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Efficacy of modified distillation sludge of rose (*Rosa centifolia*) petals for lead(II) and zinc(II) removal from aqueous solutions

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Abstract

Removal of lead(II) and zinc(II) from aqueous solutions was studied using chemically modified distillation sludge of rose (*Rosa centifolia*) petals by pretreatment with NaOH, $Ca(OH)_2$, $Al(OH)_3$, C_6H_6, C_6H_5CHO and $HgCl_2$. The adsorption capacity of biomass was found to be significantly improved. NaOH pretreated biomass showed remarkable increase in sorption capacity. Maximum adsorption of both metal ions was observed at pH 5. When Freundlich and Langmuir isotherms were tested, the latter had a better fit with the experimental data. The overall adsorption process was best described by pseudo second order kinetics. The thermodynamic assessment of the metal ion—*Rosa centifolia* biomass system indicated the feasibility and spontaneous nature of the process and ΔG° was evaluated as ranging from −26.9501 to −31.652 KJ mol^{-1} and −24.1905 to −29.8923 KJ mol^{-1} for lead(II) and zinc(II) sorption, respectively, in the concentration range 10–640 mgL^{-1}. Distribution coefficient (*D*) showed that the concentration of metal ions at the sorbent–water interface is higher than the concentration in the continuous aqueous phase. Maximum adsorption capacity of biomass tends to be in the order Pb(II) (87.74 mgg^{-1}) > Zn(II) (73.8 mg g^{-1}) by NaOH pretreated biomass.
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Keywords: *Rosa centifolia*; Biosorption; Langmuir; Freundlich; Lead; Zinc; Distribution coefficient

1. Introduction

Mobilization of heavy metals in the environment due to industrial activities is of serious concern due to their toxicity for humans and other forms of life. Removal of toxic heavy metals from industrial wastewaters is essential to control environmental pollution [1,2]. Many industries, especially electroplating, manufacturing batteries, pigments and ammunition production release continuously lead(II) and zinc(II) in wastewaters. Lead(II) is a potent neurotoxic metal [3]. Too much intake of zinc(II) can lead to respiratory incapacitation, as indicated by increased respiratory activity such as breathing rate, volume and frequency of ventilation, coughing, decrease in oxygen uptake efficiency [4]. Chemical oxidation, reduction, precipitation, adsorption, solidification, electrolytic recovery and ion exchange are some of the physicochemical wastewater treatment processes, which are being used for metal removal. Application of such methods, however, is sometimes restricted because of technical or economical constraints [5,6]. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [7].

Roses are important shrubs cultivated everywhere in the world because of their florist's demand and to meet the requirements of perfumes and fragrance and their use in medicines. Roses are the source of rose oil that is used in perfumes and fragrance. Rose oil is obtained after distillation of rose petals that is mixture of essential volatile oils. Two major species of rose are cultivated for the production of rose oil: Firstly, *Rosa damascena* which is widly grown in Bulgaria (70–80%), Turkey, Russia, India and China. Secondly, *Rosa centifolia* which is more

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commonly grown in Morocco, France and Egypt. Most rose oil is produced in Bulgaria, Morocco and Turkey. Recently, China has begun producing rose oil as well. Pakistan also contributes 8–10% to rose crop. Rose water is also obtained as a byproduct of distillsation which is also commercially valuable. To meet the requirements of rose oil and rose water, a large quantity of rose flower is required because yield of rose oil is very low as compared to quantity of rose flower used.

It takes 30 roses to make one drop of rose oil. It is reckoned that 4000 kilos of flowers yield 1 kilo of otto, of which only one-third – the green essence – comes from the first distillation and the other two-thirds – yellow – are the result of re-distilling the waters. When only first distillate of rose flower is obtained and used then about 10,000 Kg of flowers are required [8]. So, due to large-scale use of rose to meet the requirements, a large quantity of rose flower is used to distillate and rose waste becomes a problem. *Rosa centifolia* flower was used because flowering period of *Rosa centifolia* is all the year and there is no information about using *Rosa centifolia* as a biomass earlier and waste of *Rosa centifolia* has no application. So, *Rosa centifolia* waste was used as a biomass to investigate its heavy metal removal efficacy.

Metal affinity to the biomass can be manipulated by preteating the biomass with alkalies and various chemicals, which may increase the amount of metal sorbed [9,10]. In the present investigation, native and pretreated distillation sludge of *Rosa centifolia* was examined in an attempt to remove lead(II) and zinc(II) from synthetic wastewater system.

2. Materials and methods

2.1. Reagents

All the chemical reagents used in these studies were of analytical grade, including $ZnSO_4{\cdot}7H_2O$ (Merck), $Pb(NO_3)_2$, HNO_3 (Merck) and lead(II), zinc(II) atomic absorption spectrometry standard solution (1000 mg/L) (Fluka Chemicals).

To prepare stock lead(II) and zinc(II) solutions (1000 mg/L), 1.598 g of $Pb(NO_3)_2$ and 4.42 g of $ZnSO_4{\cdot}7H_2O$ were dissolved in 100 mL of deionized distilled water (DDW) and quantitatively diluting to 1000 mL using DDW. Different lead(II) and zinc(II) concentrations were prepared by diluting stock solution with DDW. Glassware used was immersed in 10% (v/v) HNO_3 and rinsed many times with DDW.

2.2. Preparation of biosorbent

Rosa centifolia biomass (distillation sludge) was taken from "Rose lab, Institute of Horticulture, University of Agriculture, Faisalabad, Pakistan" and was extensively washed with distilled water to remove particulate material from their surface and oven dried at 60 °C for 72 h. Dried biomass was ground using food processor (Moulinex, France). Biomass was pretreated with 0.1N NaOH, 0.1N $Ca(OH)_2$, 0.1N $Al(OH)_3$, 0.1N $HgCl_2$, 0.1 M C_6H_6 and 0.1 M C_6H_5CHO (50 gm of biomass/500 mL of each chemical) in Orbital shaking incubator (PA 250/25. H) at 120 rpm and 30 °C for 24 h. These pretreatments were done to analyze enhancement or decrease in adsorption capacity [11–14] of biomass. Then these pretreated biomasses were filtered and washed with distilled water up to neutral pH, followed by drying and grinding. The pretreated biomasses and native biomass were sieved through Octagon siever (OCT-DIGITAL 4527-01) to obtain adsorbent with homogenous known particle size (0.355 mm). The sieved sorbents were stored in airtight plastic containers for further experiments.

2.3. Determination of the lead(II) and zinc(II) contents in the solutions

Perkin-Elmer A Analyst 300 atomic absorption spectrometer equipped with an air–acetylene burner and controlled by Intel personal computer was used to determine concentrations of lead(II) and zinc(II) in aqueous solutions before and after the equilibrium established. The hollow cathode lamp was operated at analytical wavelength of 232 nm for lead(II) and 213.9 nm for zinc(II) and slit as 0.2 nm for both metal ions.

2.4. Batch biosorption studies

In all experiments fixed volume (100 mL) of lead(II) and zinc(II) was thoroughly mixed with 0.1 g biosorbent having size 0.355 mm at 120 rpm and 30 °C for 24 h. To check the influence of pH, initial metal concentration and contact time, different conditions of pH (1–5) for lead(II) and pH (2–7) for zinc(II), initial metal concentration (10, 20, 40, 80, 160, 320, 640 mgL^{-1}) and contact time (10, 20, 40, 80, 160, 320, 640 min) were evaluated during study. The pH of the medium was adjusted with 0.1N solutions of HCl and NaOH. The flasks were placed on a rotating shaker (PA 250/25. H) with constant shaking.

The flasks were removed from the shaker after specified time and the solutions were filtered through filter paper (Whatman No. 40, ashless). Preliminary tests were performed at 30 °C and 120 rpm using an initial lead(II) and zinc(II) concentration of 100 mg L^{-1} having pH (1–5) for lead(II) and pH (2–7) for zinc(II) for 24 h contact time for screening studies.

2.5. Metal uptake

The lead(II) and zinc(II) uptake was calculated by the simple concentration difference method [15]. Uptake of lead(II) and zinc(II) were calculated from mass balance equation:

$$q = \frac{V(C_i - C_e)}{M} \quad (1)$$

where V is the volume of the solution (L), C_i is the initial concentration, C_e is the final concentration in solution and M the mass of the sorbent (g).

2.6. FTIR analysis

The native and NaOH pretreated rose waste biomass before and after biosorption were analyzed using FTIR-BX (Perkin-Elmer) to determine the functional groups responsible for lead(II) and zinc(II) uptake from aqueous solutions.

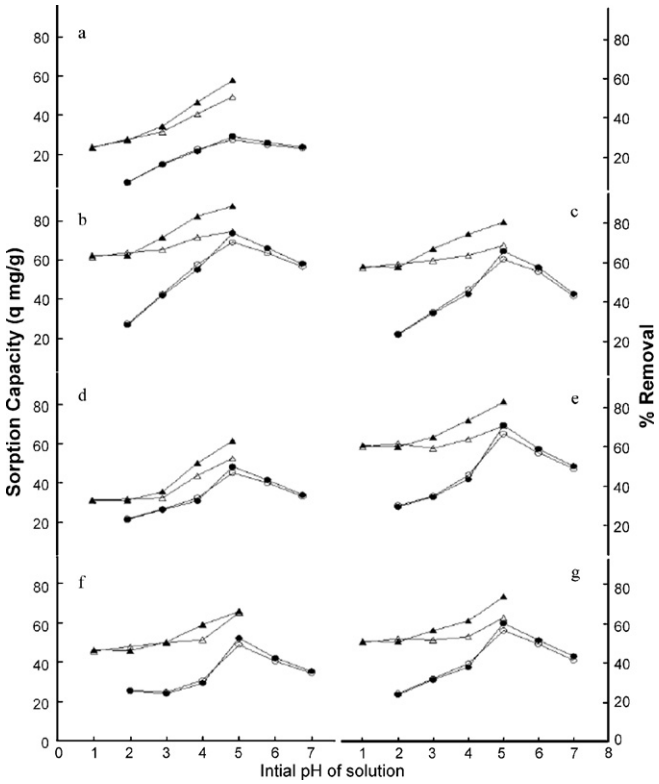


Fig. 1. Uptake capacities (Zn ●, Pb ▲) and % removal (Zn◯, Pb△) by (a) control; (b) NaOH; (c) $Ca(OH)_2$; (d) $Al(OH)_3$; (e) C_6H_6; (f) C_6H_5CHO and (g) $HgCl_2$ treated distillation sludge of rose (*Rosa centifolia*) petals at various pH values (C_i = 100 mg/L, V = 100 mL, temperature = 30 °C, agitation rate = 120 rpm, contact time = 24 h).

3. Results and discussion

3.1. Effect of pH on biosorption

pH seems to be the most important parameter for controlling the biosorption process. It affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions [16]. The pH affects the network of negative charges on the surface of the biosorbing cell walls and the chemistry of the walls, as well as physicochemistry and hydrolysis of the metal [17,18]. It was reported that at highly acidic pH (<3) lead(II) ions compete with H^+ on the binding sites of cells and adsorption is lowered. However, at higher pH (>5) solubility of lead(II) was lowered [19,20]. With an increase in pH, the functional groups on the cell wall with negative charge increase due to deprotonation of the metal binding sites, which promotes the metal uptake [21]. Results shown in Fig. 1 support the statements. Maximum adsorption by biomass (*Rosa centifolia*) was observed at pH 5 for lead(II) and zinc(II); beyond this value lead(II) precipitated and adsorption for zinc(II) that lowered at pH 6 and 7 beyond which precipitation occurred. This decrease in zinc(II) uptake at pH 6 and 7 can be explained by the fact that with increase in pH from 5 to 7, the degree of protonation of the adsorbent functional group decreased gradually. This lowered zinc removal [22]. Maximum removal of lead(II) and zinc(II) at pH 5 by *Rosa centifolia* biomass is in accordance with [23].

3.2. Effect of pretreatment

An increase in biosorption of lead(II) ions as a result of pretreatment could be due to an exposure of active metal binding sites embedded in the cell wall or chemical modifications of the cell wall components. Huang and Huang [24] stated that the increase in metal biosorption after pretreating the biomass could be due to the removal of surface impurities and to the exposure of available binding sites for metal biosorption. In the case of NaOH pretreatment, biosorption capacity was significantly enhanced in comparison with $Ca(OH)_2$, $Al(OH)_3$, C_6H_6, C_6H_5CHO and $HgCl_2$. In a study [25], NaOH treated *Penicillium digifatum* also showed enhanced biosorption of cadmium(II) and zinc(II). Removal of surface impurities, rupture of cell membrane and exposure of available binding sites for metal biosorption after pretreatment may be the reason for the increase in metal biosorption. It was also found that cell walls of *M. rouxii* could be ruptured when treated with NaOH [26]. The residual alkalinity in biomass may also result in increased hydrolysis of certain metals and thereby enhance overall metal removal by the treated biomass [27]. The pretreatment released polymers such as polysaccharides that have a high affinity towards certain metal ions [28,29]. Therefore, if lead(II) and zinc(II) are to be removed from aqueous solutions, the use of pretreatment with alkaline chemicals may improve removal efficiency. $Ca(OH)_2$ and $Al(OH)_3$ are weak bases as compared to NaOH. Enhancement in adsorption capacity due to C_6H_6, C_6H_5CHO and $HgCl_2$ is in accordance with [30].

3.3. Effect of initial metal concentrations

Different metals have different adsorption capacities at different initial metal concentrations. Results obtained in the present studies indicate that sorption capacity increased with increase in initial metal ion concentration of lead(II) and zinc(II) on

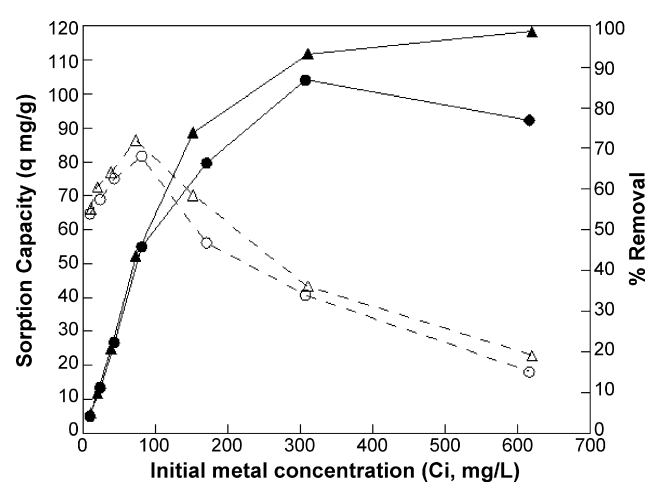


Fig. 2. Effect of different initial metal concentrations on biosorption of lead(II), uptake capacity (▲) and % removal (●), and zinc(II), uptake capacity (△) and % removal (◯) by NaOH pretreated *Rosa centifolia* biomass.

Table 1
Langmuir and Freundlich isotherm parameters for lead(II) and zinc(II) uptake by NaOH pretreated *Rosa centifolia* biomass

Metal	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters			
	X_m (q_{max}) (mg/g)	K_L (L/mg)	R^2	q_{max} (mg/g)	q_{max} (mg/g)	K (mg/g)	R^2	$1/n$
Lead	135.135	0.0163	0.9895	118.40	111.92	4.0803	0.9142	0.6234
Zinc	104.16	0.0222	0.9879	104.09	158.06	3.831	0.9052	0.5982

the biomass and percentage removal decreased with increase in initial metal concentration after 80 mg L^{-1} initial metal ion concentration (Fig. 2). This sorption characteristic has indicated that surface saturation is dependent on the initial metal ion concentrations. At low concentrations, adsorption sites have taken the available metal more quickly. However, at higher concentrations, metals need to diffuse to the biomass surface by intra particle diffusion and greatly hydrolyzed ions will diffuse at a slower rate. In all experiments, it has been noted that percentage removal of lead(II) is higher at low concentration [23,31,32]. Decrease in percent adsorption can be explained by the fact that percent adsorption decreases with increase in initial metal concentration due to rapid saturation of the metal binding sites of the biosorbent [33].

3.4. Adsorption isotherms

To examine the relationship between sorbed (q_e) and aqueous concentration (C_e) of metals at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are most frequently used. The Langmuir isotherm considers sorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. Although the Langmuir model sheds no light on the mechanistic aspects of sorption, it provides information on uptake capabilities and is capable of reflecting the usual equilibrium sorption process behavior. Langmuir assumed that the forces that are exerted by chemically unsaturated surface atoms (total number of binding sites) do not extend further than the diameter of one sorbed molecule and therefore sorption is restricted to a monolayer.

The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. To get the equilibrium data, initial lead(II) and zinc(II) concentration were varied while the adsorbent mass in each sample was kept constant. The Langmuir model [34] takes the form of equation:

$$\frac{C_e}{q_e} = \frac{1}{X_m K_L} + \frac{C_e}{X_m} \quad (2)$$

where q_e is the metal ion sorbed (mg/g), C_e the equilibrium concentration of metal ion solution, X_m and K_L are Langmuir constants. Results obtained from initial metal ion concentration tend to be in better correlation with Langmuir isotherm model (Fig. 3). If the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the sorption of the next ion, then the sorption process would follow the Langmuir adsorption isotherm.

The Freundlich relationship is an empirical equation. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration ranges. However, it is easier to handle mathematically in more complex calculations (e.g. in modeling the dynamic column behavior) where it may appear quite frequently. Freundlich model [35] can be easily linearized by plotting it in a (log–log) format. Freundlich equation is:

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

where q_e is the metal ion adsorbed (mg/g), C_e the equilibrium concentrations of metal ion solutions (mg/L). K and n are Freundlich constant. R^2 values obtained by Freundlich model indicated that Freundlich isotherm model is not applicable because R^2 value is less than 0.98 (Table 1 and Fig. 3).

3.5. Separation factor (R_L)

To predict whether a sorption system is favourable or unfavourable in a batch adsorption process, Langmuir isotherm can be used. For this purpose, an essential feature of the Lang-

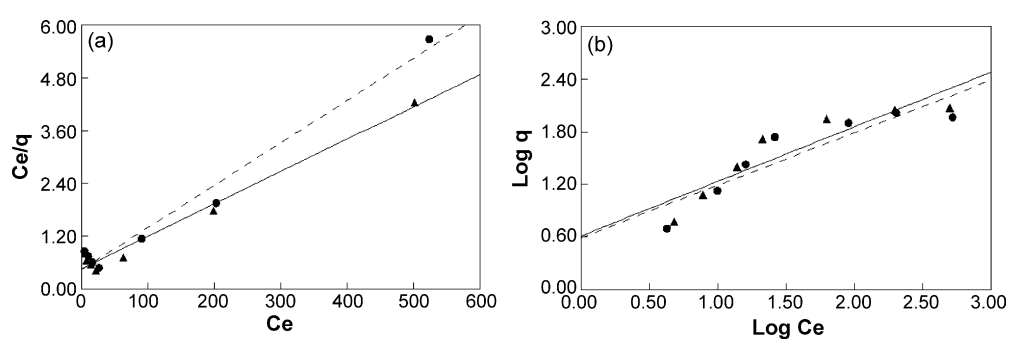


Fig. 3. Linearized Langmuir (a) and Freundlich (b) isotherm plots for biosorption of lead(II) (▲) and zinc(II) (●) cations by NaOH pretreated *Rosa centifolia* biomass.

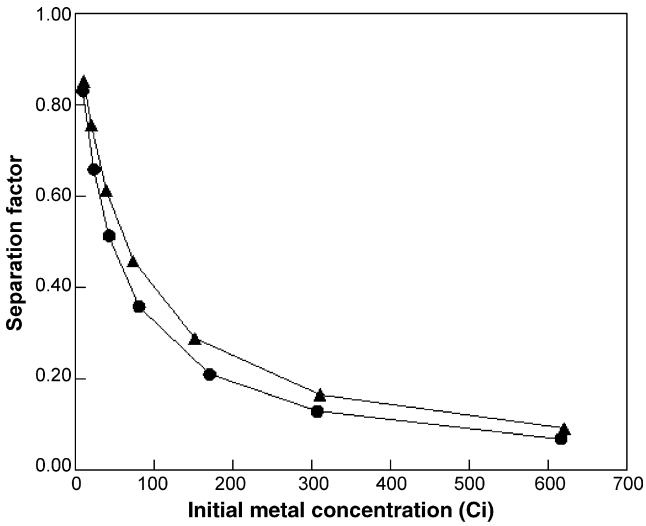


Fig. 4. Separation factor (R_L) profile for biosorption of lead(II) (▲) and zinc(II) (●) as function of initial metal concentration by NaOH pretreated *Rosa centifolia* biomass.

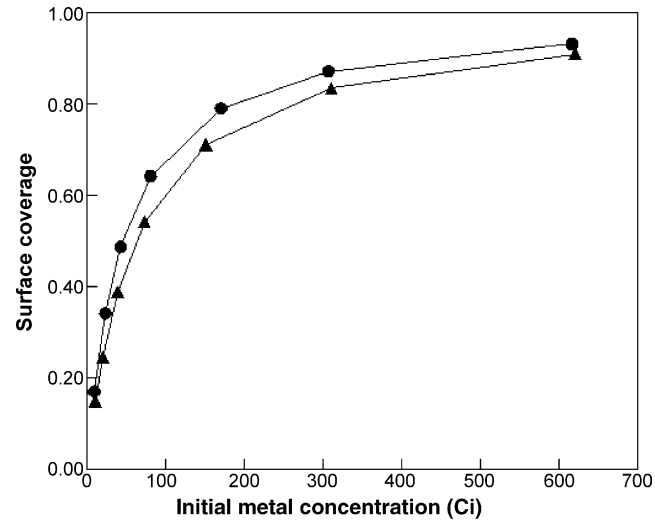


Fig. 5. A plot of surface coverage against initial metal concentration of lead(II) (▲) and zinc(II) (●) metal ions.

muir isotherm called separation parameter was used [35] (a dimensionless constant) which is defined by the following equation as:

$$R_L = \frac{1}{(1 + K_L C_i)} \tag{4}$$

Where R_L is separation factor, C_i is initial metal ion concentration and K_L Langmuir constant. Fig. 4 showed that sorption of lead(II) and zinc(II) increased concomitantly with initial metal ion concentration. Biosorbent has more sorption capacity for lead(II). R_L values between 0 and 1 represent favourable isotherm. R_L values calculated for lead(II) and zinc(II) biosorption indicate that adsorption is favourable even for higher initial metal concentrations.

3.6. Surface coverage values

Adsorption behaviour of lead(II) and zinc(II) on the *Rosa centifolia* biomass can also be calculated by surface coverage (θ). Langmuir type equation related to surface coverage [34] is as follows:

$$KCi = \frac{\theta}{1 - \theta} \tag{5}$$

where θ being the surface coverage, C_i initial metal concentration and K an adsorption coefficient. Fig. 5 shows that surface coverage on the biomass increase with increase in initial metal ion concentration.

3.7. Gibbs free energy (ΔG^0_{ads})

The thermodynamics of the exchange process depends on the number of water molecules (n) replaced by the metal ions. Since the most probable value of n is 2, the apparent Gibbs free energy of the adsorption process (ΔG^0_{ads}) corresponding to lead(II) and zinc(II) ion on the biomass are evaluated using the Bockris–Swinkel's adsorption isotherm equation as reported by Rudresh and Mayanna with θ-values and $n = 2$. The equation for Gibbs free energy [34] is expressed as:

$$\Delta G^o_{ads} = -2.303RT \log \times \left[\left\{\frac{55.4\theta}{Ci(1-\theta)}\right\}\left\{\frac{\theta + n(1-\theta)^{n-1}}{n^n}\right\}\right] \tag{6}$$

where C_i is the initial concentration of metal ion in the solution. The values of (ΔG^0_{ads}) were then evaluated with $n = 2$ at various initial metal ion concentrations. The negative values of (ΔG^o) (Table 2) indicate the spontaneous adsorption nature of zinc(II) and lead(II) by the *Rosa centifolia* biomass.

3.8. Distribution coefficient (D)

The relativeness of the biomass in removing the metal ions from aqueous solution was also evaluated in terms of the distribution coefficient, D, which can be defined as "the ratio of the metal ion concentration in the adsorbent phase, to the concentration in the aqueous phase".

Table 2 shows the value of D for a range of metal ion concentrations. These results show that the concentration of metal ions at the sorbent–water interface is higher than the concentration in the continuous aqueous phase, suggesting that the biomass is

Table 2
Distribution ratios, D, and apparent Gibbs free energy (ΔG^0_{ads}) (KJ/mol) of lead(II) and zinc(II) between *R. centifolia* biomass and aqueous phase

C_i (mg/L)	Lead(II)		Zinc(II)	
	(ΔG^0_{ads})(KJ/mol)	D	(ΔG^0_{ads})	D
10	−32.0649	0.552434	−29.8923	0.53883
20	−31.8487	0.605051	−29.4574	0.574003
40	−31.4399	0.641753	−28.9464	0.625175
80	−30.8332	0.72	−28.1599	0.680446
160	−29.7944	0.585005	−26.9178	0.467751
320	−28.4808	0.360366	−25.738	0.339188
640	−27.006	0.190918	−24.1905	0.149663

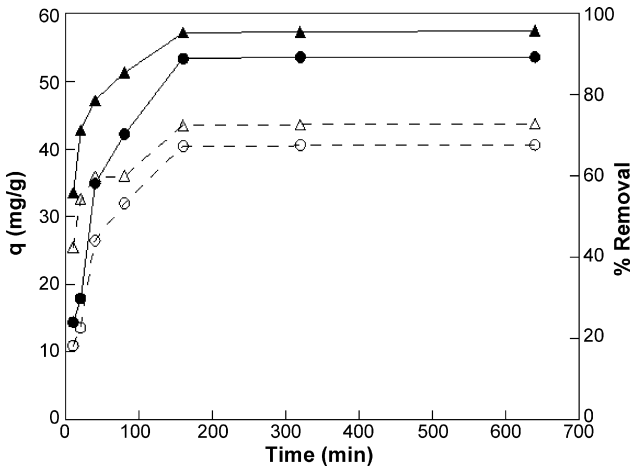


Fig. 6. Kinetic study for "lead(II) having uptake capacity (▲) and % removal (●) and zinc(II) having uptake capacity (△) and % removal (◯)" biosorption by NaOH pretreated *Rosa centifolia* biomass.

effective in the removal of metal ions from aqueous systems. The nature of the sorbed species may be deduced from the fact that the metal ions are divalent. This indicates that two molecules of biomass were associated with metals. Hence the composition of the sorbed complex and the probable mechanism may be given as follows [34,36]:

$$M^{2+} + 2\text{B}{-}\text{OH} = M(\text{BO}{-})_2 + 2\text{H}^+$$

where M^{2+} is divalent metal ion, B is biomass molecule, OH^{1-} is hydroxyl group and H^+ is proton. The sorption occurs by an ion-exchange mechanism.

3.9. Kinetic study

The data of lead(II) and zinc(II) uptake at the optimum pH 5 and initial lead(II) and zinc(II) concentration of 80 mgL^{-1} contacted with 0.1 g dried NaOH pretreated biomass showed that rapid uptake up to 74.82% occurred in the first 20 min for lead(II) while in case of zinc(II) within 20 min, maximum biosorption is 33.52% accounting for about 3.74% lead(II)/min and 1.175% zinc(II)/min. Time required for attaining equilibrium was 160 min, under the tested conditions (Fig. 6). It is known that the rate of metal uptake is influenced by factors affecting mass transfer from bulk solution to binding sites. It was indicated that various steps are involved in the transfer of metal from bulk solution to binding sites [37]. First is the bulk transport of metal ions in solution phase, which is usually rapid because of mixing and advective flow [20]. Second, film transport involves diffusion of metal through a hydrodynamic boundary layer around the biosorbent surface, and third, actual adsorption of metal ions by active sites of the biomass is considered to be rapid, equivalent to an equilibrium reaction [37]. Lead(II) sorption is seemed to follow bulk transport of metal ions in solution phase and actual adsorption of metal ions by active sites of biomass because of 74.82% lead removal within first 20 min whereas removal of zinc(II) appears to favour film transport because of only 33.52% removal within 20 min. Bulk transport and adsorption by active sites of biomass are rapid processes whereas film transport is a slow process [37,38].

3.10. Biosorption kinetic models

In order to investigate the mechanism of biosorption and potential rate controlling step, such as mass transport and chemical reaction processes, kinetic models have been used to test the experimental data. Moreover, information on the kinetics of metal uptake is required for selection of optimum conditions for full-scale batch metal removal process. A kinetic study with different time intervals with fixed metal and biosorbent concentration was performed. Kinetics of absorption by any biological material has been widely tested by first order expression given by Lagergren and pseudo second order approach. The first order Lagergren [35] equation is:

$$\log(q_e - q) = \log q_e - \frac{k_{1,\text{ads}}t}{2.303} \tag{7}$$

The pseudo second order [35] equation is:

$$\frac{t}{q} = \frac{1}{k_{2,\text{ads}}q_e^2} + \frac{t}{q_t} \tag{8}$$

where q_e is the mass of metal absorbed at equilibrium (mg/g), q_t the mass of metal at time t (min), $k_{1,\text{ads}}$ the first order reaction rate

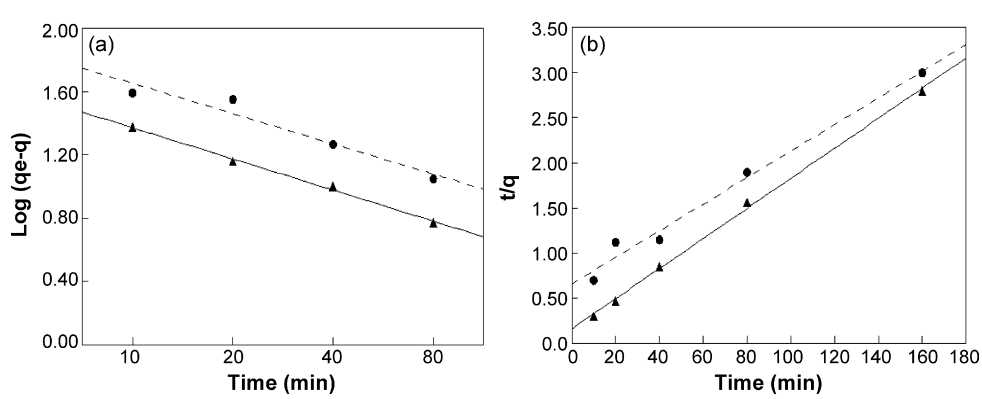


Fig. 7. Pseudo first-order (a) and Pseudo second-order (b) kinetics for biosorption of lead(II) (▲) and zinc(II) (●) metal ions by NaOH pretreated *Rosa centifolia* biomass.

Table 3
Comparison between adsorption rate constants, q_e estimated and coefficient of correlation associated to the Lagergren pseudo first order and to pseudo second order kinetic models

Metal	Pseudo first-order kinetic model			Experimental value	Pseudo second-order kinetic model		
	q_e (mg/g)	$K_{1,ads}$ (min^{-1})	R^2	q_e (mg/g)	q_e (mg/g)	$k_{2,ads}$ (mg/g min)	R^2
Lead	23.637	1.81×10^{-2}	0.9637	57.5	59.88	1.75×10^{-3}	0.9991
Zinc	46.323	2.00×10^{-2}	0.9772	53.6	67.56	3.34×10^{-4}	0.9918

constant of adsorption (per min), $k_{2,ads}$ the pseudo second order rate constant of adsorption (mg/g min). A comparison between Lagergren pseudo first order and to pseudo second order kinetic (Fig. 7) models is tabulated in Table 3. The Lagergren first order rate constant ($k_{1,ads}$) and q_e determined from the model indicate that this model failed to estimate q_e since the experimental values of q_e differed from those estimated. The correlation coefficients for the first order kinetic model obtained at various time intervals are lower than the second order rate equation (Fig. 8).

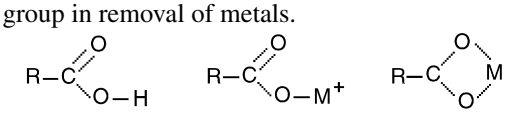
A high degree of correlation coefficient was obtained for the second order kinetic model. The theoretical q_e values were found to be in good agreement with the experimental q_e values in this second order kinetics. The results suggest that the sorption system follows the second order kinetics. The coefficients of correlation for the second order kinetic model were approximately equal to one at given temperature (30 °C). Both facts suggest that the sorption of lead(II) and zinc(II) ions followed the second order kinetic model which relies on the assumption that biosorption may be the rate limiting step. A better fitting of pseudo second order kinetic model with experimental data can also be explained by the fact that "if correlation coefficients evaluated from the isotherms are higher than 0.98 then all the models are very suitable for describing the biosorption equilibrium" [39].

3.11. FTIR analysis

FTIR analysis is an important analytical tool for determination of functional groups responsible for heavy metal removal by biomass. The changes in peak frequency and intensity suggest that carboxylic, carbonyl, sulfoxide, thioester etc. are involved in sorption process. Carboxylic acids display a broad OH stretching absorption from 3300–2500 cm^{-1}. The peaks observed on 3297.04 [40] and 1709.76 cm^{-1} are due to vibrations of OH and C=O groups belonging to carboxylic acids. Peak at position 3297.04 cm^{-1} shifts towards higher wavenumber when lead(II) and zinc(II) react with native and NaOH pretreated biomass.

$$RCOOH + NaOH \rightarrow RCOO^{-}Na^{+} + H_2O$$

These saponified ester groups in the biomass produce carboxylate, which can bind cations. The peak at 1709.06 cm^{-1} also shifts towards higher wavenumber, which indicates involvement of this group in removal of metals.



Due to this, no marked change in vibration is observed after complexation. The peak on 3023.87 cm^{-1} is attributed to C–H stretch due to presence of Ar–H (Arenes). The stretching of this group in native biomass and no vibration in native and

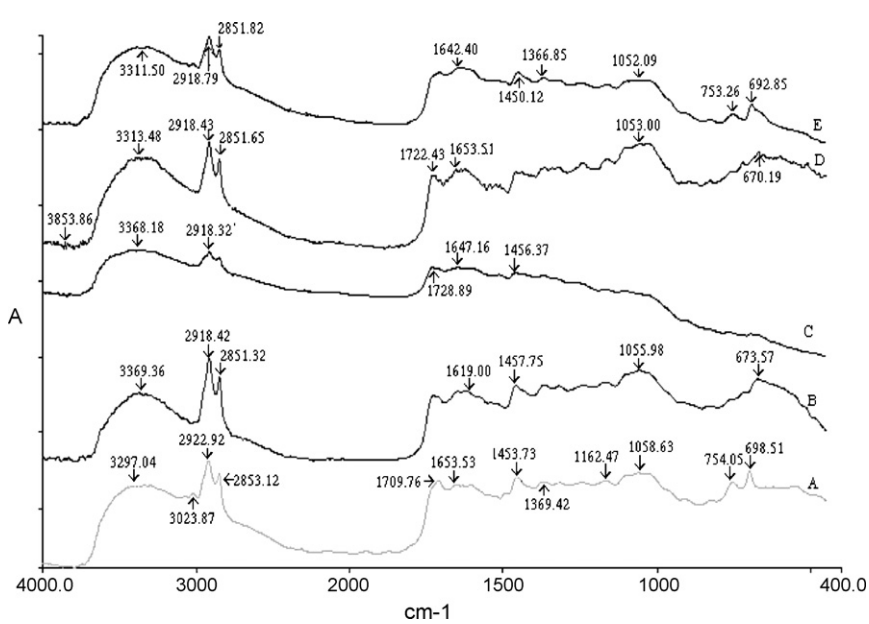


Fig. 8. FTIR spectral analysis for determination of functional groups in native NaOH pretreated *Rosa centifolia* biomass: (A) native *Rosa centifolia* biomass; (B) native *Rosa centifolia* biomass reacted with lead(II); (C) NaOH pretreated *Rosa centifolia* biomass reacted with lead(II); (D) native *Rosa centifolia* biomass reacted with zinc(II); (E) NaOH pretreated *Rosa centifolia* biomass reacted with zinc(II).

pretreated biomass when treated with lead(II) and zinc(II) is indication of involvement of this group in metal removal. This is due to the fact that after metal binding, chances of vibration of functional groups become limited. The peaks observed on 2853.12 and 2922.92 cm^{-1} are due to C–H stretch of aldehyde. This group is involved only in the removal of lead(II) because of no stretching at this position in NaOH pretreated biomass. The peak observed on 1653.53 cm^{-1} is response of C=O stretch of carbonyl group [40]. The peaks on 754.05 and 698.51 cm^{-1} correspond to S–OR stretch of thioester. This functional group is more responsible for removal of lead(II) as compared to zinc(II). The peak on 1453.73 cm^{-1} is due to C–H stretch whereas the peak 1162.47 cm^{-1} is due to P=O functional group which is also more involved in the removal of lead(II). This suggested that the dominant removal of lead(II) in case of rose biomass modified with NaOH was by functional groups in range of 1456–698.51 cm^{-1} because no vibration in the range 1456–698.51 cm^{-1} was observed after lead(II) uptake whereas removal of zinc(II) by rose biomass was less because of less variations in spectral peak positions in native and pretreated biomass when these biomasses were mixed with zinc(II).

4. Conclusion

Following are the main conclusions evaluated from present study:

- The obtained results show that sorption of lead(II) and zinc(II) was found highly dependent on experimental parameters such as pH, chemical pretreatment, initial metal concentration and contact time.
- Modification of *Rosa centifolia* waste biomass by pretreating it with chemical reagents significantly improved its sorption capacity towards the uptake of lead(II) and zinc(II) ions from aqueous solutions. The highest uptake capacity of *Rosa centifolia* waste biomass was observed after pretreatment with NaOH.
- The results of present study demonstrate that the Langmuir model fits better to the adsorption equilibrium data in the examined concentration range in comparison to the model described by Freundlich.
- Kinetic data was better described by pseudo second order model rather than pseudo first order kinetic model.
- FTIR analysis of native and NaOH pretreated *Rosa centifolia* waste biomass suggested that carboxylic, carbonyl, sulfoxide, thioester etc. are involved in lead(II) and zinc(II) sorption process.

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