

Full Length Research Paper

Kinetic and equilibrium modeling of Cu(II) and Ni(II) sorption onto physically pretreated *Rosa centifolia* distillation waste biomass

Raziya Nadeem^{1*}, Muhammad Asif Hanif¹, Muhammad Riaz¹, Abdul Aziz Azhar¹, Tahira Iqbal¹ and Tariq Mahmood Ansari²

¹Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad (38040), Pakistan.

²Department of Chemistry, Bahauddin Zakariya University, Multan (60800), Pakistan.

Accepted 14 August, 2008

The removal of Cu(II) and Ni(II) from aqueous solution by physically pretreated (boiled, heated and autoclaved) *Rosa centifolia* distillation waste biomass was conducted in batch conditions. The obtained results revealed that initial metal ion concentration, kinetics, and temperature affected the adsorption capacity of the physically pretreated *R. centifolia* distillation waste biomass. The Cu(II) and Ni(II) equilibrium sorption data agreed well to Langmuir isotherm model and the sorption kinetics were accurately described by pseudo second order kinetic model. The Cu(II) and Ni(II) uptake capacities (mg g^{-1}) of physical pretreated *R. centifolia* distillation waste biomass were in following order: boiled (66.91) > heated (52.51) > autoclaved (49.82) > native (42.68) and boiled (67.55) > heated (65.19) > autoclaved (58.09) > native (45.19), respectively. The nature of *R. centifolia* distillation waste biomass surface functionalities was analyzed by FTIR spectroscopy.

Key words: Cu(II), Ni(II), isotherms, kinetics, pretreatment, *Rosa centifolia*.

INTRODUCTION

The increased use of metals and chemicals in the process industries has resulted in the generation of large quantities of aqueous effluents that contain high levels of heavy metals, creating serious environmental disposal problems (Sarwar et al., 2004; Hanif et al., 2005; Javed et al., 2007; Hanif et al., 2007a; Hanif et al., 2007b; Bhatti et al., 2007 and Zafar et al., 2007). The presence of heavy metals in aquatic environments is known to cause severe damage to aquatic life, besides the facts that these metals kill microorganisms during biological treatment of waste water with a consequent delay of the process of water purification. Heavy metals released into the environment has been increasing continuously as a result of industrial activities and technological development, posing a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature (Nasir et al., 2007;

Nadeem et al., 2007a; Antunes et al., 2003; Hussain et al., 2004; Quek et al., 1998; Chatwal et al., 1989; Yu and Kaewsarn, 1999; Horsfall and Spiff, 2005a; Prasad and Freitas, 2000; Carson et al., 1986; Akar and Tulani, 2006). Exposure to heavy metal contamination has been found to cause kidney damage, liver damage, and anemia in low doses, and in high concentrations, heavy metals can be carcinogenic (Nasir et al., 2007). Cu(II) enters very easily in the body but is readily excreted; it stays in body, performs necessary functions but its excess is toxic and Cu(II) causes the following diseases like nausea, salivation, purgation, abdominal pain, convulsions and paralysis (Chatwal et al., 1989). Conventional methods, such as ion-exchange, chemical precipitation, ultra purification and electrochemical deposition do not seem to be economically feasible for such industries because of their relatively high costs. Therefore, there is a need to look into alternatives to investigate a low-cost method which is effective and economical, and can be on industrial scale (Quek et al., 1998). Biosorption, the uptake of heavy metals by non-living biomass, has gained increased credibility during recent years, as it

*Corresponding author. E-mail: raziyaanalyst@gmail.com.

offers a technically feasible and economical approach (Akar and Tulani, 2006). It could be considered as an eco-friendly method to the existing high cost technologies, generally, biosorptive processes can reduce capital costs by 20% operational cost by 36% and total treatment costs by 28% compared with the conventional systems (Nadeem et al., 2007b). Several biological materials were investigated for the removal of heavy metals including, yeasts, algae, fungi and other plant biomasses (Javed et al., 2007; Nasir et al., 2007; Lodeiro et al., 2006; Horsfall and Spiff 2005b; Sarin and Pant, 2006).

Rosa centifolia is commonly known as hundred-leaved rose, cabbage rose, flores rosarum incarnatarum. This is an erect shrub, 3-6 feet in height; its flowers are large and pink color (Grieve and Roses, 2007). *R. centifolia* flowers are extensively used for essential oil and rose water production by steam/hydro-distillation. The sludge left after essential oil and rose water production is a useless waste material. The present study explored the utilization of this waste material for the biosorption of Cu(II) and Ni(II) from aqueous solutions. The objectives of the present study were followings: (i) to investigate the use of *R. centifolia* biomass available in large quantities as a biosorbent for Cu(II) and Ni(II) (ii) to evaluate the effect of physical pretreatments on sorption capacity of *R. centifolia* waste biomass and (iii) to study the effect of different experimental conditions such as initial metal concentration, contact time and temperature on metal sorption process.

MATERIAL AND METHODS

Collection and pretreatment of biomass

The *R. centifolia* waste biomass left after essential oil extraction using steam distillation process was collected from Rose Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan. The collected biomass was first sun dried and then further dried in an electrical oven at 70°C to constant weight. Fully, dried biomass was grounded into powdered form and sieved to obtain biomass with uniform size (0.250 mm). *R. centifolia* biomass was subjected to three different physical treatments viz. boiled (5 g of biosorbent boiled in 250 mL of distilled water for 1 h), heated (5 g of biosorbent heated for 1 h) and auto-claved (5 g of biosorbent autoclaved at 121 °C for 15 min at 15 psi).

Batch biosorption studies

The effects of initial metal concentration (5 – 640 mg L⁻¹), contact time (5 - 320 min) and temperature (303-333 K) at fixed values of pH (5), biosorbent size (0.250 mm), biosorbent dosage (0.1 g) and shaking speed (130 rpm) on Cu(II) and Ni(II) uptake using physically pretreated *R. centifolia* biomass were evaluated in the present study. The pH of metal solution was maintained using 0.1 N NaOH and 0.1 N HCl. After equilibration solutions were filtered through Whatman filter No. 42 and stored in plastic sample bottles at 4°C till analysis (Wong et al., 2000 and Meunier et al., 2003).

Reagents

All chemical reagents used in present study including atomic ab-

sorption spectrometric standards were of analytical grade, purchased from Fluka chemicals.

Metals solutions

Stock solutions of Cu(II) and Ni(II) were prepared by dissolving 3.95 g of CuSO₄.5H₂O and 4.50 g of NiSO₄.6H₂O, respectively. The solution of appropriate concentration was prepared using deionized distilled water (DDW). The amount of Cu(II) and Ni(II) taken up by rose waste biomass in each flask was calculated using following mass balance equation (Eq.1) (Javed et al., 2007). The percentage removal was determined by equation 2.

$$q_e = (C_i - C_e) V / 1000 W \quad (1)$$

$$\% \text{ sorption} = [(C_i - C_e) 100] / C_i \quad (2)$$

Where “C_i (mg L⁻¹)” and “C_e (mg L⁻¹)” are the initial and equilibrium metal concentrations (mg L⁻¹), respectively, q_e (mg g⁻¹) is the equilibrium sorption

FTIR analysis

FTIR spectroscopy was used to detect vibration frequency changes in the *R. centifolia* distillation waste biomass. The spectra were collected by FTIR-BX (Perkin-Elmer) spectrometer within the range 400 – 4000 cm⁻¹ using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. Spectra were plotted using the same scale on the absorbance axis.

Statistical analysis

All sets of experiments were performed in triplicate to ensure the reproducibility of results. The errors bars have been shown in figures representing experimental value ± SD. All statistical analysis was performed using Microsoft Excel 2007 (Microsoft Cooperation, USA).

RESULTS AND DISCUSSION

Effect of initial metal concentration

The uptake of Cu(II) and Ni(II) increased with increase in initial metal concentration (Figures 1a and 2a). The maximum Cu(II) adsorption capacities of native, boiled, heated and autoclaved *R. centifolia* biomass were 42.68, 66.91, 52.51 and 49.82 mgg⁻¹ and maximum Ni(II) adsorption capacities of native, boiled, heated and autoclaved *R. centifolia* biomass were 45.19, 67.55, 65.19, and 58.09 mg g⁻¹, respectively. The chemistry of adsorption is relatively complicated. A number of theories have been used in an attempt to understand the adsorption process. To examine the relationship between adsorbed (q_e) and aqueous concentrations (C_e) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir (Figures 1b and 2b) and the Freundlich parameters can be determined from a linearized form of equation (Eq. 3), represented by

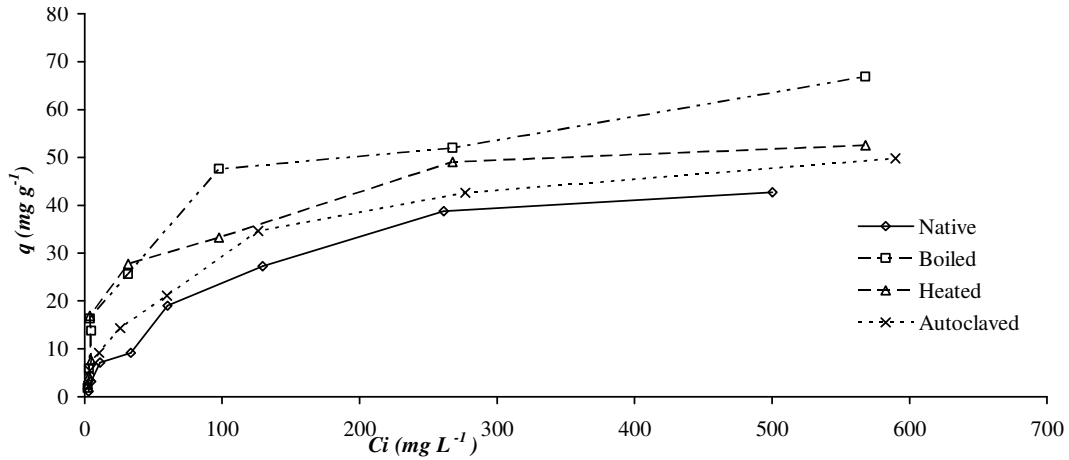


Figure 1a. Effect of initial metal concentration on biosorption of Cu(II) onto physically pretreated *Rosa centrifolia* distillation waste biomass.

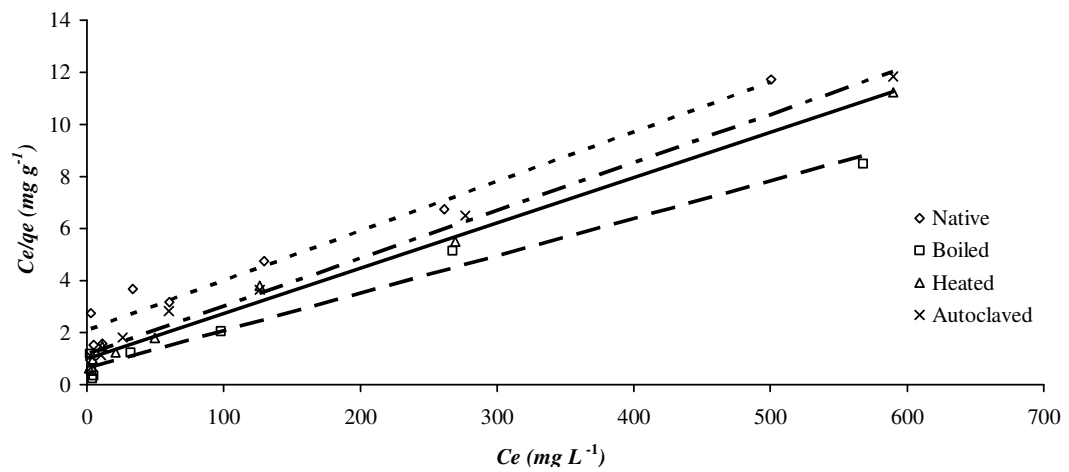


Figure 1b. Langmuir model for biosorption of Cu(II) onto physically pretreated *Rosa centrifolia* distillation waste biomass.

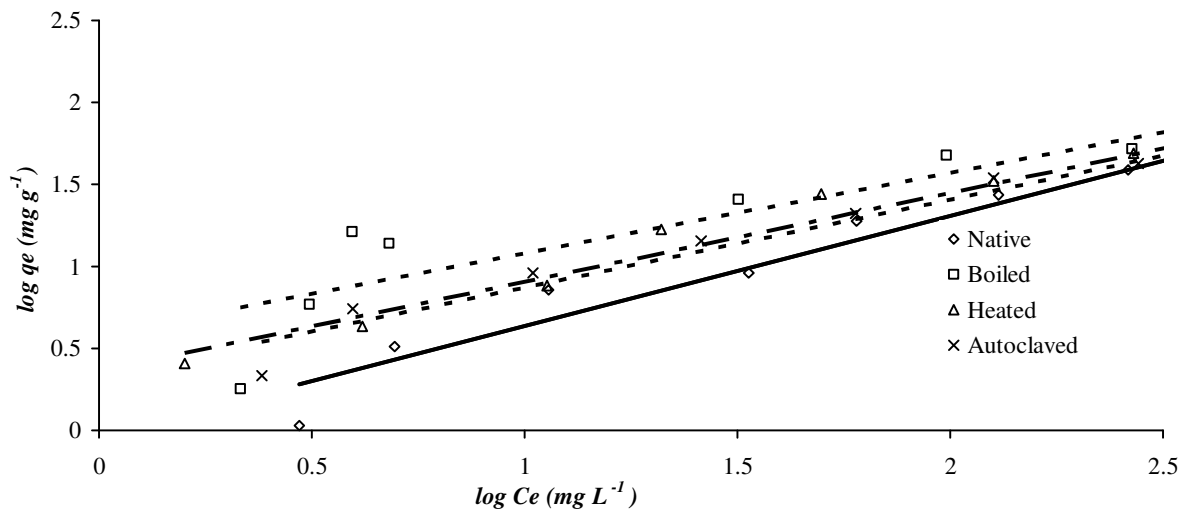


Figure 1c. Freundlich model for biosorption of Cu(II) onto physically pretreated *Rosa centrifolia* distillation waste biomass.

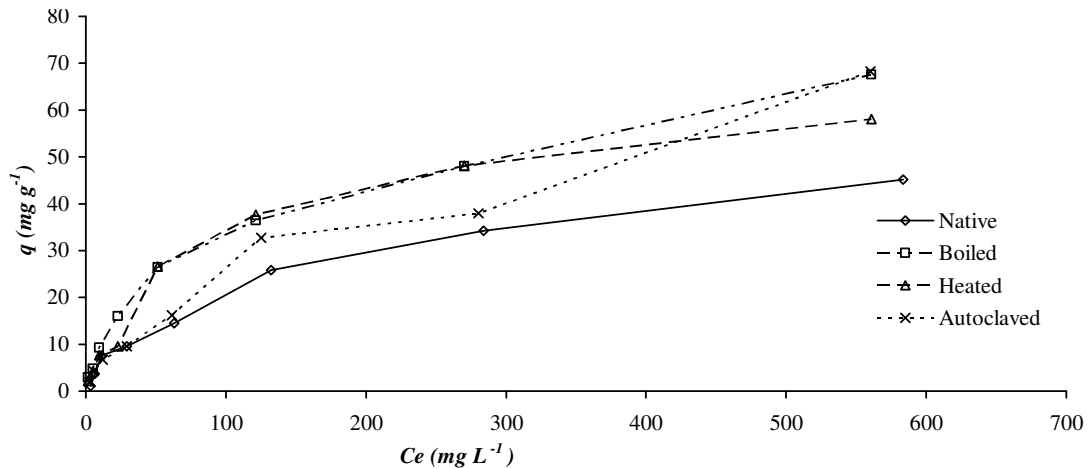


Figure 2a. Effect of initial metal concentration on biosorption of Ni(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

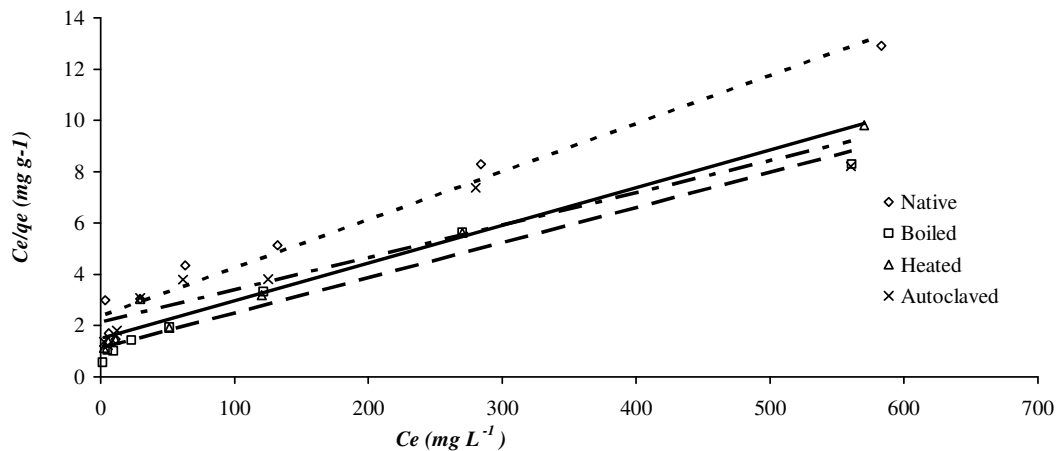


Figure 2b. Langmuir model for biosorption of Ni(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

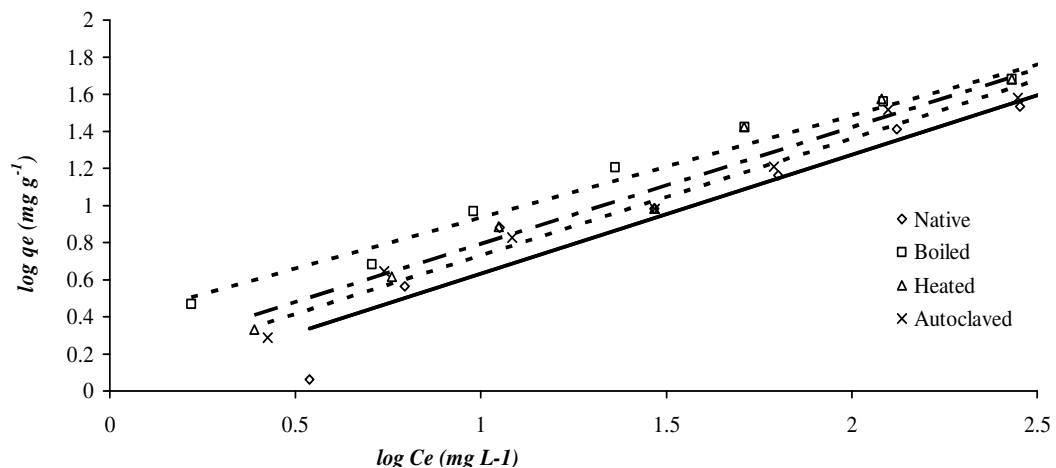


Figure 2(c). Freundlich model for biosorption of Ni(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

Table 1. Comparison between Langmuir and Freundlich isotherm parameters for Cu(II) and Ni(II) by *Rosa centifolia* biomasses.

Metal	Sample	Langmuir isotherm parameters			Experimental q(mg g ⁻¹)	Freundlich isotherm parameters			
		Xm(mg g ⁻¹)	K _L (L mg ⁻¹)	R ²		q(mg g ⁻¹)	K(mg g ⁻¹)	R ²	1/n
Cu(II)	Native	52.35	0.009	0.97	42.68	69.82	1.079	0.93	0.710
	Boiled	69.44	0.022	0.98	66.91	87.90	3.852	0.87	0.493
	Heated	57.47	0.017	0.99	52.51	73.62	2.315	0.95	0.542
	Autoclaved	54.34	0.015	0.99	49.82	65.91	2.271	0.94	0.535
Ni(II)	Native	53.19	0.030	0.96	45.19	60.37	1.021	0.92	0.631
	Boiled	72.99	0.012	0.96	67.55	44.3	3.691	0.96	0.589
	Heated	79.36	0.005	0.98	65.19	67.07	1.260	0.98	0.554
	Autoclaved	68.02	0.009	0.97	58.09	78.86	1.459	0.95	0.665

(Hanif et al., 2007a).

$$\log q_e = 1/n \log C_e + \log K \quad (3)$$

where q_e is metal ion adsorbed (mg g⁻¹), C_e is the equilibrium concentration of metal ion solution mg L⁻¹, K and $1/n$ are constants. The constants K and $1/n$ were determined by linear regression from the plot of $\log q_e$ against $\log C_e$. The Langmuir model better represented the sorption process in comparison to model of Freundlich due to its high value of correlation coefficient in case of Cu(II) as well as of Ni(II) (Table 1).

Kinetic study

While studying the effect of contact time on the uptake of Cu(II) and Ni(II) by *R. centifolia* distillation waste biomass, it was observed that the biosorption takes place in two steps, a rapid surface adsorption with in 30 min and a slow intercellular adsorption up to equilibration (Figures 3a and 4a).

Two different kinetic models were used to test the experimental data of Cu(II) and Ni(II) biosorption using physically pretreated (boiled, heated and autoclaved) *R. centifolia* distillation waste biomass. The pseudo first order model is generally expressed as (Eq. 4) (Akar and Tunali, 2006).

$$\log (q_e - q) = \log q_e - K_{1,ads} t/2.303 \quad (4)$$

where q (mg g⁻¹) is the sorption capacity, q_e (mg g⁻¹) is the equilibrium sorption capacity and $K_{1,ads}$ is the rate constant of first order kinetic model (Figures 3b and 4b).

The pseudo second order model is based on assumption that biosorption follows a second order mechanism. So, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. The pseudo second order equation is expressed as (Eq. 5):

$$t/q = 1/K_{2,ads} q_e^2 + t/q_e \quad (5)$$

where $K_{2,ads}$ is the rate constant of second order kinetic

model (g.mg⁻¹.min), q_e and $K_{2,ads}$ were calculated from the slope and intercept of the plot t/q versus t . The pseudo second order kinetic model better represented the adsorption process, in comparison to the pseudo first order kinetic model (Table 2).

Effect of temperature

Temperature is a crucial parameter in adsorption processes. The effect of temperature on the removal of Cu(II) and Ni(II) in aqueous solution by *R. centifolia* distillation waste biomass was studied by varying the temperature between 303 and 333 K. It is evident from Figures 5 and 6 that adsorption of Cu(II) and Ni(II) by the *R. centifolia* distillation waste biomass increased with increase in temperature from 303 to 313 K. However, subsequent decrease in adsorption capacity was observed when temperature was raised beyond 313 K. At high temperatures, the attractive forces between biomass surface and metal ions are weakened and the sorption decreases which results in the decrease in the thickness of the boundary layer, due to the increased tendency of the metal ion to escape from the biomass surface to the solution phase. The ultimately result is a decrease in adsorption as temperature increases (Horsfall and Spiff, 2005b).

Surface coverage (θ)

The fraction of biomass surface covered by Cu(II) and Ni(II) was calculated by the following equation (Eq. 6) derived from Langmuir adsorption isotherm (Hanif et al., 2007a).

$$\theta = K C_i (1 - \theta) \quad (6)$$

where K is the Langmuir adsorption coefficient, C_i the initial Cu(II) and Ni(II) concentration. From Figures 7 - 8, it can be concluded that fraction of biomass surface coverage value increased with increase in initial metal concentration.

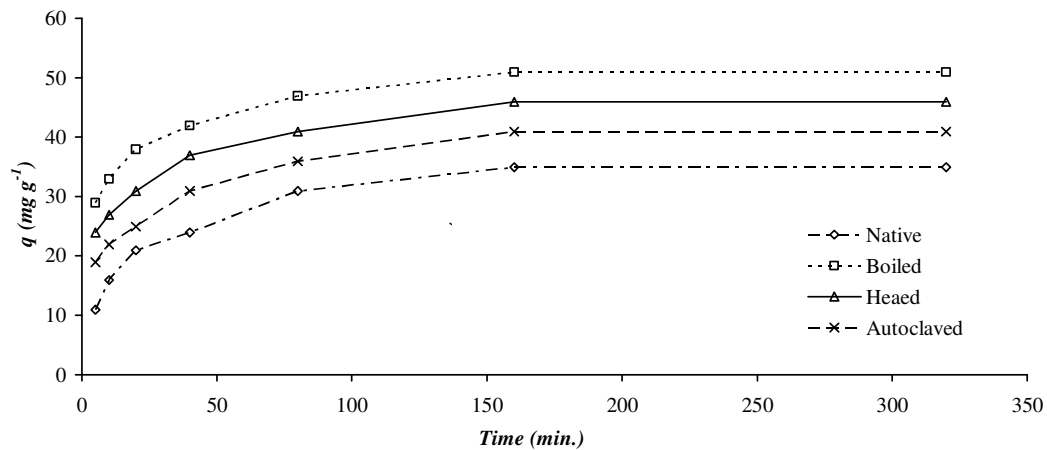


Figure 3a. Effect of contact time on biosorption of Cu(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

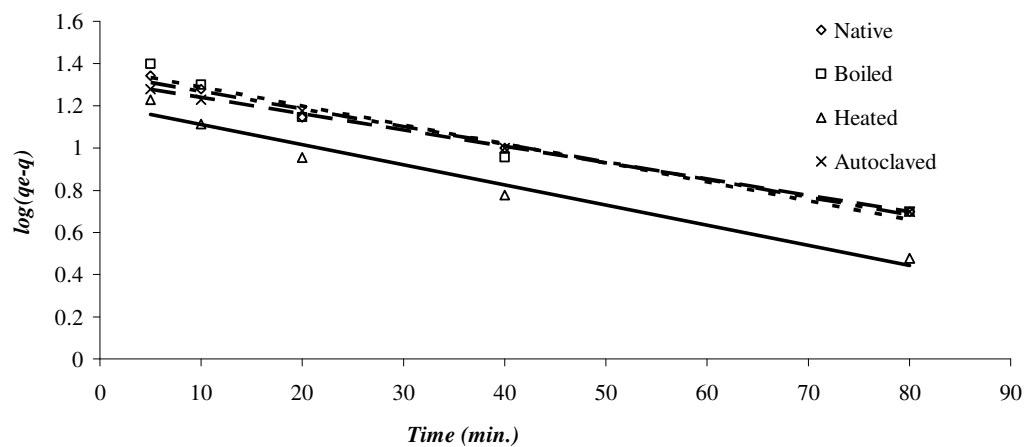


Figure 3b. Pseudo 1st order kinetic model for biosorption of Cu(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

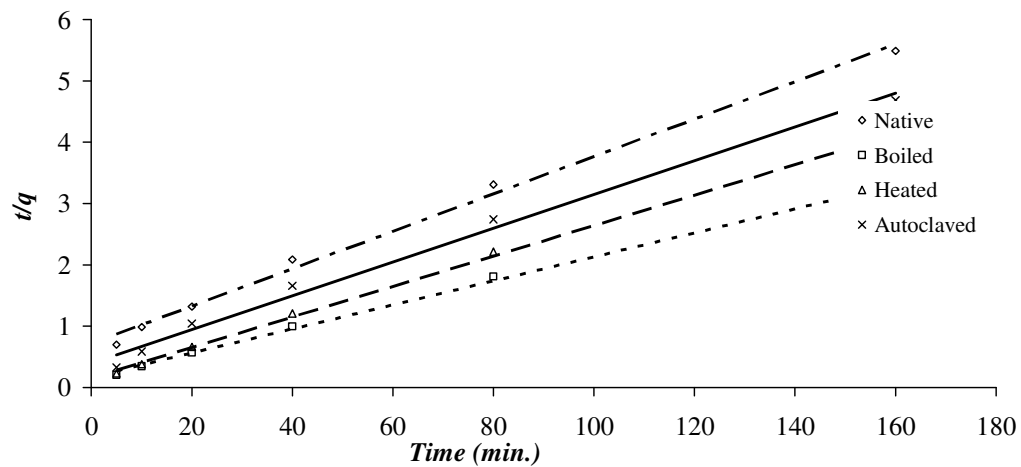


Figure 3c. Pseudo 2nd order kinetic model for biosorption of Cu(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

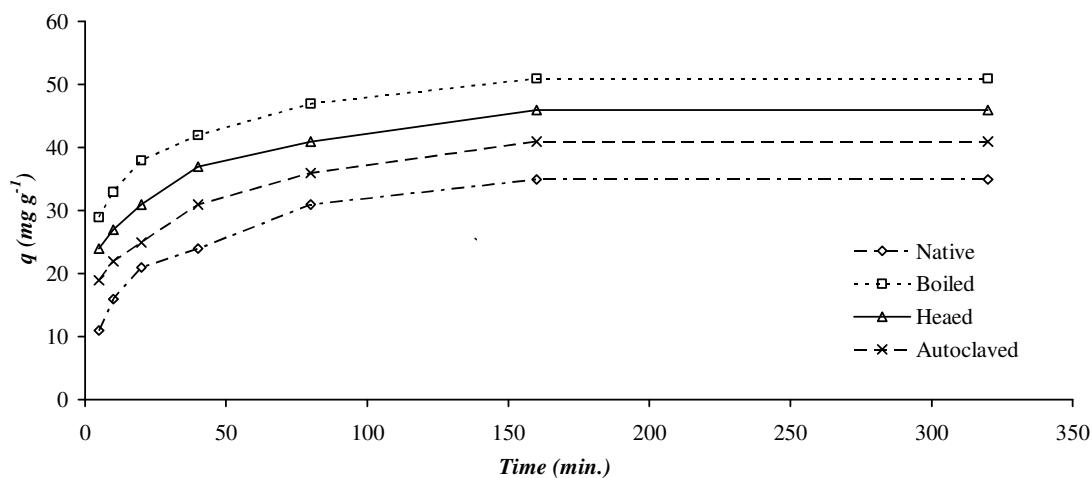


Figure 4a. Effect of contact time on biosorption of Ni(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

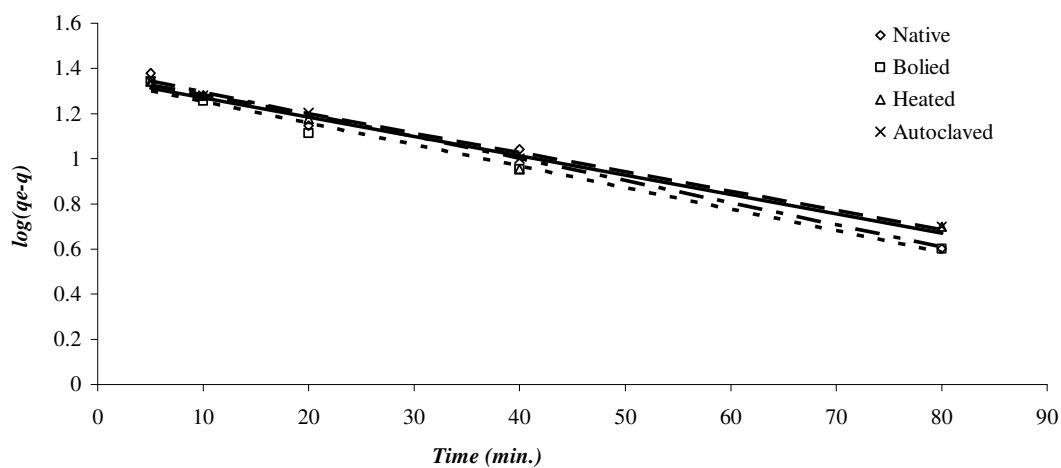


Figure 4b. Pseudo 1st order kinetic model for biosorption of Ni(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

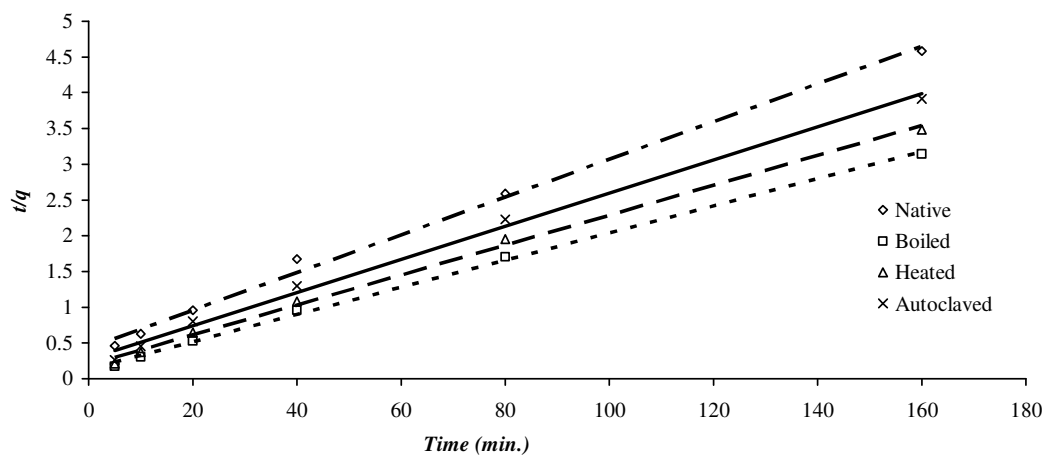


Figure 4c. Pseudo 2nd order kinetic model for biosorption of Ni(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

Table 2. Comparison between adsorption rate constants, q_e estimated and coefficient of correlation associated the Lagergren pseudo-first order and to pseudo-second order kinetic models.

Metal	Sample	Pseudo first order kinetic model			Experimental	Pseudo second order kinetic model		
		q_e (mg g^{-1})	$K_{1,ads}$ (min^{-1})	R^2	q (mg g^{-1})	q_e (mg g^{-1})	$K_{2,ads}$ ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Cu(II)	Native	22.51	0.0190	0.92	29.15	32.78	0.0013	0.99
	Boiled	25.26	0.0201	0.93	34.40	36.02	0.0022	0.98
	Heated	32.15	0.0145	0.92	39.15	40.32	0.0038	0.97
	Autoclaved	39.15	0.0032	0.90	49.50	46.36	0.0019	0.97
Ni(II)	Native	25.54	0.022	0.86	34.19	38.02	0.0016	0.99
	Boiled	41.18	0.021	0.96	50.90	52.63	0.0027	0.98
	Heated	38.89	0.019	0.87	45.91	47.84	0.00239	0.97
	Autoclaved	27.58	0.019	0.89	40.94	43.10	0.0019	0.94

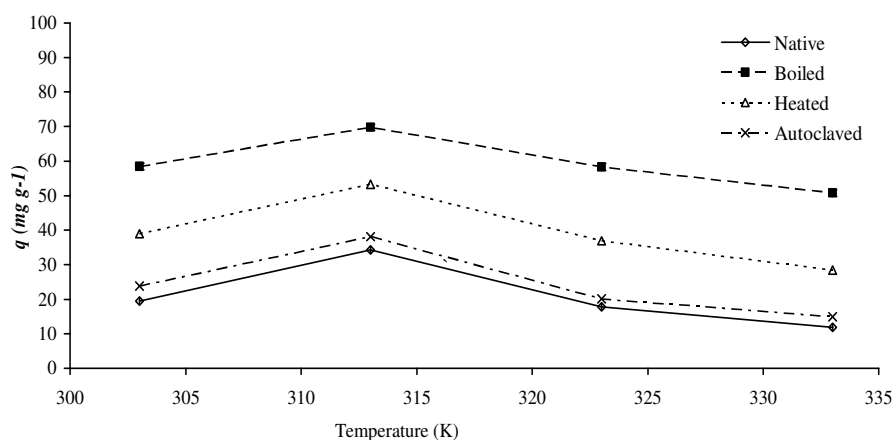


Figure 5. Effect of temperature on biosorption of Cu(II) by onto physically pretreated *Rosa centifolia* distillation waste biomass.

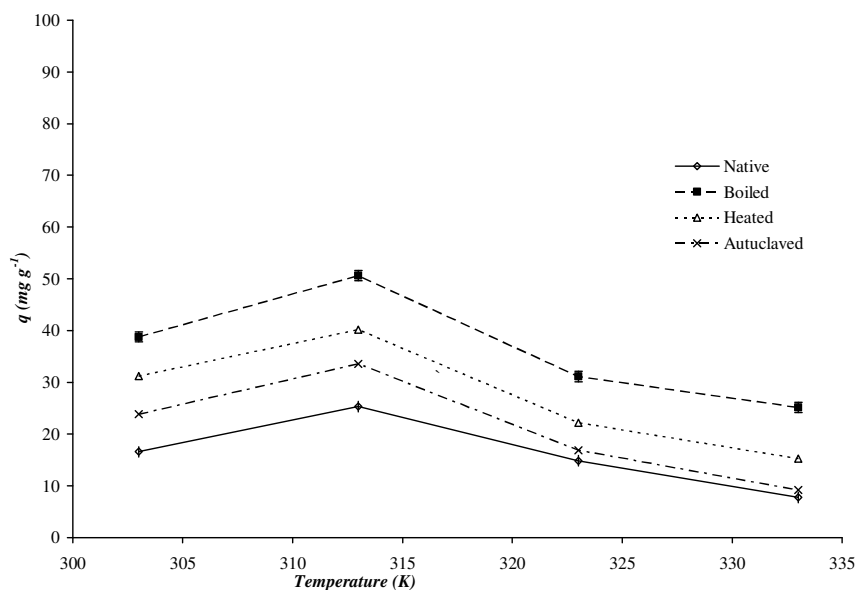


Figure 6. Effect of temperature on biosorption of Ni(II) onto physically pretreated *Rosa centifolia* distillation waste biomass.

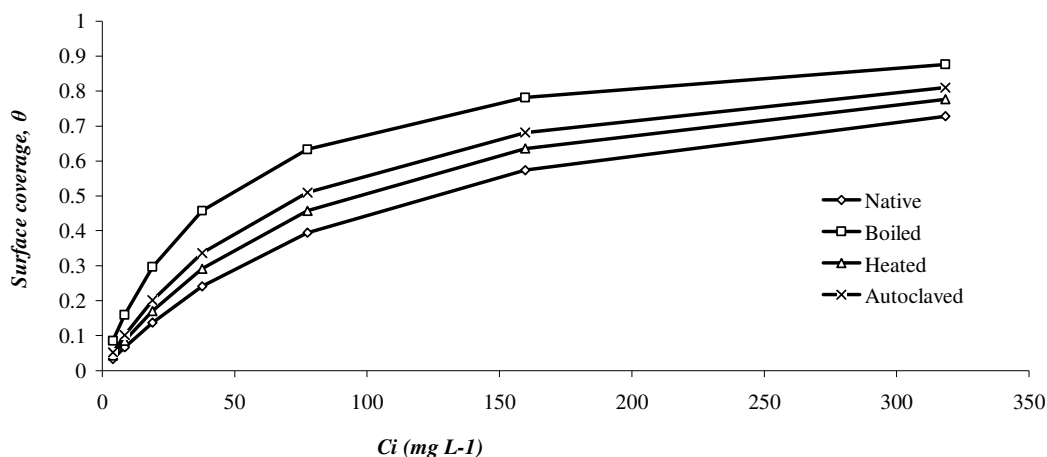


Figure 7. A plot of surface coverage (θ) against concentration of Cu(II) for physically pretreated *Rosa centifolia* distillation waste biomass.

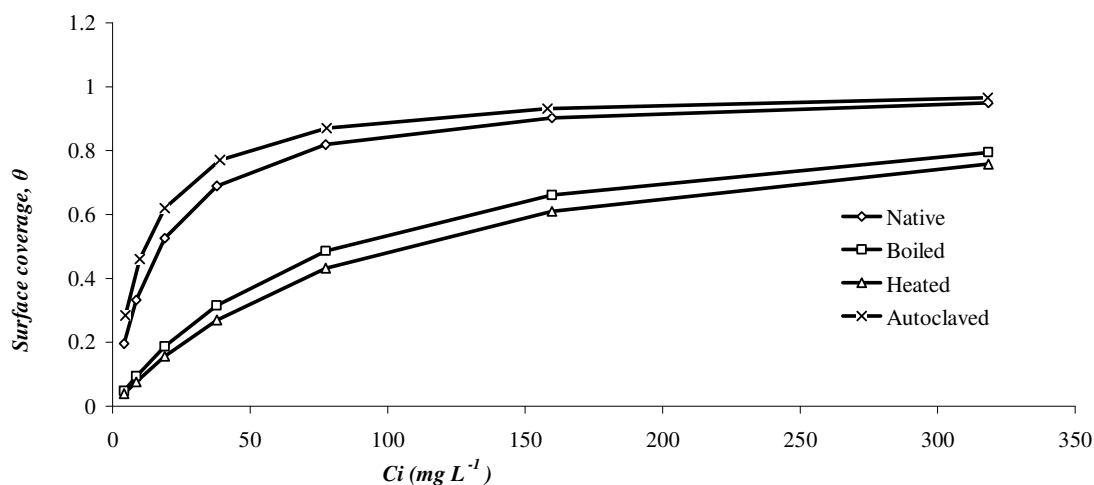


Figure 8. A plot of surface coverage (θ) against concentration of Ni(II) for physically pretreated *Rosa centifolia* distillation waste biomass.

Gibbs free energy ($\Delta G^\circ_{\text{ads}}$)

$\Delta G^\circ_{\text{ads}}$ values were calculated (Eq. 7) using Bockers Swinkel's adsorption isotherm to determine the feasibility of adsorption process (Hanif et al., 2007a).

$$\Delta G^\circ_{\text{ads}} = -2.303 RT \log \times \left[\left\{ \frac{55.4 \theta}{C_i(1-\theta)} \right\} \left\{ \theta + n(1-\theta)n^{1/n} \right\} \right] \quad (7)$$

where C_i is the initial concentration of Cu(II) and Ni(II) ions in the solution and n is charge on metal. The values of ΔG° were highly negative on all studied concentrations suggesting that the Cu(II) and Ni(II) adsorption process by *R. centifolia* biomass is spontaneous in nature at both low and high concentrations (Tables 3 - 4).

Effect of pretreatment

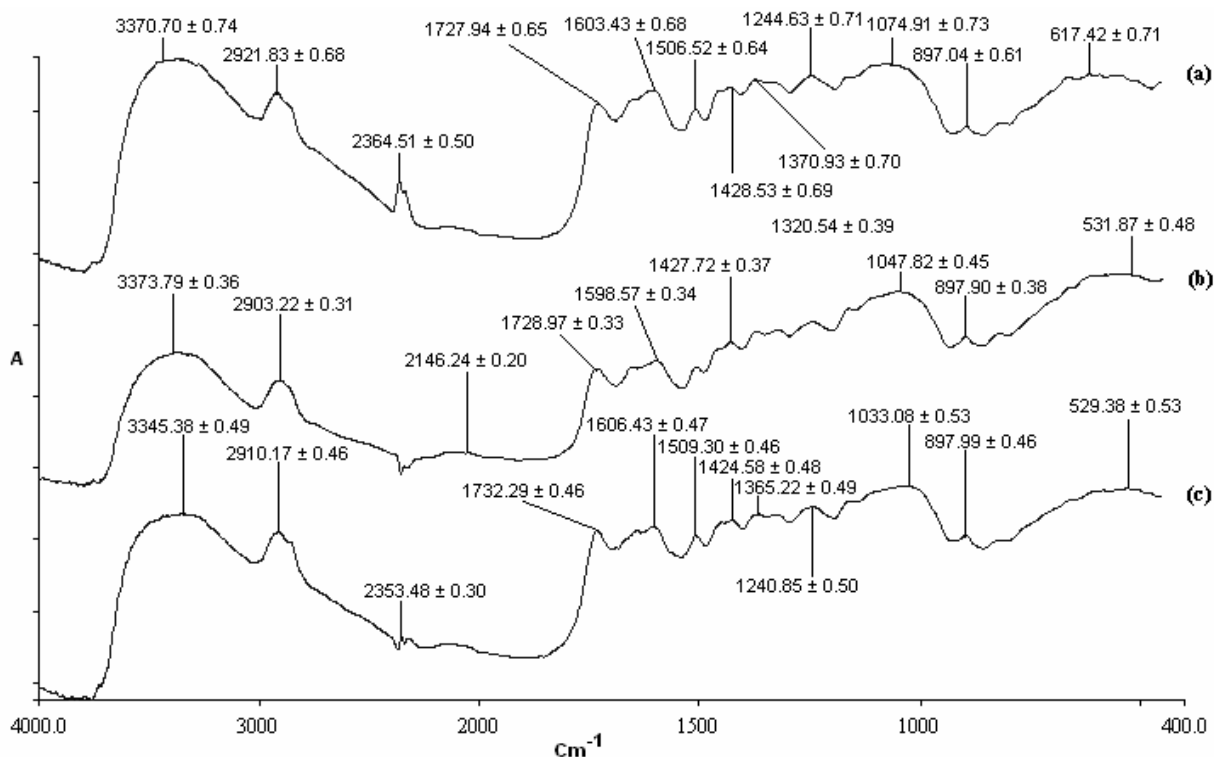
Physical pretreatment of *R. centifolia* waste biomass resulted in increase in its metal uptake capacity (Figures 1a and 2a). Cu(II) and Ni(II) uptake capacities (mg g^{-1}) of physical pretreated *R. centifolia* distillation waste biomass were in the following order: boiled (66.91) > heated (52.51) > autoclaved (49.82) > native (42.68) and boiled (67.55) > heated (65.19) > autoclaved (58.09) > native (45.19), respectively. The increase in sorption capacity of biomass after boiling and autoclaving pre-treatment may be due to the removal of mineral matter from biomass cells and subsequent creation of freer sorption sites for metal uptake. The increase in sorption capacity of preheated *R. centifolia* biomass may be attributed to the decomposition of organic matter which resulted in

Table 3. Apparent Gibbs free energy ΔG°_{ads} (KJ.mol⁻¹) of Cu(II) by *Rosa centifolia* biomass and aqueous phase.

Ci (mg L ⁻¹)	Native	Boiled	Heated	Autoclaved
5	-24.15456	-26.5424	-24.7928	-25.2936
10	-24.11197	-26.4425	-24.7389	-25.2289
25	-24.01794	-26.2465	-24.6225	-25.0925
50	-23.87304	-25.9968	-24.4502	-24.8976
80	-23.64333	-25.6919	-24.1928	-24.6212
160	-23.34586	-25.4043	-23.885	-24.3119
320	-23.05643	-25.1983	-23.6100	-24.0531
640	-22.06436	-25.0644	-23.3982	-24.3188

Table 4. Apparent Gibbs free energy ΔG°_{ads} (KJ.mol⁻¹) of Ni(II) by *Rosa centifolia* biomass and aqueous phase.

Ci (mg L ⁻¹)	Native	Boiled	Heated	Autoclaved
5	-22.4335	-25.0663	-20.7765	-22.4553
10	-22.4331	-25.0067	-20.7712	-22.4496
25	-22.4321	-24.8797	-20.7585	-21.4400
50	-22.4302	-24.6951	-19.7361	-21.4189
80	-21.4263	-24.4270	-19.6910	-21.3797
160	-20.4182	-24.1176	-19.6048	-20.3042
320	-20.4028	-23.8510	-17.4622	-20.1728
640	-19.6517	-23.6518	-17.2405	-20.3229

**Figure 9.** FTIR spectra of *Rosa centifolia* biomass (a) Unloaded *Rosa centifolia* distillation waste biomass (b) Cu(II) loaded *Rosa centifolia* distillation waste biomass (c) Ni(II) loaded *Rosa centifolia* distillation waste biomass.

availability of more sorption sites for metal uptake (Nadeem et al., 2007a).

Fourier transforms infrared (FTIR) studies

The FTIR technique is to measure the absorption of various infrared radiations by the target material, to produce an IR spectrum that can be used to identify functional groups and molecular structure in the sample. The FTIR spectra of *R. centrifolia* distillation waste biomass suggested the involvement of carbonyl ($1727.94 \pm 0.65 \text{ cm}^{-1}$), carboxylic ($3370.70 \pm 0.74 \text{ cm}^{-1}$), ethers ($1074.91 \pm 0.73 \text{ cm}^{-1}$), esters ($1244.63 \pm 0.71 \text{ cm}^{-1}$), primary amines ($1603.43 \pm 0.68 \text{ cm}^{-1}$), secondary amine ($1506.52 \pm 0.64 \text{ cm}^{-1}$), thioesters ($897.04 \pm 0.61 \text{ cm}^{-1}$), phosphine ($2364.51 \pm 0.50 \text{ cm}^{-1}$) and alkyne ($617.42 \pm 0.71 \text{ cm}^{-1}$) linkages present on the biomass surface responsible for metal uptake process (Figure 9) (Wong et al., 2000; Yu and Kaewsarn, 1999; Zafar et al., 2007). The absorbance of the peaks in the metal loaded sample was substantially lower than those in the raw sample. This indicated that bond stretching occurred to a lesser degree due to the exchange of hydrogen ions with metal ions, and subsequently peak absorbance was attenuated (Williams and Fleming, 1987).

Conclusions

The following conclusions can be drawn from the study:

- The *R. centrifolia* distillation waste biomass can be efficiently utilized as low cost biosorbent for Cu(II) and Ni(II) from aqueous solutions after physical pretreatment.
- The effectiveness of different physical pretreatments of *R. centrifolia* distillation waste biomass was in the following order: boiled > heated > autoclaved > native.
- Highly negative $\Delta G^\circ_{\text{ads}}$ values described the spontaneous nature of Cu(II) and Ni(II) sorption process by *R. centrifolia* distillation waste biomass. The metal sorption process followed well Langmuir isotherm and the metal sorption process was pseudo second order mechanism in nature.
- The fraction of biomass covered was found highly dependent on the initial concentration of metal.
- The involvement of carbonyl, carboxylic, ethers, esters, primary amines, secondary amine, thioesters, phosphine and alkyne linkages in metal adsorption process present on the biomass surface were confirmed by the FTIR spectra of *R. centrifolia* distillation waste biomass.

ACKNOWLEDGEMENT

Authors are thankful to Prof. Dr. Muhammad Aslam Khan (Director, Rose Project, Institute of Horticultural Sciences,

University of Agriculture, Faisalabad Pakistan) for providing the *R. centrifolia* distillation waste biomass.

REFERENCES

- Akar T, Tunali S (2006). Biosorption characteristics of *Aspergillus flavus* biomass for removal of Pb(II) and Cu(II) ions from an aqueous solution. *Bioresour. Technol.* 97: 1780-1787.
- Antunes WM, Luna AS, Henriques CA, da Costa ACA (2003). An evaluation of Cu(II) biosorption by brown seaweed under optimized conditions. *E. J. Biotechnol.* 6(3): 174-184.
- Bhatti HN, Mumtaz B, Hanif MA, Nadeem R (2007). Removal of Zn(II) ions from aqueous solution using *Moringa oleifera* Lam. (horseradish tree) biomass. *Proc. Biochem.* 42: 547-553.
- Carson BL, Ellis HV, Mc Cann JL (1986). Toxicology and biological monitoring of metals in human. Lewis publishers, Chelsea. Michigan. pp. 65-297.
- Chatwal GR, Mehra MC, Satake M, Katyal T, Katya ACAM, Nagahiro T (1989). *Encyclopedia of Environmental Pollution and its Control.* 2: 51-53.
- Grieve M (2008). Roses. <http://www.botanical.com/botanical/mgmhr/roses-18.html>, Last assessed on 08.11.2008.
- Hanif MA, Nadeem R, Zafar MN, Akhtar K, Bhatti HN (2007b). Kinetic studies for Ni(II) biosorption from industrial wastewater by *Cassia fistula* (Golden Shower) biomass. *J. Hazard Mater.* 145: 501-505.
- Hanif MA, Nadeem R, Bhatti HN, Ahmad NR, Ansari TM (2007a). Ni(II) biosorption by *Cassia fistula* (golden Shower) biomass. *J. Hazard. Mater.* 139: 345-355.
- Hanif MA, Bhatti HN, Nadeem R, Zia KM, Ali MA (2007c). *Cassia fistula* (Golden Shower): A Multipurpose Ornamental Tree. *Flori Orna Biotechnol.* 1(1): 21-26.
- Hanif MA, Nadeem R, Rashid U, Zafar MN (2005). Assessing pollution levels in effluents of industries in City Zone of Faisalabad, Pakistan. *J. Appl. Sci.* 5(10): 1713-1717.
- Hussain H, Ibrahim SF, Kandeel K, Moawad H (2004). Biosorption of heavy metals from waste water using *Pseudomonas* sp. *E. J. Biotechnol.* 7(1): 8-15.
- Javed MA, Bhatti HN, Hanif MA, Nadeem R (2007). Kinetic and equilibrium modeling of Pb(II) and Co(II) sorption onto rose waste biomass. *Sep Sci. Technol.* In press.
- Horsfall M, Spiff AI (2005b). Effects of temperature on the sorption of Pb²⁺ and Cd²⁺ from aqueous solution by *Caladium bicolor* (Wild Cocoyam) biomass. *E. J. Biotechnol.* 8(2): 162-169.
- Horsfall M, Spiff AI (2005a). Effect of metal ion concentration on the biosorption of Pb²⁺ and Cd²⁺ by *Caladium bicolor* (wild cocoyam), *Afr. J. Biotechnol.* 4(2): 191-196.
- Lodeiro P, Barriada JL, Herrero R, de Vicente MES (2006). The marine macroalga *Cystoseira baccata* as biosorbent for cadmium(II) and lead (II) removal: Kinetic and equilibrium studies. *Environ. Pollut.* 142: 264-273.
- Meunier NJ, Blais JF, Tyagi RD (2003). Cocoa shells for heavy metal removal from acidic solutions. *Bioresour. Technol.* 90: 255-263.
- Nadeem R, Hanif MA, Hussain A, Ali MA, Ansari TM (2007b). Biosorption of Pb (II) by local gram (*Cicer arietinum*) cultivar biomass. *J. Chem. Soc. Pak.* 2007. Accepted 18.06. In press.
- Nadeem R, Hanif MA, Shaheen F, Perveen S, Zafar MN, Iqbal T (2007a). Physical and chemical modification of distillery sludge for Pb (II) biosorption. *J. Hazard Mater;* In press.
- Nasir MH, Nadeem R, Akhtar K, Hanif MA, Khaild AM (2007). Efficacy of modified distillation sludge of rose (*Rosa centrifolia*) petals for lead (II) and Zn (II) removal from aqueous solutions. *J Hazard Mater;* In press.
- Prasad MN, Freitas (2000). Removal of toxic metals from solution by leaf, stem and root phytomass of *Quercus ilux* L. (holly oak); *Environ. Poll.* 110(2) : 277-283.
- Quek SY, Wase DAJ, Forster CF (1998). The use of sago waste for the sorption of lead and Cu(II). *Water SA,* 24(3): 251-256.
- Sarin V, Pant KK (2006). Removal of chromium from industrial waste by using eucalyptus bark. *Bioresour. Technol.* 97: 15-20.
- Sarwar MW, Hanif MA, Rashid U, Ali S, Rehman K (2004). Optimization

- of conditions of coagulation flocculation process in industrial wastewater treatment using coagulant alum. *Indian J. Biol. Sci.* 1(2): 68-70.
- Williams DH, Fleming I (1987). *Spectroscopic methods in organic chemistry*; 4th edition, McGraw Hill.
- Wong JPK, Wong YS, Tam NFY (2000). Ni(II) Biosorption by two chlorella species, *C. vulgaris* (a commercial species) and *C. miniata* (a local isolate). *Bioresour. Technol.* 73: 133-137.
- Yu Q, Kaewsarn P (1999). Binary adsorption of Cu(II) and cadmium (II) from aqueous solutions by biomass of marine alga *Ddurvillaea potatorum*. *Sci. Technol.* 34(8): 1516-1522.
- Zafar MN, Nadeem R, Hanif MA (2007). Biosorption of nickel from protonated rice bran. *J. Hazard Mater.* 143: 478-485.