Pak. J. Agri. Sci., Vol. 52(3), 619-625; 2015
ISSN (Print) 0552-9034, ISSN (Online) 2076-0906
http://www.pakjas.com.pk

REMOVAL OF ZINC AND COPPER FROM CONTAMINATED WATER USING *Ficus religiosa* LEAVES: KINETIC, EQUILIBRIUM AND MECHANISTIC STUDIES

Mohsin Kazmi[1], Naveed Ramzan[2], Nadeem Feroze[2], Qandeel Almas[1,*], Muhammad Zafar[1] and Zeeshan Saeed[2]

[1]Department of Chemical, Polymer and Composite Materials Engineering, University of Engineering and Technology, KSK Campus, 39021, Lahore, Pakistan; [2]Department of Chemical Engineering, University of Engineering & Technology, 54890, Lahore, Pakistan.
[*]Corresponding author's e-mail: qandeel_almas746@yahoo.com

The removal of copper {Cu(II)} and zinc {Zn(II)} ions from aqueous solution has been investigated using ground *ficus religiosa* leaves (GFRL). The characterization of GFRL was performed using CHNS analyzer, X-ray diffraction (XRD) and scanning electron microscope (SEM). The effect of contact time and initial concentration was observed at 33±1°C. The biosorption of Cu(II) and Zn(II) on GFRL showed fast kinetic behavior with an equilibrium time ~ 60 minutes. The pseudo second order kinetics described the kinetic behavior. The optimum GFRL dose was 10 g/L in case of both metals. The effect of initial metal concentration showed the performance of GFRL under various mass transfer driving forces and was well described by Langmuir Model with q_{max}: 28.02 mg/g for Cu(II) and 24.90 mg/g for Zn(II).

Keywords: Biosorption, heavy metals, industrial wastewater, environment, agricultural waste

INTRODUCTION

Heavy metals are natural constituents of the earth's crust. They are non-biodegradable and cannot be destroyed**.** They enter the human bodies via drinking water, food and air. A trace amounts of some of the heavy metals e.g. zinc and iron, are necessary to maintain the metabolism of human body; however, they can be poisonous at elevated concentrations. The presence of toxic heavy metals in the industrial wastewater is among the most important environmental issues (Sekhar *et al.,* 2003; Chubar *et al.,* 2004). Heavy metals are hazardous to human health and cause serious environmental problems; therefore it is essential to treat industrial wastewater to reduce the concentration of heavy metals to a minimum level and to meet the incessantly increasing legislative standards (Fuhrman *et al.,* 2007; Kazmi *et al.,* 2012). Among all the heavy metals, cadmium (Cd), copper (Cu), iron (Fe), zinc (Zn), chromium (Cr) and lead (Pb) are of most immediate concern (Volesky, 2003). Cu(II) and Zn(II) ions are serious ecological pollutants and are found in the wastewater of industries like mining, metal finishing, electroplating, metal processing, galvanizing and acid mine drainage etc. (Volesky, 2003; Kurniawan *et al.,* 2006; Bibi *et al*., 2013; Iqbal and Bhatti, 2014).

Various treatment processes such as chemical precipitation, ion-exchange, electrolytic processes, membrane technology and adsorption are available for the removal of heavy metal ions from industrial wastewater streams. However, these methods have several disadvantages including high capital and running cost, high energy requirements, incomplete removal of metals, and production of toxic chemical sludge (Kargi and Cikla, 2006; Kurniawan *et al.,* 2006; Kazmi *et al.,* 2011, 2012). Biosorption is an emerging technique that uses inexpensive biomaterials for the rejection of metal ions from dilute solutions. Biosorption is defined as the tendency of certain biomasses to bind and concentrate metal ions from aqueous solutions. The advantages of this process include high efficiency, low cost, minimal sludge production, and the possibility of metal recovery and regeneration of the biosorbent. Both living and dead biomass can be used as an adsorbent, however living cells are affected by toxic heavy metals causing cell death, hence dead or non-viable biomass is commonly used for the elimination of heavy metal from industrial wastewaters. The biomass usually employed for the elimination of toxic metal from dilute solutions is used either in its natural form-after physical treatment such as drying, autoclaving, heating, or after chemical treatment using alkalis, acids and organic chemicals (Volesky 2003; Kazmi *et al.,* 2011). Various agricultural wastes and forestry products like ground cone powder, bagasse, rice husk, *Ficus religiosa* leaves *etc.* have been used for the biosorption of toxic metals from dilute aqueous solutions (Krishnani *et al.,* 2008; Jiang *et al.,* 2009; Qaiser *et al.,* 2009; Rocha *et al.,* 2009; Aydina *et al.,* 2010; Ofomaja *et al.,* 2010).

The previous research done on ground *Ficus religiosa* leaves (GFRL) has shown that these leaves have decent biosorption efficiency for the removal of Ni (II), Cr (VI) and Pb (II) from dilute aqueous solutions (Qaiser *et al.,* 2007, 2009; Aslam *et al.,* 2010). The objective of the present study was to test the capacity of GFRL for the adsorption of Zn(II) and

Cu(II) from dilute aqueous solution. Some important factors affecting the sorption efficiency *e.g.* the amount of sorbent used, initial concentration of metal ions and initial pH of solution, were also investigated.

MATERIALS AND METHODS

Analytical grade chemicals were utilized in the present research, including $ZnSO_4.7H_2O$ (Merck), $CuSO_4.5H_2O$ (Merck), HNO_3, H_2SO_4, NaOH, and Zn (II) and Cu (II) atomic absorption spectrometry standard solutions (1000mg/L) (Fluka Chemicals). Distilled water was used for all preparations. The glassware was first washed with tap water and then 10% nitric acid solution was used to remove any traces of residual metals. The glassware was cleaned again with tap water and subsequently with distilled water.

Biomass preparation**:** *Ficus religiosa* leaves were collected from the University of Engineering and Technology Lahore. The leaves were washed with tap water to remove particulate materials from their surface and then dried in shadow. These leaves were powdered using a food processor and sieved to 50 mesh size. For chemical pretreatment, the GFRL powder was soaked in 0.1M HNO_3 solution for 24 hours (50g powder was soaked per liter of the solution). After the chemical pretreatment, distilled water was used to remove acid contents from the pretreated biomass and the suspension was filtered thoroughly. Lastly, the biomass was dried in an oven at 105°C for 1 hr. to remove moisture from the biomass. The biomass was stored in air-tight glass bottles to protect against humidity and contamination.

Biosorption study**:** To check the removal of Cu(II) ions from aqueous solutions, batch tests were carried out in 250 mL Erlenmeyer flask. A known weight of biosorbent dose (10 g/L) was thoroughly mixed with fixed volume of Cu(II) ions solution (100 mL). The flasks were then placed in an orbital shaker with water bath at a controlled temperature of 33±1°C and agitated at a constant rate of 200 rpm. The flasks were checked for equilibrium at appropriate time intervals. After the equilibrium was achieved for the adsorption of Cu(II) ions, the flasks were removed from orbital shaker to check the effect of initial metal concentration, biosorbent dose and pH of the solution on metal adsorption by GFRL. At the end of each experiment, the suspension was removed from solutions using Whatman No. 40 ash-less filter paper. Shimadzu 6800 atomic absorption spectrophotometer fortified with an air-acetylene burner and controlled by interpersonal computer was utilized to find out the concentration of Cu(II) in aqueous solution before and after the adsorption equilibrium was achieved. The wavelength used for Cu(II) sample was 213.9 nm. A similar procedure was carried out using Zn(II) ions solution and a wavelength of 327.4 nm was used in atomic absorption spectrophotometer to determine the concentration of Zn(II) ions before and after the adsorption equilibrium was achieved.

Characterization**:** *Ficus religiosa* leaves were thoroughly washed with distilled water and dried in shade. The leaves were crushed in a double roll crusher and then finely ground in a spice grinder. The particle size distribution of GFRL was established using a stack of seven ASTM screens. The GFRL particles were coated with a thin layer of graphite and observed by a SEM (JEOL JSM-6490 LV) to characterize the surface morphology and particle size and shape. The Elementar, Vario micro cube, obtained from Germany, was used to perform the elemental analysis on GFRL. Details of chacterization have been mentioned in Kazmi *et al.* (2011, 2012).

RESULTS AND DISCUSSION

Characterization of GFRL**:** The details of the organic constituents in GFRL were determined by CHNS analysis. A typical elemental analysis showed that GFRL consisted of C: 31.35 %, H: 4.894 %, N: 1.11 % and S: 0.117 %. The C/N ratio was 28.2 and C/H ratio was 6.4. Earlier, it had been shown that the nitrile (C=N), hydroxyl (-OH), carboxyl (-COOH), amine (-NH) and organosulfur (C=S) functional groups are typically present on the GFRL (Qaiser *et al.,* 2009). The structural and morphological features were explored through X-ray diffraction (XRD) and scanning electron microscope (SEM). The XRD of GFRL (not shown) represented a typical peak at ~ 22°, showing the amorphous nature of GFRL (Kazmi *et al*, 2011). Figure 1 shows the various morphological pictures of GFRL. SEM revealed that although most of the particles of GFRL were cylindrical in shape, there were few particles having needle like structure (Fig. 1a). These particles were part of the leaf vain. Figure 1b revealed an uneven surface of GFRL and displayed the presence of some pores on the surface of GFRL. Thus, SEM gave important information which may play a vital role in discussing the removal mechanism of Cu(II) and Zn(II) by GFRL.

Effect of contact time**:** Batch experiments were conducted to find the equilibrium time for the biosorption of Cu(II) and Zn(II) ions over GFRL. For each run, 1 g GFRL was thoroughly mixed with 100 mL solutions of Zn(II) and Cu(II) ions, each having 100 mg/L concentration of the respective ions, in 250 mL flask at 200 rpm. Figure 2 illustrates the typical trend for the effect of contact time on the uptake capacity of Cu(II) and Zn(II) ions, and reveals that nearly 90% Cu(II) and 80% Zn(II) ions were removed in the first 20 minutes, followed by a slight increase in the percent % removal of metal ions. The equilibrium was attained after 60 minutes as the uptake of ions remained almost constant after this interval. The equilibrium uptake of Cu(II) and Zn(II) ions was 9.54 mg/g and 8.77 mg/g, respectively.

(a)

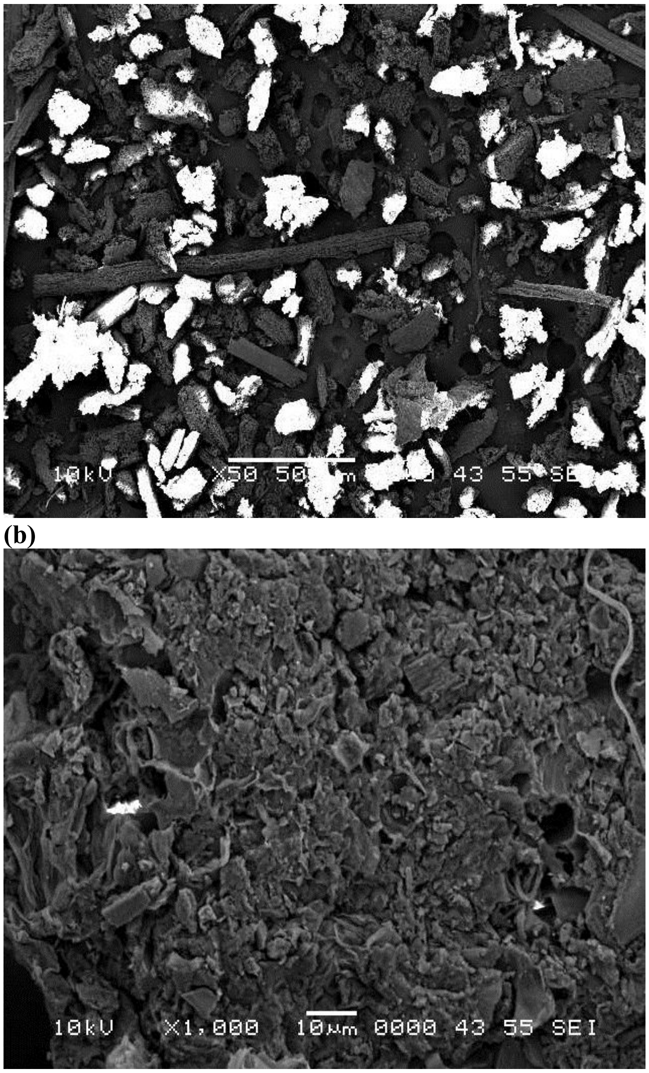

Figure 1. Structure and surface morphology of ground *Ficus religiosa* leaves (GFRL)

In the case of biosorption of both metal ions by GFRL, three regions can be identified; initial fast, intermediate slow and third slight declining. At the start of the biosorption process, the binding sites of the GFRL were vacant; hence a rapid uptake of metal ions took place in the first 20 minutes. With the passage of agitation time, a decline in the adsorption may correspond to either the competition of ions to occupy the leftover vacant sites or the transportation of ions to the intraparticle structures to interact with empty binding sites (Qaiser *et al.,* 2009; Kazmi *et al.,* 2011). The uptake continued till 60 minutes after which, an increase in agitation time resulted in a slight decrease in the uptake, indicating the establishment of equilibrium.

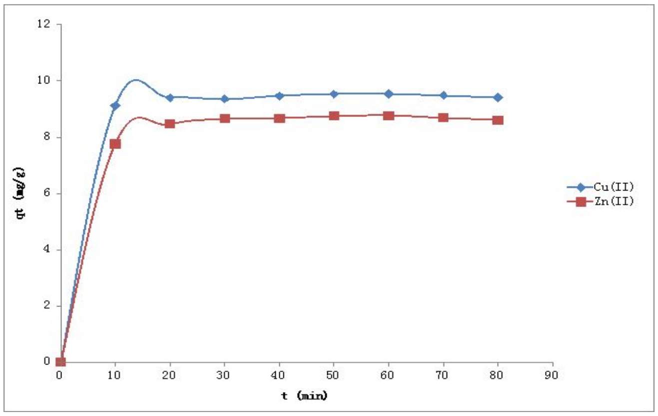

Figure 2. Effect of contact time on the uptake of Cu(II) and Zn(II) ions.

Effect of initial pH: The biosorption of metal ions is strongly dependent on the pH of the solution. To establish this effect, experiments were conducted at the same operating conditions as mentioned previously, whereas the initial solution pH was varied from 2-7. The solution pH was attuned by adding 0.1 N H_2SO_4 and 0.1 N NaOH solutions in the metal bearing solution. 100 mL of metal bearing solution was mixed with 1 g of GFRL in 250 mL flask, and the mixture was agitated on an orbital shaker at a constant speed of 200 rpm for 60 minutes for sorption to attain equilibrium.

Figure 3 shows that the uptake of metal ions sharply increased with an increase in the pH value from 2 to 4. The increase in the % removal of Cu(II) and Zn(II) ions with the increase in solution pH could be elucidated by verity that at lower pH, H^+ are present in abundance and occupy most of the negatively charged binding sites. This H^+ dominance prohibits the approach of the metallic ions (Cu(II) and Zn(II)) to the negatively charged functional groups (e.g., carboxylic acid group). As a result a lower uptake is observed at lower pH. However, it is important to notice that even in very extreme acidic conditions ($pH \leq 2$), the % removal of metal ions was not zero, indicating the existence of multiple mechanisms (electrostatic interaction, ion exchange, complexion) for the removal of metal ions (Volesky, 2003; Qaiser *et al.,* 2009; *Feroze et al.,* 2013). On the other hand, with the increase in solution pH, H^+ dominance reduces, thereby increasing the negative charge density on surface of GFRL. In this way, heavy metal ions {Cu(II) and Zn(II)} get the opportunity to link with the appropriate functional groups. Consequently, an increase in uptake was observed. However, the upper limit of pH is limited by the fact that metal salts precipitates as hydroxide, might be ($Cu(OH)_2$ and $Zn(OH)_2$ (Zhou *et al.*, 2004) at higher pH. The point (pH) of precipitation depends on the metal ion and is different for different metal salts (Hawari and Mulligan, 2006). The optimum values of solution pH for the biosorption of Cu(II) and Zn(II) ions came out to be 4.4 and 5.2, respectively.

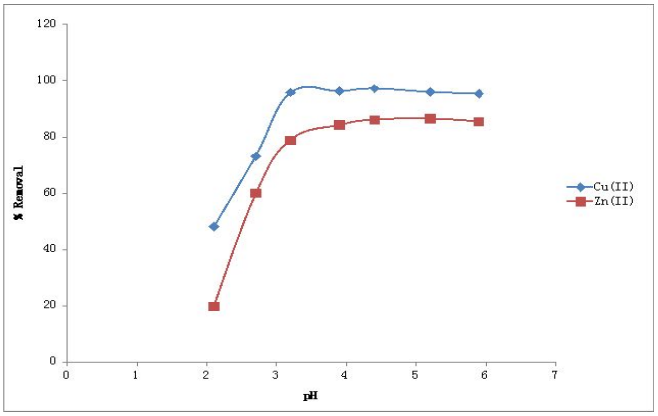

Figure 3. Effect of initial pH on the % removal of Cu(II) and Zn(II) ions.

Effect of GFRL dose**:** The effect of GFRL dose on the % removal of adsorbates was evaluated for both metal ions *i.e.,* Cu(II) and Zn(II), in the range of 5-70 g/L. The mixtures were agitated on an orbital shaker at a constant speed of 200 rpm for 60 minutes and the results are shown in Figure 4. It was observed that increasing the biosorbent dose resulted in an increase in the percentage removal of both Cu(II) and Zn(II) ions, since additional binding sites were available for metal ions. However, no significant increase in removal was observed at concentrations beyond 10 g/L, hence 10 g/L was taken as an optimum GFRL dose. The % removal of Cu(II) (95.5%) on GFRL was found to be greater than that of Zn(II) (87.4%).

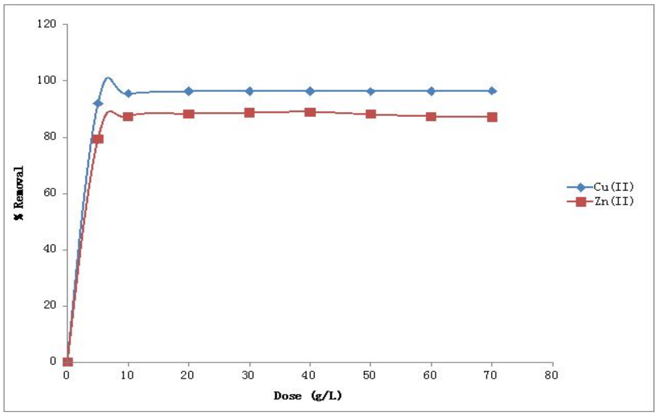

Figure 4. Effect of GFRL dose on the % removal of Cu(II) and Zn(II) ions

Effect of initial metal concentration**:** A key factor which affects the rate of adsorption is the initial concentration of the metal ions in the solution. The initial concentration of the metal ions is important because it provides the driving force for metal ions to overcome the mass transfer resistance between the solid and liquid phase. To evaluate the effect of the initial concentration of the metal ions in the solution, experiments were conducted on an orbital shaker which agitated the sample mixture at a constant speed of 200 rpm for 60 minutes for sorption to attain equilibrium. The metal ions concentration of the synthetic solution was varied from 10 – 500 g/L and the results are shown in Figure 5. It was observed that an increase in initial metal concentration resulted in an increase in the biosorption capacity since the driving force for the biosorption process *i.e.* the concentration gradient, was increased. However, it was also seen that at higher initial concentration of the metal ions, the % removal decreased, since the surface area available for adsorption was less with a fixed dose of the biosorbent (Zhu *et al.,* 2009).

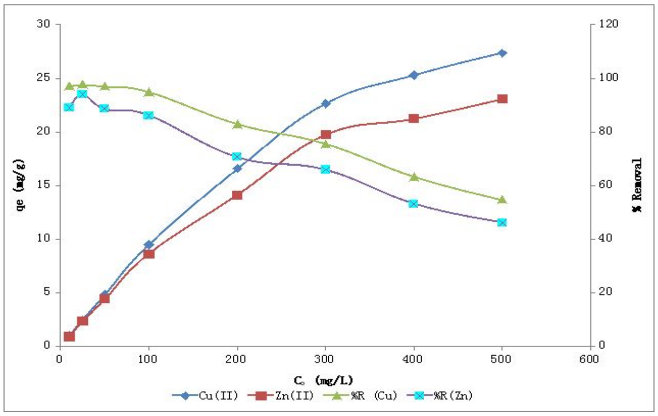

Figure 5. Effect of initial concentration on the equilibrium uptake of Cu(II) and Zn(II) ions.

Kinetic modeling**:** One of the preliminary studies to explore the biosorption potential of a particular biosorbent involves the study of its kinetic behavior for an adsorbate. Multiple kinetic models *e.g.* pseudo 1st order and pseudo 2nd order kinetic models, have been formulated to enumerate the performance of a biosorbent during the course of adsorbate uptake, as shown in Table 1. The pseudo 1st order and second 2nd order kinetics were applied, and the parameters calculated from the slope and intercept along with the coefficient of determination are given in Table 2. It was seen that the pseudo 1st order kinetics related the experimental data better in case of Zn(II) ions as compared to Cu(II) ions, since the coefficient of determination for Zn(II) ions was greater ($R^2 = 0.9427$) than that of Cu(II) ions ($R^2 = 0.8641$). The pseudo 2nd order kinetics showed an overall excellent fitting to the data, as evident from the values of coefficient of determination for both Cu(II) and Zn(II) ions. The values of equilibrium uptake obtained from the model [q_e(Cu(II)) = 9.51 mg/g, q_e(Zn(II)) = 8.78 mg/g] were in close accordance to the experimentally obtained values [q_e(Cu(II)) = 9.54 mg/g, q_e(Zn(II)) = 8.77 mg/g]. Thus, it can be suggested that the biosorption of Cu(II) and Zn(II) onto GFRL follow pseudo 2nd order kinetics.

Table 1. Details of Different Kinetic models

Kinetic Model	Differential	Integral	Plot	Reference
Pseudo 1st Order	$\frac{dq_t}{dt}=k_1(q_e-q_t)$	$\log(q_e-q_t)=\log q_e-k_1t$	$\log(q_e-q_t)$ vs t	Ho (2006)
Pseudo-2nd Order	$\frac{dq_t}{dt}=k_2(q_e-q_t)^2$	$\frac{t}{q_t}=\frac{t}{q_e}+\frac{1}{k_2{q_e}^2}$	$\frac{t}{q_t}$ vs t	Ho (2006)
Weber-Morris	-------	$q_t=kt^{0.5}$	q_t vs t	Zhu *et al.* (2009)

Table 2. Kinetic parameters for biosorption of Cu(II) and Zn(II) on GFRL.

Metal	Pseudo 1st Order			Pseudo 2nd Order		
	k_1	q_e	R^2	k_2	q_e	R^2
Cu(II)	-0.049	5.31	0.8641	0.44	9.51	0.9998
Zn(II)	-0.052	7.08	0.9427	0.17	8.78	0.9995

Table 3. Details of adsorption isotherms.

Isotherm	Linearized Form	Parameters	Plot	References
Langmuir		q_{max}, b		Zhu *et al.* (2009)
Freundlich		K_F, n		Zhu *et al.* (2009)

Table 4. Equilibrium parameters for biosorption of Cu(II) and Zn(II) on GFRL.

Metal	Langmuir			Freundlich		
	b	q_{max}	R^2	K_f	n	R^2
Cu(II)	0.084	28.02	0.9941	2.93	2.18	0.9351
Zn(II)	0.036	24.90	0.9924	1.49	1.87	0.9367

***Equilibrium modeling*:** The modeling of equilibrium data is essential for the industrial utilization of sorption process as it provides information for a comparison between different biosorbents under diverse operating conditions. A biosorption isotherm can be defined as a relationship between equilibrium concentration and the amount of substance adsorbed at a constant temperature. Freundlich and Langmuir isotherm models are extensively used for analyzing the adsorption equilibrium between metal ions and the biomaterial, as shown in Table 3. The model parameters were estimated from the slope and intercept of the individual graphs and are given in Table 4. As seen from Table 4, the Langmuir model, as compared to the Freundlich model, gave a better approximation to the biosorption of Cu(II) and Zn(II) ions by GFRL. Thus, it can be stated that a monolayer adsorption of both Cu(II) and Zn(II) ions takes place on the surface of GFRL. The value of q_{max} for Cu(II), *i.e.,* 28.02 mg/g, was higher than that for Zn(II), *i.e.* 24.90 mg/g. The Langmuir coefficient '*b*' helps to calculate an important parameter called separation coefficient (R_L) as under (Zhu *et al.,* 2009):

$$R_L=\frac{1}{1+bC_\circ}$$

where C_o is the initial concentrations of metal ions (Kazmi *et al*., 2012).

The value of R_L indicates the feasibility of the absorption process. A value of R_L between 0 and 1 indicates favorable adsorption. If $R_L > 1$, the adsorption process in unfavorable while $R_L = 0$ denotes an irreversible process.

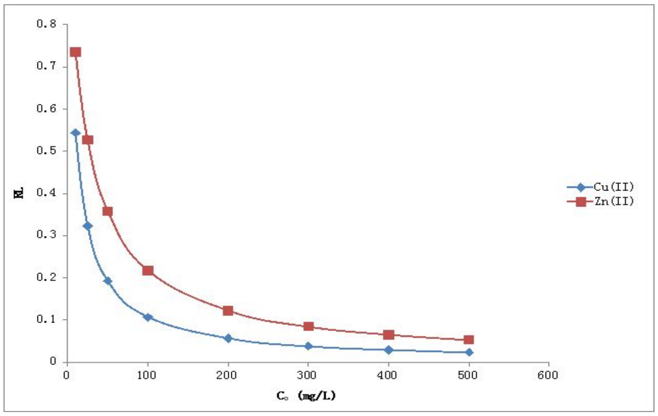

Figure 6. Effect of initial concentration on the separation coefficients for biosorption of Cu(II) and Zn(II) ions onto GFRL.

Figure 6 shows the variation of R_L with initial concentration. It was found that for all the initial concentrations of Cu(II) and Zn(II) ions, the value of separation coefficient, R_L, remained between 0 and 1, indicating a favorable biosorption of the aforementioned metal ions by GFRL.

Table 5 shows a comparison of different studies for the removal Cu(II) and Zn(II) ions. Previous studies show that a variety of natural, deceased biomasses can effectively be employed for the treatment of water polluted with heavy metals. It can be seen in Table 5 that *Ficus religiosa* leaves have shown moderate results and are better than many other biosorbents.

***Mechanistic studies*:** The pseudo 1st and 2nd order models do not elaborate the diffusion aspects of biosorption phenomenon. An adsorbate has to diffuse through liquid film around the biosorbent and the particle interstices. To explore this mechanistic aspect, the pore diffusion model was investigated as illustrated in Figure 7. The pore diffusion model states that the intraparticle diffusion may exist during the course of biosorption if the plot between q_t and is linear and will be rate controlling if the aforementioned plot passes through the origin. As shown in Figure 7, two linear regions can be observed which indicate that pore diffusion may exist in the system under consideration. However, the plots did not pass through the origin indicating that pore diffusion model was not the rate controlling step in the removal of Cu(II) and Zn(II) ions by GFRL. Since the intercepts in the Figure 7 are small, it may be stated that both the film diffusion and pore diffusion mechanisms were participating in the biosorption of Cu(II) and Zn(II) ions in varying degrees. Similar results have been reported in the literature by Kalavanthy *et al*. (2005), Zhu *et al*. (2009) and Kazmi *et al*. (2011).

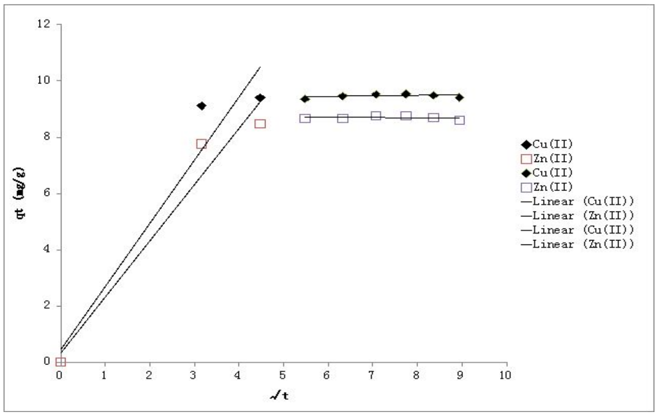

Figure 7. Plot of metal uptake against square root of time (Pore Diffusion model).

***Conclusions*:** The structural properties of GFRL enable it to effectively remove Cu(II) and Zn(II) ions from aqueous solutions. The pH of the solution displayed a radical effect on the removal of both Cu(II) and Zn(II) ions between pH 2 to 4; however, the effect is negligible at pH above 4. The kinetic behavior showed the equilibrium established in 60 minutes and the equilibrium uptakes of Cu(II) and Zn(II) ions were 9.54 mg/g and 8.77 mg/g, respectively. The optimum dosage of GFRL was found to be 10 g/L with more than 85% removal of each cation from the solution. Both metal ions were removed appreciably when adsorption isotherm study was performed at different initial metals concentrations. The kinetic modeling revealed pseudo 2nd order kinetic model as the best model to describe the time course of biosorption of Cu(II) and Zn(II) ions by GFRL. The biosorption of Cu(II) and Zn(II) ions was in the form of monolayer as shown by a good fitting of Langmuir model. The mechanistic study revealed that both pore and film diffusion phenomenon participated in the removal of Cu(II) and Zn(II) ions. The removal efficiency of Cu(II) ions was greater than Zn(II) ions in all experiments.

REFERENCES

Aslam, M.Z., N. Ramzan, S. Naveed and N. Feroze. 2010. Ni(II) Removal by biosorption using *Ficus religiosa* (peepal leaves). J. Chil. Chem. Soc. 55:81-84.

Aydina, H., Y. Buluta and C. Yerlikaya. 2008. Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. J. Environ. Manage. 87:37–45.

Bibi, I., H.N. Bhatti and M. Asgher. 2013. Bioremediation of wastewater containing reactive dyes by *Agaricus bisporus* A21: effect of supplements and redox mediators. Pak. J. Agri. Sci. 50:445-453.

Chubar, N., J.R., Carvalho and M.J.N. Correia. 2004. Cork biomass as biosorbent for Cu(II), Zn(II) and Ni(II). Colloids Surf. A. 230:57–65.

Feroze, N., M. Kazmi and N. Ramzan. 2013. Dead immobilized *Rhizopus arrhizus* as a potential biosorbent for copper removal. Korean J. Chem. Eng. 30:95-100.

Fuhrman, H.G., P.S. Mikkelsen and A. Ledin. 2007. Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: Experimental comparison of 11 different sorbents. Water Res. 41:591-602.

Hawari, A.H. and C.N. Mulligan. 2004, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass. Biores. Technol. 97: 692–700.

Ho, Y.S. 2006. Review of second-order models for adsorption systems. J. Hazard Mater. B 136: 681-689.

Iqbal, M. and I.A. Bhatti. 2014. Re-utilization option of industrial wastewater treated by advanced oxidation process. Pak. J. Agri. Sci. 51: 1041-1047.

Jiang, Y., H. Pang and B. Liao. 2009. Removal of copper(II) ions from aqueous solution by modified bagasse. J. Hazard. Mater. 164:1–9.

Kalavathy, M.H., T. Karthikeyan, S. Rajgopal and L.R. Miranda. 2005. Kinetic and isotherm studies of Cu(II) adsorption onto H_3PO_4-activated rubber wood sawdust. J. Colloid Interface Sci. 292: 354–362.

Kazmi, M., N. Feroze, S. Naveed and S.H. Javed. 2011. Biosorption of copper(II) on *Prunus amygdalus* Shell: Characterization, biosorbent size analysis, kinetic, equilibrium and mechanistic studies. Korean J. Chem. Eng. 28:2033-2040.

Kazmi, M., N. Feroze, H. Javed, M. Zafar and N. Ramzan. 2012. Biosorption of copper(II) on dry fruit by product: Characterization, kinetic and equilibrium studies. J. Chem. Soc. Pak. 34:1356-1365.

Kargi, F. and S. Cikla. 2006. Biosorption of zinc(II) ions onto powdered waste sludge (PWS): Kinetics and isotherms. Enzyme Microb. Technol. 38:705–710.

King, P., N. Rakesh, S.B. Lahari, Y.P. Kumar and V.S.R.K. Prasad. 2008. Biosorption of zinc onto *Syzygium cumini* L.: Equilibrium and kinetic studies. Chem. Eng. J. 144:181–187.

Krishnani, K.K., X. Meng, C. Christodoulatos and V.M. Boddu. 2008. Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. J. Hazard. Mater. 153:1222-1234.

Kurniawan, T.A., G.Y.S. Chan, W.H. Lo and S. Babel. 2006. Physico–chemical treatment techniques for wastewater laden with heavy metals. Chem. Eng. J. 118:83–98.

Ofomaja, A.E., E.B. Naidoo and S.J. Modise. 2010. Dynamic studies and pseudo-second order modeling of copper(II) biosorption onto pine cone powder. Desalination 251:112–122.

Qaiser, S., A.R. Saleemi and M.M. Ahmad. 2007. Heavy metal uptake by agro based waste materials. Electron. J. Biotechn. 10:410-416.

Qaiser, S., A.R. Saleemi and M. Umar. 2009. Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: Batch and column study. J. Hazard. Mater. 166:998–1005.

Rocha, C.G., D.A.M. Zaia, R.V. da S. Alfaya and A.A. da S. Alfaya. 2009. Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents. J. Hazard. Mater. 166:383–388.

Sekhar, K.C., C.T. Kamala, N.S. Chary and Y. Anjaneyulu. 2003. Removal of heavy metals using a plant biomass with reference to environmental control. Int. J. Miner. Process. 68:37– 45.

Wang, X.S., Z.Z. Li and C. Sun. 2009. A comparative study of removal of Cu(II) from aqueous solutions by locally low-cost materials: marine macroalgae and agricultural by-products. Desalination 235: 146–159.

Volesky, B. 2003. Sorption and Biosorption. Bv sorbex Inc., Montreal, Canada; pp. 35–50.

Yang, C., J. Wang, M. Lei, G. Xie, G. Zeng and S. Luo. 2010. Biosorption of zinc(II) from aqueous solution by dried activated sludge. J. Environ. Sci. 22:675–680.

Zhou, D., L. Zhang, J. Zhou and S. Guo. 2004. Cellulose/chitin beads for adsorption of heavy metals in aqueous solution. Water Res. 38:2643–2650.

Zhu, C.S., L.P. Wang and W.J. Chen. 2009. Removal of Cu (II) from aqueous solution by agricultural by-product: Peanut hull. J. Hazard. Mater. 168:739-746.