

Full Length Research Paper

Biosorption of copper(II) and lead(II) ions from aqueous solutions by modified loquats (Eriobotrya japonica) leaves (MLL)

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A modified loquat leaves (MLL) for the removal of copper(II) and lead(II) ions from aqueous solutions has been investigated. The biosorption of copper(II) and lead(II) ions was found to be dependent on solution pH, initial metal ion concentrations, biosorbent dose, contact time, and temperature. The experimental equilibrium biosorption data were analyzed by three widely used two-parameters; Langmuir, Freundlich, and Temkin isotherm models. Langmuir isotherm model provided a better fit with the experimental data than other models by high correlation coefficients $R^2$. Kinetic studies showed that pseudo-second-order described the biosorption experimental data better than the pseudo-first order kinetic model.

Key words: Biosorption, loquat leaves, copper, lead, adsorption isotherms, kinetic.

INTRODUCTION

Copper(II) and lead(II) ions have been released to the environment through electrical wiring, air conditioning tubing, plumbing, electroplating and pigments. There is a growing demand to find relatively efficient, low cost and easily available adsorbents for the adsorption of toxic heavy metals. Different agro-wastes have been investigated for the biosorption of Cu(II) and Pb(II) ions such as sugar beet pulp treated with NaOH and citric acid (Altundogan et al., 2007), *pinus pinaster* bark (Vázquez et al., 1994) apple residues (Lee et al., 1998) agricultural waste sugar beet pulp (Aksu and İsoğlu, 2005), black carrot residues (Güzel et al., 2008), acid treated sugar cane bagasse (Sousa et al., 2009), dehydrated wheat bran (Özer et al., 2004), wheat shell (Basici et al., 2004), sour orange residue (K hormaei et al., 2007), bagasse pith based sulphurised activated carbon (Krishnani and Anirudhan, 2008), chemically modified orange peel (Ning-chan et al., 2009), lemon peel (Bhatanagar et al., 2010), pine cone powder (Ofomaja et al., 2010), biomatrix from rice husk (Krishnani et al., 2008).

In the present work, We have studied the potential of copper(II) and lead(II) biosorption on a agro material which is a modified loquat leaves (MLL) coming from loquat fruit waste. Results from this study can be used to assess the utility of MLL for copper(II) and lead(II) removal from water and industrial wastewaters.

MATERIALS AND METHODS

Adsorbent

The raw loquat leaves (LL) was collected from a local plantation, Amman, Jordan. This agricultural waste was thoroughly rinsed with water to remove dust and soluble material. Then it was allowed to dry at room temperature. The dried waste was grounded to a fine powder in a grinding mill (Retsch RM 100) and sieved to get size fraction <44 µm. The fine powder was then treated with sodium hydroxide (0.2 mol/L) to improve the biosorption capacities to copper and lead ions. For this purpose, 100 gram of dried LL soaked in solution 500 mL NaOH (0.2 mol/L) for 24 h. By filtration, the sodium hydroxide modified loquat leaves (MLL) was washed with de-ionized water until the pH value of the solution reached 7.0, and then dried in an oven at 60°C for 24 h.

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Materials

All the chemicals used were of analytical reagent (AR) grade. Stock solutions of 1000 mg/L of copper(II) and lead(II) was prepared from copper nitrate [Cu(NO₃)₂*3H₂O] and lead nitrate [Pb(NO₃)₂], respectively using double distilled water. Desired test solutions of Cu(II) and Pb(II) ions were prepared using appropriate subsequent dilutions of the stock solution. The range of concentrations of Cu (II) and Pb (II) ions prepared from standard solution varies between 10 and 100 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

Analysis

The concentrations of Cu(II) and Pb(II) ions in the solutions before and after equilibrium were determined by AAS6300 Atomic absorption spectrometer (Shimadzu, Japan). The pH of the solution was measured with a WTW pH meter using a combined glass electrode. Fourier Transform Infrared Spectroscopy, FTIR (IR Prestige-21, Shimadzu, Japan) was used to identify the different chemical functional groups present in the modified loquat leaves (MLL). FTIR analyses also used to determine the functional groups which are responsible for the metal binding with MLL. The analysis was carried out using KBr and the spectral range varying from 4000 to 400 cm⁻¹.

Biosorption experiments

Batch biosorption experiments were conducted by mixing biosorbent with Cu(II) or Pb(II) ion solutions with desired concentration in 250 ml glass flask. The glass flasks were stoppered during the equilibration period and placed on a temperature controlled shaker at a speed of 120 r/min. The effect of pH on the equilibrium biosorption of Cu(II) and Pb(II) was investigated by mixing. The amount of biosorption was calculated based on the difference between the initial (C₀, mg/L) and final concentration (Cₑ, mg/L) in every flask, as follows:

$$qₑ = \frac{C₀ - Cₑ}{M} \times V \tag{1}$$

Where $qₑ$ is the metal uptake capacity (mg/g), $V$ the volume of the metal solution in the flask (L) and $M$ is the dry mass of biosorbent (g).

RESULTS AND DISCUSSION

FTIR analysis

To investigate the functional groups of MLL and metal loaded LL, a FT-IR study was carried out and the spectra are shown in Figure 1a and b. The modified loquat leaves (MLL) displays a number of absorption peaks, reflecting the complex nature of the loquat leaves. A strong and broad peak at 3410 cm⁻¹ results due to the stretching of the N–H bond of amino groups and indicative of bonded hydroxyl group. A change in peak position to 3360 cm⁻¹ Figure 1b in the spectrum of the metal loaded loquat leaves, indicates the binding of copper or lead with amino and hydroxyl groups (Nakbanpote et al., 2007; Munagapati et al., 2010). The strong absorption peak at 2927 cm⁻¹ could be assigned to –CH stretching vibrations of –CH₃ and –CH₂ functional groups. The peak at 1621 cm⁻¹ indicates the fingerprint region of CO, C–O and O–H groups, which exists as functional groups of MLL. Shifting of this peak to 1651 cm⁻¹, indicated involvement of these groups in metal binding. The region between 1520 and 1000 cm⁻¹ is the fingerprint region, OH, and C–H bending vibration and C–O stretching vibration absorption bands. The absorption peaks at 1442, 1377 and 1319 cm⁻¹ could be attributed to the presence of C–O stretching,. These peaks were shifted to 1519, 1450 and 1373 cm⁻¹, respectively. The intense band at 1060 cm⁻¹ can be assigned to the C–O of alcohols and carboxylic acids. The shift of the peak from 1060 to 1035 cm⁻¹ also suggests the involvement of C–O group in binding Cu (II) (Nakbanpote et al., 2007; Munagapati et al., 2010). The shifts in the absorption peaks generally observed indicate the existence of a metal binding process taking place on the surface of the loquat bark.

Effect of pH

To find the optimal pH for the effective biosorption of Cu(II) and Pb(II) onto MLL It was found the uptake of metal ions increased with the increase in pH from 2.0 to 6.0. At lower pH values Cu(II) and Pb(II) removal was inhibited, possibly as a result of the competition between hydrogen and metal ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the active sites in MLL would be exposed, increasing the negative charge density on the MLL surface, increasing the attraction of metal ions with positive charge and allowing the biosorption onto the MLL surface. In this study, the Cu(II) and Pb (II) ions at pH 6.0 would be expected to interact more strongly with the negatively charged binding sites in the biosorbent, Figure 2. The decrease in Cu(II) and Pb(II) biosorption above pH 6.0 was probably due to the precipitation of Cu(II) and Pb(II) ions as copper and lead hydroxides and not due to biosorption. As a result, the optimum pH for copper and lead ions biosorption was found as 6.0 and the other biosorption experiments were performed at this pH value.

Effect of contact time

The data obtained from the biosorption of Cu(II) and Pb(II) ions onto MLL powder showed that a contact time of 60 min was sufficient to achieve equilibrium, Figure 3 and the biosorption did not change significantly with further increase in contact time. Therefore, the uptake, $qₑ$ (mg/g) and the adsorbed metal concentrations $Cₑ$ (mg/L) at the end of 60 min are given as the equilibrium values
and the other biosorption experiments were conducted at this contact time of 60 min.

It was found up to 400 mg/L initial metal concentrations, the amount of adsorbed Cu(II) and Pb(II) ions per unit mass of the MLL increased. These data is reasonable and indicating the presence of many active sites on MLL surface available to bind with Cu(II) and Pb(II) ions at low concentration. Beyond the initial metal ion concentrations 400 mg/L, the adsorption capacity of MLL biosorbent remained relatively constant. This is probably due to saturation of metal ion binding sites at MLL surface at concentration higher than 300 mg/L.

**Effect of adsorbent concentration**

The adsorbent concentration effect on the percent removal at equilibrium conditions was investigated. It was observed that the amount of Cu(II) and Pb(II) biosorbed varied with varying adsorbent concentration. The amount
of Cu(II) and Pb(II) adsorbed increases with an increase in adsorbent concentration from 0.1 to 0.5 g. The percentage of metal removal was increased from 60.32 to 98.88% for an increase in MLL concentration from 0.1 to 0.5 g at initial concentration of 40 mg/L. The increase in the adsorption of the amount of solute is obvious due to increasing MLL surface area.

**Biosorption isotherms**

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of Cu(II) and Pb(II) ions onto MLL particles was modeled using four adsorption isotherms:

### Freundlich isotherm

The Freundlich isotherm model is the well known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form (Freundlich, 1939):

\[
\log q = \log K_F + \frac{1}{n} \log C_e
\]

(2)

Where \(K_F\) is the Freundlich constant related to the bonding energy, \(1/n\) is the heterogeneity factor and \(n\) (g/L) is a measure of the deviation from linearity of adsorption.

Freundlich equilibrium constants were determined from the plot of \(\log q_e\) versus \(\log C_e\), Figures 4 and 5 on the basis of the linear of Freundlich Equation (2). The \(n\) value indicates the degree of non-linearity between solution concentration and adsorption as follows: if \(n = 1\), then adsorption is linear; if \(n < 1\), then adsorption is a chemical process; if \(n > 1\), then adsorption is a physical process. The \(n\) value in Freundlich equation was found to be 2.26-3.49 for MLL, Table 1. Since \(n\) lie between 1 and 10, this indicate the physical biosorption of copper(II) and lead(II) onto MLL. The values of regression coefficients \(R^2\) are regarded as a measure of goodness of fit of the experimental data to the isotherm models.

### Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites (Langmuir, 1918). Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} Ce
\]

(3)

Where \(K_L\) is the Langmuir constant related to the energy of adsorption and \(q_{max}\) is the maximum adsorption capacity (mg/g). Values of Langmuir parameters \(q_{max}\) and \(K_L\) were calculated from the slope and intercept of the
linear plot of $C_e/q_e$ versus $C_e$ as shown in Figures 6 and 7.

Values of $q_{\text{max}}$, $K_L$ and regression coefficient $R^2$ are listed in Table 1. These values for MLL biosorbent indicated that Langmuir theory describes the biosorption phenomena favorable.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, $R_L$ expressed as in
Table 1. Langmuir, Freundlich, and Temkin constants for biosorption of Cu(II) onto MLL at different temperatures.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Q_m (mg/g)</th>
<th>b (mg/g)</th>
<th>R^2</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Langmuir</td>
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<tr>
<td>20</td>
<td>33.33</td>
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<tr>
<td></td>
<td>n</td>
<td>K_f</td>
<td>R^2</td>
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<td>40</td>
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<td>K_T</td>
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<td>434.26</td>
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<td>40</td>
<td>402.13</td>
<td>0.99</td>
<td>0.9981</td>
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</table>

Figure 6. Langmuir adsorption isotherms for Cu (II) ions onto MLL at ◊, 293 K; ■, 303 K, ∆, 313 K.

Figure 7. Langmuir adsorption isotherms for Pb (II) ions onto MLL at ◊, 293 K; ■, 303 K, ∆, 313 K.
the following equation (Özer et al., 2004):

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

(4)

Where $K_L$ is the Langmuir constant and $C_0$ is the initial concentration of nickel(II) ions. The value of separation parameter $R_L$ provides important information about the nature of adsorption. The value of $R_L$ indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

The $R_L$ was found to be 0.25 to 0.57 for concentration of 10 to 100 mg/L of Cu(II) and Pb(II). They are in the range of 0 to 1 which indicates the favorable biosorption.

**Temkin isotherm**

The Temkin isotherm model assumes the adsorption energy decreases linearly with the surface coverage due to adsorbent-adsorbate interactions. The linear form of Temkin isotherm model (Aharoni and Ungarish 1977; Boparai et al., 2011) is defined by:

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

(5)

Where $b_T$ is the Temkin constant related to heat of sorption (J/mol) and $K_T$ is the Temkin isotherm constant (L/g). These constants were obtained from plotting $q_e$ versus $\ln C_e$. Figures 8 and 9a. Values of $b_T$ and $K_T$ are listed in Table 1.

**Adsorption kinetic**

Parameters from two kinetic models, pseudo first-order
and pseudo second-order were fit to experimental data to examine the adsorption kinetics of cadmium uptake by MLL.

**Pseudo first-order kinetics**

The pseudo-first order equation of Lagergren is generally expressed as follows:

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t)
\]

(6)

Where \(q_e\) and \(q_t\) are the sorption capacities at equilibrium and at time \(t\), respectively (mg/g) and \(k_1\) is the rate constant of pseudo-first order sorption, (1/min). After integration and applying boundary conditions, \(q_t = 0\) to \(q_t = q_e\) at \(t = 0\) to \(t = t\); the integrated form of Equation (6) becomes:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]

(7)

The equation applicable to experimental results generally differs from a true first order equation in two ways: The parameter \(k_1(q_e - q_t)\) does not represent the number of available sites; and the parameter \(\log q_e\) is an adjustable parameter which is often not found equal to the intercept of a plot of \(\log(q_e - q_t)\) against \(t\), whereas in a true first order sorption reaction \(\log q_e\) should be equal to the intercept of \(\log(q_e - q_t)\) against \(t\). In order to fit Equation (7) to experimental data, the equilibrium sorption capacity, \(q_e\) must be known. In many cases it is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 min of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to \(t = \infty\), on treating \(q_e\) as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, in order to analyze the pseudo-first order model kinetics.

The pseudo first order rate constant can be obtained from the slope of plot between \(\log(q_e - q_t)\) against time, \(t\). Figure 9b shows the Lagergren pseudo-first order kinetic plot for the adsorption of copper onto MLL powder. The pseudo first order rate constant values were calculated from the slope of Figure 9b. The calculated values and their corresponding linear regression correlation coefficient values are shown in table 3. The linear regression correlation coefficient value found 0.9747, which shows that this model cannot be applied to predict the adsorption kinetic model.

**Pseudo-second order kinetics**

The pseudo second-order rate expression, which has been applied for analyzing chemisorption kinetics rate (Ho, 2006) is expressed as:

\[
\frac{dq_t}{dt} = k(q_e - q_t)^2
\]

(8)

Where \(q_e\) and \(q_t\) are the sorption capacity at equilibrium and at time \(t\), respectively (mg/g) and \(k\) is the rate constant of pseudo-second order sorption, (g/mg min).
Table 2. Langmuir, Freundlich, and Temkinm constants for biosorption of Pb (II) onto MLL at different temperatures.

<table>
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<th>b (mg/g)</th>
<th>R^2</th>
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<td>395.88</td>
<td>0.997</td>
<td>0.9943</td>
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</table>

For the boundary conditions to \( q_t = 0 \) to \( q_e = q_t \) at \( t = 0 \) to \( t = t \); the integrated form of Equation (8) becomes:

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt
\]

Equation (9) can be rearranged to obtain:

\[
q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}}
\]

(10)

The linear form of Equation (10)

\[
\frac{t}{q_e} = \frac{1}{kq_e^2} + \frac{1}{q_e} t
\]

(11)

Where \( t \) is the contact time (min), \( q_e \) (mg/g) and \( q_t \) (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, \( t \).

If pseudo-second order kinetics is applicable, the plot of \( t/q_t \) versus \( t \) of Equation (11) should give a linear relationship, from which \( q_e \) and \( k \) can be determined from the slope and intercept of the plot, Figure 10. The pseudo-second order rate constant \( k \), the calculated \( q_e \) value and the corresponding linear regression correlation coefficient value are given in Table 3. At all initial metal concentrations, the linear regression correlation coefficient \( R^2 \) values were higher. The higher values confirm that the adsorption data are well represented by pseudo-second order kinetics.

Desorption and regeneration studies

In order to investigate biosorption on Cu(II) and Pb(II) ions from metal-loaded MLL, the metal-loaded biosorbent was treated with HCl. Desorption studies were performed with different hydrochloric acids concentration. Complete elution of the loaded Cu(II) and Pb(II) 99.24% could be achieved by using 0.1N HCl. To keep the biosorption process cost down, our results indicate that MLL biosorbent could be used repeatedly in Cu(II) and Pb(II) biosorption.

Conclusion

The potential of modified loquat leaves (MLL) for the removal of Cu (II) and Pb (II) ions from aqueous solutions and electroplating wastewater was dependent on biosorption process such as pH, initial metal ions concentrations, biosorbent dose, contact time, and temperature. The equilibrium data have been analyzed using Langmuir, Freundlich and Temkin isotherms. The characteristic parameters for each isotherm and related correlation coefficients, \( R^2 \) were determined. The Langmuir biosorption isotherms were demonstrated to provide the best correlation for the biosorption of Cu(II) and Pb(II) ions onto MLL. The maximum monolayer adsorption capacity of MLL was found to be 33.33 mg of
Cu(II)/g of MLL and 34.6 mg of Pb(II)/g of MLL. The kinetic results provided the best correlation of the experimental data of biosorption of Cu(II) and Pb(II) onto MLL by pseudo second-order equation. It can be concluded that since the MLL is an easily, locally available, low-cost adsorbent and has a considerable high biosorption capacity, it may be treated as an alternative adsorbent for treatment of wastewater containing copper(II) and lead(II) ions.

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