

## Removal behaviour of Pb(II) from wastewater by composites of different sodium alginate: *Zea mays* rachis ratios

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### ABSTRACT

The composites sodium alginate (AL): *Zea mays* rachis (ZMR) with different ratios were prepared and tested for the adsorption of lead. The composite with the 1:2 ratio showed the highest adsorption capacity for lead, this material was characterized by Fourier-transform infrared spectroscopy, scanning electron microscopy and the zero point charge was determined. The wastewater was taken from one discharge to a marsh and used for the removal of Pb(II), this wastewater was acidified, the solids were allowed to sediment and water was filtered to avoid excessive fouling of the adsorbent material. The kinetic experimental data were best fitted to the pseudo-first-order model and the equilibrium data to linear models. The biosorption process was endothermic, the  $\Delta H$  value was 49.84 kJ mol<sup>-1</sup> and  $\Delta G$  decreased as increasing the temperature, suggesting a spontaneous process. 96% of initial Pb(II) concentration was removed using an optimal AL:ZMR ratio of 1:2, at pH solution value of 5. The results indicate that the adsorption of lead takes place by chemisorption.

**Keywords:** Heavy metals; *Zea Mays* rachis; Thermodynamics; Removal; Biosorption

### 1. Introduction

The marsh or Lerma Lagoon is one of the most important lacustrine water bodies of the State of Mexico. The different activities carried out by the population around this lagoon generate various wastes, which are the main sources of pollution of rivers, channels, and lakes; causing the disappearance of natural vegetation, death of fishes and other aquatic species. The direct discharge of the wastewater to the lagoon restricts the use of water, for example in irrigation or small-scale fishing and recreation [1,2]

The main sources of pollution can be attributed to the discharge of untreated industrial solid waste, the discharge of industrial effluents, agricultural activities, and leaching from landfills [3–5]. In recent decades, large amounts of

organic and inorganic pollutants have been discharged into water bodies by mining, metallurgical, electrochemical, textile industries among others. Heavy metals have a detrimental effect on aquatic animals because they are toxic and are not biodegradable; furthermore, they accumulate in food chains and can cause health problems to human beings [6]. Industrial effluents polluting water bodies with heavy metals endanger the living world and also contaminate surface, sea and groundwater resources. Wastewater from these industries has become a subject of study due to the problems caused by the presence of toxic metals such as Cu, Zn, Pb, Hg, Ni, Cr [7].

Lead is a metal of great industrial importance since it is used in the manufacture of various products, but is

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dangerous due to its toxic properties [8]. Pb can cause a wide range of biological effects depending on the concentration and time of exposure, this metal enters the body mainly by respiratory and gastrointestinal routes. Once it is in the bloodstream, it accumulates and it interferes in the synthesis of the heme group causing; anemia, alterations in the nervous, cardiovascular, reproductive and renal systems [9,10]. Heavy metals (like Pb) disposed in water from various human activities, especially industrial, even at trace levels, are of potential threat to animals and ultimately to humans. Although techniques for the treatment of effluents containing heavy metals have been developed, conventional methods are often inefficient or extremely expensive when the metal concentration is relatively low ( $<100 \text{ mg L}^{-1}$ ). In recent decades new technologies have been developed based on the biosorption of heavy metals, these processes may be very useful because natural or inorganic adsorbent materials can be used, which in some cases are wastes or are particularly abundant in nature, also the process is easy to operate [11].

Yang et al. [12] used calcium alginate beds crosslinked with  $\text{CaCl}_2$  to remove Cu(II), Cd(II), Ni(II) and Zn(II) from aqueous solution, beads exhibited a high removal efficiency for Cu(II) from the tetra metallic mixture solution and an excellent adsorption capacity of the heavy metals separately. Zvinowanda et al. [13] used *Zea mays* tassel, as an alternative low-cost biosorbent material. The potential of *Zea mays* tassel to adsorb and recover heavy metals from aqueous solution was successfully demonstrated with the removal of Pb(II) from aqueous solutions. Babarinde et al. [14] studied the removal of lead ions from dilute aqueous solution using maize (*Zea mays*) leaf as the adsorbent, results indicated that maize leaf has a good potential for removing lead from industrial wastewater.

The objective of this work was to characterize and determine the adsorption capacity of a new *Zea mays* rachis (ZMR) material supported on sodium alginate beads to remove Pb(II) from wastewater taken from one discharge to the Lerma marsh. The material support will prevent its caking because during its processing it is generated as a powder at 100 mesh. The biosorption process of Pb(II) was studied by the kinetic and isotherms using the pseudo-first and pseudo-second-order models for kinetics and, linear and Freundlich models for isotherms. On the other hand, the free energy of Gibbs, enthalpy, and entropy was also determined to elucidate if the biosorption process was chemical or physical.

## 2. Material and methods

### 2.1. Water sampling

The wastewater used for the biosorption was taken from one discharge to the marsh with a low concentration of garbage, wastewater was acidified at pH 4 to maintain Pb(II) in solution, then the solids were allowed to sediment and water was a filter to avoid sediments on the adsorbent material surface. Pb(II) in the water of Lerma marsh was measured after the filtration process [15], Pb(II) was analyzed by using atomic absorption spectroscopy (Perkin Elmer, model 31104, Osaka, Japan). A concentration of 0.18 and  $39 \text{ mg kg}^{-1}$  of Pb(II) was found in the water and sediments of the Lerma marsh, respectively, which comes from the manufacture

of furniture, due to paints and varnishes whose residues are discharged directly to the drainage of the municipality of San Pedro Cholula, which is located near Lerma River.

### 2.2. Synthesis of *Zea mays* rachis beads supported on alginate

The ZMR was ground and sieved (100 mesh), this material was washed with deionized water to remove impurities, then dried in an oven at  $40^\circ\text{C}$  for 72 h and finally stored in a desiccator. A solution of sodium alginate 1% (w/v) was prepared, at a temperature of  $65^\circ\text{C}$ . Different amounts of conditioned ZMR (2, 4, 6 and 8 g) were mixed with different aliquots of the sodium alginate solution to achieve alginate ratios (AL-ZMR) of 1:1, 1:2, 1:3 and 1:4. The resulting mixtures were dripped in a 0.1 M  $\text{CaCl}_2$  solution to form (AL-ZMR) beads, the mixtures were shaken for 24 h at 300 rpm, and then the beads were filtered, washed with deionized water to remove excess  $\text{CaCl}_2$  and finally stored in deionized water.

### 2.3. Effect of the AL-ZMR ratio on the biosorption capacity and Fourier-transform infrared spectroscopy analysis

The optimum AL-ZMR ratio of the synthesized beads to remove Pb(II) from aqueous solution was determined. A  $10 \text{ mg L}^{-1}$  Pb(II) solution was prepared and the pH was adjusted to 5. 0.5 g of beads (0.025 g dry) of different AL-ZMR ratios were placed in 10 mL of the Pb solution, the samples were stirred at room temperature ( $21^\circ\text{C}$ ) during 1 h. After the stirring time, the concentrations of Pb(II) in the remaining solutions were determined by atomic absorption using a Perkin Elmer, (Osaka, Japan) Model 31104 spectrophotometer at a wavelength ( $\lambda$ ) of 216.8 nm.

Fourier-transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) analysis was performed to identify the main functional groups of the biosorbent beads from 4,000 to  $400 \text{ cm}^{-1}$  using a Varian infrared spectrophotometer, Model 640 with a coupled attenuated total reflection device. Specific surface area and average pore diameter were determined by the Brunauer–Emmett–Teller method, using the BELSORP-MAX equipment for analysis through the adsorption and desorption processes in  $\text{N}_2$  atmosphere. The morphology of beads with different ratios of AL-ZMR was determined at a low vacuum scanning electron microscopy by using a JEOL JSM-590-LD (Tokio, Japan) electronic microscope and the elemental analysis was carried out by energy dispersive X-ray spectrometry.

### 2.4. Stability tests in acidic and basic solutions

The solubility of AL-ZMR (1:2) beads was studied in acidic and basic solutions. 0.5 g of wet beads were placed in contact with 10 mL of acid solutions ( $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) of pH 1, 2 and 3 and NaOH solutions of pH 9 and 10. The samples were kept under constant stirring for 1 h at room temperature ( $21^\circ\text{C}$ ), and then, it was determined visually whether the beads were swollen or fragmented.

### 2.5. Zero point charge (pH-ZPC)

Experiments were performed in aqueous solution varying the initial pH ( $\text{pH}_{\text{in}}$ ) between 2 and 11 (the pH was adjusted

with NaOH or HCl solutions). 0.5 g of wet beads (0.025 g dry basis) were placed in 10 mL of a 0.1 M NaNO<sub>3</sub> solution at different pH values then the mixtures were stirred for 1 h at room temperature. The equilibrium pH (pH<sub>eq</sub>) of the solution was measured and plotted ΔpH (pH<sub>in</sub> – pH<sub>eq</sub>) vs. pH<sub>in</sub>.

## 2.6. pH effect

The sampled wastewater with 0.18 mg L<sup>-1</sup> of Pb(II) was used for biosorption tests, this was performed by varying the pH of the solution between 3 and 8. 15 mL of wastewater was left in contact with 0.5 g of wet beads (0.025 g dry basis) of AL-ZMR (1: 2), the samples were shaken for 1 h at room temperature (21°C) and the remaining Pb(II) concentration in the solution was determined.

## 2.7. Biosorption kinetic and equilibrium experiments

0.5 g of wet AL-ZMR(1:2) beads samples were placed in 15 ml of a 0.18 mg L<sup>-1</sup> Pb(II) wastewater adjusted to the optimum pH, the mixtures were stirred 2, 3, 5, 10, 20, 30, 60 and 90 min, the experiments were performed at temperatures of 25°C, 30°C, and 50°C. The concentration of Pb(II) was determined and the data were treated with the kinetic models of pseudo-first and pseudo-second-order.

The equilibrium experiments were performed using Pb(II) wastewater of concentrations between 0.18 and 10 mg L<sup>-1</sup> (the concentration was adjusted using a standard solution of Pb(II)), 15 ml of each Pb(II) wastewater was left in contact with 0.5 g of wet beads (0.025 g dry basis), the samples were stirred for 60 min, at temperatures of 25°C, 35°C, and 50°C. The concentration of Pb(II) in the remaining solutions was determined by atomic absorption spectroscopy. Data were treated with the Langmuir, Freundlich and linear models.

The pseudo-first (Eq. (1)) and pseudo-second-order (Eq. (2)) models were a probe for kinetic studies [12] between the ZMR adsorbent and Pb(II) ions.

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (1)$$

where  $q_e$  and  $q_t$  are equilibrium and any time capacities (mg g<sup>-1</sup>), respectively,  $k_1$  is the rate constant of first-order adsorption (min<sup>-1</sup>).

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

where  $k_2$  is the rate constant of the pseudo-second-order equation (g mg<sup>-1</sup> min<sup>-1</sup>).

The thermodynamic biosorption parameter as enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) was determined from equilibrium value resulted in kinetics, using three different temperatures, and the Van't Hoff equation.

$$\ln(K_c) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \left(\frac{1}{T}\right) \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - T \times \Delta S^\circ \quad (4)$$

where  $K_c = \frac{q_e}{C_e}$ ,  $R$  is the universal gas constant (kJ mol<sup>-1</sup> K<sup>-1</sup>)

and  $T$  is the temperature (K).

Freundlich and Langmuir's models were used to equilibrium studies. The first model supposes a heterogeneous surface with not-uniform biosorption heat distributed over the surface. The Langmuir model (Eq. (5)) suppose that biosorption occurred at specific homogeneous sites on the biosorbent, all biosorption sites are energetically equivalent and no other interaction occurred [16,17].

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (5)$$

where  $q_e$  is the biosorption capacity at equilibrium (mg g<sup>-1</sup>),  $C_e$  the sorbate concentration in the equilibrium (mg L<sup>-1</sup>),  $q_{\max}$  is the maximum adsorption capacity (mg g<sup>-1</sup>) and  $b$  is the Langmuir constant (L mg<sup>-1</sup>).

Eq. (6) describes the empirical Freundlich isotherm based on adsorption on the heterogeneous surface:

$$q_e = K_F \times C_e^{\frac{1}{n}} \quad (6)$$

where  $K_F$  and  $n$  are the Freundlich constants indicating adsorption capacity (mg g<sup>-1</sup>) and intensity, respectively.

## 3. Results and discussion

### 3.1. Effect of the AL-ZMR ratio on the biosorption capacity and FTIR analysis

The best AL-ZMR ratio of the beads used for the removal of Pb(II) was 1: 2. Table 1 shows the removal percentages by beds of different AL-ZMR ratios, it can be seen that the highest removal percentage was 96% for the beads of 1:2 ratio.

The accumulation or aggregation of active sites as a result of the accumulation of particles may be responsible for decreasing the percentage on the removal efficiency with the increasing of the ZMR (1:2, 1:4 and 1:6) supported on the alginate [18]. It may also be due to the slower diffusion when the number of biomass increases [19]. This is consistent with the works published by Nadeem et al. [20] on the biosorption of Pb(II) using mango residues supported on alginate bead, Juárez [21] on the biosorption of Pb(II) and Cr by using the *Zea mays* rachis without support, Ullah et al. [22] where they used the sugarcane bagasse on alginate bead and noticed

Table 1  
Removal percent of Pb(II) by AL-ZMR

Material	Removal (%)
Alginate (1%)	75
<i>Zea mays</i> rachis (ZMR)	92
AL-ZMR, 1:1 ratio	93
AL-ZMR, 1:2 ratio	96
AL-ZMR, 1:4 ratio	91
AL-ZMR, 1:6 ratio	90

that the biosorption capacity of Cr (III) and Cr (VI) decreased as the amount of biomass supported increased and finally, Sadaf and Bhatti [19] reported the same behavior in the biosorption of yellow indigo by peanut shell on alginate bead.

Fig. 1 shows the infrared spectra of ZMR beads (1:2 ratio); (a) before and (b) after the biosorption of Pb(II) with a concentration of  $10 \text{ mg L}^{-1}$  (no changes were observed with lower concentrations of Pb(II)). A broadband at  $3,308 \text{ cm}^{-1}$  indicates the stretching vibrations of the  $-\text{OH}$  groups, the peak observed at  $2,918 \text{ cm}^{-1}$  describes the stretching vibrations of CH which corresponds to  $-\text{CH}_2$  and  $-\text{CH}_3$  groups; at  $1,598 \text{ cm}^{-1}$ , the band corresponds to  $\text{C}=\text{O}$  stretching vibration of carboxyl groups attributed to the aromatic groups of the lignin; the peak at  $1,421 \text{ cm}^{-1}$  corresponds to the  $\text{C}=\text{C}$  of the aromatic rings of lignin, the vibrations at  $1,245 \text{ cm}^{-1}$  correspond to the stretching of the ether group ( $\text{C}-\text{O}-\text{C}$ ) that are part of the cellulose, hemicellulose, and lignin; The band at  $1,026 \text{ cm}^{-1}$  correspond to  $-\text{OH}$  phenolic groups characteristic of cellulose, hemicellulose, and lignin [23–25]. The functional groups involved in the biosorption of Pb(II) were determined

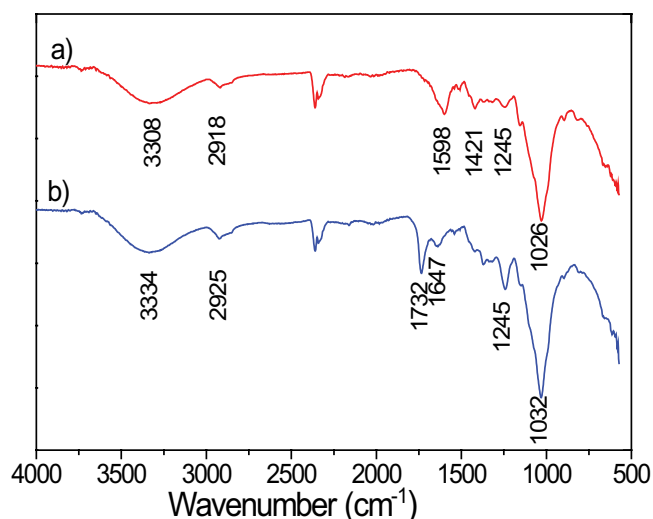


Fig. 1. FTIR spectrum of AL-ZMR(1:2) before (a) and after (b) biosorption of Pb(II).

from the shift of some bands as can be seen in Fig. 1b, as a result of the interaction between the functional groups and the metal ions in solution, the  $-\text{OH}$  groups bands shift ( $3,334$  and at  $1,032 \text{ cm}^{-1}$ ), these groups have been reported as responsible for the removal of some metal ions, including Pb(II), this behaviour can be attributed to the formation of complexes according to Petrović et al. [24]. Further evidence of interaction of AL-ZMR beads and the metal ions is the shifted of the band corresponding to  $\text{C}=\text{O}$  groups from  $1,598$  to  $1,647 \text{ cm}^{-1}$  [26]. The peak at  $1,734 \text{ cm}^{-1}$  corresponds to the stretching vibration of carboxyl groups of esters that were not observed before biosorption.

Micrographic of AL-ZMR (1:2) beads show heterogeneity of the beads, the surface of the material was not uniform, possibly associated with a certain agglomeration after the physical conditioning, the average diameter of the beads was  $1.99 \text{ mm}$ , Fig. 2 shows the micrographs at  $35\times$  and  $250\times$ , some pores in the external surface are observed.

The elemental composition showed carbon (46.38%) and oxygen (43.08%) and in a lower percentages, calcium (8.12%), silicon (0.85%), aluminum (0.68%), chlorine 0.70%) and sulfur (0.17%), the presence of these minor elements are common in *Zea mays*, due to the transport mechanism of nutrients for plant growth [27].

### 3.2. Stability of AL-ZMR (1: 2) in acidic and basic solutions

AL-ZMR beads were more stable at acidic than basic conditions (Table 2), in basic conditions, the structure of the material fragmented, this phenomenon was observed at a

Table 2  
Stability of AL-ZMR(2:1) beds in acidic and basic solutions

Solution	pH	Swelling
HCl, $\text{HNO}_3$ , $\text{H}_2\text{SO}_4$	1	Slight
	2	NO
	3	NO
NaOH	9	Slight
	10	YES

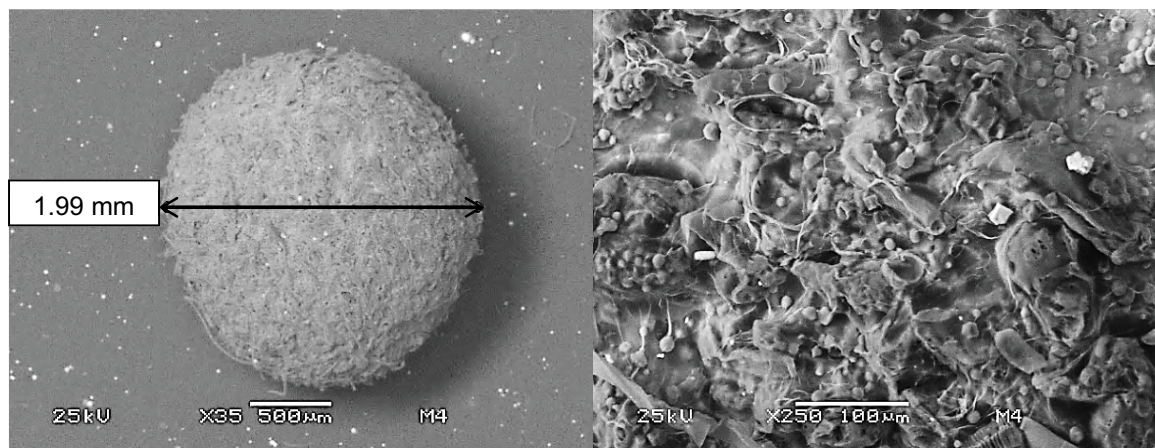


Fig. 2. Scanning electron micrographs of AL-ZMR 1:2.

pH of 9, in these conditions the beds swelled perhaps due to the excess of Na from NaOH which could replace the  $\text{Ca}^{+2}$  ions responsible for the crosslinking that binds the polymer chains of the alginate. Good mechanical stability of the beads was observed at pH 2 and 3. Slight swelling was observed at pH 1, probably due to the solubility of sodium alginate in highly acidic solutions.

### 3.3. Zero point charge (pH-ZPC)

Fig. 3 shows that the zero point charge (pH-ZPC) of AL-ZMR beads (1:2) is 6.22. This indicates that at this pH the total net charge of the surface is zero, below this pH value the predominant surface charge is positive and may adsorb negatively charged species, above this value the surface charge of the material is negative due to the deprotonation of some functional groups such as the carboxyl ions and to an increase of the number of hydroxyl ions, so the beads can attract positively charged species [28].

Fig. 3 also shows the pH ranges where the beads can change their structure, this occurs in the pH ranges from 1 to 4 and from 9 to 11, where AL-ZMR beads can undergo swelling and solubilisation of the polymer, this is consistent with the results of stability tests in acidic and basic solutions.

### 3.4. Effect of pH on the adsorption of Pb(II)

Fig. 4 shows that at pH values lower than 4, the biosorption capacity of the material for Pb(II) is lower than in the range from 4 to 6, possibly as a consequence of the protonation of the material, which prevents the Pb(II) ions interact freely with the functional groups and there is a competition with the  $\text{H}^+$  ions, in addition to a repulsion with probably protonated functional groups and to the stability of the adsorbent in acidic conditions. As the pH of the solution increased, the biosorption capacity increased. These experiments allowed to determine that the optimum pH was found to be around 5, reaching a maximum of removal, above pH 7 precipitation of Pb(II) as  $\text{Pb}(\text{OH})_2$  takes place and the adsorbent is not stable in basic conditions [29].

### 3.5. Kinetic biosorption experiments

The amount of Pb(II) sorbed by the material increased with the contact time until reaching equilibrium in approximately 20 min at the temperatures studied (25°C, 30°C and 50°C) (Fig. 5), so this time is the minimum necessary to make sure that the equilibrium was reached. The experimental data were fitted to the pseudo-first and pseudo-second-order models. Table 3 shows the kinetic parameters for the adsorption, both models adequately represent the behavior of the biosorption process, since the experimental capacities ( $q_{\text{exp}}$ ) and the calculated ones ( $q_e$ ) with each model are similar, and the adjusted coefficients of determination  $R^2$  are also similar. According to the results obtained with the FTIR spectra in which complex formation was observed, involving chemical reactions, it is suggested that the model most appropriate to be applied to the experimental data is the pseudo-first-order since  $R^2$  values are higher for this model than for the pseudo-second-order model. This model implies that the adsorption is driven by external diffusion,

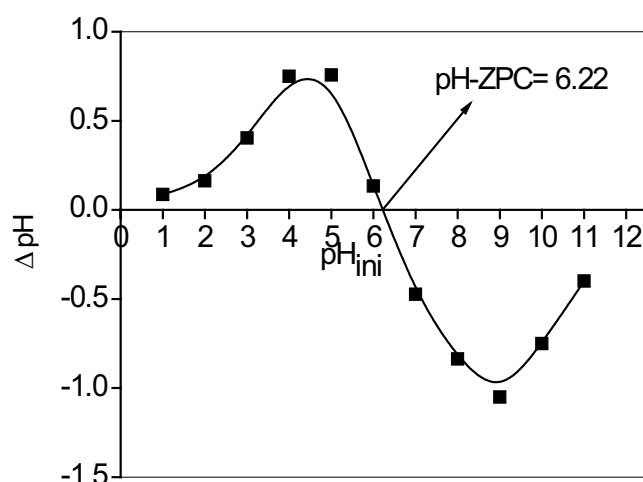


Fig. 3.  $\Delta\text{pH}$  vs.  $\text{pH}_{\text{ini}}$  of AL-ZMR(1:4).

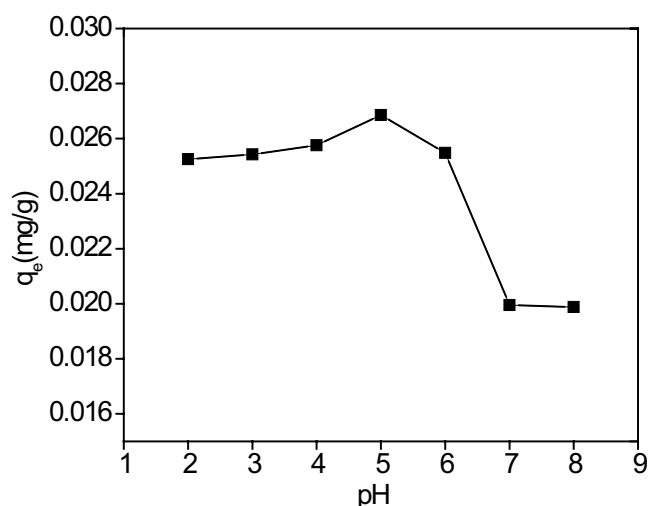


Fig. 4. Influence of initial pH on adsorption capacity of AL-ZMR for Pb(II).

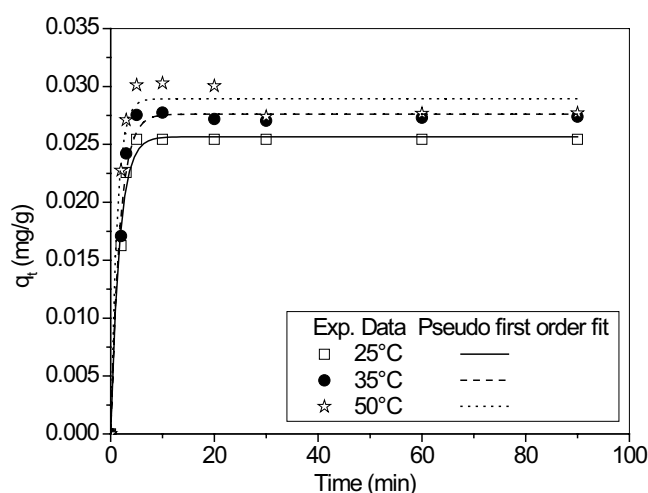


Fig. 5. Kinetic sorption behavior of Pb(II) at different temperatures adjusted to the pseudo-first-order model.

Table 3  
Kinetic adsorption parameters for Pb(II) at 25°C, 30°C, and 50°C

Kinetic model	Parameter	Temperature		
		25°C	35°C	50°C
Pseudo-first-order	$q_e$ (mg g <sup>-1</sup> )	0.026 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
	$k_1$ (min <sup>-1</sup> )	0.59 ± 0.05	0.58 ± 0.05	0.83 ± 0.11
	$R^2$	0.989	0.986	0.981
Pseudo-second-order	$q_e$ (mg g <sup>-1</sup> )	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	48.12 ± 14.78	43.76 ± 14.67	101.47 ± 55.99
	$R^2$	0.963	0.956	0.960
	$q_{exp}$ (mg g <sup>-1</sup> )	0.025	0.027	0.028

the adsorbent-phase mass transfer resistance is dominant at lower concentration and higher concentration, the mechanism switches to chemical-type adsorption [30]. The biosorption capacity increased as the temperature increases up to 35°C, it is assumed an endothermic process, then it remains almost constant. The  $k_2$  constant of the pseudo-second-order model is relatively large in all cases.

### 3.6. Thermodynamic parameters for the biosorption of Pb(II) by AL-ZMR

The enthalpy and entropy were determined by the Van't Hoff equation, this equation considers the determination of  $k_d$  from adsorption capacity and equilibrium concentration of Pb(II) from the biosorption kinetics, it is important to note that the enthalpy of the process is usually the main evidence to determine if the biosorption is physisorption or chemisorption. The results obtained are shown in Table 4, where the enthalpy was 49.84 kJ mol<sup>-1</sup>, this denotes that the predominant process is chemical, according to Eren et al. [31], low enthalpy values (5–40 kJ mol<sup>-1</sup>) indicate physisorption processes, while higher values 40–800 kJ mol<sup>-1</sup> indicates chemisorption processes. A positive value of the enthalpy indicates endothermic processes, whereas the negative values of the energy of Gibbs indicate spontaneous processes [32]. The value of  $\Delta S$  suggests the possibility of reversibility of the biosorption process [33].

### 3.7. Biosorption isotherms

The experimental results obtained from  $q_e$  and  $C_e$  at different temperatures are shown in Fig. 6, the data were treated with a linear ( $q_e = k_d \times C_e$ ) and Freundlich models to determine the isotherm parameters at the different temperatures.

According to the shape of the isotherms, the model that would be best fitted is the linear model, this was confirmed

Table 4  
Thermodynamic parameters of biosorption of Pb(II)

Temperature (K)	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (kJ mol <sup>-1</sup> )
298.15	-4.49	49.84	0.18
303.15	-8.40		
323.15	-9.27		

with the determination coefficients ( $R^2$ ) (Table 5). In this model, the distribution coefficients ( $k_d$ ) are the ratio of lead concentration in the solid phase to concentration in solution [34]. These coefficients increase as temperature increases, the biosorption capacity depends on the concentration of the sorbate in solution [25,35], and these results are valid in the concentration range used in the experiments (0.18–10 mg L<sup>-1</sup>).

The value of the constant  $k_F$  of the Freundlich model is related to the biosorption capacity,  $k_F$  value is close to  $k_d$  obtained with the linear model, while  $1/n$  is related to the biosorption intensity, a value close to unity indicates favorable biosorption intensity. The value of  $1/n$  was around the unit (0.78 and 1.14), it indicates that the interactions between the sorbate and sorbent are weak.

Fig. 6 shows the adjustment of the equilibrium data to a linear model at 25°C, 35°C and 50°C. It can be seen that the experimental data fit the linear model  $R^2$  values from 0.96 to 0.98.

The results obtained are similar to those reported by Muthusamy and Murugan, [36], used maize cob for Pb(II) removal, data were best fitted to the Freundlich model and  $k_F$  was 1.9 mg g<sup>-1</sup>. The removal percentage of Pb(II) was between 85% (0.18 mg L<sup>-1</sup> of initial concentration) and 97%

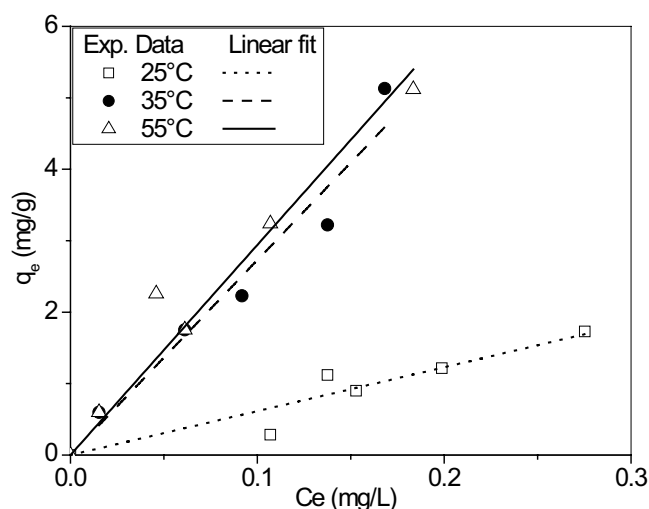


Fig. 6. Adjustment of the biosorption isotherm of Pb(II) to the linear model.

Table 5

Parameters obtained from the nonlinear adjustments of data to isotherms models

Model	Parameter	Isotherm (°C)		
		25	35	50
Linear	$k_d$ (L g <sup>-1</sup> )	6.14 ± 0.50	27.28 ± 1.70	29.40 ± 1.90
	$R^2$	0.96	0.98	0.97
	$k_F$ (mg g <sup>-1</sup> )	7.76 ± 3.60	36.13 ± 16.91	19.11 ± 4.09
Freundlich	$N$	0.87 ± 0.22	0.87 ± 0.18	1.27 ± 0.16
	$R^2$	0.87	0.92	0.96

(10 mg L<sup>-1</sup> of initial concentration). The *Zea mays* rachis supported on sodium alginate is a polymeric material that has good capacity to remove Pb(II) from aqueous solutions. According to the Freundlich model these results shows a distribution of adsorption energy onto the heterogeneous surface of the adsorbent, it describes a multilayer adsorption process of ions on the adsorbent surface [37]. Experimental data were treated with the Langmuir model, but the fit of data was not good, maybe due to the low adsorbate concentration and then the maximum adsorption capacity of the material was not reached.

#### 4. Conclusions

The *Zea mays* rachis composite is a potential adsorbent material to remove lead. The optimal ratio of AL-ZMR to remove Pb(II) was 1:2, obtaining a 96% removal of Pb(II) from wastewater and the optimum pH was 5. FTIR analysis allowed identification of the major functional groups in the beads and their interactions with Pb(II) ions, suggesting the formation of complexes, the surface of the beads was porous and heterogeneous. Tests of solubility of the material showed that the support polymer swells and solubilize at pH higher than 9, this could also be observed with the pH behavior of the material for the pH-ZPC determination which was 6.22. The pseudo-first-order model was adjusted to the experimental data. The equilibrium data were best adjusted to linear and Freundlich models.  $\Delta H$  was 57.78 kJ mol<sup>-1</sup> which indicates a chemisorption process, in addition it can be observed that when the temperature increases there is a slight increase in the biosorption capacity which indicates that the process is endothermic, the positive value of  $\Delta S$  indicates that the process is reversible, and finally  $\Delta G$  decreased as increasing temperature indicating a spontaneous process.

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