

Assessment of *Leucaena leucocephala* as bio-based adsorbent for the removal of Pb^{2+} , Cd^{2+} and Ni^{2+} from water

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ABSTRACT

This study was investigated the removal of Pb^{2+} , Cd^{2+} and Ni^{2+} from single and multicomponent aqueous solutions by *Leucaena leucocephala*. The point of zero charge and the specific surface area of the bio-based adsorbent were determined, and the Fourier-transform infrared spectroscopy and scanning electron microscopy techniques were used to characterize the biosorbent. The elemental composition before and after the heavy metal adsorption by this material was found using energy dispersive X-ray spectroscopy. The effects of various parameters such as contact time (30–1,440 min), pH (2–10), initial adsorbate concentration (10–500 mg L⁻¹) and biosorbent dosage (1–10 mg L⁻¹) were examined. Biosorption capacity was found to be dependent on all of the parameters studied. The amount of metal ions sorbed by *L. leucocephala* increased as the radius of the cations decreased. Kinetic studies show that maximum uptake of Pb^{2+} , Cd^{2+} and Ni^{2+} was reached within 60 min of contact for single and multicomponent solutions of these metallic ions. However, metal removal by biosorbent using a single metal ion solution was higher than that obtained using multicomponent solutions. Furthermore, the biosorption process of the metal ions followed a well-defined pseudo-second-order model. The data's for the single and simultaneous removal of Pb^{2+} , Cd^{2+} and Ni^{2+} were analyzed according to Langmuir and Freundlich isotherm models. The equilibrium data fit well in Freundlich isotherm model. After the biosorption process, *L. leucocephala* was treated with nitric acid at different concentrations to evaluate reusability.

Keywords: *Leucaena leucocephala*; Biosorption; Heavy metals

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1. Introduction

According to the World Health Organization (WHO) and the US Environmental Protection Agency (EPA), heavy metals such as lead (Pb), cadmium (Cd) and nickel (Ni) are considered as priority inorganic pollutants because of their high degree of toxicity, persistence and their negative effects on humans and ecosystems even at low concentrations [1]. The principal sources of these contaminants are industrial effluents such as metal plating, tanneries, mining operations, smelting, radiator manufacturing, storage battery industries and alloy industries [2]. These sources are considered among the most hazardous industries because of the toxic elements Pb^{2+} , Cd^{2+} and Ni^{2+} which are commonly found in these industrial effluents lead to water and soil pollution besides being extremely harmful to human health. For instance, lead is classified as a hazardous material since lead poisoning may result in many diseases such as dysfunction of the kidneys and the central nervous system, brain damage as well as language difficulties, among others [3]. It is also known that cadmium has strong teratogenic and mutagenic effects in living organisms and can enter into the embryo through the placenta, destroying its morphological structure and in turn restricting the fetal growth [4] whereas the hazardous health effects caused by nickel exposure to humans are mainly associated to nickel-induced carcinogenesis and allergy [5]. Additionally, as a result of the growing demand on water supply, the need of unconventional water sources such as treated wastewater has become recurrent, particularly in settlements with frequent water scarcity. Thus, besides the wastewater purification, attractive technologies are those able to recover metallic ions efficiently since the price of the noble materials such as heavy metals is constantly increasing. In order to overcome the health, environmental and economic issues mentioned above, some conventional treatment processes have been used for the removal of heavy metals from wastewater, including chemical precipitation, flotation, coagulation and membrane filtration, among others [6–8]. However, the main drawbacks of these non-eco-friendly treatments are the production of toxic chemical sludge as well as the inefficiency often observed when the heavy metal concentration is high ($10\text{--}100\text{ mg L}^{-1}$) [9]. It is therefore important to search for innovative and economical treatment methods to recover the valuable materials, water and metals, as well as to avoid the environmental and health detriment.

In this sense, bioremediation has proved to be an effective and alternative technology for the recovery of heavy metals; this technique involves the sorption of dissolved substances using renewable and very low cost-effective natural materials such as plants, microbes, yeast, algae, etc. [10]. The biosorption of Zn^{2+} by cyanobacterium *Fischerella ambigua* is an example and the maximum adsorption capacity of this biomaterial for Zn^{2+} ions was 98.03 mg g^{-1} [11].

Recently, several research groups throughout the world have focused their attention on the use of plants as a low-cost and environmentally friendly method for the elimination of metals and metalloid species from industrial wastes by biosorption treatment [12].

Many studies show that biosorbent materials of an agricultural or forestry origin such as fruit cortex [13], rice

husk [14], garlic peel [15], peanut shell [16], pine bark [17], saw dust [18], cork [19], olive tree [20], *Lemna perpusilla* Torr. [22], *Phytolacca americana* [15], and *Eupatorium adenophorum* [21] are found to be capable of removing heavy metals from water and wastewater. These materials are rich in lignin, hemicellulose and cellulose, which may contain various functional groups such as hydroxyl, carboxyl, sulfhydryl, amide, and amine groups that can be effectively bonded with metal ions [15].

Leucaena leucocephala, previously known as *L. glauca*, is a fast-growing tropical leguminous tree species, which may grow to heights of 7–18 m. Its leaves are bipinnate with 6–8 pairs of pinnae bearing 11–23 pairs of 8–16 mm long leaflets. This shrub is native to Southern Mexico (Yucatán Peninsula) and then extend throughout Nicaragua, Guatemala, Honduras, El Salvador and Northern Central America [23]. *L. leucocephala*, known as the “miracle tree”, has a wide variety of uses such as timber, firewood, pulp and in the paper industry [24]. It is also a biomass and protein source for animal feed with a yield production of $50\text{ ton ha}^{-1}\text{ y}^{-1}$ under Mediterranean conditions [25]. Its leaves and seeds are mainly composed of lipids, crude protein, carbohydrates, mimosine, saponins, coumarins, flavonoids, cardiac glycosides, steroids, phenols and a high condensed tannin content [26].

In a recent study, *L. leucocephala* bark powder was tested for single removal of Cu^{2+} , Cd^{2+} and Pb^{2+} from aqueous solutions [27]. The biosorption capacity (q_m) of *L. leucocephala* was found to be 184.2 mg g^{-1} for Pb^{2+} at $pH = 4$; 167.7 mg g^{-1} for Cd^{2+} at $pH = 5$ and 147.1 mg g^{-1} for Cu^{2+} at $pH = 6$ [27]. In pursuing this line of research, the novelty of this work lies on the systematic variation of the experimental conditions to carry out single and simultaneous biosorption of Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous solutions by *L. leucocephala* bark powder in order to elucidate the influence of the multicomponent metallic species on the biosorbent performance. Therefore, the aim of this work was to know the effects of different parameters, including contact time, biosorbent dosage, pH , and initial concentrations on the sorption capacity of the *L. leucocephala* for Pb^{2+} , Cd^{2+} and Ni^{2+} from mono- and bi-component metallic aqueous solutions. Furthermore, to the best of our knowledge this is the first time that the reusability of *L. leucocephala* as well as the possibility of heavy metal recovery after three consecutive adsorption–desorption cycles using HNO_3 as a regeneration agent is assessed in this bio-based adsorbent material.

2. Material and methods

2.1. Reagents

Stock solutions of Pb^{2+} (500 mg L^{-1}), Cd^{2+} (500 mg L^{-1}), Ni^{2+} (500 mg L^{-1}), and $Pb^{2+} + Cd^{2+} + Ni^{2+}$ (500 mg L^{-1}) were prepared by dissolving the weighed amount of $PbCl_2$ (98%, Aldrich, USA), $CdCl_2 \cdot 2.5H_2O$ (79.9%, J.T. Baker, USA) and $NiCl_2 \cdot 6H_2O$ (97%, Riedel de Haën, USA), respectively in deionized water (resistivity, $18.2\text{ M}\Omega\text{ cm}^{-1}$). The desired concentrations were prepared from the dilution of the stock solutions using deionized water. The pH of each was adjusted with 0.1 M HCl or 0.1 M NaOH.

2.2. Preparation of the biosorbent

The leave residues of *L. leucocephala* were collected from the campus area of the Autonomous University of the Ciudad Del Carmen (UNACAR) in Campeche, Mexico. The leaves were washed several times with distilled water and oven-dried at 70°C for 3 d [28,29]. The dried leaves were ground in a porcelain mortar and sieved to obtain a 40 mesh grain size. The biosorbent powder was stored in glass bottles for later use in the adsorption experiments.

2.3. pH of the point of zero charge

The pH values of the points of zero charge (pH_{PZC}) were determined for *L. leucocephala* using a 0.1 M NaNO_3 solution as a background electrolyte at different pH values. The initial pH of the solutions was adjusted between 2 and 11, using 0.1 M HCl or NaOH solutions. The experiments were carried out at 120 rpm and 303 K. After 48 h of contact, the samples were decanted and the pH was measured in the final liquid phases. Each experiment was performed in duplicate. The pH_{PZC} was determined using the intersection of the graph of initial pH (pH_i) vs. final pH (pH_f) from the lineal curve $\text{pH}_i = \text{pH}_f$.

2.4. Biosorbent characterization techniques

A nitrogen adsorption–desorption isotherm was used to determine the specific surface areas of *L. leucocephala*. The measurements were obtained with a BELSORP MAX analyzer using N_2 . The biosorbent was heated to 250°C for 24 h, afterwards the Brunauer–Emmett–Teller equation was applied to calculate the specific surface areas of the biosorbent. The monolayer volume, total pore volume and mean pore diameter were also calculated.

In order to study the interaction between the heavy metals and the biomass, vibration frequency changes in the functional groups in *L. leucocephala* were determined before and after the removal of experiments. The infrared absorption was measured out using a Fourier-transform infrared (FTIR) spectrometer (Nicolet Nexus 670 FTIR) within a range of 4,000–400 cm^{-1} and with a resolution of 4 cm^{-1} . Samples were prepared using the KBr standard method. The morphology and elemental composition of the biosorbent were examined on a scanning electron microscopy (SEM) HITACHI, S-3400N, (Manufactured in USA) fitted with an electron dispersive X100 ray (10 Kv and 30 pA; image magnification = 1,500× and a work distance of 10.5 mm).

2.5. Experimental biosorption

Biosorption experiments were performed using the batch technique previously described in Abatal and Olguín [30]. These experiments were carried out by taking the following variants into consideration: contact time = 30–1,440 min, pH = 2–10, biosorbent dose = 1–10 mg L^{-1} , and initial concentration of single and multi-component heavy metals = 10–500 mg L^{-1} . For the kinetic experiments, 0.01 g of each sample was added to 10 mL of single or multi-component heavy metal solutions with a concentration of 100 mg L^{-1} and the mixtures were placed in centrifuge tubes and shaken with a 150 rpm speed for 30, 60, 180, 360, 720 and 1,440 min, respectively. At the end of each contact time, the tubes were centrifuged at 3,500 rpm for 5 min, and the adsorbent was removed by filtration. Finally, the Pb^{2+} , Cd^{2+} and Ni^{2+} concentrations were determined by atomic absorption spectroscopy (Thermo Scientific iCE 3000 Series, Manufactured in USA).

Table 1 represents the experimental conditions used to study the effect of each parameter on sorption behavior. All experiments were conducted in duplicate to ensure reproducibility of the collected data and the results are expressed as average values.

The amount of each heavy metal sorbed was calculated using the mass balance expression (Eq. (1)):

$$q = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where q is the amount of heavy metal sorbed by the biosorbent (mg g^{-1}), V is the solution volume (mL), W is the amount of biosorbent (g), and C_0 and C_t are the initial and final metal concentrations (mg L^{-1}), at time t (min).

2.6. Desorption experiments

The desorption experiments of Pb^{2+} were carried out with a similar procedure as that described by Mata et al. [31]. After Pb^{2+} adsorption, the biosorbent was filtered, weighted and then placed in contact with 50 mL 0.1 N HNO_3 for 30 min. The solid was then separated by filtration and washed several times with deionized water to eliminate any excess acid before being reused in a new sorption/desorption cycle. The Pb^{2+} concentration in the remaining solutions following adsorption and desorption was determined by absorption atomic spectroscopy. This procedure was repeated three times in order to calculate the percentage of Pb^{2+} recovery and the reusability of *L. leucocephala* for this purpose.

Table 1
Parameters considered for the study of the biosorption processes of Pb^{2+} , Cd^{2+} and Ni^{2+} using *Leucaena leucocephala*

Parameters	Time (min)	C_i (mg L^{-1})	pH_i	Adsorbent dosage (mg L^{-1})
Contact time	30–1,440	100	5–6	1
Initial solution pH (pH_i)	1,440	100	2–10	1
Biosorbent dosage	1,440	100	5–6	1–10
Initial concentration of single and multi-component metals (C_i)	1,440	10–500	5–6	1

3. Results and discussions

3.1. Point of zero charge

The point of zero charge pH of *L. leucocephala* bark was found to be 6.3 (Fig. 1). Therefore, the adsorbent surface will be charged positively if the pH of the solution is less than the pH_{PZC} of the biomass. In this region, the negatively-charged ions present in the solution can bind by Coulombic attraction to the biosorbent. When the pH of the solution is higher than the pH_{PZC} , the surface charge of the biosorbent is negative. In this pH interval, the positively-charged ions present in the solution will be attracted by the surface of biosorbent [32].

3.2. Characterization

The specific surface area of the *L. leucocephala* sample was $6.748 \text{ m}^2 \text{ g}^{-1}$. This value is higher than those obtained for the biomasses of other aquatic plants including *Landoltia punctata* ($2.327 \text{ m}^2 \text{ g}^{-1}$), *Spirodela polyrhiza* ($1.959 \text{ m}^2 \text{ g}^{-1}$), *Lemna aequinoctialis* ($1.790 \text{ m}^2 \text{ g}^{-1}$) and *Lemna minor* ($0.640 \text{ m}^2 \text{ g}^{-1}$) [33]. Therefore, it is expected that the specific surface area from the *L. leucocephala* will play a role in retaining heavy metals from aqueous media, in a similar way that of the above mentioned aquatic plants. This point will be discussed later.

Figs. 2a–f show the IR spectra in the range of 400–4,000 cm^{-1} for *L. leucocephala* bark before and after biosorption of the metallic ions with the single and multicomponent (Pb^{2+} , Cd^{2+} and Ni^{2+}) solutions, respectively. Various absorption peaks can be observed in the spectra due to the complex nature of the biosorbent material.

Table 2 shows the characteristics infrared absorption bands and their respective associated functional groups for metal-unloaded and metal-loaded biosorbent. The primary bands corresponding to the metal-unloaded biosorbent were observed at 3,440; 2,920; 2,850; 1,628; 1,383; 1,034 and 674 cm^{-1} , and can be attributed to the $-\text{OH}$, $-(\text{CH}_2)$, $-\text{C}=\text{O}$, $-\text{CH}-$, $-\text{C}-\text{O}$, $-\text{S}-\text{H}$ and $-\text{PO}_4$ groups, respectively.

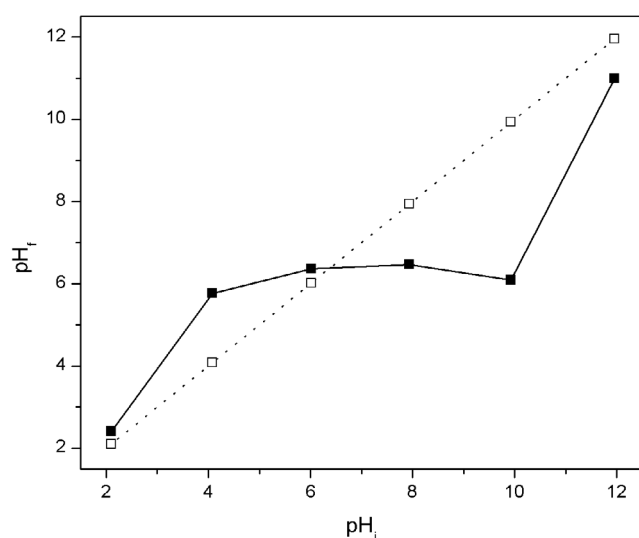


Fig. 1. pH_{PZC} for *Leucaena leucocephala* bark.

The strong and large band at $3,440 \text{ cm}^{-1}$ is associated to the polysaccharides present in *L. leucocephala* (pectin, cellulose, hemicellulose and chitin), which includes a large amount of hydroxyl groups [34]. A significant shift of this band can be observed with respect to the metal-unloaded and metal-loaded biomass, indicating that the hydroxyl groups have been changed from multimer to monomer or even a dissociative state [35]. This result also suggests that the polysaccharides present on the surface of *L. leucocephala* could be responsible for binding metal ions through chemical interactions [27].

The band observed around $1,627 \text{ cm}^{-1}$ is indicative of the presence of carboxyl groups ($-\text{C}=\text{O}$) in *L. leucocephala* bark. A minor shift of this band is observed after metal biosorption suggesting that the carboxyl group could be participating in the biosorption process [15].

The new absorption band observed in the spectra of *L. leucocephala* at $1,104 \text{ cm}^{-1}$ after single and multi-metal sorption may be due to the interaction between the metal ions and carboxyl groups from the biosorbent [26]. The bands found at $2,921$ – $2,851 \text{ cm}^{-1}$ were assigned to the C–H stretching vibrations in aromatic methoxyl groups, in the methyl and methylene groups of the side chains [36], and the band present from 671.3 to 675.5 cm^{-1} was assigned to the phosphate and sulfur functional groups [27]. Similar bands were obtained in the FTIR spectra of the metal-unloaded and metal-loaded biomasses.

The SEM image of *L. leucocephala* bark is shown in Fig. 3. It can be observed that the surface texture and morphology of the biosorbent after and before contact with metal ions displayed a rough area with detectable micropores. Elemental analysis shows that there is a major atomic percentage of carbon and oxygen in the unloaded, Pb^{2+} -, Cd^{2+} -, Ni^{2+} - and Pb^{2+} + Cd^{2+} + Ni^{2+} -loaded *L. leucocephala* bark samples and lower presence of Ca, K, Mg, Cl, S, Al, Si and P (Table 3 and Fig. 4). Furthermore, after contact of *L. leucocephala* with aqueous solution containing Pb^{2+} , Ni^{2+} and Cd^{2+} , the energy dispersive X-ray spectroscopy analysis show the presence of these elements in the surface of the samples (Table 3).

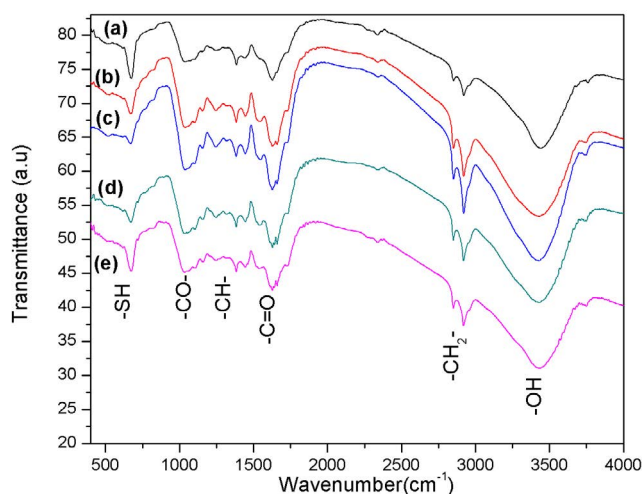


Fig. 2. IR-spectra of (a) unloaded, (b) Pb^{2+} -, (c) Cd^{2+} -, (d) Ni^{2+} - and (e) Pb^{2+} + Cd^{2+} + Ni^{2+} -loaded *Leucaena leucocephala*.

Table 2
IR absorption bands and corresponding functional groups for unloaded and loaded *Leucaena leucocephala*

Functional groups of biosorbent material	Wavenumber (cm ⁻¹)				
	Unloaded	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺ + Cd ²⁺ + Ni ²⁺
–OH or –NH ₂ stretching	3,440.8	3,426.8	3,429.3	3,428.4	3,430.1
–CH ₂ – vibration	2,921.2	2,921.8	2,920.4	2,919.6	2,940.4
	2,851.9	2,851.6	2,851.9	2,849.5	2,851.9
–COO ⁻ , C=O	1,627.2	1,628.1	1,626.4	1,628.9	1,628.1
C–H bending	1,442.5	1,444.9	1,446.6	1,446.6	1,444.1
C–O stretching	–	1,104.5	1,101.9	1,106.0	1,106.8
SH, –PO ₄	675.5	673.0	671.3	673.0	673.8

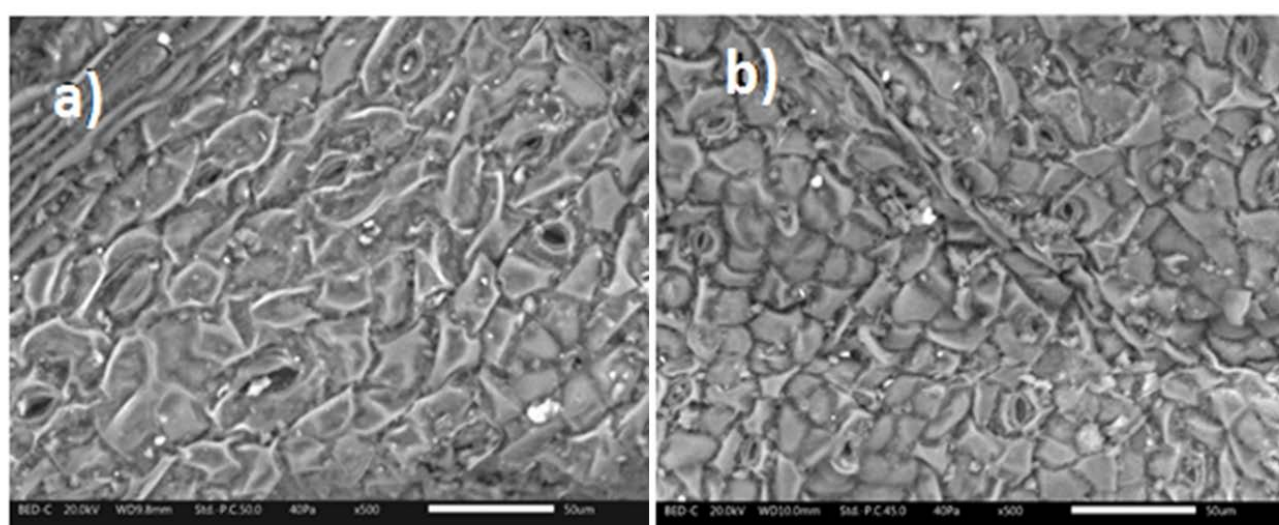


Fig. 3. SEM micrographs of (a) unloaded and b) Pb²⁺ + Cd²⁺ + Ni²⁺-loaded *Leucaena leucocephala* bark.

Table 3
EDS analysis of unloaded, Pb²⁺-loaded, Cd²⁺-loaded, Ni²⁺-loaded and Pb²⁺ + Cd²⁺ + Ni²⁺-loaded *Leucaena leucocephala*

Element	<i>Leucaena leucocephala</i>	Wt. (%)			
		Metallic loaded <i>Leucaena leucocephala</i>			
		Pb ²⁺	Ni ²⁺	Cd ²⁺	Pb ²⁺ + Cd ²⁺ + Ni ²⁺
C	68.19 ± 0.07	73.87 ± 0.10	74.49 ± 0.08	68.03 ± 0.12	74.43 ± 0.09
O	28.13 ± 0.07	23.66 ± 0.10	23.89 ± 0.08	29.17 ± 0.11	22.69 ± 0.08
Mg	0.45 ± 0.01	0.16 ± 0.01	0.09 ± 0.01	0.21 ± 0.01	0.07 ± 0.01
Al	0.10	0.06 ± 0.01	0.12 ± 0.01	0.06 ± 0.01	0.09 ± 0.01
Si	0.10	0.03 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.03
P	0.09	0.06 ± 0.01	0.06 ± 0.01	0.07 ± 0.01	0.05
S	0.18	0.09 ± 0.01	0.16 ± 0.01	0.15 ± 0.01	0.14 ± 0.01
Cl	0.36 ± 0.01	0.00	0.00	0.02 ± 0.01	0.07 ± 0.01
K	0.78 ± 0.01	0.22 ± 0.01	0.11 ± 0.01	0.18 ± 0.01	0.13 ± 0.01
Ca	1.63 ± 0.01	1.32 ± 0.01	0.62 ± 0.01	1.13 ± 0.01	0.57 ± 0.01
Pb	0.00	0.52 ± 0.040	0.00	0.00	0.70 ± 0.03
Ni	0.00	0.00	0.41 ± 0.02	0.00	0.28 ± 0.01
Cd	0.00	0.00	0.00	0.97 ± 0.02	0.75 ± 0.02
Total	100.00	100	100.00	100.00	100

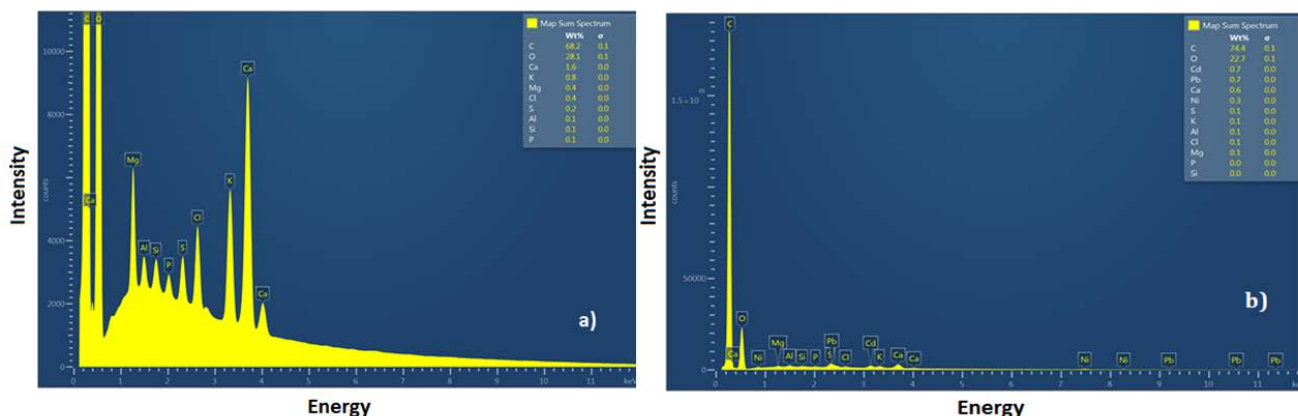


Fig. 4. Intensity (counts) vs. energy (keV) spectra of (a) unloaded and (b) $\text{Pb}^{2+} + \text{Cd}^{2+} + \text{Ni}^{2+}$ -loaded *Leucaena leucocephala* bark.

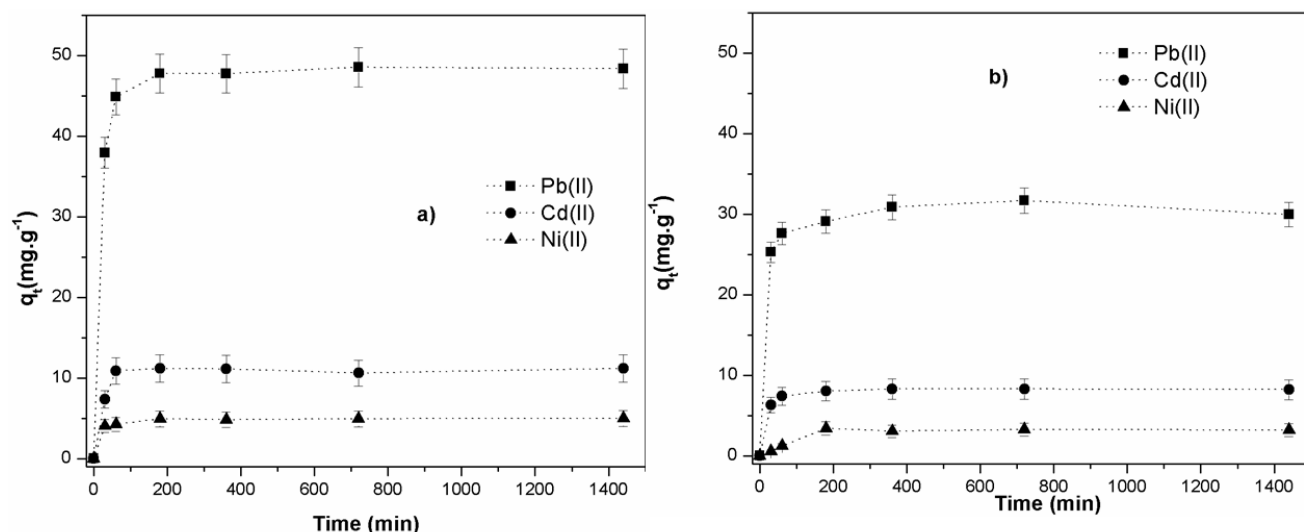


Fig. 5. Sorption of metallic ions by *Leucaena leucocephala* by mono- and multi-component solutions (Pb^{2+} , Cd^{2+} and Ni^{2+}) as a function of contact time.

3.3. Sorption

3.3.1. Kinetics

Figs. 5a and b show the plots of the sorption capacities of metallic ions from single and multi-component solutions (Pb^{2+} , Cd^{2+} and Ni^{2+}), $q_t(\text{mg g}^{-1})$ by *L. leucocephala* bark as a function of time. The results indicate that for both cases (mono-component and multi-component metal ions), biosorption of all heavy metals takes place in two steps: an initial rapid uptake followed by a slow uptake. The sorption of heavy metals by *L. leucocephala* bark is very effective within a 30–60 min time period, which can be explained by the high interaction rate of heavy metal ions in the solution with a large number of available functional groups (primarily $-\text{OH}$ and $-\text{C}=\text{O}$) from the cell wall of the biosorbent. The slow uptake of metal ions after 60 min can be attributed to saturation of the active sites on the biosorbent surface. Similar results were also obtained by other researchers [21,37]. The uptakes of Pb^{2+} , Cd^{2+} and

Ni^{2+} in equilibrium by *L. leucocephala* bark were 48.2, 12.1 and 5.2 mg g^{-1} , respectively, whereas for multicomponent metal sorption, Pb^{2+} , Cd^{2+} , and Ni^{2+} uptakes were 30.1, 7.3, and 3.7 mg g^{-1} , respectively. This difference in the uptake of metallic ions by *L. leucocephala* can be attributed to the influence of other metal ions in the same solution. The results of this investigation, in similar way with others, confirm that the presence of multiple ions in solution affects the uptake of each one as the result of the established competition for available sites on the biosorbent [38].

Pseudo-first-order (Eq. (2)) and pseudo-second-order (Eq. (3)) models were used to describe the mechanism for the sorption of heavy metals by *L. leucocephala* bark.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_t and q_e are the amounts of Pb^{2+} , Cd^{2+} , and Ni^{2+} sorbed at time t and at equilibrium ($mg\ g^{-1}$), respectively; k_1 (min^{-1}) and k_2 ($g\ mg^{-1}\ min^{-1}$) are the equilibrium rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively. Table 4 shows the parameters for the kinetic models and correlation coefficients obtained from the linear plot $\ln(q_e - q_t)$ vs. t (Eq. (2)) and t/q_t vs. t (Eq. (3)) of the experimental data. The results obtained indicate that the sorption kinetics data fit well into the pseudo-second-order kinetic model on account of the high value of the correlation coefficient ($R^2 = 0.99$) and the similarity between the experimental and theoretical q_e values.

3.3.2. Influence of solution pH

Figs. 6a and b show the removal efficiency of single and simultaneous Pb^{2+} , Cd^{2+} , and Ni^{2+} , respectively by *L. leucocephala* bark at pH = 2–10. A lower metal ion uptake by the biosorbent can be observed for a highly acidic solution

(pH ≤ 2). This can be attributed to the possible protonation of the functional groups of the biosorbent, especially, hydroxyl, carboxyl and amine groups which are important for the biosorption of heavy metals [16]. Therefore, this low removal of heavy metals is the result of the competition of H^+ ions in solution with Pb^{2+} , Cd^{2+} , and Ni^{2+} for the active sites on the biosorbent surface. Similar results were reported in other studies [16]. When the initial pH is higher than 4, single and simultaneous removal efficiency of heavy metals increases, reaching 45% and 35% for Pb^{2+} at pH 5, 20% and 8% for Cd^{2+} at pH 8, and 8% and 5% for Ni^{2+} at pH 6. The cationic chemical species of these metals predominate when the solutions have pH values ≤ 5 , 8 and 6, respectively. Therefore, this sorption behavior can be attributed to the decrease of H^+ ions in solution and the deprotonation of the functional groups of the biosorbent. Consequently, there is less competition between H^+ and the metal ions. Hydrolyzed species $Pb(OH)_2$, $Cd(OH)_2$ and $Ni(OH)_2$ can be found at pH values higher than 5, 8 and 6, respectively. The highest

Table 4

Kinetic parameters obtained from pseudo-first-order and pseudo-second-order models for the sorption of mono- and multi-component metallic ions from aqueous solutions by *Leucaena leucocephala* bark

Metallic ions	Pseudo-second-order				Pseudo-first-order		
	$q_{e,cal}$	$q_{e,exp}$	$k_2 (\times 10^{-2})$	R^2	$q_{e,cal}$	$k_1 (\times 10^{-2})$	R^2
Mono-component							
Pb^{2+}	48.54	48.39	0.39	1.00	3.43	1.60	0.52
Cd^{2+}	11.17	11.19	1.00	0.99	0.59	1.10	0.19
Ni^{2+}	5.12	5.00	0.59	0.99	0.54	1.40	0.59
Multi-component							
Pb^{2+}	30.39	29.97	0.91	0.99	3.014	0.90	0.20
Cd^{2+}	8.28	8.23	2.53	0.99	0.63	0.15	0.38
Ni^{2+}	3.45	3.20	0.38	0.99	0.84	0.11	0.18

where $q_{e,cal}$ and $q_{e,exp}$ are the amount of metallic species sorbed by *L. leucocephala* bark from the models and the experimental data.

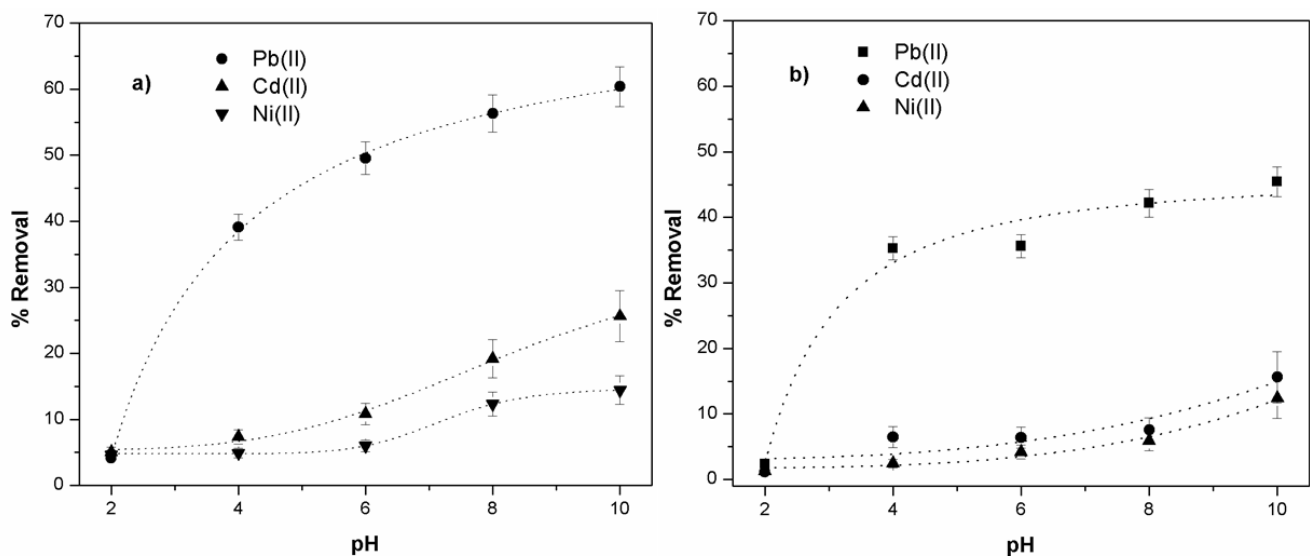


Fig. 6. Removal efficiency of (a) single and (b) simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous solutions by *Leucaena leucocephala* bark as a function of pH.

sorption of these species by *L. leucocephala* was observed at pH 10 (Fig. 6). Therefore, this behavior can be attributed to the precipitation of these hydrolyzed metallic species on the surface of the biosorbent.

3.3.3. Influence of dosage

The effect of *L. leucocephala* bark dose on the sorption efficiency for single and simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous solutions was studied. Figs. 7a and b show the results obtained. It can be observed that the removal yield for single Pb^{2+} increased from 58.42% to 90.80%, from 13.37% to 44.07% for Cd^{2+} and from 7.62% to 30.40% for Ni^{2+} , whereas for simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} removal, the percentages increased from 35% to 75%, from 8% to 40% and from 4% to 39%, respectively when the biosorbent mass increased from 10 to 100 mg per 10 mL of solution. These behaviors can be explained by the increase in the number of functional groups available for the biosorption of heavy metals. On the other hand, a negligible increase in the percentages for single and simultaneous removal can be observed when more than 2 and 8 mg additional biosorbent, respectively is supplied. Other studies have attributed this phenomenon to the possible overlapping or aggregation of active sites at higher dosage and a decrease in total sorbent surface area [16,37].

3.3.4. Isotherms

Adsorption isotherms determine the nature of the interaction between the metal ions and the biosorbent. Figs. 8a and b show the concentrations of single and simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} , respectively adsorbed by *L. leucocephala* (q_e , mg g^{-1}) and their concentration in solution (C_e , mg L^{-1}) after the sorption processes. It can be observed that biosorption of Pb^{2+} , Cd^{2+} and Ni^{2+} increased with increasing initial metal concentration. The maximum single and simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} uptake capacities were 125 and 55 mg g^{-1} , 30

and 25 mg g^{-1} and 15 and 12 mg g^{-1} , respectively. Moreover, it is worth noting that the adsorption capacities of heavy metals are higher for non-competitive conditions than for metallic species in the ternary mixture. This can be explained by the competition for adsorption sites on the surface of the *L. leucocephala* and/or the screening effect by the competing metal ions.

Langmuir and Freundlich isotherm models were used to interpret the equilibrium data for the sorption of single and simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous solutions by *L. leucocephala*. The basic assumption of the Langmuir model is the formation of a monomolecular layer when biosorption takes place without any interaction between ions adsorbed on neighboring sites [39]. The linearized form of the Langmuir isotherm model can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

where q_e (mg g^{-1}) is the amount of the metal ion corresponding to the saturation of the adsorption sites, C_e (mg L^{-1}) is the concentration of metal ion in solution at equilibrium, q_m (mg g^{-1}) is the monolayer capacity of the adsorbent and K_L (L mg^{-1}) is the Langmuir adsorption constant related to the affinity of the binding site. Figs. 9a and b show the plot of C_e/q_e vs. C_e for single and simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} removal, respectively by *L. leucocephala*. The values of q_m and K_L were obtained from the slope and the intercept of the line, respectively. The results are presented in Table 5.

The Freundlich isotherm is an empirical model based on the adsorption of the solute on a heterogeneous surface and can be applied for multilayer adsorption. The linear behavior of this model is described by the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

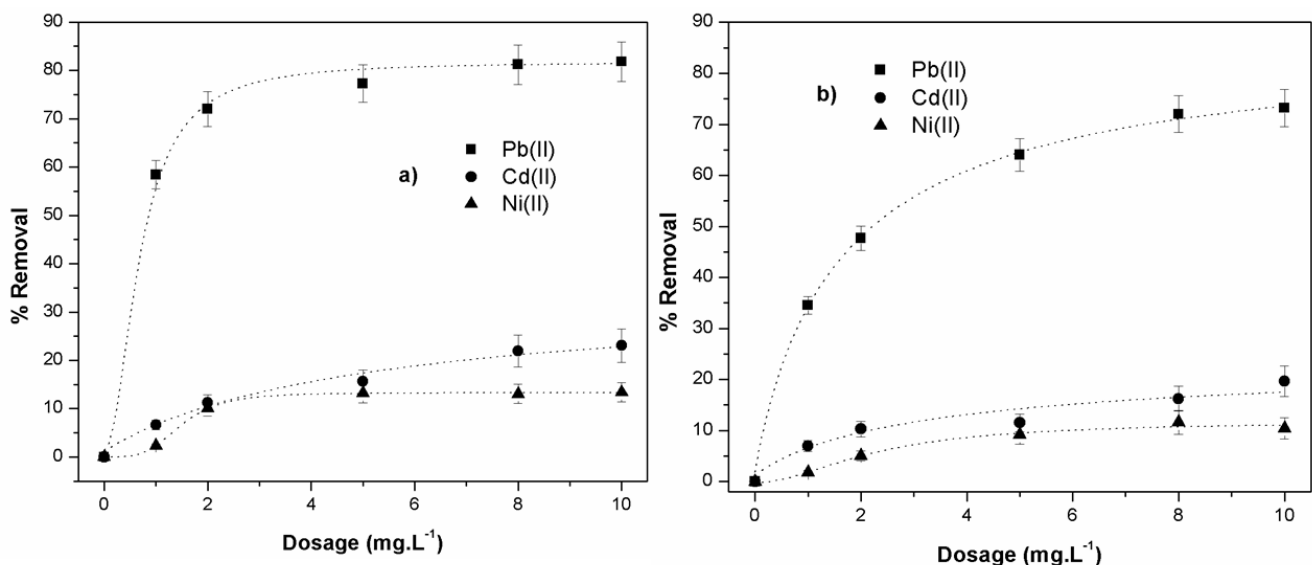


Fig. 7. Removal efficiency of (a) single and (b) simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous solutions by *Leucaena leucocephala* bark as a function of biosorbent dosage.

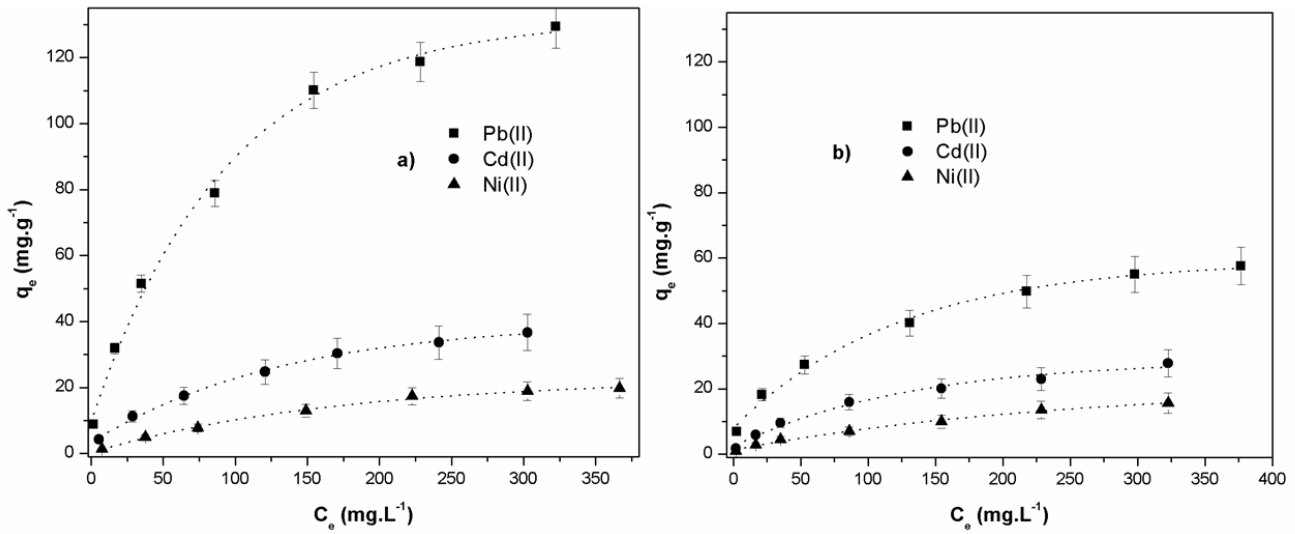


Fig. 8. Isotherms for (a) single and (b) simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} sorption by *Leucaena leucocephala*.

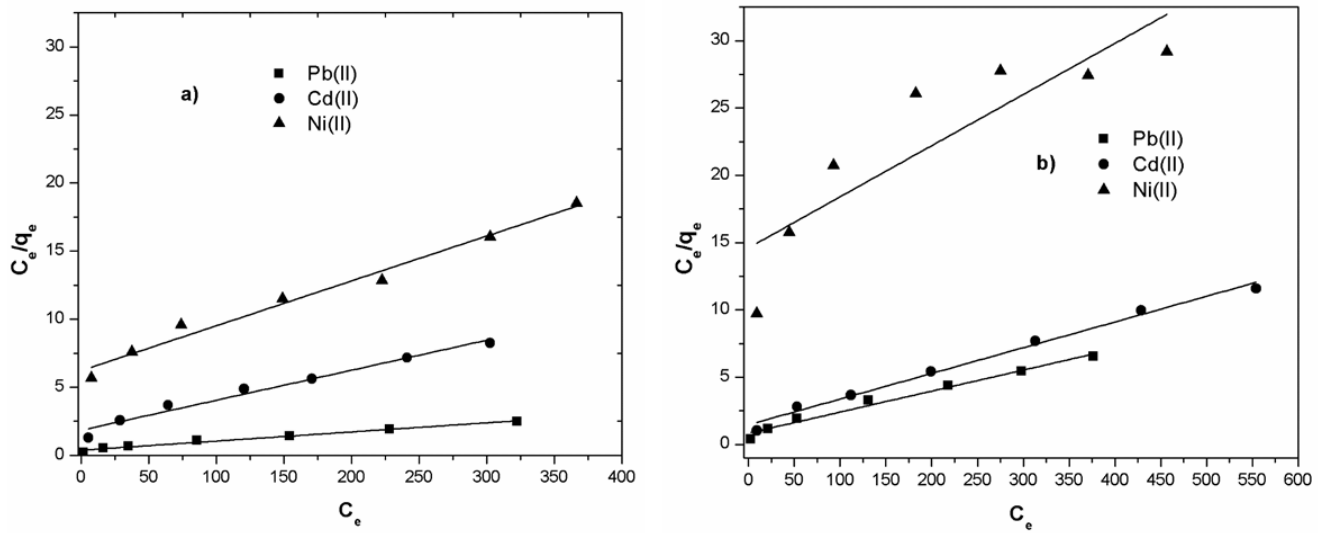


Fig. 9. Langmuir isotherm for (a) single and (b) simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} sorption by *Leucaena leucocephala*.

Table 5
Freundlich and Langmuir isotherm constants for single and simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} sorption by *Leucaena leucocephala*

Metallic ions	Isotherm models					
	Freundlich			Langmuir		
	K_F ($mg\ g^{-1}$)	$1/n$	R^2	q_m ($mg\ g^{-1}$)	K_L	R^2
Mono-component						
Pb^{2+}	7.067	0.504	0.991	149.254	0.017	0.984
Cd^{2+}	1.749	0.545	0.996	45.454	0.012	0.976
Ni^{2+}	0.349	0.707	0.991	30.395	0.005	0.982
Multi-component						
Pb^{2+}	4.779	0.430	0.998	64.102	0.018	0.982
Cd^{2+}	0.398	0.678	0.997	52.356	0.013	0.990
Ni^{2+}	0.186	0.713	0.997	26.315	0.002	0.775

where K_F (mg g^{-1}) and n are the constants indicative of adsorption capacity and adsorption intensity, respectively. Figs. 10a and b show the plot of $\ln q_e$ vs. $\ln C_e$ for single and simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} sorption by *L. leucocephala*. The values of K_F and n were obtained from the intercept and slope of the lines, respectively. The values of these parameters are shown in Table 5.

As seen from Figs. 9a and b, the experimental data did not fit the Langmuir model well ($0.775 \leq R^2 \leq 0.990$). Moreover, it can be observed that q_m values calculated from Eq. (4) are higher when compared to the experimental ones (Table 5). On the other hand, the correlation coefficient for

the Freundlich model was close to one ($0.991 \leq R^2 \leq 0.999$), thereby indicating that the experimental data adjusted well to Freundlich model.

For the sorption of single metal ions, the K_F for Pb^{2+} (7.067) $>$ K_F for Cd^{2+} (1.749) $>$ K_F for Ni^{2+} (0.349), whereas in multi-cations sorption conditions, the K_F for Pb^{2+} (4.779) $>$ K_F for Cd^{2+} (0.398) $>$ K_F for Ni^{2+} (0.186). This reveals that for both experimental conditions, the order of adsorption was $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$. According to the previous studies, the higher biosorption of Pb^{2+} in comparison with that of Cd^{2+} and Ni^{2+} is related to the hydration enthalpy of the metals ion, which indicates the necessary energy for the separation

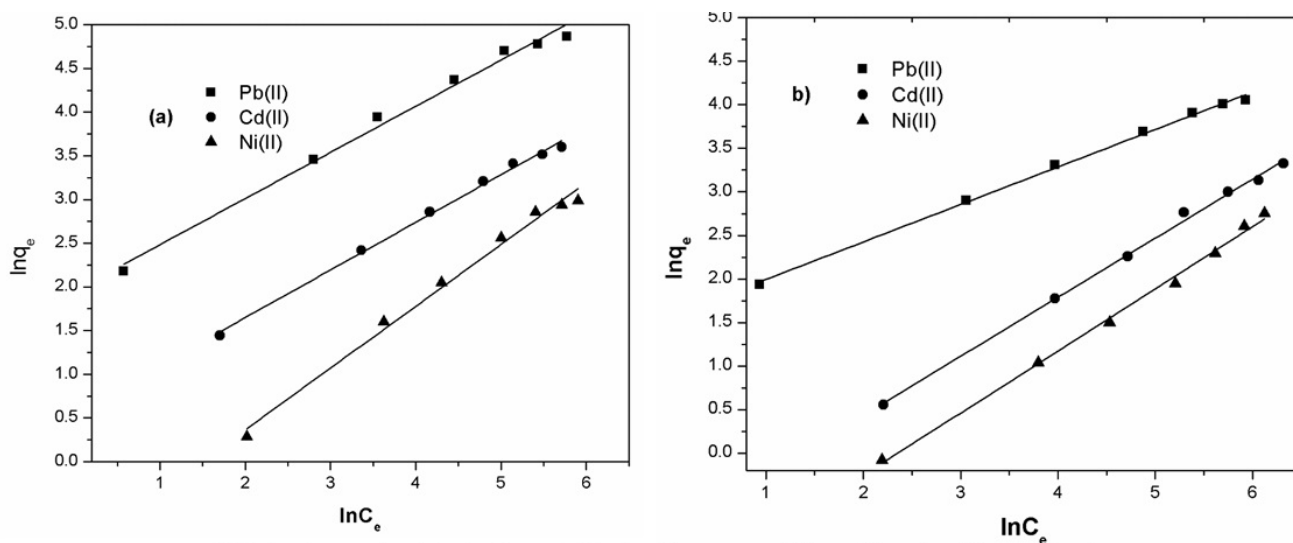


Fig. 10. Freundlich isotherm for (a) single and (b) simultaneous Pb^{2+} , Cd^{2+} and Ni^{2+} sorption by *Leucaena leucocephala*.

Table 6
Comparison of sorption capacity of *Leucaena leucocephala* with other biosorbents

Metal ions	Biosorbents	q_{\max} (mg g^{-1})	References
Pb^{2+}	<i>Myriophyllum spicatum</i>	53.87	[28]
	<i>Symphoricarpos albus</i>	62.16	[39]
	<i>Typha angustifolia</i>	3.719	[40]
	<i>Araucaria heterophylla</i>	7.256	[29]
	<i>Asplenium nidus</i> L.	12.24	[41]
	<i>Leucaena leucocephala</i>	129.40	In this study
Cd^{2+}	<i>Glebionis coronaria</i> L.	18.31	[42]
	<i>Diplotaxis harra</i>	25.24	[42]
	<i>Areca catechu</i>	10.66	[43]
	<i>Typha domingensis</i>	28.49	[44]
	<i>Leucaena leucocephala</i>	36.36	In this study
Ni^{2+}	<i>Dicerocaryum eriocarpum</i>	0.125	[37]
	<i>Ascophyllum nodosum</i>	30	[45]
	<i>Areca catechu</i>	48.72	[44]
	<i>Typha domingensis</i>	4.51	[44]
	<i>Asplenium nidus</i> L.	9.20	[41]
	<i>Leucaena leucocephala</i>	19.78	In this study

of H₂O molecules from the cations and then the facility for the ions to react with the functional group of the biosorbent [38]. The hydration enthalpies of Pb²⁺, Cd²⁺, and Ni²⁺ are -1,485; -1,829 and -2,099 kJ mol⁻¹, respectively. On the other hand, the measured solution of pH after sorption experiments was from 5.5 to 6, this indicates that the possible formation of Pb(OH)₂ and higher sorption capacity of Pb²⁺ by *L. leucocephala*. For single metal ions removal, the results show that 1/n values were 0.504, 0.545 and 0.707 for Pb²⁺, Cd²⁺ and Ni²⁺, respectively, whereas, for multi-heavy metals removal, the values of 1/n were 0.430, 0.678 and 0.713 for Pb²⁺, Cd²⁺ and Ni²⁺, respectively. In all of the cases, 0 < 1/n < 1, indicating the respective order in which Pb²⁺, Cd²⁺ and Ni²⁺ are preferably adsorbed by *L. leucocephala*.

Table 6 summarizes the comparative studies of biosorption capacity of Pb²⁺, Cd²⁺ and Ni²⁺ by *L. leucocephala* with other biosorbents reported in the literature. It was observed that the biosorption capacity of *L. leucocephala* obtained for metallic ions was found to be higher than those of many biosorbents in the literature (Table 6). These differences in sorption capacities may be attributed to different surface characteristics associated with the presence of the different functional groups of biosorbents and the experimental procedure [36,38].

3.4. Desorption and reutilization

The regeneration process of *L. leucocephala* was carried out using three adsorption and desorption cycles. As seen in Fig. 11, the sorption percentages of Pb²⁺ by *L. leucocephala* were 88.89%, 66.67% and 54.08, respectively, whereas the desorption percentages were 78.12%, 55.71% and 48.87% in the first, second and third cycles, respectively. These results indicate that *L. leucocephala* can be reused in three biosorption/desorption cycles, and that the differences in the biosorption capacity between 22% and 34.59% in the second and third cycles, respectively.

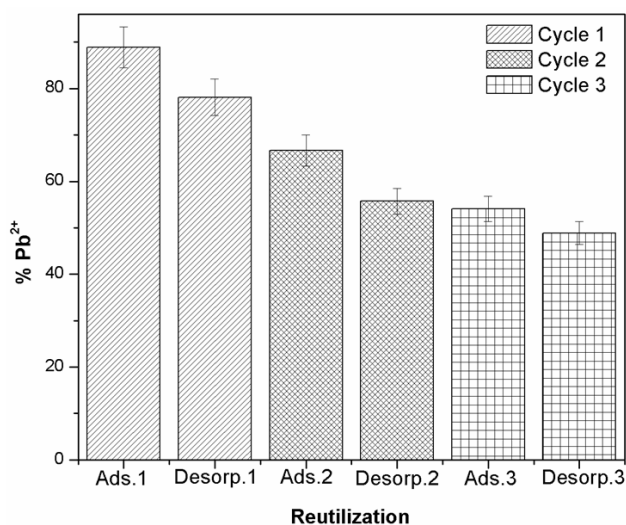


Fig. 11. Adsorption/desorption cycles for Pb²⁺ using *Leucaena leucocephala*.

4. Conclusions

This research shows that the *L. leucocephala* leaves are effective and potential biosorbent for single and simultaneous removal of Pb²⁺, Cd²⁺ and Ni²⁺ from aqueous solutions. Metallic chemical species sorption by *L. leucocephala* is confirmed by the interactions with the functional groups of the biosorbent.

Kinetic experiments show that the time required to reach the equilibrium adsorption for single and simultaneous Pb²⁺, Cd²⁺ and Ni²⁺ by the biosorbent is within 120 min. The biosorption kinetic experimental data are well described by the pseudo-second-order model.

The sorption of Pb²⁺, Cd²⁺ and Ni²⁺ by *L. leucocephala* increases with an increase in the initial pH of the metallic solution and biosorbent dosage. The Freundlich model describes the metallic sorption isotherms and the selectivity of the biosorbent for single and multicomponent metal sorption as follows: Pb²⁺ > Cd²⁺ > Ni²⁺.

The sorption efficiency of Pb²⁺, Cd²⁺ and Ni²⁺ by *L. leucocephala* is sensible to the variation of contact time, initial pH of the metallic solutions, mass of biosorbent and initial heavy metals concentration. Metallic desorption and regeneration of *L. leucocephala* is efficient for three cycles.

The outcomes obtained confirm that the presence of multiple ions in solution affects the uptake of each one as the result of the established competition for available sites on the biosorbent.

A negligible increase in the percentages for single and simultaneous removal was observed when more than 2 and 8 mg additional biosorbent was supplied, respectively. The latter was attributed to the possible overlapping or aggregation of active sites at higher dosage and a decrease in total sorbent surface area.

The higher adsorption capacities of heavy metals obtained for noncompetitive conditions in comparison with those obtained for metallic species in the ternary mixture were attributed to the competition for adsorption sites on the surface of the *L. leucocephala* and/or the screening effect by the competing metal ions.

Based on the results of this research, it would be interesting to explore the use of *L. leucocephala* for Pb²⁺, Cd²⁺ and Ni²⁺ wastewater treatment in a large-scale system due to its abundance and very low cost.

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