serbia. *Applied Clay Science,* **43:** 33-40.

Sreejalekshmi, K.G., Krishnan, K.A., Anirudhan, T.S. 2009. Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies. *Journal of Hazardous Materials,* **161:** 1506-1513.

Veli, S., Aly¨uz, B. 2007. Adsorption of copper and zinc from aqueous solutions by using natural clay. *Journal of Hazardous Materials,* **149:** 226-233.

Viladkar, S., Agarwal, R., Kamaludin, A. 1996. Adsorption of adenine, adenosine and adenosine nucleotides on nickel(II) hexacyanoferrate(II). *Bulletin of Chemical Society of Japan,* **69:** 95-100.