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Investigation of the efficacy of Pb(II) and Cd(II) ions biosorption by the Corn bran: Study equilibrium and thermodynamic parameters

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Abstract. This study focuses on investigating the efficacy of corn bran, serving as a natural biosorbent, in the biosorption of Pb(II) and Cd(II) ions. The FTIR, XRD, SEM, and pHpzc were used to characterize the biosorbent. The aim of examining the impact of contact time, pH, biosorbent dose, initial concentration, and temperature was to thoroughly comprehend how these factors affect the biosorption process. The equilibrium was defined through the Langmuir and the Freundlich isotherm models. The Langmuir model exhibited a satisfactory linear correlation (R^2 = 0.999 for Pb and R^2 = 0.989 for Cd), than the Frundlich isotherm. At the optimal conditions for each metal, the maximum loading capacity (qmax) was 40.98 mg/g and 29.41 mg/g for Pb(II) and Cd(II) ions, respectively. These results emphasize the possibility of utilizing corn bran as a low-cost and eco-friendly material for removing lead and cadmium ions. The biosorption capacity of lead and cadmium ions in a single system was higher than in a binary system, at optimum conditions. Over 99.18 % and 97.54 % of lead and cadmium ions were successfully recovered through desorption using 0.5M HNO_3. The examination of thermodynamic parameters (ΔH^o, ΔS^o, and ΔG^o) suggests that the biosorption process is exothermic, spontaneous, and favorable.

Keywords: biosorption; cadmium; corn bran; isotherm; lead; thermodynamic parameters

1. Introduction

Numerous industrial and metallurgical processes, as well as particular human activities, contribute to the ongoing production of growing amounts of wastewater. These include mining, smelting, metal plating, pigment production, battery manufacturing, metallurgical processes, and activities related to tannery and fabrication [1, 2]. The wastewater often contains substantial concentrations of heavy metal ions [3]. The presence of these metals in ponds, drains, and rivers affects both the environment and the quality of life for local communities that depend on these water sources. In this group of metals are lead, cadmium, aluminum, arsenic, beryllium, chromium, mercury, nickel, zinc, and others.

They are not naturally decomposable and present a risk to the environment. The critical issue of heavy metal contamination requires immediate and effective solutions to minimize the related risks as much as feasible [4, 5]. Exposure to lead, whether acute or chronic, results in various abnormalities within the human body. Prolonged exposure to lead can bring up to conditions such

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as arteriosclerosis, hypertension, thrombosis, and cardiac disease [6]. Children are at a heightened risk of lead, particularly when exposed to dust containing environmental lead, which can intensify the severity of poisoning [7]. The global presence of cadmium pollution is evident in both groundwater and soil [8]. Cadmium is a metal widely used in a range of industries, such as cadmium plating, alkaline batteries, copper alloys, and the manufacturing of paints and plastics [9]. Cadmium has been associated with the induction of apoptosis, oxidative stress, DNA methylation, and DNA damage. Furthermore, it is well known as a carcinogen, affecting organs such as the kidneys, bones, lungs, pancreas, and prostate, and contributing to neurodegenerative diseases [10]. Hence, it is crucial to treat wastewater before discharge. According to studies, heavy metal removal from industrial waterways has gained traction due to the negative influence on species' life cycles [11]. The commonly used methods for removing heavy metals from wastewater include ion exchange, chemical precipitation, reverse osmosis, ultrafiltration, coagulation, electrochemical treatment, and biosorption [12]. Nevertheless, certain limitations exist in applying these methods, including elevated operating costs, the energy-intensive nature of using hazardous chemicals, and the generation of residual metal sludge, which poses a risk of secondary contamination during disposal [13]. Biosorption proves to be an affordable, environmentally friendly, and easily operable method [14]. This is attributed to the fact that biomasses, being biodegradable, readily available, and low-cost materials, are employed in the process [15].

Last decades, several biomasses such as Potato and Banana peels [16], Plantain peels [17], Pistachio shells [18], Date palm leaves [19], Almond green hull [20], Melon peel [21], Broadleaf Cattail, and Water hyacinth [22], Mango seed [23], Alga Anabaena sphaerica [24], White bran and Coffee waste [25], Agave bagasse [26], etc., have been used for heavy metal removal from aqueous solution.

In this research, milled corn bran is used without chemical treatment as a biosorbent, aiming to minimize costs and simplify the biosorption process. Therefore, the objectives of this study include characterizing the biomass and exploring its potential as a biosorbent for the removal of lead and cadmium ions in both forms, single and binary systems from aqueous solutions.

2. Methods and materials

Corn bran was gathered from the Peja region in Kosovo. It was washed several times with distillated water to remove dust and then dried at 80°C for 20 hours [27]. The dried samples were grinded and sieved through < 0.2 mm, which was used for experiments.

The biosorption of Pb (II) and Cd (II) ions onto corn bran was investigated through a batch technique. Experimental runs used a stock solution of individual metals with various concentrations (100, 60, 30, and 15 mg/dm^3). A predetermined amount of biosorbent (0.05, 0.125, 0.25, and 0.50 g) was balanced with 50 cm^3 metal solutions in a stopper Pyrex glass flask for specific time (5, 10, 20, 30, 60, 90, and 120 min) at different temperature (15, 25, 35, and 45°C) and different pH values (2, 3, 4, 5, 6, and 7), within a thermostatic shaker bath (200 rpm). The pH of the solutions was adjusted to the desired level using 0.1 M HCl or 0.1 M NaOH. (pH-meter HANA Model, HI 98130). The concentration of metal ions (Pb^{2+} and Cd^{2+}) was determined by AAS (Atomic Adsorption Spectrometer, flame Contra AA 300, Analytik Jena).

The capacity of biosorbent (q_e), and the removal percentage (% A) were calculated using the following Eqs. (1-2):

Table 1. Elementary analysis of Corn bran

Elem.	C	H	N	S	O	Mg	Al	Cl	Si	K	Ca	Fe
(%)	43.9	6.45	0.71	0.05	46.95	<0.01	<0.01	0.03	0.14	0.35	0.03	0.007

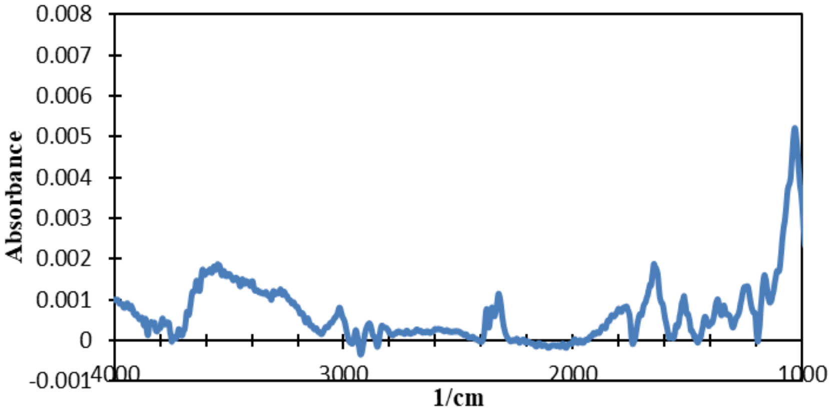


Figure 1. FTIR spectrum of corn bran

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\%(A) = \frac{C_o - C_e}{C_0} x\, 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of metal ions (mg/dm^3); V is the volume of solution (dm^3), and m is the amount of the biosorbent (g). The determination of the point of zero charge (pH_{PZC}) for the biosorbent was carried out through the pH drift method [27].

Regeneration of corn bran is crucial for ensuring its sustainability as a raw material for water purification [28]. The desorption of Pb(II) and Cd(II) ions was done by 0.5M HNO_3, 0.5 M HCl, 0.5M CH_3COOH, and distilled water. The corn bran containing metal ions was placed into the desorption medium (0.125g/50cm^3) and agitated at 200 rpm for 2 hours, at a temperature of 25°C.

3. Results and discussion

3.1 Characterization of biosorbent

Elementary analysis is very important when examining the properties of any carbon-based material, including cellulose/lignocellulose. Typically, these investigations are employed to evaluate the energy value of a material and information on its chemical composition [29]. It involves a quantitative examination of different components (C, H, N, S, O, etc.) Table 1 presents the elementary analysis for corn bran. Based on the values presented in this table, it can be observed that the predominant elements are carbon and oxygen. Furthermore, the combustion of 1 g of corn bran resulted in the formation of 23.30 mg of ash.

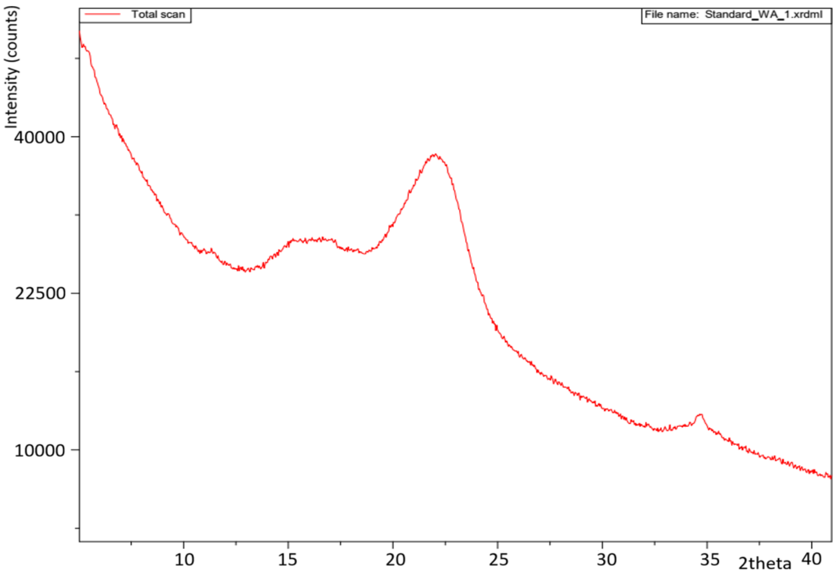


Figure 2. XRD of corn bran

3.1.1 FTIR analysis

The analysis of Fourier transform infrared spectroscopy (FTIR) determines the functional groups existing in corn bran. These groups could play a role in the binding of Pb(II) and Cd(II) ions, as well as in biomass interactions [30]. The FTIR spectroscopy technique (PerkinElmer Spectrum IR Version 10.6.1) was used to determine the functional groups present in corn bran over a scan range of 1000-4000 cm^{-1}. For the spectrum, 1,000 scans were accumulated with a spectral resolution of 4 cm^{-1}. Fig. 1 displays this spectrum.

From Fig. 1, it was noticed the presence of carboxyl, carbonyl, hydroxyl, and amino groups on the biosorbent surfaces. These functional groups play a significant role in the biosorption of heavy metals due to the affinity of metal ions towards them [21]. The peaks observed at 3542, 3008, and 2882 cm^{-1} correspond to the stretching vibrations of O-H, N-H, and C-H, respectively. Nevertheless, the bands detected at 1755 and 1635 cm^{-1} may be associated with the stretching vibrations of C=O and N-H, respectively [24]. Additionally, the three peaks at 1532, 1406, and 1360 cm^{-1} suggest stretching vibrations of N-H, C=O, and C-N. Furthermore, a large biosorption band observed with the peak at 1024 cm^{-1} indicates the stretching vibration of the C-O bond.

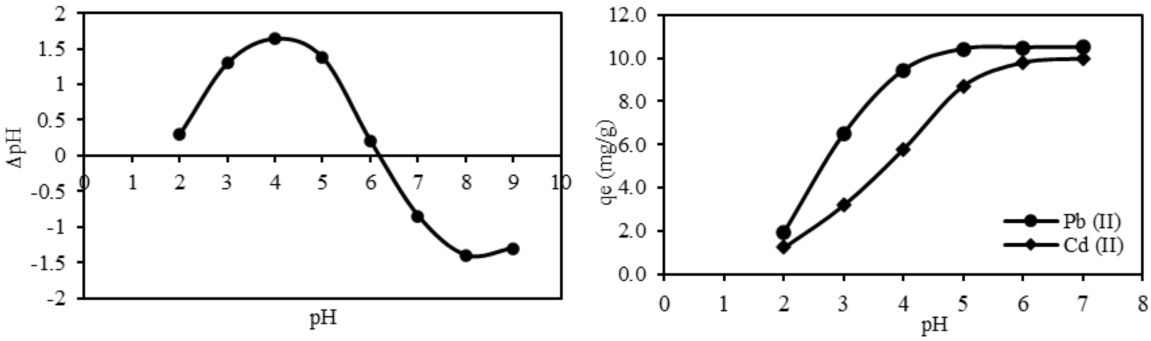
3.1.2 X-ray diffraction

The X-ray diffraction (XRD) of the corn bran was analyzed and recorded as a function of 2θ at a scan speed of 1.2^{o} min^{-1}, and XRD patterns were recorded from 5 to 40^{o} (see Fig. 2). This examination facilitated the identification of the amorphous segment within this biomass. Several peaks were discerned at 2θ angles of 15°, 22°, and 34.5°, indicative of characteristic cellulose patterns [31].

3.1.3 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) serves as an effective tool for examining the surface morphology of biosorbents. Through this technique, qualitative insights into the surface structure

Figure 3. SEM image of the corn bran



(a) pH_{PZC} of corn bran (b) Biosorption capacity vs pH

Figure 4. Determination of the pH_{PZC} and impact of pH on biosorption of Pb(II) and Cd(II)

can be obtained, offering valuable information for the characterization of materials [32]. The SEM image of the biosorbent used is presented in Fig. 3. This image clearly shows that the surface of corn bran was very porous. This biomass exhibits numerous heterogeneous porous layers, suggesting a favorable environment for the biosorption of metal ions like lead and cadmium on its surface.

3.1.4 Determination of PH_{PZC} and impact of pH

The zeta potential is a key parameter, encompassing numerous surface phenomena, including biosorption and the stability of metal ions on biomass surfaces. This parameter enables the assessment of how the charge of particles influences the biosorption of metal ions [33]. The biosorption of metal ions such as lead and cadmium by corn bran can be effectively explained by the point of zero charge (pH_{PZC}). This pH value relies on the chemical composition and electronic characteristics of the functional groups present on the surface of the biosorbent [32]. The pH_{PZC} was obtained from the equation $\Delta pH = pH_f - pH_o$, where pH_f – is the final pH and pH_o – is the initial pH. These results are presented in Fig. 4(a).

Based on Fig. 4, the corn bran exhibits a pH_{PZC} value of 6.2. At pH levels below 6.2, the surface of the biosorbent carries a positive charge, whereas at pH levels above 6.2, the surface becomes negatively charged. The increased bisorption of metal ions above the pH_{PZC} is due to heightened attractive forces between the negatively charged surface of corn bran and the positively charged

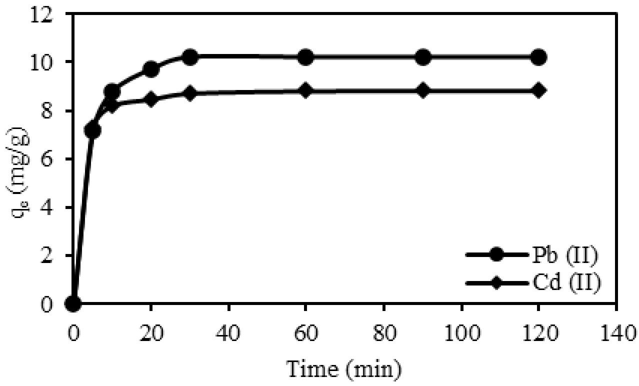


Figure 5. Effect of different contact times on biosorption of Pb(II) and Cd(II), by corn bran

metal ions. Conversely, below the pH_{PZC}, there is competition between hydrogen ions and metal ions (Pb^{2+}, Cd^{2+}) to interact with the biomass surface [24].

The pH of the solution significantly impacts the biosorption process of metal ions as it directly affects the binding capacity of hydrogen ions relative to that of metal ions to the active sites on the biosorption surface [34]. The figure described the correlation between different pH values and the biosorption capacity of Pb(II) and Cd(II), as presented in Fig. 4(b). The data suggest that as the pH of the liquid phase rises, the biosorption of metal ions increases accordingly. The optimal pH for the maximum biosorption of Pb(II) and Cd(II) was determined to be 6 and 7, respectively. At a low pH value (pH 2), the removal rates of lead and cadmium by the corn bran were only 1.94 and 1.26 mg/g, respectively. However, at pH 6, these rates increased significantly to 10.47 for lead and 9.79 mg/g for cadmium. In addition, at pH 7, the biosorption of cadmium reached 9.98 mg/g. At lower pH levels, the increased presence of hydrogen ions on the corn bran surface leads to a higher occupation of sites. As a result, fewer sites are available for the biosorption of metal ions, thereby reducing the efficiency of biosorption [21]. As the pH value increases, fewer sites on the surface are occupied by hydrogen ions. Consequently, there is an increase in the bisorption of metal ions due to the availability of more sites for their attachment. Furthermore, metal ions tend to precipitate at pH levels above 7, which is indicated by a decrease in biosorption capacity [29].

3.2 Effect of contact time

The contact time is a vital parameter in studying the biosorption mechanism and helps to find out the pathway towards determining the rate of biosorption [30]. Influence of contact time on the removal of lead and cadmium ions by corn bran was examined for a time interval of 5 - 120 min. This investigation was conducted under conditions of pH 5.0, biosorbent dose 0.125g, and temperature 25°C, which is illustrated in Fig. 5.

These data suggested that the biosorption of both metal ions was quite rapid in the first 5 min, followed by a gradual increase until equilibrium was attained at 30 minutes for both metals. Subsequently, the biosorption remained constant thereafter. At contact time 5 min, the capacity of biosorption of Pb(II) and Cd(II) ions was 7.81, 7.69 mg/g, but after 30 min, it increased to 10.51, 8.17 mg/g. Therefore, when contact time increased from 5 to 30 min (~ 500 %), the biosorption capacity increased by just 2.70 and 0.48 mg/g for lead and cadmium, respectively. Contact time of

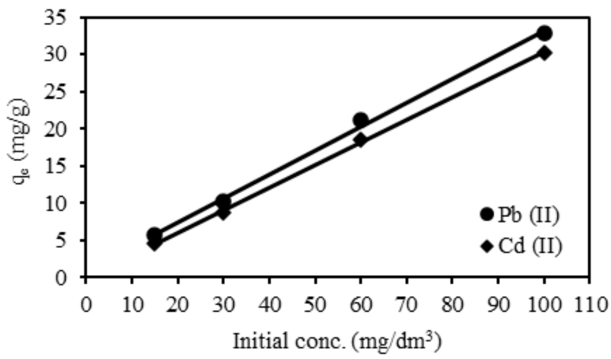


Figure 6. The effect of initial concentrations of metal ions Pb(II) and Cd(II), on the biosorption by corn bran

30 min was used as the optimum time for the biosorption process of Pb(II) and Cd(II) ions by corn bran.

3.3 Effect of initial concentration

The interaction of metal ions with the biosorbent is notably influenced by the initial concentration of metal ions [30]. The investigation of the impact of the initial concentration of lead and cadmium ions by corn bran was chosen from 15-100 mg/dm^3. A graph was plotted to illustrate the relationship between various concentrations of lead and cadmium ions and their respective biosorption capacities, as shown in Fig. 6.

It was observed that the removal of metal ions varied significantly by the solution's initial concentration [34]. Fig. 6 illustrates the enhanced biosorbent capacity as the concentration of metal ions increases. The experimental results exhibited that, if the initial concentration of lead increases from 15 to 100 mg/dm^3, the uptake rises from 5.71 mg/g to 33.28 mg/g, and from 4.52 mg/g to 30.25 mg/g for cadmium, respectively. This elevation may be attributed to an increase in the initial concentration of metal ions, thereby creating a stronger driving force for the ions to move from the solution to the biosorbent [35]. On the other hand, a higher concentration gradient diminishes the resistance to mass transfer between the bulk phase and the biomass surface [29].

3.4 Effect of biosorbent dose

The dosage of biosorbent represents an important parameter in determining the optimal quantity needed to achieve maximum biosorption of metal ions at certain conditions [30]. Different biomass dosages of biosorbent from 0.05, 0.125, 0.250, and 0.50 g were used to investigate this effect on the removal of Pb (II) and Cd(II) ions by corn bran. These results are represented in Fig. 7.

From experimental data, it can be concluded that the biosorption capacity of lead and cadmium ions decreases as the biosorbent dose increases, notably within the range of 0.05 to 0.25g. Otherwise, raising the biosorbent dose from 0.25 to 0.50 g did not yield any significant impact on the biosorption of metal ions. Because a specific mass of corn bran can absorb a constant quantity of metal ions. This phenomenon could be clarified by the formation of aggregates or particle interactions, which consequently decrease the total surface area of the biomass [36, 37]. Hence, a biosorbent dose of 0.125g/50 cm^3 was identified as the optimal dosage for Pb(II) and Cd(II) ions.

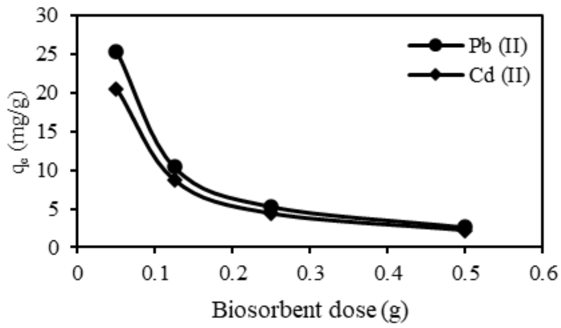
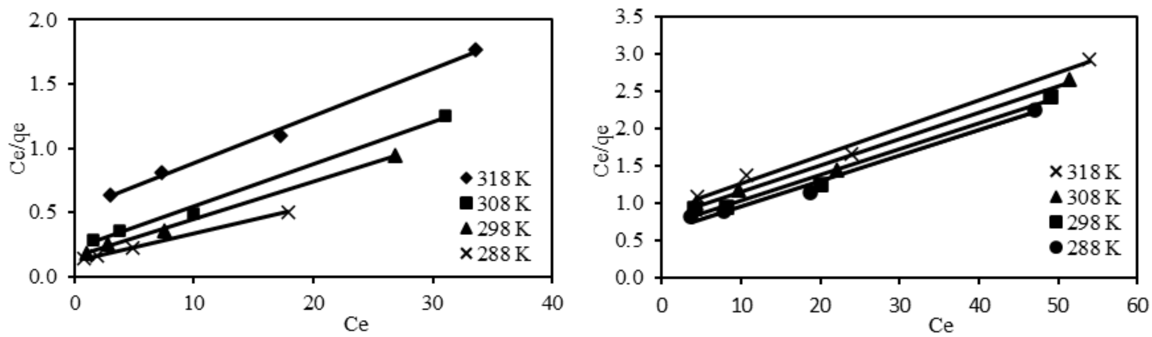


Figure 7. Effect of biosorbent dose on the biosorption of Pb(II) and Cd(II) ions by corn bran



(a) Pb(II) (b) Cd(II)

Figure 8. Langmuir isotherms for biosorption of metal ions by corn bran

3.5 Biosorption Isotherms models

The biosorption isotherm models serve to characterize the equilibrium biosorption data, illustrating the relationship between the mass of solute absorbed per unit mass of biosorbent at equilibrium [24]. Typically, two primary isotherms are utilized, the Langmuir and the Freundlich biosorption isotherms. The Langmuir isotherm model is predicated on the theory of monolayer biosorption. The equation describing the biosorption isotherm is given by [38]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{3}$$

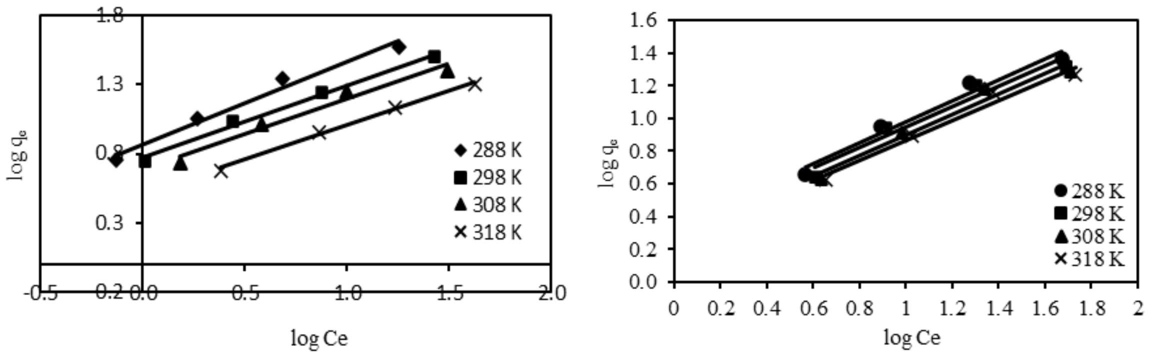
q_m is the saturated monolayer biosorbent capacity (mg/g); K_L (dm^3/mg) is the Langmuir constant and it is an affinity parameter related to the energy of biosorption; C_e is the equilibrium metal ions concentration in the solution (mg/dm^3) and q_e, is the equilibrium of lead, cadmium ion concentration on the biosorbent (mg/g). Plotting C_e/q_e versus C_e should result in a straight line of slope $1/q_m$ and intercepts $1/K_L q_m$. Langmuir isotherms for the biosorption of Pb (II) and Cd(II) ions by pine cones are presented in Fig. 8(a, b).

To determine if the biosorption process is favorable, the dimensionless separation factor R_L, is calculated using the equation [26]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

Table 2. Separation factor R_L of corn bran for Pb(II) and Cd(II) ions in different concentrations, and temperatures

Temp.(K)	Conc. of Pb(II) (mol/dm^3)				Conc. of Cd(II) (mol/dm^3)			
	15	30	60	100	15	30	60	100
288	0.237	0.134	0.072	0.044	0.548	0.377	0.232	0.154
298	0.262	0.151	0.082	0.050	0.566	0.395	0.246	0.164
308	0.303	0.179	0.098	0.061	0.602	0.395	0.275	0.185
318	0.484	0.319	0.190	0.123	0.619	0.309	0.289	0.196



(a) Pb(II) (b) Cd(II)

Figure 9. Freundlich isotherms for biosorption of metal ions by corn bran

For favorable biosorption, the condition 0< R_L< 1 must hold [27]. These data are exhibited in Table 2.

The dimensionless separation factor R_L for corn bran at various concentrations and temperatures decreases within the range of 0 to 1, indicating favorable biosorption of metal ions used in this research. Analysis of Table 2 reveals that as the concentration of lead ions rises from 15 to 100 mg/dm^3 (at 288 K), the separation factor decreases from 0.237 to 0.044 and from 0.548 to 0.154 for cadmium, respectively. Conversely, with an increase in temperature from 288 K to 318 K (at 100 mg/dm^3), the R_L factor raising from 0.044 to 0.123 for lead and from 0.154 to 0.196 for cadmium. Hence, the biosorption process tends to be more favorable at higher concentrations and lower temperatures for the two metals used.

The Freundlich biosorption isotherm presents an alternative model with distinct assumptions. Unlike the Langmuir model, the Freundlich model posits a heterogeneous distribution of active sites, offering an expression that characterizes surface heterogeneity [39]. The Freundlich biosorption isotherm is not limited to the formation of a monolayer, offering a large-scale perspective on biosorption mechanisms. The Freundlich equation is expressed as follows [26]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

K_F (mg/g) is the Freundlich isotherm constant, and *1/n* is the biosorption intensity, which varies with the heterogeneity of the material. The constants *1/n* and *log*K_F are determined from the slope and intercept of the plot, respectively. Freundlich isotherms for corn bran are illustrated in Fig. 9(a, b).

Table 3. Langmuir and Freundlich isotherm data for Pb(II) and Cd (II) ions

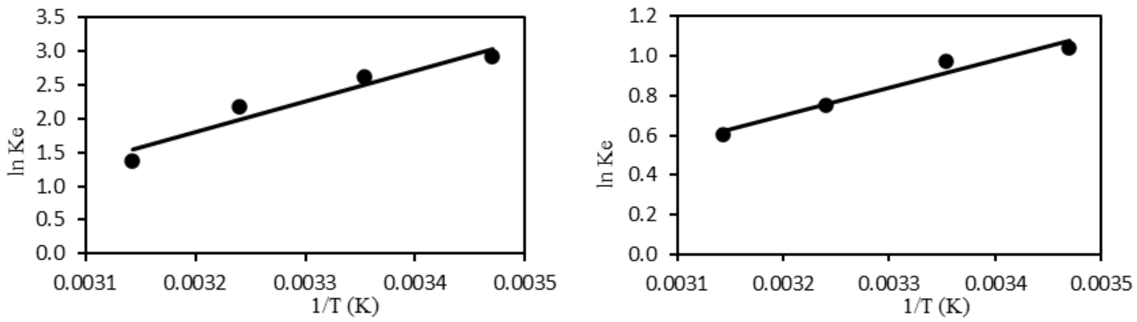
Isotherm		Parameter for Pb(II)				Parameter for Cd(II)			
Langmuir	Temp. (K)	288	298	308	318	288	298	308	318
	q_{max} (mg/g)	40.98	34.25	30.30	27.25	29.41	28.80	28.30	27.10
	K_L (dm^3/mg)	0.215	0.187	0.153	0.071	0.055	0.051	0.044	0.041
	R^2	0.996	0.995	0.999	0.998	0.985	0.980	0.986	0.988
Freundlich	K_F (mg/g)	7.413	5.902	4.853	3.191	2.183	2.089	1.888	1.770
	1/n	0.597	0.524	0.510	0.501	0.642	0.626	0.623	0.613
	R^2	0.979	0.991	0.964	0.995	0.967	0.947	0.962	0.970

Table 4. Data of the Pb(II) and Cd(II) ion biosorption capacity of the various biosorbents

Bisorbents	Biosorption capacity of Pb(II) (mg/g)	Biosorption capacity of Cd (II) (mg/g)	Ref.
Anabaena sphaerica	121.95	111.1	[24]
Agave Bagasse	93.14	28.50	[26]
Posidonia Oceanica Fibers	48.33	30.22	[40]
Agave Americana fibers	40	12.5	[41]
Pinus bark	-	10.38	[42]
Phytolacca americana L	13.19	-	[43]
Wheat bran	12.34	6.25	[44]
Araucaria heterophylla	-	9.28	[45]
Broadleaf Cattail	1.76	0.13	[22]
Sugarcane bagasse	0.26	0.03	[46]
Corn Stalk	1.04	0.08	[46]

The findings demonstrate that the biosorption of metal ions onto the biosorbent fits better to the Langmuir than the Freundlich isotherms. A higher linear coefficient value (R^2>0.999 for lead, and R^2>0.988 for cadmium) indicates that the Langmuir isotherm is a more suitable model for explaining the biosorption process than the Freundlich isotherm (with R^2 values of 0.995 for lead and 0.970 for cadmium) using corn bran, which supports the idea of biosorption with monolayer coverage. The reduction values of q_{max} and K_L with increasing temperature affirm the exothermic nature of the process for the two metal ions. The maximum biosorption capacity for Pb(II) ions was 40.98 mg/g, while for Cd(II) ions, it was 29.41mg/g, respectively. Therefore, it can be concluded that corn bran manifests a higher affinity for lead compared to cadmium. The preference of sorption exhibited by the corn bran for lead over cadmium may be attributed to Pb's smaller hydrated radius (Pb^{2+} = 0.401 nm, Cd^{2+} = 0.426 nm) and hydration energy (Pb^{2+} = 1481 kJ/mol, Cd^{2+} = 1807 kJ/mol) [40]. The data calculated from the Freundlich isotherm Table 5 showed that the *1/n* value was from 0.597 to 0.501 for lead, and from 0.642 to 0.613 for cadmium, which is an indication that the biosorption process was favorable [24].

A comparison of the lead and cadmium ions biosorption capacity of some biosorbents is presented in Table 4.



(a) Pb(II) (b) Cd(II)

Figure 10. The plot of lnK_e vs $1/T$ for metal ions biosorption by corn bran

3.6 Thermodynamic parameters

Another very important parameter in the interpretation of the interaction between the biosorbent and the metal ions is temperature. The rising temperature could either facilitate or impede the metal biosorption process [38]. The biosorption of metal ions Pb(II) and Cd(II) was analyzed under varying temperatures, 288-318 K. The thermodynamic parameters ΔH^o, ΔS^o, and ΔG^o offer insights into the mechanism and biosorption process. The Gibbs free energy change (ΔG^o) is a fundamental criterion used to determine the feasibility of a chemical process [45]. If the Gibbs free energy has a negative value, it suggests that the chemical process is spontaneous; conversely, a positive value indicates non-spontaneity. The thermodynamic parameters (ΔH^o, ΔS^o, and ΔG^o) may be computed using the following Eqs. (6-9) [45]:

$$\Delta G^o = -RTlnK_e \tag{6}$$

$$K_e = \frac{(C_o - Ce)}{C_e} \tag{7}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{8}$$

$$lnK_e = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{9}$$

ΔG^o– Gibss free energy change, R- universal gas constant, T– absolute temperature, ΔH^o– enthalpy change, ΔS^o– entropy change, K_e– the equilibrium constant. A plot of lnK_e versus $1/T$ was found to be linear, where the slope and the intercept can be calculated ΔH^o and ΔS^o, and are illustrated in Fig. 10.

As can be seen in Table 5, it is evident that temperature has a negative effect on the biosorption of Pb(II) and Cd(II) ions onto corn bran, suggesting that higher temperatures are not convenient to the biosorption process. In reality, elevated temperatures support the desorption process in this case. The negative Gibbs free energy value denotes the spontaneous and feasible nature of metal ion biosorption [47]. The decreasingly negative value of ΔG^o with increasing temperature indicates that the sorption of lead and cadmium ions by corn bran is more favorable at lower temperatures [47]. The negative values of standard enthalpy changes observed during the biosorption of Pb(II)

Table 5. Thermodynamic parameters of Pb(II) and Cd(II) for corn bran

	Pb(II)			Cd(II)		
Temp. (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
288	-7.372			-2.578		
298	-6.322	-37.911	-106.32	-2.263	-11.612	-31.37
308	-5.262			-1.952		
318	-4.202			-1.636		

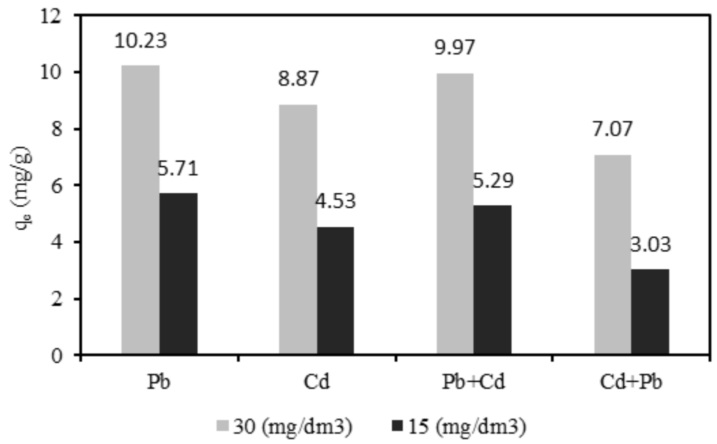


Figure 11. Comparison of the biosorption capacities of Pb(II) and Cd(II) with corn bran in single and binary systems

and Cd(II) ions onto corn bran suggest that this process is exothermic [24]. The ΔH° was -37.911 kJ/mol, -11.612, for lead and cadmium, demonstrating that the physical chemical process was predominant at lead, and the physical process at cadmium, with a weak force of attraction. The negative entropy change (Pb^{2+} -106.32 J/molK, Cd^{2+} -31.37 J/molK), values indicate a decrease in the degree of freedom of the sorbed species [37].

3.7 Biosorption behavior in a binary system

The results presented earlier describe the biosorption of Pb(II) and Cd(II) ions using corn bran from single solutions, without considering the interaction of different ions. Fig. 11 illustrates the biosorption capacity of lead and cadmium ions onto corn bran in both binary and single systems.

The biosorption capacity of Pb(II) ions decreases from 10.23 to 9.97 mg/g in the presence of Cd(II), and the biosorption capacity of Cd(II) is reduced from 8.87 to 7.07 mg/dm^3 in the presence of Pb(II), at an initial concentration of 30mg/dm^3. It is the same trend that has been seen, and the initial concentration is 15 mg/dm^3. The impact on biosorption capacity in a binary system was determined using the following equation [26]:

$$r = \frac{q_e^m}{q_e^o} \tag{10}$$

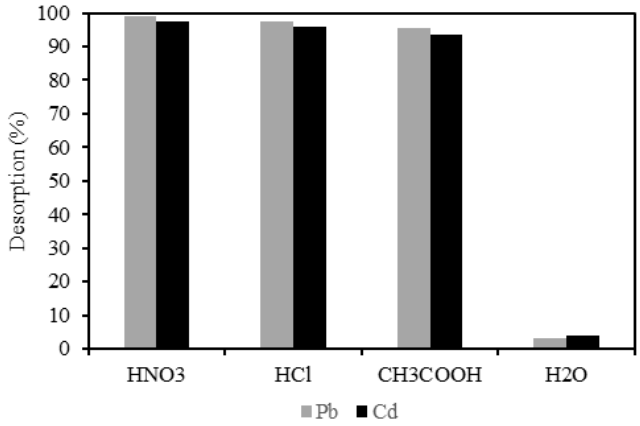


Figure 12. Desorption efficiencies of Pb(II) and Cd(II) ions using different agents

where q_e^m and q_e^o represent the biosorption capacity of the metal ions in a binary system and a single system. When *r* is greater than 1, it indicates an enhancement in the biosorption of the metal ions in the binary system. Conversely, a value smaller than 1 suggests a reduced biosorption capacity. Finally, a value equal to 1, signifies no interaction between the two metal ions [26]. Based on the results calculated by Eq. (10), the *r-factor* values for both metals are less than 1. Thus, it can be concluded that the biosorption capacity of Pb(II) and Cd(II) ions decreases in the binary system, owing to the competition effect. According to that described above, the presence of Pb(II) or Cd(II) induces an antagonistic effect, obtaining *r* values of 0.974 and 0.797, respectively [26]. Based on these results, it is very clear that this effect is more affected by cadmium than lead.

3.8 Desorption and regeneration

Biosorbents that come from different biomasses are usually characterized by high biosorption/ desorption capacity [39]. That makes these materials very useful in the processes of treating polluted waters. Desorption plays a crucial role in recovering metal ions from corn bran, enabling the reuse of this biosorbent for subsequent biosorption processes. This effect of lead and cadmium ions is presented in Fig. 12.

Data presented in Fig. 12 showed that corn bran can be regenerated through the utilization of 0.5M HNO_3, 0.5M HCl, 0.5M CH_3COOH, was 99.18, 97.62, 95.54% of the Pb(II), and 97.54, 95.93, 93.47% of the Cd(II). On the other hand, by distilled water, it was only 3.21% of Pb(II) and 3.87 % of Cd(II). The primary agent demonstrating high desorption efficiencies for corn bran in the resorption of metal ions is 0.5M HNO_3, while distilled water makes a negligible contribution. The desorption experiments implied that the corn bran could undergo multiple reuses.

4. Conclusions

• ATR-IR spectrum confirmed the presence of hydroxyl, carboxyl, carbonyl, and amine groups in corn bran, which are responsible for binding sites of lead and cadmium ions.

• The Langmuir isotherm model was indicated to be the most suitable for describing the biosorption process. From these isotherms, the maximum biosorption capacities of Pb(II) and Cd(II) ions were 40.98 mg/g and 29.41 mg/g, using the optimal conditions.

• The standard enthalpy change of lead and cadmium was -37.911 kJ/mol, -11.612 kJ/mol, which confirmed a stronger interaction between lead ions by corn bran than cadmium. Gibbs free energy was negative at all temperatures, showing that biosorption is spontaneous.

• Mixtures of metals have much less coating than biosorption by biosorbent in single metal conditions. The most efficient substance in corn bran regeneration is 0.5 M HNO_3.

• It can be described that corn bran has a high potential for the removal of lead and cadmium ions from an aqueous solution.

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