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Cd (II) and Pb (II) biosorption in aqueous solutions using agricultural residues of *Phaseolus vulgaris* L.: Optimization, kinetics, isotherms and desorption

Biosorción de Cd (II) y Pb (II) de soluciones acousas en residuos agrícolas de *Phaseolus vulgaris* L.: Optimización, cinética, isotermas y desorción

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Abstract

Industrial activities are the most common cause of water contamination by heavy metals, which endanger the quality of water resources and human health, due to their bioaccumulation capacity and consequent biomagnification. For this reason, the removal of metals from effluents before their discharge into the receiving water bodies is of crucial importance. This is why, in the present investigation, the biosorption processes of Cd (II) and Pb (II) in *Phaseolus vulgaris* L. (bean) agricultural residues (stems, leaves and leaf sheaths) were optimized. The influence of pH, biosorbent doses and initial concentration levels of metallic ions was evaluated using the response surface methodology (RSM). Quadratic models were developed for the percent removal of Cd (II) and Pb (II). Optimal biosorption conditions were attained at pH = 4.3, a 7.4 g/L biosorbent dose and an initial 9.14 mg/L concentration of each metal, achieving percent removals of 87.70 and 95.58% for Cd (II) and Pb (II), respectively. The FT-IR characterization showed that the functional groups involved in adsorption would be in the range of 2300 to 2400 cm^{-1}. The biosorption kinetics were described by the pseudo first order model and the equilibrium data was adjusted to the Freundlich isotherm. An approximate desorption of 98% of Cd (II) and Pb (II) was achieved. The *Phaseolus vulgaris* L. residue showed a great biosorption capacity of Cd (II) and Pb (II) simultaneously.

Keywords: *Phaseolus vulgaris* L. residues, Biosorption, response surface methodology, Cd (II) and Pb (II) desorption.

Resumen

Las actividades industriales son la fuente más común de contaminación del agua por metales pesados que resultan ser un peligro para la calidad de los recursos hídricos y la salud humana, debido a su capacidad de bioacumulación y consecuente biomagnificación, por tal motivo, la remoción de metales de efluentes antes de ser vertidos a los cuerpos receptores es de crucial importancia. Razón por la cual, en la presente investigación se optimizó el proceso de biosorción de Cd (II) y Pb (II) en residuos agrícolas de *Phaseolus vulgaris* L. (frejol) que constó de tallos, hojas y vainas. Se evaluó la influencia del pH, dosis de biosorbente y concentración inicial del ion metálico mediante la metodología de superficie de respuesta (RSM). Se desarrollaron modelos cuadráticos para las remociones porcentuales de Cd (II) y Pb (II). Las condiciones óptimas de biosorción fueron pH=4.3, dosis de biosorbente 7.4 g/L y una concentración inicial de cada metal de 9.14 mg/L logrando remociones de 87.70 y 95.58% para Cd (II) y Pb (II), respectivamente. La caracterización por FT-IR mostró que, los grupos funcionales involucrados en la adsorción estarían en el rango de 2300 a 2400 cm^{-1}. La cinética de biosorción fue descrita por el modelo de pseudo primer orden y los datos en equilibrio se ajustaron a la isoterma de Freundlich. Se logró una desorción aproximada de 98% de Cd (II) y Pb (II). El residuo de *Phaseolus vulgaris* L. mostró gran capacidad de biosorción de Cd (II) y Pb (II) simultáneamente.

Palabras clave: Residuos de *Phaseolus vulgaris* L., Biosorción, metodología de superficie de respuesta, desorción de Cd (II) y Pb (II).

1   Introduction

Aquatic ecosystems play a fundamental role in providing water resources to the human population (Häder *et al*., 2020). However, the constant growth of the population generates important changes and/or transitions in the environment (Nriagu, 2019). Rapid economic and social development in recent decades has caused negative impacts (Yu *et al*., 2017) such as water pollution, which is a threat to human health, water resources and ecosystems (Tarazona, 2014). Moreover, water pollution is one of the main environmental challenges of the 21st century due to the release of toxic substances resulting from anthropogenic activities (Harikishore, 2017). Pollution can originate in point sources (when the contamination source is localized and easy to identify) and in non-point sources (when contamination is generated by diffuse sources and its treatment requires more effort) (Wilhelm, 2009). Industrial activities are generally the most common source of pollution by heavy metals. These metals deposit in the environment (Paul, 2017) and, being bioavailable, tend to bioaccumulate throughout the food chain (Millward *et al*., 2019) until their concentrations become toxic to living beings (Chojnacka and Mikulewicz, 2014). Among the heavy metals of greatest concern are cadmium, copper, mercury, lead and zinc (Millward *et al*., 2019), which can bioaccumulate and lead to biomagnification, which is the trophic enrichment of pollutants within the food chain, producing a progressive increase of the concentration of the toxic elements (Drouillard, 2008).

Cadmium is a highly toxic metal generated mainly by industrial activity (Mendez-Armenta and Rios, 2011). It is used as a pigment and to galvanize other metals (Gad, 2014). Upon entering the environment it can remain intact for long periods of time (Zang and Bolger, 2014). Acute poisoning generally occurs in people exposed directly to this toxic element, while chronic poisoning can be the consequence of eating food contaminated with this metal (Cataldi *et al*., 2017). High levels of Cd (II) are generally found in animal offal, oilseeds, spices, some vegetables, grains (Zang, 2016), mollusks, crustaceans, and other fishery products (Storelli, 2013). Chronic exposure to Cd (II) can produce adverse effects on the heart, lungs, bones, gonads, kidneys (Gad, 2014) and the central nervous system (Mendez-Armenta and Rios, 2011).

Lead and its useful properties have been exploited for millennia. However, in the 20th century, Pb (II)

was recognized as a major public health problem, after large amounts of this metal were added to fuel and paint, and used to supply water (Bellinger, 2018). Thus, the knowledge of lead's toxic effects dates back to a distant past (Needleman and Bellinger, 2017). Lead's toxicity targets the central nervous system: at high doses encephalopathy is the most serious consequence, and at lower doses cognitive and behavioral problems are observed (Needleman and Bellinger, 2017). Also, it negatively affects the kidneys, the heart and the blood-forming organs, and it could also increase the risk of cavities (Azadani, 2019). This is why, the expert's current opinion is that no lead exposure limit is "safe" (Bellinger, 2018) The nervous system of fetus, infants and children are the most susceptible: a chronic exposure to lead of 30 μg/day corresponds to a 1-point decrease in IQ. In adults, 80 μg/day corresponds to a 1 mmHg increase in systolic blood pressure (Carrington and Bolger, 2014). Hence, treating industrial effluents before they are deposited in receiving water bodies would be adequate to prevent contaminants from bioaccumulating and biomagnifying. For this reason, alternatives are needed to remove contaminants from water/wastewater (El-Sayed, 2020). Several physical, chemical, electrochemical, and biological remediation methods are currently being developed and discussed (Hashim *et al*., 2011; Speight, 2020). Among them, the adsorption process has become highly important as a suitable technology for water/wastewater remediation (El-Sayed, 2020). In addition, there is a growing need to use ecological waste and low-cost supplies for biosorption processes, i.e. adsorption on the surface of biological-origin compounds (El-Sayed and El-Sayed, 2014). This is because the basic components of agricultural residues include cellulose, hemicellulose, lignin, lipids, proteins, simple sugars, amylum, and these contain a variety of functional groups (Bhatnagar and Sillanpää, 2010), which would provide the residues with a powerful biosorption capacity for several contaminants, including Cd (II) (Ding *et al*., 2012; Kumar *et al*., 2012) and Pb (II) (Shakeri *et al*., 2012; Surisetty *et al*., 2013). Furthermore, biosorbents have advantages over conventional adsorbents since they turn out to be an effective, sustainable, profitable and environmentally friendly technology, which justifies their application (Singh *et al*., 2020).

Research on surfaces and adsorption phenomena has been carried out mainly by Fourier transform infrared spectroscopy (FT-IR) (Sheppard, 2017), since it is one of the available techniques to explore

solid/liquid phenomena in situ, allowing for easy obtention of information about the nature of the adsorbed species, the adsorbate, speciation and mechanisms (Hind *et al.*, 2001). It also allows the identification of the presence of functional groups of the organic and inorganic components present in the biosorbent (Ramón de los Santos *et al.*, 2019; Rojas-Morales *et al.*, 2016; Suárez-Vázquez *et al.*, 2019).

Some research on residues, such as rice husk (Ding *et al.*, 2012), walnuts (Şencan *et al.*, 2015), sugar cane (Garg *et al.*, 2008), coconut (Shakeri *et al.*, 2012), banana (Akpomie and Conradie, 2020), grape (Torab-Mostaedi *et al.*, 2013), citrus peel (Chatterjee and Schiewer, 2011), grapefruit (Saikaew *et al.*, 2009), etc. has shown that they were effective in removing Cd (II) and Pb (II). The residue of *Phaseolus vulgaris* L. (beans) has been reported to remove metals such as Pb (II) (Safa Özcan *et al.*, 2009), Cr (VI) (Srivastava *et al.*, 2016) and dyes from aqueous solutions as Acid Red 57 (Tunali *et al.*, 2007). Also, being an agricultural residue, it is likely to be composed of hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch. In addition, it may contain certain functional groups responsible for its optimal capacity for biosorption of contaminants, such as hydroxyl groups (-OH), carbonyls (-CO), amines (-NH) and groups $-CH_3$ and $-CH_2$ (Bhatnagar and Sillanpää, 2010). Therefore, in the present research study, we sought to (i) evaluate and optimize the biosorption process of Cd (II) and Pb (II) separately in synthetically prepared bimetallic solutions using residues of *P. vulgaris* L. (bean), and (ii) propose a desorption procedure for both metals.

2 Materials and methods

2.1 Reagents, materials and equipment

All reagents and standards used were obtained from Merck. Standard solutions of Cd (II) and Pb (II) of 1000 mg/L were used. The nitric acid used was Suprapure. ASTM (American Society for Testing and Materials) sieves were used for size classification. Ultrapure water was obtained from the Thermo Scientific Barnstead Easypure II water purifier. The quantification of Cd (II) and Pb (II) was performed at the Metrohm voltammetric station, model VA 797 Computrace with a three-electrode system consisting of a dropping mercury electrode (DME) as a working electrode, platinum (Pt) as an auxiliary electrode and Ag/AgCl/KCl (3 mol/L) as a reference electrode. For the characterization of the biosorbent, the Varian 640-IR FT-IR spectrophotometer was used. Biosorption studies were carried out in a batch-type stirred system consisting of 8 stirrers in series with a temperature control system and constant stirring speed of 200 rpm.

2.2 Preparation of the biosorbent

The *P. vulgaris* L. residues (Figure 1-A). (stems, leaves sheaths and leaves) were collected in the province of Camaná, Arequipa, Perú (-16.6236924, -72.7199288). These residues were crushed (Figure 1-B). in a knife mill, then classified by size using ASTM sieves, obtaining three fractions "Fraction 1" was constituted of particles larger than 1.18 mm; "Fraction 2" was made up of particles from 850 μm to 1.18 mm; and "Fraction 3", of particles from 150 to 850 μm. The fractions were washed with distilled water until attaining a constant pH (Ramón de los Santos *et al.*, 2019), then dried at 70-75 °C for 24 hours (Torab-Mostaedi *et al.*, 2013).

2.3 Metallic ions biosorption experiments

The biosorption experiments evaluated the importance of different factors (pH, biosorbent doses and initial metal concentration) in the percent removal (%R) of Cd (II) and Pb (II), since the performance of the adsorption process depends on these factors and varies with the types of biosorbents (Karimi *et al.*, 2019).

The experiments were carried out in a Batch-type system (Figure 1) where metallic ions solutions (100 mL) were shaken individually and in bimetallic solutions at 200 rpm (S. T. Akar *et al.*, 2009; Safa Özcan *et al.*, 2009) and 20.0 ± 1.0 °C.

Cd (II) and Pb (II) in aqueous samples were quantified using differential pulse anodic stripping voltammetry (DPASV) on the dropping mercury electrode (DME) (Raj *et al.*, 2013). Quantification was developed using the standard addition method. 100 μL of filtered sample were measured in the reaction cell, then 10 mL of 0.1 M acetate buffer (pH = 4.6) were added, as well as two standards of Cd (II) and Pb (II) solutions with concentrations of 0.5 and 1.0 mg/L, respectively. The parameters were: purge time, 300 s; deposition potential, -1.2 V; deposition time, 60 s; equilibration time, 10 s; start potential, -0.8 V; and final potential, -0.25 V. The method was previously validated evaluating the linearity, precision and accuracy parameters. Limits of detection (LoD) and quantification (LoQ) were

also calculated (Quattrocchi *et al.*, 1992). The percent removal (%R) of each aqueous sample was evaluated using the following equation:

$$\%R = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

where "*R*" corresponds to removal, "C_0" is the initial concentration of the metal under study and "C_f" is the concentration of the metal at the end of the experiment (Tejada-Tovar *et al.*, 2020).

2.3.1 *Particle size evaluation, pre-treatment and biosorbent contact time*

In order to identify the appropriate values for particle size, pre-treatment and contact time, tests were carried out using 100 mL bimetallic solutions at an initial concentration of Cd (II) and Pb (II) of 1 mg/L at pH = 5. The solutions were put in contact with the biosorbent with the following considerations: a) For the choice of particle size, the removal capacity of the three fractions was evaluated using a dose of 10 g/L; b) For the determination of the effect of the pre-treatment on the removal of both metals, the fraction with the highest removal capacity was treated with HCl and 0.1 N NaOH for 24 hours, filtered and washed with distilled water until a constant pH was attained, and dried between 70-75 °C for 24 h to obtain a constant weight (Akar *et al.*, 2009) (the removal capacity of this fraction would be later evaluated). Tests were carried out without prior treatment, as well. c) With the particle size and pre-treatment previously defined, contact time was evaluated by taking samples at times 0, 2, 4, 6, 8, 10, 20, 40, 80 and 120 min.

2.3.2 *Factorial design and optimization*

Factorial design achieves greater precision in estimating the effects of the interactions between different input factors established at at least two levels, called "high" and "low" or "+1" and "-1", respectively. If there are "*k*" factors, each of them on two levels, a complete factorial design has 2^k executions (Gottipati and Mishra, 2010). In the present biosorption investigation, three factors were evaluated (Table 1), which were: pH (3.5 and 5 adjusted with NaOH and HCl 0.1 N and controlled with a pH meter), initial concentration of metallic ions (1 and 10 mg/L) and biosorbent dose (5 and 10 g/L). A 2^k factorial design was developed three times ($2^3 \times 3$), yielding a total of 24 experiments that were carried out randomly in order to evaluate the removal of Cd (II) and Pb (II) in separate (individual) studies.

Once the factors' optimal values for the removal of the maximum amount of each metallic ion separately, were identified, the authors proceeded to the simple optimization of biosorption in bimetallic solutions of Cd (II) and Pb (II). Central "0" and axial points (values above the maximum "+2" and below the minimum "-2") were added to the values in Table 1, in order to further extend the working area and analyze possible trends and interactions (Table 2). These axial points were calculated with previously determined factors (-1.7888 and 1.7888) for pH (2.9 and 5.6), initial concentration (0.1 and 13.5 mg/L) and biosorbent concentration (3 and 12 g/L). A total of 18 additional experiments were performed. The data obtained was processed individually to evaluate the removal behavior of both metals in the bimetallic solution, and dual optimization (both metals) was also performed using the response surface methodology (RSM) (Garba *et al.*, 2016).

Table 1. Experimental design of Cd (II) and Pb (II) biosorption of individual metallic solutions.

Factors	Codified levels	
	-1	+1
A: pH	3.5	5
B: Biosorbent dose (g/L)	5	10
C: Initial concentration of each metallic ion (mg/L)	1	10

Table 2. Experimental design of Cd (II) and Pb (II) biosorption of bimetallic solutions.

Factors	Codified levels				
	-2	-1	0	+1	+2
A: pH	2.9	3.5	4.25	5.0	5.6
B: Biosorbent dose (g/L)	3	5	7.5	10	12
C: Initial concentration of each metallic ion (mg/L)	0.1	1	5.5	10	13.5

2.4 Kinetic studies

Literature suggests several adsorption models to correlate adsorption data in batch systems (Ramón de los Santos *et al.*, 2019). The kinetic study of the biosorption process was performed with the optimal values for each factor, 9 mg/L of initial metal ion concentration, pH 4.3 adjusted with 1 N NaOH and 0.1 N HCl, and 7.4 g/L of biosorbent concentration with a stirring speed of 200 rpm, during 40 min. A bimetallic system was used, during 40 minutes at a temperature of 30 °C, thrice. As indicated by the literature, two nonlinear kinetic models were used: the pseudo first order and pseudo second order equation, which provide information on the rate of biosorption by the adsorbate, both based on biosorption capacity (qe) (Lin and Wang, 2009). The pseudo first order model assumes that the rate of adsorption depends on the concentration of a single reactant and the pseudo second order model explains the relationship between the active sites filled and empty, the square of the number of sites not occupied by an ion is equal to the rate at which the active sites are filled; in other words, physical adsorption is faster than chemosorption.

The pseudo first order kinetic equation for biosorption analysis is presented below:

$$q_t = q_e \left(1 - e^{K_1 t}\right) \quad (2)$$

where K_1, q_t and qe are representing model's speed constant, biosorption capacity at time "t" and biosorption capacity at equilibrium, respectively (Lin and Wang, 2009; Tejada-Tovar *et al.*, 2020).

The pseudo second order equation is shown below:

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (3)$$

where "K_2" is the model's speed constant (Bonilla-Petriciolet *et al.*, 2019; Lin and Wang, 2009).

2.5 Biosorption isotherms

The experiments were performed three times with the optimal values for each factor, 9 mg/L of initial metal ion concentration, pH 4.3 and the biosorbent concentration was varied from 0 to 13.4 g/L at 200 rpm, during 40 min y at temperatures of 20, 30 and 40 °C. The equilibrium characteristics, biosorption capacity, of this biosorption study were described using Langmuir and Freundlich isotherm models to determine the type of biosorption phenomenon that occurs between the *P. vulgaris* L. residue and the two metals in question.

Langmuir's model assumes monolayer adsorption on a surface containing a finite number of adsorption sites (Garba *et al.*, 2016), where the adsorbent surface is homogeneous with binding sites that are energetically equivalent (Bonilla-Petriciolet *et al.*, 2019). The model is shown below:

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

where, q_m, K_L, q_e and C_e are representing monolayer adsorption capacity (mg/g), Langmuir adsorption constant, biosorption capacity (mg/g) at equilibrium and adsorbate or biosorbent concentration (mg/L) at equilibrium (Bonilla-Petriciolet *et al.*, 2019). On the other hand, the Freundlich model assumes heterogeneous surface energies (Garba *et al.*, 2016), where the amount that is adsorbed increases infinitely with an increase in concentration (Bonilla-Petriciolet *et al.*, 2019). It is expressed using the following general equation:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where "K_F" is the Freundlich constant and "n" is a heterogeneity factor (Bonilla-Petriciolet *et al.*, 2019).

2.6 Waste characterization using FT-IR

In the present investigation, *P. vulgaris* L. residues were analyzed by FT-IR spectroscopy before and after the biosorption process to identify the functional groups present in the residue, as well as the interactions with the metallic ions under study, using the KBr tablet method. The relation *P. vulgaris* L. residues/KBr employed was approximately 1% in weight(Ding *et al.*, 2012).

2.7 Cd (II) and Pb (II) desorption

Desorption represents a process of chemical species emission on a solid surface, which evaluates the emission of the species without chemical conversions right after breaking its bond with the surface atoms (Matsushima, 2018).

In the present investigation, the percentage of the desorption of Cd (II) and Pb (II) was developed by stirring (200 rpm) 0.37 g of the biosorbents loaded with the metals in 50 mL HNO$_3$ solution at different molarities (0.05, 0.1, 0.2 and 0.3 M) for 20 minutes at a temperature of 20 ± 1 °C. Once the most appropriate HNO$_3$ concentration had been determined, the effect of time (5, 10 and 20 min) was evaluated.

2.8 Statistical analysis

The experimental design and data analysis were performed in *Statgraphics Centurion XVI.I* software. For the analysis of the data related to kinetics and isotherms, a nonlinear least squares fitting was performed using Microsoft Excel 2019 Solver. The comparison of experimental groups was carried out using a two-way analysis of variance (ANOVA) where the p-value $p \leq 0.05$ indicated significant difference. Subsequently, the least significant difference method (LSD) was used as test for confirmation (Lira-Pérez *et al.*, 2019).

3 Results and discussion

3.1 Quantification of Cd (II) and Pb (II) in solutions by voltammetry

The calibration graphs resulted in determination coefficients (R^2) of 0.9997 and 0.9956 for Cd (II) and Pb (II), respectively. The relative standard deviations (RSD) were 0.56 and 0.43% for Cd (II) and Pb (II), respectively with recovery percentages of 98.76% and 97.89%. The detection and quantification limits (LoD and LoQ) were (0.612 and 2.58 μg/L) and (0.836 and 1.96 μg/L) for Cd (II) and Pb (II), respectively. With these results, it was shown that the method is linear ($R^2 > 0.995$), precise (RSD <2.7%) and exact with percent recoveries between 90 and 110% (Quattrocchi *et al.*, 1992).

3.2 Choice of particle size, pre-treatment and contact time

Table 3 shows the removal percentages of each metal with different particle sizes. Analysis of variance indicated significant difference in at least one of the fractions ($p \leq 0.05$). The LSD test confirmed the significant difference between the treatments at 95% confidence. Hereafter for all the experiments, Fraction 3, which had the smallest particle size, was used, since the literature indicates that, the smallest particle sizes have larger surface areas, thus display better performances (Mo *et al.*, 2018). On the other hand, the previous treatments of the biosorbent with HCl 0.1 N, NaOH 0.1 N and distilled water, resulted in biosorption percentages of 85.56, 94.35 and 93.44% for Cd (II) and 85.37, 87.95 and 85.58% for Pb (II). The two-way analysis of variance indicated that there was no difference when using the waste treatments (p>0.05), therefore, it was decided not to carry out previous treatments in order to avoid additional costs.

Finally, Figure 1-C shows that the removal of Cd (II) and Pb (II) at 2 minutes exceeded 70% and after 20 minutes, it reached values greater than 90%.

Table 3. Removal by particle size.

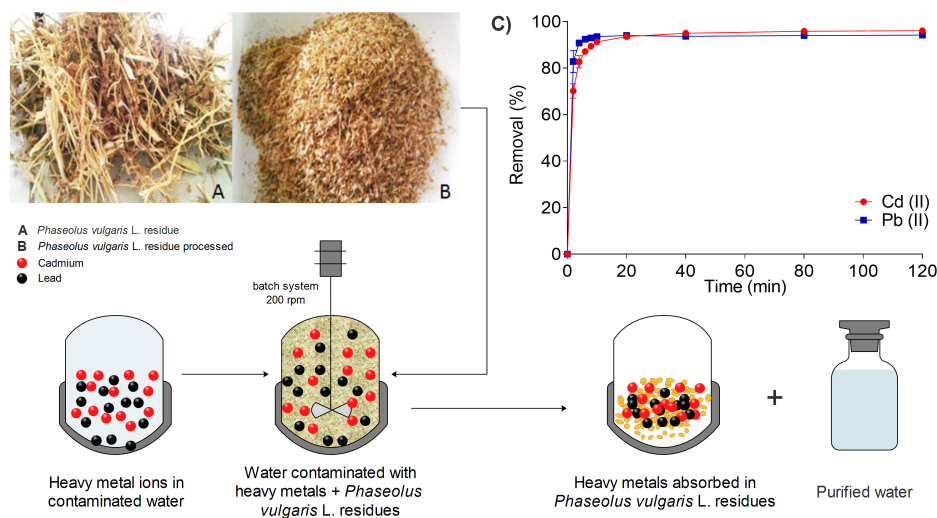| Particle size	Removal, %	
	Cd (II)	Pb (II)
Fraction 1 (> 1.18 mm)	91.40	81.18
Fraction 2 (850 μm at 1.18 mm)	95.16	82.87
Fraction 3 (150 to 850 μm)	94.36	86.99

Fig. 1. Cadmium and lead removal system A) *Phaseolus vulgaris* L. residue B) *Phaseolus vulgaris* L. residue processed C) Removal of Cd (II) and Pb (II) as a function of time.

A similar study indicates that the amount of Pb (II) ions adsorbed by *P. vulgaris* L. residues increased with contact time until 20 minutes; after maximum removal at 20 °C was achieved (Safa Özcan *et al.*, 2009). In the present research study, it was effectively observed that, at 20 minutes, a constant removal of Pb (II) is attained. However, since the study is performed on bimetallic solutions, it is noted that the removal of Cd (II) continues until 40 minutes, where it tends to become constant. Therefore, it was decided to carry out the experiments during 40 minutes.

3.3 Evaluation of the individual biosorption processes of Cd (II) and Pb (II)

The results of the factorial design analysis are shown in Table 4, where it is observed that, at pH = 5, 10 g/L biosorbent dose, and an initial Cd (II) concentration of 10 mg/L, a maximum 93.14% removal of Cd (II) was achieved. The same table shows that, for Pb (II), the

maximum removal percentage was 96.62%, under the following conditions: pH = 3.5, a 10 g/L biosorbent dose, and initial Pb (II) concentration of 10 mg/L.

Figure 2 shows the Pareto diagrams, which allow the determination of the effect of each factor on the system where the biosorption process was carried out. Basically, it is a process that involves two phases, one solid (sorbent) and another liquid (solvent) that contains the species to be sorbed. Due to the great affinity of the sorbent for metallic ions, the latter are attracted and united by complex processes that are affected by mechanisms such as chemosorption, complexation, surface and pore adsorption, ion exchange, chelation, adsorption by physical forces, diffusion and others (Sud *et al.*, 2008). In the case of Cd (II) removal, it is noted that the factors that have a significant effect on the removal process are the pH and the biosorbent dose (Figure 2-A). On the other hand, in the Pb (II) test it is observed that the factors that affect in greater proportion are the concentration and the interaction between the pH and the initial concentration of the metal (Figure 2-B).
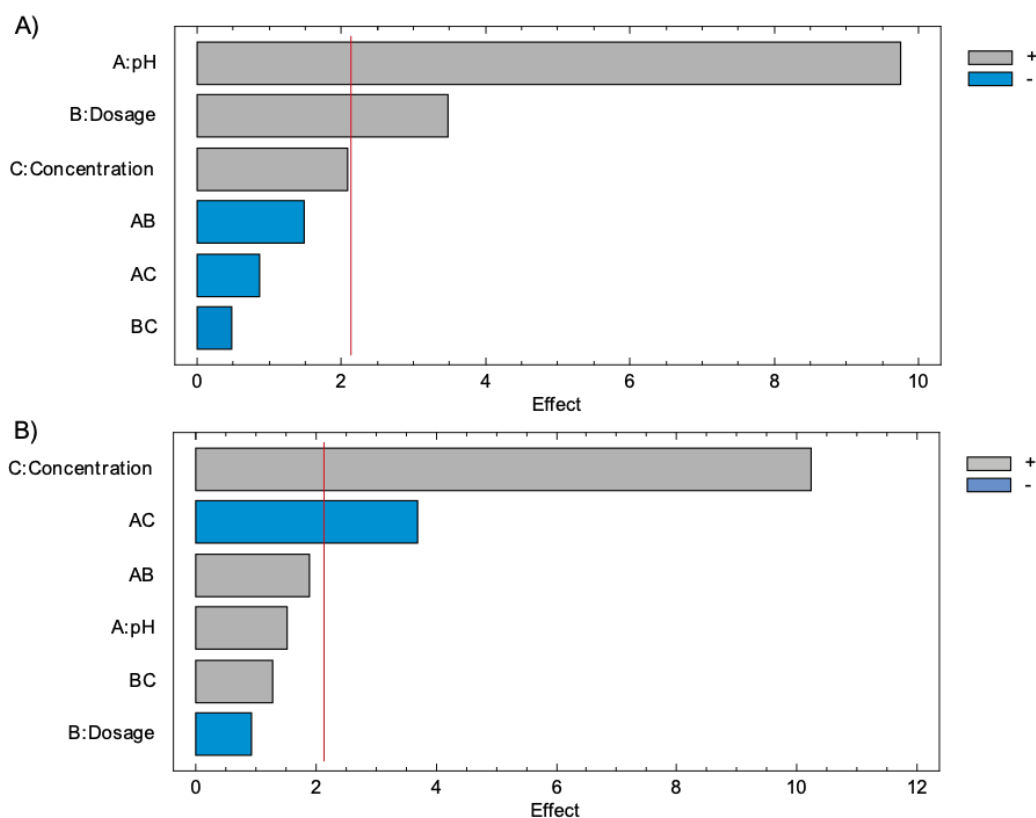

Fig. 2. Standardized Pareto diagram of the biosorption studies on metallic solutions evaluated individually. A) Experiment with Cd (II) and B) Experiment with Pb (II).

Table 4. Factorial design results.

Nº	Factors' codes			Factors' values			Cd (II) Removal %R	Pb (II) Removal %R
	A	B	C	A	B	C		
1	-1	1	1	3.5	10	10	83.99	93.04
2	1	-1	1	5	5	10	92.42	70.29
3	-1	-1	-1	3.5	5	1	72.62	42.45
4	1	1	-1	5	10	1	93.51	69.6
5	-1	1	-1	3.5	10	1	69.73	23.18
6	-1	-1	1	3.5	5	10	75.73	96.12
7	1	1	1	5	10	10	92.48	93.31
8	1	-1	-1	5	5	1	93.98	54
9	-1	1	1	3.5	10	10	83.33	95.84
10	1	-1	1	5	5	10	91.3	91.88
11	-1	-1	-1	3.5	5	1	67.8	50.46
12	1	1	-1	5	10	1	93.53	73.8
13	-1	1	-1	3.5	10	1	81.56	31.15
14	-1	-1	1	3.5	5	10	74.73	96.6
15	1	1	1	5	10	10	93.02	79.6
16	1	-1	-1	5	5	1	85	71.32
17	-1	1	1	3.5	10	10	82.25	96.62
18	1	-1	1	5	5	10	91.93	93.7
19	-1	-1	-1	3.5	5	1	74.18	61.9
20	1	1	-1	5	10	1	92.02	46.71
21	-1	1	-1	3.5	10	1	84.3	36.78
22	-1	-1	1	3.5	5	10	76.25	95.86
23	1	1	1	5	10	10	93.8	94.44
24	1	-1	-1	5	5	1	86.02	53.44

*A= pH, **B**= Doses, **C**= Initial concentration of the metals [Cd (II) and Pb (II)], R=Removal.

Currently, it is known that pH is the most important factor in adsorption processes: a study shows that *P. vulgaris* L. residues has a lower biosorption capacity of Pb (II) at low pH (pH = 1-3) and that when the pH is above 3, biosorption increases sharply until pH = 5 since more metal binding sites may be exposed and have negative charges, and there would be a subsequent attraction of positively charged metallic ions with the biosorbent surface (Safa Özcan *et al.*, 2009). In the present research study, a decrease in Cd (II) removal was observed at pH 3.5, however, it was found that a pH = 3.5 favored removal of Pb (II).

Concerning the biosorbent dose, it was found that when it increased, a greater removal was achieved for the Pb (II) trial, since the number of possible binding sites increased (Safa Özcan *et al.*, 2009). However, regarding Cd (II) removal, it was found that a lower dose achieved better results. These preliminary studies would indicate that both metals tend to behave differently when contacted with *P. vulgaris* L residues, which creates the need for studying both metals in the same solution. The final equations of the empirical model for the percent removal of Cd (II) and Pb (II) responses studied individually are presented below:

$$\%R_{Cd(II)} = 9.87 + 14.97A + 3.67B + 1.38C - 0.51AB - 0.19AC - 0.031B$$

(6)

$$\%R_{Pb(II)} = 57.83 + 0.87A - 10.43B + 11.90C - 1.99AB - 2.15AC - 0.23B$$

(7)

where "A" corresponds to pH, "B" is the biosorbent dose and "C" is the initial concentration of the metal.

Table 5. Results of optimization on bimetallic solutions.

Nº	Factors' codes			Factors' values			Cd (II) Removal %R	Pb (II) Removal %R
	A	**B**	**C**	**A**	**B**	**C**		
1	0	0	0	4.25	7.5	5.5	94.32	91.26
2	-1	-1	-1	3.5	5	1	72.53	72.08
3	0	0	0	4.25	7.5	5.5	92.92	92.86
4	1	1	-1	5	10	1	93.54	83.32
5	1	-1	1	5	5	10	91.75	97.25
6	-1	1	-1	3.5	10	1	81.05	71.82
7	-1	-1	1	3.5	5	10	73.28	92.41
8	1	-1	-1	5	5	1	87.06	81.62
9	1	1	1	5	10	10	92.24	97.45
10	-1	1	1	3.5	10	10	86.49	94.62
11	0	1.78885	0	4.25	12	5.5	91.69	92.31
12	0	0	1.78885	4.25	7.5	13.5	94.73	93.54
13	0	0	0	4.25	7.5	5.5	92.43	92.6
14	0	0	0	4.25	7.5	5.5	91.08	93.08
15	1.78885	0	0	5.6	7.5	5.5	93.18	85.86
16	0	-1.78885	0	4.25	3	5.5	88.25	93.46
17	-1.78885	0	0	2.9	7.5	5.5	58.59	88.61
18	0	0	-1.78885	4.25	7.5	0.1	47.86	48.65

A= pH, **B**= Doses, **C**= Initial concentration of the metals [Cd (II) and Pb (II)], R=Removal.

3.4 Simultaneous evaluation of the biosorption process of Cd (II) and Pb (II)

After finding that the factors that have the greatest influence on the removal of Cd (II) differ from the factors that influence the removal of Pb (II) after the individual evaluations (Figure 2), it was necessary to optimize the process to evaluate the factors that influence the removal of both metals simultaneously (bimetallic solution) according to the design shown in Table 2. The percent removals obtained from the 18 additional experiments for optimization are presented in Table 5, where it is observed that, at pH = 4.25, a 7.4 g/L biosorbent dose and an initial concentration of each metal of 13.5 mg/L, a maximum removal of 94.73% Cd (II) and 97.45% of Pb (II) were achieved, respectively, demonstrating that *P. vulgaris* L. residues can remove both metals simultaneously. It was also confirmed that, by raising the pH above 5, the removal of Cd (II) and Pb (II) decrease. A similar result indicates that there was also a decrease in Pb (II) biosorption above pH = 5 in the same residue (Safa Özcan *et al.*, 2009).

According to the Cd (II) Pareto diagram (Figure 3-A), it can be deduced that the pH (A), initial concentration (C), as well as the quadratic effect of pH (AA) and the initial concentration (CC), all significantly influence the biosorption process. Concerning Pb (II) in Figure 3-B, it is observed that the initial concentration (C) and its quadratic effect (CC) have a greater effect on the removal of said metal.

The empirical model for the percent removal of Cd (II) and Pb (II) responses studied simultaneously revealed a behavior defined by the following quadratic equations:

$$\%R_{Cd(II)} = 92.88 + 7.86A + 2.42B + 6.49C - 4.45A^2 - 5.89C^2 \tag{8}$$

$$\%R_{Pb(II)} = 93.13 + 1.65A + 10.64C - 1.42A^2 - 1.67AC - 6.47C^2 \tag{9}$$

where "*A*" indicates the pH of the process, "*B*" represents the biosorbent concentration, "*C*" refers to the initial concentration of the metal, and A^2 and C^2 correspond to the quadratic interaction of the pH and the initial concentration of the metal, respectively.

Table 6. Optimal values for simultaneous biosorption of Cd (II) and Pb (II) using bean residues.

Factor	Optimal value	Theoretical removal (%)		Experimental removal (%)	
		Cd(II)	Pb(II)	Cd(II)	Pb(II)
A	4.30				
B	7.40	94.74	97.44	87.70	95.58
C	9.14				

*A= pH, B= Doses, C= Initial concentration of the metals [Cd (II) and Pb (II)], R=Removal.
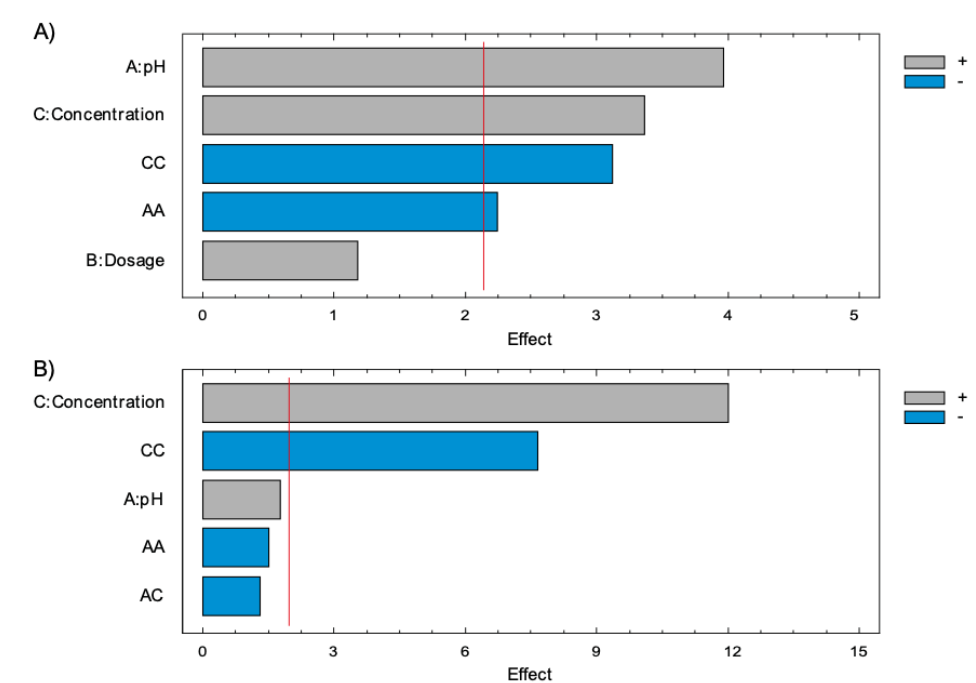
Fig. 3. Standardized Pareto diagram of the biosorption study on bimetallic solutions. A) Cd (II) diagram and B) Pb (II) diagram.

Finally, based on the response surface graphs for each metal studied separately on bimetallic solutions (Figure 4-A and B) and the optimization graph of both metals (Figure 4-C), the biosorption process could be theoretically analyzed and optimized (Table 6) showing that the optimal factors to achieve theoretical removals of 94.74 and 97.44% for Cd (II) and Pb (II), respectively, are a pH = 4.30, a 7.40 biosorbent dose and a concentration of each metal of 9.14 mg/L. However, in practice, 87.70% removals were obtained for Cd (II) and 95.58% for Pb (II), which would indicate some competition between the metallic ions (Figure 4-D). This preference for Pb(II) could be due to the binding capacity of each ion which depends on several factors such as ionic potential, ionic radius, hydrolysis and its chemical properties (Low *et al.*, 2000). However, it was reported that most biosorption studies show that functional groups have a greater affinity for ions with a higher ionic radius and covalent index, which is just higher for Pb (II) than for Cd (II) (Pacheco *et al.*, 2010).

3.5 Kinetic study and biosorption isotherms

For the kinetic studies and isotherms, the optimal parameters found in Table 6 were used. The biosorption kinetics for both metals and their respective parameters are shown in Table 7, where it is observed that the mathematical model that best fits the removal process of Cd (II) and Pb (II) is that of the pseudo first order ($R^2 = 0.9842$, Cd (II) and $R^2 = 0.9625$, Pb (II)). It was found that the amount of Cd (II) and Pb (II) adsorbed in equilibrium, "q_e", was 0.9623 mg/g and 1.0654 mg/g, respectively.

Table 7. Kinetic models parameters for each metallic ion.

Model	Parameter	Value	
		Cd(II)	Pb(II)
Pseudo first order	q_e (mg/g)	0.9623	1.0654
	K_1 (min^{-1})	1.1321	2.5822
	R^2	0.9843	0.9625
Pseudo second order	q_e (mg/g)	0.9884	1.0607
	K_2 (g/mg.min)	2.7371	4.9286
	R^2	0.9782	0.9566
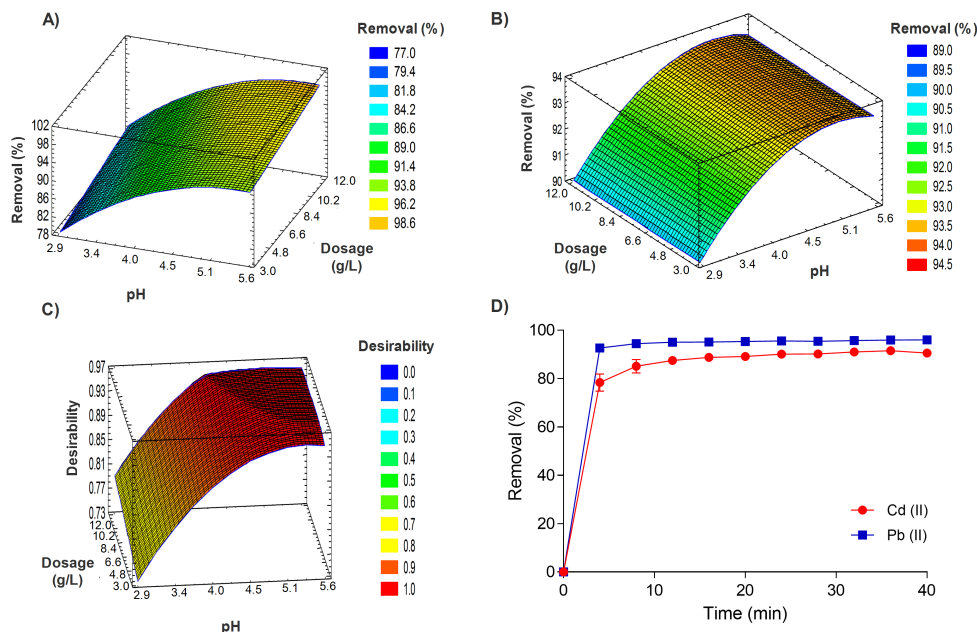
Fig. 4. Surface response graphs for A) Cd (II) and B) Pb (II), C) Surface response graphs for Cd (II) and Pb (II) simultaneously, D) Competition between metallic ions.

On the other hand, in Figure 5 and Table 6, the comparison between the Langmuir isotherm and Freundlich is shown. For Cd (II), the experimental data trend shows the pattern of the Freundlich isotherm (Figure 5-A, B and C). The same behavior is observed for Pb (II) (Figure 5-D, E and F).

Table 6 shows that for Cd (II), at 20, 30 and 40 °C, the R^2 values for the Freundlich isotherm are 0.9525, 0.9794, 0.9845, and for Pb (II), they were 0.8562, 0.9466 and 0.7834, respectively.

These values are higher than those obtained in the Langmuir isotherm. Therefore, according to Freundlich's model, the adsorption of Cd (II) and Pb (II) would occur on a heterogeneous surface (surface of the *P. vulgaris* L. residue) where the amount

that is adsorbed increases infinitely with increasing concentration. According to literature, at first, the strongest binding sites would be occupied and then an exponential decrease in adsorption energy would occur upon completion of the adsorption process (Al-Ghouti and Da'ana, 2020).

The values of the K_F constant at temperatures of 20, 30 and 40 °C are 0.9985, 0.9730 and 1.0243 mg/g, respectively, for Cd (II), and 2.7998, 2.6179 and 2.5176 mg/g, respectively, for Pb (II). Concerning the heterogeneity of the surface area of the biosorbent, "*n*", it is suggested that at values closer to 0 the surface is less heterogeneous and for values closer to 1, it is the opposite.

Table 8. Isotherm parameters for Cd (II) y Pb (II) at different temperatures.

Adsorbate	Temperature ºC	Biosorption Isotherms					
		Langmuir			Freundlich		
		K_L (L/g)	q_m (mg/g)	R^2	K_F (L$^{1/n}$.mg$^{1-1/n}$/g)	n	R^2
Cd(II)	**20**	0.0014	0.9086	0.8848	0.9985	0.7579	0.9525
	30	0.0014	0.9737	0.8068	0.973	0.6156	0.9794
	40	0.0015	0.9626	0.82	1.0243	0.6242	0.9845
Pb(II)	**20**	0.0042	1.1906	0.3644	2.7998	0.3187	0.8562
	30	0.0028	1.7329	0.3427	2.6179	0.2639	0.9466
	40	0.0031	1.5192	0.2276	2.5176	0.207	0.7834
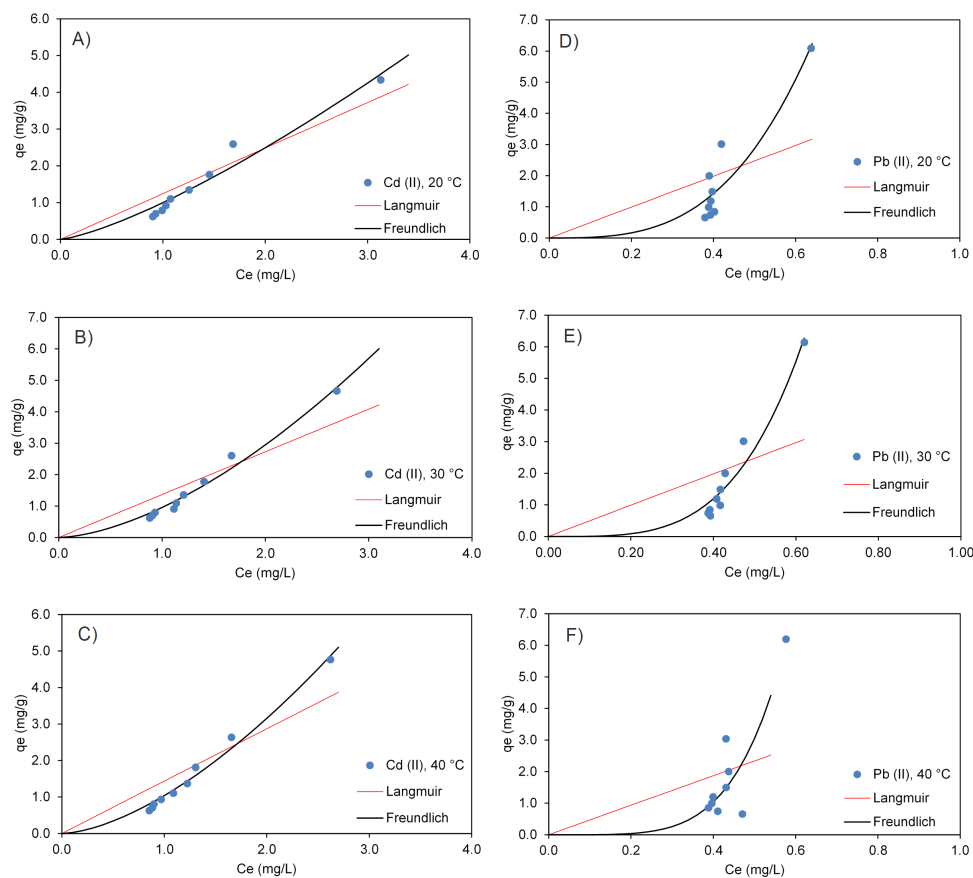
Fig. 5. Langmuir and Freundlich isotherms for Cd (II) and Pb (II) at different temperatures. A) Cd (II) at 20 °C, B) Cd (II) at 30 °C, C) Cd (II) at 40 °C, D) Pb (II) at 20 °C, E) Pb (II) at 30 °C, and F) Pb (II) at 40 °C.

Thus, heterogeneous surface of the *P. vulgaris* L. residue turned out to be more heterogeneous, which would indicate a better disposition for Cd (II) than for Pb (II). On the other hand, the literature indicates that, when n is greater than zero, but less than 1 ($0 > n > 1$), adsorption is favorable, when n is greater than 1, the adsorption process is unfavorable, and, when $n = 1$, it is irreversible (Al-Ghouti and Da'ana, 2020). In the present research study (Table 8), biosorption for both

Cd (II) and Pb (II) would be favorable to the studied conditions.

Regarding temperature, the equilibrium biosorption capacity of Cd (II) on *P. vulgaris* L. residues was enhanced at higher temperatures. A temperature increase from 20 to 50 °C leads to an increase in biosorption capacity. After equilibrium is reached, absorption increases with increasing temperature. This effect can be explained by the

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availability of more active biosorbent sites at higher temperatures (Safa Özcan *et al.*, 2009). However, in the present research study, it is observed that when adding Cd (II) to the adsorption system, the temperature enhances the removal of Cd (II) and not that of Pb (II), which would indicate some type of competition for adsorption sites.

3.6 Desorption

The authors worked with HNO_3 at different concentrations (Figure 6-A). It was determined that at a concentration of 0.3 M the highest percentage of desorption of the metallic ions was attained, achieving 97.65% for Cd (II) and 96.22% for Pb (II). Similar studies also used 0.1 M HNO_3 reaching a 98% desorption of Cd (II) in a biosorbent prepared with orange peel and Fe_2O_3 nanoparticles (Gupta and Nayak, 2012). Other studies used HCl and EDTA solutions to desorb Cd (II) in 65% using grape stem residues (Martínez *et al.*, 2006).

Once the nitric acid concentration required to improve the desorption process was determined, the contact time needed to reach the maximum percentage of desorption was evaluated. As shown in Figure 6-B, the contact time was short: after 5 minutes there was already a 90.86% desorption for Cd (II), and 87.30% for Pb (II). However, it is not until 20 minutes that both metals achieve a desorption of 98%, a convenient time for bimetallic systems like the one used in this work.

3.7 FT-IR Analysis

The infrared spectrum of the dry residue of *Phaseolus vulgaris* L. before the biosorption process is presented in Figure 7-A. According to the literature (Mohamed *et al.*, 2017), for wavenumbers between 3200 cm^{-1} and 3300 cm^{-1} single OH bonds are observed; between 2800 and 3000 cm^{-1} the presence of $-CH_3$ and $-CH_2$ is observed; between 2000 and 2500 cm^{-1} C≡N and C≡C groups are normally present; and between 1500 and 2000 cm^{-1} C=C would be present. Moreover, in Figure 7-B, which corresponds to the IR spectrum after the adsorption of Cd (II) and Pb (II), it is observed that vibrations occur at 2300-2400 cm^{-1}, which would mean that in this wavenumbers range the adsorption of both metals would be taking place on the surface of the dry residue of *Phaseolus vulgaris* L. A previous study for which the adsorption of only Pb (II) was evaluated showed that the bean residue displayed wide absorption bands, which stretched at 3290-3345 cm^{-1}, corresponding to bound $-NH$ and $-OH$ groups. Thus, evidence of a change in the decrease of the intensities in the amino and hydroxyl groups indicated that these two groups are possibly involved in the biosorption of Pb (II) (Safa Özcan *et al.*, 2009). This behavior was not observed in the present study: there were no variations in the wavenumber corresponding to O−H.
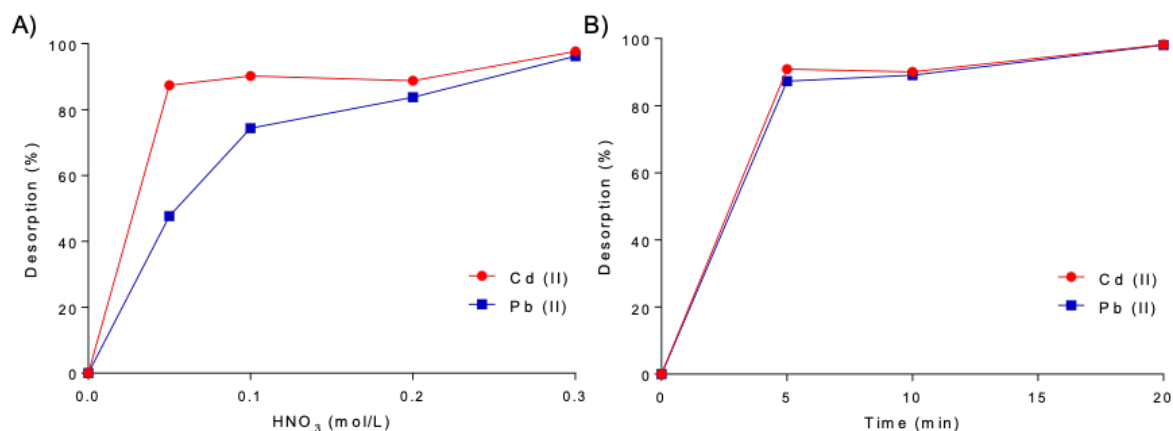

Fig. 6. Cd (II) and Pb (II) desorption in function of time. A) Effect of acid concentration on desorption, B) Effect of time on desorption.
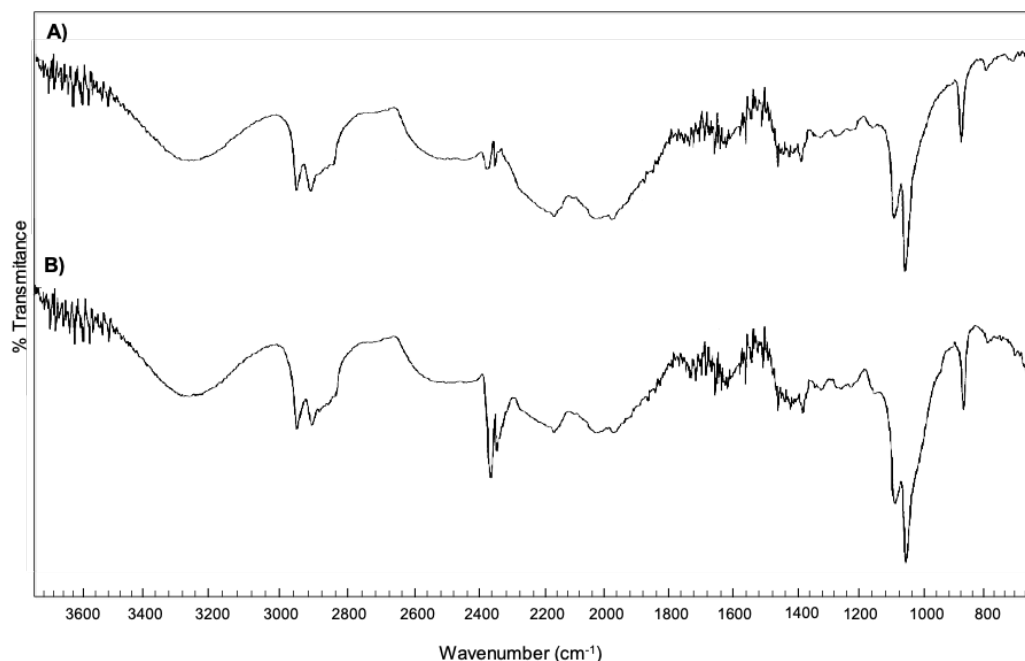
Fig. 7. FTIR spectrum for unloaded *Phaseolus vulgaris* L. residues (A) and Cd (II) and Pb (II) loaded *Phaseolus vulgaris* L. residues (B).

Conclusions

Using the Response Surface Methodology, the pH (4.30), biosorbent dose (7.4 g/L) and initial concentrations (9.14 mg/L) factors of Cd (II) and Pb (II) were optimized for removal of both metallic ions in bimetallic solutions obtaining percent removals of 87.70 and 95.58%, respectively, for 20 min, particle size 150 to 850 μm and at a temperature of 20 °C. The performed analyses indicate that the biosorption behavior of both metals is different when they are studied separately, than when they are studied simultaneously. The pH and initial concentration factors are the most important in the process of removing both metals from bimetallic solutions. The biosorption behavior follows a pseudo first order kinetics. The analyzed equilibrium data revealed that the Freundlich isotherm is the best fitted model for the biosorption process. Approximately 98% desorption of Cd (II) and Pb (II) adsorbed on the surface of *P. vulgaris* L. residues was achieved using a 0.3 M HNO_3 solution in 20 minutes. Finally, FT-IR analysis of *P. vulgaris* L residues showed the presence of O-H, −CH_3, −CH_2, C≡N, C≡C and C=C groups. Biosorption could occur between 2300 and 2400 cm^{-1}, as shown by the vibrations observed during the analysis of the material loaded with metals. The residue of *Phaseolus vulgaris* L. showed great biosorption capacity for these metallic ions and the optimization conditions reduce the time and cost of application, acquiring an added value and being destined for the treatment of residual waters or industrial effluents.

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