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Factors affect on bioremediation of Co(II) and Pb(II) onto *Lonicera japonica* flowers powder

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ABSTRACT

Bioremediation is a low-cost eco-friendly separation technique for the treatment of pollutants such as heavy metals and organics from wastewaters. In the present study, a biosorbent, *Lonicera japonica* flowers powder (LJFP) was prepared from *Lonicera japonica* flowers (LJF) for treating Pb (II) and Co(II) from aqueous solutions and was well characterized by FT-IR and SEM–EDX. The kinetic results showed that the kinetics of both metal ions was rate limiting pseudo-second order. However, Pb(II) was also involved in chemisorptions, which was proved by the Elovich kinetic model. The equilibrium data of Pb(II) were tuned with Langmuir isotherm whereas Co (II) was fit to Freundlich isotherm model. The maximum uptake capacities of LJFP for Pb(II) and Co(II) were 19.61 and 43.48 mg/g at 298 ± 2 K, pH 6.0. Thermodynamic studies were conducted in the range of temperature, 298–313 ± 2 K, and were revealed that the sorption process of Pb(II) and Co(II) on LJFP was endothermic. Overall studies demonstrated that the biomass, LJFP is a promising, efficient, economical, and reusable sorbent.

Keywords: Bioremediation; Heavy metals; *Lonicera japonica* flowers; Kinetics; Sorption mechanism; Thermodynamics

1. Introduction

Many industrial activities (e.g. metal plating and fertilizer) introduce heavy metals into the environment via their waste effluents such as combustion of fuel, industrial emissions, varnishes, and chemical colorants [1,2]. Particular attention has been paid to the presence of heavy metals, because of their irreversible deleterious effects on human [3].

Co(II) and Pb(II), heavy metal ions, were chose as a target in the present study. The natural levels of Co(II) are not harmful to the organism including human. But, at higher concentration, it is toxic because adverse health impacts, such as anthropogenic activities in human beings [4,5]. Pb(II) is toxic to human

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even at trace levels. Both causes an acute and chronic poisoning, adverse effects on human body parts such as kidney, liver, and heart, damage the functioning of the thyroid gland, the vascular system, the immune system, and causes asthma [6,7]. Co(II) causes genetic changes in living cells and exposure to its ionization radiation is associated with an increasing risk of developing cancer. Likewise, Pb(II) exposure can cause chromosome aberration, skin allergies, cancer, and birth defects [8–11].

Currently several methods being used for the treatment of heavy metals from contaminated wastewaters including filtration, membrane separation, electrochemical treatment, ion exchange, adsorption, and bioremediation [12–16]. However, bioremediation has been investigated as a cost effective, highly efficient process, and with the ability of biosorbent to bind and sequester the metal ions from wastewaters [17]. Several agricultural-based biosorbents have been used for the removal of heavy metals such as *Portulaca oleracea* [18], orange peel [19], *Annona squamosal* shell [20], rice husk and rice bran [21,22], tea wastes [23], neem biomass [24], *Ficus carcia* leaves [25], green algae biomass [26], tamarind bark, potato peel waste [27], and *Peganum harmala* seeds [28]. This literature survey reveals that the uses of agricultural wastes as biosorbents for treatment of heavy metals laden wastewaters have advantages due to the presence of multifunctional groups on material surface, an eco-friendly nature, and high biosorption capacity.

This aforesaid demonstrate that the use of modified agricultural waste material from *Lonicera japonica* flowers (LJF) is an excellent source of biomass for the treatment of heavy metals that can eliminate these contaminants from underground water at a reasonable cost without waste generation in the environment as well as contribute or reduce the organic pollution of this kind from waste. It belongs to *Lonicera* genus of plantae kingdom, called Japanese honeysuckle, and is native to Asia, mainly in China, Japan, and Korea. It has simple green leaves and has double-tongued white flowers that can fade to yellow color [29,30]. The LJF vine has natural antibacterial and anti-inflammatory properties. It is usually combined with other herbs and used as a medicine to treat fevers and remove toxins from a person's body [29–31].

The aim of the present work was to examine the efficiency of biosorbent, *Lonicera japonica* flowers powder (LJFP) for the removal of Co(II) and Pb(II) from aqueous solutions. Experimental parameters, such as equilibrium pH, adsorbent dosage, and kinetic studies, were performed to develop an effective biosorption process for the removal of Co(II) and Pb(II). Biosorption isotherms were also tested to determine the rate and mechanism of the biosoprtion process. This developed method can be successfully applied for the removal of Co(II) and Pb(II) from aqueous environments. To the best of our knowledge, this report is the first of its kind about using biomass, LJFP, as a biosorbent for the removal of heavy metal ions.

2. Materials and methods

2.1. LJFP preparation

LJF (Fig. 1) were collected from Oriental Medical College, Gyeongju, South Korea. These flowers were washed with deionized water and were cut into small pieces, dried, and ground in a mill to get a fine powder. The powder was boiled with deionized water at 60˚C for 2 h, changing the water repeatedly until the water becomes colorless, indicating that the LJFP was free from soluble color compounds. The washed fine powder was oven dried at 60˚C for 24 h and stored in desiccators to prevent moisture adsorption, which was shown in Fig. 1.

2.2. Chemicals and equipment

$Co(CH_3COO)_2{\cdot}4H_2O$ and anhydrate $Pb(NO_3)_2$ purchased from Sigma–Aldrich (Ireland) were used for the preparation of standard metal ion (1,000 mg/L) solutions. Required working solutions were prepared by diluting the standard metal solution. pH 340i, WTW, Germany, were used for adjusting pH of the samples. ICP–OES (Optima 2100 DV, Perkin-Elmer, USA) was used for metal concentration determination. Scanning electron microscope with an energy dispersive X-ray spectroscopy (S-4300 & EDX-350, Hitachi, Japan) was used only for measuring surface morphology and composition. Surface area and pore sizes of the biosorbent were measured by the Brunauer–Emmett–Teller method (BET) (Autosorb-1, Quanta Chrome Instrument,

Lonicera Japonica Flowers *Lonicera Japonica* Flower Powder

Fig. 1. Visual appearance of LJF and LJFP.

USA). Spectrum GX & Auto image FT-IR (Perkin-Elmer, USA) was used for analyzing functional groups in the biosorbents.

2.3. Batch biosorption studies

Batch studies were employed to evaluate the biosorption characteristics of LJFP. A 0.05 g of biomass (LJFP) with 50 mL of Co(II) and Pb(II) (2–25 mg/L) solutions at pH 6.0 were taken in a falcon tube and shaken with 200 rpm in a temperature (298 ± 2 K)-controlled shaker (SI-600R, JEIO Tech, Korea) by batch sorption studies. At the end of pre-determined time interval (120 min), filtered out aqueous solution and the metal ion concentrations were determined using ICP–OES. The amount of metal biosorption was determined by mass balance. All investigations were carried out in triplicate to avoid discrepancies in experimental results and the values reported were mean ± SD. Origin 8.0© was used to fit the kinetics and equilibrium models using linear regression analysis. Metal solution controls were utilized to maintain quality control. Metal ions biosorption removal percentage (R_s) and biosorption capacity (q_e) for unit LJFP were calculated according to these equations:

$$R_s = ((C_o - C_f)/C_o)\ 100 \tag{1}$$

$$q_e = (C_o - C_e)V/m \tag{2}$$

Kinetic studies were used to assess the time influence on the amount of biosorption capacity at time (t) and were calculated according to this equation:

$$q_t = (C_o - C_t)V/m \tag{3}$$

where C_o, and C_e, C_f, or C_t are the initial, equilibrium, final, or at time t, concentration of metal ion (mg/L) in the solution, respectively. q_e is the biosorption capacity (mg/g), V is the volume of metal ion solution (L), and m is the weight of the biosorbent (g).

3. Results and discussion

3.1. Physical characterization of the LJFP biosorbent

Characteristics of LJFP biomass such as density (bulk), moisture content, surface area/composition, ash content, and other physical parameters were evaluated. The bulk density of the biomass was found to be 0.420 g/mL with 1.25% moisture and 12.45% ash content. The BET surface area of biomass was considered to be 135 m^2/g by using N_2 gas adsorption method. The pore volume (0.22 m^2/g) and pore mean diameter (25.5×10^{-8} cm) of LJFP were measured and was confirmed as mesopores sorbent (20×10^{-8} cm < d < 500×10^{-8} cm; International Union of Pure and Applied Chemistry).

3.2. Optimization of batch biosorption of Pb(II) and Co(II) on biomass LJFP

Biosorption of heavy metal ions onto the surface of LJFP is affected by several factors, including biomass dosage, initial pH, initial metal ion concentration, time, and temperature. In order to optimize the effect of these parameters, batch biosorption tests were carried out.

3.2.1. Biomass, LJFP dosage effect

The number of sites available on sorbent depends upon the amount of the biosorbent. Effect of biosorbent dosage (Fig. 2) (0.25 to 8.0 g/L) on metal ion removal efficiency was studied in a temperature-controlled shaker. The percentage of metal ion uptake was found to be increased with increasing concentration of the LJFP is due to the increase in active sites on the sorbent, making easier penetration of the metal ions into active sites. But the amount of metal adsorbed per unit LJFP decreased considerably (data not shown). It is due to the sorbent atoms agglomerates, or interactions between sorbent atoms are reduced the available surface area and blocked some of the active sorption sites causing decreased available unit surface area [32,33]. It was found from the results that 1.0 g/L biosorbent dosage was required to achieve maximum biosorption of Co(II) and Pb(II)

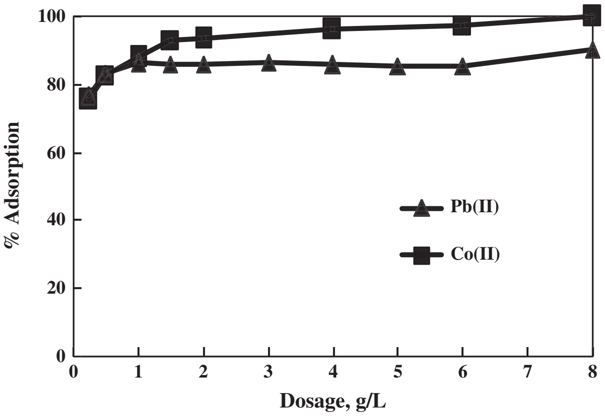

Fig. 2. Effect of the LJFP dosage on biosorption of Pb(II) and Co(II) (10.0 mg/L) at pH 6.0, and 298 ± 2 K for 120 min equilibrium.

ions. A slow increase in the removal percentage was found to reach a constant value with respect to the biosorbent dosage beyond 1.0 g/L.

3.2.2. Effect of pH

The pH of the solution is a well-known characteristic that affects the surface charge of adsorbents by the protonation of functional groups in the biomass. The degree of ionization, as well as the chemistry of the metal ions, is influenced by the solution pH. In aqueous systems, the surface of LJFP can be protolyzed in two ways:

$$\equiv \mathrm{SOH} + \mathrm{H}^+ \rightleftharpoons \ \equiv \mathrm{SOH}_2^+ \text{ (In acidic media)} \tag{4}$$

$$\equiv \mathrm{SOH} + \mathrm{OH}^- \rightleftharpoons \ \equiv \mathrm{SO}^- + \mathrm{H}^+ \text{ (In basic media)} \tag{5}$$

where $\equiv \mathrm{SOH}$: Adsorbent surface

As shown in Fig. 3, metal uptake was increased with an increase in pH from 2.0 to 6.5 and achieved maximum sorption capacity values above pH 6.0. Lower uptake capacity was observed at lower pH. This is due to the known fact that the concentrations of protons or hydronium (H_3O^+) ions was higher and may form as positive adduct (Eq. (4)) or compete with metal ions for the binding of active sites on the surface of the biosorbent. Further, with increasing pH there is a decrease in competition between the protons surrounded by the adsorbent/metal ions. When the pH of the solution was increased from 2.0 to 6.0, the number of negatively charged sites increased as protons dissociated from the sorbent surface (Eq. (5)), resulting in an increased biosorption of positive metal ions. Further the biosoprtion capacity was almost constant above the pH 6.5, where no significant change in adsorption was observed. The biosorption mechanism of Pb(II) and Co(II) on the surface of the biosorbent may be predicted in the following ways:

$$2(\equiv \mathrm{SO}^-) \ + \mathrm{M}^{2+} \rightleftharpoons (\equiv \mathrm{SO}^-)_2 \ - \mathrm{M}^{2+} \tag{6}$$

$$2(\equiv \mathrm{SOH}) \ + \mathrm{M}^{2+} \rightleftharpoons (\equiv \mathrm{SO})_2 \ - \mathrm{M}^{2+} \ + 2\mathrm{H}^+ \tag{7}$$

where M^{2+} : Pb(II) & Co(II), $\equiv \mathrm{SOH}$
: Adsorbent surface

3.2.3. The effect of contact time and initial metal ion concentration on biosorption

The effect of contact time is one of the most important factors that affect the biosorption efficiency. From the results (Fig. 4), it has been observed that rapid biosorption of the metal ion was achieved at initial period (within 10 min). After this period, biosorption of metal ions slowly increased until it reached the equilibrium. The possible reason for the phenomenon is a large number of vacant surface sites are available for biosorption initially. After an interval of time, the left over vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and aqueous phases. Similar results were seen by some researchers for other sorbate-sorbent systems [33–38]. Based on the results, 30 and 120 min were assumed based on the equilibrium times required for Co(II) and Pb(II),

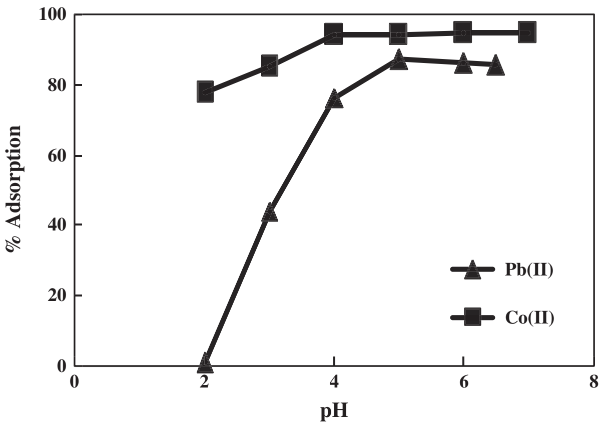

Fig. 3. Evaluation of the pH effect on Co(II) and Pb(II) (10.0 mg/L) biosorption onto LJFP (1.0 g/L) for 120 min equilibration with 200 rpm at pH 6.0, and 298 ± 2 K.

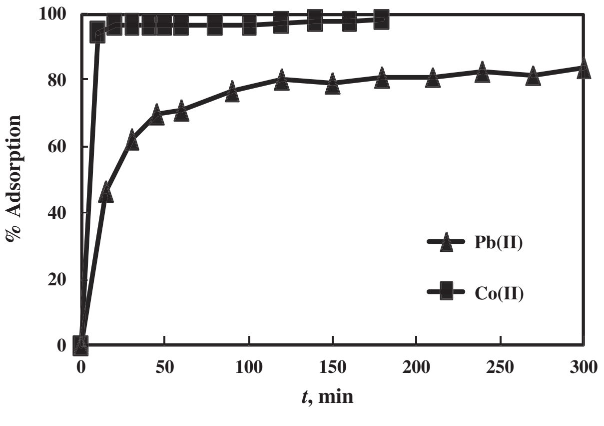

Fig. 4. The effect of equilibration time on biosorption of Pb(II) and Co(II) ions (10.0 mg/L) onto LJFP (1.0 g/L) at 200 rpm, 298 ± 2 K temperature, and pH 6.0.

respectively. Hence, 120 min was fixed for further batch biosorption experiments of both metal ions. When initial concentration of both metal ions was increased from 5.0 to 20.0 mg/L, the absolute sorption per unit weight of biosorbent increased. However, the percentage of both metal ions biosorption decreased with increasing initial concentration (data not shown) because the existing active sorption sites became fewer at higher initial concentration. It is concluded that metal ions biosorption onto LJFP is concentration dependent. Similar results were observed by some researchers for various sorption systems [33,35].

3.3. *Kinetic studies of biosorption of Pb(II)and Co(II) on LJFP*

The kinetics for the biosorption of Pb(II) and Co(II) onto biomass, LJFP have been investigated for three initial concentrations varying between 5.0 and 20.0 mg/L. The order of the reaction of the obtained experimental kinetic data was analyzed by the pseudo-first-order [39], and pseudo-second-order [40] kinetic models. The suitability of models was expressed by correlation coefficient (R^2), sorption capacity (q_e), and chi-square (χ^2) function test. The linear pseudo-first and second-order kinetic models are expressed in Eqs. (8) and (9):

$$\log(q_e - q_t) = \log(q_e) - (K_1/2.303)t \quad (8)$$

$$t/q_t = (1/K_2q_e^2) + (1/q_e)t \quad (9)$$

where q_t and q_e are the metal ion concentrations (mg/g) at any time (t) and at the equilibrium (mg/g), respectively, K_1 is the first-order rate constant (min^{-1}) which is obtained from slope of the $\log(q_e - q_t)$ vs. t at different initial concentration of metal ions (Fig. 5). K_2 is the pseudo- second-order rate constant (g/mg.min) and was calculated from the slope of t/q_t vs. t (Fig. 6). The K_1, K_2, and the correlation coefficient (R^2) values are summarized in Table 1. Equilibrium data were further correlated, to predict the chemisorptions studies by using the Elovich kinetic model [41], expressed as:

$$q_t = 1/b \log(ab) + 1/b \log t \quad (10)$$

where a (mg/gh) is the rate of sorption at the initial stage and b (mg/g) is the activation energy. The linear plots of this model are shown in Fig. 7. The calculated parameters are given in Table 1.

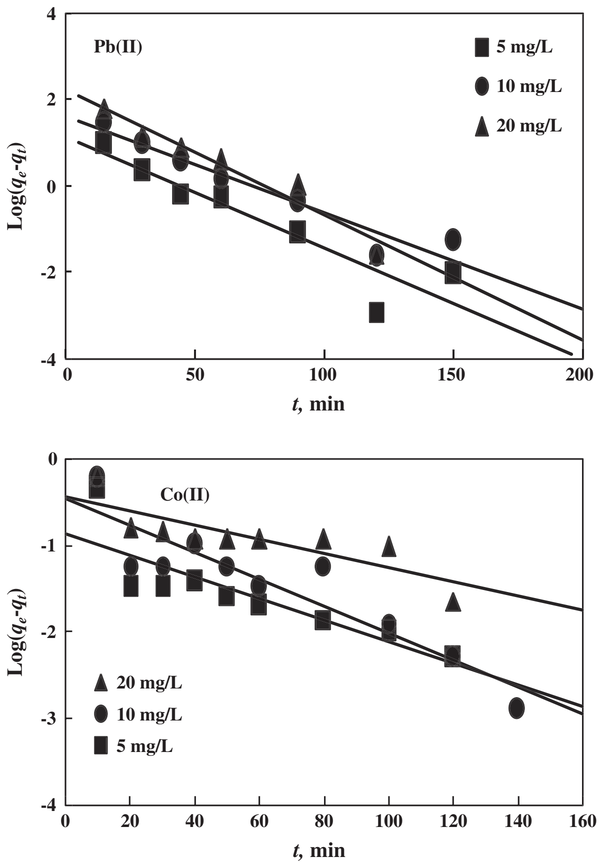

Fig. 5. Pseudo-first-order kinetics for the biosorption of Pb(II) and Co(II) onto LJFP (1.0 g/L) at pH 6.0, 200 rpm, and 298 ± 2 K.

The obtained (Table 1) high correlation coefficient (R^2), low χ^2, and closeness of biosorption capacity values showed that the pseudo-second-order model provides a better fit to the experimental results than the pseudo-first-order and the Elovich models for both metal ions. However, the pseudo-first-order works effectively in the region where biosorption occurs rapidly. Although, the Elovich model was suitable for Pb(II), but not Co(II). Hence, from this kinetic results concluded that the biosorption of either metal ion onto LJFP biomass was the rate controlling step involving pseudo-second-order kinetics, where Pb(II) was involved in chemisorption along with diffusion kinetics.

3.4. *Isotherm studies for biosorption of Pb(II) and Co(II) onto LJFP*

The three most common isotherm models described in literature, Langmuir (Eq. (11)) [42], Freundlich (Eq. (12)) [43], and Temkin and Pyzhev (Eq. (13)) [44]

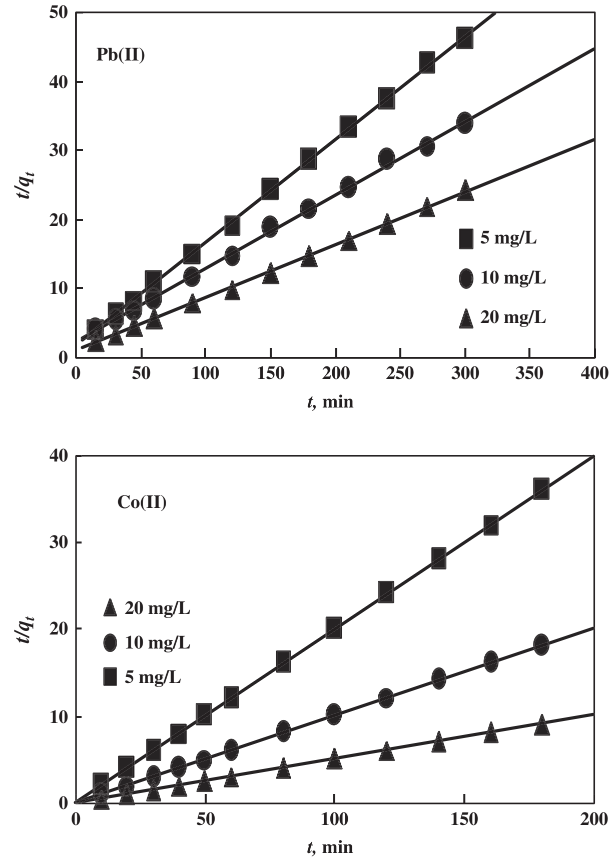

Fig. 6. Pseudo-second-order kinetics for the biosorption data of Pb(II) and Co(II) onto LJFP (1.0 g/L) at pH 6.0, 200 rpm, and 298 ± 2 K.

were used to correlate the equilibrium data obtained in the temperature range, 298 to 323 ± 2 K.

$$c_e/q_e = 1/b(1/K_L) + (1/b)\, C_e \quad (11)$$

$$\log q_e = \log K_F + (1/n) \log C_e \quad (12)$$

$$q_e = B \log K_T + B \log C_e \quad (13)$$

where q_e is the metal ion uptake capacity and C_e is the equilibrium concentration of metal ion. The maximum uptake capacity, *b*, and Langmuir equilibrium constants K_L were calculated, respectively, from the slope and intercept of the plot of C_e/q_e vs. C_e (Fig. 8). The Freundlich constants, $1/n$ and K_F were calculated from the slope and intercepts of the plot of log C_e vs. log q_e (Fig. 9), where Temkin's constant, $B = (RT/b)$, was obtained from the slope of the plot of q_e vs. log C_e (Fig. 10). The intercept of the curve indicates B log K_T. The isotherm constants K_T and BK_T are the Temkin equilibrium binding constants (L/mg).

Table 1
Kinetic parameters of Pb(II) and Co(II) biosorption onto LJFP

			Pseudo-first order				Pseudo-second order				Elovich model			
Metal ion	Initial metal ion concentration, (mg/L)	$q_{e,exp.}$, (mg/g)	$q_{e,cal.}$, (mg/g)	K_1, (min^{-1})	R^2	χ^2	$q_{e,cal.}$, (mg/g)	K_2, (g/mg min)	R^2	χ^2	b, (mg/g)	$1/b \times \log (ab)$	R^2	χ^2
Pb(II)	5	6.25 ± 0.21	14.45 ± 0.28	0.06 ± 0.004	0.869	0.371	6.71 ± 0.12	0.01 ± 0.001	0.999	0.051	1.18 ± 0.021	1.88 ± 0.25	0.903	0.786
	10	8.52 ± 0.16	44.16 ± 0.37	0.05 ± 0.005	0.928	0.276	9.43 ± 0.21	0.01 ± 0.002	0.998	0.062	0.64 ± 0.024	0.27 ± 0.19	0.947	0.652
	20	12.11 ± 0.25	179.47 ± 0.32	0.07 ± 0.004	0.954	0.284	13.16 ± 0.18	0.01 ± 0.001	0.999	0.087	0.52 ± 0.018	2.11 ± 0.26	0.902	0.743
Co(II)	5	4.97 ± 0.18	0.13 ± 0.35	0.03 ± 0.003	0.724	0.381	5.01 ± 0.23	1.65 ± 0.002	0.999	0.091	4.22 ± 0.032	4.49 ± 0.32	0.537	0.654
	10	9.87 ± 0.23	0.34 ± 0.34	0.04 ± 0.005	0.840	0.243	10.02 ± 0.27	1.96 ± 0.003	0.999	0.076	3.05 ± 0.024	9.21 ± 0.32	0.584	0.870
	20	19.50 ± 0.12	0.35 ± 0.28	0.02 ± 0.004	0.683	0.286	20.01 ± 0.24	1.28 ± 0.002	0.999	0.064	2.12 ± 0.027	18.57 ± 0.23	0.773	0.901

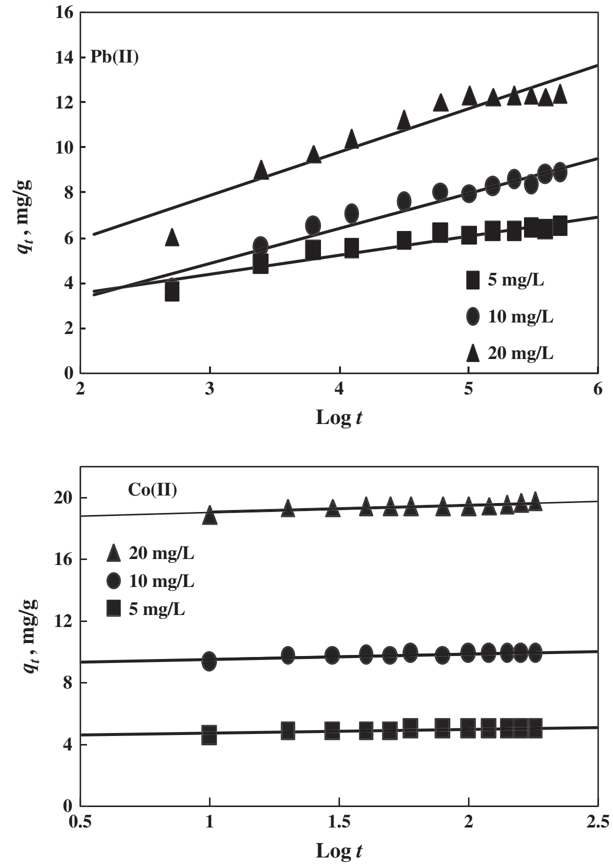

Fig. 7. The Elivoch kinetic studies for the biosorption data of Pb(II) and Co(II) onto LJFP (1.0 g/L) at pH 6.0, 200 rpm, and 298 ± 2 K.

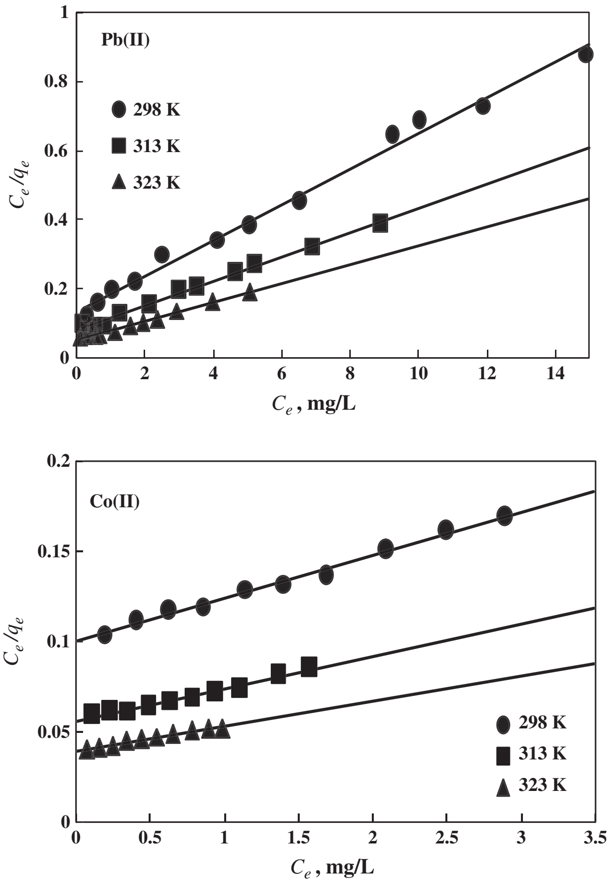

Fig. 8. Langmuir isotherm studies for Pb(II) (2.0 to 25.0 mg/L) and Co(II) (2.0 to 20.0 mg/L) biosorption onto LJFP (1.0 g/L) at pH 6.0, and various temperatures for 120 min equilibrium.

The obtained isotherm parameters are shown in Table 2 and were found to be the Langmuir and Freundlich adsorption isotherm models yielded the best results, as indicated by the highest R^2 and low χ^2 values at different biosorbent dosage compared to Temkin isotherm models. These isotherm results suggest that the biosorbent surface contains both homogeneous and heterogeneously distributed active sites. However, the favorable order (Langmuir > Freundlich > Temkin for Pb(II), and Frendlich > Langmuir > Temkin for Co(II)) and low χ^2 values of studied isotherms were concluded that the monolayer biosorption on a homogeneous surface of biomass was more favorable for Pb(II), whereas multilayer biosorption on the heterogeneous surface of biomass was more favorable for Co(II). When compared to both metal ions maximum biosorption capacities, Co(II) was found to have a higher sorption capacity than Pb(II). Further, the suitability of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_{L}, expressed as [45,46]: $R_{\mathrm{L}} = 1/(1+K_{\mathrm{L}}C_{\mathrm{o}})$, where C_{o} is the highest initial concentration of adsorbate (mg/L) and K_{L} (L/mg) is the Langmuir constant. The R_{L} value indicates the shape of the isotherm to be either favorable ($0 < R_{\mathrm{L}} < 1$), linear ($R_{\mathrm{L}} = 1$), unfavorable ($R_{\mathrm{L}} > 1$), or irreversible ($R_{\mathrm{L}} = 0$). The R_{L} values in the present investigations were found to be $0 < R_{\mathrm{L}} < 1$ at 298, 313, and 323 K (Table 2) for both metal ions indicating that the sorption of Pb(II) and Co(II) onto LJFP is favorable.

3.5. Comparison of Co(II) and Pb(II) biosorption onto LJFP with other biosorbents

Biosorption capacities of LJFP for Co(II) and Pb(II) removal were compared with literature-reported biosorbents (Table 3) [25,47–55]. Maximum biosorption capacity of LJFP biomass is found to be 19.61 mg/g

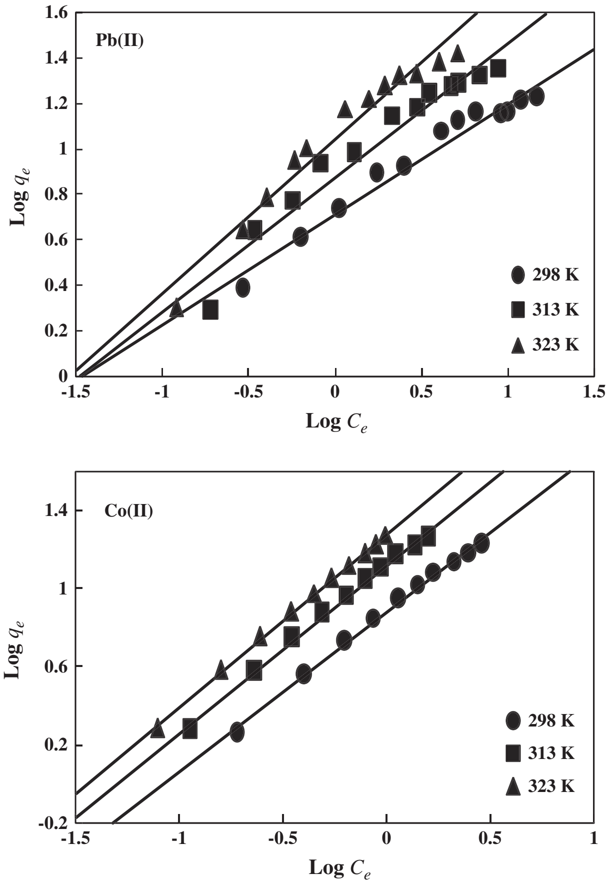

Fig. 9. Freundlich isotherm studies for Pb(II) (2.0 to 25.0 mg/L) and Co(II) (2.0 to 20.0 mg/L) biosorption onto LJFP (1.0 g/L) at pH 6.0 and various temperatures for 120 min equilibrium.

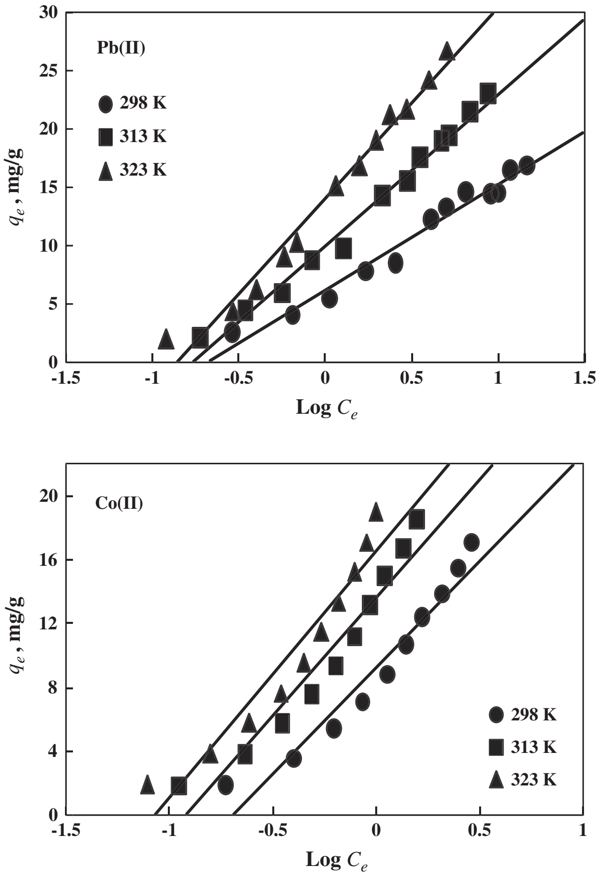

Fig. 10. Temkin isotherm studies for Pb(II) (2.0 to 25.0 mg/L) and Co(II) (2.0 to 20.0 mg/L) biosorption onto LJFP (1.0 g/L) at pH 6.0, and various temperatures for 120 min equilibrium.

Pb(II) and 43.48 mg/g Co(II) at 298 ± 2 K by 1.0 g/L biomass, LJFP dosage is relatively large and comparable with other biomasses. These obtained results show that LJFP might be a promising and economically an efficient material for the removal of Co(II) and Pb(II) ions from aqueous environments.

3.6. Biosorption mechanism of Pb(II) and Co(II) on biomass, LJFP

It is essential to understand mechanisms of biosorption processes. Hence, in this study employed FT-IR and SEM–EDX analysis to understand the biosorption mechanism of metal ions. In the FT-IR spectrum (Fig. 11(a)) of LJFP, a broad and strong absorption peak at 3,421 cm^{-1} is attributed to aromatic and aliphatic –OH groups. The peaks between 2,853 and 3,016 cm^{-1} indicate –C–H stretching vibrations in the hetero aromatic structure and the strong peaks between 2,853 and 2,943 cm^{-1} are related to the –C–H vibration of alkyl and ethylene groups of side chains and aromatic methoxyl groups, while the weak absorption peaks between 2,323 and 2,348 cm^{-1} indicate C–C triple bonds at the side chain of the aromatic ring (or) aliphatic chains. The strong stretching absorption peaks around 1,744 cm^{-1} are assigned as carbonyl stretching vibrations. The absorption peaks between 1,635 and 1,640 cm^{-1} indicate an aromatic ring alkenes and amide group –C–O stretching frequency, while the peaks between 1,468 and 1,357 cm^{-1} are typical vibrations in the alkynes skeleton on an aromatic ring. The absorption peaks between 1,275 and 1,036 cm^{-1} indicate –C–O stretching vibrations in the side chains of an aromatic ring unit. The vibration bands appeared between 925 and 710 cm^{-1} indicate the presence of substituted phenyl rings. The absorption peaks observed between 650 and 416 cm^{-1} are related to –C–X (X=Cl^{-1}, S^{2-}) stretching vibrations. After loading with Pb(II) and

Co(II) onto LJFP, the FT-IR absorptions peaks of LJFP shifted to higher wavelengths when compared with bare LJFP (Fig. 11(a)). The shifting absorption peaks are associated with the involvement of aromatic and aliphatic –OH, –COOH, –C=O, and –C–X (X=S^{2-}, halides, O^{2-}) groups in the biosorption of metal ions, Pb(II) or Co(II) onto the LJFP surface.

Further SEM–EDX analysis was conducted to identify surface morphology and composition. From the EDX analysis of LJFP biomass (Fig. 11(b)) observed that the weight percentage of carbon (65.89 wt.%) and oxygen (29.48 wt.%) were more than calcium (0.73 wt.%), sulfur (1.36 wt.%), and chlorine (2.55 wt.%). The presence of sulfur in LJFP is beneficial because, sulfur groups are soft bases and have chemical affinity toward soft acids, Pb(II) or Co(II). Thus, the presence of sulfur in LJFP makes it as a potential biosorbent. The SEM morphology of biomass and metal-loaded biomass are shown in Fig. 12. It was observed that the biomass has rough surface morphology, which is favorable for the biosorption of metal ions. The surface morphology of Co(II)- or Pb(II)-loaded biomass (Fig. 12) exhibited different morphology than bare LJFP biomass, indicating that metal ions were adsorbed onto the LJFP surface. The preceding results concluded that the multilayer sorption on a heterogeneous surface of LJFP involved in the rate controlling step plays an important role for the removal of Co(II) from aqueous solution. Whereas monolayer chemisorptions on a homogeneous surface of LJFP involved in the rate controlling step was favorable for Pb(II). Moreover, it has good desorption capacity with high biosorption capacity.

3.7. Thermodynamic studies on biosorption of Pb(II) and Co(II)

The interactions between biosorbent and target and energy changes in the biosorption process mainly depend on the thermodynamic parameters, Gibb's free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). These thermodynamic parameters of the present system were determined using the following equations:

$$\Delta G^\circ = -RT \log K_c \tag{14}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{15}$$

where R is the universal gas constant (8.314×10^{-3} kJ mol/K), T is the temperature of the system in K, K_c is the equilibrium constant that was product of the maximum amount biosorbed by the biosorbent (q_{max}) and the Langmuir equilibrium constant (K_L).

Table 2
Isotherm parameters of Pb(II) and Co(II) biosorption onto LJFP

Metal ion	Temperature, ±2 (K)	Langmuir isotherm parameters					Freundlich isotherm parameters				Tempkin isotherm parameters			
		q_m, (mg/g)	K_L, (L/mg)	R^2	χ^2	R_L	K_F, (mg/g (L/mg)$^{1/n}$)	1/n	R^2	χ^2	K_T, (L/mg)	B	R^2	χ^2
Pb(II)	298	19.61 ± 0.482	2.59 ± 0.021	0.991	0.143	0.015 ± 0.001	5.22 ± 0.431	0.49 ± 0.021	0.967	0.184	4.733 ± 0.421	9.044 ± 0.452	0.974	0.484
	313	28.57 ± 0.342	2.23 ± 0.024	0.992	0.186	0.018 ± 0.002	7.66 ± 0.531	0.59 ± 0.014	0.948	0.210	5.911 ± 0.541	12.910 ± 0.642	0.987	0.420
	323	37.04 ± 0.452	1.89 ± 0.034	0.990	0.133	0.021 ± 0.001	11.14 ± 0.610	0.68 ± 0.024	0.958	0.165	7.312 ± 0.610	16.330 ± 0.552	0.977	0.365
Co(II)	298	43.48 ± 0.512	4.35 ± 0.028	0.993	0.124	0.011 ± 0.003	7.66 ± 0.521	0.83 ± 0.019	0.995	0.204	5.01 ± 0.578	13.32 ± 0.652	0.943	0.512
	313	58.82 ± 0.335	3.29 ± 0.038	0.986	0.156	0.015 ± 0.001	13.40 ± 0.641	0.86 ± 0.016	0.995	0.174	8.33 ± 0.601	14.85 ± 0.466	0.940	0.474
	323	76.92 ± 0.475	3.00 ± 0.027	0.975	0.16	0.016 ± 0.002	19.41 ± 0.488	0.89 ± 0.023	0.998	0.197	11.81 ± 0.467	15.48 ± 0.588	0.922	0.397

Table 3
Comparison of maximum metal up take capacity of LJFP with other biomasses for Pb(II) and Co(II) at 298 ± 2 K

Biomass	Metal up take capacity (mg/g)		Remarks
	Pb(II)	Co(II)	
Ficus carcia leaves [25]	34.36	N.R.	pH 6.0 at room temperature
Pretreated *Rhizopus oryzae* (Bread Mold) [47]	69.73	13.56	pH 4 for Pb(II) & 7 for Co(II) at $C_o = 200$ mg/L, 298 K
Red rose waste biomass [48]	51.53	68.67	pH 5 for Pb(II) & 7 for Co(II) at $C_o = 100$ mg/L, 298 K
Coconut tree sawdust (CTS) [49]	25.0	N.R.	pH 6.0 at room temperature
Sugarcane bagasse (SB) [49]	21.28	N.R.	pH 6.0 at room temperature
Neochloris pseudoalveolaris [50]	96.2	20.1	N.D.
Hypogymnia physodes (Foliose lichen) [51]	N.R.	9.90	N.D
Ficus religiosa leaf powder [52]	N.R.	5.0	pH 7.0, $C_o = 92$ mg/L, at 303 K
Eriobotrya japonica leaves [53]	34.60	N.R.	pH 6 at room temperature
R. arrhizus (fungi)[54]	56.0	2.9 0	pH 5 for Pb(II) & pH 7 for Co(II) at room temperature
Saccharomyces cerevisiae [54]	N.R.	5.80	pH 6.5 for Co(II) at room temperature
Aspergillus niger [54]	30.0	95.0	pH 4 for Pb(II) & pH 7 for Co(II) at room temperature
Evernia prunastri (fruticose lichen) [55]	N.R.	5.72	N.D.
Present study	19.61	43.41	pH 6.0, $C_o = 20$ mg/L at 298 ± 2 K

Note: N.R. = Not Report; N.D. = No Data.

Based on Eq. (15), linear plots drawn between ΔG° vs. T of both metal ions were shown in Fig. 13. The intercept and slope of the linear plots indicate the ΔH° and ΔS°, respectively, and were summarized in Table 4.

The negative values (Table 4) of ΔG° indicate the spontaneous nature of biosorption of both metal ions onto LJFP. The positive values of ΔH° and ΔS° indicate the randomness of the sorbate–sorbent interaction with the endothermic nature of the sorption mechanism of Pb(II) and Co(II) onto LJFP in the temperature range of 298–323 ± 2 K [56,57]. Endothermicity of the enthalpy of the present sorption mechanism can be explained. It is the well known that metal ions are well solvated in water. So, in order to get sorption of aqueous metal ions on the sorbent, it is required to expend some energy to the ion dehydration from its hydration sheath in aqueous solution. This dehydration energy exceeds the exothermicity of the ion attaching to the surface. The dissociation of water from ions is essentially an endothermic process that exceeds the enthalpy of sorption to a considerable extent [33,58,59].

3.8. Effect of ionic strength on biosorption of Pb(II) and Co(II)

Numerous types of suspended and dissolved compounds, apart from the metal ions, are released from industrial wastewaters. These impurities might be acids, alkalis, other ions, or metal ions. Total ionic

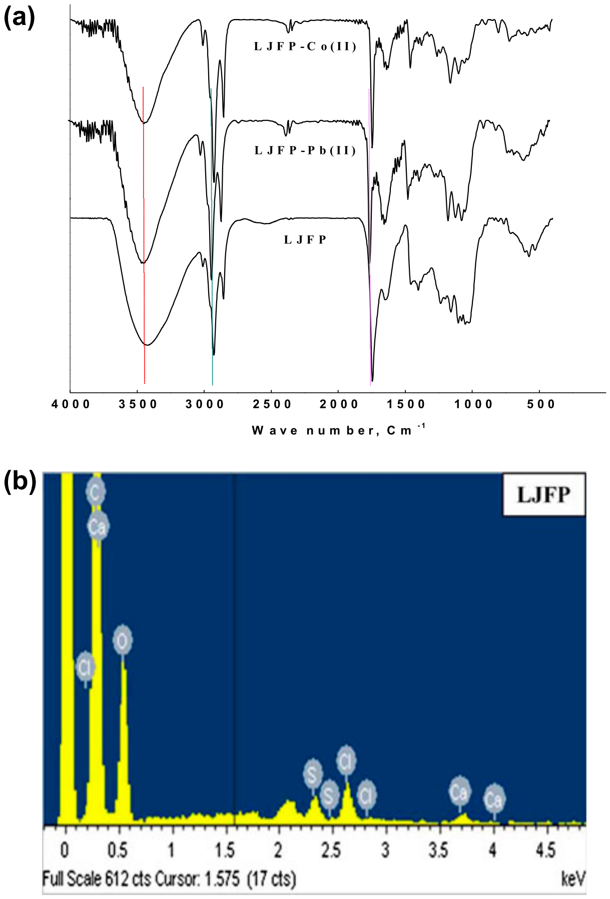

Fig. 11. FT-IR spectrum of bare LJFP and metal ion loaded, LJFP–Pb(II) and LJFP–Co(II) (a) and SEM–EDX of bare LJFP (b).

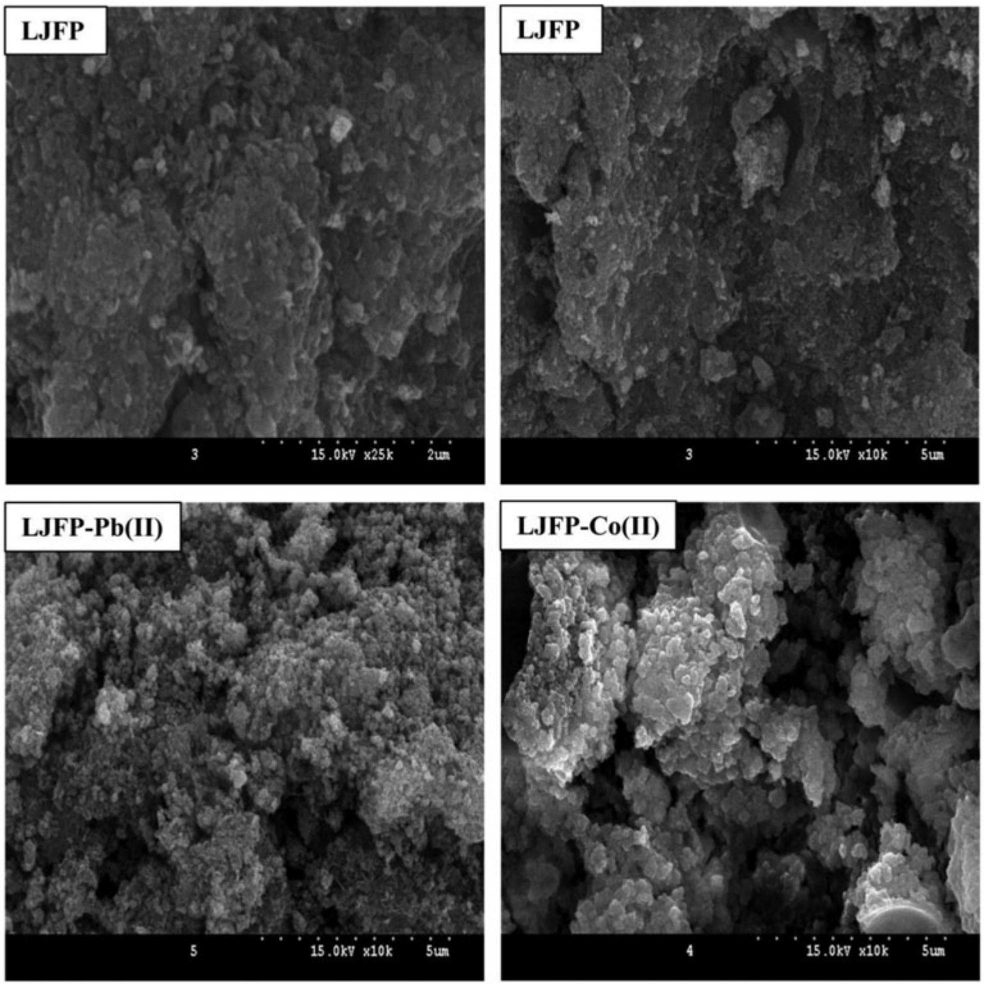

Fig. 12. Scanning electron microscopy (SEM) surface morphology of bare LJFP and metal ions loaded LJFP.

strength is an important factor that is adverse to the biosorption of metal ions. The effect of ionic strength on biosorption of Pb(II) and Co(II) was studied in the 0.005 to 0.045 mol/L NaCl concentration range at room temperature. From the results (Fig. 14) it is observed that increased total ionic strength led to a slight decrease in the amount of biosorbed Pb(II). This is due to the competitive interaction of salt ions and metal ions with the surface active sites of the biosorbent. However, the amount of biosorbed Co(II) was not significantly affected by total ionic strength.

3.9. Desorption studies

The desorption studies of Co(II) and Pb(II) in biomass were carried out with sodium salts of EDTA, HCl, HNO_3, and Na_2CO_3. As the concentration of the

Table 4
Thermodynamic parameters of Pb(II) and Co(II) biosorption onto LJFP

Metal ion	Temperature, ±2 (K)	log K_C	ΔG°, (kJ/mol)	ΔH°, (kJ/mol)	ΔS°, (kJ/mol K)	R^2
Pb(II)	298	1.71 ± 0.012	−4.23 ± 0.008	4.51 ± 0.008	0.029 ± 0.009	0.997
	313	1.80 ± 0.016	−4.69 ± 0.013			
	323	1.85 ± 0.012	−4.96 ± 0.014			
Co(II)	298	2.28 ± 0.007	−5.64 ± 0.006	2.62 ± 0.012	0.027 ± 0.011	0.966
	313	2.29 ± 0.009	−5.95 ± 0.007			
	323	2.36 ± 0.014	−6.35 ± 0.001			

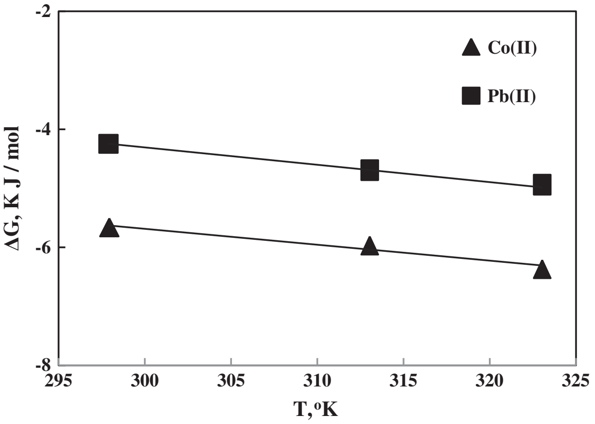

Fig. 13. Temperature effect study on Gibb's free energy of Pb(II)–LJFP or Co(II)–LJFP biosorption system at pH 6.0, and 200 rpm for 120 min equilibrium.

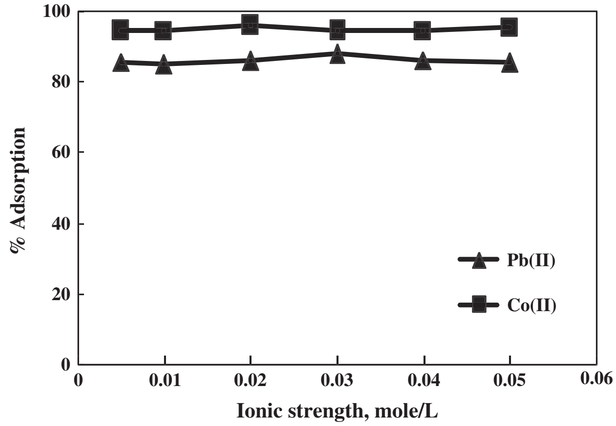

Fig. 14. Effect of ionic strength study on biosorption of Pb(II) and Co(II) (10.0 mg/L) onto LJFP (1.0 g/L) for 120 min equilibration at pH 6.0, and 298 ± 2 K.

Table 5
Desorption studies of Pb(II) and Co(II) from LJFP biomass

Desorbing solution	Concentration of desorbing solution, (mol/L)	Desorption of metal ion (%)	
		Pb(II)	Co(II)
EDTA	0.005	57.85 ± 0.021	64.58 ± 0.031
	0.001	78.75 ± 0.033	84.32 ± 0.051
	0.015	89.54 ± 0.053	94.46 ± 0.028
	0.020	93.26 ± 0.042	94.70 ± 0.033
	0.025	97.06 ± 0.050	98.15 ± 0.047
HCl	0.005	15.76 ± 0.041	20.43 ± 0.045
	0.001	26.57 ± 0.033	33.27 ± 0.037
	0.015	55.48 ± 0.046	67.86 ± 0.027
	0.020	79.96 ± 0.052	89.95 ± 0.044
	0.025	92.15 ± 0.028	93.23 ± 0.036
HNO_3	0.005	23.56 ± 0.058	30.62 ± 0.024
	0.001	39.98 ± 0.062	63.56 ± 0.029
	0.015	68.46 ± 0.038	85.27 ± 0.032
	0.020	80.76 ± 0.052	90.35 ± 0.041
	0.025	95.44 ± 0.040	96.78 ± 0.036
Na_2CO_3	0.005	32.34 ± 0.028	13.18 ± 0.025
	0.001	35.67 ± 0.066	14.25 ± 0.029
	0.015	55.24 ± 0.057	28.92 ± 0.045
	0.020	77.21 ± 0.045	52.31 ± 0.034
	0.025	97.21 ± 0.044	79.65 ± 0.038

desorbing solutions (HCl, HNO_3, EDTA, and Na_2CO_3) increased, both metal ions were desorbed. As showed in Table 5, more than 90% of Pb(II) and Co(II) ions were desorbed from biomass using 0.025 mol/L HCl, HNO_3, and EDTA solutions. Especially, 98% of Co(II) and 97% of Pb(II) recovery was achieved with that concentration of EDTA. This may be due to fact that the stability of the aqueous metal ion-EDTA complex is greater than the metal ion-sorbent complex. Ninety-seven percent Pb(II) was desorbed in Na_2CO_3 solvent.

These results prompted that LJFP could be reused without significant losses in its initial biosorption capacity. It will help to elucidate the biosorption and desorption behavior of Pb(II) and Co(II) in aqueous solutions for recovery and recycling of sorbent in particular treatment of effluents.

4. Conclusions

LJFP is an eco-friendly potential biosorbent for heavy metals removal. This work considered the efficiency of biomass, LJFP in the removal of Pb(II) and Co(II) ions from an aqueous environment. From the obtained results it conclude that:

(1) The biosorption kinetics of both metal ions, Pb (II) and Co(II) was the rate limiting step pseudo-second-order kinetic. However, Pb(II) also followed the Elovich kinetic, indicating the chemisorptions kinetic of Pb(II) onto LJFP.

(2) The isotherm data of the biosorption of Pb(II) were better explained by the Langmuir isotherm model than the Freundlich and Temkin. Co(II) sorption data which better tune to Freundlich model than the other two models. It concluded that the monolayer sorption on a homogeneous surface is favorable for biosorption of Pb(II), whereas multilayer sorption on a heterogeneous surface is favorable for Co(II). It is also observed that the biosorption capacity of LJFP for Co(II) is greater than Pb(II).

(3) The maximum biosorption capacity for Pb(II) and Co(II) was 19.61 and 43.48 mg/g, respectively, at 298 ± 2 K with 1.0 g/L biomass and an optimum pH 6.0, indicating that the present biomass should be considered to be a promising and potential biosorbent for the removal of Pb(II) and Co(II). The biosorption capacity of LJFP for Pb(II) and Co(II) was near or more than the reported results of various other biosorbents.

(4) FT-IR studies were concluded that the sorption mechanism is associated with aromatic and aliphatic –OH, –COOH, –C=O, and –C–X (X= S^{2-}, halides, O^{2-}) groups in the adsorption of both metal ions, Pb(II) or Co(II), on the LJFP surface.

(5) From the thermodynamic results, it is concluded that the metal ion–biomass interaction was spontaneous, although endothermic for the present both metal ions biosorption system at 298–313 ± 2 K.

(6) The effect of ionic (NaCl) strength was no significant affect the biosorption of either metal ion. Moreover, EDTA caused desorption of both metal ions.

(7) The overall results suggest that LJFP can be successfully employed for the regular sorption of metal ions on a large scale from hydrometallurgical industries.

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