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Muhammad Abdullah Javed[a]; Haq Nawaz Bhatti[a]; Muhammad Asif Hanif[a]; Raziya Nadeem[a]
[a] Industrial Biotechnology Laboratory, Department of Chemistry, University of Agriculture, Faisalabad, Pakistan.

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Kinetic and Equilibrium Modeling of Pb(II) and Co(II) Sorption onto Rose Waste Biomass

Muhammad Abdullah Javed, Haq Nawaz Bhatti,
Muhammad Asif Hanif, and Raziya Nadeem
Industrial Biotechnology Laboratory, Department of Chemistry,
University of Agriculture, Faisalabad, Pakistan.

Abstract: An attempt was made to assess the biosorption potential of rose waste biomass for the removal of Pb(II) and Co(II) ions from synthetic effluents. Biosorption of heavy metal ions (>90%) reached equilibrium in 30 min. Maximum removal of Pb(II) and Co(II) occurred at pH 5 and 6 respectively. The biosorbent dose for efficient uptake of Pb(II) and Co(II) was 0.5 g/L for both metals. The biosorbent size affected the Pb(II) and Co(II) biosorption rate and capacity. Rose waste biomass was found effective for Pb(II) and Co(II) removal from synthetic effluents in the concentration range 10–640 mg/L. Equilibrium sorption studies showed that the extent of Pb(II) and Co(II) uptake by the rose waste biomass was better described by the Langmuir isotherm in comparison to the Freundlich model. The uptake capacities of the two metal ions were 156 and 27.15 mg/g for Pb(II) and Co(II) respectively.

Keywords: Pb(II), Co(II), biosorption, isotherms, rose waste biomass

INTRODUCTION

Modern industry is, to a large degree, responsible for the contamination of the environment. Lakes, rivers, and oceans are being overwhelmed with hazardous levels of metals.

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Address correspondence to Haq Nawaz Bhatti, Industrial Biotechnology Laboratory, Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan. Tel.: + 92-41-9200161/3309; Fax: +92-41-9200764; E-mail: hnbhatti2005@yahoo.com

Heavy metals are usually classified as

1. toxic metals
2. precious metals
3. radionuclides

Pb(II) and Co(II) are frequently encountered toxic metals in industrially effluents (1). The toxic characteristics of Pb(II) and Co(II) are displayed as follows:

1. toxicity can last for a long time in nature;
2. could be transformed from relevant less toxic species into more toxic forms in a certain environment;
3. the bioaccumulation and bioaugmentation through food chain could damage normal physiological activity and endanger human life finally.

Due to their increasing applications and the above immutable nature, the Pb(II) and Co(II) pollution has naturally become one of the most serious environmental problems today.

Biosorption can be a solution to clean the environment contaminated by heavy metals. The cost of decontamination of toxic metals from industrial wastewaters using conventional methods such as precipitation, oxidation/reduction, ion-exchange, filtration, membranes, and evaporation is exorbitant (2). The biological process of biosorption is favored because of an abundance of certain biomasses, generated as a byproduct in industrial processes and agriculture wastes (3). When choosing the biomass for metal biosorption experiments, its origin is a major factor to be taken into account. Biomass can come from

i. industrial wastes which should be obtained free of charge
ii. organisms easily available in large amounts in nature
iii. organism of quick growth, especially cultivated or propagated for biosorption purposes (4–12).

Cost effectiveness is the main attraction of metal biosorption, and it should be kept in mind. Although both living and dead cells are being used for biosorption, but the latter biomass is the more favored one (13). When living biomass is used, the physiological state of the organism, the age of the cell, the availability during their growth and environmental conditions during biosorption process (such as pH and temperature), are important parameters that affect its performance and a small change in these conditions may result in the death of living organisms. Living cells are subjected to metal toxicity and nutrient supply is also necessary. These are the main drawbacks of using living biosorbents for the biosorption process. Metal solution chemical features also influence the efficiency of metal concentration on the living biomass. All these factors favor the use of dead biomass as a suitable biosorbent for heavy metals removal (13, 14).

Roses are one of the most popular garden shrubs and are also among the most common flowers sold by florists. Roses are of great economic importance both as a crop for florists' use and for use in perfume. Thousands of rose hybrids and cultivars have been bred and selected for garden use. Roses are mainly used for their amazing fragrance which is difficult to put in words. Rose perfumes are made from rose oil, which is a mixture of volatile essential oils obtained by steam-distilling of crushed petals of roses. As the yield of rose oil is very much low, so huge amounts of rose flowers are being used for production of rose oil and rose water. Rose water is another commercially viable product of roses, which is produced on a pilot scale around the globe. Rose waste biomass is the sludge that remains after the rose oil extraction from rose flowers. As a result of processing, waste material disposal becomes an issue. Rose waste biomass is produced in large amounts and has no useful application. The purpose of the present study was to investigate the Pb(III) and Co(II) ions sorption characteristics of this useful biomass.

MATERIAL AND METHODS

Biomass

Rose (*Rosa centifolia*) waste biomass (RWB) was obtained from Rose Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan. The biomass was sun dried for seven days to constant weight. Dried material was ground to homogenous powder using food processor (Monlinex, France) and then sieved (OCT-DIGTAL 4527-01) to obtain a fraction with a known particle size ($<0.25-0.1$ mm) for use in the subsequent sorption studies. The sieved biomass was stored in airtight polypropylene plastic containers at 303 ± 1 K for further experiments.

Reagents

All reagents used in present study were of analytical grade, including $Pb(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, NaOH, HCl, Pb(II) and Co(II) atomic absorption spectrometry standard solutions (1000 mg/L), which were purchased from Fluka chemicals.

Biosorption Studies

Batch experiments were carried out in 250 mL flasks to check the influence of pH (4–7), biosorption dosage (0.5–2 g/L), biosorbent particle size (0.25–1.0 mm), initial metal concentration (10–640 mg/L), contact time (0–320 min) and temperature (303–333 K) on the sorption of Pb(II) and Co(II) by rose waste biomass. Metal solution (100 mL) was added into

250 mL conical flask, which was agitated at 130 rmp at 303 ± 1 K. The solution pH was adjust using 0.1 N NH_4OH and/or 0.1 N HNO_3. After equilibration, solution samples were filtered though 0.45 μm membrane filter and analyzed for residual Pb(II) and Co(II) concentration by an atomic absorption spectrophotometer (Perkin Elmer, A Analyst 300). The hollow cathode lamp was operated at analytical wavelength of 232 nm for Pb(II) and 240.7 nm for Co(II) using air acetylene flame.

The amount of Pb(II) and Co(II) taken up by rose waste biomass in each flask were calculated using following mass balance equation Eq.(1):

$$qe = \frac{V(Ci - Ce)}{W} \tag{1}$$

All the experiments were performed in triplicate, and the results are represented as mean ± standard deviation (SD).

RESULTS AND DISCUSSION

Effect of pH

The results regarding the effect of pH on biosorption of Pb(II) and Co(II) by rose waste biomass are shown in Fig. 1a. At low pH value (<4.0), Pb(II) and Co(II) removal was inhibited, possibly as a result of the competition between hydrogen and metal ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricted the approach of metal cations as a consequence of the repulsive forces. However, as pH was increased, negative charge density on the biomass surface increased, which subsequently resulted in an increase in the uptake of metal cation. pH is an important parameter for biosorption of heavy metal ions from aqueous solution as it affects the solubility of metal ions and concentration of counter ions on the biomass cell walls (15). Further sorption experiments were carried out with initial pH 5 and 6 for Pb(II) and Co(II) respectively, since their respective hydroxide starts precipitating from solutions at higher pH values, making true sorption studies impossible.

Effect of Biosorbent Dose

The effect of biosorbent dosage on Pb(II) and Co(II) is presented in Fig. 1b. The experimental results indicate that biosorbent dosage influences the Pb(II) and Co(II) uptake capacity of rose waste biomass. A dosage of 0.5 g/L was enough for the maximum uptake of Pb(II) and Co(II) from aqueous solution. On increasing biomass concentration further, the removal of Pb(II) and Co(II) decreased; which may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in the total adsorbent area (16).

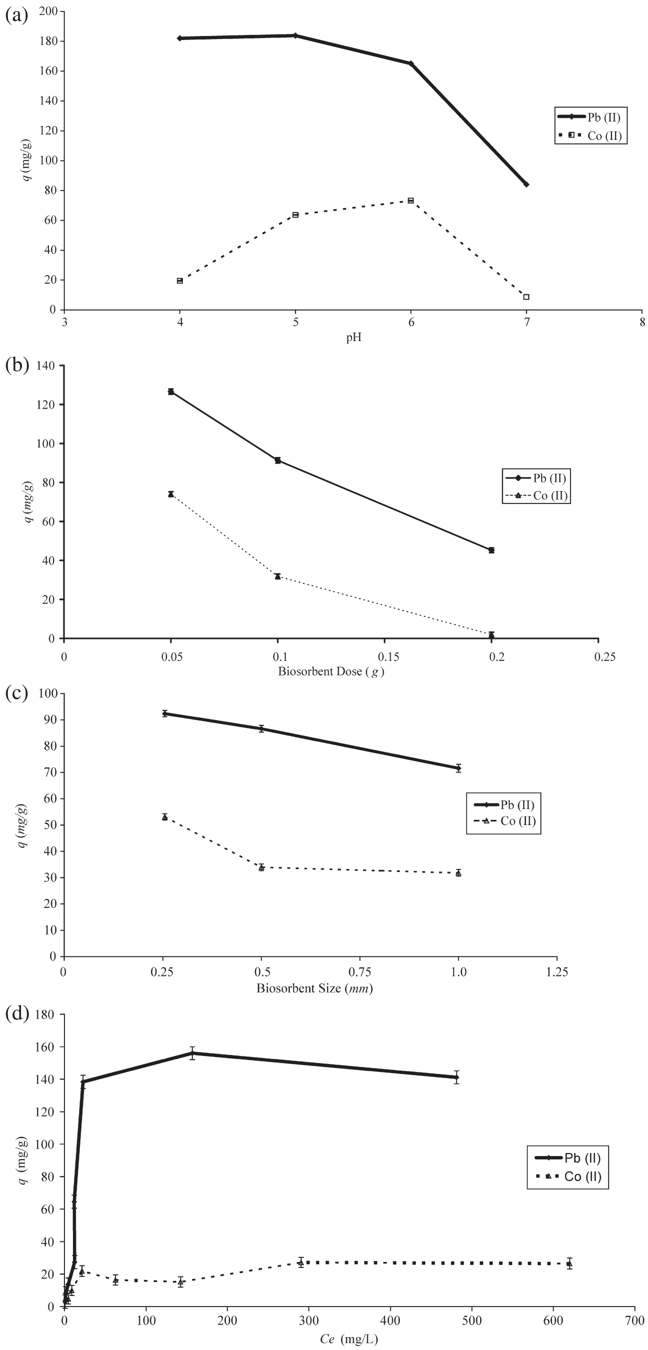

Figure 1. Effect of pH (a) biosorbent dosage (b), particle size (c) and initial metal concentration (d) on Pb(II) and Co(II) uptake by rose waste biomass.

Effect of Particle Size

The effect of altering the particle size on the Pb(II) and Co(II) uptake by rose waste biomass showed that there was a more dominate removal of metal ions by smaller particles (Fig. 1c). This was most probably due to the increase in total surface area (16, 17).

Initial Metal Concentration

The uptake of Pb(II) and Co(II) increased with increase in initial metal concentration (Fig. 1d) (7). The chemistry of adsorption is relatively complicated. A number of theories have been used in an attempt to understand the adsorption process. Modeling of equilibrium data was done using most widely used Langmuir and Freundlich isotherm models. In the Langmuir model, maximum monolayer adsorption capacity, q_{max} (mg/g) and other parameters were determined from following linearlized form of equation Eq. (2):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{2}$$

Where q_e is the metal ion sorbed (mg/g), C_e the equilibrium concentration of metal ions solution, and K_L is the Langmuir adsorption constant. The heterogeneous adsorption capacity, q_e (mg/g) of rose waste biomass for Pb(II) and Co(II) was determined by following the log form of the Freundlich isotherm Eq. (3):

$$log\, q_e = \frac{1}{n} log\, C_e + log\, k \tag{3}$$

The linearlized regression plots of Langmuir and Freundlich isotherms for Pb(II) and Co(II) uptake by rose waste biomass are presented in Fig. 2a and b respectively. The magnitude of experimental q_{max} for rose waste biomass was 156 and 27.15 mg/g for Pb(II) and Co(II), respectively. A comparison between Langmuir and Freundlich isotherm models is tabulated in Table 1. The Langmuir constant (K), q_{max} and R^2 determined from the model indicated that this model better described the adsorption process in comparison to the model of Freundlich. The Langmuir isotherm model has following three assumptions.

1. Adsorption cannot proceed beyond monolayer coverage.
2. All surface sites are equivalent and can accommodate, at most, one adsorbed atom.
3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites.

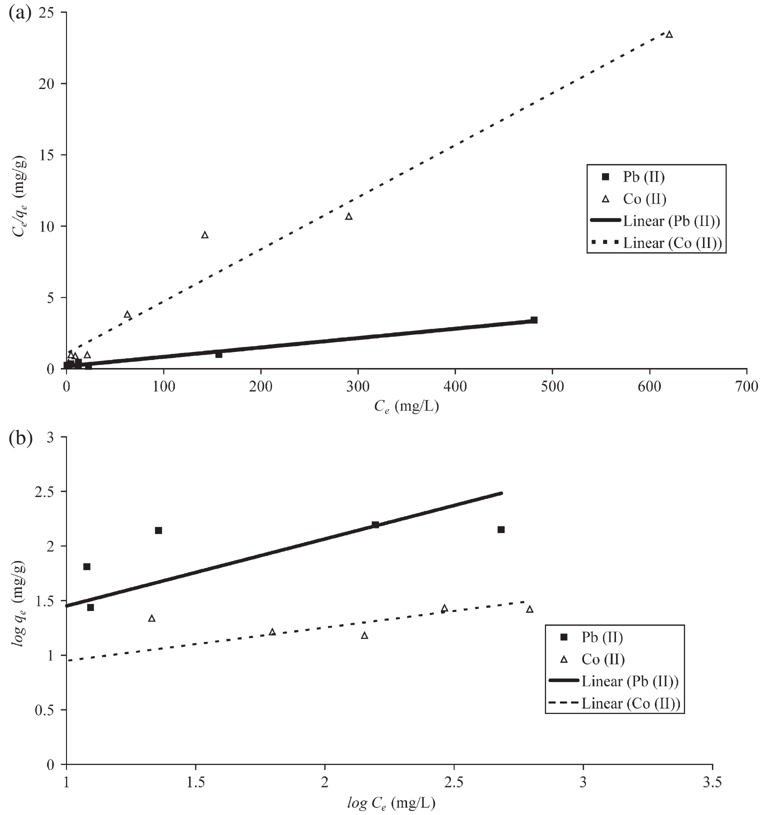

Figure 2. Linearlized Langmuir (a) and Freundlich (b) isotherm models for the sorption of Pb(II) and Co(II) by rose waste biomass.

Table 1. Langmuir and Freundlich isotherm models parameters for Pb(II) and Co(II) uptake by rose waste biomass

Metal	Pb (II)	Co(II)
Langmuir isotherm parameters		
q_{max} (mg/g)	151.51	27.62
K_L (L/mg)	0.028	0.037
R^2	0.9852	0.982
Experimental value		
q (mg/g)	156	27.15
Freundlich isotherm parameters		
q (mg/g)	388.54	19.75
K (mg/g)	6.75	19.75
R^2	0.8423	0.9234
$1/n$	0.3198	0.6344

Kinetic Study

In Figs 3a and b, the Pb(II) and Co(II) uptake capacity (mg/g) of rose waste biomass respectively, has graphically been shown as a function of constant time at 100 mg/g initial metal concentration. The rate of removal of Pb(II) was extremely rapid in first 20 min and equilibrium was reached in only 40 min. The rate of Co(II) uptake by rose waste biomass was significantly slower in comparison to the Pb(II) uptake, and an equilibrium was reached in 160 min. Atomic radius of Pb(II) and Co(II) is 1.75 and 2.25 Å respectively. The smaller the cation, the greater is its radius in an aqueous medium (18). The Pb(II) and Co(II) kinetic data revealed that waste rose biomass sorption capacity increased with a decrease in hydrated radius of metals ion in aqueous solutions. This sorption characteristic represented that surface saturation was dependent on the hydrated radius of Pb(II) and Co(II) cations, at a lower hydrated radius of metal ion sorption sites took up the available metal more quickly; however, at higher aqueous atomic radius, metal ions need to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate (19). Kinetic experiments were performed at four different temperatures (Figs. 3a–d). Results indicated that there was no effect of temperature on the equilibrium sorption time.

Kinetic data was fitted using Lagergren pseudo first order model and the pseudo second order model (20, 21). The linearlized form of first order Lagergren equation is given as Eq. (4) (Figs. 4a–d):

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

The pseudo second order equation Eq. (5) is (Figs. 5a–d):

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

where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t the mass of metal at time t (min.), $k_{1,ads}$ the first order reaction rate of adsorption (per min.), $k_{2,ads}$ the pseudo second order rate constant of adsorption mg/g min^{-1}. A comparison between the Lagergren pseudo-first order and pseudo second order kinetic model is tabulated in Table 2. The obtained kinetic data suggest that the sorption of Pb(II) and Co(II) ions followed the second kinetic model which relies on the assumption that biosorption may be the rate limiting step (22).

Effect of Temperature

The temperature dependence of Pb(II) and Co(II) biosorption by rose waste biomass showed a good compliance with the pseudo second order equation,

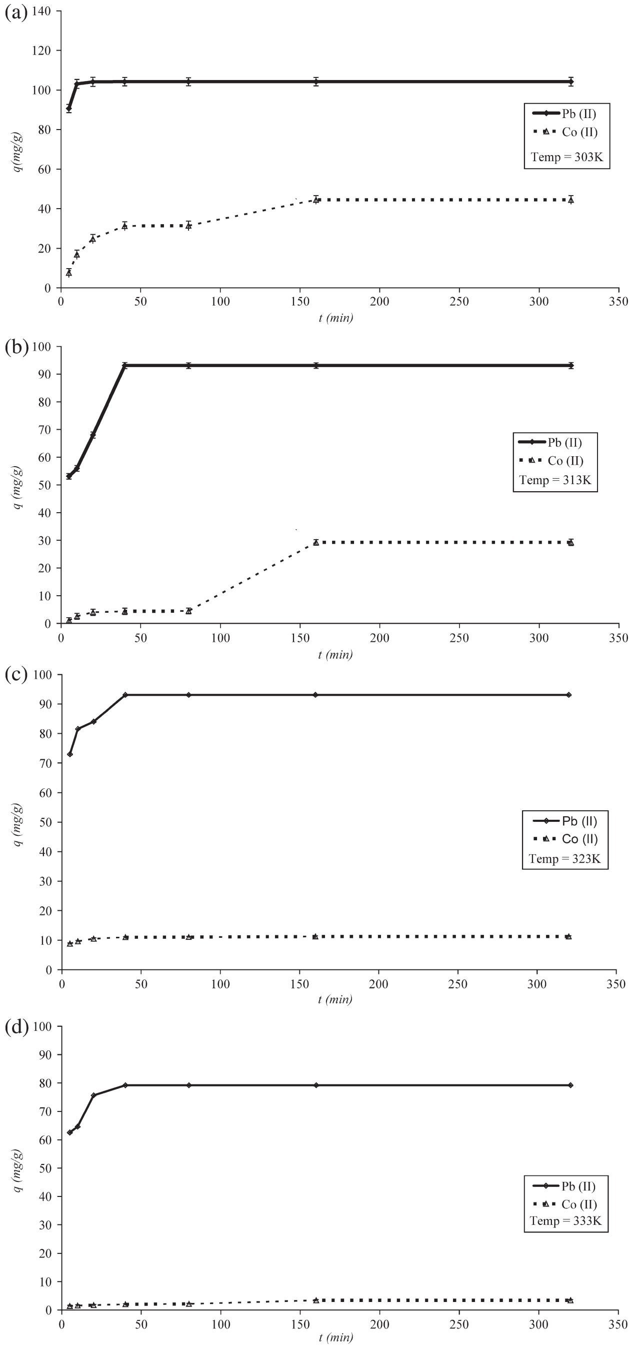

Figure 3. Effect of contact time on the uptake of Pb(II) and Co(II) by rose waste biomass (a) 303 K (b) 313 K (c) 323 K (d) 333 K.

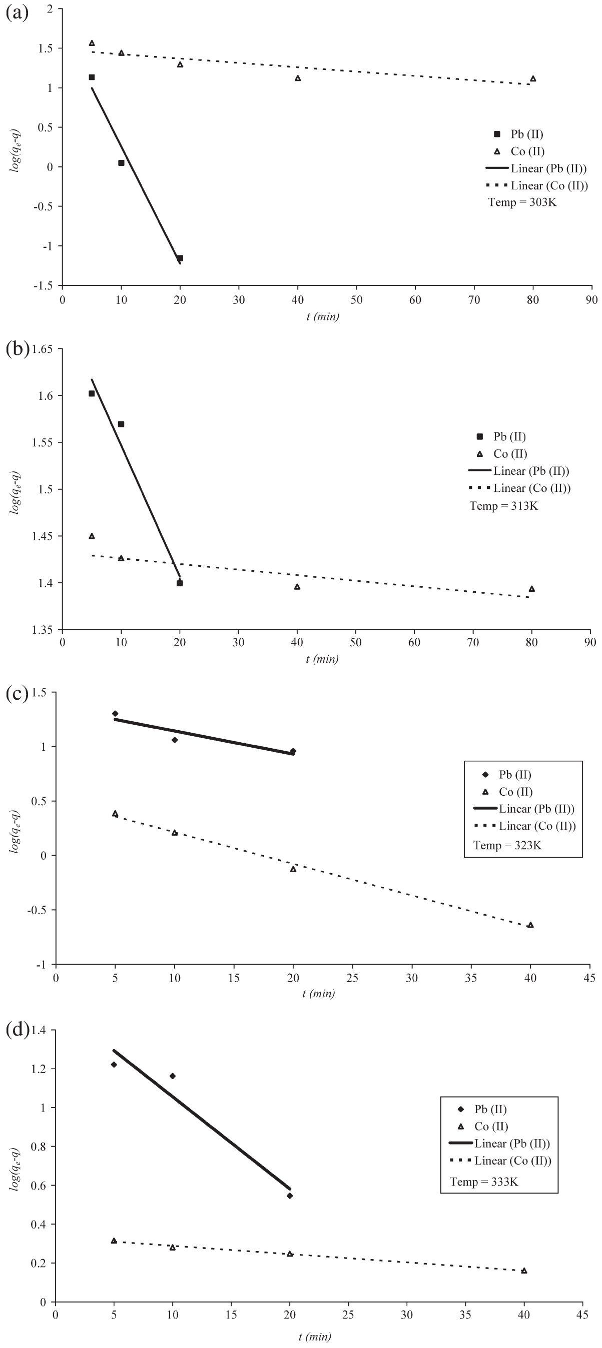

Figure 4. Lagregren pseudo first order kinetic model for biosorption of Pb(II) and Co(II) by rose waste biomass (a) 303 K (b) 313 K (c) 323 K (d) 333 K.

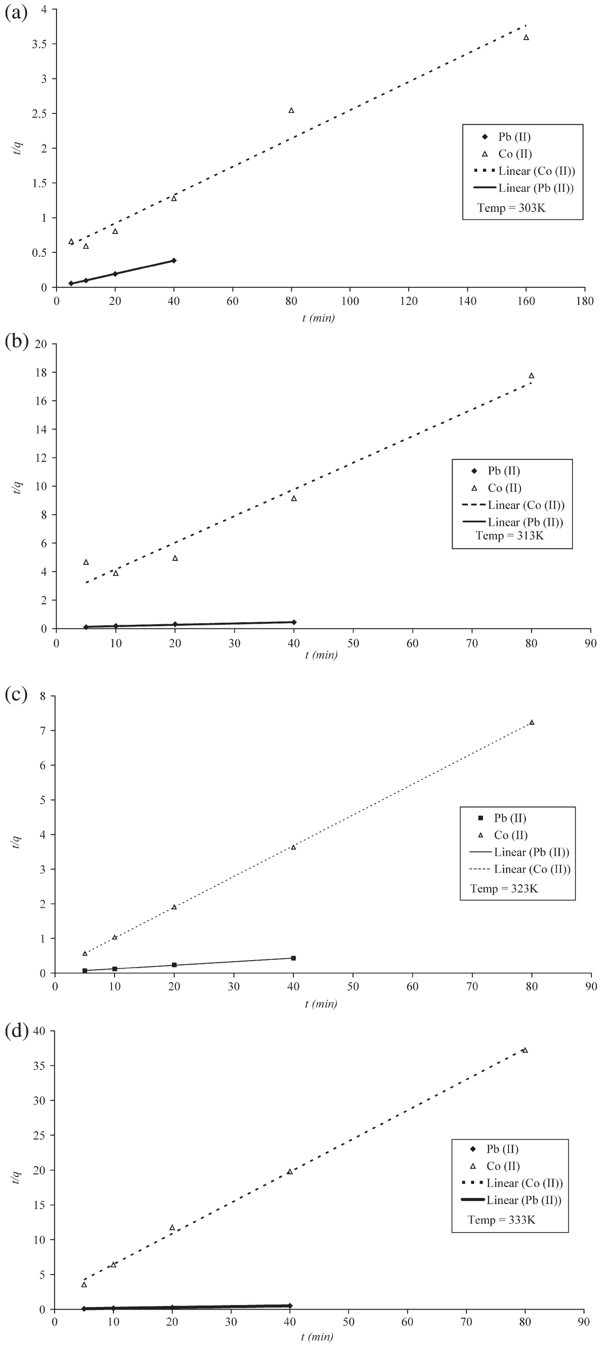

Figure 5. Pseudo second order kinetic model for biosorption of Pb(II) and Co(II) by rose waste biomass (a) 303 K (b) 313 K (c) 323 K (d) 333 K.

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

	Pseudo first order kinetic model				Experimental value	Pseudo second order kinetic model		
Metal	Temp. K	q_e mg/g	k_1,*ads* min^{-1}	R^2	q mg/g	q_e mg/g	k_2,*ads* g/mg min^{-1}	R^2
Pb (II)	303	72.26	0.32	0.986	47.77	51.02	0.0087	0.999
Co (II)	303	64.46	0.97	0.902	36.37	49.75	0.00075	0.941
Pb (II)	313	3.097	0.07	0.83	11.30	13.75	0.0096	0.954
Co (II)	313	4.949	0.01	0.849	6.79	8.143	0.0056	0.940
Pb (II)	323	1.51	0.32	0.925	3.22	3.97	0.033	0.950
Co (II)	323	2.343	0.009	0.944	5.37	5.69	0.017	0.952
Pb (II)	333	2.873	0.19	0.859	2.86	3.35	0.051	0.962
Co (II)	333	1.50	0.17	0.935	4.50	4.68	0.0391	0.990

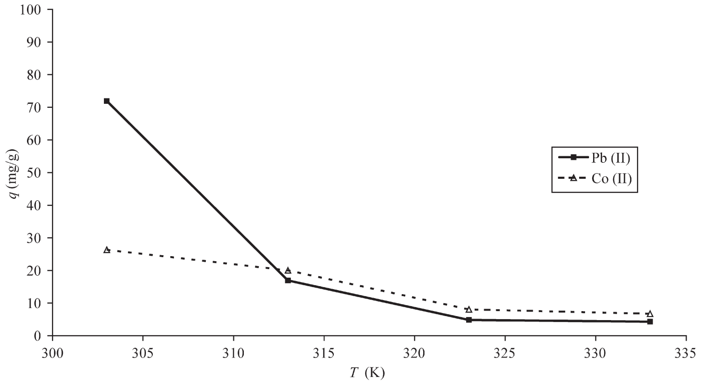

Figure 6. Effect of temperature on the uptake of Pb(II) and Co(II) by rose waste biomass.

Table 3. Comparison between rose waste biomass and previously used biosorbent for the uptake of Pb(II) and Co(II)

Metal	Biosorbents	$q_{\max}$ (mg/g)	Reference
Pb(II)	Rose waste biomass	156	Present study
	Cocoa shells	6.2	(26)
	Crop milling waste (black gram husk)	49.97	(27)
	Ceratophyllum demersum	44.8	(28)
	Myriophyllum spicatum	46.49	(29)
	Brown seaweed *Cystoseira baccata.*	186	(30)
	Phellinus badius.	0.82 mmol/gram	(31)
	Aspergillus flavus	10.82 mg/g	(32)
	Baker's yeast modified by crosslinking cystine	45.87	(33)
	Waste chinese herb Pang Da Hai	27.1	(34)
	Bacillus sp.	92.27	(35)
	Chlamydomonas reinhardtii	96.3	(36)
Co(II)	*Rosa centifolia* distillation sludge	27.15	Present study
	Sludge fed with glucose and sulfate	18.76	(37)
	Sargassum wightii	20.63	(38)
	Marine green alga *Ulva reticulata* in a packed column	46.1	(39)
	Sargassum wightii	20.63	(40)
	Oscillatoria angustissima	7.02	(41)

which are reflected by the high values of the correlation coefficients. The equilibrium Co(II) biosorption capacity of rose waste biomass decreased with temperature (Fig. 6). These results are in accordance with the earlier reported work(23–25). The adsorption of Pb (II) and Co(II) onto rose waste biomass decreased with increase in temperature suggested that the adsorption process is exothermic in nature (Fig. 6). A comparison of rose waste biomass with previously used biosorbents is given in Table 3 (26–41). From the same table it can be noted that rose waste biomass has more sorption capacity in comparison to most of the earlier reported biosorbents.

CONCLUSIONS

Studies pertaining to the assessment of Pb(II) and Co(II) uptake by rose waste biomass revealed that the sorption process was diffusion controlled and was dependent on the hydrated radius of the metal ion being biosorbed. Further, from the results of the present study it can be concluded that the sorption process was strongly affected by experimental conditions such as pH, the sorbent dose, the sorbent particles size, the initial metal concentration, and the contact time and solution temperature. Pb(II) and Co(II) sorption by rose waste biomass was well-described by the Langmuir isotherm and the pseudo-second-order kinetic model.

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