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Evaluation of Pb (II) and Cd (II) biosorption from aqueous solution by *Ziziphus lotus* stem powder (ZLSP)

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Abstract. The ability of *Zizyphus lotus* stem powder (ZLSP) to remove Pb (II) and Cd (II) ions from an aqueous solution was evaluated. The present phenomenon of biosorption was revealed to depend on pH, biosorbent dosage, temperature, initial ionic concentration, time of contact and biosorbent's particle size. The sorption process was exothermic ($\Delta H°<0$), and showing a strong Pb(II)/Cd(II)-ZLSP affinity ($\Delta S°>0$). Gibbs free energy data ($\Delta G°<0$, and decreases as temperature increase) reveals that the process studied is characterized by its feasibility and spontaneous nature. The best fits of the equilibrium data were obtained by the Temkin model and the Langmuir model. The maximum Pb(II)/Cd(II)-ZLSP biosorption capacities were 33.02 mg/g for Pb (II) and 20.73 mg/g for Cd (II). The pseudo-second order model was the most appropriate for fitting the kinetic data. The characterization of the biochemical groups essentially involved in the sorption phenomenon was made possible by FTIR spectral analysis. The capacity of ZLSP as an effective and ecofriendly biosorbent is confirmed through this study.

Keywords: biosorption; isotherm; kinetic; thermodynamic; Ziziphus lotus

1. Introduction

The emergence of life on earth was found to be closely related to the water molecule (White *et al.* 2020). Human owe a lot of their survival on water (Rosinger and Brewis 2020). The last century has seen a strong demand for water in relation to the great industrial revolution and the demographic explosion in several corners of the world (Saatsaz 2020). Therefore, both domestic and industrial activities have contributed significantly to water pollution, which has led to a shortage of resources of drinking water for populations (Abdul Maulud *et al.* 2021). Many various types of organic and inorganic chemical pollutants are detected in wastewater wastewaters (Elgarahy *et al.* 2021). A plethora of pollutants, including heavy metals, have been discovered in a number of natural media, including soils, surface waters, aquifers, and many others (Sadeghi *et al.* 2022). Metal pollution is generated by a number of industrial sectors (Jia *et al.* 2019). Thus, Lead (Pb) and cadmium (Cd) contamination is caused by a number of anthropogenic activities, including the manufacturing of batteries (Dehghani-Sanij *et al.* 2019), oil refining (Naseri *et al.* 2021), utilization of fertilizer products (Wei *et al.* 2020), mining (Chirinos-Peinado and Castro-Bedriñana 2020), textile industry (Kishor *et al.* 2021), etc.

The direct release of polluted wastewaters poses a major hazard to the environment's health (Tariq *et al.* 2020). One of the places where these metallic discharges are released is the aquatic area, and a variety of these discharges are bioavailable to the biocenosis and mainly to the bio-accumulating organisms (Butnariu 2022). Thus, according to a process known as biomagnification, the concentration of harmful metallic elements rises from one link to the next along the trophic chains until it reaches levels that are dangerous to human health (Murtaza *et al.* 2022). The literature reports that lead and cadmium can cause a range of dysfunctions and physiological disorders in humans (Sall *et al.* 2020).

The scarcity of potable water, together with the awareness of the importance of ecosystem health, has stimulated research aimed at the treatment and reuse of water for a wide range of consuming sectors. Thus, diverse technologies for wastewater treatments have been conceived and then put to use, such as: chemical precipitation (Zhang and Duan 2020), reverse osmosis (Arola *et al.* 2019), adsorption (Ampiaw *et al.* 2019), ion- exchange membrane (Khan *et al.* 2017), and coagulation- flocculation (Jorge *et al.* 2022). Despite the fact that a number of procedures have undergone testing to determine whether they can remove metallic elements from a metal solution that has been contaminated, adsorption has shown great promise in providing a less expensive, clean and efficient means for metal sequestration (Rashid *et al.* 2021). The adsorption process is closely linked to the topological and electrical properties of the adsorbent, which is capable of trapping adjacent ionic species by its electrically charged surface patterns distributed over a large surface (Liu *et al.* 2019, Begum *et al.* 2021).

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Several studies have focused on exploring the adsorbent properties of biomass, particularly plant biomass, and several types of waste, part of the quest for low-cost and environmentally friendly substances (Boloy *et al*. 2021). The literature revealed a variety of biosorbents that have undergone testing to determine their biosorption capacity, such as: orange peels (Parashar and Gandhimathi 2022), banana peel (Akpomie and Conradie 2020), brown algae (Jayakumar *et al*. 2022), bacteria and fungi (Oyewole *et al*. 2019), etc. By containing a diversity of biochemical molecules such as lignin, polyphenols, polysaccharides, biosorbents of vegetable nature, expose a multitude of chemical functions such as amine groups, phosphate groups, acid groups, sulphonate groups, and hydroxyl groups, capable, thanks to their electrical properties, of carrying out electrostatic interactions with other electrically charged species such as metal ions (Elahi *et al*. 2020).

Due to a number of edaphic variables and microclimates as well as other reasons, the north of Morocco has a rich floristic diversity (El Maaiden *et al*. 2019). Thus, shrubs of the *Ziziphus lotus* species are widely distributed there. This species' reproductive phase is recognized by the development of drupe fruits, which turn brown when ripe, inside of a shrub with numerous branches covered in dense foliage. The fruits, known as Nbeg in the region, can be consumed either raw or after being traditionally processed to make a flour called Zemmita (Abcha *et al*. 2021). *Z. Lotus*'s phytochemical diversity in bioactive compounds (Berkani *et al*. 2022), as well as its biological activities (Hammi *et al*. 2022), have been revealed through the exploration of its biomass. Environmentally, *Ziziphus Lotus* was tested according to what several studies bring for its capacity to eliminate dyes (Boudechiche *et al*. 2019), cadmium ions (El Yakoubi *et al*. 2023a), lead ions (El Yakoubi *et al*. 2023b), and to show an anticorrosive potential (Oukhrib *et al*. 2017).

Our present work aimed to evaluate the elimination potential of *Ziziphus Lotus* stem powder (ZLSP) towards Pb (II) and Cd (II) enriching an ionic solution, while examining the effect of several parameters related to the reaction bath, the biosorbent particles, and the adsorbate. Elovich, Pseudo-first order, and pseudo-second order models, were involved in the kinetic study of pollutant sorption. Equilibrium data were examined using the Langmuir (L), Freundlich (F) and Temkin (T) isotherms. Additionally, biosorption was studied thermodynamically.

2. Materials and methods

2.1 Harvesting and preparing stems:

In September 2021, the *Ziziphus lotus* stems were harvested from some shrubs, located east of Targuist in Morocco. With distilled water, the collected samples underwent several washes to remove debris. Subsequently, they were sun-dried and further dried in an electric oven at 60°C for 24 hours. An electric mixer was utilized to grind the samples into a fine powder. The resulting ZLSP was then directly poured into a glass beaker without any additional preparation steps.

2.2 Preparation of ionic adrobats

By dissolving a mass of 1.6 g of $Pb(NO_3)_2$ and 2.74 g of $Cd(NO_3)_2.4H_2O$ in demineralized water, For Pb (II) and Cd (II) respectively, a concentration of 1 g/L was generated. A set of dilutions for each of the stock solutions made it possible to generate a series of concentrations.

2.3 Batch experiment of Cd (II) and Pb (II) biosorption onto ZLSP

In a batch system, the sequestering potential of ZLSP against the two metal species was evaluated. The biosorption process was investigated with respect to various parameters, including pH, dosage of ZLSP, temperature, initial ions concentration, time of contact, and ZLSP particle size. The experiments were carried out in 500-ml Erlenmeyer flasks equipped with continuous agitation. Using a HANNA pH meter and either a 100 mmol/L HCl solution or a 100 mmol/L NaOH solution, the pH values were brought to the appropriate levels. Freshly prepared and diluted solutions were utilized for each experiment. All chemicals employed in the study were of the highest quality. Optimal parameters for better biosorption efficiency have been deduced by experimenting in ranges of pH (2-10), Temperature (15-60°C), ZLSP dosage (0.5-9g/L), initial concentration (0.25-100 mg/g), particle size (Ø <100μm - Ø > 500 μm), and ZLS– Pb (II)/Cd (II) interaction time.

2.4 Analysis and characterization of samples

Assessment of elimination potential was based on the measurement of the Pb (II) and Cd (II) concentration before sorption process and after sorption process using a GBC 932 plus as an atomic absorption spectrophotometry. To estimate the adsorbed quantity qe (mg/g) and the removal percentage (%R) of the two metal species by ZLSP, equation (1) and equation (2) were applied respectively.

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

$$(\%\mathrm{R}) = \frac{\mathrm{C_i} - \mathrm{C_e}}{\mathrm{C_i}} * 100 \tag{2}$$

where:
C_i (mg/L): initial ion concentration.
C_e (mg/L): equilibrium ion concentration.
m (g/L): concentration of ZLSP.

To explore the correlation between ZLSP particle size variable (Ps) and specific surface area (SSA) variable in the powders, measurements of SSA were performed for various size ranges. The BET method (Brunauer–Emmett–Teller) has been employed to calculate the SSA of ZLSP, by the sorption isotherms of N_2 at -196 °C (77K) on an ASAP 2020, Micromeritics, USA. Prior to each test, the samples of ZLSP underwent degassing at 433 K for 12 hours. FTIR spectroscopy was deployed using a Bruker Alpha equipment to determine different kinds of chemical functions present in each sample of ZLSP. Thus, multiple discs of potassium bromide (KBr) were established, where each disk is composed of 0.1 g of KBr and 1 mg of ZLFP. FTIR spectra were obtained in the range of 400 to 4000 cm^{-1} with a detector resolution of 2 cm^{-1}.

By fixing the other parameters to their optimal values (particles size <100 µm, pH=6 for Pb (II) and pH=7 for Cd (II), C_i = 100 mg/L, T (°C) = 25-50 °C, m = 4-5 g/L, and contact time = 90 min), the effect of each parameter is assessed.

2.5 Biosorption kinetics and Biosorption isotherms biosorption kinetics

In order to understand the mechanism that governs the adsorption process, the experimental results were interpreted using pseudo first order kinetic model (PFOK), pseudo second order kinetic model (PSOK), and Elovich model. Referring to the quantity of each pollutant biosorbed and the values of regression coefficient (r^2) relating to each model, the kinetic data were analyzed. The following Eqs. (3)-(5) give the expressions relating to PFOK, PSOK, and the Elovich model respectively:

$$q_t = q_e(1 - e^{-K_1 * t}) \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

$$q_t = \frac{1}{\beta}\,\mathrm{Ln}(1 + \alpha\beta t) \qquad (5)$$

with:
q_e (mg/g): amount of ions trapped at equilibrium.
q_t (mg/g): amount of ions trapped at any time « t » (min).
K_1: rate constant for the PFOK model.
K_2: rate constant for the PSOK model.
α (mg/g min): The initial rate of adsorption.
(g/mg): Desorption constant.

Cd(II)/Pb(II)-ZLSP biosorption isotherm

These are Langmuir (L), Temkin (T) and Freundlich (F) models which were recruited to analyze the experimental data relating to Pb(II)/Cd(II)-ZLSP biosorption. Thus, the adsorbent-adsorbate contact surface is assumed to be homogeneous in the Langmuir model, with an identical adsorption sites, and the adsorption occurs in a monolayer fashion, where adsorbate molecules occupy the accessible surface adsorption sites. The model is described mathematically by Eq. (6) below:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \qquad (6)$$

with:
q_e (mg/g), q_m (mg/g), K_L (L/mg), C_e (mg/L) represent biosorbed quantity at equilibrium state, maximum adsorption capacity, Langmuir equilibrium constant, and equilibrium concentration of Cd (II) and Pb (II), respectively.

The Freundlich isotherm expressed by formula (7) presented below, describes a multilayer apposition of the adsorbate on a heterogeneous surface of the adsorbent:

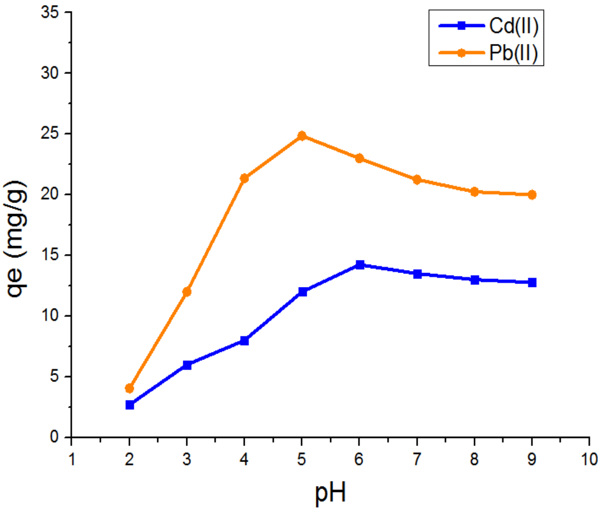


Fig. 1 Evolution of the biosorption capacity on ZLSP as a function of pH

$$q_e = K_F C_e^{1/n} \qquad (7)$$

with:
K_F: Freundlich constant ($mg^{1-1/n}\, g^{-1}\, L^{1/n}$).
n: a heterogeneity factor.
K_F: constant relating to the adsorption capacity.
1/n: relating to the biosorption intensity.

The model which best corresponds to the experimental data recorded is the one having offered the value of the correlation coefficient (r^2) closest to 1.

By studying Pb(II)/Cd(II)-ZLSP interactions, the Temkin model suggests that due to repulsive molecular interactions, the molecular adsorption heat of the layer decreases linearly with coverage, as expressed mathematically by Eq. (8) below:

$$q_e = \frac{RT}{B}\,\mathrm{Ln}\,(A\, C_e) \qquad (8)$$

3. Results and discussion

3.1 Cr (VI) elimination study pH effect

The pH of the solution may have an impact on an adsorbent's characteristic adsorption sites, which would consequently affect the efficiency of adsorption in the process of removing pollutants contaminating wastewater (Beni and Esmaeili 2020). The values of q_e were estimated over a pH range (2 - 9) as described in Fig. 1. Thus, the biosorbed metal quantity, for Pb (II) and Cd (II), raises from 4.04 to 23.00 mg/g and from 2.69 to 14.23 mg/g, respectively, when the pH of the solution rises from 2 to 6. The biosorption capacity of ZLSP then gradually decreases, with increasing pH, to reach 20.00 mg/g and 12.77 mg/g for Pb(II) and Cd(II), respectively, at pH = 9. It turned out that the pH of the solution has an impact on ZLSP's capacity to

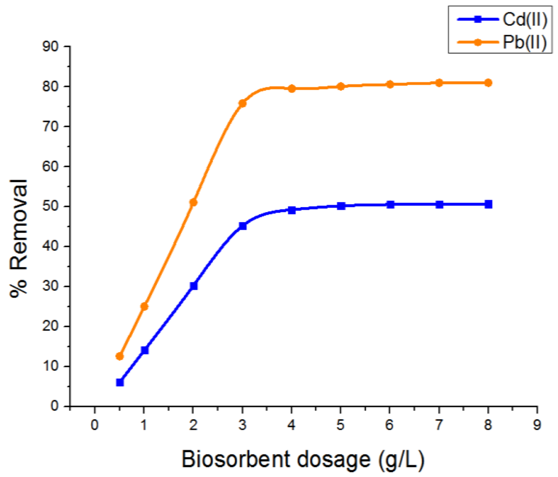
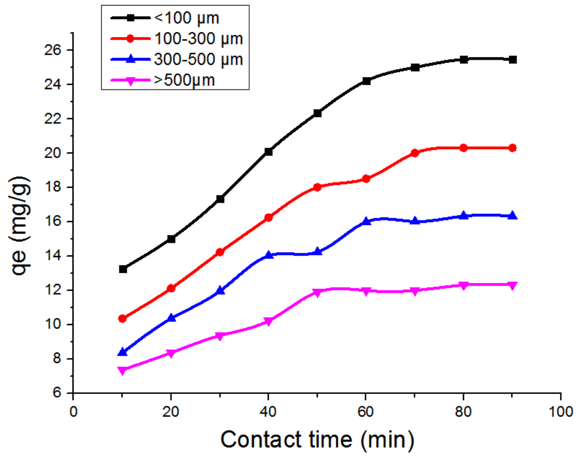
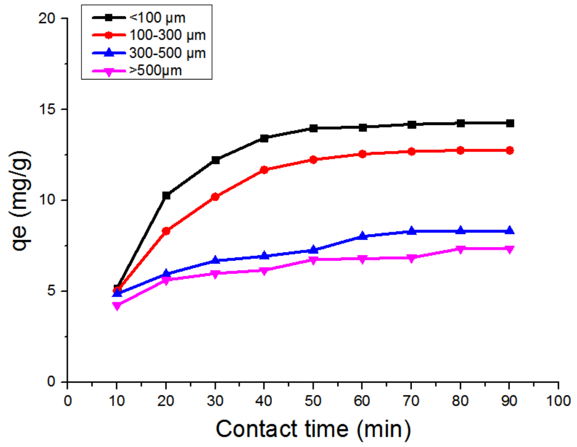


Fig. 2 Cd (II) / Pb (II) Biosorbent dosage effect on biosorption capacity onto ZLSP



(a) Pb(II) biosorption



(b) Cd(II) biosorption

Fig. 3 Biosorption of Pb (II) and Cd (II) by ZLSP as a function of particle size/contact time

sequester Pb (II) and Cd (II). Therefore, this capacity is reduced in an acidic environment and grows in tandem with pH up to an optimal value, beyond which it gradually decreases.

In an acidic environment, sufficiently concentrated oxonium H_3O^+ ions, result of water's protonation, enter with the two bivalent cations Pb (II) and Cd (II) in competition on the negatively charged surface of the biosorbent, which could explain the low ionic sequestration in an acidic environment.

When the pH of the solution increases, the reduction of oxonium ions allows the surface of the ZLSP to be more and more negative, which favors cationic fixation and would therefore increase the adsorption capacity of Pb (II) and Cd (II) (Quyen *et al*. 2021). In a basic reaction environment, Cd (II) and Pb (II), would be neutralized by the hydroxide anions OH^-, which could explain the inefficiency of the elimination process of the two cationic pollutants at pH>7 (Bhattacharjee *et al*. 2020).

ZLSP dosage effect

The possible influence of the ZLSP dosage on the elimination potential against the two ions object of the study was investigated by maintaining the other parameters at their optimum, and the results of which are presented in Fig 2. When passing the dosage of ZLSP from 0.5 to 8 g/L, the elimination percentage increases from 12.56 to 81.02% and from 6.06 to 50.69 %, for Pb (II) and Cd (II) respectively. By gradually increasing the dosage of ZLSP, we indirectly increase the Cd(II)/Pb(II)-ZLSP binding sites, which would be the origin of the progressive increase in the cation trapping capacity of ZLSP (Kumar *et al*. 2018).

Effect of ZLSP particle size / time of contact

Cation trapping were investigated for samples particles of various sizes, ranging from less than 100 µm to more than 500 µm, in relation to the time of interaction, as indicated in Fig. 3. The data collected demonstrates that the process's kinetics of Pb (II) and Cd (II) is influenced by both the time of contact and size of ZLSP particles. The ZLSP sample whose size is less than 100 µm expresses a considerable equilibrium biosorption rate, with 25.49 and 14.26 mg/g, at equilibrium, for Pb (II) and Cd (II) respectively. Clearly, it was the small ZLSP particles (Ø <100 µm) that were able to offer the highest ionic removal rate, and which increases with increasing ZLSP – Cd(II)/Pb(II) contact time. The results demonstrate that the removal efficiency of Cd (II) and Pb (II) increases as the size of the biosorbent particles decreases. The greater SSA that smaller biosorbent particles display helps to explain this observation, as shown in Table 1 [43]. Because they are the most effective in this depolluting process, particles smaller than 100 µm were used to study the effects of different parameters on the removal percentage and biosorption capacity.

Differential elimination Cd(II)/Pb(II)-ZLSP

The adsorption property of each ionic variety is influenced by its fundamental characteristics. For example, lead acts as a harder Lewis acid, exhibiting a higher electro-negativity (2.33), while cadmium behaves as a softer Lewis acid, characterized by a lower electronegativity (1.69). Furthermore, the hydrated radius of lead (0.401 nm) is smaller than that of cadmium (0.426 nm) (Cheng *et al*. 2021). All these reasons seem to explain the adsorption preference of lead over cadmium on ZLSP surface (Dias *et al*. 2021).

Table 1 Particle size groups (PSG) and specific surface area (SSA) of ZLSP

PSG	SSA (m^2/g)
<100µm	1.532
100-300µm	1.004
300-500µm	0.810
>500µm	0.222

Table 2 Elementary atomic analysis of ZLSP

Biosorbent	Atomic percentages			
	C %	H %	N %	O %
ZLSP	51.74 ± 1.88	4.95 ± 0.19	1.01 ± 0.02	42.22 ± 1.15

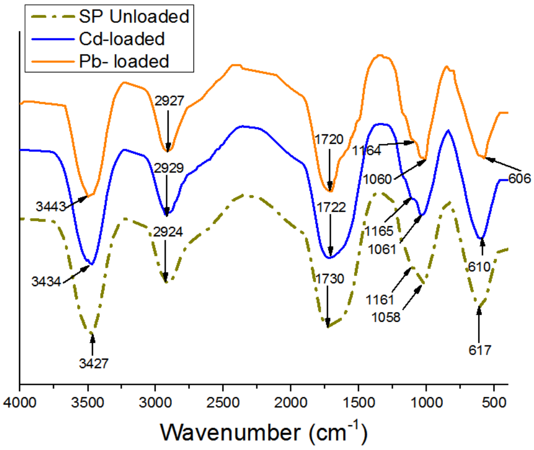


Fig. 4 Unloaded ZLSP and Cd(II)/Pb(II) loaded ZLSP by FTIR analysis

3.2 ZLSP characterization elementary atomic analysis

In an attempt to understand how the metallic pollutant is sequestered on the adsorption surface, it was wise to carry out a composition analysis of the biosorbent. Thus, the ZLSP was found to be made of 51.74 ± 1.88 % carbon, 42.22 ± 1.15 % oxygen, 4.95 ± 0.19 % hydrogen, and 1.01 ± 0.02 % nitrogen, as shown in Table 2.

3.3 FTIR spectra analysis and characterization of ZLSP samples

To identify the most significant biological groups present in the biosorbent and their contribution during the Cd (II) and Pb (II) trapping process, FTIR spectra are employed as a qualitative study technique. This allowed to deduce the nature of the biochemical groups at the origin of the interaction coreing the Cd (II) – ZLSP and Pb(II) - ZLSP adsorption phenomenon. The FTIR spectra (400 to 4000 cm^{-1}) for the unloaded sample and the Cd (II) and Pb (II) loaded sample are shown in Fig. 4. The composition and molecular structure of the biomass employed have a major effect on the FTIR spectrum's shape (Marmouzi *et al.* 2019, Lazzari *et al.* 2018).

The involvement of O-H groups (carboxylic acids, alcohols, and phenols), which are typical of pectins, lignin, and cellulose, is indicated by the broad high peak at 3427cm cm^{-1} for ZLSP. The seen peaks at 2924 cm^{-1} would have been attributed to aliphatic acids' C-H stretching vibrations (Chen *et al.* 2018). The peak noted at 1730 cm^{-1} in the FTIR spectra of the ZLSP sample would possibly be due to the stretching vibration of the C=O bond. This indicates the presence of carboxylic and esters groups in the ZLSP. The peak observed at 1161cm cm^{-1} in the FTIR spectrum of the ZLSP biosorbent is likely attributed to the stretching of the C-O antisymmetric bridge in the cellulosic components of the biomass. The presence of lignin can be recognized by an absorption band at about 1058 cm^{-1} generated by the -O-CH$_3$ group in the Biosorbent sample. Vibrational bending mode of the aromatic compounds would produce a strong band at 617 cm^{-1}. The Fig. shows also that following the process of Cd (II) and Pb (II) biosorption, there is a significantly decrease in the intensities of the peaks, particularly those associated with hydroxyl and carboxyl radicals. Furthermore, slight shifts in the positions of these peaks are also noted. Thanks to the FTIR results, it seemed that from the ZLSP various chemical groups insinuate themselves, to interact electro-statically with cationic units as was demonstrated for Cd (II) and Pb (II).

3.4 Kinetics of the elimination process

In order to understand the dominant mechanism during the sequestration of the two metals studied on the surface of ZLSP, chemisorption or physisorption, the experimental data collected are analyzed by recruiting the use of three models: pseudo second order kinetic model (PSOK), pseudo first order kinetic model (PFOK) and Elovich model as indicated in the Table 3. Thus, and by comparing their parameters and particularly the correlation coefficients noted from the nonlinear regression, it turned out that the PSOK model best described the kinetics relating to the Cd(II)/Pb(II)-ZLSP interaction, suggesting the dominant involvement of chemisorption in the process. Furthermore, the Elovich kinetic model, by referring to the correlation coefficient (r^2), can model the Cd(II)/Pb(II)-ZLSP biosorption kinetics, and which would suggest that the binding sites on ZLSP are diverse and exhibit a range of activation energies by chemical sorption. Previous studies relating to the biosorption of Pb (II) and Cd (II), align with our results, as is the case with *Leucaena leucocephala* (Cimá-Mukul *et al.* 2019), Korshinsk pea shrub (Wang *et al.* 2021), and scrobiculate milk cap (Anayurt *et al.* 2009).

3.5 Cd(II)/Pb(II)-ZLSP biosorption isotherm

Several previous studies reported that increasing the ionic concentration tends to intensify the molecular Brownian motion which maximizes the chances of incorporation of ions at their appropriate sites in the adsorbate (Feisther *et al.* 2019). To test the effect of the concentration of the metalpollutant on the adsorption capacity by ZLSP, a range of concentrations was applied and the results obtained are presented in both Figs. 5 and 6. The curve generated by the

Table 3 Main variables of Cd(II)/Pb(II)-ZLSP adsorption kinetics

	kinetic parameters	Metals	
		Cd	Pb
Model	$q_{e,\,exp}$	14,26 ± 1.11	25,49 ± 1.77
PFOK	$q_{e,\,cal}$ (mg/g)	12,88 ± 1.33	22,66 ± 1.77
	K_1 (min^{-1})	0,072 ± 0.005	0,059 ± 0.007
	r^2	0,987	0,985
PSOK	$q_{e,\,cal}$ (mg/g)	14,99 ± 1.23	27,001 ± 2.012
	K_2 (g/mg.min)	0,00522 ± 0.0002	0,0022 ± 0.0007
	r^2	0,996	0,997
Elovich	α (mg/g.min)	1,826 ± 0.666	2,357 ± 0.818
	β (g/mg)	0,292 ± 0.008	0,151 ± 0.006
	r^2	0,986	0,994

Table 4 Constants of isotherms: Langmuir (L), Temkin (T) and Freundlich (F), that characterize the adsorption of Pb(II) and Cd (II) onto ZLSP

Isotherms constants		Metal	
		Cd	Pb
Langmuir (L)	q_m (mg/g)	20,73± 1.07	33,02± 1.34
	K_L (L/mg)	0,451± 0.019	0,277± 0.019
	r^2	0,998	0,998
Freundlich (F)	K_F ($mg^{1-1/n}\,g^{-1}\,L^{1/n}$)	7,054± 1.001	9,264± 1.234
	n	0,255± 0.019	0,294± 0.047
	r^2	0,876	0,874
Temkin (T)	A (L/g)	7,275± 0.766	4,436± 0.569
	B	3,357± 1.009	5,629± 1.001
	r^2	0,973	0,974

Table 5 ZLSP-Cd (II)/Pb (II) maximum biosorption capacity compared to other biomaterials

Biosorbents	q_m (mg/g) Cd (II)	q_m (mg/g) Pb (II)	References
Banana peel	5.71	2.18	(Anwar *et al.* 2010)
Grape Bagasse	23.20	14.40	(De Gisi *et al.* 2016)
Brewery yeast	14.3	48.9	(Kim *et al.* 2005)
Eucalyptus leaf	15	45	(Feisther *et al.* 2019)
Flammulina velutipes	8.43	18.34	(Zhang *et al.* 2010)
Eichhornia crassipes	12.55	12.60	(Nharingo and Moyo 2016)
Lactarius scrobiculatus	53.1	56.2	(Anayurt *et al.* 2009)
Ulva lactuca	29.1	-	(Ghoneim *et al.* 2014)
American pokeweed	-	13.19	(Wang *et al.* 2018)
Ziziphus lotus (Stem)	20,73	33,02	Present study

experimental data is type L according to the Giles classification (Medyńska-Juraszek *et al.* 2021), which suggests a possible competition between Cd (II)/Pb (II) and the solutes dissolved in the solvent. In order to understand how the adsorbate molecules are spread on the ZLSP surface, three models were tested and whose parameters are compared to those obtained experimentally. These are the isothermal models of Langmuir, Freundlich and Temkin, and whose general expression of their parameterizations obtained as well as those relevant to the experiment are given in Table 4. It clearly appears that the best fit of the experimental data, was offered by the Langmuir and Temkin models, with an r^2 value close to 1, which suggests a homogeneous, monolayer arrangement of Pb (II)/Cd (II) on the ZLSP's surface. Thus, the maximum monolayer adsorption capacities are higher for Pb (II) than for Cd (II)

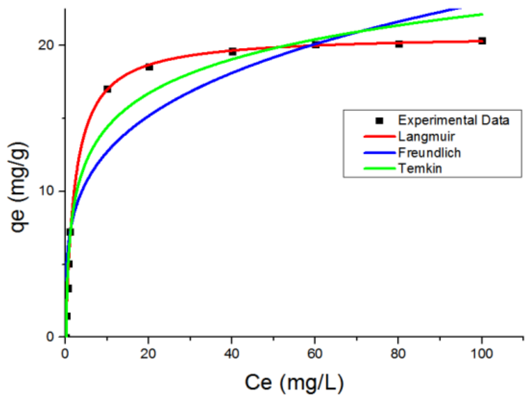


Fig. 5 Langmuir (L), Temkin (T) and Freundlich (F) isotherms of Cd (II) biosorption onto ZLSP

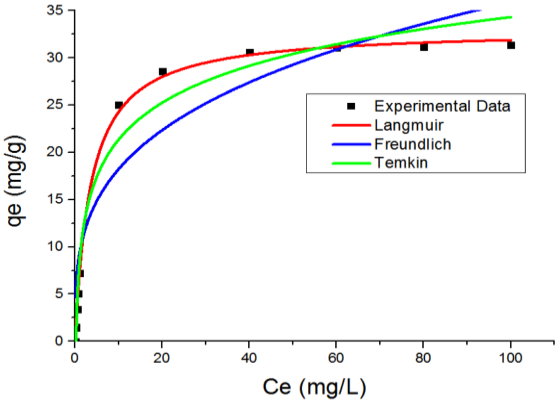


Fig. 6 Langmuir (L), Temkin (T) and Freundlich (F) isotherms of Pb (II) biosorption onto ZLSP

and in the following order:

$$q_m\left\{\begin{matrix}ZLSP\\ Cd\end{matrix}\right. (=20,73\ mg/g) < q_m\left\{\begin{matrix}ZLSP\\ Pb\end{matrix}\right. (=33,02\ mg/g)$$

The maximum capacities of ZLSP to biosorb Cd (II) and Pb (II) expressed by our study were compared to previous results concerning the behavior of the two metals against other types of plant materials, as shown in Table 5.

3.6 Elution and regeneration

The efficiency of using biomaterials in the removal of pollutants from wastewater is determined by their regenerative capacity during successive cycles of adsorption, elution and regeneration. Using HCl (0.20 M), as eluent for Cd (II) and Pb (II), and in four consecutive cycles, ZLSP was regenerated, still retaining eliminatory power against lead and cadmium. According to this result, the use of ZLSP as an efficient and economically affordable biosorbent is recommended.

3.7 Process's thermodynamic aspects and temperature effect:

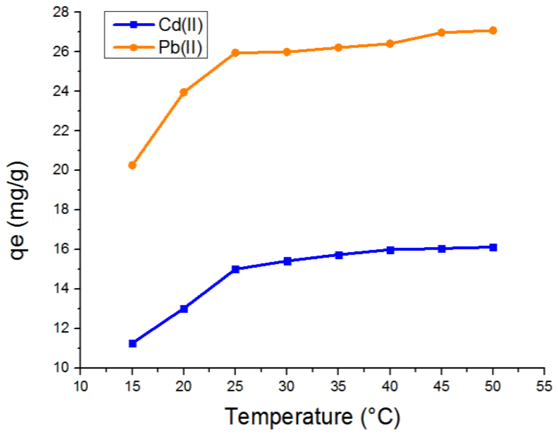


Fig. 7 Impact of temperature on Cd(II)/ Pb(II) elimination by ZLSP

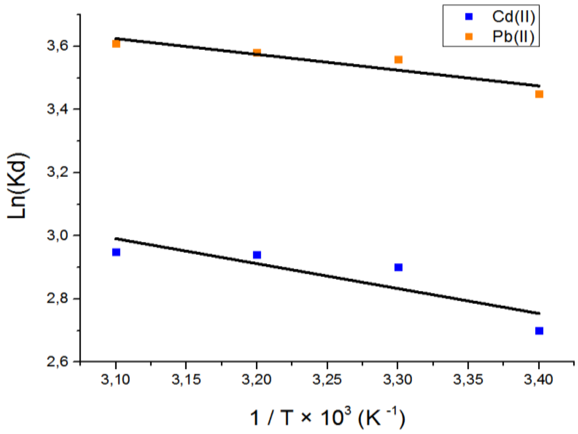


Fig. 8 Plot of Ln K_d = f (1/T) for the Cd(II) and Pb(II) biosorption on ZLSP

It is in the thermal range (15–50°C) that the effect of temperature on the elimination capacity of ZLSP towards the two metal species was examined, as shown in Fig 7. The biosorption potentiel increases with the increase in the temperature of the medium, although from 25°C the quantity of the two adsorbed metals increases only slightly. The increase in the biosorption rate is explained by the fact that as the medium's temperature rises, molecular agitation also rises.

To comprehend the thermodynamic traits of the biosorption Cr (VI)-ZLFP, the following equations were utilized to compute several parameters, including ΔG°, ΔH°, and ΔS°:

$$K_d = \frac{q_e}{C_e} \quad (9)$$

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

$$Ln\ K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (11)$$

where:
K_d: distribution coefficient (mL/g).
ΔH°: enthalpy change (kJ/mol).
ΔG°: Gibbs free energy change (kJ/mol).
ΔS°: entropy change (J/mol K).
R: universal gas constant (8.314 J/ mol K).
T: temperature (K).

Table 6 The thermodynamic variables relating to Pb(II)/Cd(II)-ZLSP biosorption

Heavy Metal	T (K)	K_d	ΔG^0 (KJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K mol)
Cd (II)	293	14.96	- 18,932	- 9,946	53,87
	303	18.23	- 20,291		
	313	19.03	- 20,743		
	323	19.21	- 21,196		
Pb (II)	293	31.50	- 16,762	- 9,228	57,57
	303	35.13	- 17,192		
	313	35.90	- 17,622		
	323	37.15	- 18,052		

Using the slopes and intercepts of the linear regression of Ln K_d = f (1/T), corresponding to the curves of Cd(II) and Pb(II) which are illustrated in Fig. 8, the thermodynamic variables were estimated and indicated in Table 6.

The negative values of ΔH° (ΔH° = - 9,228 kJ/mol for Pb (II) and ΔH° = - 9,946 kJ/mol for Cd (II)) implies that the process is exothermic, and the positive values of entropy ΔS° (57,57 J/K mol for Pb (II), and ΔS° = 53,87 J/K mol for Cd (II)), suggest a considerable Pb(II) and affinity Cd(II) for ZLSP. Moreover, the Gibbs free energy (ΔG°) is negative, and it decreases when the temperature increases from 293 to 323 K, which confirms the feasibility of the biosorption and the spontaneous nature of the process.

4. Conclusions

The main aim of the current work was to examine the use of *ziziphus lotus* stem powder as a biosorbent in the removal of Pb (II) and Cd (II) ions from an ionic solution. Conventional methods for eliminating Pb (II) and Cd (II) ions from wastewater are known to be costly, making the utilization of ZLSP an attractive alternative. The biosorption capacity was found to be strongly affected by factors such as dosage of ZLSP, particle size, temperature, initial Pb(II) / Cd(II) concentration, pH, and contact time. The characterization of ZLSP material using the BET method revealed that particles smaller than 100 µm exhibited the highest SSA, indicating their suitability for enhanced metal ion adsorption. Kinetic and isothermal modeling of the data collected suggested that the Pb (II) / Cd (II) biosorption could be well described by the PSOK model and the Langmuir isotherm (L) respectively. The maximum capacity of biosorption (q_m), calculated from the model of Langmuir (L), were: 33,02 mg/g and 20,73 mg/g for Pb (II) and Cd (II) respectively. The successful application of the biosorption method using *ziziphus lotus* stems suggests its potential use in different water treatment processes in terms of Pb (II) and Cd (II), offering an alternative to conventional methods. Furthermore, it was demonstrated that even after five cycles of adsorption, elution, and regeneration, the Pb (II)/Cd (II) elimination process could still be successful.

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