Research Article

Disposal of Heavy Transition Cd\(^{2+}\) Ions from Aqueous Solution Utilizing Nanosized Flamboyant Pod (Delonix regia)

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Abstract The absorption of toxic heavy metal by natural adsorbents from water was indicated by investigating the effect of nanosized Delonix regia (D. regia) and the chemically modified adsorbent citric acid D. regia (CA-D. regia) for removing the Cd\(^{2+}\) ions. Different techniques were employed for characterizing the adsorbent D. regia such as energy-dispersive X-ray (EDX) analysis, Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and scanning electron microscopy (SEM). The effect of temperature, dosage of adsorbent, contact time, pH, and Cd\(^{2+}\) ion concentration on the adsorption process was studied. The maximum adsorption capacity of Cd\(^{2+}\) ions by D. regia, \(q_m\), was 37.2 mg g\(^{-1}\). The highest removal efficiency (RE) was 96.00% at pH 4.0. FT-IR peaks indicated that the main functional groups (hydroxyl and carboxylic groups) are responsible for Cd\(^{2+}\) ions binding in the adsorption. The adsorption process was endothermic and was best described by a pseudo-second-order kinetics model. The Freundlich isotherm has a better fit with the experimental data compared to the Langmuir isotherm. These results indicated that D. regia is an environment-friendly, available, and low cost adsorbent for adsorbing the Cd\(^{2+}\) ions.

Keywords nanosized Delonix regia; kinetics; removal efficiency; adsorption; thermodynamics; isotherm

1. Introduction

The high importance of wastewater treatment lies in being a source to reduce the problem of limited and scarce water resources, which is considered the most important obstacle at all that prevents the continued implementation of plans for the state’s expansion. So the addition of this resource is going to maximize the benefit from the available water resources, reduce the growing gap between available water resources and the required water needs, and maintain the international water security and human health. Water bodies and wastewater are contaminated with bacteria, waste matter, and toxic heavy metals [1]. Toxic heavy metals release into the environment causes food contamination and so food safety for the human consumption is a serious worldwide public issue and is widely addressed [2]. Cd\(^{2+}\) ion is one of the most toxic heavy metals and it is responsible for causing kidney damage, bone fraction, and red blood cells damage [3]. Ion exchange, chemical precipitation, and membrane separation methods can be used for the removal of Cd\(^{2+}\) ions from water, but these methods are considered ineffective and costly [4,5]. Waste materials generated due to agricultural by-products as a whole were 320,000,000,000 kg annually [6], such as sugar cane bagasse, peat, rice husks and straw, soya bean, saw dust, walnut and seeds hull, corn cobs, banana peels and Psidium guajava, maize leaves, Ulmus leaves, and Eriobotrya japonica [7,8]. Nowadays we face solid waste disposal problem; hence there is a need to convert this waste to be a useful, economic value product for the removal of heavy metal from aqueous solution which would be useful to the environment. Treating biomass with NaOH and citric acid increases Cd\(^{2+}\) ions uptake as the carboxyl groups increase [9]. On the other hand, Delonix regia (D. regia) plant contains chemical constituents such as flavonoid, terpenoids and its glycosides, phenolics, and phytosterol which play an important role in medicine [10]. Moreover, as this plant is considered a cheap adsorbent material this increases subsequently its economic value. From this point of view, our aim of this work is to investigate the ability of nanosized D. regia pods powder to remove Cd\(^{2+}\) ions from aqueous solution.

2. Experimental methods

Chemicals used in this investigation were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.1. Sample collection

The D. regia pods were collected from Shandawil Research Station, Sohag, Egypt.
2.2. Instruments

The investigated D. regia pod sample was grinded to nanosize using Retsch Muhle Brinkmann Spectro Mill MS Microgrinding Mixing Pulverizer. The structure of investigated plant was characterized by X-ray powder diffraction (XRPD), with X-ray patterns from 5° to 80° and at 2θ collected by a Philips X’Pert PRO-MPD (PANalytical, The Netherlands) using graphite-monochromatized Cu Kα radiation (λ = 1.54184 Å) operating at 45 kV and 40 mA. The morphology of samples was studied by field-emission scanning electron microscopy (FE-SEM) and was performed on a JSM-6100 microscope (JEOL, Japan) with an acceleration voltage of 30 kV. The chemical composition of the synthesized nanostructures was also analyzed using energy dispersive analysis of X-ray (EDAX) unit attached with the FE-SEM. Transmission electron microscopy (TEM) images were obtained with a 2000 EX(H) microscope (JEOL, Japan) at an acceleration voltage of 200 kV. Particle-size distribution of the studied nanosized D. regia pod was evaluated using imageJ Launcher, broken-symmetry software, version (1.4.3.6.7) [11,12,13]. Hettich Centrifuge EBA 20 (D-78532 Tuttlingen) was used to centrifuge the sample after the adsorption process. The concentration of Cd²⁺ was determined using Flame Atomic Absorption Spectrometer (Flame AAS; Perkin-Elmer model; Analyst 200). AD1000 and AD1020 pH/mV/ISE/temperature bench meters were used to adjust pH of the prepared solutions. The shaking was carried out in a thermostated electronic shaker bath, Heidolph MR 3001, and centrifugation was performed on a Hettich EBA 20 centrifuge. Fourier transform infrared spectroscopy (FTIR-2000, Perkin-Elmer) was used for detection of the surface functional groups on the prepared biosorbents.

2.3. Sample pretreatment

Pods of D. regia were washed with water, dried, grinded, and sieved to obtain a very fine powder less than 100 nm.

2.3.1. Treatment of D. regia by citric acid

Chemical modification of nanosized D. regia powder was performed using NaOH followed by citric acid treatment [14].

2.4. Preparation of aqueous solution

Stock solution of Cd²⁺ ions was prepared by weighing out 2.726 g of Cd(NO₃)₂·4H₂O and dissolving it in a 1,000 mL volumetric flask; the result concentration was 1,000 mg/L.

2.5. Adsorption experiments

2.5.1. Initial Cd²⁺ ions concentration

The amount of 50 mL of Cd²⁺ ions solution of different concentrations was added to 0.3 g of the adsorbent in a bottle.

2.5.2. pH values

Experiments were carried out at different pH values (2–10) and pH was adjusted by using 0.1 M NaOH or 0.1 M HCl.

2.5.3. Adsorbent dosage

In each experiment, 50 mL of Cd²⁺ ions solution of concentration (20 mg/L) were added to different dosages of the adsorbent in a bottle.

2.5.4. Contact time

In the adsorption kinetics experiment, 0.2 L of Cd²⁺ ions solution of different concentrations were added to 1.2 g of the adsorbent in a flat bottle and then the mixture was stirred on a shaker and a contact time 20 min–120 min with time interval 20 min.

2.5.5. Adsorption isotherm

The Cd²⁺ ions distribution between the solid and liquid phases can be described by the Freundlich and Langmuir isotherms. The amount of Cd²⁺ ions adsorbed at equilibrium (qe) increased with the initial concentration of Cd²⁺ ions, as expected [15,16,17,18]. The amount of qm is 15.26 mg/g of D. regia. Langmuir isotherm equation is represented in a linear form [16,17,18] as follows:

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad \text{(1)}
\]

Plot of \(\frac{C_e}{q_e}\) against \(\frac{1}{q_m}\) gives a line with intercept \(\frac{1}{q_m b}\) and slope \(\frac{1}{q_m}\) is obtained, which shows Cd²⁺ ions adsorption isotherms of Langmuir. From the intercept and slope, the Langmuir parameters \(b\) and \(q_m\) are calculated [16,17,18]. The Freundlich equation has the general form [16,17,18,19]

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{(2)}
\]

From a plot, a line with slope and intercept, \(1/n\) and \(\log K_f\), respectively, can be calculated. The slope, \(1/n\), indicates the intensity of adsorption and \(\log K_f\) indicates the adsorption capacity [20]. A dimensionless constant separator factor \(R_L\) can classify the isotherms [21] stated as

\[
R_L = \frac{1}{1 + bC_o} \quad \text{(3)}
\]

2.5.6. Temperature

An amount of 50 mL of different concentrations of Cd²⁺ ions solution was added to 0.3 g of the adsorbent in a bottle at different temperatures and then the mixture was stirred for 60 min on a shaker at 300 rpm. Then, it was centrifuged and the concentration of Cd²⁺ ions was determined. The relationships (1) and (2) [21] can be used to calculate \(\Delta S^o\).
ΔH°, and ΔG° (the thermodynamic parameters for the adsorption process) [22,23,24] as follows:

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

2.5.7. Calculation of Cd²⁺ ions absorption capacity (qₑ)

The amount of qₑ was calculated by

\[ qₑ = \frac{v(C₀ - Cₑ)}{w}. \]  

The RE of the Cd²⁺ ions was determined using

\[ \text{RE} = \left( \frac{C₀ - Cₑ}{C₀} \right) \times 100 \]

where RE% is the percentage of the removed Cd²⁺ ions.

2.5.8. Kinetics study

The mechanism of the adsorption of Cd²⁺ ions was tested using pseudo-first-order [25] and pseudo-second-order kinetic models displayed by the following equations, respectively [26,27]:

\[ \ln (qₑ - q₉) = \ln qₑ - k₁t, \]
\[ \left( \frac{t}{q₉} \right) = \frac{1}{k₂qₑ^2} + \left( \frac{t}{qₑ} \right). \]

Both models are tested for suitability using correlation coefficient R² [26,28].

2.5.9. Chemical treatment of the adsorbent

An amount of 50 mL of Cd²⁺ ions solution of initial concentration 20 mg/L was added to 300 mg of a chemically treated adsorbent citric acid D. regia (CA-D. regia); the mixture was stirred for 60 min. After each experiment, the mixture was centrifuged and the concentration of each was determined using the Flame AAS.

3. Results and discussion

3.1. Characteristics of the adsorbent

3.1.1. FT-IR analysis of the adsorbent

An FT-IR analysis of D. regia and Cd²⁺ ions loaded D. regia (Cd-D. regia) (Figure 1(a)) was carried out. The FT-IR spectrum of D. regia indicates the functional groups. The peak appears in the region of 1,000 cm⁻¹–1,200 cm⁻¹, which is characteristic of cellulose [29]. A strong peak at 3,298 cm⁻¹ was attributed to N–H bond. The shift in the peak position to 3,332 cm⁻¹ in the spectrum of the Cd-D. regia indicates the binding of Cd²⁺ ions with amino and hydroxyl groups [30,31,32]. The peak at 2,917 cm⁻¹ was assigned to CH stretching vibrations. A peak at 1,036 cm⁻¹ indicated the C–O of alcohols and the shift to 1,040 cm⁻¹ indicated a binding of Cd²⁺ ions with C–O group [30,31,32,33]. A peak was observed at 1,738 cm⁻¹, which is characteristic of carbonyl group and is shifted to a wave number of 1,731 cm⁻¹ on Cd²⁺ adsorption [34,35]. A peak at 1,243 cm⁻¹ indicates the presence of carboxylic acids which shifted to a wave number of 1,229 cm⁻¹ after Cd²⁺ ions absorption [36].

Also, an FT-IR analysis for detecting the functional groups of CA-D. regia and Cd²⁺ loaded CA-D. regia (Cd-CA-D. regia) is shown in Figure 1(b). A comparison of the IR spectra of the samples of D. regia and CA-D. regia revealed that a characteristic vibration absorption band of carboxyl group at 1,733 cm⁻¹ is present in the IR spectrum of CA-D. regia samples. This indicates the esterification between alcohol groups of cellulose in D. regia and citric acid. The peak at 1,733 cm⁻¹ shifted to
1,731 cm\(^{-1}\) in the spectrum of Cd-CA-D. regia indicating the adsorption of Cd\(^{2+}\) ions on carboxylic group. The peak around 2,550 cm\(^{-1}\) to 3,550 cm\(^{-1}\) centered at 3,343 indicates the existence of carboxylic OH groups and COOH group after CA treatment. It appears from Figure 1(b) that the different functional groups on CA-D. regia are responsible for the adsorption of Cd\(^{2+}\) ions. A change in peaks’ position at 3,323 cm\(^{-1}\) in the spectrum of Cd-CA-D. regia indicates the adsorption of these Cd\(^{2+}\) ions on hydroxyl groups \[14\].

3.1.2. EDX analysis
To determine the composition of the investigated plant, EDX elemental analysis of D. regia is shown in Figure 2.

3.1.3. SEM analysis
An SEM analysis of the adsorbent D. regia (Figure 3) is used to show the morphology. The surface morphology of powder showed that the powder is composed of fine particles.

Figure 4: XRD patterns of the adsorbent D. regia and Cd-D. regia.

3.1.4. XRD analysis
XRD patterns of the D. regia powder (shown in Figure 4) indicate the presence of a significant amount of amorphous material due to lignin in the sample and show that the structure of D. regia has a different change at the appearance of amorphous peak at \(2\theta = 42.16^\circ\) after the adsorption of Cd\(^{2+}\) ions.

3.1.5. TEM analysis
The adsorbent was subjected to a TEM analysis (cf. Figure 5(a)) to examine the particle size. Figure 5(b) shows the diameter distribution histogram of the nanosized adsorbent estimated by public image analysis product (ImageJ, NIH, USA) and the size of the majority of particles was found to be 18 nm. The small size of the studied adsorbent allows it to be more efficient in the adsorption of cadmium ions.
Figure 5: (a) TEM image of nanosized adsorbent *D. regia*. (b) Calculated histogram for particle size distribution of *D. regia*.

Figure 6: Effect of initial Cd$^{2+}$ ions concentration on Cd$^{2+}$ ions RE and $q_e$ by *D. regia*.

Table 1: Cd$^{2+}$ ions RE and $q_e$ at different initial concentrations.

| $C_e$ (mg/L) | $C_e$ (mg/L) ±SD | Cd$^{2+}$ ions RE ± SD | $q_e$ (mg/g) ± SD |
|-------------|------------------|------------------------|------------------|
| 10          | 0.64 ± 0.04      | 93.57 ± 0.04           | 1.56 ± 0.05      |
| 20          | 1.52 ± 0.10      | 92.42 ± 0.16           | 3.80 ± 0.06      |
| 50          | 4.46 ± 0.22      | 91.08 ± 0.22           | 7.59 ± 0.09      |
| 100         | 9.60 ± 0.15      | 90.39 ± 0.09           | 15.10 ± 0.08     |
| 200         | 23.01 ± 0.60     | 88.49 ± 0.06           | 29.50 ± 0.01     |
| 300         | 78.51 ± 0.70     | 73.75 ± 0.21           | 36.88 ± 0.03     |
| 400         | 176.64 ± 0.97    | 55.84 ± 0.27           | 37.23 ± 0.20     |

*aSD* = standard deviation.

3.1.6. Effect of initial concentration

Table 1 and Figure 6 illustrate the effect of Cd$^{2+}$ ions concentration on the adsorption. The Cd$^{2+}$ ions $q_e$ increases as the concentration rises, as Cd$^{2+}$ ions are more available for interaction with the adsorbent. The Cd$^{2+}$ ions RE for initial concentration 10 mg/L is 93.57% and decreases as the concentration increases. At low concentrations of Cd$^{2+}$ ions, a greater chance was available for metal removal as adsorption sites took up the available Cd$^{2+}$ ions with increasing concentrations [37,38,39,40].

3.1.7. Effect of pH

Table 2 and Figure 7 illustrate the effect of pH on the adsorption process. The Cd$^{2+}$ ions RE and $q_e$ increase as the pH value increases. The amount of Cd$^{2+}$ ions removed
Figure 8: Effect of adsorbent dosage on Cd\(^{2+}\) ions RE and \(q_e\) by \textit{D. regia}.

Table 3: Cd\(^{2+}\) ions RE and \(q_e\) at different adsorbent dosages by \textit{D. regia}.

| Adsorbent dosage (mg) | \(C_e\) (mg/L) \(\pm SD\) | Cd\(^{2+}\) ions RE \(\pm SD\) | \(q_e\) (mg/g) \(\pm SD\) |
|-----------------------|------------------|-----------------|-----------------|
| 25                    | 2.84 ± 0.08      | 85.79 ± 0.09    | 34.32 ± 0.16    |
| 50                    | 2.22 ± 0.06      | 88.90 ± 0.31    | 17.98 ± 0.17    |
| 100                   | 1.88 ± 0.03      | 90.54 ± 0.22    | 9.05 ± 0.10     |
| 200                   | 1.77 ± 0.01      | 91.10 ± 0.31    | 4.56 ± 0.09     |
| 300                   | 1.36 ± 0.03      | 93.21 ± 0.17    | 3.11 ± 0.06     |
| 400                   | 1.24 ± 0.02      | 93.80 ± 0.07    | 2.35 ± 0.05     |
| 500                   | 1.04 ± 0.01      | 94.82 ± 0.05    | 1.90 ± 0.01     |

by the \textit{D. regia} at low pH 2 was low (0.65 mg/g) with RE of 19.5% compared to the amounts removed at pH 4 to pH 10 which ranged from 3.2 mg/g (RE 96%) at pH 4 to 2.98 mg/g (RE 89.29%) at pH 5. This is because at low pH value the concentration of H\(^+\) is high [33], as H\(^+\) ions were being removed by the adsorbent instead of the Cd\(^{2+}\) ions [34, 41]. At a higher concentration of H\(^+\) ions, the adsorbent surface becomes positive charge thus reducing the attraction between \textit{D. regia} and Cd\(^{2+}\) ions [42].

3.1.8. Effect of the adsorbent dosage

Table 3 and Figure 8 illustrate the effect of the adsorbent dosage. RE increases with the lowest value of 85.79% and the highest value of 94.82% obtained with 25 mg and 500 mg of the adsorbent, respectively. This is because at high dosage, there is an increase in surface area and availability of adsorption sites, but \(q_e\) decreases with a decrease in the amount of Cd\(^{2+}\) ions adsorbed per unit weight of adsorbent [43,44,45].

3.1.9. Effect of contact time

Figure 9 and Table 4 illustrate the effect of contact time on the adsorption of Cd\(^{2+}\) ions by \textit{D. regia}. The amount of Cd\(^{2+}\) ions absorbed increased with an increase in the contact time and reached equilibrium in 60 min. This is because a long contact time and availability of active sites was followed by a reduction in the Cd\(^{2+}\) ion uptake. The removal of Cd\(^{2+}\) ions remains constant as the active sites are less available [46, 47].

3.1.10. Effect of temperature

Table 3 and Figure 10 illustrate the effect of temperature on the adsorption. The Cd\(^{2+}\) ions RE and \(q_e\) by \textit{D. regia} increase while the temperature is increasing, as the active sites have increased and encouraged the process of adsorption, due to an increase in the movement of the Cd\(^{2+}\) ions and pore size indicating an endothermic process [48,49].

3.1.11. Adsorption isotherm

Parameters of Cd\(^{2+}\) ions adsorption are given in Table 6. A dimensionless constant separator factor (\(R_L\)) can classify
Cd²⁺ ions adsorption on ions and the adsorbent and also a favorable adsorption (i.e., Effect of temperature on Cd²⁺ ions RE by D. regia).

Table 4: Effect of contact time on Cd²⁺ ions RE and qₑ at different initial concentrations (10 mg/L, 30 mg/L, and 50 mg/L) by D. regia.

| Time (min) | Cd²⁺ RE% at Cₒ (10) | Cd²⁺ RE% at Cₒ (30) | Cd²⁺ RE% at Cₒ (50) | qₑ at Cₒ (10) | qₑ at Cₒ (30) | qₑ at Cₒ (50) | Cₑ at Cₒ (10) | Cₑ at Cₒ (30) | Cₑ at Cₒ (50) |
|-----------|---------------------|---------------------|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 20        | 90.97               | 90.20               | 80.99               | 1.52           | 4.51           | 6.67           | 0.90           | 2.93           | 10.00          |
| 40        | 93.57               | 94.07               | 93.16               | 1.56           | 4.70           | 7.76           | 0.64           | 1.78           | 3.42           |
| 60        | 93.98               | 92.80               | 91.08               | 1.57           | 4.64           | 7.59           | 0.60           | 2.16           | 4.46           |
| 80        | 96.29               | 95.40               | 90.87               | 1.61           | 4.73           | 7.57           | 0.37           | 1.37           | 4.56           |
| 100       | 93.88               | 88.92               | 86.86               | 1.56           | 4.45           | 7.24           | 0.61           | 3.32           | 6.57           |
| 120       | 92.95               | 91.86               | 88.55               | 1.55           | 4.58           | 7.38           | 0.70           | 2.50           | 5.73           |

Table 5: Effect of temperature on Cd²⁺ RE and qₑ by D. regia.

| Temperature (°C) | Cd²⁺ RE% at Cₒ (10) | Cd²⁺ RE% at Cₒ (30) | Cd²⁺ RE% at Cₒ (50) | qₑ at Cₒ (10) | qₑ at Cₒ (30) | qₑ at Cₒ (50) | Cₑ at Cₒ (10) | Cₑ at Cₒ (30) | Cₑ at Cₒ (50) |
|------------------|---------------------|---------------------|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 25               | 93.57               | 92.42               | 91.08               | 1.56           | 3.08           | 7.59           | 0.64           | 1.52           | 4.46           |
| 30               | 93.93               | 93.21               | 92.63               | 1.57           | 3.11           | 7.72           | 0.61           | 1.36           | 3.68           |
| 40               | 95.88               | 93.81               | 93.69               | 1.60           | 3.13           | 7.81           | 0.41           | 1.24           | 3.15           |
| 50               | 94.69               | 92.03               | 92.48               | 1.58           | 3.07           | 7.71           | 0.53           | 1.59           | 3.76           |

Table 6: Isotherm constants of Cd²⁺ ions adsorption at various temperatures.

| T(K) | qₑ (mg/g) ±SD | b(L/mg) ±SD | Rₑ | L | n ±SD | 1/n | Kₑ (mg/g) ±SD | Rₑ |
|------|---------------|-------------|----|---|--------|-----|---------------|----|
| 298  | 23.49 ± 0.12  | 0.11 ± 0.03 | 0.94 | 1.22 ± 0.09 | 0.81 | 2.22 ± 0.15 | 0.99 |
| 303  | 38.63 ± 0.15  | 0.07 ± 0.01 | 0.88 | 1.13 ± 0.05 | 0.88 | 2.41 ± 0.08 | 0.99 |
| 313  | 22.34 ± 0.11  | 0.16 ± 0.06 | 0.59 | 1.29 ± 0.07 | 0.77 | 3.00 ± 0.14 | 0.98 |
| 323  | 26.42 ± 0.19  | 0.10 ± 0.06 | 0.40 | 1.25 ± 0.06 | 0.80 | 2.46 ± 0.31 | 0.97 |

Table 7: A dimensionless constant separator factor (Rₑ) for Langmuir type adsorption process.

| Cₒ (mg/L) | Rₑ at 25°C | Rₑ at 30°C | Rₑ at 40°C | Rₑ at 50°C |
|-----------|------------|------------|------------|------------|
| 10        | 0.49       | 0.60       | 0.39       | 0.50       |
| 20        | 0.32       | 0.43       | 0.24       | 0.33       |
| 50        | 0.16       | 0.23       | 0.11       | 0.17       |

Table 8: Thermodynamic parameters for the adsorption process.

| Temperature (K) | ΔG° (KJ/mol) | ΔH° (KJ/mol) | ΔS° (J/mol K) |
|-----------------|--------------|--------------|---------------|
| 298             | 6.19         |               |               |
| 303             | 5.83         | 27.50         | 71.51         |
| 313             | 5.12         |               |               |
| 323             | 5.01         |               |               |

3.1.12. Thermodynamic studies

From a plot ln(b) against 1/T, thermodynamic parameters were obtained. The Cd²⁺ ions qₑ by D. regia increased as temperature increased, indicating that the adsorption process was endothermic. Thermodynamic parameters (ΔG°, ΔH°, and ΔS°) (Table 8) were determined using (1) and (2) [52]. The adsorption process of Cd²⁺ ions on the D. regia was endothermic as ΔH° values were positive. A positive ΔG° value suggested an ion-exchange mechanism [53]. The more positive value of ΔS°, the more randomness there is during the adsorption process [25, 54].

Figure 10: Effect of temperature on Cd²⁺ ions RE by D. regia.

The isotherms [50] stated in (3). Rₑ values have arranged from 0.1114 to 0.5979 (Table 7). The n values were greater than 1 [51], indicating a formation of a bond between Cd²⁺ ions and the adsorbent and also a favorable adsorption (i.e., Cd²⁺ ions adsorption on D. regia is favorable). According to linearity coefficients (Rₑ² = 0.999), Freundlich model has a good fit to the adsorption of Cd²⁺ ions on D. regia (Figures 11 and 12).
Table 9: Kinetic parameters of Cd$^{2+}$ ions adsorption onto *D. regia*.

| $C_0$ (mg/L) | Pseudo-first-order kinetics | Pseudo-second-order kinetics | Observed $q_e$ (mg/g) ±SD |
|--------------|----------------------------|----------------------------|--------------------------|
|              | $k_1$ (1/min) ±SD | $q_e$ (mg/g) ±SD | $R^2$ | $k_2$ (g/mg.min) ±SD | $q_e$ (mg/g) ±SD | $R^2$ |
| 10           | 0.12 ± 0.01        | 0.99 ± 0.03           | 0.98 | 0.97 ± 0.04        | 1.60 ± 0.06       | 0.999 | 1.57 ± 0.05 |
| 30           | 0.08 ± 0.003       | 1.65 ± 0.05           | 0.61 | 0.49 ± 0.02        | 4.73 ± 0.04       | 0.999 | 4.71 ± 0.04 |
| 50           | 0.14 ± 0.02        | 13.37 ± 0.09          | 0.93 | 0.14 ± 0.01        | 7.69 ± 0.08       | 0.998 | 7.59 ± 0.09 |

3.1.13. Kinetic studies

Pseudo-first-order and pseudo-second-order kinetics can be used to test the mechanism of the adsorption of metal ions [28,29]. The adsorption kinetic of the adsorbed Cd$^{2+}$ ions was studied (Figures 13 and 14). The pseudo-first-order model is not good in studying the kinetics of the adsorption of Cd$^{2+}$ ions compared to pseudo-second-order model ($R^2 = 0.999$) for Cd$^{2+}$ ions (Table 9) [28]. So the second-order kinetics is good in studying the kinetics of the adsorption of Cd$^{2+}$ ions, as the calculated $q_e$ (7.69 mg/g) is very close to the experimental $q_e$ (7.59 mg/g), suggesting that the adsorption solutions involve the Cd$^{2+}$ ion and the adsorbent [51,52].
Table 10: Effect of chemical treatment of the adsorbent on the adsorption efficiency.

| Adsorbent                          | $C_0$ (20 mg/L) of metal ions | $C_e$ (mg/L) ±SD | RE% ±SD | $C_0$ (mg/L) ±SD | RE% ±SD |
|-----------------------------------|-----------------------------|------------------|---------|------------------|---------|
| D. regia                          | 1.52 ± 0.02                 | 92.42 ± 0.19     | 0.259 ± 0.03 | 98.71 ± 0.15     |

3.1.14. Effect of chemical treatment of the adsorbent on the adsorption efficiency

The effect of chemical treatment of the adsorbent D. regia by esterifying with NaOH followed by citric acid treatment (CA-D. regia) on the RE compared with D. regia was studied and shown in Table 10. It was observed that the RE percentage of metal ions by CA-D. regia was higher than that of Cd$^{2+}$ ions by D. regia, as the chemical treatment of D. regia with NaOH and citric acid increases Cd$^{2+}$ ions adsorption as the carboxyl group of the biomass increases [14, 43, 55].

4. Conclusion

Nanosized flamboyant pod D. regia was used for the adsorption of Cd$^{2+}$ from aqueous solution. The investigated biosorbent was characterized by using FT-IR, SEM, TEM, XRD, and EDX techniques. The adsorption process depends on temperature, pH, contact time, dosage, and Cd$^{2+}$ ions concentration.

Adsorption of Cd$^{2+}$ ions from solution obeyed the Freundlich isotherm model. The $q_m$ of Cd$^{2+}$ ions on D. regia is 37.2 mg·g$^{-1}$. The adsorption process was endothermic having an ion exchange mechanism. Second-order kinetics models are better in studying the kinetics of adsorption. The results showed that D. regia pod biosorbent proved to be a very effective biosorbent in the removal of Cd$^{2+}$ ions from water.

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Conflict of interest
The authors declare that they have no conflict of interest.

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