Kinetic and thermodynamic aspects of Cu(II) and Cr(III) removal from aqueous solutions using rose waste biomass

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ABSTRACT

Distillation waste of rose petals was used to remove Cu(II) and Cr(III) from aqueous solutions. The results demonstrated the dependency of metal sorption on pH, sorbent dose, sorbent size, initial bulk concentration, time and temperature. A dosage of 1 g/L of rose waste biomass was found to be effective for maximum uptake of Cu(II) and Cr(III). Optimum sorption temperature and pH for Cu(II) and Cr(III) were 303 ± 1 K and 5, respectively. The Freundlich regression model and pseudo-second-order kinetic model were resulted in high correlation coefficients and described well the sorption of Cu(II) and Cr(III) on rose waste biomass. At equilibrium q_{max} (mg/g) of Cu(II) and Cr(III) was 55.79 and 67.34, respectively. The free energy change ($\Delta G°$) for Cu(II) and Cr(III) sorption process was found to be -0.829 kJ/mol and -1.85 kJ/mol, respectively, which indicates the spontaneous nature of sorption process. Other thermodynamic parameters such as entropy change ($\Delta S°$), enthalpy ($\Delta H°$) and activation energy (ΔE) were found to be 0.604 J mol^{-1} K^{-1}, -186.95 kJ/mol and 68.53 kJ/mol, respectively for Cu(II) and 0.397 J mol^{-1} K^{-1}, -119.79 kJ/mol and 114.45 kJ/mol, respectively for Cr(III). The main novelty of this work was the determination of shortest possible sorption time for Cu(II) and Cr(III) in comparison to earlier studies. Almost over 98% of Cu(II) and Cr(III) were removed in only first 20 min at an initial concentration of 100 mg/L.

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1. Introduction

The effective removal of heavy metals from aqueous waste is among the most important issues of world [1]. A number of methods exist for removal of heavy metal pollutants from liquid waste where they are present in high concentrations. These include methods such as precipitation, electroplating, ion exchange and membrane processes. These processes are difficult to implement on large scale due to expensiveness, and other shortcomings such as ineffectiveness at low concentration (<100 mg/L) and production of toxic sludge and/or other waste products that also need disposal [2]. A development in the past decade has been the use of many biological sorbents to accumulate heavy metals [3]. Cu(II) and Cr(III) among the most widely used heavy metals, are mainly employed in electrical, electroplating, paper manufacturing, pesticides, herbicides and tannery industries. The effluents of these industries contain Cu(II) and Cr(III) ions which cause serious toxicological concerns. These are usually known to deposit in brain, spleen, liver, pancreas and myocardium [4–6]. Activated carbon is a commonly used biosorbent in sugar refining, chemical and pharmaceutical industries wastewater treatment [7]. Installations of bioreactors are rapidly growing worldwide especially in Canada and the United States. Some municipal wastewaters are already being used in British Columbia, Ontario and North America [8,9]. A number of abundant, inexpensive materials have been suggested as potential biosorbents [6,10,11]. Although, several advance techniques have been developed but the steam distillation still remains the preferred process for the extraction of essential oils from plant material. This is due to the simplicity and transparency of the process which gives reassurance of purity, as the process uses only water. Perhaps no flower is more recognizable and no aroma more evocative than that of the rose. And among roses *Rosa centifolia* is most renowned for its delightful fragrance. For the commercial production of *R. centifolia* essential oil (yield = 0.02%) large quantities of plant material are being used in steam distillation process. It takes about 10,000£ of rose blossoms to produce 1£ of oil. The *R. centifolia* biomass left after essential oil extraction is a waste material of no commercial importance. The chemical composition of *R. centifolia* waste biomass is described later on in this manuscript. In continuation of our investigation [11], the purpose of the present study was to investigate the use of rose waste biomass in Cu(II) and Cr(III) removal. The effects of pH, sorbent dose, size, initial metal concentration, content time and temperature on Cu(II) and Cr(III) biosorption are described here in detail.

2. Materials and methods

All reagents including $CuSO_4 \cdot 5H_2O$, $Cr_2(SO_4)_3$, NaOH, Conc. HCl, Cu(II) and Cr(III) atomic absorption spectrometry standards were purchased from Fluka Chemicals. Rose petals biomass was obtained from Rose Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan. This biomass was a waste material remained after essential oil extraction using distillation process. Rose waste biomass was sun dried for 7 days to constant weight. Dried biomass was ground into powdered form (Moulinex, France) and then sieved through octagon siever (OCT-DIDGITAL 4527-01) to obtain particles with homogenous size. Pure cellulose, moisture content, ash content, crude protein, crude lipids, total carbohydrates and tannin were determined using standard methods [12]. The rose waste biomass samples were wet digested [13]. The Na, K and Li were analyzed using flame photometer (Sheerwood 450 flame photometer) and trace metals (Cr, Cu, Pb, Co, Zn, Mn, Ni, Ca, Fe and Mg) were determined by PerkinElmer AAnalyst 300 spectrometer [14]. The fraction with <0.25 mm to 1.00 mm was selected for use in the biosorbent tests. Stock Cu(II) and Cr(III) solutions ($1000\,mg\,L^{-1}$) were prepared by dissolving 3.927 g and 3.77 g of $CuSO_4 \cdot 5H_2O$ and $Cr_2(SO_4)_3$, respectively using deionized distilled water (DDW). Cu(II) and Cr(III) solutions of different concentrations for sorption experiments were prepared by diluting stock solution with DDW. In order to investigate the effect of pH, metal solutions at various initial pHs were prepared using 0.1 M HCl or 0.1 M NaOH. The biomass (at 1.0 g/L) was added into the conical flasks containing the 100 mL of metal solution (100 mg/L). The flasks were agitated at 130 rpm for 24 h. The experiments were conducted at 303 ± 1 K. The final pH of the solution was measured with an ORION 525A pH meter. The metal concentrations were measured using atomic absorption spectrophotometer (AAS) (PerkinElmer AAnalyst 300). In the dose (0.5–2 g/L), size (0.250–1.00 mm) and metal concentration (10–640 mg/L) experiments, 100 mL solution was taken in 250 mL conical flask and the initial pH was maintained at the optimum value of 5.0 for Cu(II) and Cr(III). All flasks were shaken at 130 rpm at 303 ± 1 K. Kinetic experiments (0–320 min) were performed at four different temperatures (303–333 K) to evaluate the effect of contact time and temperature. The initial and final concentrations were determined using AAS. Biosorption of the metal ions (q_e) in the sorption system was calculated using the following mass balance equation:

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

where V is the solution volume, W is the amount of biomass, and C_i and C_e are the initial and final (or equilibrium) metal concentrations, respectively.

All data represents the mean $\pm$ S.D. of three independent experiments. All statistical analysis was done using Microsoft Excel 2004, Version office Xp.

3. Results and discussion

The chemical composition of *R. centifolia* waste biomass is shown in Table 1. The obtained results clearly indicated that the rose waste biomass is cellulosic in nature and have replaceable hydrogen, alkali and alkaline metals. Thus, it can be regarded as potential Cu(II) and Cr(III) adsorbent. The effect of different experimental parameters on Cu(II) and Cr(III) biosorption is described in detail below.

Table 1
The elemental (mg/kg) and proximate composition of *Rosa centifolia* waste biomass

Sample: *Rosa centifolia*	
Na^+	58.26 ± 0.55
K^+	24.59 ± 0.29
Li^+	63.52 ± 0.83
Fe^{2+}/Fe^{3+}	9.13 ± 0.11
Mn^{2+}	4.55 ± 0.39
Zn^{2+}	3.34 ± 0.24
Cu^{2+}	9.04 ± 0.03
Pb^{2+}	5.25 ± 0.15
Ca^{2+}	41.02 ± 0.12
Cr^{3+}/Cr^{6+}	7.53 ± 0.21
Ni^{2+}	6.35 ± 0.39
Mg^{2+}	34.26 ± 0.51
Co^{2+}	8.59 ± 0.31
Moisture contents (%)	23.16 ± 0.14
Ash contents (%)	10.26 ± 0.22
Crude protein (%)	0.21 ± 0.05
Tannin (g/100 g)	8.58 ± 0.14
Lipid contents (%)	5.31 ± 0.12
Fiber (%)	74.26 ± 1.03
Carbohydrate (%)	61.06

3.1. Effect of pH

Solution pH is an important parameter that affects biosorbent capacity of heavy metals. The influence of hydrogen ion concentration on the biosorption of Cu(II) and Cr(III) was investigated by varying the pH of metal solution in the range 2–5 (Fig. 1). Little biosorption of Cu(II) and Cr(III) occurred at low pH value (<4). In fact, it is known that at low pH, most of the carboxylic groups are not dissociated and cannot bind the metal ions in the solution. Biosorption capacity of rose waste biomass increased rapidly with increase in pH, i.e., 4–5. The increase in biosorption is due to dissociation of carboxylic groups at higher pH values. This could be explained by the increase in density of the negative charge on cell surface, causing proton removal on the cell binding sites, thereby increasing its biosorption capacity [2,15,16]. Further experiments were carried out with initial pH value of 5 for both Cu(II) and Cr(III), since their respective hydroxides start precipitating from solutions at higher pH values, making true sorption studies impossible.

3.2. Effect of biosorbent dose

Biosorbent dose is a significant factor to be considered for effective metal removal as it determines sorbent–sorbate equilibrium of the system [10,17]. In order to investigate the effect of the amount of biomass on Cu(II) and Cr(III) biosorption, biosorbent dose in the range of 0.05–0.2 g/100 mL was subjected to biosorption tests
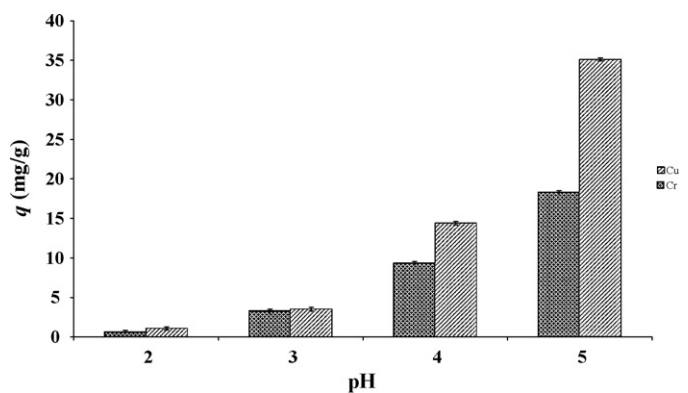
Fig. 1. Effect of pH on the biosorption of Cu(II) and Cr(III) by rose waste.
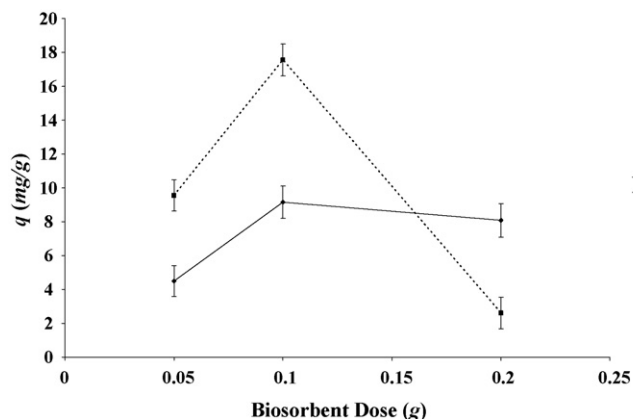
Fig. 2. Effect of biosorbent dosage on the biosorption of Cu(II) and Cr(III) by rose waste biomass.
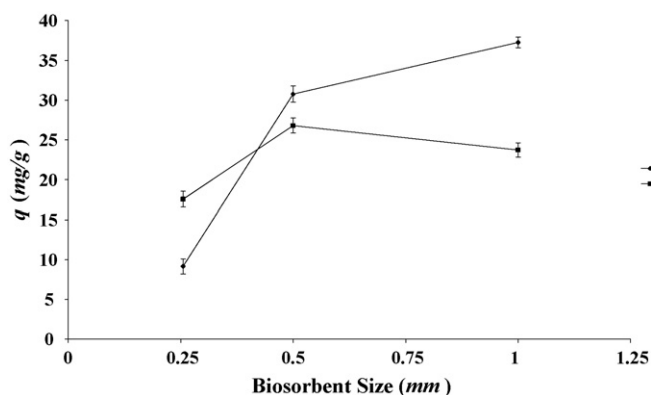

Fig. 3. Effect of biosorbent particle size on the biosorption of Cu(II) and Cr(III) by rose waste biomass.

(Fig. 2). The bisorption capacity of the rose waste biomass increased first with an increasing amount of biomass and then reached a saturation value and decreased. The effective amount of biomass was found to be 0.1 g per 100 mL for both Cu(II) and Cr(III). The initial increase in the biosorption capacity can be attributed to increased biosorbent surface area and the availability of more adsorption sites. The decrease in Cu(II) and Cr(III) removal thereafter may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area. Similar type of observations has been reported earlier [15].

3.3. Effect of particle size

The effect of varying biosorbent particle size is presented in Fig. 3. Significant removal of Cu(II) and Cr(III) ions was recorded for 1.00 mm and 0.50 mm sized biosorbent particles, respectively. The increase was probably due to the interrelationship between the total surface area and molecular size of hydrolyzed metal ions. The atomic radius (Å) of Cu(II) and Cr(III) is 1.27 and 1.24, respectively. As the Cr(III) had small atomic radius, so in aqueous solution it was surrounded by more water molecules resulting in large atomic size
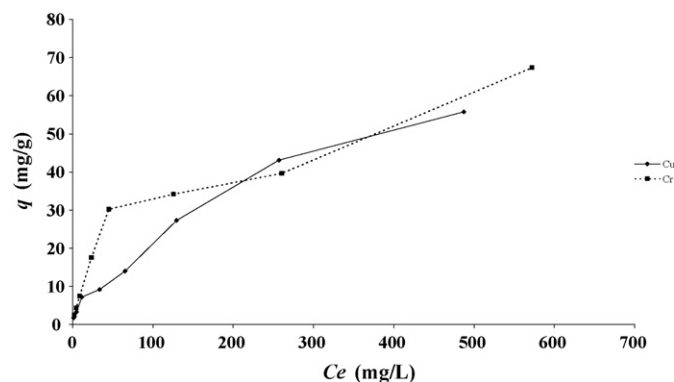

Fig. 4. Effect of initial metal concentration on the biosorption of Cu(II) and Cr(III) by rose waste biomass.

in aqueous phase in comparison to Cu(II). Thus, hydrated ion of Cr(III) needs more surface area which is achieved by decreasing the particle size of the biosorbent [11].

3.4. Effect of initial metal concentration

Biosorption of metals by any biosorbent is highly dependent on the initial concentration of metal ions [17]. In general, the data indicates that sorption capacity increased with increase in initial metal ion concentration for both metals on the biomass (Fig. 4). Similar type of uptake trend for Cr(III) and Cd(II) by *Cadmium bicolor* (wild cocoyam) biomass, has also been reported [18].

3.5. Biosorption of isotherm analysis

Most commonly used Langmuir and Freundlich models were employed to describe the uptake of Cu(II) and Cr(III) by rose waste biomass. The Langmuir parameters were determined from the following linearized equation [19]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}k_L} + \frac{C_e}{q_{max}} \qquad (2)$$

where C_e (mg/L) is the equilibrium concentration of metal ion solution, q_e is the metal ion sorbed (mg/g), q_{max} is a measure of the maximum adsorption capacity corresponding to complete monolayer capacity and K_L (L mg^{-1}) is Langmuir constant.

Freundlich isotherm parameters were calculated from the following equation as described earlier [10]:

$$\log q_e = \frac{1}{n} \log C_e + \log k \qquad (3)$$

where C_e (mg/L) is the equilibrium concentration of metal ion solution, q is the metal ion sorbed (mg/g), k and n are Freundlich constants. A comparison between Langmuir and Freundlich isotherms is presented in Table 2. The R^2 values suggested that Freundlich isotherm provides a good model of the sorption system, which is based on heterogeneous adsorption of metal ions by biosorbent.

Table 2
Langmuir and Freundlich isotherm models parameters for Cu(II) and Pb(II) sorption by rose waste biomass

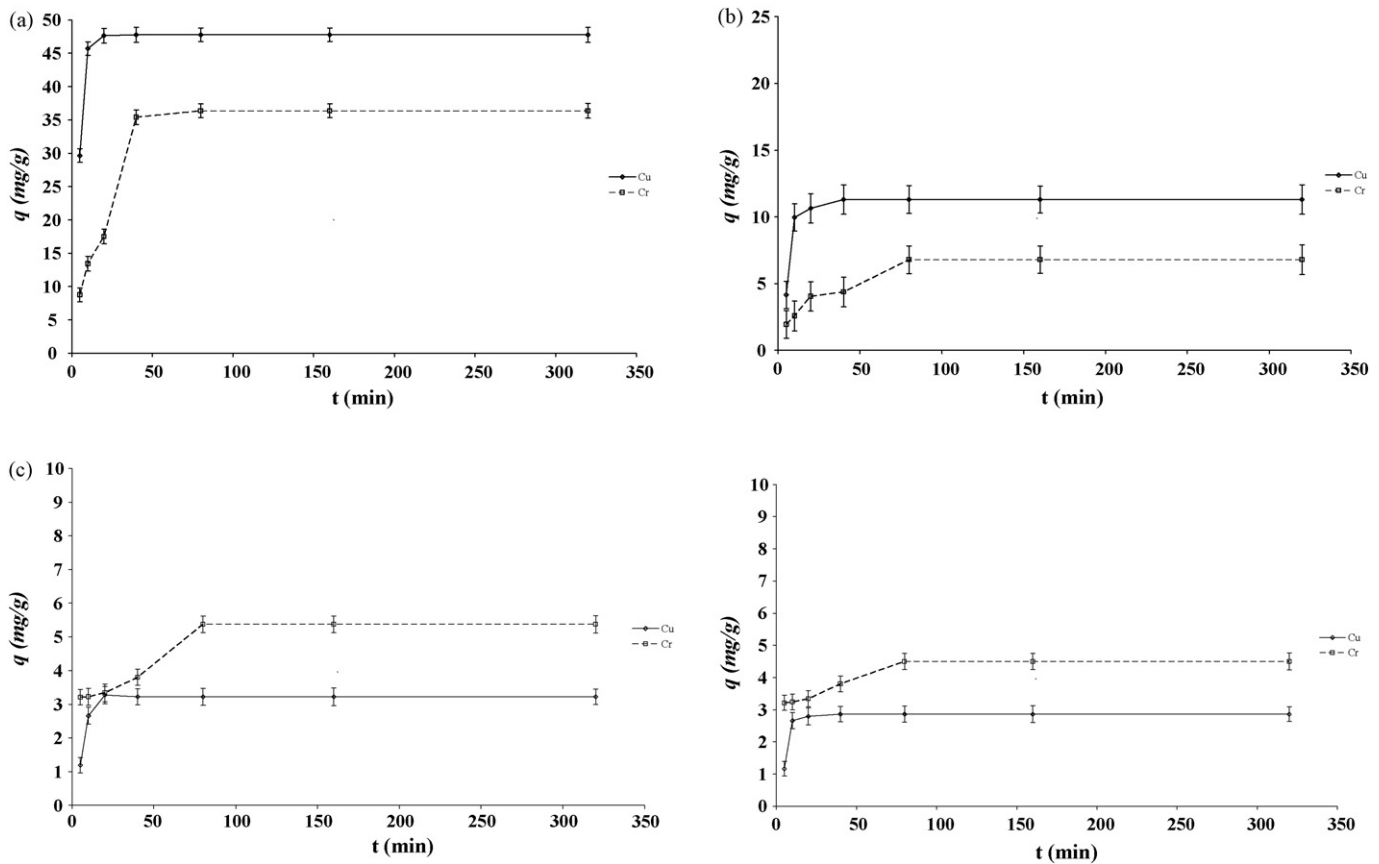| Metal	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	q (mg g^{-1})	q (mg g^{-1})	K (mg g^{-1})	R^2
Cu(II)	68.96	0.00671	0.8517	55.79	55.32	1.39	0.985
Cr(III)	70.42	0.014	0.928	67.34	80.37	2.088	0.9472

Fig. 5. Effect of sorption time on Cu(II) and Cr(III) uptake by rose waste biomass: (a) at 303 K, (b) at 313 K, (c) at 323 K and (d) at 333 K.

3.6. Biosorption kinetics

The dependency of Cu(II) and Cr(III) sorption on time was studied by varying sorption time from 10 to 320 min at four different temperatures (303–333 K), while keeping other parameters such as pH, biosorbent dose, biosorbent particle size and initial metal concentration constant at 5, 1 g/L, 0.250 mm and 60 mg/L, respectively (Fig. 5a–d). It is obvious that the rate of removal of Cu(II) and Cr(III) ions was extremely rapid in first few minutes regardless the effect of temperature. However, the biosorption capacity reached up to a constant value after equilibrium and almost 98% of total metal was removed in first 20 min. The sorption equilibria were attained in 40 min and 80 min of contact time for Cu(II) and Cr(III), respectively. The shapes of q versus t curves are similar to those reported in literature [2,7,20,21]. The kinetic data was fitted to the Lagergren pseudo-first-order model [22] and pseudo-second-order kinetic model [23]. The pseudo-first-order kinetic

model considers the rate of occupation of the adsorption sites to be proportional to the number of unoccupied sites. Whereas pseudo-second-order kinetic model assumes that the rate limiting step may be biosorption involving valence forces through sharing or exchange of electrons between the biosorbent and sorbate [24].

The first-order Lagergren equation is

$$\log(q_e - q) = \log q_e - \frac{k_{1,\text{ads}}t}{2.303} \tag{4}$$

The pseudo-second-order equation is

$$\frac{t}{q} = \frac{1}{k_{2,\text{ads}}q_e^2} + \frac{t}{q_t} \tag{5}$$

where q_e is the mass of the metal absorbed at equilibrium (mg/g), q_t (mg/g) is the mass of the metal absorbed at time (t in min), $k_{1,\text{ads}}$ (min^{-1}) $k_{2,\text{ads}}$ (mg/g min) are pseudo-first order and pseudo-second-order rate constants of adsorption, respectively. It was

Table 3
Comparison between Lagergren pseudo-first order- and pseudo-second-order kinetic models for the uptake of Cu(II) and Cr(III) by rose waste biomass

| Metal		Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order kinetic model		
		q_e (mg g^{-1})	$K_{1,\text{ads}}$ (min^{-1})	R^2	q (mg g^{-1})	q_e (mg g^{-1})	$K_{2,\text{ads}}$ (g mg^{-1} min^{-1})	R^2
Cu(II)	303	72.26	0.32	0.986	47.77	51.02	0.0087	0.999
	313	3.097	0.07	0.83	11.30	13.75	0.0096	0.954
	323	1.51	0.32	0.925	3.22	3.97	0.033	0.950
	333	2.873	0.19	0.859	2.86	3.35	0.051	0.962
Cr(III)	303	64.46	0.97	0.902	36.37	49.75	0.00075	0.941
	313	4.949	0.01	0.849	6.79	8.143	0.0056	0.940
	323	2.343	0.009	0.944	5.37	5.69	0.017	0.952
	333	1.50	0.17	0.935	4.50	4.68	0.0391	0.990
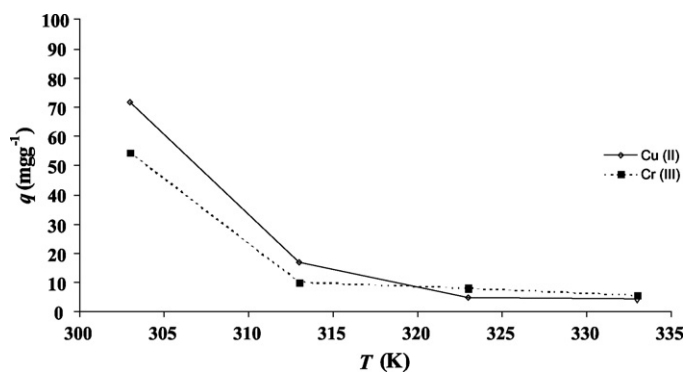
Fig. 6. Effect of solution temperature on Cu(II) and Cr(III) sorption onto rose waste biomass.

found that pseudo-second-order reaction model, was applicable to adsorption data of Cu(II) and Cr(III) on to rose waste biomass in comparison to model of Lagergren. The values of the reaction rate constants and correlation coefficient for each metal are listed in Table 3.

3.7. Effect of temperature

The effect of temperature on the metal biosorption experiments was investigated at four different temperatures, i.e., from 30 °C to 60 °C. Fig. 6 compares the equilibrium uptake capacity of rose waste biomass for Cu(II) and Cr(III) at different temperatures. The results indicated that the temperature highly influenced the adsorption of Cu(II) and Cr(III) on to rose waste biomass. Maximum biosorption of Cu(II) and Cr(III) ions by rose waste biomass was obtained at 303 K. The equilibrium biosorption capacity of both metals decreased sharply with increase in temperature. The decrease in equilibrium biosorption capacity indicates that lower temperature favor Cu(II) and Cr(III) removal. The biosorption of Cu(II) and Cr(III) ions by rose waste biomass seems to be the diffusion of metals on the surface of biomass. The mechanism may be explained, as the surface diffusion is an exothermic type reaction. Increasing the medium temperature decreases metal uptake capacity by rose waste biomass. It is also possible that as the temperature increases, denaturation of active sites of biomass also increases. Results indicated that metal-biosorbent adsorption process is exothermic in nature [25].

3.8. Thermodynamic parameters

The thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°), entropy change (ΔS°) activation energy (ΔE) were estimated to evaluate the feasibility and nature of adsorption process [16,22,26].

The Gibbs free energy (ΔG°) for the biosorption Cu(II) and Cr(III) by rose waste biomass was calculated using the following equation:

$$\Delta G^\circ = -RT \ln K_c \tag{6}$$

where K_c is the equilibrium constant, R is gas constant (8.314 kJ mol^{-1} K^{-1}), and T is the solution temperature (K). The free energy change (ΔG°) for Cu(II) and Cr(III) adsorption process was found to be −0.829 kJ/mol and −1.85 kJ/mol, respectively. The negative value of ΔG° of Cu(II) and Cr(III) suggested the spontaneous nature of process. The enthalpy and entropy for the sorption of Cu(II) and Cr(III) was calculated using the following equation (Fig. 6) [26]:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

$$\therefore K_c = \frac{C_a}{C_e}$$

where C_a is milligram of adsorbate adsorbed per liter, C_e is the equilibrium concentration of solution (mg/L), T is the temperature in K, and R is the gas constant (8.314 J mol^{-1} K^{-1}). The value of enthalpy change (ΔH°) and entropy change (ΔS°) were found out to be as −186.950 kJ/mol and 0.604 J mol^{-1} K^{-1}, respectively for Cu(II) and −119.788 kJ/mol and 0.397 J mol^{-1} K^{-1}, respectively for Cr(III).

The negative values of ΔH° for Cu(II) and Cr(III) removal with rose waste biomass indicated that the metal adsorption process was exothermic in nature. In an exothermic process, the total energy absorbed in bond breaking is less than the total energy released in bond making between metal and biomass, resulting in the release of extra energy in the form of heat. The positive values of ΔS° for both Cu(II) and Cr(III) showed that increased randomness at solid solutions interface during the adsorption of Cu(II) and Cr(III) on rose waste biomass. The activation energy for Cu(II) and Cr(III) biosorp-
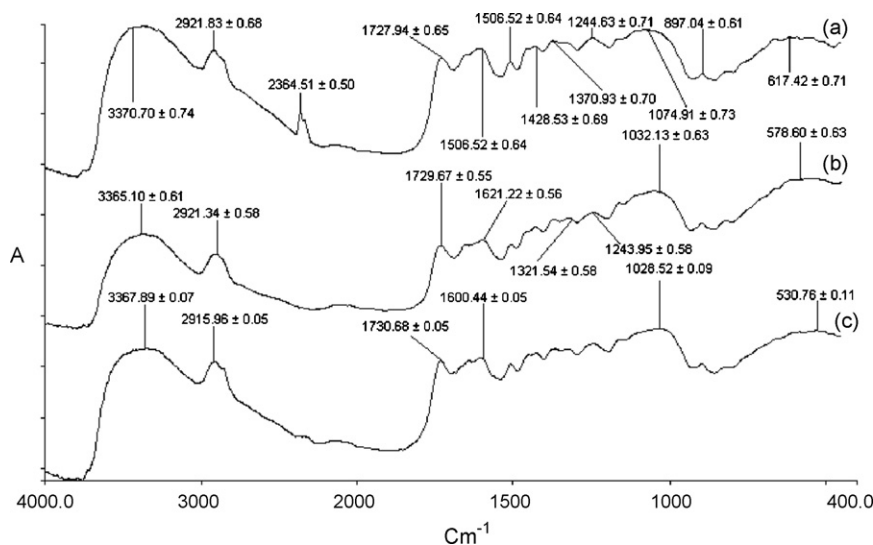

Fig. 7. FTIR spectra of rose distillation waste biomass.

tion studies were calculated from the following equation (Fig. 6) [13]:

$$\ln k = \ln k_0 - \frac{E}{RT} \tag{8}$$

where k (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant k_0 is the temperature independent factor also have the same units. E is the activation energy of sorption (kJ/mol), R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature in K. The activation energy for Cu(II) and Cr(III) was 68.53 kJ/mol and 114.45 kJ/mol, respectively.

3.9. Fourier transforms infrared (FTIR) studies

In order to determine the functional groups responsible for metal uptake, the FTIR was employed as an analytical [27]. A raw unreacted rose waste biomass sample and biomass sample treated with 100 mg/L solutions of Cu(II) and Cr(III) ions, respectively were analyzed (Fig. 7). The spectra indicate the presence of different functional groups which are responsible for metal sorption process: e.g., carboxylic acids display a broad intense –OH stretching absorption from 3300 to 2500 cm^{-1}, phosphine (2364 cm^{-1}), carbonyl (1727 cm^{-1}), primary amines (1603 cm^{-1}), secondary amine (1506 cm^{-1}), esters (1244 cm^{-1}), ethers (1074 cm^{-1}), thioesters (897 cm^{-1}), and alkyne (617 cm^{-1}). When infrared light interacted with the biomass, it caused stretching, contraction and bending of its chemical bonds. Hence, chemical functional group tends to absorb infrared radiation in a specific wavelength range. The absorbance of the peaks in the reacted sample is substantially lower than those in the raw sample of the biomass. This indicates that the bond stretching occurs to a lesser degree due to the presence of Cu(II) and Cr(III) ions, and subsequently absorbance peak is attenuated.

4. Conclusions

The following conclusions were drawn from the present study:

1. The obtained results showed that pH, sorbent dose, sorbent particles size, initial metal concentration uptake time and solution temperature highly affected the Cu(II) and Cr(III) uptake capacity of the rose waste biomass.
2. The distillation waste rose biomass demonstrated a good capacity of Cu(II) and Cr(III) biosorption, highlighting its potential for effluents treatment process.
3. Cu(II) and Cr(III) biosorption capacity rose biomass varied highly with temperature the maximum adsorption capacity of 55.79 mg/g of Cu(II) and 67.34 mg/g of Cr(III) were obtained at 303 ± 1 K. A comparison between rose biomass and other biosorbents is presented in Table 4.
4. Freundlich sorption model adequately described the biosorption of both Cu(II) and Cr(III) by rose waste biomass. The kinetics of Cu(II) and Cr(III) biosorption by rose waste biomass was extraordinary fast, reaching 98% of the total biosorption capacity in first 20 min. Kinetics results were well described by pseudo-second-order model.
5. The calculated thermodynamic parameters showed that reactions were exothermic and spontaneous in nature that proceeds with increase in entropy.

These all facts confirmed that rose waste biomass is a potential material to remove toxic Cu(II) and Cr(III) ions with high uptake capacity.

Table 4
Cu(II) and Cr(III) uptake capacities of different biomasses

Biosorbent used for Cu(II)	q_{max} (mg/g)	References
Rose waste biomass	55.79	Present study
Sago waste	12.4	[28]
Pseudomonas sp.	8.9	[29]
Saccharomyces cerevisiae	0.246	
Phanerochaete chrysosporium	0.398	
Sargassum fluitans	50.85	[6]
Myriophyllum spicatum	10.37	[23]
Gallan gum gel beads	47.66	[3]
Ochrobactrum anthropi	32.6	[30]
Biosorbent used for Cr(III) (mg/g)		
Rose waste biomass	67.34	Present study
Sargassum sp.	67.6	[31]
Saccharomyces cerevisiae	11.85	[32]
Sargassum seaweed	40	[33]

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