Research Article

Eco-Efficient Biosorbent Based on *Leucaena leucocephala* Residues for the Simultaneous Removal of Pb(II) and Cd(II) Ions from Water System: Sorption and Mechanism

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*Leucaena leucocephala* is a potential source of polyphenols widely available in southern Mexico. This work highlights the extraction of polyphenols from *Leucaena leucocephala* leaves waste (LLEPs) and the evaluation of their efficiency to remove the single and multicomponent Pb(II) and Cd(II) metal ions from aqueous solutions. Batch test conditions were carried out to examine the effects of contact time, initial metal ion concentration, and adsorbent dosage on the biosorption process. The surface textures and the composition of the LLEP biosorbent was characterized using pH of point of zero charge (pH\textsubscript{PZC}), attenuated total reflectance Fourier transform infrared (ATR-FTIR), and matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry, respectively. Further analysis using ATR-FTIR after adsorption contact of biosorbent was also investigated. The highest Langmuir saturation monolayer adsorption capacity, \(q_{\text{m}}\) for the removal of Pb(II) by LLEPs was obtained as 25.51 and 21.55 mg/g in mono- and bimetal solutions, respectively. The pseudo-second-order model provided the best fit for the kinetic data obtained for the removal of Pb(II), Cd(II), and their mixture, and the \(k_{2}\) values depend on the adsorbent mass. This implied that the chemisorption process might be the mechanism of the solute ions-LLEPs interaction in this study. Furthermore, nearly 100% removal of lead and cadmium individually and 95% of their mixture was found using 0.9 g of LLEPs.

1. Introduction

Biosorption has emerged as a potential and promising solution to remove toxic heavy metals from water and wastewater, and is also considered as an alternative process to the conventional methods such as those based on ion exchange, precipitation, membranes, and electrochemistry processes widely applied in industrial effluents treatments which are very costly and have many limitations [1, 2]. Recent research studies have directed attention to biosorption processes owing to the high metal-binding capacities of various biosorbent materials [3]. Algae-, fungi-, agricultural-, and forestry-based materials have proved to be eco-efficient and environmentally friendly sorbent for heavy metals [3, 4]. Diverse waste materials have been used as low-cost bioadsorbents for heavy metals from water solutions; in
et al. studied the application of hybrid low-cost SiO2/Cd(II) from aqueous solutions. In this context, Copello et al. demonstrated a high total phenol content with more than 15.0 mg gallic acid equivalent (GAE)/g dried sample, whereas Geranium purpureum, Matricaria chamomilla, and Lavandula vera showed a content less than 7 mg GAE/g dried sample [16, 17].

Leucaena leucocephala as a potential source of polyphenols is a fast-growing, tropical, leguminous tree species that belongs to Mimosaceae, native to southern Mexico (Yucatán Peninsula), and then extends to Nicaragua, including Guatemala, Honduras, El Salvador, and northern Central America [18, 19]. Leucaena leucocephala, named the miracle tree, is considered as a multipurpose tree species for its wider uses as timber and firewood, in pulp and paper industry [20] also as a biomass and protein source for animal feed with yield production of 50 ton ha⁻¹ year⁻¹ under Mediterranean conditions [21]. Their leaves and seeds are composed mainly of lipids, crude protein, carbohydrates, mimosine, saponins, coumarins, flavonoids, cardiac glycosides, steroids, and phenols and have a high condensed tannin content [18, 22, 23]. Recently, Abu Zarin et al. reported the total phenolic content in Leucaena leucocephala hybrid-Rendang from its crude extract to be 3.21 mg GAE/g [22].

Polyphenols, extracted from plants, are characterized by the abundant phenolic hydroxyls that are capable of chelating with transition-metal ions, especially for those metal species with d-orbits [24]. Because of the strong chelating ability of phenolic hydroxyls towards transition metals, the polyphenol-based adsorbent showed to be potential and efficient sorbent for the removal of Pb(II) and Cd(II) from aqueous solutions. In this context, Copello et al. studied the application of hybrid low-cost SiO2/ polyphenol matrices as a bioadsorbent for Pb(II), Cr(III), and Cr(VI) [16]. Waseem et al. have used biomass derived from of Acacia nilotica leaves as an adsorbent material for the removal of cadmium and lead, and they found the maximum adsorption to be 2.51 mg/g and 4.99 mg/g for Pb(II) and Cd(II), respectively [13]. Recently, Zhang et al. have evaluated the effectiveness of Sagittaria trifolia L. stalk plant to remove Pb(II), Cd(II), and Cr(III) [14]. However, the maximum adsorption capacities of Pb(II) reported by Jayaram and Prasad were 45.454 mg/g using Prosopis juliflora as a source of polyphenols [25].

However, to the best of our knowledge, there are no reports of polyphenols extracted from L. leucocephala as potential metal removers from mono- and multicomponent systems. Indeed, L. leucocephala residues have no application for human consumption here in Mexico; therefore, it is expected that it will remain a waste that could be considered a sustainable low-cost source of polyphenol adsorbents. Therefore, the aim of this work was to describe the simultaneous sorption mechanism of Cd and Pb from aqueous solution using L. leucocephala-extracted polyphenols (LLEPs) considering various experimental parameters such as contact time, adsorbent dosage, and initial concentration.

2. Materials and Methods

2.1. Chemicals. Deionized water (18.2 MΩ cm⁻¹, conductivity) was used for all dilutions and to prepare the synthetic stock solutions of Pb(II) and Cd(II) using PbCl₂ (98%, Aldrich) and CdCl₂.2.5H₂O (79.9 %, J.T. Baker) salts, respectively. Methanol (70%), Folin–Ciocalteu reagent, and Na₂CO₃ were used in the procedures for extraction and quantification of total polyphenols.

2.2. Plant Preparation. Leaf residues of Leucaena leucocephala tree were collected from the campus area of the Autonomous University of Ciudad Del Carmen identified by our botanist Dr. Enrique Lopez, washed with deionized water, dried at 70°C, and then stored in glass bottles to be used for the polyphenols' extraction.

2.3. Extraction of Polyphenols. The extraction method of polyphenols was described by Scalbert et al.; 15 g of plant leaf samples was extracted three times with 300 mL of 80% methanol solution under magnetic agitation at room temperature (3 × 2 h). The supernatant was collected after each extraction by filtration and then the sample solution was used for polyphenol quantification. The methanol was evaporated under reduced pressure, and then the polyphenols were dried and ready to be used in the sorption process [26].

2.4. Total Polyphenolic Content. Total polyphenolic contents were determined according to the method of Scalbert et al. [26]. 0.5 mL of a 200-fold diluted aqueous extract was mixed with 2.5 mL of 10-fold diluted Folin–Ciocalteu phenol reagent and incubated for 1 min, before 2 mL of 7.5% Na₂CO₃ was added. The mixture was allowed to stand for 15 min at 50°C in a water bath and then transferred into cold water. Samples absorbance was measured at 760 nm in a UV-Vis spectrophotometer (Evolution 220) after 30 min of incubation. A gallic acid aqueous solution (80 µg/mL) was used for calibration, and the final results were expressed as mg gallic acid equivalent (GAE) per g of dry weight (DW).

2.5. Characterization Methods

2.5.1. Point of Zero Charge (pH_PZC). The pH of the point of zero charge (pH_PZC) of LLEPs has been described as
following: 0.10 g of each adsorbent with 50 mL of 0.01 M NaCl adjusted to different initial pH values (pH = 2, 4, 5, 6, 8, 10, and 12). The suspensions were allowed to equilibrate for 24 h under agitation, decanted, and the final pH values of each remaining solution were measured using the pH meter Thermo Scientific (ORION 3-Star pH Benchtop). The experiments were conducted in duplicate, and the measurement temperature was set at 25.0 ± 0.1°C. The pH of the biosorbent was determined from the point of intersection of the curves obtained in the plot of pH_initial vs. pH_final.

2.6.2. Isotherms. For isotherms, 0.1 g of LLEPs was mixed with 10 mL of aqueous solution of Pb(II) and Cd(II) with known initial concentrations (10–500 mg L⁻¹). The mixtures were shaken for 24 h in a rotary shaker at room temperature. At the end of equilibrium time, the suspensions were centrifuged at 3500 rpm for 10 min, and the concentration of lead metals was analyzed by AAS.

2.6.3. Influence of LLEPs Dosage. In order to study the effect of LLEPs dosage on the Pb(II) and Cd(II) removal efficiency, 10 mL of Pb(II) and Cd(II) solutions with an initial concentration of 100 mg/L was mixed in centrifuge tubes containing 0.1 g, 0.5 g, and 0.9 g of LLEPs. The mixtures were shaken for 30, 60, 180, and 360 min. At the end of each specific contact time, the mixtures were centrifuged, and the metallic ions were determined by AAS.

3. Results and Discussions

3.1. Total Phenol Content. In order to determine the total phenolic content, the curves of calibration were obtained using known quantities of commercial gallic acid. Total phenolic content of the L. leucocephala extracts were measured using the Folin-Ciocalteu method in terms of gallic acid equivalent. The total polyphenols content of methanol extracts of Leucaena leucocephala waste was found to be 3.71 ± 0.1 mg of gallic acid/g of dried extract. This result was higher than the one reported from Leucaena hybrid-Rendang [22].

3.2. Point of Zero Charge (pH_PZC). Figure 1 shows the point of zero charge results of LLEPs. The pH_PZC was found at pH = 5.10 ± 0.01; furthermore, a shift of the final pH (pH_f) of the solution toward the slightly acidic region was observed, which could be attributed to the amphoteric character of the polyphenols surface that approximates the pH of a solution to their PZC value [27]. The effect of the amphoteric character of the surface can be observed in slight increase in the pHf on the point of pHz = 5. However, with respect to the surface charge of LLEPs, above the pH_PZC (pH > 5.1), the adsorbent surface is negatively charged, which could promote the attraction of cations, which is the case of our study. Therefore, it is plausible that a slight acidic range is favorable for metal retention onto LLEPs.

3.3. Mass Spectroscopy MALDI-TOF. To get more detailed information on the chemical composition and structure of natural compounds presented in LLEPs, MALDI-TOF mass spectroscopy analysis was performed. The flavonoid constituents in the extracts of Leucaena leucocephala foliage have been identified earlier by mass spectrometry techniques as caffeic acid, isorhamnetin,
chrysoeriol, isorhamnetin 3-O-galactoside, kaempferol-3-O-rutinoside, quercetin-3-O-rhamnoside, as well as luteolin-7-glucoside, among others [28–30]. In order to determine the different natural compounds in the extract of Leucaena leucocephala leaves studied in this work, we have analyzed the MALDI-TOF spectrum of a sample without using any cationizing agent (Figure 2). Considering that MALDI-TOF is not a quantitative method and the intensities of the signals do not necessarily reflect the fractions of the constituents in the sample, in this case, MALDI-TOF analysis is treated only as a confirmation of the presence or absence of natural products such as the aforementioned flavonoids in the tested sample.

From Figure 2, it is observed that the signals of at least 9 populations of natural constituents are clearly dominating. For the dimers of isorhamnetin 3-O-galactoside, kaempferol-3-O-rutinoside, and chrysoeriol, the observed m/z values are 959.9, 1187.3, and 1203.4, respectively. The m/z signals for the trimers of luteolin-7-glucoside and quercetin-3-O-rhamnoside are both observed at 1345.2. Finally, for the tetramer of nonanoic acid, 9-(o-propylphenyl), methyl ester, the observed m/z value is 1161.2. The base chemical structures of some of these natural compounds are shown in Figure 3. It is worth noting that no data were found in the literature that would allow adequate identification of the natural compounds present in the sample with m/z values observed at 979.1, 1469.7, 2502.4, and 2687.0, respectively. Further research involving nuclear magnetic resonance spectroscopy (NMR) and the use of advanced sample purification techniques are necessary in order to clarify this issue.

3.4. ATR-FTIR Spectroscopy. ATR-FTIR spectroscopy was used to confirm the heavy metal adsorption carried out by LLEPs after 6 h of contact with cationic solutions of Pb²⁺, Cd²⁺, and the mixture of both metals, respectively. The comparative FTIR spectra before and after the different heavy metal adsorption experiments are shown in Figure 4. In order to better appreciate the differences in the absorption bands of the functional groups present in the chemical structure of the samples, the infrared spectra have been shifted by 3% from each other starting from the one corresponding to (d) (the sample taken after the simultaneous Pb²⁺ and Cd²⁺ adsorption experiment), followed by (c) (the sample taken after Cd²⁺ adsorption experiment), then (b) (the sample taken after Pb²⁺ adsorption experiment), and finally (a) (the sample taken before metal adsorption experiments).

Taking into account the base chemical structures elucidated by MALDI-TOF analysis for the LLEPs (Figure 3), one would expect for all of the samples the presence of characteristic absorption bands corresponding to the stretching vibrations of the O–H group around 3600 cm⁻¹, the stretching vibrations of the =CH– (aromatic) group above 3000 cm⁻¹, the stretching vibrations of the C=O (carbonyl) group around 1700 cm⁻¹, and the stretching vibrations of the C–O (ether) group around 1100–1200 cm⁻¹, among others. However, it is not possible to assign bands in the spectra of these samples unambiguously, as the absorbance bands are overlapping and poorly resolved. In this sense, since we have wet samples, the stretch signal H–O–H appears and overlaps the characteristic peak regarding the stretching vibrations of the O–H bond observed around 3314.35 cm⁻¹ in Figure 4. Likewise, the representative flexion vibration band associated to H–O–H is also observed at 1635.73 cm⁻¹.

It is worth noting that there are two well-resolved characteristic bands that appeared only in the blank sample (a) and clearly indicate that the heavy metal adsorptions have successfully taken place in the molecular architectures.
For instance, the band displayed at 1113.62 cm$^{-1}$ is attributed to the stretching vibrations of the C–O (ether) bond, whereas that shown at 1015.75 cm$^{-1}$ is assigned to the stretching vibrations of the C–OH bond. As the metal adsorption has proceeded (b, c, and d), the absorption band due to the C–OH stretching decreases considerably, suggesting on the one hand that the LLEPs has effectively adsorbed the heavy metal ions and on the other hand that after 6 h of contact with the cationic solution active sites still remain to undergo metal adsorption. In contrast, the absorption band of aromatic C–O stretching completely disappears after deadsorption experiments pointing out that the ether moieties in the sorbent also participate effectively in the metal uptake. It is likely that steric hindrance plays an important role in the adsorption efficiency of the active sites described above. At this stage, FTIR analysis has been performed just in a qualitative fashion to corroborate the effectiveness of the sorbent to capture Pb$^{2+}$ and Cd$^{2+}$ from monocationic as well as polycationic solutions of both metals.

3.5. Kinetics. The sorption equilibrium for Pb(II) and Cd(II) in mono- and bimetal system at pH = 6 by LLEPs was examined. Figure 5 shows the plots of the sorption capacities of single and simultaneous Pb(II) and Cd(II), $q$(mg/g), as a function of time. It can be well seen that the adsorption increases sharply within the first 60 min while the equilibrium time ($t_{eq}$) was reached within 120 min for both Pb(II) and Cd(II). The simultaneous adsorption in bimetal system showed a slight decrease in adsorption capacity due to the presence of a second metal whilst the equilibrium time did not changed. Generally, for both the cases, the adsorption process consisted of two main reaction stages, initial fast adsorption process, up to 65% of Pb(II) and 63% Cd(II) in mono- and bimetal system, followed by a slow continuous sorption reaction with 8–9% of metal. The first stage can be explained by the abundance of active binding sites that are gradually occupied by Pb(II) and Cd(II) as the contact time is increasing. In the second stage, the access to active sites becomes limited. This could be attributed to the possible metal ions repulsion from the LLEPs surface.
In order to describe the mechanism of sorption of Pb(II) and Cd(II) in mono- and bimetal systems onto LLEPs, the pseudo-first-order (Equation (2)), pseudo-second-order (Equation (3)), and Elovich (Equation (4)) models were used.

\[
\ln(q_e - q_t) = \ln(q_e) - k_1t,
\]

\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}
\]

Figure 4: FT-IR spectra of LLEPs (a) before metal adsorption experiments (blank sample), (b) after Pb\(^{2+}\) adsorption experiment, (c) after Cd\(^{2+}\) adsorption experiment, and (d) after simultaneous Pb\(^{2+}\) and Cd\(^{2+}\) adsorption experiment, respectively.

Figure 5: Effect of contact time on the adsorption percentage of Pb(II) and Cd(II) by LLEPs in (a) monometal and (b) bimetal systems (C\(_i\) = 100 mg/L; pH = 6).
where $q_t$ (mg·g⁻¹) and $q_e$ (mg·g⁻¹) are the amounts of metal ions adsorbed at time $t$ and equilibrium, respectively, $k_1$ (min⁻¹) and $k_2$ (g·mg⁻¹·min⁻¹) are the equilibrium rate constants of pseudo-first-order and pseudo-second-order sorption process, respectively. $\alpha$ is the sorption rate (mg·g⁻¹·min⁻¹), and $\beta$ is a desorption constant related to the extent of surface coverage and activation energy for chemisorption. Table 1 shows the parameters of the kinetic models and correlation coefficients obtained from the lineal plots of ln($q_e - q_t$) vs. $t$ (Equation (2)), $t/q_t$ vs. $t$ (Equation (3)), and $q_t$ vs. ln$t$ (Equation (4)) of experimental data.

Figures 6(a) and 6(b) show the plot of $t/q_t$ vs. $t$, for the single and simultaneous Pb²⁺ and Cd²⁺, respectively. As seen from Figure 6, the experimental data well adjusts to the pseudo-second-order kinetic model ($R^2 \geq 0.999$). Moreover, it can be observed that $q_m$ values calculated from Equation (3) are similar with the experimental $q_m$ values (Table 1). This indicates that the sorption kinetics of Pb(II) and Cd(II) show better agreement for the pseudo-second-order model. Similar results are reported.

| $m_{LLEPs}$ (g) | Metallic ions | Pseudo-second-order | Pseudo-first-order | Elovich model |
|----------------|---------------|---------------------|--------------------|--------------|
|               | $q_e$ (cal)   | $q_e$ (exp)         | $k_2$              | $r^2$        | $q_e$ (cal) | $k_1$  | $r^2$ | $\alpha$ | $\beta$ | $r^2$ |
| **Single removal** | Pb²⁺ | 8.203 | 8.199 | 0.007 | 0.999 | 1.497 | 0.004 | 0.814 | 0.008 | 0.288 | 0.584 |
|                 | Cd²⁺ | 6.887 | 6.844 | 0.007 | 0.999 | 1.105 | 0.002 | 0.957 | 0.003 | 0.267 | 0.954 |
| **Simultaneous removal** | Pb²⁺ | 8.025 | 8.021 | 0.006 | 0.999 | 1.476 | 0.004 | 0.814 | 0.009 | 0.282 | 0.584 |
|                 | Cd²⁺ | 6.447 | 6.404 | 0.007 | 0.999 | 1.029 | 0.002 | 0.959 | 0.043 | 0.250 | 0.954 |
| **Single removal** | Pb²⁺ | 2.008 | 2.003 | 0.042 | 0.999 | 0.192 | 0.002 | 0.908 | 4.329 | 0.043 | 0.906 |
|                 | Cd²⁺ | 1.588 | 1.589 | 0.285 | 0.999 | 0.022 | 0.002 | 0.461 | 13.70 | 0.016 | 0.686 |
| **Simultaneous removal** | Pb²⁺ | 1.872 | 1.869 | 0.204 | 0.999 | 0.044 | 0.002 | 0.995 | 12.83 | 0.013 | 0.947 |
|                 | Cd²⁺ | 1.530 | 1.525 | 0.101 | 0.999 | 0.088 | 0.002 | 0.979 | 10.06 | 0.026 | 0.960 |
| **Single removal** | Pb²⁺ | 1.243 | 1.242 | 0.798 | 0.999 | 0.011 | 0.002 | 0.995 | 94.10 | 0.003 | 0.996 |
|                 | Cd²⁺ | 1.118 | 1.117 | 1.427 | 0.999 | 0.005 | 0.002 | 0.961 | 184.6 | 0.002 | 0.967 |
| **Simultaneous removal** | Pb²⁺ | 1.201 | 1.200 | 0.748 | 0.999 | 0.012 | 0.002 | 0.946 | 54.59 | 0.006 | 0.795 |
|                 | Cd²⁺ | 1.055 | 1.054 | 0.278 | 0.999 | 0.033 | 0.002 | 0.931 | 39.88 | 0.009 | 0.927 |

**Figure 6**: Pseudo-second-order kinetic plot for (a) single removal and (b) simultaneous removal of Pb(II) and Cd(II) sorption by LLEPs.
in the literature, where mentioned that in most cases of biosorption, pseudo-second-order equation fit better for the whole range of contact times than the pseudo-first-order [16].

3.6. Effect of Polyphenols Dosage. The study of the effect of LLEPs dosage is essential as the adsorbent dosage showed to be an important parameter that influences the metal uptake from the solution. Figure 7 shows the initial mass introduced of LLEPs as a function of time; the results showed that the percentage removal of metal ions increases with increasing the amount of LLEPs 0.1g to 0.9g in mono- and bimetal systems; This could be attributed to the availability of active binding sites.

As the Figures 7(a) and 7(b) show, 0.9g of LLEPs was enough to remove over 98% of Pb(II) and Cd(II) (C_i = 100 mg/L; pH = 6).
95% of both metals. In general, the removal of Pb(II) was faster than Cd(II) ions as it will be discussed in the next section.

3.7. Isotherms. Figure 8 presents the isotherms of Pb(II) and Cd(II) in mono- and bimetal system at pH = 6 by LLEPs. The metal removal capacity as a function of metal concentration at the equilibrium state was analyzed using Langmuir and Freundlich models. The Langmuir isotherm describes monolayer adsorption on the surface of an adsorbent with a finite number of identical adsorption sites and no interaction between sites. This model is represented as follows:
The Freundlich isotherm is an empirical equation used to describe heterogeneous systems, and it is expressed by the following linear equation:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \]  

where \( q_e \) (mg/g) is the maximum adsorption capacity of the monolayer and \( K_F \) (L·mg\(^{-1}\)) is the Freundlich isotherm constant and \( n \) is the adsorption intensity. A plot of \( \ln q_e \) versus \( \ln C_e \) gives a straight line of slope \( 1/n \) and intercepts \( \ln K_F \).

In the present work, the experimental data were fitted to the Langmuir model for describing the obtained isotherms to propose the sorption mechanism involved with the energy of adsorption. \( q_m \) and \( K_L \) were determined from the slope and intercept of the plots of \( C_e/q_e \) versus \( C_e \).

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems, and it is expressed by the following linear equation:

\[ q_m = \frac{1}{q_m K_L} + \frac{C_e}{q_m}, \]  

where \( q_m \) (mg·g\(^{-1}\)) is the maximum adsorption capacity of Pb(II) individually by LLEPs \( (q_{m,Pb} = 25.510 \text{ mg·g}^{-1}) \) than that observed in the presence of the second metal \( (q_{m,Pb+Cd} = 21.552) \), whereas the maximum Cd(II) adsorption capacity showed the reverse results when it was higher in bimetal system \( (q_{mb,Cd+Cd+Pb} = 16.807) \) than monometal system \( (q_{mb,Cd} = 14.792) \). The constant related to the affinity of the binding site \( (K_L) \) is lower for competent solution metals compared to the one with individual metal, which is in agreement with the abundant binding sites in the latter.

It is generally well known that the specific adsorption of metals on different adsorption surfaces is dependent on their hydration energies; however, higher hydration energy of cations implies higher hydration radii. From the above results, the adsorption capacity toward Pb(II) was obviously higher as compared to Cd(II) due to big coordination sphere offered in its case since it has an energy of hydration higher \((\Delta H_{h,Pb(II)} = -1485 \text{ kJ/mol})\) than Cd(II) \((\Delta H_{h,Cd(II)} = -1809 \text{ kJ/mol})\), thus, an ionic radius (1.19 Å) higher than Cd (0.95 Å) [31]. Hence, Pb(II) ions can bind better with polyphenols groups. Moreover, the electronegativity also has an important role in the preference of biosorbents for metals; however, as the metal is more electronegative, it will be rapidly attracted to the negative surface of a biosorbent, in our case, to the negative-charged surface of LLEPs at the studied pH as confirmed by PZC measure. Therefore, as the lead cation Pb(II) provides the higher electronegativity (2.33) than the cadmium Cd(II) with value of 1.69, the Pb\(^{2+}\) ions were rapidly diffused to the LLEPs surface negatively charged.

### 4. Plausible Mechanism

Polyphenols have been widely reported as metal scavengers such as flavonoids, stilbenes, and lignans compounds [32–34]. In our case, three potential metal-binding sites are identified in flavonoid compounds of LLEPs (Figure 9). It is well known that the deprotonated phenolic is a particularly good ligand for metal cations, once the oxygen center is generated possessing a high charge density, called Hard ligand (Figure 9(a)). On the contrary, the presence of a C=C double bond conjugated with a 3-oxo group is also of great importance for partial delocalization that could also bind heavy metal cations (Figure 9(b)) [35]. Besides, the hydroxyl groups presented the molecules R-C\(_6\)O\(_6\)H\(_9\) is probably involved in the biosorption process of heavy metals as suggested in the Figure 9(c). However, the major contribution to metal chelation is due to the catechol moiety (Figure 9(a)) owing to the presence of two hydroxyl groups in ortho-positions provides a strong metal-chelating character [36].

Therefore, since lead (Pb\(^{2+}\)) and cadmium (Cd\(^{2+}\)) were effectively sorbed onto the LLEPs, they should combine with hydroxyl ions (–OH) and pyrone oxygen of flavonoids compounds as it is exemplified in luteolin-7-glucoside. In general, the binding of metal ions on polyphenolic groups as well as alcoholic groups was considered to take place by the ion-exchange mechanism leading to the formation of a 5-membered chelate complex. A similar phenomenon for Cs(VI)-catechol complex has also been reported [37].

### 5. Conclusions

From this work, it can be concluded that L. leucocephala-extracted polyphenols are an effective low-cost biosorbent of Pb(II) and Cd(II) in monosystem and binary system.

Successful extraction of polyphenols from Leucaena leucocephala plant was identified by MALDI-TOF mass spectroscopy, with high rate compared to reported results of this plant.
ATR-FTIR spectroscopy clearly indicated that the heavy metal adsorptions have successfully taken place in the molecular architectures.

Nearly 100% removal of lead and cadmium was possible at a neutral pH value by 0.9 g of LLEPs, while 95% removal of the mixture Pb-Cd was possible at a pH value of 5 under the batch test conditions.

The pseudo-second-order model best describes the sorption behavior of Pb(II), Cd(II), and their mixture, and the $k_2$ values depend on the adsorbent mass. This implied...
that the chemisorption process might be the mechanism of the solute ion-LLEPs interaction in this research work.

The experimental data of both metals Pb(II) and Cd(II) sorption isotherms well fit the Langmuir model. The \( K_L \) parameter is lower for competent solution metals compared to the one with individual metal. The maximum adsorption capacity (\( q_m \)) of Pb(II) ions was obtained as 25.51 and 21.55 mg/g in mono- and bimetal solutions.

**Data Availability**

The authors declare that they have no inconvenience to share the data generated on this study.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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