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Kinetics and Bioadsortion Equilibrium of Lead and Cadmium in Batch Systems with Cocoa Shell (*Theobroma Cacao* L.)

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Abstract

Residual biomass waste is used as an efficient and low-cost means of removing heavy metals (nickel, cobalt, chromium, lead, mercury, arsenic, among others) from wastewater, so it is important to evaluate the potential of cocoa shell waste (*Theobroma cacao L.*), with three particle sizes (0.35, 0.5 and 1 mm), as an adsorber of cadmium ions and lead in aqueous solution (100 ppm) in a batch system, that was the objective of this research. It was hypothesized that the smaller the particle size, the higher the percentage of removal of cadmium and lead ions. A factorial experimental design with three levels of variation and two study factors (particle size and initial metal concentration) was implemented, carrying out 9 experiments per metal, for a total of 18. Plant segments were washed and dried, then adsorption was determined. The process of removal of Cd (II) and Pb (II) ions was favored by particles of 0.35 mm, with which the maximum percentage (95 and 86%) of removal of Cd and Pb was obtained. The kinetic model that best fitted the experimental adsorption data was Elovich and the isothermal model that best described the results was that proposed by Freundlich. It is concluded from the results obtained in this study that cocoa shells have great potential for removal of Cd and Pb in aqueous solutions in a satisfactory manner.

Keywords: Bioadsorption, Elovich, Freundlich, isothermal adsorption, Theobroma cacao L.

1. Introduction

Heavy metals are pollutants released into the environment and are highly available as a result of increased anthropogenic activities, such as industrial, mining, and agricultural activities [1]. There is currently a worldwide concern about the significant increase in pollution rates from the improper release and treatment of heavy metal industrial effluents. This leads to the search for economical techniques for the treatment of wastewater with these pollutants, which guarantee their elimination. In relation to this, bioadsorption has become very important because it is a process in which biological materials can be used to accumulate pollutants in aqueous solutions, considering them as an ion exchanger of natural origin [2, 3, 4, 5, 6].

The use of residual biomasses has been documented from orange peel (*Citrus sinensis*), cassava (*Manihot esculenta*), yam (*Dioscorea rotundata*), lemon (*Citrus limon*), cocoa (*Theobroma cacao L.*), bagasse of African palm (*Elaeis guineensis*) and others, in the removal of heavy metals such as nickel, cobalt, chromium, lead, mercury, arsenic, among others; good adsorption results are obtained, which place waste biomass as an efficient and low-cost means of eliminating these wastewater pollutants [7, 8, 9].

Zhang et al. [10] investigated cadmium adsorption using magnetic alginate beads linked to Rhizopus sp., determined that under optimal conditions the removal of Cd was 89% and that the addition of Pb could reduce the rate of removal of Cd under the same conditions.

Similar studies were carried out by Abdelwahab et al. [11] with modified and unmodified guava leaves in the adsorption of cadmium ions from aqueous solutions, reporting the rapid removal of these ions, following a pseudo-second order model; Rosique et al. [12], reported similar results in the removal of Cd with Opuntia; Iqbal and Khera [13] studied the removal of Pb and Cu in aqueous solution using *Fumaria indica*, adapting the Freundlich isothermal model to the adsorption data for both metals. De Moraes-Ferreira et al. [14], used two biosorbents obtained from the aquatic plants Salviniasp. And Pistiastratiotes, achieving efficient elimination of Pb (II) from aqueous solutions, with a maximum observed adsorption capacity of 202 mg g^{-1} and 210.1 mg g^{-1}.

The objective of this research was to evaluate the potential of cocoa shell waste, with different particle sizes, such as Cd and Pb ion bioadsorbents, by studying kinetic and adsorption isotherms. It was hypothesized that the smaller the particle size, the higher the percentage of removal of cadmium and lead ions.

2. Methodology

This study was carried out in the Energy and Environment laboratories of the University of Cartagena, Cartagena (Bolivar). Cocoa was obtained from Tierra Alta (Cordoba).

2.1. *Preparation of biomass*

The seeds were manually extracted and the shell separated. This was cut into small pieces that were easy to handle. The biomass was collected and washed with distilled water in order to eliminate soluble impurities; it was then dried in a laboratory furnace Esco, Model Isotherm® OFA-32-8 that is located in the Laboratory of Physicochemistry of the University of Cartagena, Piedra de Bolívar; Cartagena - Colombia; at 90 ºC for 24 h. Subsequently, it was crushed in a manual conventional stainless steel mill called corona, which is located in the Laboratory of Physicochemistry of the University of Cartagena, Piedra de Bolívar; Cartagena - Colombia; and sieved with a stainless steel sieve AISI 316 laboratory, mesh sizes of 0.35, 0.5 and 1 mm. The characterization of biomass was obtained in the previous study of lead and cadmium adsorption in a continuous fixed bed system on cocoa residues carried out by Lara et al. [15].

2.2. *Adsorption experiments for determining the best particle size*

All working solutions were prepared from cadmium sulphate (CdSO4) and lead nitrate Pb $(NO_3)_2$ of analytical grade Merck brand, for Cd and Pb respectively. The solutions were prepared with deionized water in a stirrer at 25 ºC and 150 rpm for two hours at pH 6 [16]. Thus, adsorption tests with different particle sizes: 0.35, 0.5 and 1 mm, in order to know their influence on the process, were carried out using a solution of 100 ppm of Cd and Pb. With the particle size that presented a higher percentage of removal, later studies were carried out to construct the kinetic curve and evaluate the adjustment of experimental data to different models of adsorption isotherms.

2.3. *Kinetic tests and adsorption isotherms*

Kinetic tests were carried out to determine the saturation time of biomass by taking aliquots of 5 mL every half hour between 10 and 270 min, evaluating the kinetic models of pseudo-primer order, pseudo-second order and Elovich. Adsorption isotherms were constructed to determine the amount of metal adsorbed in the interface with the concentration of the metal adsorbed in the phase and Langmuir and Freundlich isotherms models were used to determine which one best fits the data [16].

3. Results

3.1. *Effect of particle size*

The best adsorption conditions were observed with particles of 0.35 mm (Figure 1). As the particle size decreases, the retention rate increases due to the possible increase in contact area, and therefore of accessible sites, coinciding with that reported by Tejada-Tovar et al. [17] in its study on the removal of lead from residue biomass from orange peel (*Citrus sinensis*) and corn husk (*Zea mays*), however, this could not be directly related to particle size, as particles of the same thickness are actually being used, which is what determines diffusion distance, and the particle size classification of a biomass by standard sieves works in length and width [18]. For example, studies have shown that the largest biomass particles of *Sargassum fluitans* and *Ascophylum Nodosum* had greater metal adsorption than the smallest particles, increasing from 0.15 to 0.85 mm, but decreasing from particle size 0.85 mm to 1.00 mm [19, 20].

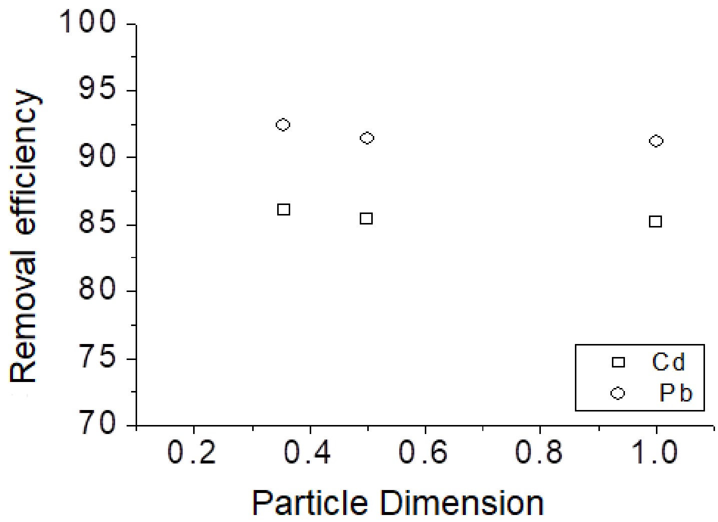

Figure 1. Effects of particle size on Pb and Cd adsorption using cocoa shell.

3.2. *Kinetics and adsorption isotherms*

Studies of biosorption kinetics are important in the treatment of effluents, as they provide good information about the adsorption mechanism and the nature of the process. In this research, the adjustment of the experimental data to the kinetic models of pseudo-primer order, pseudo-second order and Elovich for Pb and Cd, respectively (Figure 2).

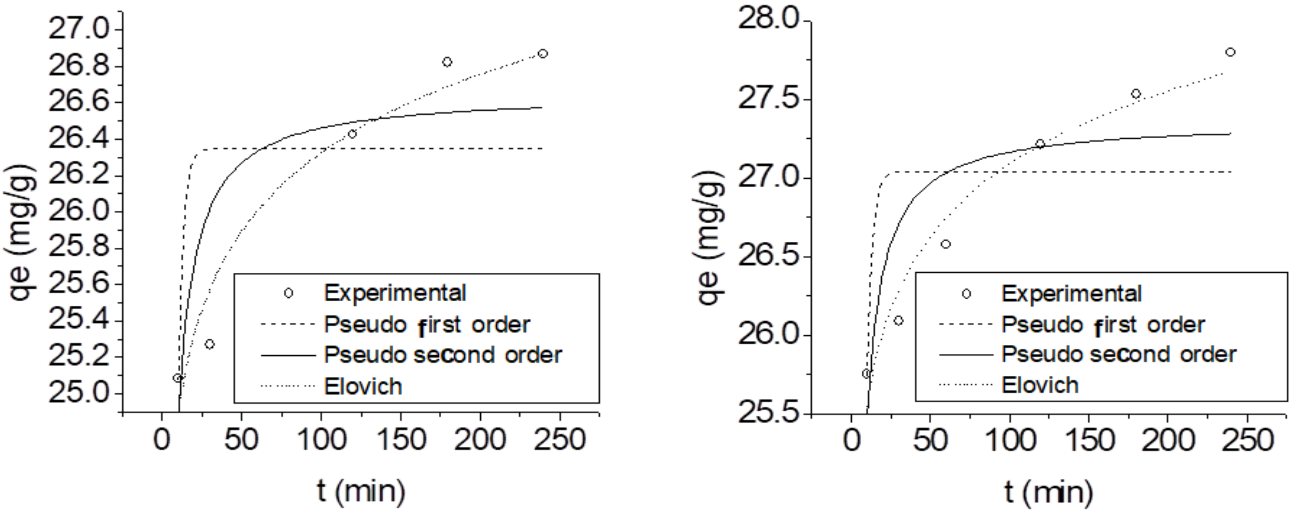

Figure 2. Adjustment of the kinetic models of Pb (left) and Cd (right) adsorption using cocoa shell.

The kinetic model that best fits the experimental adsorption data of Pb and Cd in residual cocoa biomass is that of Elovich with R^2 of 0.953 and 0.933 for each metal, respectively, as shown in Table 1; therefore there is an exchange of species on the non-homogeneous surface of the solid, this involves different processes of isotope exchange at the same time and that the process is highly dominated by chemisorption, which is expected after the complexity shown by the material in the FTIR analysis obtained in previous studies by Lara et al. [15]., thus demonstrating the wide interaction of metallic ions with the functional groups of biomass.

In this model α, it is related to the chemisorption energy and β with the covered surface, so of the calculated parameters, it is observed that although the initial adsorption velocity is higher for cadmium, the greater efficiency is given for lead.

Analyzing the results of the adsorption isotherms of Pb and Cd in cocoa shell presented in Table 2, it was found that the model that best adjusted the adsorption and better decayed the behavior of the adsorption process using cocoa shell in the removal of Pb and Cd was Freundlich's, with correlation coefficient (R^2) of 0.916 and 0.922 for each metal, respectively. Because of this, it is established that the surface of biomass is heterogeneous in nature as shown by the FTIR analysis reported in the previous study by Lara et al. [15], as well as that during the adsorption process multilayers are formed on the surface of the biomaterial and the ions occupy active sites, initially with strong bonds and this strength decreases to measures that are occupied by the ions of Cd (II) and Pb (II).

Table 1. Parameters of kinetic models for Pb and Cd.

Model	Parameters	Cadmium	Lead
First order	q_e	0.304	0.303
	k_1	27.043	26.348
	R^2	0.269	0.247
Second order	q_e	27.366	26.654
	k_2	0.049	0.051
	R^2	0.624	0.641
Elovich	β	1.497	1.605
	α	2.734 E15	1.387E16
	R^2	0.953	0.933

Table 2. Parameters of Pb and Cd adsorption isotherms in cocoa shell.

Model	Parameters	Cadmium	Lead
Langmuir	q_{max}	4.508	4 6930.90
	b	0.744	3.18E-5
	R^2	0.880	0.849
Freundlich	K_f	37.818	0.453
	1/n	1.119	1.476
	R^2	0.922	0.916

The adsorption intensity, given by the Freundlich parameter (n) is higher than expected and compared to other works: 0.1376 for the Pb [21], 0.0616 for Cd [22], 1.046 for Ni and 0.602 for Zn [23], it was confirmed that the process can be classified as favourable for adsorption. The closer the value from (1/n) to zero, the greater the adsorbent heterogeneity [24]. Regarding adsorption capacity, a high capacity was found in the present study compared to other reports for Pb (19.69 mg g^{-1}- 47.07 mg g^{-1}) [25, 26, 27], using from rock minerals, fruit husks and tree leaves, however for cadmium (6.85 mg g^{-1} - 90.09 mg g^{-1}) using diverse materials such as coffee residues, Leaves of trees and fruit peels the adsorption capacity of this study was low, suggesting the variation of other parameters to improve this capacity [26, 28, 29, 30].

4. Conclusion

Adsorption experiments showed the effectiveness of cocoa shell to remove Cd (II) and Pb (II) in aqueous solutions, using particle sizes of 0.35 mm, suggesting it as an alternative use of waste materials. Elovich's kinetics and Freundlich's isothermal model explained precisely the kinetics and equilibrium data, respectively, finding that the adsorption system is controlled by chemisorption. It is concluded from the results obtained in this study that cocoa shells are a good precursor when generating adsorbent material for use in the removal of Lead and Cadmium present in aqueous solution in a satisfactory manner.

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