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# Detoxification of lead(II) ions in aqueous solutions using chemically modified *Ziziphus jojoba* and *Eriobotrya japonica* leaves: thermodynamic and kinetics considerations

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## ABSTRACT

The current study deals with the Pb(II) ions removal by chemically modified ($HNO_3$ and $CaCl_2$) *Ziziphus jojoba* (CMZJL) and *Eriobotrya Japonica* leaves (CMEJL). Batch experiments were conducted to find out the optimal conditions of pH, temperature, biosorbent dose, initial metal concentration and contact time for maximum metal biosorption. The maximum biosorption capacity onto CMZJL and CMEJL were 80 and 73.10 mg/g respectively at optimal conditions i.e. contact time 120 min, temperature 50°C and pH 6.0. The Tempkin, Langmuir and Freundlich isotherms were applied to find out best fit for the equilibrium data. The Langmuir model best fitted the equilibrium data with regression correlation coefficient ($R^2$) of 0.999. Kinetic studies suggested that the process obeys the pseudo second order kinetic model in a better way than the first order kinetic model with $R^2 = 0.999$ for both the adsorbents. The calculated thermodynamics functions like change in enthalpy ($\Delta H^\circ = -51.366$ and $-42.202$), entropy ($\Delta S^\circ = 21.975$ and $18.149$) and Gibbs free energy ($\Delta G^\circ = -6.598$, $-6.709$, $-6.929$, $-7.149$ and $-5.450$, $-5.541$, $-5.722$, $-5.904$ corresponding to 298, 303, 313 and 323K) revealed the removal of Pb(II) ions onto the CMEJL and CMZJL was feasible, exothermic and spontaneous in nature.

*Keywords:* Biosorption; Pb(II); Kinetics; Equilibrium; Thermodynamics

## 1. Introduction

Pollution of heavy metals in the aquatic system is a serious global issue. The discharge of hazardous heavy metals from different anthropogenic sources into the aqueous system poses a serious threat to the health of organisms [1]. Heavy metals are persistent in nature as they are non-degradable and can reach to human bodies through the food chain [2]. Heavy metals are discharged into water by various industries including mining, lead batteries, smelting, metal electroplating, firearms ammunition, oil refineries, ceramics and glass industries, matches, pigments, and paint industries [3]. Amongst the heavy metals, Pb(II) (the chief pollutant in aqueous systems) pollution is due to its vast use in industries and petroleum. In third world countries, the wastes effluents from industries are put directly into water stream without any prior primary or secondary treatments thus carries a number of pollutants into the water system. Lead is also a component amongst them which is a hazardous substance and is harmful to living organisms [4]. The contamination of aquatic system with Pb(II) ions causes many diseases like nephritic syndrome, anemia, and hepatitis. In humans, it affects the reproductive system, nervous system, brain, and liver [5]. The maximum allowable limit of Pb(II) ions in drinking water, as per the World Health

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Organization (WHO), is 0.010 to 0.005 ppm [6]. Therefore, it is very necessary to eliminate Pb(II) ions from the industrial effluents before they mix with water.

Conventional techniques used for the elimination of Pb(II) ion include membrane filtration, ion exchange, chemical precipitation, reverse osmosis, reduction, chelation, solvent extraction, electroplating, and evaporation [7]. The conventional methods for the removal of lead from water are effective even if the metals are present in the low concentrations (1–100 ppm) [8]. However, from an economical point of view, they are expensive. Furthermore, they produce excessive chemical sludge which is difficult to dispose of, leading to other environmental problems which would further increase the cost of the process, thus hampering their application on a commercial scale [9]. Removal of heavy metals through biosorption, on the other hand, is a preferred alternative approach as they are economic, effective, easy recycling of the biomass, and are environment-friendly and do not produces chemical sludge [10]. Various biosorbents including *Cinnamomum camphora* [11], *Moringa oleifera* [12] , *Hevea brasiliensis* [13], *Ficus religiosa* [14], *Ulmus carpinifolia, Fraxinus excelsior* [15], *Imperata cylindrica* [16], *Atriplex canescens* [17], *Saraca indica* [17], *Azadirachta indica* [18], etc. have been used for the elimination of Pb(II) ions from waste waters.

In present work, the biosorption capability of chemically modified leaves of *Ziziphus jojoba* (CMZJL) and *Eriobotrya japonica* (CMEJL) were evaluated for the removal of Pb(II) ions from industrial waste effluents. The influences of different experimental parameters like biomass dosage, pH, initial concentration of metal ion, contact time, and temperature on biosorption of Pb(II) ions were also evaluated. The adsorption kinetics were studied employing pseudo-first order and second order kinetics models. The experimental data were correlated by isotherm models of Langmuir, Temkin, and Freundlich. To confirm biosorption, various characterization techniques such as FTIR spectroscopy, pore size and area analyses were used. Finally, thermodynamic parameters such as enthalpy change, entropy, and Gibbs free energy were calculated from experimental data.

## 2.Materials and methods

### 2.1. Preparation of biomass

The leaves of *Eriobotrya japonica* and *Ziziphus jojoba* were collected from Peshawar district, Pakistan. The plant's leaves were cleaned with distilled water and dried in shade at room temperature for one-month and then in an electric oven at 40°C for 24 h to ensure the complete removal of moisture. The dried leaves were powdered using an electrical grinder and then sieved onto 45 mesh screens. The powdered biosorbents were stored in an airtight bottle before use. About 100 g leaves powder were soaked into 2 L of 0.1 M nitric acid ($HNO_3$) solution for twenty-four hours, then passed through a filter and frequently washed with distilled water to eliminate the remaining acid. Both the biosorbents were first dried in open container and then in an electric oven at 100°C for 120 min. Subsequently, 50 g of the acid-treated biosorbent was soaked in 1 L of 0.1 M $CaCl_2$ solution for 24 h. The biosorbent was passed through filter and then clean with distilled water to eliminate excess $CaCl_2$. The chemically modified biosorbent was dried in open container and then at 105°C in an electric oven, and stored in a desiccator.

### 2.2. Heavy metal solution preparation

About 1000 ppm, Pb(II) ions stock solution was prepared by dissolving $Pb(NO_3)_2$ in distilled water. Various concentrations of solutions of Pb(II) ions were prepared using double distilled water.

### 2.3. Characterization of biosorbent

Perkin Elmer spectrometer Fourier Transform Infrared (FTIR) was used in the range of 400–4000 $cm^{-1}$ wave number to record the unloaded and Pb(II) ions loaded spectra of CMZJL and CMEJL to recognize the functional groups which were involved in removal process and the effect of loaded lead ion on functional groups.

Barret Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) pore volume, surface area, and pore diameter were determined using surface area analyzer (NOVA 2000e, Quantachrome USA).

### 2.4. Biosorption experiments

Batch biosorption experiments were carried out in order to find out different isothermal, kinetics, and thermodynamic parameters. In batch experiments, 100 mL Pb(II) solutions were contacted with 0.5 g of biosorbent. The pH of the solutions were adjusted with dilute HCl and NaOH solutions. To determine the effect of various physicochemical parameters on biosorption like pH (2–7), biosorbent dosage (0.1–3 g), contact time duration (10–150 min) and temperature (20–50°C) were determined by contacting the specified amount of adsorbent with lead solutions for a specified interval of time. The solution was shaken in a temperature-controlled shaker at an agitation speed of 180 rpm for desired contact time and temperature. After complete shaking, the solution was filtered through Whattman filter paper and the concentration of remaining Pb(II) ions in the filtrate was detected using atomic absorption spectrometer. Following equation was used to calculate biosorption capability of adsorbent.

$$q_e = V\frac{\left(C_o - C_e\right)}{m} \tag{1}$$

where $m$ is the biomass dosage (g), $V$ is the Pb(II) solution volume (L), $q_e$ is biosorption capacity of Pb(II) ions onto biomass (mg/g), $C_o$ is the initial Pb(II) ions concentration and $C_e$ is the equilibrium Pb(II) ion concentration (mg/L). All experiments were carried in triplicate and only mean value are presented.

### 2.5. Statistics

The regression coefficient correlation ($R^2$) values of the various models i.e. Langmuir isotherm, Freundlich isotherm, pseudo-first order and second-order kinetic models were determined using Microsoft Excel, 2016.

## 3. Results and explanation

### 3.1. Pore size, pore diameter and surface area

The CMZJL and CMEJL pore volume, surface area, and pore diameter were determined by Brunauer Emmett Teller (BET) and Barret Joyner Halenda (BJH) techniques. The results are shown in Table 1. The results show that both biosorbents have the comparable surface area and pore volume. However, the surface area of CMZJL was relatively larger than the surface area of CMEJL.

### 3.2. FTIR spectra

The Fourier transformed infrared (FTIR) spectra of CMZJL, CMEJL, Pb(II) ions loaded CMZJL, and CMEJL displays a number of peaks indicating the complex nature of biomass (Figs. 1 a–d). The spectral peak at 2930 cm$^{-1}$ is due to hydroxyl (–OH) functional group. Aliphatic stretching vibration was evident from the peak at 2860 cm$^{-1}$. The peak at 1319 cm$^{-1}$ represents –NH group [19]. The presence of a peak at 1162 cm$^{-1}$ shows stretching of C-N [20]. The peak at 1022 cm$^{-1}$ indicates stretching of C-OH [9]. The spectrum of FT-IR for Pb(II) loaded CMZJL indicates that some peaks were shifted. The spectral peak from 2928 cm$^{-1}$ shifted to 2932 cm$^{-1}$. Peaks at 2861 cm$^{-1}$ and 1318 cm$^{-1}$ shifted to 2868 cm$^{-1}$ and 1325 cm$^{-1}$ respectively. Peak present at 1022 cm$^{-1}$ moved to 1018 cm$^{-1}$.

Table 1
CMZJL and CMEJL pore volume, pore diameter and surface area

| Biomass | CMZJL | CMEJL |
|---|---|---|
| (BET) surface area, m$^2$ g$^{-1}$ | 97. 91 | 63.32 |
| (BJH) surface area, m$^2$ g$^{-1}$ | 366.71 | 148.90 |
| Pore volume, cm$^3$ g$^{-1}$ | 1.20 | 0.49 |
| Pore diameter, Å | 130.45 | 129.14 |

The FT-IR spectrum of CMEJL indicates -OH stretching at 3374 cm$^{-1}$. Absorption peak between 2951 cm$^{-1}$ and 2889 cm$^{-1}$ shows the -OH group due to stretching and methyl substituent (Figs. 1c and d). The absorption peak at 1751 cm$^{-1}$ shows the C=O group from -COOH functional group. Peaks at 1516 cm$^{-1}$ presenting the C-C stretching of aromatic compounds [21]. The peak at 1433 cm$^{-1}$ is due to –C=S functional group. The peak present at 1385 cm$^{-1}$ originates from -OH bending. The peaks at 1357 cm$^{-1}$ and 1324 cm$^{-1}$ indicates –NH functional groups. The -CN peak appeared at 1160 cm$^{-1}$ [22]. The peak at 1029 cm$^{-1}$ is due to C-OH vibration [23]. The FTIR spectrum of Pb(II) deposited CMEJL shows clear variations. The peak present at 2919 cm$^{-1}$shifted to 2925 cm$^{-1}$. The absorption peaks present at 2835 cm$^{-1}$, 1357 cm$^{-1}$, 1162 cm$^{-1}$ and 1029 cm$^{-1}$ were shifted to 2838 cm$^{-1}$, 1361 cm$^{-1}$, 1164 cm$^{-1}$ and 1038 cm$^{-1}$ respectively. The changes in peaks of various functional groups indicate the role of -O, C-OH, -NH, and CO functional groups on CMEJL in the elimination of Pb(II) ions.

### 3.3. Effect of pH on biosorption

The pH influences the biosorption process of heavy metals and other contaminants from the aqueous phase [24]. The effect of pH on the biosorption of Pb(II) was tested

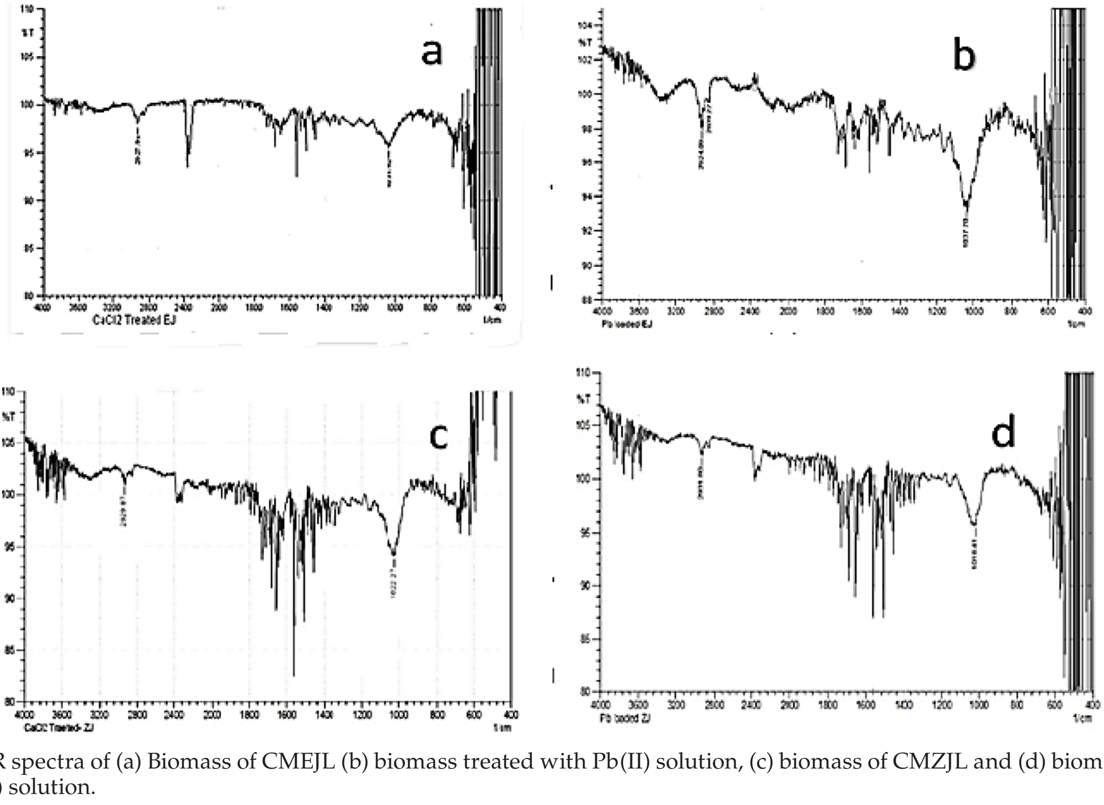

Fig. 1. FTIR spectra of (a) Biomass of CMEJL (b) biomass treated with Pb(II) solution, (c) biomass of CMZJL and (d) biomass treated with Pb(II) solution.

in pH range from 2 to 7. Fig. 2 shows that pH also has an effect on the biosorption capabilities of CMZJL and CMEJL. Highest biosorption was observed at pH 6, i.e. the optimum pH. Operating conditions like initial Pb(II) ions concentration (100 ppm), contact time (2 h), biomass quantity (0.1 g) and shaking speed (180 rpm) were kept constant in all the testing samples. The biosorption capacities of both biosorbents for Pb increased from pH 2–7.

On the surface of biosorbent, functional groups like $-OH^-$, $-COO^-$ are free dominant (FTIR analysis). At low pH, they interact with hydronium ions positively. The removal of Pb(II) at low pH was low as a large number of hydronium ions present at low pH which compete with metal ions (Pb(II) ions) and prevented the metal ions from approaching to the active sites present on the sorbent surface [6]. At high pH, the biomass surface have a negative charge and now the competing hydronium ions are few in number, therefore increases the elimination of Pb(II) ions through electrostatic interactions [25]. Thus, the increase in lead ion removal with an increase in pH can be explained on the basis of a decrease in competition between hydronium and metal ions for the surface active sites. Above pH 7, biosorption of Pb(II) ions decreases due to the low polarity of Pb(II) ions at high pH [26]. Therefore, pH 6 was taken as optimum pH and was used in the subsequent experiments.

### 3.4. Biomass dosage

The effect of biosorbent dosage on the Pb(II) removal was investigated in a range of 0.1 to 3 g for both the adsorbents. The results are graphically shown in Fig. 3. The other parameters such as initial Pb(II) ions concentration (100 ppm), contact time (2 h), pH (6) and shaking speed (180 rpm) were kept constant. It was observed that the percent biosorption increases with an increase in biosorbent dosage from 0.1 to 0.5 g. However, above 0.5 g, a further increase in the biomass dosage did not cause any significant increase in the biosorption. This is due to the fact that equilibrium establishes between biomass and metal ions at the existing operating parameters rendering biosorbent incapable of further biosorption [27].

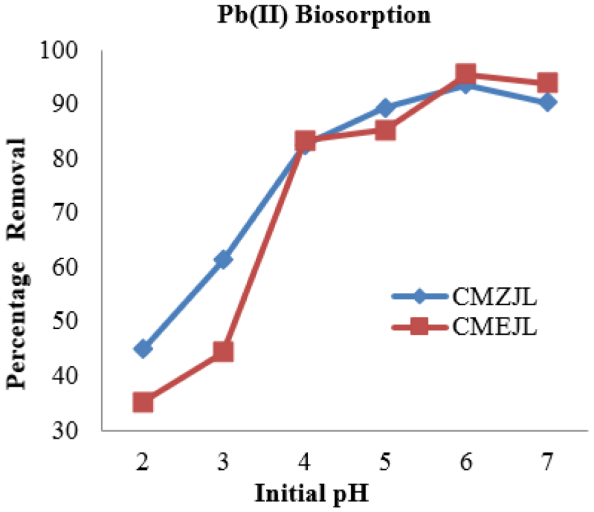

Fig. 2. The effect of pH on the biosorption of Pb(II) ions onto CMZJL and CMEJL (concentration = 100 mg/L, volume = 100 ml, time = 120 min, Shaking speed = 180 rpm, temperature = 25°C and biosorbent dosage = 0.5 g).

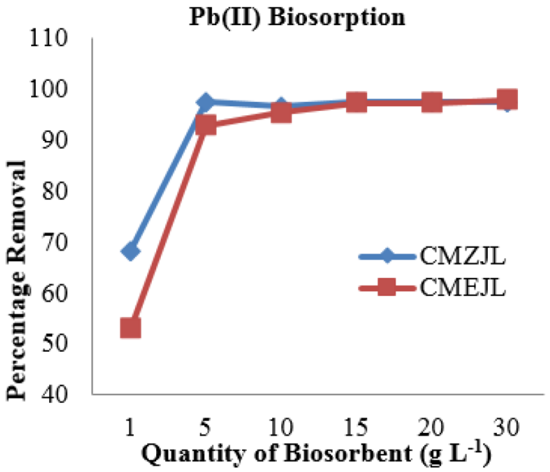

Fig. 3. The effect biosorbent dosage on Pb(II) ions adsorption onto CMZJL and CMEJL (pH = 6, concentration = 100 mg/L, volume = 100 ml, time = 120 min, shaking speed = 180 rpm, temperature = 25°C).

### 3.5. Effect of initial metal concentration

The effect of initial lead concentration on the adsorption of lead onto CMZJL and CMEJL was studied in the range of 20–700 mg/L and the obtained results are shown in Fig. 4. The other operating conditions such as biosorbent dosage (0.5 g), contact time (2 h), pH (6.0) and shaking speed (180 rpm) were kept constant. At lower metal concentrations all Pb(II) ions present in the aqueous solution were readily biosorbed as more active binding sites were available on the adsorbent surface [28]. However, when the Pb(II) ions concentration was increased, the available bind-

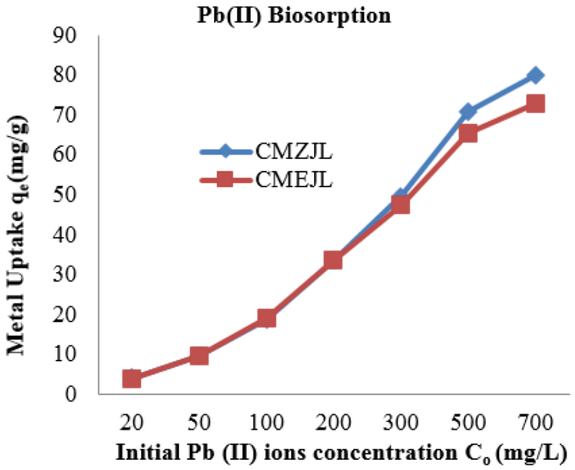

Fig. 4. The effect of initial Pb(II) ions concentration on biosorption over the surface of CMZJL & CMEJL (pH = 6, biomass dosage = 0.5 g, volume = 100 ml, time = 120 min, Shaking speed = 180 rpm, temperature = 25°C).

ing sites decreased as most of the pores were occupied by metal ions. Thus competition for active sites on the biosorbent surface were encountered [29].

### *3.6. Effect of contact time*

The effect of contact time on the Pb(II) ions biosorption onto CMZJL and CMEJL was studied over an interval of 10–150 min (Fig. 5). A gradual increase in Pb(II) ions elimination was observed for 10–120 min. The optimum biosorption level was attained within 120 min and afterwards, no significant increase in percent biosorption with time was observed as equilibrium was already established [27].

### *3.7. Effect temperature*

The effect of temperature on the adsorption of Pb(II) onto CMZJL and CMEJL was studied in the temperature range of 20–50°C (Fig. 6). The higher temperature usually increases biosorption as with an increase in temperature kinetic energy of molecules increases. However, physical damage to the biomass can be expected at high temperatures. It is usually useful to carry biosorption at room temperature as these experimental conditions can easily be replicated [30].

### *3.8. Kinetics models*

Biosorption kinetics models are mainly dependent on the physical and chemical characteristics of the biosorbent [31]. Pseudo first-order and pseudo second-order kinetic models were applied to explain the experimentally observed adsorption kinetics [32]. Linear equation of the pseudo-first order kinetics is given below:

$$ln\left(q_e - q_t\right) = ln\, q_e - k_1 t \tag{2}$$

where $q_t$ and $q_e$ (mg g$^{-1}$) are the quantity of Pb(II) ions biosorbed per unit weight of biomass at time *t* and equilibrium. $k_1$ (min$^{-1}$) is the biosorption equilibrium constant, derived from the graph of $ln\,(q_e - q_t)$ vs. *t*.

The linear equation of pseudo second order model is given as [33]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where $q_t$ and $q_e$ (mg g$^{-1}$) are the biosorbed amounts of Pb(II) ions per unit weight of biosorbent at time t and equilibrium respectively. $k_2$ is the rate constant (g/mg min). $k_2$ and $q_e$ are derived from the intercept ($1/k$) and slope ($1/q_e$) determined from the plots of *t* vs. $t/q_t$ (Fig. 7).

The regression correlation coefficients of the pseudo second order model were very high as compared to the pseudo first order model. Thus it was concluded that better fit of the kinetics data can be obtained with pseudo second order model rather than the pseudo first order kinetic model which is also evident from the theoretical value of $q_e$ obtained from the pseudo second order equation (Table 2). Similar observations for various biosorbent have been reported in the literature as well [34].

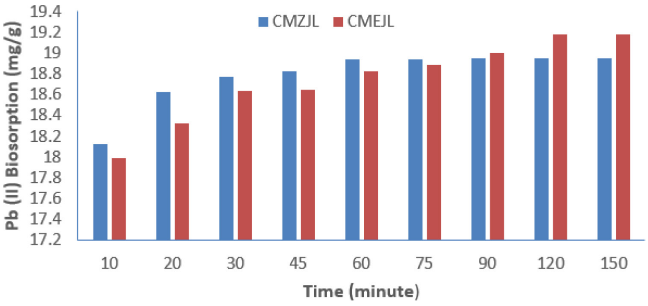

Fig. 5. Effect of contact time on the removal of Pb(II) ions by CMZJL and CMEJL (concentration = 00 mg/L), volume = 100 mL, shaking speed = 180 rpm, temperature = 25°C and biosorbent dosage = 0.5 g).

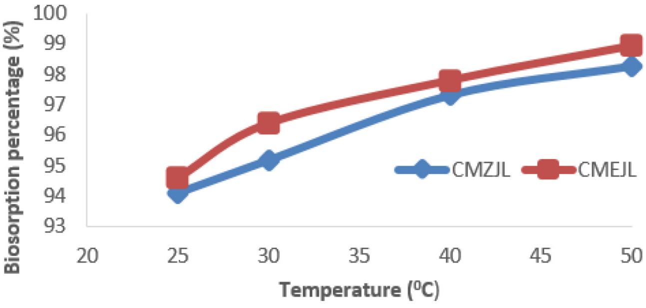

Fig. 6. The effect of temperature on the biosorption of Pb(II) onto CMZJL and CMEJL.

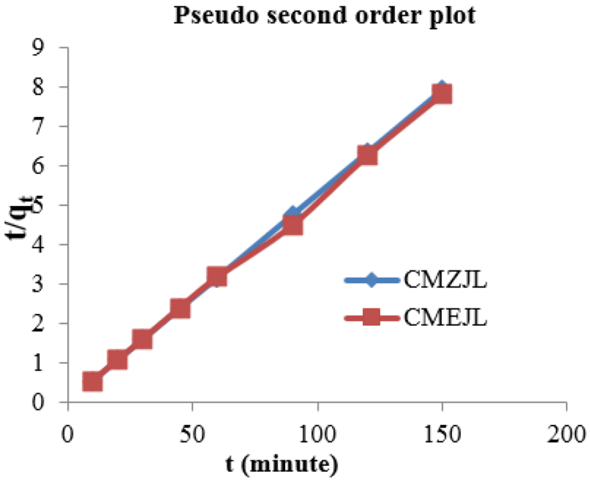

Fig. 7. Pseudo second order kinetics of the biosorption of Pb(II) ions onto CMZJL and CMEJL.

Table 2
Pseudo second order rate constants and regression correlation coefficient of Pb(II) ions adsorption onto CMZJL and CMEJL

| Biosorbent | $C_0$ (mg L$^{-1}$) | Pseudo second order | | |
|---|---|---|---|---|
| | | $K_2$ (g mg$^{-1}$ min$^{-1}$) | $q_e$ (cal) mg g$^{-1}$ | R$^2$ |
| CMZJL | 100 | 0.01901 | 14.72 | 0.999 |
| CMEJL | 100 | 0.01937 | 15.52 | 0.999 |

### 3.9. Equilibrium adsorption isotherms

Temkin, Langmuir and Freundlich isotherm models were applied to explain the adsorption equilibrium data. The Langmuir model is usually applied to mono layer adsorption on the surface of an adsorbent and according to this model a mono layer surface phase is formed on an energetically homogenous surface of an adsorbent. Further this assume that, the adsorption energy is constant and no transmigration of adsorbates occurs on the adsorbent surface [35]. The mathematical form of Langmuir model is given as follows [36]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{4}$$

where $C_e$ is the equilibrium concentration (mg L$^{-1}$), $q_e$ is the quantity biosorbed at equilibrium in mg/g, $q_m$ is the maximum theoretical mono layer biosorption capacity in mg g$^{-1}$ and where $K_L$ is equilibrium Langmuir constant (L mg$^{-1}$) related to the affinity of biosorption on active sites.

The Freundlich model is applied to explain biosorption on both homogenous and heterogenous surfaces. It considers the interactions between the biosorbed molecules as well. The linear form of Freundlich isotherm is given as follow [37]:

$$\ln q_e = \ln K_F + \frac{1}{n} + \ln C_e \tag{5}$$

where $q_e$ is Pb(II) ions biosorbed per gram of the biomass (mg g$^{-1}$), $C_e$ is equilibrium concentration of Pb(II) ions (mg L$^{-1}$), $n$ is adsorption intensity (g L$^{-1}$) and $K_F$ is isotherm Freundlich constant (L g$^{-1}$).

The Temkin isotherm explains the relation between Pb(II) ions and biosorbent. It assumes that the biosorption energy in a layer linearly decreases with the surface coverage due to the interactions and can be presented as [38]:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \tag{6}$$

where $q_e$ is Pb(II) ions adsorbed per gram of the biomass (mg/g), $C_e$ is equilibrium concentration of Pb(II) ions (mg/L), $T$ is temperature in (K), $R$ is universal gas constant (8.314 × 10$^{-3}$ kJ/mol·K), $K_T$ is Temkin isotherm equilibrium constant in L/g, $b_T$ is Temkin isotherm constant in J/mol.

The results obtained are shown in Fig. 8. The values of maximum biosorption capacity and isotherm constants for both biosorbents were calculated from the slope and intercept of the graphs and are given in Table 3. The regression correlation coefficient (R$^2$) for Langmuir model is high when compared to other two isotherms and thus this isotherm best explains the equilibrium biosorption data lead onto prepared adsorbents. Among the adsorbent used the regression correlation coefficient (R$^2$) value for the CMEJL was higher than CMZJL. Although the values of $K_F$ and $n$ were high but lower value of R$^2$ indicated that Freundlich isotherm is not suitable to the explain experimental data [39].

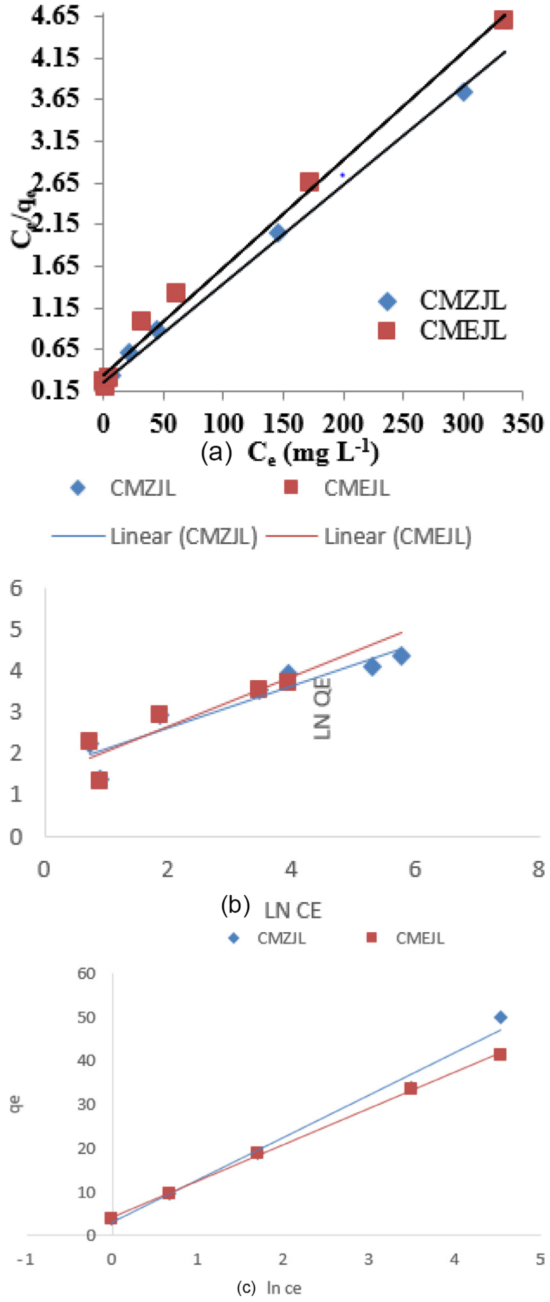

Fig. 8. Isotherm plots for the biosorption of Pb(II) on to CMEJL and CMZJL a. Langmuir b. Freundlich c. Temkin.

### 3.10. Biosorption thermodynamics

Thermodynamic parameters; enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG), were calculated to explain the effect of temperature on Pb(II) biosorption onto CMZJL and CMEJL. The ΔG was calculated from the equation given as follow:

$$\Delta G = -RT \ln K_d \tag{7}$$

where $R$ (8.314 J mol$^{-1}$ K$^{-1}$) is the universal gas constant, $T$ (K) is the absolute temperature and $K_D$ ($K_D = q_e/C_e$) is the distribution coefficient which is temperature dependent

Table 3
Isotherm parameters of the biosorption of Pb(II) ion onto CMEJL and CMZJL

| Model | Langmuir model | | | | Freundlich model | | | Temkin model | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Biosorbent | $C_0$ (mg L$^{-1}$) | $q_{max}$ (mg g$^{-1}$) | $b$ (L mg$^{-1}$) | R$^2$ | $n$ (g L$^{-1}$) | $K_F$ (L g$^{-1}$) | R$^2$ | $K_T$ (L g$^{-1}$) | $b_T$ (J mol$^{-1}$) | R$^2$ |
| CMZJL | 100 | 58.47 | 0.0939 | 0.9930 | 2.269 | 86.99 | 0.9762 | 1.573 | 227.48 | 0.9351 |
| CMEJL | 100 | 45.24 | 0.1116 | 0.9977 | 2.060 | 56.16 | 0.8963 | 1.660 | 297.50 | 0.9992 |

[40]. The entropy ΔS and ΔH were obtained from the given equation.

$$\ln K_D = \frac{-\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (8)$$

The entropy (ΔS) and enthalpy changes (ΔH) of biosorption were estimated from the intercept and slope of the graph of $\ln K_D$ verses $1/T$ respectively (Fig. 9). The values of the Gibbs free energy change are given in Table 4. The negative values of ΔG indicates the spontaneous nature and thermodynamic feasibility of the biosorption of Pb(II) onto prepared adsorbent. An increase in Gibbs free energy values with an increase temperature pointed confirmed that high temperature would play a key role in the biosorption of lead onto prepared adsorbent. The negative values of the ΔH suggests that the adsorption process of the Pb(II) ions onto the CMZJL and CMEJL is exothermic. The process was a chemisorption as the ΔH higher than 20.9 kJ/mol and thus followed second order kinetics [41]. The ΔS > 0.0 for Pb(II) ions shows increase in randomness at the solid and solution interface resulting in stronger favorable interaction for Pb(II) adsorption onto CMZJL and CMEJL. The increase adsorption capacities of the adsorbents with an increase in the temperature might be due to the chemical interaction between lead ion and active sites of adsorbents or the increased intra particle diffusion rate of Pb$^{2+}$ molecules into the pores of the prepared adsorbents as a result of decreasing solution viscosity at elevated temperatures and the number of active sites generated on adsorbent surface [42–46].

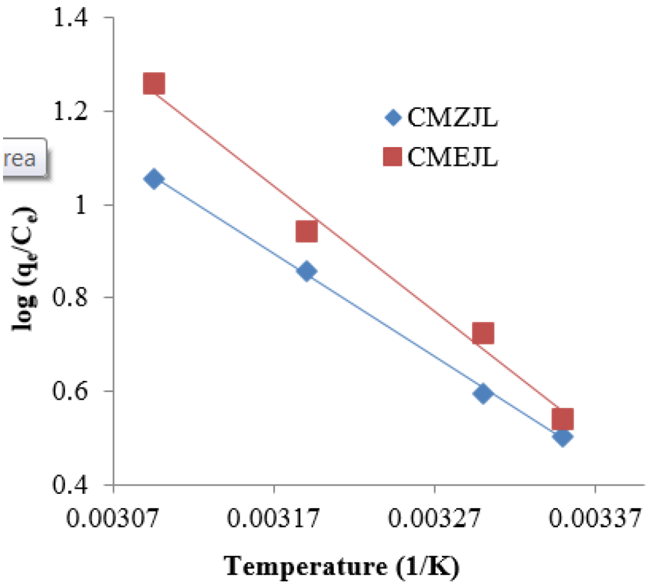

Fig. 9. The Van't Hoff's graph for the adsorption of Pb(II) onto CMEJL and CMZJL (concentration = 100 mg/L, volume = 100 mL, biosorbent = 0.5 g, shaking speed = 180 rpm, pH = 6).

Table 4
Thermodynamics parameters of the biosorption of Pb(II) onto CMZJL and CMEJL

| Biomass | ΔH (kJ mol$^{-1}$) | ΔS (J mol$^{-1}$ K$^{-1}$) | ΔG (kJ mol$^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | 298K | 303K | 313K | 323K |
| CMZJL | −42.202 | 18.149 | −5.450 | −5.541 | −5.722 | −5.904 |
| CMEJL | −51.366 | 21.975 | −6.598 | −6.709 | −6.929 | −7.149 |

### 3.11. Comparative biosorption capacity of CMZJL and CMEJL with other biosorbents

A comparison of maximum biosorption capacities of CMZJL and CMEJL with other biosorbents has given in Table 5. It was concluded from table that the biosorption capacities of the prepared adsorbents were high as com-

Table 5
Comparison of CMZJL and CMEJL for Pb(II) removal with other low-cost biomasses

| Biosorbents | $q_{max}$ (mg g$^{-1}$) for Pb(II) | Reference |
|---|---|---|
| *Moringa oleifera* tree leaves | 210 | [12] |
| Xanthated rubber leaf powder | 202 | [13] |
| *Fraxinus excelsior* leaves | 172. | [15] |
| *Ulmus carpinifolia* leaves | 167 | [15] |
| Sludge of rose petals | 88 | [25] |
| Sago waste | 65 | [47] |
| Rubber leaf powder | 47 | [22] |
| Tree fern | 40 | [45] |
| *Ficus religiosa* leaves | 38 | [9] |
| Groundnut hull | 31 | [14] |
| Rice husk ash | 12 | [46] |
| Lalang leaf powder | 05 | [16] |
| Tobacco stem | 05 | [23] |
| CMZJL | 80 | This study |
| CMEJL | 73 | This study |

pared to the reported biosorbents capacities, CMZJL was relatively more potent than CMEJL.

## 4. Conclusion

In this research, chemically modified leaves of *Ziziphus jojoba* and *Eriobotrya japonica* were used as readily available and inexpensive biomass for the elimination of Pb(II) ions from aqueous medium. The CMZJL and CMEJL exhibited maximum biosorption capabilities of 80 and 73.10 mg $g^{-1}$ respectively at temperature 323 K, initial pH 6.0, initial concentration of 100 mg/L, biomass quantity of 5 g $L^{-1}$ and contact time of 120 min. Kinetic data of the biosorption of Pb(II) onto CMZJL and CMEJL followed pseudo second order kinetics. Equilibrium biosorption was explained well by the Langmuir model rather than the Freundlich and Temkin models. The thermodynamic calculations indicated exothermic ($\Delta H^o = -51.366$ and $-42.202$), chemisorption, favourable and spontaneous ($\Delta S^o = 21.975$ and 18.149, and ($\Delta G^o = -6.598$, –6.709, –6.929, –7.149 and –5.450, –5.541, –5.722, –5.904 corresponding to 298, 303, 313 and 323K) nature of the process. The CMZJL was more efficient than CMEJL. It was concluded that CMZJL and CMEJL are effective, inexpensive, easily available and natural low-cost biomass that can be used as biosorbent for the removal of Pb(II) ions from contaminated waste water. Further research is required to evaluate efficacy of these biosorbents for removal of other metal pollutants as well.

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