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Removal of Cd(II) and Pb(II) from aqueous solution using *Ziziphus lotus* leaves as a potential biosorbent

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ABSTRACT

Ziziphus lotus is a wild plant that has recently become appreciated mainly due to the antioxidant and nutrient-rich properties of its fruits. The powder of the inedible leaves was investigated in this research in batch mode for its capacity to remove cadmium(II) and lead(II) ions as an eco-friendly and cost-effective biosorbent. Leaves powder revealed the highest uptake rate at pH = 8 and pH = 7 for Cd(II) and Pb(II), consecutively. The best metal adsorption rate is obtained with a temperature ranging from 25°C to 30°C, a contact time of 90 min, an initial ionic concentration of 100 mg/L, and a biosorbent dosage ranging from 3.5 to 5 g/L. The experimental kinetic data of the biosorption process for both heavy metal ions were fitted by the pseudo-second-order model. The equilibrium data fitted very well to the Langmuir model and Temkin model. The maximum monolayer biosorption capacities were 70.78 and 80.75 mg/g for Cd(II) and Pb(II), respectively. The main chemical groups which are involved in the trapping of Cd(II) and Pb(II) and which have been revealed by Fourier-transform infrared spectral analysis are: O–C, O=C, H–O, H–C, and N–C. The biosorption was endothermic ($\Delta H°$ = 7.33 kJ/mol for Cd(II), and 5.33 kJ/mol for Pb(II)). The reaction was accompanied by a decrease in entropy ($\Delta S°$ = –19.87 J/K·mol for Cd(II), and –8.38 J/K·mol for Pb(II)). When the temperature increases from 293 to 333 K, the Gibbs energy ($\Delta G°$) increased, indicating that biosorption was less feasible at higher temperatures. The present research confirms that *Z. lotus* leaves could be exploited as a low-cost and an effective biosorbent for the elimination of Cd(II) and Pb(II) ions from aqueous solution.

Keywords: Heavy metals biosorption; *Ziziphus lotus*; Wastewater treatment; Kinetic isotherms

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1. Introduction

One of the great scourges that preoccupy the majority of industrial countries today is the impact of industrial activities on the ecosystem integrity of natural environments [1]. Several types of chemical substances are involved in altering the quality of natural environments and are qualified for this reason as pollutants [2]. Heavy metals form a range of chemical pollutants, which can alter environmental health and threaten life in many natural ecosystems [3]. Water is a main ingredient for the activity of several industrial sectors integrating metallic substances in their processes such as metallurgical industry [4], mining activities [5], fossil fuel burning [6], alloy and solder [7], etc. Thus, wastewater from industrial effluents is the main vector of heavy metal pollution affecting natural environments. Several organisms express an important bioconcentrating character of heavy metals, which are thus accumulated in their tissues, and pass from one trophic level to another until they can threaten human health at the pyramidal summit of the trophic chains [8].

Water scarcity amplified by the effects of climate change, and the overexploitation of drinking water, has prompted scientists to investigate the various possible techniques capable of treating wastewater for its use, especially in industries [9]. Several techniques have been developed to purify polluted water, including: reverse osmosis [10], adsorption [11], coagulation/flocculation [12], membrane filtration [13] and chemical precipitation [14].

Adsorption is one of the techniques that have given good results in the treatment of wastewater, including for heavy metals [15]. This technique consists of using a material called the adsorbent, characterized by a large specific surface and by the presence on its surface of chemical molecules capable of trapping ions or molecules which are thus qualified as adsorbate [16]. The adsorbent could be natural or composite. Thus, although composite materials are designed in such a way that they offer better adsorption potential, they often have a high cost and could affect environmental health. Thus, finding a natural material with a high adsorption capacity would be an alternative to the use of expensive materials that threaten environmental health during their degradation. Inspired by the circular economy and looking for less expensive and eco-friendly solutions, natural biomaterials have been widely examined to assess their potential for use in wastewater treatment [17]. Therefore, biosorption has demonstrated its effectiveness and cost-efficiency in replacing conventional methods that are often expensive. [18].

Several biosorbents have been evaluated for their ability to sequester pollutants and particularly heavy metal ions, of which we cite: palm fruit bunch [19], orange peel [20], apple pomace [21], banana peel [22], coir pith [23], wheat straw [24], aquatic plants [25] and other materials. Plant biomass is coated on its surface with different chemical groups such as carboxyl groups, hydroxyl groups, and aromatic groups that enter into its biomolecular constitution [26]. Thus, several of these electrically charged surface chemical groups enter into electrostatic interactions with other electrical charges, including those carried by the metal ions [27].

In addition to its reputation for cannabis cultivation in certain regions, the northern part of Morocco is also well-known for its rich floristic diversity [28]. *Ziziphus lotus* shrubs are among the wild plants that colonize various locations in northern Morocco [29]. These shrubs are exploited mainly for their fruit, small and rounded, which is eaten when ripe or sometimes used to make flour in a traditional culinary preparation [30]. The leaves of this plant, mentioned in the Koran, are used in certain spiritual practices such as Roqya [31]. Many studies have recently focused on *Z. lotus* to explore its possible nutritional and therapeutic virtues [32]. The biomass of *Z. lotus* was found to be rich in protein substances, carbohydrate substances, and lipid substances, as well as a richness in mineral salts [33]. On the other hand, *Z. lotus* has also been shown to be able to manifest an antihyperlipidemic effect [34], an antiglycaemic effect [35],and treat some chronic inflammatory diseases [36]. In addition to its nutritional and therapeutic virtues, the biomass of *Z. lotus* has demonstrated its potential for environmental applications, serving as a biosorbent for various pollutants [37] or even as an anticorrosive [38]. The evaluation of the potential of a biosorbent is linked to the influence of certain parameters intrinsic to the biomass such as the particle size and the mass used, and to certain extrinsic parameters such as the pH and the temperature of the solution, the contact time [39]. Some studies additionally rely on the contributions of artificial intelligence in order to optimize the experimental conditions and maximize the efficiency of biosorption [40,41].

In this work, the potential of *Z. lotus* leaves powder (LP) as an ecofriendly biosorbent to remove two heavy metal ions, cadmium Cd(II) and lead(Pb), from an aqueous solution has been investigated. The biosorption capacity was evaluated under the effect of several parameters such as: biosorbent dosage, particle size, pH, initial ion concentration, contact time, and temperature. The biosorption kinetic data of the LP were tested by pseudo-first-order model, pseudo-second-order model, and Elovich model. The Langmuir, Freundlich, and Temkin isotherm models were used to study the equilibrium data. Moreover, the biosorption's thermodynamics were assessed.

2. Materials and methods

2.1. Biosorbent preparation

In September 2021, *Z. lotus* leaves were taken from fruiting bushes in the west of Al Hoceima (Morocco). The samples were cleaned several times with distilled water to remove debris, and then dried in the sun before being dried at 60°C for 24 h using an electric oven. Samples were reduced to powder using an electric mixer. Then and without any prior treatment, the LP was placed in a glass beaker for later use.

2.2. Ionic stock solutions

Before utilization, all glassware had been cleaned with nitric acid and then rinsed with deionized water. An initial concentration of 1 g/L was prepared for both Cd(II) and Pb(II), after dissolving in distilled water 2.74 g of $Cd(NO_3)_2{\cdot}4H_2O$ and 1.6 g of $Pb(NO_3)_2$, respectively. The different concentrations are obtained through a series of dilutions of the ionic stock solution.

2.3. Batch biosorption studies

In a batch system, the biosorption experiments of Cd(II) and Pb(II) on the LP sample were evaluated. The biosorption process was studied in relation to pH, temperature, dosage of biosorbent, initial metal concentration, contact time, and size of biosorbent particles. In 300 mL Erlenmeyer flasks with continuous agitation, the biosorption tests were conducted.

2.3.1. pH

Using a HANNA instruments (pH 209) pH meter, the pH values were adjusted to preferred values with 0.1 mol/L HCl or 0.1 mol/L NaOH solution. For each experiment, freshly diluted solutions were applied. The chemicals used were all of the highest quality. Under the optimized condition, for the two ions, the pH was varied from 2 to 10.

2.3.2. Temperature

The influence of temperature, in the range of 15°C–60°C, was studied under optimal conditions. An isothermal shaker was used to regulate the temperature.

2.3.3. Amount of biomass

The optimum biosorbent dose was identified using a range of biosorbent dosages from 0.5 to 9 g/L.

2.3.4. Initial metal concentration

The range of metal ion concentrations was from 0.25 to 100 mg/L.

2.3.5. Contact time

The adsorbate–adsorbent contact time ranged from 10 to 90 min.

2.3.6. Biosorbent particle size

Changing the size of the biosorbent particles from less than 100 μm to more than 500 μm was utilized to study how particle size impacted biosorption process. The pH was 8 for Cd(II) and 7 for Pb(II), the temperature was 25°C, the initial metal concentration was 100 mg/L, and the biosorbent dosage was 1 g/L.

At 3,000 rpm for 10 min, the samples were centrifuged to separate the liquid phase from the solid phase at the end of each batch adsorption test.

2.3.7. Adsorption capacity q_e (mg/g) and removal percentages (%R)

The adsorption capacity q_e (mg/g) and removal percentages (%*R*) of Cd(II) and Pb(II) from their aqueous solutions by the LP were calculated by Eqs. (1) and (2), consecutively, based on the quantification of the metal ions in the ionic solution before and after the adsorption process employing an atomic absorption spectrophotometry (GBC 932 plus).

$$q_e = \frac{C_i - C_e}{m} \tag{1}$$

$$\left(\%R\right) = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

where C_i (mg/L) is the initial ions concentration, C_e (mg/L) is the equilibrium cations concentration after adsorption, while m (g/L) represents the mass of the biosorbent per litre of ionic solution.

2.4. Characterization of samples

2.4.1. Elemental analysis (C, H, N and O)

The elemental analysis of the LP was performed using Vario EL, Elementar, Germany.

2.4.2. Estimation of the specific surface area

The specific surface area (SSA) of LP was calculated by the adsorption isotherms of N_2 at –196°C (77 K), using the BET (Brunauer–Emmett–Teller) method (ASAP 2020, Micromeritics, USA).

The samples of our study were degassed at 160°C for 12 h before each test.

2.4.3. Fourier-transform infrared spectroscopy analysis

Using a Bruker ALPHA spectrometer, the Fourier-transform infrared spectroscopy (FTIR) analysis was carried out, in order to identify different functional groups in each sample. KBr discs were prepared with each containing 1 mg of the sample and 100 mg of KBr. In the range 400–4,000 cm^{-1} that FTIR spectra were generated with detector at 2 cm^{-1} resolution.

2.5. Kinetic study of biosorption

In seeking to characterize the kinetics that would be involved in the process of Cd(II) and Pb(II) ions sequestration by LP, the pseudo-first-order, pseudo-second-order and Elovich models were adopted and the kinetic data were exploited based on the regression coefficient (r^2) and the amount of Cd(II) and Pb(II) adsorbed per unit weight of FP. The pseudo-first-order kinetic model is expressed in Eq. (3), the pseudo-second-order kinetic model is given by Eq. (4), while Elovich model is given as shown in Eq. (5):

$$q_t = q_e\left(1 - e^{-K_1 t}\right) \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

$$q_t = \frac{1}{\beta}\ln\left(1 + \alpha\beta t\right) \tag{5}$$

where q_e and q_t (both in mg/g) are respectively the quantities of heavy metal ions adsorbed at equilibrium and at

any time "t" (min); K_1 and K_2 are the rate constants for the pseudo-first-order kinetic and pseudo-second-order kinetic models, respectively; α is the initial adsorption rate (mg/g·min) and β is the desorption constant (g/mg).

2.6. Biosorption isotherm

The obtained biosorption measurements were examined using the Langmuir model and Freundlich model. Thus, the Langmuir model is based on the assumptions of a homogeneous adsorption surface containing similar adsorption sites, and a single monolayer is formed when adsorption is maximal. Eq. (6) is a description of this model:

$$q_e = q_m \frac{1 + K_L C_e}{K_L C_e} \tag{6}$$

where q_e (mg/g) is the biosorbed quantity at equilibrium state, C_e is the equilibrium concentration of the metal ion (mg/L), K_L represents the Langmuir equilibrium constant (L/mg), and q_m is the maximum adsorption capacity (mg/g).

The Freundlich isotherm model assumes that the adsorption surface is heterogeneous. It is a model which can be used to describe the multilayer adsorption, and for which the following equation provides a description Eq. (7):

$$q_e = K_F C_e^{1/n} \tag{7}$$

where K_F ($mg^{1-1/n}/g{\cdot}L^{1/n}$) represents the Freundlich constant and n represents a heterogeneity factor. While the K_F constant is associated to adsorption capacity, the $1/n$ value is associated to the intensity of biosorption. Based on the correlation coefficients (r^2) values obtained, the best model that fits with experimental data was chosen.

By studying the different adsorbent/adsorbate interactions, the Temkin model suggests that the heat of the adsorption of the molecules of the layer decreases linearly with the coverage because of the repulsive molecular interactions. Eq. (8) expresses the nonlinear form of the Temkin model:

$$q_e = \frac{RT}{B} \ln\left(AC_e\right) \tag{8}$$

3. Results and discussion

3.1. Biosorption studies

3.1.1. pH effect

The efficacy of the adsorption during the wastewater treatment process is influenced by pH solution. The distinctive adsorption sites of the biosorbent could be impacted by any change affecting the pH of the solution [42]. The influence of pH on the biosorption of Cd(II) and Pb(II) by LP was evaluated over a pH range of 2–10 as shown in Fig. 1. Thus, the elimination of both Cd(II) and Pb(II) from ionic solution has proved to be strongly linked to the variation of the pH solution. In highly acid medium, the capacity to trap metal ions was limited, and gradually increases with the increase in the pH value before starting to decrease when the pH of the medium exceeds certain values for both Cd(II) and Pb(II). Over the pH range from 2 to 8, the adsorption capacity increases from 5.3 to 70 mg/g and from 12.1 to 80.7 mg/g for Cd(II) and Pb(II), respectively. From pH = 8, this same capacity of LP to adsorb metal ions progressively decreases to reach 64.2 and 76.8 mg/g for Cd(II) and Pb(II), respectively, in pH = 10.

When the pH is low, the environment contains a lot of H^+ protons, which interact with the negative charges of the biosorbent, and thus could explain the low capacity of the LP to adsorb the two metal cations in an acidic medium. When the pH gradually increases, the surface of the biomaterial becomes more and more negative which increases gradually, through the electrostatic interactions, the adsorbed quantity of the two metallic species charged positively [43]. For pH values higher than 8, the reaction medium is enriched with OH^- ions that can form complexes with the Cd(II) and Pb(II) cations, which could explain the progressive decrease in the adsorption capacity beyond pH = 8 [44].

3.1.2. Biosorbent dosage effect

The efficiency of both Cd(II) and Pb(II) removal as a function of LP dosage was evaluated. The results are illustrated in Fig. 2. The dosage of biosorbent was adjusted from 0.5 to 9 g/L, while the other study parameters (temperature, pH, initial ion concentration, contact time, and particle size) were kept constant. The LP elimination efficiency increased from 40.56% to 84.30% and from 48.56% to 97.30%, when the dosage of biosorbent was increased from 0.5 to 9 g/L, respectively for Cd(II) and Pb(II). The results obtained show that, as the dosage of the biosorbent increases the efficiency of the elimination also increases. This trend could be explained by the increase in the number of metal ion adsorption sites on the surface of the biosorbent when its dosage increases [45].

3.1.3. Effects of biomaterial particle size/contact time

The adsorption kinetics of Cd(II) and Pb(II) were studied for different sizes of LP particles ranging from less than

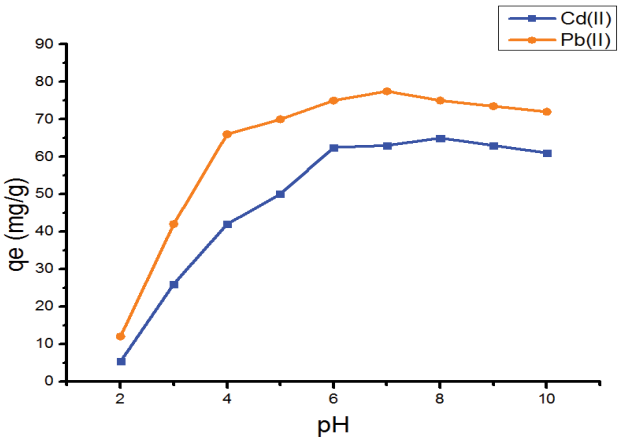

Fig. 1. pH effect on Cd(II) and Pb(II) biosorption by leaves powder: C_i = 100 mg/L, size of particles <100 µm, m = 1 g/L, T (°C) = 25°C, and contact time = 90 min.

100 μm to more than 500 μm, and as a function of contact time. The results are illustrated in Fig. 3. The data obtained indicate that the biosorption kinetic depends on both the contact time and particle size of the biosorbent. The best rate of Cd(II) and Pb(II) adsorption by LP, is obtained by particles smaller than 100 μm. Generally, with increasing contact time, the biosorption process slows down before stagnating beyond 80 min. With a particle size less than 100 μm, the amounts adsorbed at equilibrium are 66.35 and 78.36 mg/g, respectively for Cd(II) and Pb(II). It was clear that the biosorption efficiency increases with the decrease of the biosorbent particle size. This result could be explained by the increase in the SSA of the biosorbent particles when they decrease in size [46], as indicated in Table 1. Thus, in order to examine the impact of various parameters on the biosorption process, particles smaller than 100 μm were utilized because they are the most efficient at removing metal ions.

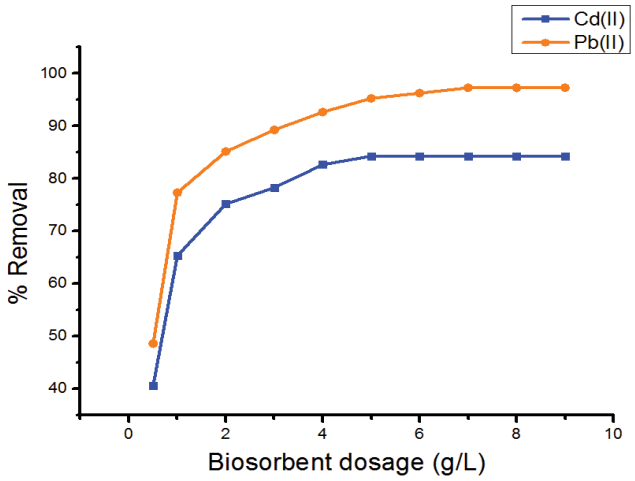

Fig. 2. Biosorbent dosage effect on Cd(II) and Pb(II) biosorption by leaves powder: C_i = 100 mg/L, size of particles <100 μm, T (°C) = 25°C, pH = 8 for Cd(II)/pH = 7 for Pb(II), and contact time = 90 min.

3.1.4. Preferential cation trapping

The intrinsic properties of metal ions affect the ability of their adsorption on the biosorbent surface. Thus, Cd(II) is a soft Lewis acid with a lower electronegativity (1.69), whereas Pb(II) is a hard Lewis acid with a higher electronegativity (2.33). Furthermore, the hydrated radius of Cd(II) (0.426 nm) is greater than that of lead Pb(II) (0.401 nm) [47]. All these factors could explain the preferential adsorption of lead compared to that of cadmium on the biosorbent surface [48].

3.2. Characterization of samples

3.2.1. Elemental analysis (C, H, N and O)

To comprehend the metals' binding mechanism to the biomass, it is crucial to determine the composition and structure of the biosorbent. The elementary analysis of the LP is shown in Table 2. Thus, results showed that LP is composed of 50.51% ± 1.42% carbon, 5.01% ± 0.22% hydrogen, 1.05% ± 0.10% nitrogen, and 42.45% ± 1.02% oxygen.

Table 1
Particle-size groups and specific surface area of leaves powder

Particle-size groups	Specific surface area (m^2/g)
<100 μm	3.031
100–300 μm	2.484
300–500 μm	1.940
>500 μm	1.493

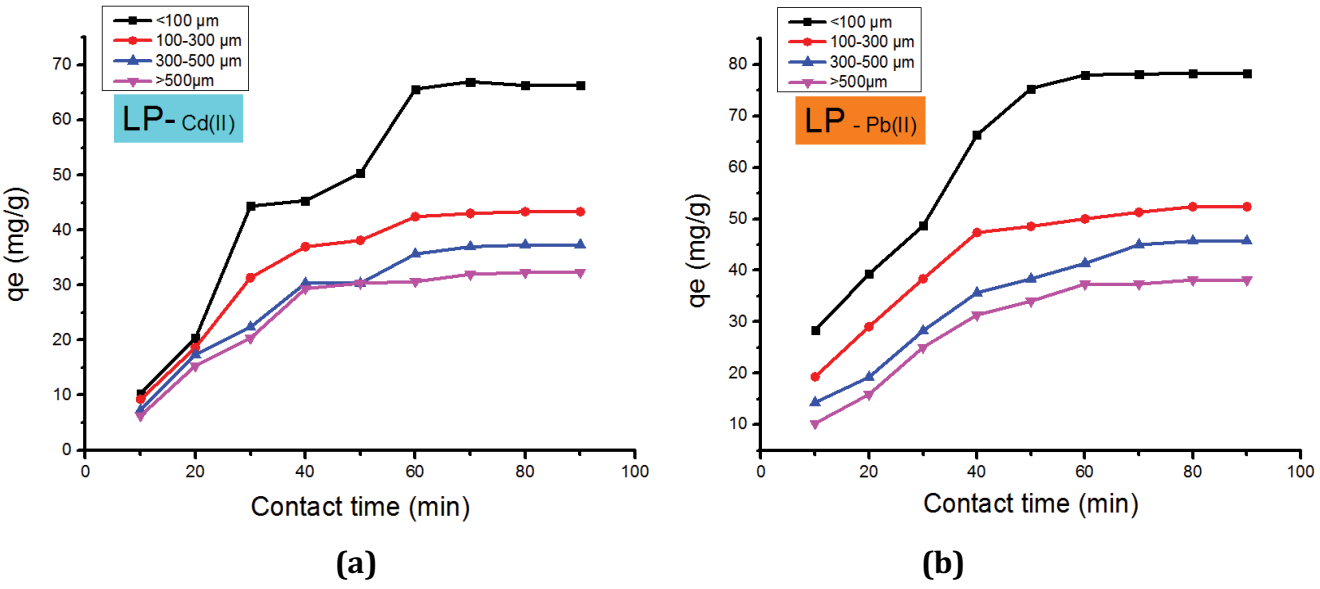

Fig. 3. Effect of biomaterial particle size/contact time on Cd(II) (a) and Pb(II) (b) biosorption by leaves powder: C_i = 100 mg/L, m = 1 g/L, T (°C) = 25°C, and pH = 8 for Cd(II)/pH = 7 for Pb(II).

3.2.2. FTIR analysis

To determine the main biochemical groups contained in the biosorbent, and which have been involved in the process of cationic trapping highlighted, the FTIR spectra was utilized as a qualitative analysis. Fig. 4 shows the infrared spectra (400–4,000 cm^{-1}) of LP. The appearance of any FTIR spectra is intimately linked to the phytochemical composition of the biosorbent biomass [49,50]. The broad and intense absorption peak at 3,421 cm^{-1} for FP indicates the presence of O–H groups (phenols, alcohols, and carboxylic acids) characteristic of pectins, lignin, and cellulose [51]. The observed peaks at 2,920 cm^{-1}, would have been generated by the C–H stretching vibrations of aliphatic acids. A stretching vibration of the C=O bond would be due to the carboxylic groups and their esters, which had probably given the peak at 1,732 cm^{-1}. The peak at 1,159 cm^{-1} would result from stretching of the C–O antisymmetric bridge of LP biomass's cellulosic components. An absorption band, at around 1,062 cm^{-1}, due to –O–CH_3 group, indicates the presence of lignin in the LP samples. An intense band at 621 cm^{-1} would be generated by the bending modes of the aromatic compounds. Additionally, the same Fig. 4 shows that for LP loaded with heavy metals (Cd and Pb), the intensities of the peaks corresponding especially to the hydroxyl and carboxyl groups decrease or slightly shifted after the ionic adsorption process. The FTIR spectra reveal that the hydroxyl and carboxyl groups, abundantly present in LP biomass, contribute significantly in the adsorption of Cd(II) and Pb(II) by involving electrostatic interactions.

Table 2
Elemental composition of leaves powder

Biosorbent	Elemental analysis			
Leaves powder	C %	H %	N %	O %
	50.51 ± 1.42	5.01 ± 0.12	0.95 ± 0.02	43.45 ± 1.02

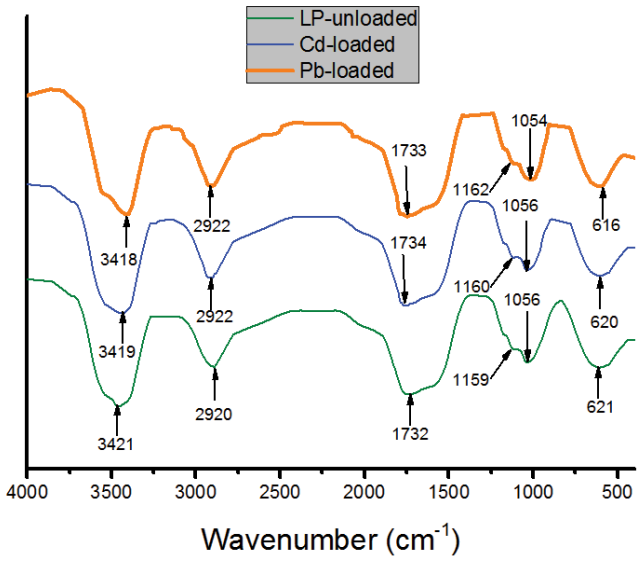

Fig. 4. Fourier-transform infrared spectroscopy analysis of fruits powder (leaves powder): spectra of leaves powder-unloaded, spectra of Cd-loaded, and spectra of Pb-loaded.

3.3. Kinetic study of biosorption

The pseudo-second-order kinetic model, the pseudo-first-order kinetic model and Elovich model were used to interpret the experimental data in order to understand the mechanism that controls the adsorption process. Nonlinear regression was used to estimate the parameters of both models. Table 3 presents the obtained data and correlation coefficients (r^2). The kinetic parameters of Cd(II) and Pb(II) adsorption onto *Z. lotus* LP indicate that the correlation coefficients (r^2) are closer to 1 for the pseudo-second-order kinetic model compared to the correlation coefficients given by the pseudo-first-order kinetic model. Moreover, the calculated values ($q_{e,cal}$) which were predicted by the pseudo-second-order kinetic model are nearer to the experimental values ($q_{e,exp}$), contrary to the values predicted by the pseudo-first-order kinetic model, which are different and far from the values obtained experimentally. We can conclude that Cd(II) and Pb(II) adsorption onto LP of *Z. lotus* appears to be more pseudo-second-order kinetic, suggesting a predominant chemisorption process.

Furthermore, according to the Elovich kinetic model's high correlation coefficients (r^2), the kinetic process of Cd(II) and Pb(II) biosorption onto LP can be properly described by this model. The Elovich model's applicability suggests that the active sites of the LP are diverse in nature and thus exhibit a range of chemisorption activation energies.

Similar results were reported on Cd(II) and Pb(II) biosorption by *Leucaena leucocephala* [52], *Caragana korshinskii* [53], and *Lactarius scrobiculatus* [54].

3.4. Biosorption isotherm

The biosorption capacities of LP for cadmium Cd(II) and lead Pb(II) were investigated for different initial metal concentrations as shown in Figs. 5 and 6. According to the experimental data, the biosorption capacity increases with the increase in the ionic concentration in the reaction medium. Strong driving forces for mass flow could explain

Table 3
Kinetic parameters of Cd(II) and Pb(II) uptake by leaves powder

Model	Kinetic parameters	Metals	
		Cd	Pb
Pseudo-first-order model	$q_{e,exp}$	66.35 ± 1.01	78.36 ± 1.17
	$q_{e,cal}$ (mg/g)	56.15 ± 1.23	67.76 ± 1.11
	K_1 (min^{-1})	0.0651 ± 0.0005	0.0655 ± 0.005
	r^2	0.989	0.995
Pseudo-second-order model	$q_{e,cal}$ (mg/g)	66.47 ± 1.98	80.11 ± 2.02
	K_2 (g/mg·min)	0.0010 ± 0.0002	0.0008 ± 0.0004
	r^2	0.9975	0.9970
Elovich model	α (mg/g·min)	6.433 ± 0.851	7.799 ± 0989
	β (g/mg)	0.062 ± 0.009	0.051 ± 0.008
	r^2	0.987	0.981

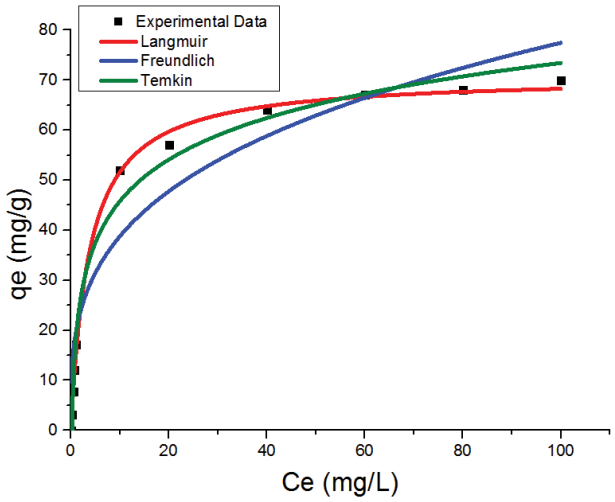

Fig. 5. Langmuir, Freundlich, and Temkin isotherms of Cd(II) biosorption on leaves powder: biosorbent dosage = 1 g/L, size of particles <100 μm, pH = 8, T (°C) = 25°C and contact time = 90 min.

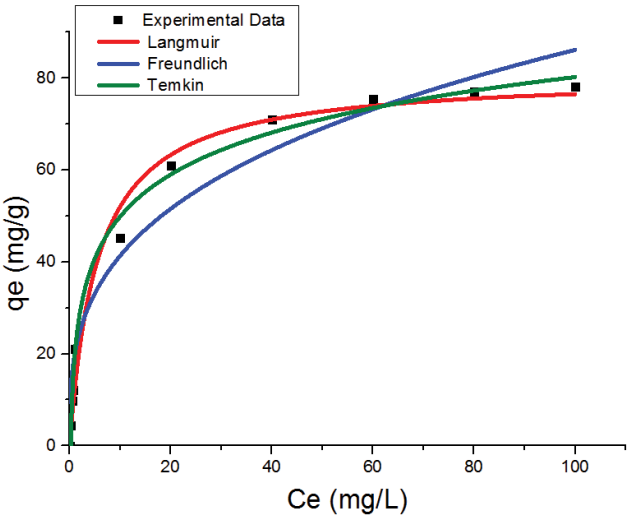

Fig. 6. Langmuir, Freundlich, and Temkin of Pb(II) biosorption on leaves powder: biosorbent dosage = 1 g/L, size of particles <100 μm, pH = 7, T (°C) = 25°C and contact time = 90 min.

the tendency of an increase in adsorption capacity with the increasing of metal ions concentration [55].

A high concentration of dissolved ions in solution implies a high quantity of these ions will be adsorbed on the surface of the biosorbent. Therefore, the initial metal concentration determines the biosorption capacity.

According to Giles categorization, the obtained isotherms form was type L. Generally, this type of isotherm is characteristic of adsorption with little competition between the adsorbate and the molecules composing the solvent.

The experimental biosorption isotherms obtained were compared with the biosorption isotherm models. The Langmuir, Freundlich and Temkin sorption parameters obtained from the isotherms as well as the correlation coefficients are indicated in Table 4. The table shows that the

Table 4
Isotherms constants (Langmuir, Freundlich and Temkin) that describe the sorption of Cd(II) and Pb(II) onto leaves powder

Isotherms		Metal	
		Cd	Pb
Langmuir parameters	q_m (mg/g)	70.78 ± 1.12	80.75 ± 1.09
	K_L (L/mg)	0.269 ± 0.011	0.181 ± 0.028
	r^2	0.997	0.983
Freundlich parameters	K_F (mg$^{1-1/n}$/g·L$^{1/n}$)	19.43 ± 1.23	19.84 ± 1.11
	n	3.331 ± 0.012	3.137 ± 0.038
	r^2	0.911	0.950
Temkin parameters	A (L/g)	4.567 ± 0.854	4.419 ± 0.799
	B	11.98 ± 1.00	13.16 ± 1.06
	r^2	0.989	0.992

Langmuir model and Temkin model, with a r^2 value close to 1, generated the best fit of experimental data. This result suggests that Cd(II) and Pb(II) are homogeneously adsorbed on a monolayer surface of the biosorbent.

The maximum monolayer adsorption capacities are higher for Pb(II) than for Cd(II) and this with the following order:

$$q_m\begin{Bmatrix}\text{LP}\\ \text{Pb}\end{Bmatrix}\left(=80.75\ \text{mg/g}\right) > q_m\begin{Bmatrix}\text{LP}\\ \text{Cd}\end{Bmatrix}\left(=70.78\ \text{mg/g}\right)$$

The obtained biosorption capacity of LP was compared with the results obtained from previous studies on the sequestration of Pb(II) and Cd(II) by plant biomass.

The biosorbent potential of *Z. lotus* LP has been revealed by the present study to be clearly superior to that of several biosorbents cited in the literature, as shown in Table 5.

4. Elution and regeneration

The capacity to regenerate during the several adsorption–elution–regeneration cycles determines the efficacy of utilizing materials to remove pollutants from wastewater. using hydrochloric acid (0.10 M) as eluent, LP was regenerated as a natural biosorbent of Cd(II) and Pb(II) ions for 5 consecutive cycles. Although experimental data have shown that the removal capacity of the two heavy metals gradually decreases after reaching 5 consecutive cycles, LP can be used for several cycles and thus constitute a natural and efficient biosorbent for the removal of Cd(II) and Pb(II) from polluted ionic solutions.

5. Temperature effect and thermodynamic study

The influence of temperature on the biosorption of Cd(II) and Pb(II) onto LP was studied in the temperature range of 15°C–60°C as shown in Fig. 7. For both Cd(II) and Pb(II), the adsorption capacity increases with the increase in the temperature of the medium. This capacity reaches its optimum value at 25°C, and beyond which it gradually decreases. For

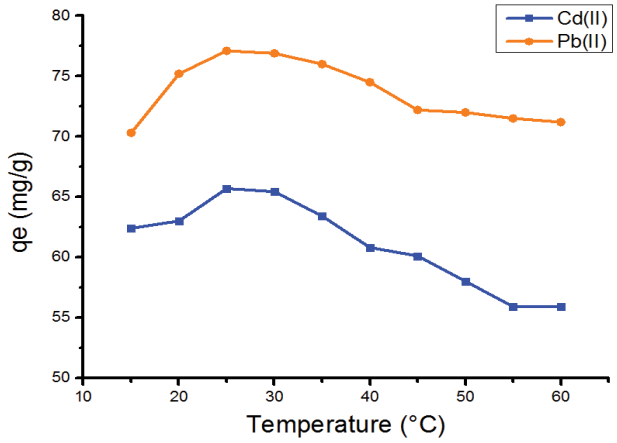

Fig. 7. Temperature effect on Cd(II) and Pb(II) biosorption by leaves powder: C_i = 100 mg/L, size of particles <100 µm, m = 1 g/L, pH = 8 for Cd(II)/pH = 7 for Pb(II), and contact time = 90 min.

Table 5
Comparison of maximum biosorption capacity of *Ziziphus lotus* leaves powder for Cd(II) and Pb(II) with other environmentally friendly biosorbents

Biosorbents	q_m (mg/g) Cd(II)	q_m (mg/g) Pb(II)	References
Lactarius scrobiculatus	53.1	56.2	[54]
Eichhornia crassipes	12.55	12.60	[56]
Flammulina velutipes	8.43	18.34	[57]
Brewery yeast	14.3	48.9	[58]
Grape bagasse	23.20	14.40	[59]
Cladophora biomass	12.07	20.65	[60]
Banana peel	5.71	2.18	[61]
Eucalyptus leaf residue	15	45	[62]
Ulva lactuca	29.1	–	[63]
Pokeweed	–	13.19	[64]
Ziziphus lotus (leaves)	70.78	80.75	Present study

both Cd(II) and Pb(II), the adsorption capacity increases with increasing medium temperature. This capacity reaches its optimum value at 25°C, before gradually decreasing when the temperature exceeds its optimum. When the temperature of the medium increases the molecular agitation increases, which explains the increase in the biosorption capacity. The decrease in this capacity beyond 25°C would be due to the weakening of the interactions between the ionic species and the adsorbent.

Considering the results of how temperature affects the biosorption of the two heavy metals, the measurement of some thermodynamic parameters, such as entropy ($\Delta S°$), enthalpy ($\Delta H°$) and free energy ($\Delta G°$) was carried out to describe the thermodynamic behavior of the biosorption of Cd(II) and Pb(II) on LP, using the following equations:

$$K_d = \frac{q_e}{C_e} \tag{9}$$

Table 6
Thermodynamic parameters estimated for the biosorption of Cd(II) and Pb(II) by leaves powder

Heavy metal	T (K)	K_d	$\Delta G°$	$\Delta H°$	$\Delta S°$
			(J/mol)	(kJ/mol)	(J/K·mol)
Cd(II)	293	1.702	13.158	7.335	–19.872
	303	1.892	13.357		
	313	1.551	13.555		
	323	1.380	13.754		
	333	1.267	13.953		
Pb(II)	293	3.032	7.791	5.336	–8.381
	303	3.329	7.875		
	313	2.921	7.959		
	323	2.570	8.043		
	333	2.472	8.127		

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

where K_d is the distribution coefficient (mL/g), $\Delta H°$ is the enthalpy change (kJ/mol), $\Delta S°$ is the entropy change (J/mol·K), $\Delta G°$ is Gibbs free energy change (kJ/mol), T is the temperature (K), and R is the universal gas constant (8.314 J/mol·K). The thermodynamic parameters given in Table 6 were calculated by taking use of the slopes and intercepts of linear regression of $\ln K_d = f(1/T)$.

The results obtained are presented in Table 6. The positive enthalpy values for the biosorption of the two heavy metals ($\Delta H°$ = 7.33 kJ/mol for Cd(II), and 5.33 kJ/mol for Pb(II)) suggest that the chemical process is endothermic. The negative entropy value ($\Delta S°$ = –19.87 J/K·mol for Cd(II), and –8.38 J/K·mol for Pb(II)) indicates a reduction in randomness at the solid/liquid interface during the biosorption. When the temperature increases from 293 to 333 K, the Gibbs energy ($\Delta G°$) increased, indicating that biosorption was less feasible at higher temperatures.

6. Conclusion

This study shows that powdered *Z. lotus* leaves powder is an effective biosorbent for the removal of Cd(II) and Pb(II) ions from aqueous solutions. The biosorption capacity was strongly dependent on biosorbent dosage, Temperature, pH, contact time, initial metal concentration, and particle size. The characterization of the material by the BET method revealed that particles whose size is less than 100 µm have the highest SSA and can be selected for better metal ions adsorption.

The kinetic biosorption of the obtained results show that the process is well described by the pseudo-second-order kinetic model. The Langmuir model and the Temkin model, among the tested isotherm models, accurately describe the experimental results for the sequestration of Pb(II) and Cd(II). Thus, the values of the maximum biosorption capacity, obtained from the Langmuir model, were: 70.78 and 80.75 mg/g for Cd(II) and Pb(II), respectively.

All these considerations reflect that the biosorption method using *Z. lotus* leaves, as an inexpensive and as an environmentally friendly biosorbent, could be used in industrial treatment processes for the elimination of Cd(II) and Pb(II), and also offering an alternative to conventional processes. The maximum adsorption capacities of the two metal ions decrease with increasing temperature, and the thermodynamic parameters indicate that the process of biosorption is endothermic and less feasible at higher temperatures. Moreover, it was shown that the ionic elimination process could be effective even after five adsorption–elution–regeneration cycles.

References

[1] W.-J. Liu, H. Jiang, H.-Q. Yu, Emerging applications of biochar-based materials for energy storage and conversion, Energy Environ. Sci., 12 (2019)1751–1779.

[2] A. Tolosana-Moranchel, S. McMichael, J.W.J. Hamilton, J.A. Byrne, P. Fernández-Ibañez, Electrochemically assisted photocatalytic degradation of contaminants of emerging concern in simulated wastewater using WO_3 – elucidation of mechanisms, Chem. Eng. J., 458 (2023) 141442, doi: 10.1016/j.cej.2023.141442.

[3] G. Qin, Z. Niu, J. Yu, Z. Li, J. Ma, P. Xiang, Soil heavy metal pollution and food safety in China: effects, sources and removing technology, Chemosphere, 267 (2021)129–205.

[4] Z.F. Gao, H.M. Long, B. Dai, X.P. Gao, Investigation of reducing particulate matter (PM) and heavy metals pollutions by adding a novel additive from metallurgical dust (MD) during coal combustion, J. Hazard. Mater., 373 (2019) 335–346.

[5] G. Tepanosyan, L. Sahakyan, O. Belyaeva, S. Asmaryan, A. Saghatelyan, Continuous impact of mining activities on soil heavy metals levels and human health, Sci. Total Environ., 639 (2018) 900–909.

[6] M. Kapahi, S. Sachdeva, Bioremediation options for heavy metal pollution, J. Health Pollut., 9 (2019) 191–203.

[7] M. Safiur Rahman, M.D.H. Khan, Y.N. Jolly, J. Kabir, S. Akter, A. Salam, Assessing risk to human health for heavy metal contamination through street dust in the Southeast Asian Megacity: Dhaka, Bangladesh, Sci. Total Environ., 660 (2019) 1610–1622.

[8] H. Li, J. Watson, Y. Zhang, H. Lu, Z. Liu, Environment-enhancing process for algal wastewater treatment, heavy metal control and hydrothermal biofuel production: a critical review, Bioresour. Technol., 298 (2020) 122–421.

[9] N. Ungureanu, V. Vlăduț, G. Voicu, Water scarcity and wastewater reuse in crop irrigation, Sustainability, 12 (2020) 55–90.

[10] L. Gao, G. Liu, A. Zamyadi, Q. Wang, M. Li, Life-cycle cost analysis of a hybrid algae-based biological desalination – low pressure reverse osmosis system, Water Res., 195 (2021) 116–957.

[11] W.S. Chai, J.Y. Cheun, P.S. Kumar, M. Mubashir, Z. Majeed, F. Banat, S.H. Ho, P.L. Show, A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application, J. Cleaner Prod., 296 (2021) 126589, doi: 10.1016/j.jclepro.2021.126589.

[12] C. Zhao, J. Zhou, Y. Yan, L. Yang, G. Xing, H. Li, P. Wu, M. Wang, H. Zheng, Application of coagulation/flocculation in oily wastewater treatment: a review, Sci. Total Environ., 765 (2021) 142–795.

[13] S. Hube, M. Eskafi, K.F. Hrafnkelsdóttir, B. Bjarnadóttir, M.Á. Bjarnadóttir, S. Axelsdóttir, B. Wu, Direct membrane filtration for wastewater treatment and resource recovery: a review, Sci. Total Environ., 710 (2020) 136–375.

[14] H. Peng, J. Guo, Removal of chromium from wastewater by membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology: a review, Environ. Chem. Lett., 18 (2020) 2055–2068.

[15] W. Zhang, S. Wang, X. Cao, N. Gu, Y. Qin, Y. Luo, Z. Liu, J. Wu, G. Meng, X. Guo, A facile coordinate complexing of Na(I) to fabricate SPB-ACE@MS-4A for selective adsorption to monovalent alkali metal ions, Desalination, 520 (2021) 115–337.

[16] W. Li, B. Mu, Y. Yang, Feasibility of industrial-scale treatment of dye wastewater via bio-adsorption technology, Bioresour. Technol., 277 (2019) 157–170.

[17] S.H. Kee, J.B.V. Chiongson, J.P. Saludes, S. Vigneswari, S. Ramakrishna, K. Bhubalan, Bioconversion of agro-industry sourced biowaste into biomaterials via microbial factories – a viable domain of circular economy, Environ. Pollut., 271 (2021) 116–311.

[18] P.A. Deyris, F. Pelissier, C.M. Grison, P. Hesemann, E. Petit, C. Grison, Efficient removal of persistent and emerging organic pollutants by biosorption using abundant biomass wastes, Chemosphere, 313 (2023) 137–307.

[19] K. Rambabu, G. Bharath, F. Banat, P.L. Show, Biosorption performance of date palm empty fruit bunch wastes for toxic hexavalent chromium removal, Environ. Res., 187 (2020) 109–694.

[20] S. Dey, S.R. Basha, G.V. Babu, T. Nagendra, Characteristic and biosorption capacities of orange peels biosorbents for removal of ammonia and nitrate from contaminated water, Cleaner Mater., 1 (2021) 100–1001.

[21] S. Zhang, Y. Ji, J. Dang, J. Zhao, S. Chen, Magnetic apple pomace biochar: simple preparation, characterization, and application for enriching Ag(I) in effluents, Sci. Total Environ., 668 (2019) 115–123.

[22] K.G. Akpomie, J. Conradie, Banana peel as a biosorbent for the decontamination of water pollutants. A review, Environ. Chem. Lett., 18 (2020) 1085–1112.

[23] H. Parab, M. Sudersanan, Engineering a lignocellulosic biosorbent – coir pith for removal of cesium from aqueous solutions: equilibrium and kinetic studies, Water Res., 44 (2010) 854–860.

[24] M. Wu, H. Liu, C. Yang, Effects of pretreatment methods of wheat straw on adsorption of Cd(II) from waterlogged paddy soil, Int. J. Environ. Res. Public Health., 6 (2019) 205, doi: 10.3390/ijerph16020205.

[25] Z. Lin, J. Li, Y. Luan, W. Dai, Application of algae for heavy metal adsorption: a 20-year meta-analysis, Ecotoxicol. Environ. Saf., 190 (2019) 110–189.

[26] J.Y. Zhu, U.P. Agarwal, P.N. Ciesielski, M.E. Himmel, R. Gao, Y. Deng, M. Morits, M. Österberg, Towards sustainable production and utilization of plant-biomass-based nanomaterials: a review and analysis of recent developments, Biotechnol. Biofuels, 14 (2021) 114, doi: 10.1186/s13068-021-01963-5.

[27] A. Kurniawan, Y. Fukuda, Analysis of the electric charge properties of biofilm for the development of biofilm matrices as biosorbents for water pollutant, Energy Ecol. Environ., 8 (2023) 62–68.

[28] Y. Chebli, S.E. Otmani, F. Elame, N. Moula, M. Chentouf, J.L. Hornick, J.F. Cabaraux, Silvopastoral system in Morocco: focus on their importance, strategic functions, and recent changes in the Mediterranean side, Sustainability, 13 (2021) 10744, doi: 10.3390/su131910744.

[29] E.E. Maaiden, Y.E. Kharrassi, K. Moustaid, A.K. Essamadi, B. Nasser, Comparative study of phytochemical profile between *Ziziphus spina christi* and *Ziziphus lotus* from Morocco, Food Meas., 13 (2019) 121–130.

[30] H.A. Bouzid, E.H. Sakar, L. Bijla, M. Ibourki, A. Zeroual, J. Gagour, J. Koubachi, K. Majourhat, S. Gharby, Physical fruit traits, proximate composition, antioxidant activity, and profiling of fatty acids and minerals of wild jujube (*Ziziphus lotus* L. (Desf.)) fruits from eleven Moroccan origins, J. Food Qual., 2022 (2022) 9362366, doi: 10.1155/2022/9362366.

[31] F. Elkhalloufi, S. Boutayeb, F. Mamouch, L. Rakibi, S. Elazzouzi, H. Errihani, The evolution of the socio-cultural and religious characteristics of cancer patients in Morocco: case of the National Institute of Oncology Rabat, BMC Cancer., 21 (2021) 516, doi: 10.1186/s12885-021-08175-y.

[32] I. Marmouzi, M. Kharbach, M.E. Jemli, A. Bouyahya, Y. Cherrah, A. Bouklouze, Y.V. Heyden, M.E.A. Faouzia, Antidiabetic, dermatoprotective, antioxidant and chemical functionalities in *Zizyphus lotus* leaves and fruits, Ind. Crops Prod., 132 (2019) 134–139.
[33] A.K. Rashwan, N. Karim, M.R.I. Shishir, T. Bao, Y. Lu, W. Chen, Jujube fruit: a potential nutritious fruit for the development of functional food products, J. Funct. Foods, 75 (2020) 104–205.
[34] N. Bencheikh, M. Bouhrim, I.A. Merrouni, S. Boutahiri, L. Kharchouf, M. Addi, D. Tungmunnithum, C. Hano, B. Eto, A. Legssyer, M. Elachouri, Antihyperlipidemic and antioxidant activities of flavonoid-rich extract of *Ziziphus lotus* (L.) Lam. fruits, Appl. Sci., 11 (2021) 77–88.
[35] F. Dahlia, S. Barouagui, H. Hemida, D. Bousaadia, B. Rahmoune, Influence of environment variations on anti-glycaemic, anti-cholesterolemic, antioxidant and antimicrobial activities of natural wild fruits of *Ziziphus lotus* (L.), S. Afr. J. Bot., 132 (2020) 215–225.
[36] A. Alsayari, S. Wahab, Genus *Ziziphus* for the treatment of chronic inflammatory diseases, Saudi J. Biol. Sci., 28 (2021) 6897–6914.
[37] N.E. Messaoudi, M.E. Khomri, N. Chlif, Z.G. Chegini, A. Dbik, S. Bentahar, A. Lacherai, Desorption of Congo red from dye-loaded *Phoenix dactylifera* date stones and *Ziziphus lotus* jujube shells, Groundwater Sustainable Dev., 12 (2021) 100–552.
[38] A. Jmiai, B.E. Ibrahimi, A. Tara, M. Chadili, S.E. Issami, O. Jbara, A. Khallaayoun, L. Bazzi, Application of *Zizyphus Lotuse* - pulp of Jujube extract as green and promising corrosion inhibitor for copper in acidic medium, J. Mol. Liq., 268 (2018) 102–113.
[39] I.K. Rind, A. Sarı, M. Tuzen, M.F. Lanjwani, I. Karaman, T.A. Saleh, Influential biosorption of lead from aquatic solution using *Escherichia coli*/carbon nanofibers, Environ. Nanotechnol., 19 (2023) 100–776.
[40] M. Fawzy, M. Nasr, H. Nagy, S. Helmi, Artificial intelligence and regression analysis for Cd(II) ion biosorption from aqueous solution by *Gossypium barbadense* waste, Environ. Sci. Pollut. Res., 25 (2018) 5875–5888.
[41] M. Nasr, A.E.D. Mahmoud, M. Fawzy, A. Radwan, Artificial intelligence modeling of cadmium(II) biosorption using rice straw, Appl. Water Sci., 7 (2017) 823–831.
[42] A.A. Beni, A. Esmaeili, Biosorption, an efficient method for removing heavy metals from industrial effluents: a review, Environ. Technol. Innovation, 17 (2020) 100503, doi: 10.1016/j.eti.2019.100503.
[43] V.t. Quyen, T.H. Pham, J. Kim, D.M. Thanh, P.Q. Thang, Q.V. Le, S.H. Jung, T.Y. Kim, Biosorbent derived from coffee husk for efficient removal of toxic heavy metals from wastewater, Chemosphere, 284 (2021) 131312, doi: 10.1016/j.chemosphere.2021.131312.
[44] C. Bhattacharjee, S. Dutta, V.K. Saxena, A review on biosorptive removal of dyes and heavy metals from wastewater using watermelon rind as biosorbent, Environ. Adv., 2 (2020) 100007, doi: 10.1016/j.envadv.2020.100007.
[45] M. Kumar, A.K. Singh, Mohd. Sikandar, Study of sorption and desorption of Cd(II) from aqueous solution using isolated green algae *Chlorella vulgaris*, Appl. Water Sci., 8 (2018) 225, doi: 10.1007/s13201-018-0871-y.
[46] V. Mishra, C. Balomajumder, V.K. Agarwal, Biosorption of Zn(II) onto the surface of non-living biomasses: a comparative study of adsorbent particle size and removal capacity of three different biomasses, Water Air Soil Pollut., 211 (2010) 489–500.
[47] S. Cheng, Y. Liu, B. Xing, X. Qin, C. Zhang, H. Xia, Lead and cadmium clean removal from wastewater by sustainable biochar derived from poplar saw dust, J. Cleaner Prod., 314 (2021) 128074, doi: 10.1016/j.jclepro.2021.128074.
[48] M. Dias, J. Pinto, B. Henriques, P. Figueira, E. Fabre, D. Tavares, C. Vale, E. Pereira, Nutshells as efficient biosorbents to remove cadmium, lead, and mercury from contaminated solutions, Int. J. Environ. Res. Public Health., 18 (2021) 1580, doi: 10.3390/ijerph18041580.
[49] I. Marmouzi, M. Kharbach, M.E. Jemli, A. Bouyahya, Y. Cherrah, A. Bouklouze, Y.V. Heyden, M.E.A. Faouzia, Antidiabetic, dermatoprotective, antioxidant and chemical functionalities in *Zizyphus lotus* leaves and fruits, Ind. Crops Prod., 132 (2019) 134–139.
[50] E. Lazzari, T. Schena, M.C.A. Marcelo, C.T. Primaz, A.N. Silva, M.F. Ferrão, T. Bjerk, E.B. Caramão, Classification of biomass through their pyrolytic bio-oil composition using FTIR and PCA analysis, Ind. Crops Prod., 111 (2018) 856–864.
[51] Y. Chen, H. Wang, W. Zhao, S. Huang, Four different kinds of peels as adsorbents for the removal of Cd(II) from aqueous solution: kinetics, isotherm and mechanism, J. Taiwan Inst. Chem. Eng., 88 (2018) 146–151.
[52] C.A. Cimá-Mukul, Y. Abdellaoui, M. Abatal, J. Vargas, A.A. Santiago, J.A. Barrón-Zambrano, 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, Bioinorg. Chem. Appl., 2019 (2019) 2814047, doi: 10.1155/2019/2814047.
[53] T. Wang, J. Zheng, H. Liu, Q. Peng, H. Zhou, X. Zhang, Adsorption characteristics and mechanisms of Pb^{2+} and Cd^{2+} by a new agricultural waste–*Caragana korshinskii* biomass derived biochar, Environ. Sci. Pollut. Res., 28 (2021) 13800–13818.
[54] R.A. Anayurt, A. Sari, M. Tuzen, Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass, Chem. Eng. J., 151 (2009) 255–261.
[55] V.A. Feisther, J.S. Filho, F.V. Hackbarth, D.A. Mayer, A.A.U. de Souza, S.M.A.G.U. de Souza, Raw leaves and leaf residues from the extraction of essential oils as biosorbents for metal removal, J. Environ. Chem. Eng., 7 (2019) 103047, doi: 10.1016/j.jece.2019.103047.
[56] T. Nharingo, M. Moyo, Application of *Opuntia ficus-indica* in bioremediation of wastewaters. A critical review, J. Environ. Manage., 166 (2016) 55–72.
[57] D. Zhang, H. Hea, W. Li, T. Gao, P. Ma, Biosorption of cadmium(II) and lead(II) from aqueous solutions by fruiting body waste of fungus *Flammulina velutipes*, Desal. Water Treat., 20 (2010) 160–167.
[58] T.Y. Kim, S.K. Park, S.Y. Cho, H.B. Kim, Y. Kang, S. Done Kim, S.J. Kim, Adsorption of heavy metals by brewery biomass, Korean J. Chem. Eng., 22 (2005) 91–98.
[59] S. De Gisi, G. Lofrano, M. Grassi, M. Notarnicola, Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review, Sustainable Mater. Technol., 9 (2016) 10–40.
[60] A. Amro, M. Abhary, Removal of lead and cadmium ions from water using Cladophora biomass, Pol. J. Environ. Stud., 28 (2019) 3589–3596.
[61] J. Anwar, U. Shafique, Waheed-uz-Zaman, M. Salman, A. Dar, S. Anwar, Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana, Bioresour. Technol., 101 (2010) 1752–1755.
[62] V.A. Feisther, J.S. Filho, F.V. Hackbarth, D.A. Mayer, A.A.U. de Souza, S.M.A.G.U. de Souza, Raw leaves and leaf residues from the extraction of essential oils as biosorbents for metal removal, J. Environ. Chem. Eng., 7 (2019) 103047, doi: 10.1016/j.jece.2019.103047.
[63] M.M. Ghoneim, H.S.E. Desoky, K.M.E. Moselhy, A. Amer, E.H.A.E. Naga, L.I. Mohamedein, A.E. Al. Prol, Removal of cadmium from aqueous solution using marine green algae, *Ulva lactuca*, Egypt. J. Aquat. Res., 40 (2014) 235–242.
[64] G. Wang, S. Zhang, P. Yao, Y. Chen, X. Xu, T. Li, G. Gong, Removal of Pb(II) from aqueous solutions by *Phytolacca americana* L. biomass as a low-cost biosorbent, Arabian J. Chem., 11 (2018) 99–110.