Kinetics and Isotherms of a Green Method for the Sorption of Metal Ions from Aqueous Solution

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Abstract. Owing to their toxicity, the existence of heavy metals in the environment has become a major global concern. In this study, the ability of albizia-lebbeck tree leaves (ALTL) as green and low cost adsorbent to remove Pb²⁺, Zn²⁺ and Cd²⁺ from Synthetic wastewater by adsorption was investigated. The initial metals’ concentrations of 10-80 mg/l, adsorbent dosage of 0.3-1.0 gm, pH of 3-8, contact time of 30-240 min, and shaking speed of 200 rpm, have been studied by batch adsorption technique. Four ranges of adsorbent particle size were tested: 75-150; 150-300; 300-600; 600-1000 μm. Five different temperatures (20, 30, 40, 50 and 60°C) were selected to demonstrate the influence of temperature on metals’ adsorption onto ALTL. Langmuir and Freundlich models were used to analyze the experimental data. Equilibrium data fitted well with the Freundlich isotherm model with maximum adsorption capacity of 9.124 mg/g at 20°C for metals’ concentration of 40 mg/L. Pseudo-first-order and pseudo-second-order equations were utilized for analysis of the kinetic data. The second-order model was fitting very well with the experimental data. Thermodynamic parameters like entropy, enthalpy and Gibbs free energy changes were estimated to determine the spontaneity of the sorption process. The results revealed that the ALTL adsorbent performed good removal of metals.

Keywords: Green adsorbent; Metal ions; Sorption; Kinetics; Isotherms.

1. Introduction

Different types of heavy metals like lead, cadmium, copper, zinc and mercury, which are the result of anthropogenic activities, were revealed in industrial wastewaters. These metals existing at low concentration, will be hazardous to human health and the ecosystem and because they are non-biodegradable, it is difficult to remove them. Heavy metals represent an ecological burden that brings attention. Furthermore, the toxicity of all metals annually is greater than collective total toxicity of the annually discharged radioactive and organic wastes [1].

As an attractive and efficient treatment, the adsorption method can be utilized for removal of heavy metals from wastewater [2], in addition this method has a characteristic quality that surpasses other treatment modes because of its clean operation which is sludge-free, but the cost of manufacturing and regeneration of adsorbent material are very high [3]. Therefore, it is important to find an inexpensive mode of adsorption. Thus, efforts are made to discover a low-cost substitute adsorbent material with high treatment effectiveness [4]. The bio-sorption is a favorable technique for the adsorption of heavy metals.
metals from aqueous solutions, particularly when adsorbent is produced from biological sources such as agricultural wastes, lignocelluloses carbonaceous materials, plant wastes, and natural resources [5].

The current study aims at investigating ALTL as green and low-cost adsorbent for removal of lead, zinc and cadmium in wastewater. The parameters like time, pH, adsorbent dosage, initial concentration, temperature and adsorbent particle size were studied. The adsorption isotherms and kinetic data are further demonstrated to understand the adsorption mechanism of metal ions onto ALTL. It also involves a thermodynamic study on removal of these metals.

2. Methodology

2.1 Materials

2.1.1 Preparation of Simulated Wastewater

To simulate the water's lead, zinc and cadmium contamination, three salts of Pb(NO₃)₂, ZnCl₂ and Cd(NO₃)₂·4H₂O (manufactured by Analar Company, England) were dissolved in distilled water to prepare three solutions of 1000 mg/L of lead, zinc and cadmium ions, respectively. These solutions were used to prepare the other desired experimental solutions, five concentrations (10, 20, 40, 60 and 80 mg/L) of every metal ion were prepared using equation (1). Metal ion concentrations were measured by using AAS(GBC, SensAA, Australia). The following equation was adopted in the present study to prepare the desired concentrations [6]:

\[ W = V \times C_i \times \frac{M_{wt}}{At_{wt}} \]  

where \( W \) : the metal salt weight (mg), \( C_i \): required metal ion concentration in the solution (mg/L), \( V \) : solution volume (L), \( At_{wt} \) : atomic weight of metal ion (g/mol), \( M_{wt} \) : molecular weight of metal salt (g/mol).

2.1.2 Preparation of Adsorbent

Albizia lebbeck tree leaves (ALTL) were collected from the trees in the campus of Wasit University (Iraq) to be prepared and used in the experiments. Preparation of ALTL adsorbent included some steps starting from cutting tree leaves and cleaning using distilled water to wash ALTL three times to remove impurities. After washing, leaves were dried in an oven for three hours at 110°C. In order to obtain small volumes less than 1000 microns, dried ALTL was grinded in a mill. The last step of the preparation process is sieving to get four ranges of particle size (75-150, 150-300, 300-600 and 600-1000 μm).

2.2 Experimental Procedure

Batch experimental mode was conducted to obtain the equilibrium data. Five initial concentration solutions (10, 20, 40, 60 and 80 mg/L) of every metal ion (lead, zinc and cadmium) were used. The solutions were adjusted at pH of 3, 5, 6, 7 and 8. Amounts of 0.3, 0.5, 0.7, 0.9 and 1.0 g of adsorbent (ALTL) were placed in five flasks of 250 ml volume, and five samples of 100 ml of metal ion solution were added in these flasks. The flasks were placed in the orbital shaker (incubated AAH23212K, model S1-600R, Korea) and mixed continuously for 30, 60, 90, 120, 150, 180, 210 and 240 min at 200 rpm speed and temperature of 20°C. The solution and adsorbent were separated by filter paper. Concentration of metal ions in the filtrable solution was measured by using AAS. Adjustment of the pH was achieved by adding a solution of NaOH (0.1N) or HCl (0.1N) and recording pH continuously using a pH meter (Type EZDO model 6011, China) until reaching the desired value. The uptake percentage was estimated by using the following equation.

\[ \text{% uptake} = \left[ \frac{(C_i - C_f)}{C_i} \right] \times 100 \]  

where \( C_i \) = initial concentration of metal (mg/l), and \( C_f \) = final concentration of metal (mg/l).

3. Results and Discussion

3.1 Factors affecting the adsorption performance

Different factors affected the adsorption performance of Pb²⁺, Zn²⁺ and Cd²⁺ in aqueous solution on the ALTL.
3.1.1 pH
For the purpose of making the optimum sorption of metal ions on the solid-liquid interface at the active sites at the surface of sorbent, it is necessary to study the change in initial pH value [7]. Figure 1 illustrates the influence of pH on metals ions uptake by ALTL. As shown in this figure, solution pH is in the range of 3 to 8. The uptake efficiencies of metals ions are increased slowly with increasing initial pH, but they are decreased after pH 7.

When pH level increases from 3 to 7 the adsorbed amount is increased from 2.8 to 4.6 mg/g, 2.2 to 3.6 mg/g and 2.0 to 3.6 mg/g for Pb\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\) respectively. At pH = 7, the solubility of the Pb(NO\(_3\))\(_2\), ZnCl\(_2\) and Cd(NO\(_3\))\(_2\)-4H\(_2\)O are very high, thus the Pb\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) are the main present species. Rising in the value of pH leads to decrease the solubility of the above compounds and they are starting to precipitate. The sedimentation performs a substantial function in the uptake of metals from water [8]. Accordingly, all experimental tests were carried out at pH less than or equal to 8. The adsorption of Pb\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) on the surface of the adsorbent is basically affected by the surface charge on ALTL as adsorbent which is affected by the solution pH. Therefore, the high uptake efficiency of metal ions may be because of the attraction electrostatic force between adsorbate and adsorbent [9]. On the other hand, at lower pH, the competition of hydrogen ions to substitute in unoccupied adsorption sites of ALTL will lead to a comprehensive disharmony of metal ions [10]. According to their ion concentration in the aqueous solution and the ion transfer rate, the H\(^+\) ions are more easily adsorbed than metal ions. Additionally, the H\(^+\) ions surround the surface of the sorbent that prohibit Pb, Zn and Cd from reaching the binding sites of the adsorbent, therefore, the adsorption process will be unfavorable at low pH [11].

3.1.2 Contact time
Figure 2 shows the influence of agitation time on lead, zinc and cadmium uptake efficiency. The uptake of metal ions was calculated at different shaking time keeping the other parameters (pH, initial concentration, adsorbent dosage, agitation speed and temperature) constant. During the experiments, 100 ml of each metal solution with initial concentration of 40 mg/L has been investigated with 0.5 g of adsorbent at 20°C temperature and 200 rpm agitation speed. The optimum pH (pH=7) has been dedicated. The sorption of metal ions increases as the contact time increases. The maximum percentages of metal uptake were 57.5% for lead and 45% for zinc and cadmium, which was attained at a shaking time of 210 min. The rapid increase occurs before this time due to the large number of available vacant locations at the primary period of the sorption process. The equilibrium time of 210 min was adopted for the other sequential experiments.

3.1.3 Adsorbent Dosage
Figure 3 depicted the effect of ALTL dosage with particle size of 75-150 mm on the uptake efficiency of metals under other fixed operational conditions. When the weight of ALTL increases from 0.3 to 1.0 g at initial metal concentration of 40 mg/L, the uptake percentage increased from 55-72.5, 35-60, and 30-65 for Pb, Zn and Cd, respectively. The reason for that is attributed to the adsorption capacity of ALTL which is relying on the activity at the surface. Namely, the number of adsorption sites available for metal-surface interactions increases according to the specific surface area [12]. Therefore, the uptake efficiency of metal ions from solution increases with increasing the amount of ALTL. On the other hand, the cause probably related to gathering of the ALTL surface area which is ready to metal ion adsorption and increasing in diffusion track length. The results agreed with [13].

3.1.4 Initial Concentration
Initial concentration is one of the parameters investigated in this study. The changing of uptake efficiency with initial concentration is shown in figure 4. Initial concentration was varied from 10 to 80 mg/L. The other parameters which are pH, time, agitation speed, adsorbent dosage, temperature were kept fixed. As shown graphically, the change of uptake efficiency with variation of initial concentration was from 65 to 50%, 55 to 40% and 57.5 to 42.5% for Pb, Zn and Cd, respectively. It is obvious that the efficiency decreases with the increase in initial concentration. Higher uptake percentage was at lower concentration. This attributed to the vacant binding locations available on the ALTL adsorbent. At high
metal concentrations all binding locations are occupied, therefore, the uptake efficiency reduced with increasing concentration.

3.1.5 Temperature
Nassar 2012 [14] illustrate that the temperature is an important factor for the adsorption technique. The viscosity of the solution decreases when the temperature increases, which leads to increase in the diffusion rate of the metal molecules at the layer of external boundary, then the capacity of adsorption increases. Thus, the information of enthalpy, entropy and Gibbs free energy changes accompanying the adsorption can be provided by studying the effect of temperature on the adsorption process. In the present study, influence of temperature factor on the adsorption process was studied as depicted in figure 5. Experiments were conducted at initial concentrations of lead, zinc and cadmium of 40 mg/L at 210 min agitation time and 0.5g amount of adsorbent at pH 7 at five different temperatures (20, 30, 40, 50 and 60°C) under a fixed agitation speed of 200 rpm. It is obvious that the capacity of adsorption increases when the temperature increases from 20 to 60°C. The amount of metal ions adsorbed is increased with increasing the temperature of the solution. The uptake efficiency increased from 58 to 73 % for lead, while the uptake range for zinc and cadmium was from 45 to 63 %.

3.1.6 Adsorbent Particle Size
Investigation on the effect of particle size of ALTL adsorbent was carried out by testing four ranges of particle sizes (75-150, 150 -300, 300-600 and 600-1000 μm). As illustrated in figure 6 the uptake efficiency increased with decreasing average particle size of ALTL. The maximum uptake of metals occurred at the lower range of particle size (75-150 μm). The reason behind that is the smaller particle...
size of adsorbent lead to increase in surface area, additionally display relatively greater number of available binding sites. Therefore, this increases the removal percentage of metals.

3.2 Adsorption Isotherms

3.2.1 Langmuir Isotherm Model

It is monolayer coverage of surfaces and supposes that sorption happens in an adsorbent which is structurally homogenous, and all the sorption locations are energetically similar. The following expression represents the saturated monolayer curve [15]:

\[
\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0}
\]

where \( C_e \) is the metal concentration in solution at equilibrium (mg/l), \( Q_e \) is the metal ion amount adsorbed on adsorbent (mg/g). The symbols \( b \) and \( Q_0 \) are the Langmuir constants which represent the constants at equilibrium for the adsorbate-adsorbent equilibrium and capacity of monolayer. Values of \( b \) and \( Q_0 \) were obtained from the slope and intercept of the Langmuir plot figure 7.

3.2.2 Freundlich Isotherm Model

Freundlich isotherm equation is a concept that the metal ions uptake occurs on the heterogeneous surfaces of multilayer sorption, the adsorbed amount of metal increases by increasing the adsorbate concentration [15]. The Freundlich model is:

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e
\]

where \( Q_e \) is the solute concentration in the bulk solution at equilibrium (mg/l), \( Q_e \) is the solute amount adsorbed per unit mass of adsorbent (mg/g), \( K_f \) is a constant that refers to the relative sorption capacity of the adsorbent (mg/g), \( 1/n \) is a constant that refers to the adsorption intensity. The constants \( n \) and \( K_f \) indicate the adsorption extent and nonlinearity between concentration and solution, respectively.

The linear plotting of the Freundlich model can be obtained by drawing \( \log Q_e \) versus \( \log C_e \), the coefficients of adsorption could be determined from this plot (figure 8). Table 1 shows all constants which are obtained from the Langmuir and Freundlich isotherm models.

3.3 Adsorption Kinetics

Valuable information about the adsorption mechanism is provided by kinetics of adsorption [16]. Rate of uptake in adsorption process, which is desired for choosing best operation conditions in batch process, can be explained with kinetics of adsorption [17].

3.3.1 Pseudo First-Order Reaction Kinetic

The simple equation of reaction kinetics for pseudo first-order is [18]:

\[
\frac{dQ}{dt} = K \cdot Q
\]
\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]  
(5)

where \( q_e \) is the heavy metal amount adsorbed at saturation (mg/g), \( q_t \) is the heavy metal amount adsorbed at time \( t \) (mg/g), \( k_1 \) is the rate constant of the first-order adsorption. Drawing of \( \ln (q_e - q_t) \) versus \( t \) permits estimation of the rate constant \( k_1 \) and \( q_e \) (figure 9).

\[ y = 0.1403x + 5.3306 \\
R^2 = 0.5157 \\
\]
(a) Lead

\[ y = 0.1363x + 9.4981 \\
R^2 = 0.3485 \\
\]
(b) Zinc

\[ y = 0.1096x + 4.233 \\
R^2 = 0.4227 \\
\]
(c) Cadmium

\[ y = 1.5977x + 1.2209 \\
R^2 = 0.847 \\
\]
(a) Lead

\[ y = 1.3801x + 1.3196 \\
R^2 = 0.8447 \\
\]
(b) Zinc

\[ y = 0.836x - 0.3971 \\
R^2 = 0.7544 \\
\]
(c) Cadmium

**Figure 7.** Langmuir adsorption isotherm for removal of heavy metals by ALTL adsorbent.

**Figure 8.** Freundlich adsorption isotherm for removal of heavy metals by ALTL adsorbent.

| Metal | \( q_{\text{max}} \) (mg/g) | \( K \) | \( R^2 \) | \( n \) | \( 1/n \) | \( R^2 \) | \( K_f \) [(mg/g) (L/mg)\(^{1/n} \)] |
|-------|-----------------|------|-------|------|------|-------|---------------------|
| Pb    | 7.127           | 0.025| 0.516 | 0.626| 1.597| 0.847 | 0.060               |
| Zn    | 7.336           | 0.014| 0.348 | 0.724| 1.380| 0.844 | 0.047               |
| Cd    | 9.124           | 0.025| 0.422 | 1.570| 0.636| 0.754 | 0.460               |

**Table 1.** Langmuir and Freundlich Parameters.
3.3.2 Pseudo Second-Order Reaction Kinetic

Reaction kinetic of pseudo second order can be expressed as in equation (6) [19]:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  \hspace{1cm} (6)

where \( q_e \) is the equilibrium adsorbed amount, \( q_t \) is the metal amount adsorbed at time \( t \), and \( k_2 \) is the rate constant for pseudo second order (g/mg h). As in the reaction kinetic of pseudo first order, \( q_e \) and \( k_2 \) can be estimated from the slope and intercepts of drawing \( t/q_t \) versus \( t \) (figure 10).

**Figure 9.** Pseudo first order for sorption of heavy metals ions onto ALTL at 20°C, and pH 7.

**Figure 10.** Pseudo second order for sorption of heavy metals ions onto ALTL at 20°C, and pH 7.
Table 2 reveals the estimated rate constants ($k_1$, $k_2$), heavy metals adsorbed amounts per unit mass adsorbed ($q_e$) and correlation coefficients ($R^2$) of linear regression for reaction kinetics of pseudo first order and pseudo second order. In the reaction kinetic of pseudo second order, estimated values of $q_e$ are nearer to experimental values of lead, zinc and cadmium. Moreover, as illustrated in table 2, second-order kinetic studies have the higher correlation coefficients.

| Metal | $q_e$-experimental (mg/g) | $q_e$-calculated (mg/g) | $K_1$ (min$^{-1}$) | $R^2$ | $q_e$-calculated (mg/g) | $K_2$ (min$^{-1}$) | $R^2$ |
|-------|--------------------------|------------------------|-------------------|-------|------------------------|-------------------|-------|
| Pb    | 4.6                      | 1.90                   | -0.008            | 0.947 | 4.90                   | 0.008             | 0.988 |
| Zn    | 3.6                      | 1.15                   | -0.006            | 0.583 | 3.70                   | 0.015             | 0.979 |
| Cd    | 3.6                      | 1.93                   | -0.008            | 0.732 | 3.91                   | 0.007             | 0.974 |

3.4 Sorption Thermodynamics

For best understanding the effect of temperature on adsorption, and to know the kind of adsorption process, sorption of metals was studied at various temperatures (293 to 333°K). Thermodynamic parameters like Gibbs free energy changes ($\Delta G^0$), enthalpy changes ($\Delta H^0$) and entropy changes ($\Delta S^0$) were used to set the spontaneity of sorption process. Using equilibrium constants variation with temperature, the above parameters can be determined. The change of Gibbs free energy of the sorption reaction can be estimated by the following equation [20]:

$$\Delta G^0_{ads} = -RT \ln (K_d)$$ (7)

where $R$ is the universal gas constant ($R = 8.314$ J/mol K), $\Delta G^0$ is the standard Gibbs free energy change (J/mol), $T$ is the absolute temperature (°K), and $K_d$ is the coefficient of distribution (dimensionless).

$\Delta S^0$ and $\Delta H^0$ can be determined from van’t Hoff equation [20]:

$$\ln (K_d) = - \frac{\Delta H^0_{ads}}{RT} + \frac{\Delta S^0_{ads}}{R}$$ (8)

The enthalpy and entropy values were obtained from the slope and intercept of $\ln K_d$ versus 1000/T (figure 11). Table 3 recapitulates the coefficient of distribution for a series of experiments at various temperatures.

![Figure 11](image-url). Coefficient of Distribution versus 1000/Temperature.
The negative values of change in enthalpy ($\Delta G$) and entropy ($\Delta S$) indicate the spontaneity of the adsorption process. From the results of this study, it can be concluded that ALTA has the ability to remove these metals from water. The negative $\Delta G$ values become more negative supported that the adsorption process is preferable with increasing temperature.

The following well-known equation was adopted to calculate Gibbs free energy ($\Delta G$):

$$G = \Delta H - T\Delta S$$

(9)

The estimated values of the thermodynamic parameters ($\Delta H^\circ$, $\Delta S^\circ$, $\Delta G^\circ$) for the adsorption of metal ions on ALTL are shown in table 4. The negative values of change in enthalpy ($\Delta H^\circ$) indicate an endothermic adsorption process, while the positive entropy change values ($\Delta S^\circ$) refer to an increase in the randomness of ions at the solid/solution interface during adsorption process [21].

Temperature and consumed heat are the main factors that $\Delta G^\circ$ depends on. Negative values of $\Delta G^\circ$ point out feasibility and spontaneity nature of the ions sorption and getting of an additional stable energy level after adsorption process of metal ions [22]. As illustrated in table 4, the free energy change for all adsorption process is negative at all temperature ranges, referring that the adsorbent has a greatest predilection for metal ions. When the temperature is increased, $\Delta G^\circ$ values become more negative supported that the adsorption process is preferable with increasing temperature.

### Table 4. Thermodynamic parameters for adsorption of Pb, Zn and Cd on ALTL.

| Metal | $\Delta H$ (J/mol) | $\Delta S$ (J/mol K) | $\Delta G$ (KJ/mol) |
|-------|-------------------|----------------------|---------------------|
|       | 293 K             | 303 K                | 313 K               | 323 K | 333 K |
| Pb    | -1.729            | 4.556                | -1.337              | -1.382 | -1.428 | -1.473 | -1.519 |
| Zn    | -1.893            | 4.658                | -1.367              | -1.413 | -1.460 | -1.506 | -1.553 |
| Cd    | -1.715            | 3.953                | -1.160              | -1.199 | -1.239 | -1.279 | -1.318 |

4. Conclusion

In this study, the optimum conditions for removal of heavy metals (Pb$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$) on low-cost adsorbent have been investigated in batch mode experiments. The best operating conditions were 40 mg/l initial metal concentration, 0.5 gm dosage of adsorbent, neutral pH, 210 min contact time, and particle size 75-150μm. Langmuir and Freundlich isotherms were analyzed with the experimental data. Equilibrium data were fitted well with the Freundlich model with maximum adsorption capacity of 7.127, 7.336 and 9.124 mg/l for the above three metals, respectively, at 20°C. The kinetic data is analyzed using pseudo first-order and pseudo second-order equations. The experimental data was fitted very well with the pseudo second-order kinetic model. The obtained results reveal that the ALTL adsorbent performed good uptake removal 72.5%, 60% and 65% for lead, zinc and cadmium, respectively. Potentially, ALTA can be used as a solid-phase extraction material for the initial concentration, separation and removal of metals from water. The negative $\Delta G^\circ$ value was referring to the spontaneity nature of the adsorption process. From the results of this study, it can be concluded that ALTA has the ability to remove these metals from water.

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