RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.2, No.4 (2009), 791-806
ISSN: 0974-1496
CODEN: RJCABP

ADSORPTION OF ZINC (II) AND NICKEL (II) FROM AQUEOUS SOLUTION USING SYZYGIUM AROMATICUM (CLOVES): KINETIC AND ISOTHERM STUDIES

Masood Alam, Mohd. Aslam* and Sumbul Rais
Department of Applied Sciences & Humanities, Faculty of Engineering and Technology, Jamia Millia Islamia, New Delhi 110025
*E-mail: aslam312@gmail.com

ABSTRACT

Present study deals with the adsorption of Zn(II) and Ni(II) onto cloves (Syzygium aromaticum) from aqueous solution under different process conditions. The adsorption was carried out in a batch process taking different concentrations of the metal ion in aqueous solution with variation in adsorbent dose, pH and agitation time. The solution initial pH values affected metal sorption. Over the pH range of 6 - 9, pH-related effects were significant. Meanwhile, at lower pH values the percentage of metal removal decreased. The sorption was found to decrease with increase in initial concentration and increases with increasing adsorbent dose. The equilibrium nature of Zn (II) and Ni (II) adsorption at different metal ion concentration were described by Langmuir, Tempkin and Freundlich Isotherm. The equilibrium data indicates the following order to fit the isotherms: Freundlich > Tempkin > Langmuir. In order to evaluate kinetic parameters Lagergren's first-order, pseudo-second-order, Elovich kinetic model and intra-particle diffusion models were explored. Among the kinetic models studied, the pseudo-second-order equation was the best applicable model to describe the sorption process. FTIR spectra of the adsorbent were recorded to explore the number and position of functional groups available for the binding of Zn (II) and Ni (II) ions of the studied adsorbent.

Keywords: Adsorption; Heavy metals; Cloves; Isotherms; Kinetics.

INTRODUCTION

The release of large quantities of heavy metals into natural environment through mining, refining of ores, combustion of fossil fuels, agricultural runoff, industrial and domestic effluents has not only intensified environmental pollution problems but also the deterioration of several aquatic ecosystems with the accumulation of metals in biota and flora. Although these metals are essential to life at low concentration but may become hazardous at high concentration[1].

Ni and Zn are the most common pollutants which are arising from industries such as electroplating, mineral processing, galvanization plants, paints formulation, porcelain enameling, nonferrous metal and vegetable fat producing industries[2]. Acute nickel poisoning causes headache, nausea and vomiting, chest pain, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness[3]. Zinc participates in various body functions at low concentration but can pose various health hazards when present at higher concentration. Abdominal pain, dizziness, lack of muscular coordination, and acute renal failure are some of the health complication at high concentration of Zinc[4-5].

In India, acceptable limit of Ni and Zn in drinking water are 0.01mg/l and 3.0 mg/l respectively which the industrial discharge limit in waste water is 2.0 mg/l for Ni and 5.0 mg/l For Zn[6]. Hence it is necessary to remove Ni and Zn from the industrial waste water before being allowed to interact with the natural environment. Several physicochemical methods such as precipitation, chemical oxidation or reduction, electrochemical treatment, evaporation recovery, filtration, ion exchange and membrane technologies have been widely used to remove heavy metal ions from waste water. These processes may be ineffective or technically limited with economical viability[7-11]. Biosorption which is the ability of certain biomaterials to bind with heavy metals from even the most diluted aqueous solutions offer a technically feasible and economically attractive alternative to the conventional technologies for the removal of heavy metal from the contaminated effluents.

Cloves (*Syzygium aromaticum*) are the aromatic dried flower buds of a evergreen tree in the family Mytraceae. Cloves are used in Ayurveda called Lavang in India. Chinese medicine and western herbalism and dentistry, where the essential oil is used as an anodyne (pain killer) for dental emergencies. Cloves are used as a carminative, to increase hydrochloric acid in the stomach and to improve peristalsis. Cloves are also said to be a natural anti helmintic[12]. A clove kills intestinal parasites and exhibit broad antimicrobial properties against fungi and bacteria, thus supporting its traditional use as a treatment for diarrhea, intestinal worms and other digestive ailments.

The compound responsible for the cloves aroma is eugenol. It is the main compound of cloves, comprising 72-90% of the total which has pronounced antiseptic and anesthetic properties. Other important constituents include acetyl eugenol, beta-caryophyllene and vanillin; crategolic acid; tannins, gallotannic acid, methyl salicylate(pain killer); the flavonoids eugenin, kaempferol, rhamnetin and eugenetin; triterpenoids like oleanolic acid, stigmasterol and campesterol; and several sesquiterpenes[13].

EXPERIMENTAL

Biosorbent preparation

Syzygium aromaticum (cloves) was used as a biosorbent for the removal of heavy metals. Cloves was washed with double distilled water (DDW) repeatedly to remove dust and solid impurities, dried in an oven for 24 hr at 60ºC, ground and sieved. Finally, it again washed with double distilled water several times and dried in an air oven at 105±5ºC for 6 hr and cooled to room temperature in desiccators. Powdered material of 40-50 mesh BSS screens was used for metal sorption studies.

Preparation of Zn(II) and Ni(II) standards

The stock aqueous solution of Zn(II) and Ni(II) containing 1000mg/l were prepared by dissolving 4.39 gm of $ZnSO_4.7H_2O$ and 4.95 gm of $Ni(NO_3)_3.6H_2O$ in 1 liter of DDW. The stock solutions were used to prepare dilute solutions of different working concentrations.

Analysis of metal ions

The concentration of Zn(II) and Ni(II) ions were analyzed using Perkin Elmer AAnalyst 3100 Atomic Absorption Spectrophotometer (AAS) using an air acetylene flame. The hollow cathode lamp was operated at 15 mA for Zinc and at 25 mA for Nickel.

Biosorption Studies

The batch experiments are carried out in 250 ml Erlenmeyer flasks containing 0.5 g of the biosorbent in 50 ml of Zn(II) and Ni(II) solutions (100 mg/l) separately at 25 ± 2 ºC on a rotary shaker at 120 rpm. The effect of pH on biosorption rate was investigated in a pH range of 2 to 9, which was regulated by micro additions of 0.1 N HCl or 0.1 N NaOH at the beginning of the experiment. The best amount of biomass was determined by changing the biomass dosage between 0.25g to 1 g in 50 ml of metal solution. For optimization of contact time samples were taken at predetermined time intervals (10-120 min) for determination of the residual metal ion concentration in the solution. Before analysis, the samples were centrifuged at 5000 rpm to separate the biomass. The residual metal concentrations in the supernatant were analyzed by AAS (Perkin Elmer, model 3100).

The amount of the metal adsorbed (mg) per unit mass of biomatrix was obtained by using the equation[14]:

$$q = \frac{\left(C_o - C_e\right)}{W} \times V \tag{1}$$

Where q is amount of metal ion adsorbed per gram of biomass in mg g^{-1}, C_o is the initial metal ion concentration in mg l^{-1}, C_e is the final metal ion concentration in mg l^{-1}, V is the volume of the reaction mixture in liter, and W is the weight of biomass in the reaction mixture in g.

The percentage biosorption of metal ion was calculated as follows:

$$\text{Biosorption}(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

Where C_o and C_e (mg l^{-1}) are the initial and equilibrium metal concentration of solution.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH was found to be the highest amongst studied variables. In these experiments, the initial pH of Zn(II) and Ni(II) containing solution was adjusted to the desired value using either 0.1 N HCl or 0.1 N NaOH solutions. To the pH adjusted zinc and nickel solutions, clove was added. A sharp increase from negligible to maximum values in the pH range of 2-7 for Ni(II) and 2-8 for Zn(II) was observed (Fig.1). This can be explained by the fact that the pH of the biosorption medium affects the solubility of metal ions. In the low pH (2-3) adsorption sites are more protonated and they are less attractive against various cationic forms of metals i.e. electrostatic repulsion will be high. Electrostatic repulsion decreases with the increasing in pH due to reduction of positive charge density on the sorption edges thus resulting in an increase metal biosorption[15]. It reaches maximum around pH 7 and 8 for Ni(II) and Zn(II) respectively. At pH values higher than 7-8, the amount of metallic ions taken up was decreased due to the formation of soluble complexes of the metal ions and their competition with the active sites.

Effect of adsorbent dose

The number of available sites and exchanging ions for adsorption depends upon the amount of adsorbent in the biosorption process. It can be observed from Fig.2 that the metal uptake was found to increase with increasing concentration of adsorbent by keeping other parameters constant. At very low adsorbent concentration, the adsorbent surface becomes saturated with the metal ions and the residual metal ion concentration in the solution is large. The increase in percentage metal ion adsorption with increase in biosorbent concentration can be attributed to increase in binding sites[16].

Effect of contact time

The rate at which adsorption takes place is of most important when designing batch adsorption experiments. Consequently it is important to establish the time dependence of such system under various process conditions. The experimental runs measuring the effect of contact time on the batch adsorption of 100 mg l^{-1} at initial pH of 5 and 0.5 gm adsorbent dosage for Zn(II) and Ni(II) is shown in Fig.3.

The adsorption rate for Ni(II) is very fast initially and it reaches plateau value with in 40 min where as the rapid adsorption of Zn(II) tapers off after 30 min, as equilibrium is approached. The initial high adsorption rate is probably due to the abundance of active binding sites on the adsorbent, and with gradual occupancy of these sites, the sorption becomes less efficient in the later stage[17].

Effect of initial metal ion concentration

Solutions containing different metal concentration were used to study the effect of initial concentration upon metal uptake once equilibrium was attained. The extent of removal was suppressed by approximately 18.73% for Zn(II) and 16.91% for Ni(II) when initial concentration was increased from 25 to 100mgl^{-1} for constant pH and adsorbent dose levels as shown in Fig.4. At low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency[18] and it may also be explained by K_d value. The distribution coefficient, K_d has been used to indicate the adsorption affinity of a solid adsorbent towards a solute. In present K_d may be written as[19]

$$K_d = \frac{(C_o - C_e)}{C_e} \times \frac{V}{M} \tag{3}$$

Here, the metal ion adsorption mainly is attributed to ion-exchange reactions in the micropores of the adsorbent. Fig.5 represents K_d as a function of metal ion concentration. The K_d values increased with the decreasing concentration of Zn(II) and Ni(II) ions.

The data for the adsorption of zinc and nickel ions on clove has been analyzed in the light of the Langmuir, Tempkin and Freundlich mode of adsorptions. It was found that the analyzed adsorption isotherms were capable of describing the data over the entire concentration range studied.

FTIR analysis

Various functional groups such as amine (-NH), carboxylate anions ($-COO^-$), hydroxyl (-OH), and others (-C=C), (-C-C), (-C=O), (-C-O), (-C-N), (-C-H) have been proposed to be responsible for sorption metal binding by different biosorbent and their importance for metal uptake depends on factors such as the quantity of sites its accessibility, chemical state or affinity between site and metal. The FTIR spectra of metal unloaded and loaded forms of the biosorbent in the range of 400-4000 cm^{-1} were taken and presented in Table 1 to confirm the presence of the above groups in biosorbent.

FTIR spectra of metal Ni(II) and Zn(II)-sorbed biosorbent showed that the peaks expected at 3434, 2928, 2362, 1627, 1454, 1320, 1259, and 588 cm^{-1}(Fig. 6 a) had shifted, respectively to 3436/3437, 2927, 2363/2362, 1628, 1517/1516, 1456, 1267,and 456/591 cm^{-1} due to Ni(II) and Zn(II) sorption[20] (Fig.6 b, c). The shift in the wavelength showed that there was a metal binding process taking place at the surface of biosorbent.

The spectral analysis unloaded and loaded metal binding indicated that –OH, -NH, -C=O, $-COO^-$, -C-O, -C=C, -C-H, -CN was involved in metal biosorption. It should also be noted that FTIR results did not provide any quantitative analysis as well as the information about the level of affinity to metal of the functional groups presented in the adsorbents. They only presented the possibility of the coupling between the metal species and the functional group of the adsorbents.

Adsorption isotherm

The adsorption isotherm is the relationship between equilibrium concentration of solute in the solution and equilibrium concentration of solute in the sorbent at constant temperature[30]. The data of sorption equilibrium in this work were tested with Langmuir [31], Freundlich[32] and Tempkin isotherms[33].

Langmuir isotherm

The Langmuir equation assumes that (i) the solid surface presents a finite number of identical sites which have uniform energy; (ii) there is no interaction between adsorbed species meaning that the amount adsorbed has no influence on the rate of adsorption; (iii) a monolayer is formed when the solid surface reaches saturation[34].

Langmuir equation can be described as:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{4}$$

Where q_e and q_m are the equilibrium and monolayer biosorption capacities of the biosorbent (mol g^{-1}) respectively. C_e is the metal ion concentration at equilibrium in the solution (mol l^{-1}) and K_L is the Langmuir constant (l mol^{-1}) related to the free energy of biosorption. Equation 4 is usually linearized to obtain the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{5}$$

By plotting C_e/q_e versus C_e , K_L and q_m can be determined when a straight line is obtained. The applicability of the Langmuir isotherm to the adsorption of Zn(II) and Ni(II) ions onto clove was proved by correlation coefficients R^2= 0.9082 and 0.9824 for Zn(II) and Ni(II) ions respectively. Fig. 7 explains this applicability.

The Langmuir constant, K_L, can be used to determine the suitability of the biosorbent to sorbate by using Hall separation factor (R_L, dimensionless)[35] and R_L can be calculated as follows:

$$R_L = \frac{1}{1 + K_L C_o} \tag{6}$$

Where C_o is the initial concentration in the solution (mg l^{-1}), for favorable adsorption 0< R_L<1; while R_L>1, R_L=1 and R_L=0 describe unfavorable, linear and irreversible adsorption, respectively[36]. The data obtained represent a favorable adsorption (Table 2).

Tempkin isotherm

Tempkin isotherm model considered the effects of indirect adsorbate-adsorbate interaction isotherms which explained that the heat of adsorption of all the molecules on the adsorbent surface layer would decrease linearly with coverage due to adsorbate-adsorbate interactions[37]. Therefore, the adsorption potentials of the adsorbent for the adsorbate can be evaluated using tempkin adsorption isotherm model, which assumes that the fall in the heat of sorption is linear rather than logarithmic as implied in the Freundlich equation.

The tempkin isotherm can be simplified by the following equation:

$$q_e = a + b \ln C_e \tag{7}$$

Where b is the tempkin isotherm constant and can be determined by a plot of q_e versus ln $C_{e.}$

The linear plot of the Tempkin isotherm for the adsorption data are shown in Fig. 8. The obtained correlation coefficient (R^2) for Tempkin isotherm model is 0.9447 for Zn(II) and 0.9910 for Ni(II).

Freundlich isotherm

The Freundlich isotherm is an empirical expression based on biosorption on a heterogeneous surface. The Freundlich model is represented by the equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{8}$$

Where K_F (l g^{-1}) and n are freundlich isotherm constants being indicative of the extent of the biosorption and the degree of non linearity between solution concentration and adsorption, respectively. The plot of ln q_e versus ln C_e (Fig. 9) for the biosorption was employed to generate K_F and n from the intercept and slope values. Examination of the correlation coefficients reported in the Table 3 shows that the Freundlich model is more applicable to clove than Langmuir and Tempkin model. The correlation obtained for Zn(II) and Ni(II) ions are 0.9946 and 0.9944 respectively which indicates that the experimental data fitted well to freundlich model. The n values 3.5803 and 4.4306 are higher than 1.0 indicates that both Zn(II) and Ni(II) is favorably adsorbed by clove at 25 ºC[38].

Adsorption kinetics

Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full scale batch process. In order to clarify the adsorption kinetics of heavy metal ions, experimental data are mostly tested for the pseudo-first-order, pseudo-second-order, elovich kinetic and intra particle diffusion equations.

Pseudo first-order kinetic model

The integrated form of pseudo first-order kinetic model as proposed by Lagergren[39] generally expressed as:

$$\ln(q_e - q) = \ln q_e - K_1 t \tag{9}$$

Where q_e (mmolg^{-1}) and q (mmolg^{-1}) are the mass of metal adsorbed at equilibrium and at time t, respectively, K_1 (min^{-1}) is the first order rate constant of adsorption. A straight line of ln(q_e-q) versus t suggest the applicability if this kinetic model (Fig.10). q_e and K_1 can be determined from the intercept and slope of the plot, respectively. The R^2 values for this model at studied concentration are 0.8775 & 0.9774 as seen in Table 4. The low correlation coefficient values obtained from the pseudo first-order kinetic model indicates that sorption is not occurring exclusively onto one site per ion[40].

Pseudo second-order kinetic model

The pseudo second-order kinetic model is expressed as[41]:

$$\frac{t}{q}=\frac{1}{K_2 \times q_e^2}+q_e \tag{10}$$

Where q_e (mmolg^{-1}) and q (mmolg^{-1}) is the same as defined for equation 9 and K_2 (gmmol^{-1}min^{-1}) is the pseudo second order rate constant of adsorption. The best fit for the experimental data of this study was achieved by the application of pseudo second-order kinetic equation (Fig 11). The coefficient of correlation for pseudo second order kinetic model was equal to 0.9820 (Zn) and 0.9974 (Ni) and the estimated value of q_e also agreed with the experimental one. Both factors suggest that the biosorption of Zn(II) and Ni(II) ions followed the pseudo second-order kinetic model, indicating that the rate limiting step was a chemical biosorption process between metal ions and clove biosorbent through the exchange of electrons between the particles involves[42-43]. Similar conclusions were found by Ho and McKay as a result of an analysis of data from literature. They reported that most of the sorption systems follow a pseudo-second-order kinetic[44].

Elovich kinetic model

The Elovich kinetic model is for general application to chemisorption kinetics. The general explanation for this form of kinetic law involves that the active sites are heterogeneous in nature and therefore exhibit different activation energies for chemisorptions[45]. The Elovich model can be expressed in the following form:

$$q_t = \alpha + \beta \ln t \tag{11}$$

Where α is the initial adsorption rate (mgg^{-1}min^{-1}) and β is the desorption constant which are obtained from the intercept and the slope of a plot of q_t versus In t. The plot should give a linear relationship for the applicability of simple Elovich kinetics as in Fig. 12. The correlation coefficient R^2 are obtained as 0.7353 and 0.8146 for Zn(II) and Ni(II) ions respectively which are found to be less than the values calculated using pseudo-first-order kinetic model and pseudo-second-order kinetic model as shown in Table 4.

Intra particle diffusion

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and the adsorption on the pore surface or a combination of more than one steps. The adsorption rate parameter which controls the batch process for most of the contact time is the intra particle diffusion. The possibility of intra particle diffusion resistance affecting adsorption was explored by using the intra particle diffusion model as[46] which was explored by using Weber & Morris equation[47].

$$q_t = K_{id} t^{1/2} + I \tag{12}$$

The slope and intercept of plot q_t versus $t^{1/2}$ were used to calculate the intra particle diffusion rate constant, K_{id} and I. Values of I give an idea about the thickness of the boundary layer i.e. the larger the intercept the greater is the boundary layer effect. The deviation of straight lines from the origin, as shown in the Fig. 13, may be because of the difference between the rate of mass transfer in the initial and final steps of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step[48]. It can also be concluded on the basis of I value as $I \neq 0$ thus suggesting that intra-particle diffusion is not the rate-limiting step[49]. R^2 values given in Table 4 are ranged between 0.6752 and 0.9572.

CONCLUSION

This paper presented the results of a detailed study of the adsorption process that removed Ni(II) and Zn(II) ions from aqueous solution using cloves. The experimental data indicates that higher the pH of the solution, the lower the initial metal ion concentration, and higher the adsorbent dose, more Nickel and Zinc are adsorbed on cloves. The experimental data were evaluated by Langmuir, Freundlich, and Tempkin adsorption isotherms. Equilibrium adsorption fitted well in Freundlich adsorption isotherm. The pseudo first-order, pseudo second-order, Elovich kinetic and Intra-particle diffusion models were used to test the kinetic data. Kinetics data tends to fit well in pseudo second-order kinetic model confirming the chemisorptions of Ni(II) and Zn(II) onto cloves. The possibility of Intra-particle diffusion has been studied by using Weber-Morris model. The interaction between metal ions and functional groups on the biomass surface were estimated by FTIR spectroscopy analysis. The results of the study indicated that clove has great potential to remove Ni(II) and Zn(II) ions from aqueous solution through a low-cost and eco-friendly way.

REFERENCES

1. M. Kazemipour, M. Ansari, S. Tajrobehkar, M. Majdzadeh and H.R. Kermani, *J. Hazard. Mater.* **150**, 322 (2008).
2. A.K. Meena, G. K. Mishra, Satish, C. Rajagopal and P. N. Nagar, *IJEP* **25 (1)**, 8(2005)
3. P. Parker, Encyclopedia of environmental science (2nd edn). McGraw Hill, New York. 1980.
4. S.A. Abbasi, N. Abbasi and R. Soni, Heavy metals in the environment, Mittal Publications. New Delhi, India. (1998)
5. A.S. Prasad and D. Oberleas, Trace elements in human health and disease. Zinc and Copper. Academic Press, New York, **1**, 470(1976).
6. Y.C. Sharma, G. Prasad and D.C. Rupainwar, *Int. J. Env. Stud.,* **40**, 535(1992).
7. B. Volesky and Z.R. Holan, *Biotechnol. Prog.* **11**, 235 (1995).
8. B. Volesky, *Hydrometallurgy* **59**, 203(2001).
9. R.H.S.F. Viera and B. Volesky, *Int. Microbiol,* **3**, 17(2000).
10. N. Ahalya, T.V. Ramachandra and R.D. Kanamadi, *J. Chem. Environ.* **7**, 71(2003).
11. K.K. Singh, M. Talat and S.H. Hasan, *Bioresour. Technol.* **97**, 2124(2006).
12. B. Phyllis and B. James, Prescription for Nutritional Healing, 3rd ed., Avery Publishing, 94(2000).
13. D. Bensky, S. Clavery, E. Stoger and A. Gamble, Chinese Herbal Medicines*:* Material Medica, 3rd ed. (2004).
14. X.S. Wang, Y.P. Tang and S.R. Tao, *Chem. Eng. J.* **148**, 217(2009).
15. A. Sari, D. Mendil, M. Tuzen and M. Soylak, *J. Hazard. Mater.* **162**, 874(2009).
16. M. Riaz, R. Nadeem, M.A Hanif, T.M. Ansari and Khalil-ur-Rehman, *J. Hazard. Mater.* **161**, 88(2009).
17. A.C.A. Costa and S.G.F. Leite, *Biotechnol. Lett.* **13**, 559(1991).
18. A.K. Bhattacharya, S.N. Mandal and S.K. Das, *Chem. Eng. J.* **123**, 43(2006).
19. N. Khalid, S. Ahmad, A. Toheed and J. Ahmed, *Appl. Radiat. Isot.* **52**, 31(2000).
20. M.L. Hair, Infra red Spectroscopy in Surface Chemistry, Marcel Dekker, New York., 49(1967).
21. H. Eroglu, S. Yapici, C. Nuhoglu and E. Varoglu, *J. Hazard. Mater.* **163**, 607(2009).
22. A. Sari and M. Tuzen, *J. Hazard. Mater.* **164**, 1372(2009).
23. H.P. Yuan, J.H. Zhang, Z.M. Lu, H. Min and C. Wu, *J. Hazard. Mater.* **164**, 423(2009).
24. G. Tan and D. Xiao, *J. Hazard. Mater.* **164**, 1359(2009).
25. M. Jain, V.K. Garg and K. Kadirvelu, *J. Hazard. Mater.* **162**, 365(2009).
26. T.K. Naiya, P. Chowdhury, A.K. Bhattacharya ad S.K. Das, *Chem. Engg. J.* **148**, 68(2009).
27. A.B. Perez- Marin, V. Mesegeur-Zapata, J.F. Ortuno. M. Aguilar, J. Saes and M. Llorens, *J. Hazard. Mater.* **139**, 122(2007).
28. M. Khormaei, B. Nasernajad, M. Edrisi and T. Eslamzadeh, *J. Hazard. Mater.* **149**, 269(2007).
29. S. Kushwaha, S. Sodaye and P. Padmaja, *PWASET.* **33**, 617(2008).
30. Q. Feng, Q. Lin, F. Gong, S. Sugita and M. Shoya, *J. Colloid Interf. Sci.* **278**, 1(2004).
31. I. Langmuir, *J. Am. Chem. Soc.* **40**, 1361(1918).
32. H. Freundlich, *Phys. Chem. Soc.* **40**, 1361(1906).
33. E.S.Z. El-Ashtoukhy, N.K. Amin and O. Abdelwahab, *Desalination* **223**, 162(2008).
34. Y.H. Huang, C.L. Hsueh, C.P. Huang, L.C. Su and C.Y. Chen, *Sep. Purif. Technol.* **55**, 23(2007).
35. K.R. Hall, E.C. Lee, A. Acrivos and T. Vermeulen, *Ind. Eng. Chem. Fun.*, **5**, 212(1996).
36. H. Arslanoglu, H.S. Altundogan and F. Tumen, *J. Hazard. Mater.* **164**, 1406 (2009).
37. A.E. Nemr, *J. Hazard. Mater.* **161**, 132(2009).
38. V. Sarin and K.K. Pant, *Bioresour. Technol.* **97**, 15(2006).
39. S. Lagergren, *Handlingar*, **24**, 1(1898).
40. Y. Nuhoglu and E. Malkoc, *Bioresour.Technol.,* **100(8)**, 2375(2009).

41. R.A.K. Rao and M.A. Khan, Colloids and Surfaces A. *Physicochem. Eng. Aspects*, **332**, 121(2009).
42. M. Dundar, C. Nuhoglu and Y. Nuhoglu, *J. Hazard. Mater.* **151**, 186(2008).
43. Y.S. Ho and G. McKay, *Water Res.* **34**, 735(2000).
44. Y.S. Ho and G. McKay, *Process Biochem.* **34(5)**, 451(1999).
45. X.S. Wang, Y.P. Tang and S.R. Tao, *Chem. Engg.* J. **148**, 217(2009).
46. G. McKay, *Chem. Eng. Sci.* **39**, 129(1984).
47. W.J. Weber and J.C. Morris, J. Sanit. *Eng. Div. Am. Soc. Civ. Eng.* **89**, 31(1963).
48. M.E. Argun, S. Dursun, C. Ozdemir and M. Karats, *J. Hazard. Mater.* **141**, 77(2007).
49. K. Vijayaraghavan, J. Mao and Y.S. Yun, *Bioresour. Technol.* **99**, 2864(2008).

Table-1: FTIR spectral characteristics of biosorbent before and after adsorption.

IR peak	Frequency (cm^{-1})					Assignment	Ref.
	Before adsorption	After adsorption Ni(II)	After adsorption Zn(II)	Difference in Ni(II)	Difference in Zn (II)		
1	3434	3436	3437	+2	+3	-OH, -NH	[21, 22]
2	2928	2927	2927	-1	-1	-CH, -OH	[23,24,25, 26,27]
3	2362	2363	2362	+1	0	-CH	[25]
4	1627	1628	1628	+1	+1	-C=O, $-COO^-$	[21,24,25, 27,28]
5	1454	1517	1516	+63	+62	-C=C	[23,27]
6	1320	1456	1456	+136	+136	-CN, -CO	[26,27]
7	1259	1267	1267	+8	+8	-C-O, -OH	[26,28,29]
8	1032	1032	1032	0	0	-C-O, -OH	[22,25,26]
9	588	456	591	-132	+3	C-C, amine	[21]

Table-2: R_L Values

Heavy Metal	Concentration	R_L Values
Zn(II)	25 ppm	0.6309
Ni(II)		0.8456
Zn(II)	50 ppm	0.4608
Ni(II)		0.7323
Zn(II)	75 ppm	0.3629
Ni(II)		0.6459
Zn(II)	100 ppm	0.2994
Ni(II)		0.5777

Table-3. Adsorption Isotherms

Metal	Langmuir isotherm			Freundlich isotherm			Tempkin isotherm		
	q_m	K_L	R^2	K_F	1/n	R^2	a	b	R^2
Zn	10.582	0.02342	0.9082	2.0675	0.2793	0.9946	2.20673	1.98436	0.9447
Ni	9.1324	0.00731	0.9824	1.3938	0.2257	0.9944	1.15546	0.90704	0.991

Table 4. Adsorption Kinetic

Metal	Pseudo first-order			Pseudo second-order			Elovich kinetic model			Intra-particle diffusion		
	R^2	K_1	q_e	R^2	K_2	q_e	R^2	α	β	R^2	K_{id}	I
Zn	0.8775	0.01264	4.2469	0.982	0.00753	6.629	0.7353	2.6413	1.66	0.9572	0.3389	2.2587
Ni	0.9774	0.02415	2.1055	0.9974	0.05918	3.2467	0.8146	1.6617	0.9738	0.6752	0.1631	1.696

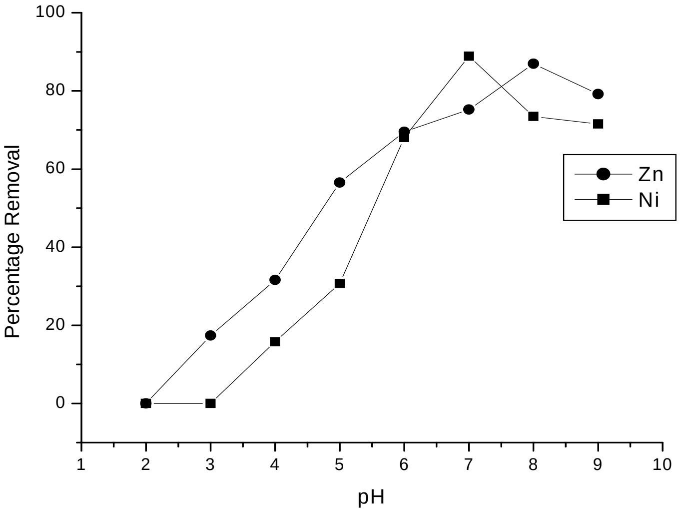

Fig. 1. Effect of pH

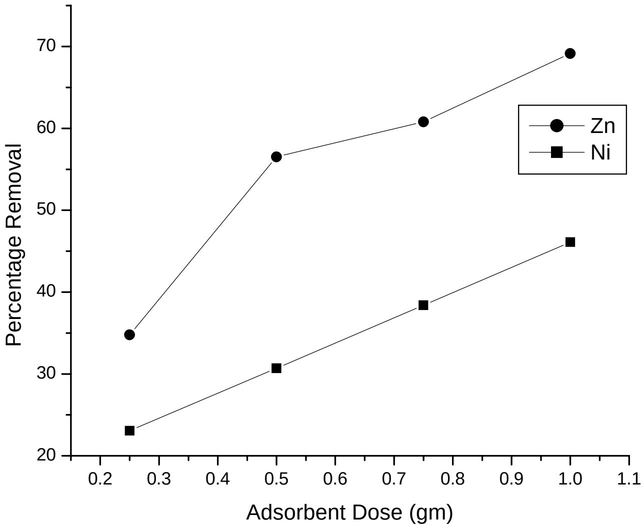

Fig. 2. Effect of adsorbent dose

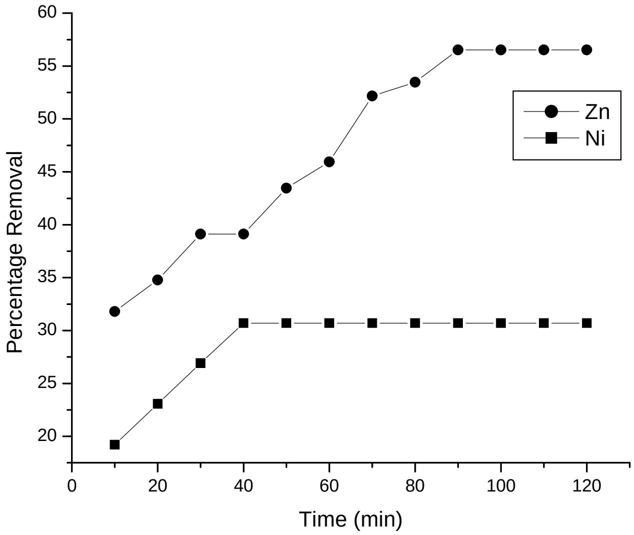

Fig. 3. Effect of contact time

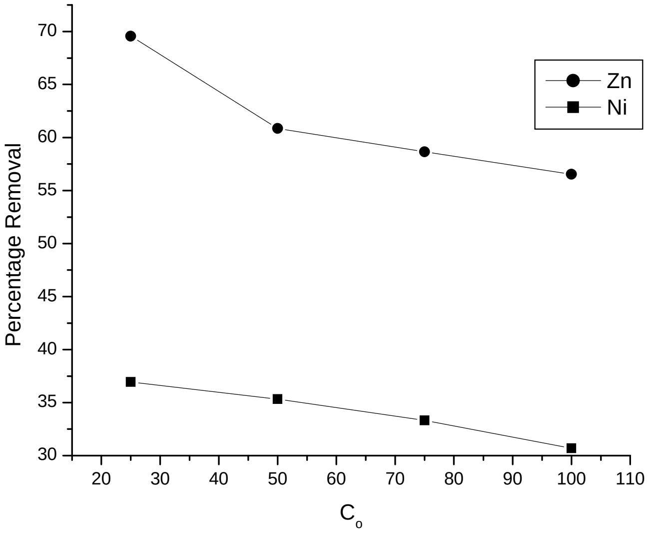

Fig. 4. Effect of initial metal ion concentration

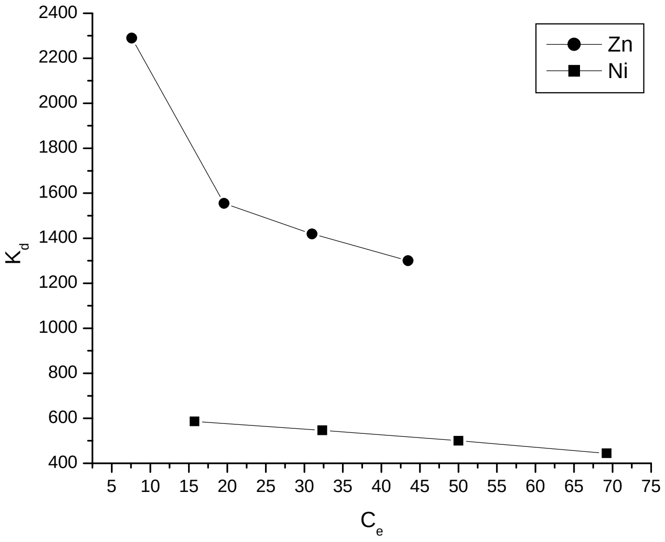

Fig. 5. K_d value as a function of metal ion concentration

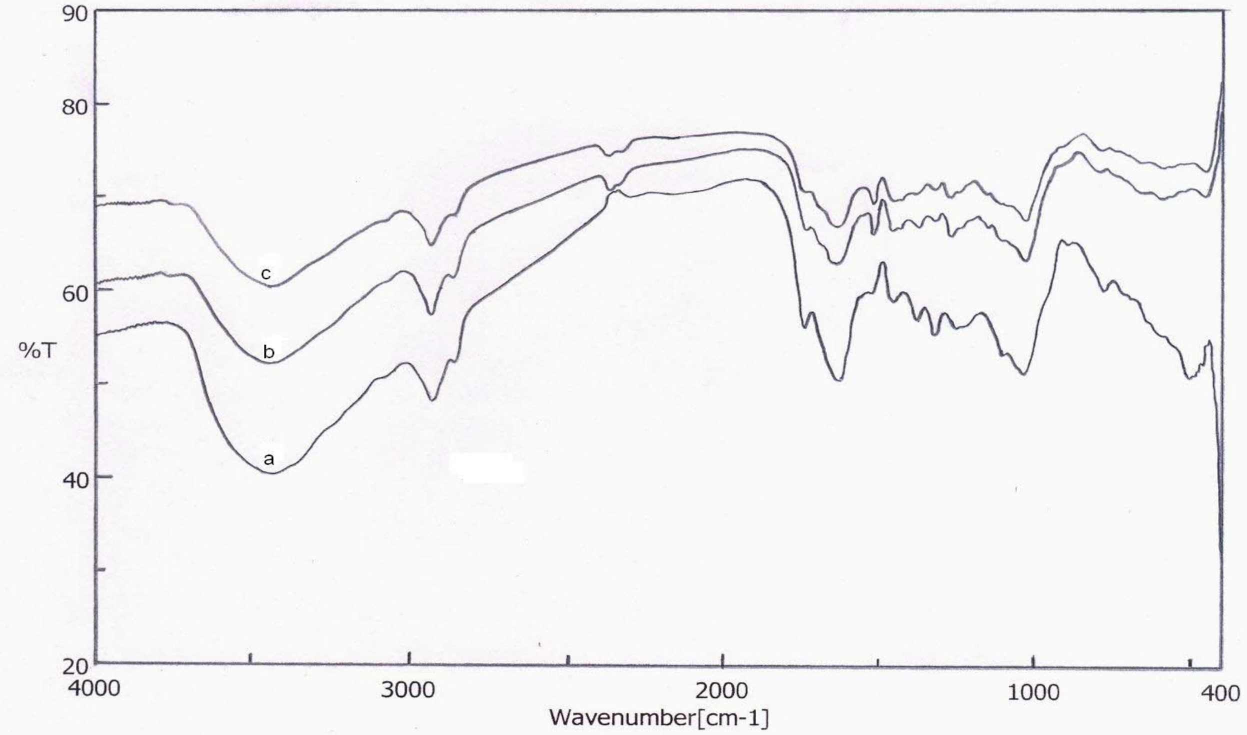

Fig. 6. FTIR Spectra of Biosorbent.

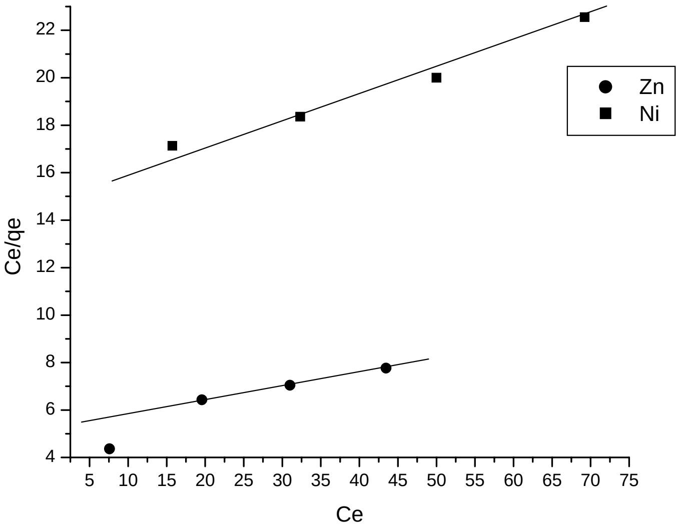

Fig. 7. Langmuir Isotherm

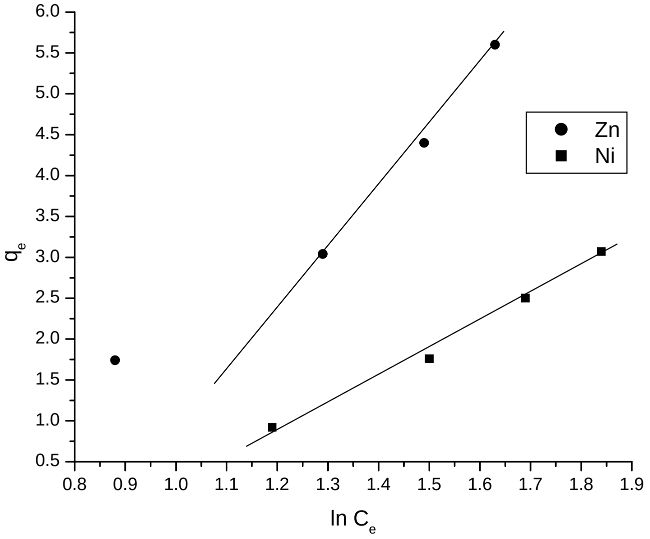

Fig. 8. Tempkin Isotherm

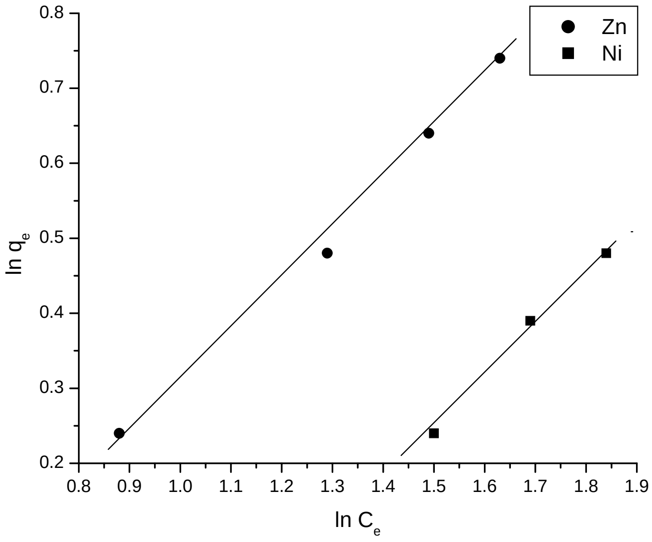

Fig. 9. Freundlich Isotherm

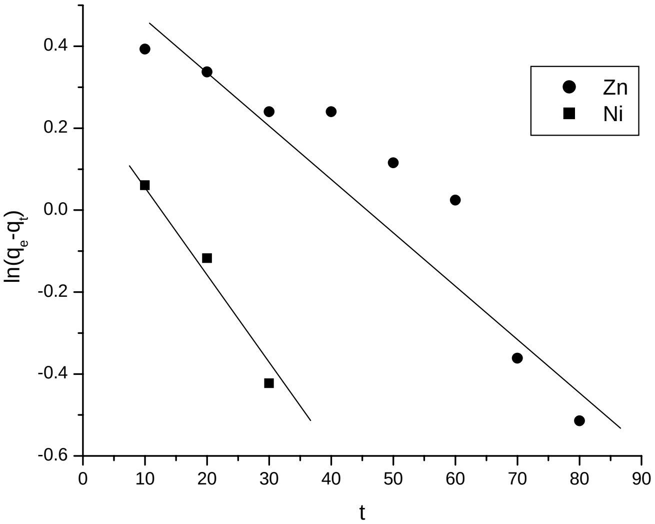

Fig.10. Pseudo first-order kinetic model

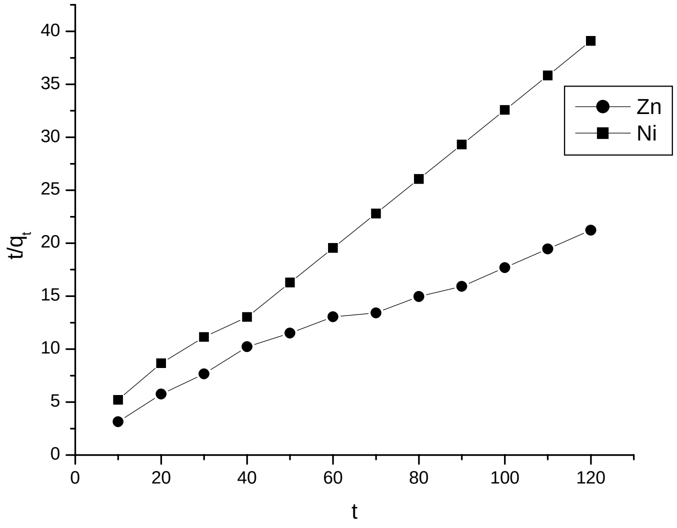

Fig. 11. Pseudo second-order kinetic model

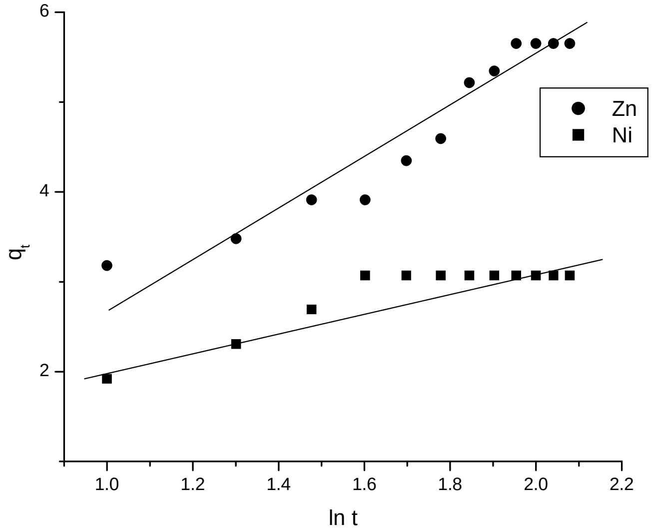

Fig. 12. Elovich Kinetic model

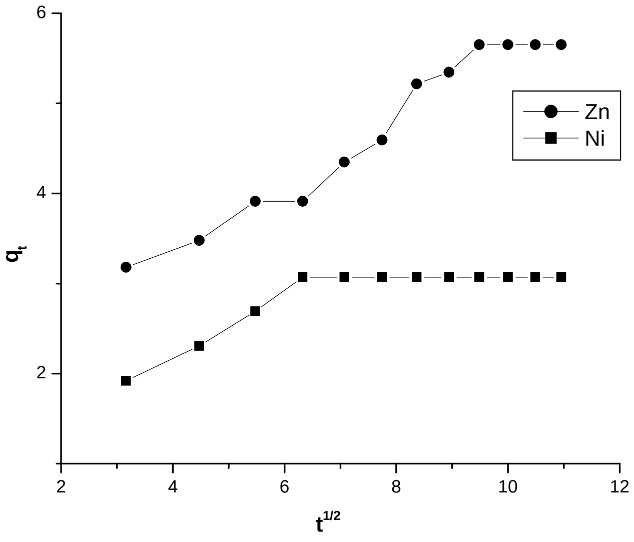

Fig. 13. Intra particle diffusion

(Received: 3 December 2009 Accepted: 11 December 2009 RJC-495)

RJC
http:// www.rasayanjournal.com

Be a Proud Life Member of RJC

Life Membership for Individuals: Rs.8000/- for Indians and USD 1000 for others.
Life Membership for Institutional: Rs.10000/- for Indians and USD 1500 for others.

BENEFITS OF LIFEMEMBERSHIP:

1. You will receive the journal and all its special issues regularly life long.
2. You will receive all other future publications (Proceedings, Edited Books, Monographs etc.) published by RJC on 50% discount.
3. If you are a LIFE MEMBER, you need not to pay subscription fee every time for publication of your paper in RJC.
4. You'll be a Reviewer for RJC manuscripts of your Field Interest and we'll publish your name in our journal.
5. You will be exempted from Registration Fee of any National or International future events (i.e. workshop, seminars, Conferences etc.) organized by RJC.
6. You may be elected as Editorial Member of RJC (Note: It'll depend upon your publication and scientific achievements).
7. You'll have a very personalized gift from RJC with Complements.

For being a **Life Membership**, just mail to Editor-in-Chief with your detailed Resume.