Biosorption of lead ions from aqueous environment using Henna biomass

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ABSTRACT

The purpose of this study was to use Henna as a biosorbent to remove lead ions (Pb²⁺) from an aqueous environment as an effective method for wastewater treatment. Dried leaves of Henna were ground and then passed through the standard screens to be used for the treatment process. The effects of main operating conditions, that is, time (20–200 min), biosorbent amount (0.1–1.2 g/L), and pH (2–9) on the percentage of removal of Pb²⁺ ions from aqueous solution using Henna were investigated. Maximum Pb²⁺ biosorption reached 90% at pH 5.5, 55 ppm initial concentration of Pb²⁺ ions, 1 g/L biosorbent amount, and 110 min time. Properties of biosorbent (before and after biosorption process) were characterized by Fourier-transform infrared spectroscopy and scanning electron microscopy. The Freundlich and Langmuir isotherm models were used to represent biosorption mechanisms so that the results of the Langmuir model with $R^2 = 0.9473$, are in better agreement with experimental data. Thermodynamic study indicates the biosorption process is exothermic in nature and thermodynamic parameters, ΔH = −25.16 (kJ/mol) and ΔS = +55.146 (J/mol K) were obtained. Kinetic studies were undertaken to determine the biosorption mechanism. The $R^2$ value of the pseudo-second-order kinetic model was found close to unity ($R^2 = 0.994$) indicating that the outcomes can adapt to this model better than a first-order kinetic model with $R^2 = 0.923$. The most important impact of using Henna is the high performance for the removal of the Pb²⁺ ions (90% removal efficiency) as the possible reason is due to its irregular surface structures and its availability and low price.

Keywords: Biosorption; Henna; Lead ions removal; Thermodynamic study; Kinetics; Isotherm

1. Introduction

Heavy metal (e.g., Pb, Hg, Cr, Cd, etc) ions in industrial wastewaters can pollute groundwater resources [1]. Lead is a shiny, toxic, soft metal with atomic number of 82, atomic mass equal to 207.2 g mol⁻¹, and Van der Waals radius of 202 × 10⁻¹² m which is produced through industrial activities such as mining, pigments, and printing processes, car batteries, petroleum and plating industries [2]. Heavy metals ions are considered as the top environmental pollutants and can cause serious environmental problems. Due to the high solubilities of heavy metals ions in aqueous environments, living organisms can adsorb them. By entering the food chain, they can cause harmful effects on human and
animal’s health [3]. Thus, it is essential to remove heavy metals ions from wastewaters using conventional treatment processes to protect the environment [4].

There are various approaches for the development of technologies for wastewater treatment such as chemical precipitation [5], osmosis [6,7], ion exchange [8], filtration [9], electrochemical treatment [10], photocatalytic degradation [11,12], oxidation/reduction [13] and adsorption [14]. On the other hand, there are many limitations and problems in the application of these technologies, such as high-energy requirements, high costs, imperfect removal, and fabrication of toxic sludge. Adsorption process is strongly recommended for heavy metals ions removal as an effective and reasonably priced process. Selecting the right adsorbent with maximum adsorption characteristics and adsorption capacity and minimum consumption has been the subject of many studies in the last decade. In this regard, several research studies have been conducted to evaluate natural materials, agricultural waste materials, and agricultural products as adsorbents to remove Cd, Cr, Pb, Cu ions from aqueous solutions. [15–23] This approach is called biosorption and these natural adsorbents are well known as biosorbents that can be used without functionalization with high efficiency. Sometimes in order to make the biosorption process more suitable for industrial applications, natural materials are functionalized with numerous chemical reagents [24]. Local accessibility, technical possibility, being economical and technical applicability are the important factors in selecting these adsorbents for wastewater treatment processes. These natural materials have several compounds for instance lignin, cellulose, and pectin with different functional groups such as amino, carbonyl, hydroxyl, alkoxy, and carboxylic on their cells walls that have high affinities for the metal ions [25]. Some reported biosorption such as tomato waste and apple juice residue [26], pine nuts shell [27], banana peels [18], rice husk [28], etc have proven that these natural compounds can be considered appropriate choices to remove heavy metals ions from aqueous solutions in the adsorption process.

Henna is a plant 5–6 m long with green, gray, elliptical leaves that mainly grows in some areas of Iran and some tropical areas of Asia and Africa [29]. Numerous studies have given the idea to use Henna as a potential adsorbent for removing heavy metals ions [29–32]. It is decided to use Henna in the biosorption process because of its availability and its low price. The main objective was to use Henna leaves as biosorbent for removing Pb2+ ions from an aqueous solution. Also, effective parameters on the percentage removal of Pb2+ such as time, biosorbent amount, and pH were investigated and analyzed carefully. Thermodynamic and kinetic studies were conducted to determine the biosorption mechanism and thermodynamic parameters such as ΔH, ΔG, and ΔS. In order to study the interaction of Pb2+ ions with Henna, Freundlich, and Langmuir isotherm models [33,34] were applied. Furthermore, scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) studies were conducted before and after the biosorption process. This process is facile and cheap for the treatment of the aqueous environment from the hazardous effects of Pb2+ ions.

2. Experimental section

2.1. Equipment and materials

SEM was performed using a LEO1450 VP microscope with a scanning range from 0 to 30 keV. FTIR was recorded as KBr pellets using a PerkinElmer spectrophotometer (USA) in the 400–4,000 cm⁻¹ range. Pb2+ ions sorption capacity was measured using a Shimadzu Model AA-680 (Japan) atomic absorption spectrophotometer (AA). The solution pH was measured using a Metrohm pH meter model 691. Henna leaves powder was dried using a laboratory oven model OF-11E (JeioTech Company, South Korea). The solutions were stirred and heated using LABINCO mixer-heater model L-81. Pb(NO₃)₂ (Merck, Germany) was used as purchased. High-grade NaOH and HCl 37% (Merck, Germany) were used for the tests without further purification. Distilled water (Merck, Germany) was used in all experiments. Henna leaves were collected from Golbadestan, Yazd, Iran.

2.2. Preparation of biosorbent

Henna leaves powder was washed carefully with distilled water in order to remove dust and the soluble particles or the other contaminants present in it and it was then dried in an air oven at about 100°C for 24 h. Then, the powder was separated using an ASTM filter (70–100 mesh) and it was stored in a sample for subsequent experiments.

2.3. Batch biosorption studies

First, an aqueous solution of Pb(NO₃)₂ 55 ppm was prepared. Then, 100 mL of solution with pH (2–9) was poured into a 250 mL beaker [29]. The desired amount of biosorbent (0.1–1.2 g/L) was then weighed and shed in a beaker [29]. The mixture was intermixed using a mixer-heater (600 rpm) according to the desired temperature. After each test, the biosorbent was removed by filtration from the solution using the Whatman filter paper (no. 42). A few drops of HCl were added to the filtrated sample to prevent metal deposits. The samples were stored in a refrigerator at 4°C to be analyzed by the AA. Moreover, FTIR analysis was conducted to investigate the bonds position and changes of functional groups of biosorbent during the Pb2+ ions removal process. The surface morphology of Henna was investigated using SEM. All experiments were performed in a beaker with a volume of 250 mL at room temperature (24°C). Every test was carried out with 100 mL of solution. In order to investigate the effect of pH, solution of HCl or NaOH of 0.1 M was used.

2.4. Thermodynamic study, isotherm, and kinetic models

Different isotherm models have been developed for describing sorption equilibrium. In this study, Freundlich and Langmuir adsorption models [33,34] were used [17] to study the interaction of Pb2+ with biosorbent (Henna).

The Langmuir sorption isotherm [33] assumes that the adsorption takes place on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules [21] that is given by Eq. (1) [33]:
The adsorption kinetics can also be explained by the pseudo-second-order kinetic model that can be described by Eq. (6) [38]:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

where $k_2$ (g/mg min) is the pseudo-second-order rate constant, $q_e$ (mg/g) represents the amount of adsorbate adsorbed at any time $t$, and $q_e$ (mg/g) stands for the amount of adsorbate adsorbed in equilibrium.

3. Results and discussion

3.1. Thermodynamic study

The thermodynamic parameters at different temperatures are listed in Table 1 and are shown in Fig. 1. The negative values of $\Delta G$ and $\Delta H$ confirm the spontaneous and exothermic nature of the biosorption process of Pb$^{2+}$ ions from an aqueous solution onto Henna. In addition, considering the data of Table 1, decreased solution temperature would result in increased values of $\Delta G$ that is desirable from thermodynamics point of view. There is a physical biosorption between Pb$^{2+}$ and Henna because of the low value of $\Delta H$ (<40 kJ/mol). The positive value of entropy suggests spontaneity of the Pb$^{2+}$ ions biosorption process [35,39].

3.2. SEM study

SEM was used to investigate the morphology of the biosorbent before and after the metal ions removal process. Fig. 2 illustrates that the Henna is made up of irregular surface structures with some pores, which are very suitable for metal ions biosorption. It can be observed that the structure of treated Henna is aggregated after the metal ions removal process and indicates Pb$^{2+}$ biosorption and binding on its surface porosity [32].

3.3. FTIR analysis

The FTIR spectra is useful to study the characteristics of the biosorbent functional groups involved in Pb$^{2+}$ ions during biosorption processes. FTIR spectrum of Henna is illustrated in Fig. 3, comparing with that of the after Pb$^{2+}$ ions removal processes. The broadband around 3,409 cm$^{-1}$ is related to O-H functional group and its shift of band position to 3,400 cm$^{-1}$ indicates Pb$^{2+}$ ions binding to the O-H group. The strong band at 1,632 cm$^{-1}$ is assigned to the C=O inner coordination group. The strong band at 1,398 cm$^{-1}$ is assigned to the COO$^{-}$ mode.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-8.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>-8.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>-7.65</td>
<td>-25.166</td>
<td>+55.146</td>
</tr>
<tr>
<td>328</td>
<td>-7.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
functional group while shows a slight shift to 1,641 cm\(^{-1}\) indicating Pb\(^{2+}\) ions biosorption onto C=O functional group. Additionally, the band at 1,055 cm\(^{-1}\) can be attributed to the presence of C–O stretching vibration along with a shift to 1,035 cm\(^{-1}\) due to Pb\(^{2+}\) ions binding to C–O [32]. The new bands at 500–700 cm\(^{-1}\) are probably due to the presence of the (Pb–O) band [19]. These observations once more confirm that the functional groups existing in Henna provide an electron, which increases Pb\(^{2+}\) biosorption tendency [29–31].

3.4. Effect of pH

pH is a significant factor in the biosorption process that can affect the surface charge of the biosorbent, the amount of ionization, and speciation of the adsorbate. On the other hand, the sorption process is pH-dependent. Hence, biosorption efficiency was assayed in the pH range of 2–9 and adjusted using NaOH or HCl solution. The tests were carried out at a mixing rate of 600 rpm, 55 ppm initial concentration of Pb\(^{2+}\) ions, 0.55 g/L biosorbent, and 110 min time. Pb\(^{2+}\) ions removal as a function of pH is shown in Fig. 4a. Initially, at pH = 2, Pb\(^{2+}\) ions removal was 19.77%. By increasing the pH to 5.5, the efficiency of Pb\(^{2+}\) ions removal was improved and reached 72%. This trend is due to competition between Pb\(^{2+}\) ions and the protons on the active sites of biosorbent surface in high concentration of H\(^{+}\) ions. There are many protons at lower pH, which surround the binding sites of Henna and easily adsorb functional groups on its surface [19,21,40,41]. Increasing the pH to a higher value, 9, showed 45.2% Pb\(^{2+}\) ions removal, which was decreased since at higher pH, most of the functional groups are protonated and Pb\(^{2+}\) ions precipitate as they form hydroxides like Pb(OH)\(_{2}\) and Pb(OH)\(_{3}\) in the solution [19,21,40,41]. Considering the aforementioned results, pH = 5.5 was chosen as the optimum value and this state was used in the further steps of this study. This trend is in good agreement with the experimental results, which report a pH between 5–6 as the optimum value for the biosorption of Pb\(^{2+}\) ions onto several biosorbents [42].

3.5. Effect of biosorbent–adsorbate contact time

Fig. 4b demonstrates the effect of biosorbent–adsorbate contact time during the removal of the Pb\(^{2+}\) ions. These tests were carried out at a mixing rate of 600 rpm, pH of 5.5, 55 ppm initial concentration of Pb\(^{2+}\) ions, 0.55 g/L biosorbent, and time period of 20–200 min. The biosorption process involves two fast and slow steps.

With a biosorption time period of 0–110 min, the efficiency of Pb\(^{2+}\) ions removal was reached 80%. The initial
biosorption rate increased due to mass transfer driving force between the active sites of the biosorbent and the Pb$^{2+}$ ions, and it remained constant until 200 min. Since Pb$^{2+}$ ions occupied a portion of the active sites, the biosorption process remained constant (equilibrium) after 110 min. The parameters that affect the equilibrium adsorption time are the biosorbent’s physical properties. Notably, equilibrium states were reached following the saturation of active sites [26]. Consequently, the optimum biosorption time for Pb$^{2+}$ ions binding onto the Henna surface was estimated to be 110 min.

3.6. Effect of biosorbent amount

Biosorbent amount is an important factor that affects the metal removal process. Fig. 4c reveals the effect of biosorbent mass on the Pb$^{2+}$ biosorption at pH of 5.5, contact time of 110 min, 55 ppm initial concentration of Pb$^{2+}$ ions, and 0.1–1.2 g/L biosorbent amount. With the increase in biosorbent amount, Pb$^{2+}$ removal increased, maximizing at 90.5%. This might be due to an increase of sorptive surface area and the more availability of biosorption active sites [43,44]. Further increase in biosorbent does not enhance metal removal because the available metal ions are already adsorbed by the biosorbent [45]. Considering the abovementioned results, 1 g/L biosorbent was chosen as the optimum amount.

3.7. Biosorption isotherms study

Two isotherm models namely Langmuir [33] and Freundlich [34] were used in this study. The calculated
isotherm parameters are presented in Table 2 and Fig. 5. The $R^2$ coefficient is considered as a measure of agreement of experimental data with the isotherm models results [40]. In two cases, the $R^2$ values reveal the good applicability of both models for describing the biosorption of Pb$^{2+}$ ions onto the biosorbent. However, as can be seen, the Freundlich isotherm model [34] is not suitable ($R^2 = 0.8185$). The $R^2$ value for the Langmuir [33] model ($R^2 = 0.9473$) is higher than the other so that it displays a better fit compared to the Freundlich model [34]. This indicates that there is likely a homogeneous distribution of active sites on the biosorbent surface and monolayer biosorption (considering the initial assumptions of the Langmuir model [33]). A dimensionless constant separation factor or the equilibrium parameter $R_L$ specified by Eq. (7) can be used to represent the feasibility of the Langmuir isotherm model [33]:

$$R_L = \frac{1}{(1 + K_L C_0)}$$

where the Langmuir constant is represented by $K_L$, and the initial metal concentration is $C_0$ (mg/L). The $R_L$ value indicates whether the isotherm is unfavourable ($R_L > 1$), linear ($R_L = 1$), irreversible ($R_L = 0$), or favourable ($0 > R_L > 1$). The $R_L$ value obtained in this work during the biosorption of Pb$^{2+}$ by Henna was 0.17 indicating Pb$^{2+}$ ions biosorption onto the Henna surface is favorable.

Fig. 4. Effect of pH on biosorption of Pb$^{2+}$ ions from aqueous solution using Henna at mixing rate of 600 rpm, 55 ppm initial concentration of Pb$^{2+}$ ions, 0.55 g/L biosorbent, 110 min time and 2–9 pH range (a), Effect of time on biosorption of Pb$^{2+}$ ions from aqueous solution using Henna at mixing rate of 600 rpm, pH of 5.5, 55 ppm initial concentration of Pb$^{2+}$ ions, 0.55 g/L biosorbent and 20–200 min time period (b), Effect of biosorbent on amount of biosorption of Pb$^{2+}$ ions from aqueous solution using Henna at mixing rate of 600 rpm, pH of 5.5, contact time of 110 min, 55 ppm initial concentration of Pb$^{2+}$ ions and 0.1–1.2 g/L biosorbent amount (c).

Table 2
Calculated isotherm parameters

<table>
<thead>
<tr>
<th>Freundlich [34]</th>
<th>Langmuir [33]</th>
<th>Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln q_e$ vs. $\ln C_e$</td>
<td>$C_q/\eta_q = 0.5524\ln C_e + 1.5374$</td>
<td>Plot</td>
</tr>
<tr>
<td>$K_F = 4.65$ (L/mg)</td>
<td>$C_q/\eta_q = 0.5524\ln C_e + 1.5374$</td>
<td>Model</td>
</tr>
<tr>
<td>$n = 1.81$</td>
<td>$K_L = 0.0262C_q + 0.3058$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>$R^2 = 0.8185$</td>
<td>$\eta_q = 0.0262C_q + 0.3058$</td>
<td>Adsorption isotherm parameters</td>
</tr>
<tr>
<td>$q_{max} = 38.46$ (mg/g)</td>
<td>$K_L = 0.085$ (L/mg)</td>
<td></td>
</tr>
</tbody>
</table>

The $R^2$ values reveal the good applicability of both models for describing the biosorption of Pb$^{2+}$ ions onto the biosorbent.
3.8. Biosorption kinetics

The adsorption rate is one of the most important factors in an adsorption process [46]. The biosorption kinetics depends on the physical and chemical properties of the adsorbent, which affects the biosorption mechanism [36]. In this section, the kinetic study of the biosorption process was undertaken and the results of the pseudo-first-order kinetic model [37] were compared with the results of the pseudo-second-order kinetic model [38] to have an idea about the rate of adsorption and its nature such as chemical adsorption or physical adsorption. Curves for these models are shown in Fig. 6. Also, the results of the comparison

![Graph showing comparison of pseudo-first-order and pseudo-second-order kinetic models](image-url)

Fig. 5. Langmuir (a) and Freundlich (b) biosorption isotherms [33,34] for Pb²⁺ ions removal from aqueous solution using Henna.

![Graph showing comparison of pseudo-first-order and pseudo-second-order kinetic models](image-url)

Fig. 6. Pseudo-first-order [37] and pseudo-second-order [38] kinetic plots for biosorption of Pb²⁺ ions from aqueous solution using Henna.
between pseudo-first-order and pseudo-second-order kinetic models [37,38] are displayed in Table 3.

According to the obtained results, the $R^2$ value of the first-order kinetic model [37] is 0.923, indicating that the results are not fully consistent with the first-order kinetic model [37]. On the other hand, the $R^2$ value of the pseudo-second-order kinetic model [38] is close to unity ($R^2 = 0.994$) indicating that the outcomes are more able to adapt to this model. Table 3 shows that the experimental value of $q_e$ ($q_e = 8$) is closer to the value of $q_e$ obtained from the pseudo-second-order model [38] ($q_e = 8.25$) rather than the value of $q_e$ obtained from the pseudo-first-order model [37] ($q_e = 6.42$). This indicates that the chemical sorption incorporating valence forces through the exchange or sharing of electrons between Henna and Pb$^{2+}$ ions is likely the rate-limiting stage in the biosorption process [23,26].

### 3.9. Proposed removal mechanism

There are many functional groups on the cell wall of the biosorbents, such as amine (NH$_2$), carboxyl (C=O), hydroxyl (R–OH), and sulfhydryl that carry out the removal of metal ions from the aqueous environment. These functional groups can serve as coordination and electrostatic interaction sites to adsorb metal ions. As mentioned in the FTIR section, OH and C=O functional groups get involved in Pb$^{2+}$ ions removal during biosorption process. A solid phase (Henna) and an aqueous phase containing lead ions are involved in the process. The following is a brief description of the proposed adsorption mechanism [17]:

- Ion exchange: $2(R'OH) + Pb^{2+} \leftrightarrow (R'O) -, Pb + 2H^+$
- Hydrogen bonding: $(R'OH) + Pb^{2+} \leftrightarrow (R'OH)-Pb^{2+}$

where $R'$ represents the matrix of Henna.

### 3.10. Other studies

In recent years, various studies have been carried out using biosorbents to remove toxic metals from an aqueous environment, especially Pb$^{2+}$ ions. A few examples of them with their experimental conditions are given in Table 4 [47–51]. Farooq et al. [47] reported the usage of powdered straw from Triticum aestivum for 80% removal of Pb$^{2+}$ ions from aqueous solution. Abdelfattah et al. [48] worked on peanut husk powder for the removal of some metal ions like Pb$^{2+}$ with over 90% removal efficiency from their aqueous solutions. Biosorption of Pb$^{2+}$, Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ ions using agricultural waste, unmodified coconut husk from industrial wastewater with 72.4% removal of Pb$^{2+}$ ions was reported by Lata’s group [49]. There is a study on the use of fungus Absidia cylindrospora against three trace metals: Cd$^{2+}$, Cu$^{2+}$, and Pb$^{2+}$ having 59% removal efficiency for Pb$^{2+}$ ions [50]. Investigation of removal efficiency of Pb$^{2+}$ (over 69% removal efficiency) and Cd$^{2+}$ from their aqueous solutions using Lactobacillus acidophilus was carried out by Afraz et al. [51] to optimize the operational parameters. Their results are very promising indicating the good capabilities of these natural materials as adsorbents to replace other types of adsorbents. Comparing the results of this work with other results yields two points: First, the high performance of biosorbent for the removal of the Pb$^{2+}$ ions (90% removal efficiency) using Henna after 110 min, which the possible reason is irregular surface structures with some pores of adsorbent, and second important point is the availability and low price of Henna.

### 4. Conclusion

This work confirms the application of Henna as an efficient biosorbent for removing Pb$^{2+}$ ions from an aqueous solution. Different tests were conducted to assess the effect of process variables including biosorbent amount (0.1–1.2 g/L), pH of the solution (2–9), and time (20–200 min). Maximum Pb$^{2+}$ biosorption reached 90% at pH 5.5, 55 ppm initial concentration of Pb$^{2+}$ ions, 1 g/L biosorbent amount, and 110 min time. Thermodynamic results reveal the endothermic nature of the biosorption of Pb$^{2+}$ ions from an aqueous solution using Henna.
isotherm models [33,34] were used to fit the experimental data. The data are in better agreement with the results of the Langmuir isotherm model [33] considering a better $R^2$ value. FTIR and SEM techniques clearly show that Pb$^{2+}$ ions are stabilized and coated on the surface of Henna. The pseudo-second-order kinetic model [38] is a suitable model for representing the kinetics of the studied system. From the obtained results, it is concluded that this water treatment method can offer several benefits such as facile and low-cost rout that makes it an interesting method for applying and extending this biosorbent for removing heavy metals from an aqueous environment.

References


