Removal of Toxic Pb(II) Ions from Aqueous Solution by Nano Sized Flamboyant Pod (Delonix regia)

Abstract
The removing of toxic heavy metals from aqueous solution by agricultural biosorbents was investigated by studying the effect of nano sized (Delonix regia) and chemically modified biosorbent citric acid Delonix regia (CADR) for removing of Pb²⁺ ions. TEM, XRD and EDS, FT-IR, SEM methods were used for characterizing the biosorbent (Delonix regia). The effect of contact time, pH, temperature, dosage of biosorbent, and Pb²⁺ ion concentration on adsorption process were studied. The maximum biosorption capacities (qₑ) of Pb²⁺ by Delonix regia biosorbent was 43.62 mg/g. The highest R. E was (93.5%) at pH 5. FT-IR method showed that the adsorption of metal ions occurs by functional groups on the surface of Delonix regia powder. The biosorption process was endothermic from thermodynamic parameters. The pseudo second-order model more fit (R²=0.999) than the pseudo first-order model (R²=0.985) from studying the kinetic parameters. The experimental data fit with Freundlich isotherm (R² close to 1). This results indicated that Delonix regia is available agricultural, low cost and environment friendly biosorbent for removing the Pb²⁺ ions.

Keywords: Lead; Biosorbent; Kinetic parameters; Biosorption capacities; Delonix regia pod

Introduction
Toxic Heavy metals can be released into water through metal smelters, effluents from plastics, textiles, There is evidence that present in the environment, even in low concentration of heavy metals cause dermal damage and cancer [1,2]. Lead is considered as the most toxic metal exists in several industrial wastes, such as chemicals, lead acid storage batteries. Lead poisoning in human causes damaging to the kidneys, liver, and brain [2,3]. The removal of heavy metal from contaminated sites is very important to restore ecosystem functions and stability [4]. The search for low-cost techniques to remove heavy metals from wastewater using agricultural materials such as Maize leaves, loquat leaves (Eriobotrya japonica), Psidium guajava leaves, Scolymus hispanicus, Azadirachta indica (Neem leaves), Ulmus leaves, Oleaeuropaea (Olive leaves), and Prunusvium leaves [5], rice straw, rice bran, rice husk, hyacinthroots, neem leaves [6]. Delonix regia is a species of flowering plant in the family Fabaceae, subfamily Caesalpinioideae [7]. Delonix regia possesses several medicinal characters [8]. The effect Delonix regia biomass for the removing of Methylene Blue dye [9], Hg (II) ion from water [10] and Pb, Cu and Co ions [11]. Chemical treatment of biomass with NaOH and citric acid increases its cation uptake ability as the carboxyl groups of the biomass increases [12] Ion-exchange has been suggested as one the mechanisms for heavy metal...
removal from aqueous solution [2,13]. This study can introduce an economic value biosorbent for removing of toxic heavy metal by using nanosized Delonix regia pod.

Experimental
From Sigma-Aldrich, Pb(NO$_3$)$_2$, HCl, citric acid and NaOH were purchased.

Sample collection
The pods of Delonix regia were obtained from Shandawil Research Station, Agriculture Research Center, Sohag, Egypt.

Instruments
Nano size of the investigated biosorbent was obtained by using Retsch Muhle Brinkann Spectro Mill MS Micro-Grinding Mixing. Biosorbent was characterized by X-ray powder diffraction using a Philips X’Pert PRO MPD. (EDAX) unit was used to analyse the chemical composition of the synthesized nanostructures. Field-emission scanning electron microscopy was used for studying the morphology of sample. Functional groups on the biosorbent surface were detected by using (FT-IR, 2000, PerkinElmer). mV-ISE-pH-temperature bench Meters was used to adjust pH of the solutions. Transmission electron microscopy images were obtained with a 2000 EX (II0 microscope (J E O L-Japan). A shaker bath (Heidolph M R-3001) was used for shaking. E-B-A, 20 zentrifugen D78532 tuttinglen was used to centrifuge the sample after the adsorption process. The concentration of Pb$^{2+}$ ions was determined using (AAS) (model PerkinElmer-Analyst, 200).

Sample pretreatment
Delonix regia pods were cleaned with water, and then dried. Delonix regia pods were grinded to obtain a fine powder. The fine powder was used as biosorbent in the experiments.

Treatment of Delonix regia (DR) by Citric Acid
Chemical modification of nano sized powder Delonix regia (DR) using NaOH followed by citric acid treatment. The synthesis of CADR was carried out as followed, 200 grams of the powder was placed in 4 L of 0.1 N NaOH,
then was stirred at 300 rpm for 1 h at 23°C to remove base. The powder was rinsed with water and added to 4 L of distilled water. This biomass was mixed with citric acid (CA) in a ratio of 1.0 g powder to 7.0 mL of CA (0.6 M). The acid/powder Slurry was dried overnight at 50°C and then heated to 120°C for 1.5 h. Citric acid (CA) treated DR powder (CADR) was filtered and washed in a Buchner funnel under vacuum with 150–200 mL of distilled water per gram of the product to remove excess CA. This volume of water was sufficient to remove un reacted CA since no turbidity from lead citrate was observed when the washed powder was suspended in 10 mL of water to which 10 mL of 0.1 M lead nitrate was added. The modified powder was dried at 50°C overnight [2,14,15].

Preparation of Solution
Aqueous solution of Pb$^{2+}$ ions was prepared by weighing out 1.60 g of Pb(NO$_3$)$_2$ and dissolved in a 1000 ml volumetric flask with de-ionized water to obtain a 1000 mg/L concentration. Different initial concentrations of Pb$^{2+}$ ions were prepared by Dilution.

Batch Biosorption Experiments
Effect of concentration of metal ion
A total of 50 ml of Pb$^{2+}$ ions solution of different concentrations was added to 0.3 g of the Adsorbent in a flat bottle and then the mixture was stirred for 1 hr on a shaker at 300 rpm.

Effect of pH
Experiments were carried out at different pH (2:10) and pH was adjusted by using 0.1 M (NaOH) or 0.1 M (HCl). A total of 50 ml of Pb$^{2+}$ ions solution of concentration (20 mg/L) was added to 0.3 g of the Adsorbent in a flat bottle, then the mixture was stirred for 1 hr on a shaker at 300 rpm.

Effect of dosage
In each biosorption experiment, 50 ml of Pb$^{2+}$ ions solution of concentration (20 mg/L) was added to different dosage of the adsorbent in bottle and then the mixture was stirred for 1 hr on a shaker at 300 rpm.

Effect of contact time
In the biosorption kinetics experiment, 0.2 L of Pb$^{2+}$ ions solution of different concentrations was added to 1.2 g of the adsorbent in flat bottle and then the mixture was stirred for 1 hr on a shaker at 300 rpm and a contact time (20: 120) minutes with time interval 20 minutes.

Effect of temperature and determination of thermodynamic parameters
A total of 50 ml of different concentrations of Pb$^{2+}$ ions solution was added to 0.3 g of the adsorbent in bottle at different temperature and then the mixture was stirred for 1 hr on a shaker at 300 rpm. Then the mixture was centrifuged and the concentration of Pb$^{2+}$ ions was determined. Were calculated using the relationships (1) and (2) [2,16,17] can be used to calculate ΔH, ΔS, and ΔG (the thermodynamic parameters for the adsorption process.

\[ \ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \]  
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

Calculation of metal uptake
The Pb$^{2+}$ions uptake at equilibrium was calculated by:
\[ q_e = \frac{v(C_e - C_i)}{w} \]  
where $q_e$ is Pb$^{2+}$ ions absorption capacity, $v$ is the volume of the Pb$^{2+}$ ions solution and $w$ is the amount of the adsorbent, $C_i$ and $C_e$ are initial Pb$^{2+}$ ion concentrations and $C_e$ are final (equilibrium) Pb$^{2+}$ ion concentrations. The efficiency of the Pb$^{2+}$ ions removal was also determined using:
\[ RE\% = \left(1 - \frac{C_e}{C_i}\right) \times 100 \]
Where, RE% is the percentage of the removed Pb$^{2+}$ions.
Kinetics study

The mechanism of the adsorption of Pb\textsuperscript{2+} ions was studied using pseudo first order kinetic models, the intraparticle diffusion and pseudo second order kinetic models [2,18-20] and they are giving in a linear form by Equations 5, 6 and 7, respectively.

\[
\ln(q_e - q_t) = -k_1 t
\]

(5)

\[
\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e}
\]

(6)

\[
q_t = k_{3t} t^{0.5}
\]

(7)

kinetic models are tested for suitability using correlation coefficient \(R^2\) [2,20,21].

Effect of chemical treatment

A total of 50 ml of Pb\textsuperscript{2+} ions solution of (20 mg/L) concentration was added to 0.3 g of the chemically treatment adsorbent (CADR) in bottle, then the mixture was stirred on a shaker for 1 hr at 300 rpm and the concentration of Pb\textsuperscript{2+} ions was determined.

Results and Discussion

Characteristics of the biosorbent

FTIR spectral analysis: FTIR spectral analysis of Delonix regia pod (DR) and Pb\textsuperscript{2+} ions loaded Delonix regia pod (Pb-DR) (Figure 1a) were carried out. FTIR data of Delonix regia (DR) indicates the functional groups. The main characteristic cellulose peak appears in the region of 1000-1200 cm\textsuperscript{-1} [22]. The strong and broad peak at 3298 cm\textsuperscript{-1}, indicated the N-H bond of amino groups and broad peak at 3298 cm\textsuperscript{-1}, indicated the N-H bond of amino groups and hydroxyl group. The shift in the peak to 3330 cm\textsuperscript{-1} in the spectra of the metal loaded Delonix regia pod powder shows the binding of Lead ions with hydroxyl and amino groups [23-25] peak at 2916 cm\textsuperscript{-1} in the spectra of the Delonix regia pod powder indicates CH\textsubscript{3} and CH\textsubscript{2} groups. The peak at 1594 cm\textsuperscript{-1} indicates CO, OH and C-O groups, the Shift to 1612 cm\textsuperscript{-1} indicated the metal binding. Band at 1036 cm\textsuperscript{-1} indicated the C-O of alcohols, the shift to 1028 cm\textsuperscript{-1} indicated binding of Pb\textsuperscript{2+} ions with C-O group [2,24-26]. Peak at 1738 cm\textsuperscript{-1}, which is indicative of carbonyl group, shifted to wave number of 1732 cm\textsuperscript{-1} after Pb\textsuperscript{2+} adsorption [2,27,28]. Band at 1243 cm\textsuperscript{-1} indicates carboxylic acids which shifted to 1233 cm\textsuperscript{-1} after adsorption of Pb\textsuperscript{2+} [29]. The shifts in the absorption peaks indicate the binding of metal ions on the surface of the Delonix regia powder.

Also FT-IR for detection the groups on the modified biosorbents [Citric Acid (CA) treated DR powder (CADR) before and after the biosorption of Pb\textsuperscript{2+} ions (Pb-CADR) was shown in Figure 1b.

Comparison of the IR spectra of samples of DR and CA modified DR (CADR) revealed that a characteristic stretching vibration absorption band of carboxyl group at 1733 cm\textsuperscript{-1} is present in the IR spectrum of CADR samples. This indicates the esterification between alcohol groups of cellulose in DR and citric acid.

The broad absorptions around 2500-3500 cm\textsuperscript{-1} centered at 3343 confirm the existence of carboxylic OH groups and free COOH groups after CA modification. It appears from Figure 1b that the different functional groups on CADR are responsible for biosorption of Pb\textsuperscript{2+}. A change in peaks position at 3328 cm\textsuperscript{-1} in the spectrum of Pb\textsuperscript{2+} loaded CADR indicates the binding with hydroxyl groups. The peak at 1733 cm\textsuperscript{-1} shifted to 1728 cm\textsuperscript{-1} in the spectrum of Pb\textsuperscript{2+} loaded CAMO indicating the binding of metal ions to carboxylic groups also [2,30,31].

Elemental analysis: To determine the chemical composition of the biosorbent. Elemental analysis of Delonix regia (pod) is shown in Figure 2.

Scanning electron micrograph (SEM): SEM of biosorbent Delonix regia pod (D-R) (Figure 3) are used to show the morphology of Delonix regia pod, which exhibits the structure porosity of biomass. The surface morphology of Delonix regia pod powder showed that the powder was a fine particle. The particles have a large number of steps and edges.

XRD analysis: XRD of the Delonix regia pod powder is shown in Figure 4 indicates the amount of amorphous material in the sample. XRD of the adsorbent Delonix regia indicate that the structure of Delonix regia pod powder has a small different
change due to the appearance of amorphous peak at 2θ=44.7 after adsorption process confirming adsorption of Pb²⁺ ions.

Transmission electron microscopy (TEM): The sample was subjected to TEM analysis (Figure 5a) to indicate the particle size and the major size of the particles was found to be 18 nm (Figure 5b).

Effect of initial concentration: Figure 6 and Table 1 illustrated the effect of metal ions concentration on Pb²⁺ ions biosorption is in (qₑ) increases as the concentration rises, as Pb²⁺ ions are more available for interaction with the biosorbent. The Pb²⁺ ions R. E for initial concentration 10 and 20 mg/L are 94.3% and 93.5%, respectively and decreases as the concentration increases. A greater chance was available for metal removal at low concentrations, biosorption sites took up the available Pb²⁺ ions when increasing concentrations. So, initial concentration of Pb²⁺ ions solutions increases the biosorption [2,32-34].

Effect of pH: Figure 7 and Table 2 illustrated the effect of pH of a solution in the adsorption process. R.E. and qₑ increase as the pH increase. The amount of Pb²⁺ ions removed by the Delonix regia at low pH 2 was low (1.91 mg/g) and R.E. 57.3% compared to the amounts removed at pH 4 to 10 were ranged from (2.7 mg/g and R.E. 81% at pH 4) to 3.12 mg/g and R.E. 93.5% at pH 5. Because at low pH the concentration of H⁺ is high [19], as H⁺ ions were being removed by the biosorbent, instead of the Pb²⁺ ions, [21,35] at higher concentration of H⁺ ions, the biosorbent becomes more positive charge on the surface and the attraction between biosorbent and Pb²⁺ ions is reduced [36]. At higher pH the capacity of the adsorbent reduced, the reduction in adsorption may be due to the increasing of OH⁻ ions, or Pb²⁺ ions were precipitated as lead hydroxide [2,37].

Effect of biosorbent dosage: It is an effective factor to study the capacity of a biosorbent. R.E. increases with least value of 64.65% obtained with 25 mg and highest value of 95.04% with 500 mg of the biosorbent, this because at high dosage, there is an increase in surface area and availability of biosorption sites, but qₑ decreases as a decrease in the amount of Pb²⁺ ions adsorbed per unit weight of biosorbent [2,38-40]. These results are illustrated in Figure 8 and Table 3.

Effect of contact time: Table 4 and Figure 9 illustrated the effect of contact time for the adsorption of Pb²⁺ ions by Delonix regia. The amount of Pb²⁺ ions absorbed increased with an increase in the contact time and reach equilibrium in 60 minutes. This because long contact time and availability of active sites, it was followed by a reduction in the metal uptake. There was a slightly increasing or remain constant in the Pb²⁺ ions removal, as the sites are less available [2,41,42].

Effect of temperature: Table 5 and Figure 10 illustrated the effect of the temperature on adsorption, the Pb²⁺ R.E. and qₑ by Delonix regia increases while the temperature is increasing, as the active sites have increased and encourages the process of biosorption, due to increase in the movement of the Pb²⁺ ions and pore size indicating an endothermic process [2,43-45].

Adsorption isotherm: Pb²⁺ ions distribution between the solid and liquid phases can be described by the Freundlich and Langmuir
Table 1 Pb$^{2+}$ ions Removal Efficiency and $q_e$ at different initial concentrations.

| C$_i$ (mg/L) | C$_e$ (mg/L) ± Sd | Pb$^{2+}$ ions R. E.% ± Sd | $q_e$ (mg/g) ± Sd |
|-------------|-----------------|-----------------------------|-----------------|
| 10          | 0.57 ± 0.03     | 94.30 ± 0.06                | 1.57 ± 0.02     |
| 20          | 1.30 ± 0.10     | 93.50 ± 0.09                | 3.16 ± 0.04     |
| 50          | 4.84 ± 0.12     | 90.33 ± 0.30                | 7.53 ± 0.10     |
| 100         | 15.30 ± 0.13    | 84.70 ± 0.40                | 14.12 ± 0.13    |
| 200         | 35.88 ± 0.23    | 82.06 ± 0.06                | 27.35 ± 0.11    |
| 300         | 69.08 ± 0.20    | 76.97 ± 0.08                | 38.49 ± 0.07    |
| 400         | 138.28 ± 0.34   | 65.43 ± 0.23                | 43.62 ± 0.21    |

Table 2 Pb$^{2+}$ ions removal efficiency $q_e$ at initial concentration of 20 mg/L at different pH values.

| pH | C$_e$ (mg/L) ± Sd | Pb$^{2+}$ ions R. E.% ± Sd | $q_e$ (mg/g) ± Sd |
|----|----------------|-----------------------------|-----------------|
| 2  | 8.54 ± 0.09     | 57.30 ± 0.12                | 1.91 ± 0.04     |
| 4  | 3.80 ± 0.05     | 81.00 ± 0.08                | 2.70 ± 0.07     |
| 5  | 1.30 ± 0.02     | 93.50 ± 0.32                | 3.12 ± 0.03     |
| 6  | 1.32 ± 0.04     | 93.40 ± 0.07                | 3.11 ± 0.06     |
| 7  | 1.430.02        | 92.85 ± 0.61                | 3.10 ± 0.01     |
| 8  | 1.62 ± 0.013    | 91.92 ± 0.18                | 3.06 ± 0.02     |
| 10 | 1.60 ± 0.01     | 92.00 ± 0.43                | 3.07 ± 0.03     |

$C_i/q_e = 1/q_m b + C_e/q_m$  

(8)

Plot of $C_i/q_e$ against $C_e$ give a line with intercept $1/q_m b$ and slope $1/q_m$ is obtained (Figure 11), which shows Lead biosorption isotherms of Langmuir. From the intercept and slope the Langmuir parameters ($b$ and $q_m$) are calculated. These values may be used for compared and correlate the biosorptive properties of Delonix regia of the Freundlich has the linear form [2,50].

$\log q_e = \log K_f +1/n \log C_e$

(9)

From a plot, a line with slope and intercept $1/n$ and log $K_f$ respectively is obtained (Figure 12). The slope, $1/n$, indicate the intensity of adsorption and log $K_f$ indicate the adsorption capacity.

isotherms [46] $q_e$ increased with the initial concentration of Pb$^{2+}$, as expected [47,48]. $q_m$ is 15.26 mg/g of Delonix regia. Langmuir model suggests that the adsorption take places on homogeneous sites. Langmuir isotherm equation is represented by equation 8 in a linear form [2,49].
Table 3 Pb²⁺ ions removal efficiency and qₑ at different biosorbent dosage.

| qₑ (mg/g) ± Sd | Pb²⁺ ions R. E.% ± Sd | Cₑ(mg/L) ± Sd | Biosorbent Dosage(mg) |
|----------------|-----------------------|----------------|-----------------------|
| 25.98 ± 0.20   | 64.95 ± 0.33          | 7.01 ± 0.09    | 25                    |
| 13.18 ± 0.13   | 65.90 ± 0.41          | 6.82 ± 0.05    | 50                    |
| 8.12 ± 0.09    | 81.24 ± 0.09          | 3.75 ± 0.02    | 100                   |
| 4.37 ± 0.07    | 87.30 ± 0.012         | 2.54 ± 0.04    | 200                   |
| 3.12 ± 0.04    | 93.50 ± 0.07          | 1.30 ± 0.001   | 300                   |
| 2.36 ± 0.02    | 94.25 ± 0.16          | 1.15 ± 0.02    | 400                   |
| 1.91 ± 0.01    | 95.04 ± 0.07          | 0.99 ± 0.01    | 500                   |

Figure 8 Effect of biosorbent dosage on Pb²⁺ ions removal efficiency and qₑ.

Figure 9 Effect of contact time on Pb²⁺ ions removal efficiency and qₑ at different initial concentrations (10, 30 and 50) mg/L by Delonix regia pod.

Figure 10 Effect of temperature on Pb²⁺ ions removal efficiency at different Initial concentrations (10, 20, 50) mg/L by Delonix regia pod.

Figure 11 Linearized biosorption isotherms of Langmuir.

[51] parameters of Pb²⁺ ions adsorption was given in Table 6a dimensionless constant separator factor (Rₑ) can classify the Isotherms [52] stated as:

\[ Rₑ = \frac{1}{1 + b C^*} \] (10)

Rₑ Mathematical calculation indicates the shape of isotherm, irreversible if (Rₑ=0), linear if (Rₑ=1), unfavorable if (Rₑ>1) favorable if (0<Rₑ<1). Rₑ values have arrange from 0.059 to 0.333 (Table 7) n values were greater than 1 [53], these values indicating a formation of a bond between Pb²⁺ ions and adsorbent and indicating favorable biosorption. This indicate that Pb(II) ions adsorption on Delonix regia is favorable. Linearity coefficient (R²) can be used to examine the fitting of the models. According to linearity coefficients (R²=1) Freundlich models has a good fit models and adsorption of Lead ion on Delonix regia follow Freundlich isotherm models.

Thermodynamic studies

From a plot lnb against 1/T, thermodynamics equilibrium constant was used to obtain the other thermodynamic parameters. The biosorption capacity of the Delonix regia for Lead increased as temperature increased, indicating the adsorption process was...
Table 4 Effect of contact time on Pb²⁺ ions removal efficiency and qₑ at different initial concentrations (10, 30 and 50) mg/L by Delonix regia pod.

| Time (min) | Pb²⁺ R. E. % at Cₑ(10) | Pb²⁺ R. E. % at Cₑ(20) | Pb²⁺ R. E. % at Cₑ(50) | qₑ at Cₑ(10) | qₑ at Cₑ(20) | qₑ at Cₑ(50) | Cₑ at Cₑ(10) | Cₑ at Cₑ(20) | Cₑ at Cₑ(50) |
|------------|--------------------------|--------------------------|--------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 20         | 83.9                     | 81.9                      | 80.32                    | 1.4            | 4.1            | 6.69           | 1.61           | 5.41           | 9.84           |
| 40         | 91                       | 86.43                     | 86.51                    | 1.52           | 4.3            | 7.2            | 0.9            | 4.1            | 6.74           |
| 60         | 94.2                     | 90.6                      | 90.0                     | 1.57           | 4.53           | 7.52           | 0.57           | 2.81           | 4.9            |
| 80         | 94.8                     | 91.73                     | 90.49                    | 1.58           | 4.59           | 7.54           | 0.52           | 2.5            | 4.75           |
| 120        | 94.97                    | 91.97                     | 90.71                    | 1.58           | 4.6            | 7.59           | 0.5            | 2.4            | 4.65           |

Table 5 Effect of temperature on Pb²⁺ ions removal efficiency and qₑ at different initial concentrations (10, 20, 50) mg/L by Delonix regia pod.

| Temp.(°C) | Pb²⁺ R. E. % at Cₑ(10) | Pb²⁺ R. E. % at Cₑ(20) | Pb²⁺ R. E. % at Cₑ(50) | qₑ at Cₑ(10) | qₑ at Cₑ(20) | qₑ at Cₑ(50) | Cₑ at Cₑ(10) | Cₑ at Cₑ(20) | Cₑ at Cₑ(50) |
|-----------|--------------------------|--------------------------|--------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 25        | 94.30                    | 93.50                     | 90.33                    | 1.57           | 3.17           | 7.53           | 0.57           | 1.30           | 4.84           |
| 30        | 94.46                    | 93.92                     | 90.70                    | 1.57           | 3.13           | 7.56           | 0.55           | 1.22           | 4.65           |
| 40        | 95.99                    | 94.44                     | 91.21                    | 1.60           | 3.15           | 7.60           | 0.41           | 1.11           | 4.40           |
| 50        | 95.70                    | 94.34                     | 90.62                    | 1.59           | 3.14           | 7.55           | 0.43           | 1.13           | 4.69           |

Table 6 Isotherm constants of Pb²⁺ ions biosorption on Delonix regia pod at various temperatures.

| T (K) | qₑ(mg/g) ± Sd | b(L/mg) ± Sd | R² | n ± Sd | 1/n | Kₑ(mg/g) ± Sd | R² |
|-------|---------------|--------------|-----|--------|-----|---------------|-----|
| 298   | 15.26 ± 0.18  | 0.200 ± 0.01 | 0.995 | 1.377 ± 0.09 | 0.726 | 2.46 ± 0.01 | 0.999 |
| 303   | 15.41 ± 0.09  | 0.207 ± 0.02 | 0.994 | 1.372 ± 0.01 | 0.73 | 2.53 ± 0.09 | 0.999 |
| 313   | 12.99 ± 0.23  | 0.315 ± 0.06 | 0.983 | 1.520 ± 0.06 | 0.657 | 2.91 ± 0.03 | 0.999 |
| 323   | 12.56 ± 0.35  | 0.317 ± 0.05 | 0.991 | 1.540 ± 0.07 | 0.65 | 2.81 ± 0.05 | 0.998 |

endothermic. Thermodynamic parameters (ΔG°, ΔS° and ΔH°) were determined using the equations (1), (2) [54], the slope ΔH°/R and intercept ΔS°/R are obtained and the values of ΔH° and ΔS° were calculated (Table 8). The adsorption process of Lead ions on the Delonix regia was endothermic as ΔH° values were Positive. A positive ΔG° value suggested an ion-exchange mechanism occur in the biosorption of Pb²⁺ and a complex formed by Pb²⁺ with the Delonix regia [2,55] An increase in randomness during the biosorption as the Positive ΔS° value [2,56-58].

**Kinetic studies on the biosorption of Pb²⁺ ions**

Pseudo first order, pseudo second order kinetic and the intra particle diffusion models can be used to test the mechanism of the adsorption of metal ions [2,19-21]. The adsorption kinetic of the adsorbed Pb²⁺ ions was studied (Figures 13 and 14). Correlation coefficient, R² can be used to test the suitability of these models [2,21]. The variable and constant of each kinetic model were calculated and were presented in Table 9, the calculated qₑ determined from the plot of the pseudo first order model differs from the experimental qₑ. This indicates that pseudo first order model is not good in studying the kinetics of the biosorption of Pb²⁺ ions compared to pseudo second order models (R²=0.999) for Pb²⁺ ions, Table 9. So the second order kinetics is good in studying...
Table 8 Thermodynamic parameters for the biosorption process.

| Temperature (K) | \( \Delta G^\circ \) (KJ/mol) | \( \Delta H^\circ \) (KJ/mol) | \( \Delta S^\circ \) (J/mol. K) |
|-----------------|-----------------|-----------------|-----------------|
| 298             | 4.73            | 17.69           | 43.84           |
| 303             | 4.51            |                  |                 |
| 313             | 4.08            |                  |                 |
| 323             | 3.64            |                  |                 |

Table 9 Kinetic parameters of Pb\(^{2+}\) ions biosorption at different initial concentration.

| \( C_0 \) (mg/L) | Pseudo-first order | Pseudo-second order | Intraparticle diffusion | Observed \( q_e \) (mg/g) ± Sd |
|------------------|--------------------|---------------------|-------------------------|-------------------------------|
|                  | \( k_1 \) (1/min) | \( q_e \) (mg/g) ± Sd | \( k_2 \) (g/mg.min) ± Sd | \( q_e \) (mg/g) ± Sd | \( K_{in} \) | C | R\(^2\) ± Sd |
| 10               | 0.083 ± 0.005     | 1.36 ± 0.06         | 0.448 ± 0.01           | 1.6 ± 0.03 | 0.9988 | 0.027 | 0.57 | 0.755 | 1.58 ± 0.02 |
| 30               | 0.069 ± 0.003     | 3.41 ± 0.07         | 0.148 ± 0.03           | 4.6 ± 0.05 | 0.9986 | 0.818 | 2.81 | 0.861 | 4.59 ± 0.06 |
| 50               | 0.091 ± 0.009     | 7.23 ± 0.12         | 0.094 ± 0.01           | 7.6 ± 0.09 | 0.9987 | 0.137 | 4.9  | 0.807 | 7.54 ± 0.10 |

Table 10 Effect of chemical treatment of Biosorbent on biosorption efficiency.

| Biosorbent | Delonix regia |
|------------|---------------|
| \( C_0 \) (20 mg/L) of metal ions | DR | CADR |
| \( C_e \) (mg/L) ± Sd | R. E.% ± Sd | \( C_e \) (mg/L) ± Sd | R. E.% ± Sd |
| Cd\(^{2+}\) | 1.52 ± 0.02 | 92.42 ± 0.19 | 0.259 ± 0.03 | 98.71 ± 0.15 |
| Pb\(^{2+}\) | 1.30 ± 0.06 | 93.50 ± 0.11 | 0.390 ± 0.01 | 98.05 ± 0.17 |

The kinetics of the biosorption of Pb\(^{2+}\) ions, as the calculated \( q_e \) (7.54 mg/g are very close to the experimental \( q_e \) (7.6 mg/g), suggesting that the biosorption of the Pb\(^{2+}\) ions solutions involves the Pb\(^{2+}\) ion and the Delonix regia biosorbent particles [2,58,59].

**Effect of chemical treatment of the biosorbents on biosorption efficiency**

The effect of chemical treatment of the biosorbents by esterifying with NaOH followed by citric acid treatment (CADR) on the R. E compared with (DR) was studied and shown in **Table 10**. It was observed that the R.E.% of metal ions by (CADR) was higher than the R.E.% of metal ions by (DR) and this was due to the Chemical treatment of biomass with NaOH and citric acid increases its cation uptake ability as the carboxyl groups of the biomass increases [2,31,32].

**Conclusion**

1. Nano size of Flamboyant Pod (Delonix regia) was used for biosorption of toxic Pb\(^{2+}\) ions from solution and is consider a very effective biosorbent in the removal of heavy metals. This study indicated that: The Adsorption process depends on temperature, pH, Contact time, dosage and metal ion concentration.
2. Adsorption of Pb\(^{2+}\) ions from solutions obeyed Freundlich isotherm models. \( q_m \) of Pb\(^{2+}\) ions on Delonix regia is 43.62 mg g\(^{-1}\).
3. The biosorption process was endothermic an ion-exchange mechanism applies in the biosorption of (Pb\(^{2+}\) ions). This confirmed by thermodynamic studies.
4. Second order kinetics models is a better than the pseudo first order in studying the kinetics of the biosorption of Pb\(^{2+}\) ions.
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