Original Article

Adsorption isotherms for copper and lead removal from landfill leachate

Isotermas de adsorción para la remoción de cobre y plomo de lixiviados de rellenos sanitarios

Elizabeth Carvajal Flórez 🆔 ✉

Universidad Nacional de Colombia. Bogotá, Colombia.

Abstract

Introduction: the treatment of leachates containing heavy metals, such as copper (Cu) and lead (Pb), is crucial as their levels often exceed permissible limits established by regulations. This study focuses on evaluating the efficiency of treating these metals using adsorption with processed coffee pulp.
Objective: the objective of this study is to determine the removal rates and adsorption capacity of copper and lead in landfill leachates.
Methods: adsorption isotherms were conducted in individual solutions using the Langmuir and Freundlich models. A 2^3 experimental design and response surface analysis were applied to evaluate the variables. Additionally, thermodynamic parameters were determined to understand the type of adsorption.
Results: the results indicate that the Langmuir model best fits the adsorption of copper and lead. The maximum adsorption capacities for copper at doses of 1.3 and 5 g of adsorbent material were 0.29, 0.12, and 0.59 mg/g, while for lead, they were 0.05, 0.02, and 0.02 mg/g. The adsorption rates for copper were 65.3%, 71.0%, and 69.4%, and for lead, they were 30.30%, 13.80%, and 25.40% at the respective doses.
Conclusion: the thermodynamic parameters suggest that the adsorption mechanism is chemical in nature, supporting the effectiveness of processed coffee pulp as an adsorbent material for the removal of heavy metals in leachates.

Keywords: adsorption isotherms, sorption, leachate, landfill

Resumen

Introducción: el tratamiento de lixiviados que contienen metales pesados, como el cobre (Cu) y el plomo (Pb), es fundamental debido a que sus niveles a menudo superan los límites permisibles establecidos por la normatividad. Este estudio se centra en evaluar la eficiencia del tratamiento de estos metales utilizando sorción con pulpa de café procesada.
Objetivo: el objetivo de este estudio es determinar las tasas de remoción y la capacidad de adsorción del cobre y plomo en lixiviados de rellenos sanitarios.
Métodos: se realizaron isotermas de adsorción en soluciones individuales utilizando los modelos de Langmuir y Freundlich. Se aplicó un diseño experimental 2^3 y análisis de superficies de respuesta para evaluar las variables. Además, se determinaron parámetros termodinámicos para comprender el tipo de sorción.
Resultados: los resultados indican que el modelo de Langmuir se ajusta mejor a la sorción de cobre y plomo. Las capacidades de adsorción máximas para el cobre en dosis de 1,3 y 5 g de material adsorbente fueron de 0.29, 0.12 y 0.59 mg/g, mientras que para el plomo fueron 0.05, 0.02 y 0.02 mg/g. Las tasas de adsorción para el cobre fueron del 65.3%, 71.0% y 69.4%, y para el plomo del 30.30%, 13.80% y 25.40%, en las respectivas dosis.
Conclusión: Los parámetros termodinámicos sugieren que el mecanismo de adsorción es de tipo químico, lo que respalda la efectividad de la pulpa de café procesada como material adsorbente para la remoción de metales pesados en lixiviados.

Palabras clave: metamodelo, Bodega de datos, Arquitectura, Calidad de aire, Salud pública.

Why was it conducted?
To explore new adsorbents, such as coffee pulp, that could help remove contaminants from water, such as heavy metals, particularly in landfill leachates.

What were the most relevant results?
Coffee pulp is a suitable biomass for the removal of heavy metals. However, further research is needed on the characteristics and properties of coffee pulp and the adsorption process, in order to enable its implementation on a real scale.

What do these results contribute?
They explore new ways to remove contaminants from water compared to conventional techniques. They also seek effective environmental solutions for managing agro-industrial waste, such as coffee pulp.
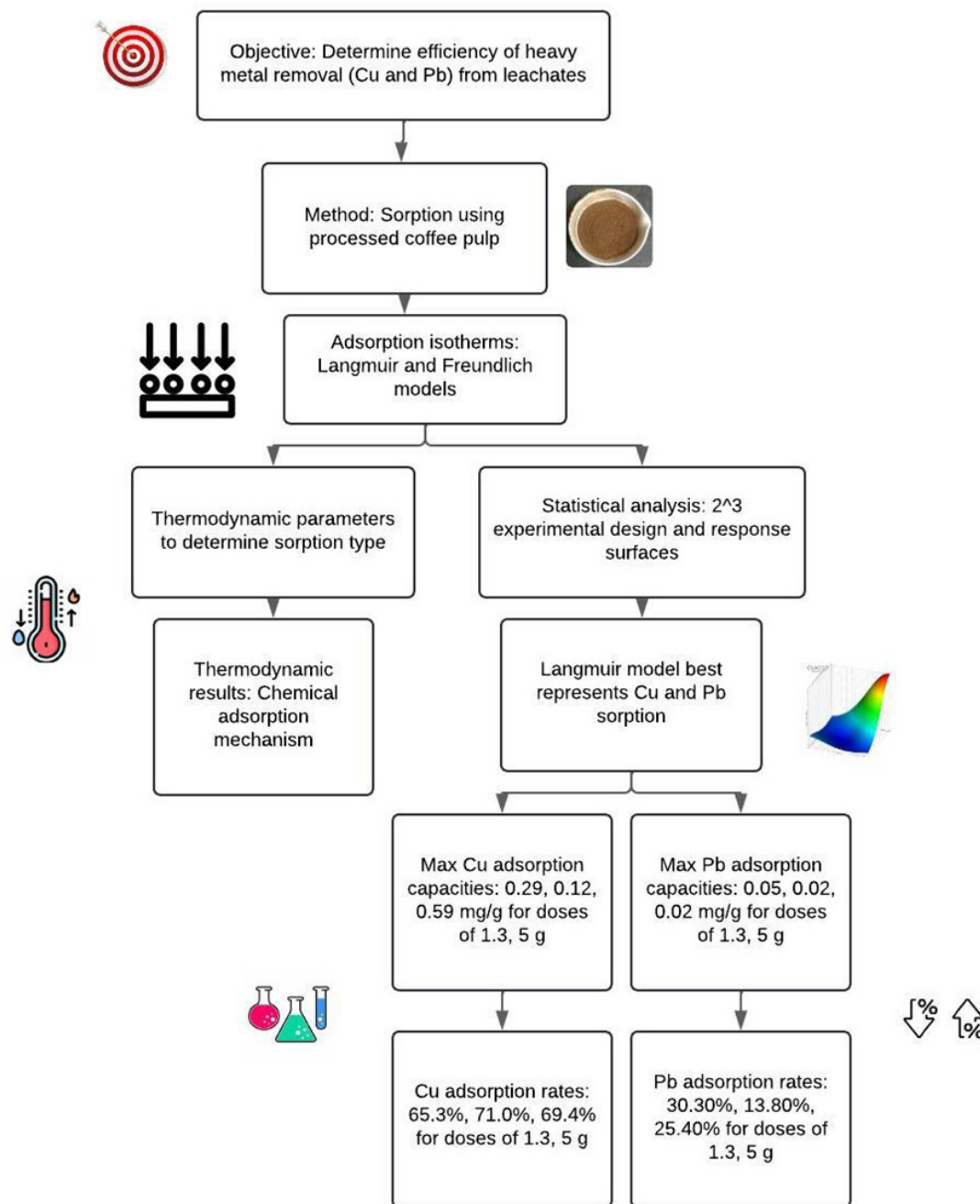
Graphical Abstract

Introduction

Solid waste generation is directly related to the development of human activities, consumption patterns and purchasing power. At a global level, technological advances, demographic growth, and the population concentration of large cities have led to an increase in the consumption of products and, consequently, contributing more rapidly to the growth of excessive waste production. Solids that are discarded annually, a fact that if it continues to occur, puts the planet´s stability at risk (1). According to the World Bank, in 2016, 0.74 kg of waste per capita per day was generated; resulting in a total of 2.01 billion tons. It is projected that by 2050, this will increase to 3.40 billion tons (2). There are different methods for the disposal, treatment, and elimination of solid waste, such as the use of landfills or open dumps, incineration, which seeks the chemical reduction of the volume of waste with energy recovery in the form of heat, and composting for the reuse of organic waste. organic through biological processes, among others (3). In most countries, including Colombia, waste is disposed of in controlled landfills or open dumps, which remains one of the primary forms of final disposal. According to a survey conducted by the World Bank in 90 countries, the latter method has been widely applied and accepted as the primary treatment option for municipal waste (4). Final disposal through landfills or open dumps generates countless environmental problems, with the generation of leachate being one of the main concerns due to the negative impacts it causes on the environment (5). Leachate is considered highly polluting effluent due to the complex composition, which includes a high concentration of organic material (biodegradable and refractory), in which humic compounds constitute an important group, as well as nitrogenous compounds, heavy metals and salts. inorganic. Its composition can be highly variable given the different types of waste that can reach landfills, the quantity, environmental conditions, and age of the landfill (5). It has been reported that leachates have concentrations of toxic substances, including heavy metals. Various treatment methods are available for the removal of heavy metals, both conventional and non-conventional, including precipitation, adsorption, electrocoagulation, ion exchange, sorption, and bioremediation, among others. For this reason, it is expected to know the efficiency levels in the treatment of heavy metals such as copper and lead from leachates since these are found in most cases above the permissible limits established in the regulations. In this context, sorption was investigated as a non-conventional alternative for removing these metals. The percentage (%) removal and adsorption capacity (mg/g) were determined using chemically and thermally modified coffee pulp (a waste generated in the processing of the grain) as the adsorbent material. These removal rates provide insight into the efficiency of the process and the feasibility of using processed and transformed waste as an adsorbent material.

Materials and methods

Selection and preparation of adsorbent material

The coffee pulp was obtained from a coffee farm in the municipality Santa Bárbara (Antioquia, Colombia). It was collected through the wet method, which separates the outer shell of the bean. The pulp was thoroughly washed with distilled water and dried for 72 hours in a conventional oven. After drying, it was ground and sieved until a particle size of less than 0.5 mm was achieved. For chemical modification, the coffee pulp was mixed with phosphoric acid (H3PO4) at 50%, in a ratio of 2:1 W/V, per 48 hours. It was rinsed with plenty of distilled water to remove the most significance amount of acid, and its pH was adjusted to a range of 6.5 to 7 with NaOH. 0.1 M. The sample was filtered and placed at 150°C for 24 hours to remove moisture. Thermal modification or carbonization, after chemical modification, was carried out in three phases, according to the method proposed by Pap et al., 2017 (6). In the first phase, the material was placed in crucibles inside a muffle furnace at a rate of 10°C per minute to 180°C for 35 minutes. In the second phase, the temperature was

increased to 400°C at a rate of 10°C per minute for 30 minutes. And in the final phase, the temperature was increased to 400°C at the same rate for 30 minutes. After cooling in a desiccator, the coffee pulp was stored in airtight bags. This material will hereafter be referred to as MCP (Modified Coffee Pulp).

Leachates Characterization

The leachates were obtained from the Neil Road landfill in Chico, Northern California. The landfill operates in a mechanized manner, and non-hazardous waste disposed of after source separation by the community. The analysis of anions and cations was performed by a private laboratory in the Chico-California, using EPA methods 300.0 and 200.7, respectively. The ionic strength of the leachate was set at 0.1M with sodium perchlorate. Heavy metals were analyzed in a Thermo Electron S4 AA spectrophotometer.

Experimental desing

An experimental design central composition was carried out, the factorial part of which corresponds to a 2^3 design. The tests were carried out in duplicate. The initial concentration that makes up the experimental region was chosen, taking the actual conditions of the leachates in Colombia as a reference (7). The contact time was chosen according to previous studies using coffee pulp and values reported in the literature (8), (9), (10). The adsorbent dose used was 1 g. The tests were conducted with continuous stirring at 150 rpm in a jar test equipment. The pH was adjusted based on the point zero charge (PZC), determined using the drift method and potentiometric titrations. The experimental region is detailed in Table 1.

Table 1. Experimental region for statistical design

Factor		Level			Star	
		Low	Central	High	+	-
X_1	Initial concentration for copper and lead (ppm)	1	1.5	2	1.67	2
X_2	Contact Time (h)	6	9	12	1.68	1.6
X_3	pH	4	5	6	1.7	1.7

To evaluate the response, total heavy metal removal was chosen as the dependent variable:

$$Y_i = C - C_0 \qquad \text{Eq. (1)}$$

To find the values that allow obtaining the greatest removal, the response surface method, whose acronym in English is (RSM), was used, using the R software. Surfaces are built from the fitted models where C is the final heavy metal concentration after running each treatment and C_0 the initial heavy metal concentration The response surfaces were analyzed for two scenarios: i) $i = 1$, copper solution; ii) $i = 2$, lead solution. The surfaces were constructed from the selection of models, which have the following form:

$$\hat{Y}_i = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{23} X_2 X_3 + \beta_{13} X_1 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{123} X_1 X_2 X_3$$

The final model for each case was selected to include only significant terms, adhering to the principle of parsimony.

Adsorption isotherms

The leachates were individually contacted with copper and lead solutions, considering the concentrations, pH, and optimal contact times obtained through the experimental design and response surfaces. The doses of Modified Coffee Pulp (MCP) used were 1, 3, and 5 grams. The system was kept under constant agitation at 150 rpm. After the contact time had elapsed, the equilibrium concentrations (C_e, mg/L) and the adsorbed metal amount per mass of adsorbent (q_e, mg heavy metal/g adsorbent) were measured. The experimental data were fitted to mathematical models using non-linear regression, minimizing the sum of squared errors (SSE) via the Microsoft Excel® Solver tool.

Single-component or individual solutions

The adsorbate loading per mass of adsorbent was quantified using the following equation:

$$q_t = C_0 - C_t * \frac{V}{W} \qquad \text{Eq. (3)}$$

Where, C_0 is the initial concentration of the solution (mg/L); C_t is the concentration at a time t after the process has started (mg/L); V: volume of the solution (L); W is the dosage of the adsorbent (g); q_t is the adsorbed mass per mass of the adsorbent (mg/g) at a given time. The models used in this study were the Langmuir and Freundlich isotherms.

Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy were determined, and calculated from the temperature based on the tests and standard conditions (25°C). This information allows us to establish the spontaneity of the process, the mechanism by which sorption occurs, and whether the process is exothermic or endothermic. The change in Gibbs free energy was calculated from the Eq. (4).

$$\Delta G^0 = -RT \ln K_{eq} \qquad \text{Eq. (4)}$$

The enthalpy of formation was calculated from the Van't Hoff equation (Eq. (5)), using the constant (K_1), and the temperature (T_1) at standard conditions (25°C). K_2 and T_2 correspond to the temperature of the tests (23°C).

$$\ln K_1 - \ln K_2 = \frac{\Delta H^0}{R} * \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{Eq. (5)} \qquad \Delta G^0 = \Delta H^0 - \Delta S^0 \qquad \text{Eq. (6)}$$

The enthalpy also determines the type of adsorption (physical or chemical). Physical adsorption occurs when the enthalpy is less than 40 kJ/mol. When it is greater than 200 kJ/mol, it is chemical adsorption, that is, here monolayer adsorption occurs, forming strong bonds at the active sites on the adsorbent surface [11] [12]. About ☐S (Eq. (6)), positive values, indicate an increase in randomness or disorder at the solid/liquid interface. Negative values indicate that the interaction between the adsorbent and the metal at the solid/liquid interface occurs in an orderly manner [13] [14].

Results and discussion

Design of experiments, individual copper solution

The scatter plot (Figure 1) shows that the amount of copper removed does not have exhibit a clear trend in relation to contact time. About the initial concentration, greater removal is observed at initial concentrations higher than 1.5 ppm and pH between 3.5 and 4.5.
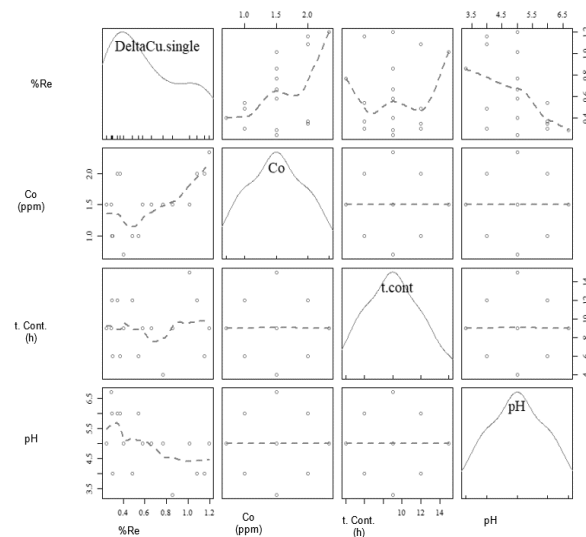
Figure 1. Scatter plot for the amount of copper removed in individual solution (Delta. Cu.single), the initial concentration (Co), the contact time in hours (t.cont), and the pH**.**

Figure 2 presents the response surface for the removal of individual copper. It shows that the region with the highest removal corresponds to pH less than 4.5 and initial concentration between 1 and 1.5 ppm. The plot on the right (contour lines) corroborates the response surface graph since, in the region where greater removal occurs, it corresponds to an initial concentration between 1 and 1.5 ppm and pH between 3.5 and 4.5.
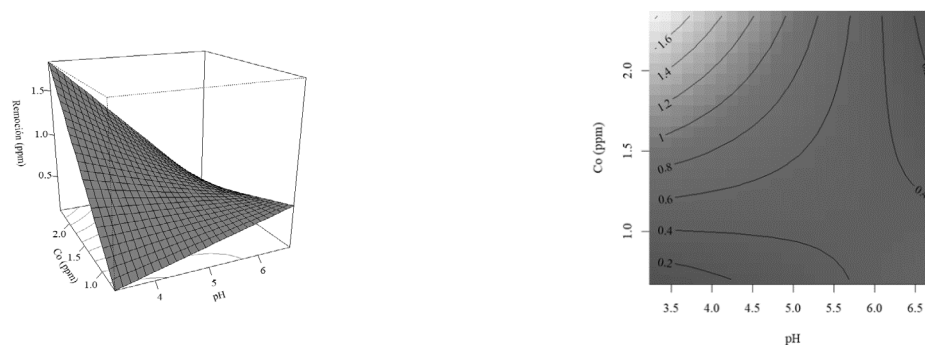

Figure 2. Response surface (left) and contour (right) for individual Cu

The data comply with the assumptions of homoscedasticity and normality. The Shapiro-Wilk test, which test for the normality of the residuals, resulted in a p-value of 0.4738, indicating sufficient evidence to accept the hypothesis as accurate, for this reason, the assumption of normality is met. The Breusch-Pagan test defines homoscedasticity in the null hypothesis. A p-value of 0.1423 indicates that there is evidence to support this hypothesis being true, and therefore the model exhibits homoscedasticity. In this case, it is observed that the contact time was not significant, so it is not reported in the final model. The initial concentration, and pH significantly affected the amount of heavy metal removed (p-values of 0.0022 and 0.0044, respectively). The estimated coefficients show that an increase in 1 ppm of initial copper generates an increase of 0.20 ppm in the amount removed, while increasing the pH by 1 unit produces a decrease of 0.18 ppm in the amount of copper removed. The R^2 value of 0.7279 indicates that the model is acceptable, as it explains 72.79%. the variability in the data.

Individual lead solution

Figure 3 shows that lead exhibits high variability in the experimental region. Contact time has no impact on the response variable (% removal), while the initial concentration and pH do. The optimal region corresponds to an initial concentration between 1.5 and 2ppm, and a pH between 3 and 3.5.
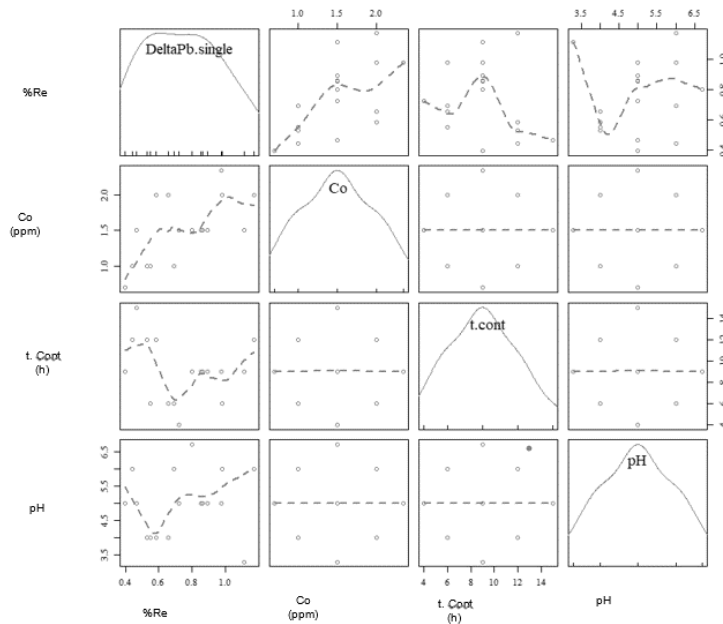

Figure 3. Scatter plot for the amount of lead removed in individual solution (Delta,Pb,single), the initial concentration (Co), the contact time in hours (t,cont) and the pH.

Homoscedasticity and normality are accepted, making the valid model. Since the p-value is greater than 0.05, the hypotheses of normality and homoscedasticity are not rejected. The linear model is valid. But the R^2 coefficient, whose value is (0.43), shows a lack of adjustment. Figure 4 show that the amount removed is the only variable correlated with the initial concentration, and that the amount of metal removed increases as the initial concentration increases. From this, it is observed that between 1.5 ppm and 2 ppm there is no apparent significant difference. The model fits moderately whenever $R^2 \geq 0.7$ (15). It is evident that between 1.5 ppm and 2 ppm, there is no apparent significant difference.
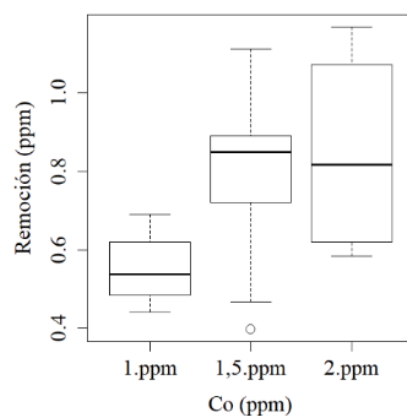

Figure 4. Box and whisker diagram for lead removal according to initial concentration

According to the previous analyses, Table 2 shows the variables values that results the highest removal rate in individual solutions. These values will be used to carry out the isotherm tests.

Table 2. Levels of selected factors

Solution	Contact time (h)	pH	Initial Concentration (ppm or mg/L)
Individual copper	15	4.0	2.0
Individual lead	9	3.3	1.5

Adsorption isotherms

Adsorption isotherms were conducted in a batch-type system, with the parameter values set according to Table 2. The isotherms were performed in triplicate, varying the adsorbent dose at 1, 3, and 5 grams.

Isotherms in individual systems

Table 3, Table 4 and Table 5 present the maximum adsorption capacities, constants, and errors obtained through the least squares method (SSE) for the Langmuir and Freundlich models with Pb and Cu.

Table 3. Individual isotherm of Cu and Pb, MCP dose 1g

Copper												Lead		
Langmuir			**Freundlich**			**Langmuir**			**Freundlich**					
q_{max} mg/g	K_{ads}	SSE	N	K_F mg/g	SSE	q_{max} mg/g	K_{ads}	SSE	n	K_F mg/g	SSE			
0.29	0.27	0.00016	0.71	0.10	0.000079	0.050	0.318	0.0000058	1.14	0.012	0.0000057			

Table 4. Individual isotherm of Cu and Pb, MCP dose 3g

Copper						Lead					
Langmuir			**Freundlich**			**Langmuir**			**Freundlich**		
q_{max} mg/g	K_{ads}	SSE	n	K_F mg/g	SSE	q_{max} mg/g	K_{ads}	SSE	n	K_F mg/g	SSE
0.12	0.202	0.0000063	0.357	0.084	0.00004	0.02	0.103	0.00000031	0.93	0.002	0.00000029

Table 5. Individual isotherm of Cu and Pb, MCP dose 5g

Copper						Lead					
Langmuir			Freundlich			Langmuir			Freundlich		
q_{max} mg/g	K_{ads}	SSE	n	K_F mg/g	SSE	q_{max} mg/g	K_{ads}	SSE	n	K_F mg/g	SSE
0.059	0.20	0.00001158	0.385	0.031	0.00000106	0.020	0.103	0.00000002	1.97	0.002	0.00000007

According to the results, the Freundlich model presents the best fit to the experimental data of Cu for the doses of 1 and 5 g of MCP, while the Langmuir model fits best for the 3-gram dose, as these models exhibit the lowest error values. However, the maximum adsorption capacities fitted to the Langmuir model are higher than those of the Freundlich model. For example, for the isotherm with a dose of 1 g, q_{max} is 0.289 mg/g with the Langmuir model, and K_F is 0.104 mg/g with the Freudlich model. For the isotherm with a dose of 3g q_{max} is 0.120 mg/g with the Langmuir model, and for example, for the isotherm with a dose of 1 g, q_{max} is 0.289 mg/g with the Langmuir model and K_F is 0.104 mg/g with the Freudlich model. The isotherm with a dose of 3g q_{max} is 0.120 mg/g with the Langmuir model and K_F is 0.084 mg/g with the Freudlich model. For the isotherm with a dose of 5 gs, qmax is 0.059 mg/g with the Langmuir model and K_F is 0.031 mg/g with the Freudlich model. From these values, it can be concluded that although the error is lower with the Freundlich model, the adsorption capacity calculated with the Langmuir model has a much higher value, which represents that there is a greater amount of copper retained on the surface of the pulp coffee is 0.084 mg/g with the Freudlich model. For the isotherm with a dose of 5 gs, q_{max} is 0.059 mg/g with the Langmuir model and K_F is 0.031 mg/g with the Freudlich model. From these values, it can be concluded that although the error is lower with the Freundlich model, the adsorption capacity calculated with the Langmuir model has a much higher value, which represents that there is a greater amount of copper retained on the surface of the pulp coffee. About the maximum adsorption capacities (K_f y q_{max}) obtained for the different doses, it can be deduced that the values found for Cu (0.104, 0.120, 0.031 mg/g) are low compared to others reported in the literature (Table 6), denoting that the surface of the coffee pulp is easily saturated.

There is little availability of active sites to retain a greater amount of heavy metals. Regarding the sorption speed or affinity, for doses of 1 and 5, the values n are greater than zero (0.715 and 0.385, respectively), concluding that the pulp surface has a partial affinity for Cu. For the 3 g dose, the affinity is related to the Langmuir constant, K_{ads}, whose value is 0.103, indicating that there is also relative affinity for said metal to be retained. In the case of the individual Pb isotherms, it can be seen that for the doses of 1 and 3g, the experimental data fit the Freundlich model and for the 5g dose, they fit the Langmuir model; however, as happened with copper, the maximum adsorption capacities are greater with the Langmuir model compared to that of Freundlich. The maximum adsorption capacities (K_f) according to the Freundlich model are 0.012 and 0.002 mg/g, for doses of 1 and 3 respectively, and 0.002 mg/g for the dose of 5 gs with the Langmuir model (q_{max}). Like copper, these adsorption capacities are very low compared to other adsorbents derived from coffee waste (Table 6), indicating that MCP has a high saturation capacity, and there are few active sites available to capture heavy metals compared to the amount of metal to be retained, which may explain these low values. In terms of affinity, the values for the 1- and 3-gram doses are greater than 1, indicating that the metal affinity to the coffee pulp

surface is lower compared to Cu. The same holds for the 3-gram dose, where the affinity constant is low at 0.103.

Table 6. Maximum adsorption capacities with coffee wastes

Metal	Isoterma	q_{max}(mg/g)	adsorbent Material	Source
Pb	Langmuir	158.70	Coffee waste drink	(16)
Cu		97.10		
Cu	Freundlich	13.60	Used coffee beans	(17)
Cr (VI)	Langmuir	4.27	Activated carbon prepared from coffee waste	(18)
Ni	Langmuir	146.72	Activated carbon from coffee husks	(19)
Ni (II)	Langmuir	57.14	Coffee husks	(20)
	Langmuir	51.91	Activated carbon prepared from coffee waste	
Pb	Freundlich	9.18	Coffee husks	(21)
Pb	Langmuir	41.15	Magnetic nanoparticle with coffee residue	(22)
Pb	Langmuir	285.7	Used coffee grounds	(23)
Cu	Langmuir	11.60	Used coffee grounds	(24)
Cu	Langmuir	31.20	Coffee and clay waste	(25)
Pb		19.50		
Cd	Langmuir	15.65	Coffee beans	(14)
Pb	Langmuir	22.50	Coffee Beans	(26)
Pb	Langmuir	49.48	Used coffee grounds	(27)
Cu	Langmuir	1.95		
Cd	Langmuir	6.73	Spent and degreased coffee beans	(28)
Pb	Freundlich	63.30	Activated carbon prepared from coffee waste	(29)
Pb	Freundlich	9.88	Modified plum seeds	(6)

Figures 5 and 6 show the fit of the experimental data to the Freundlich and Langmuir models. Although visually the models do not fit 100% of the data obtained from the tests, the errors are tolerable, allowing us to infer which model is a better fit. The model that best fits the experimental data is the Freundlich model; however, the Langmuir model provided the best results for estimating the maximum adsorption capacity. The Langmuir model assumes that adsorption occurs on a homogeneous surface of the adsorbent, meaning that all binding sites are equally interactive, resulting in chemical adsorption. In contrast, the Freundlich model assumes that the forces at all binding sites on the adsorbent

are heterogeneous, where the adsorbed molecules interact with each other, pointing to physical adsorption (30) (6). Based on the assumptions of each model and the maximum adsorption capacity found, it is concluded that the Langmuir model adequately represents the adsorption of copper and lead using coffee pulp.
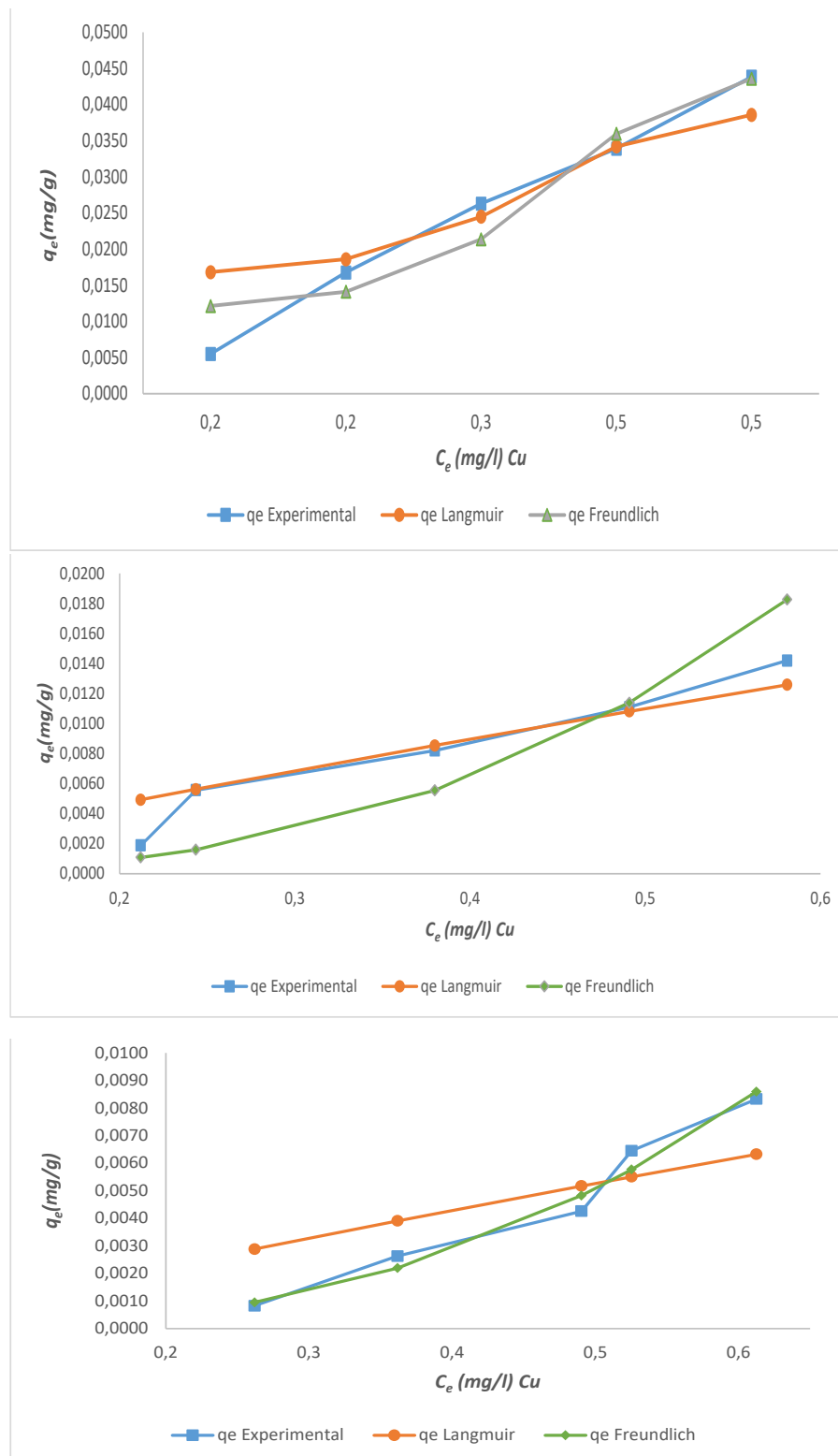

Figure 5. Cu isotherms with different dosages of adsorbent material (a)1g,(b) 3g, (c)5g
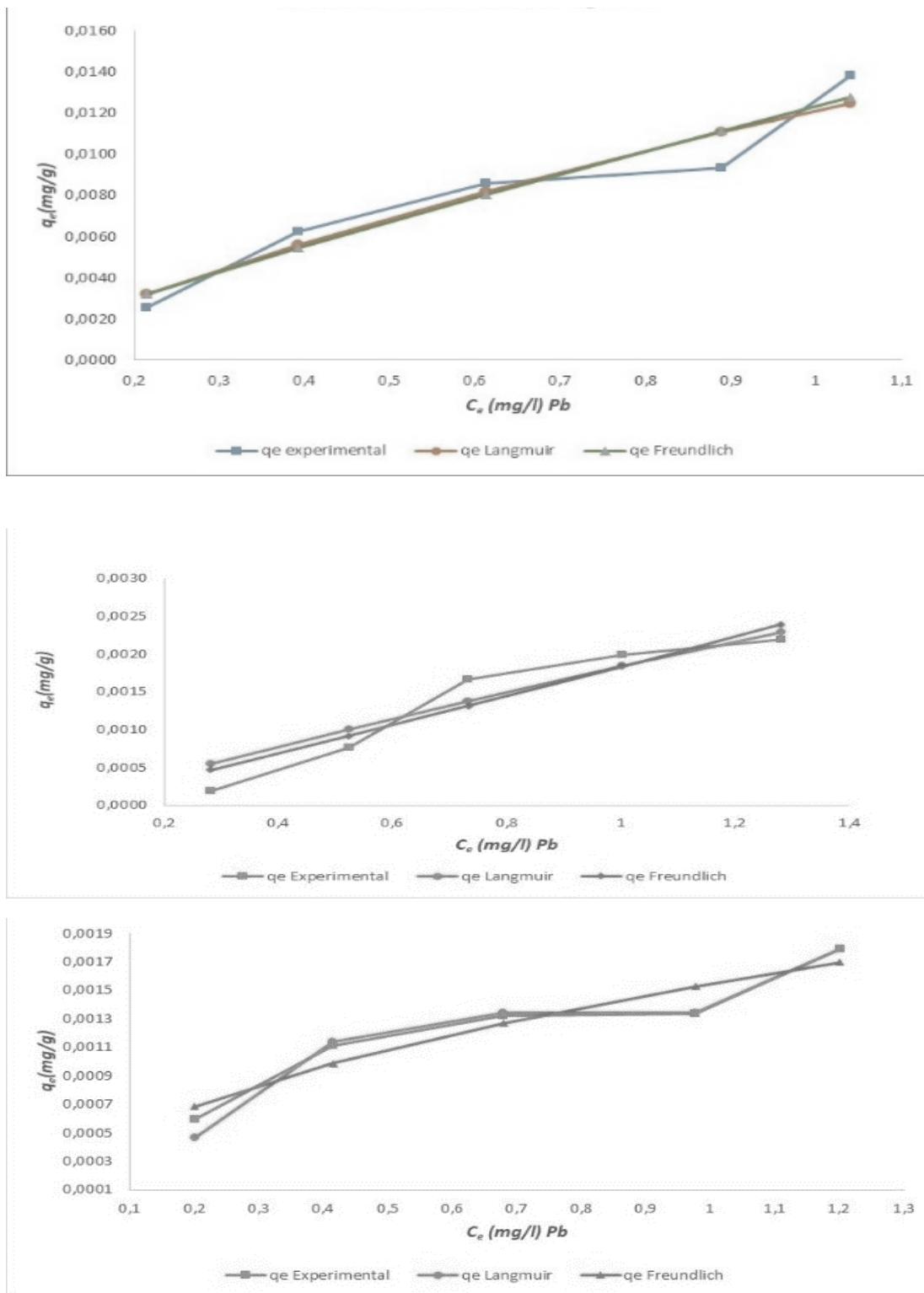
Figure 6. Pb isotherms with different dosages of adsorbent material a)1g,(b) 3g, (c)5g

From the study conducted with coffee husks (21), the removal of lead was found to fit the Freundlich model, with an adsorption capacity of 9.18 mg/g, a value significantly higher than that observed in the present study. These results suggest that the adsorption

mechanism is heterogeneous and multilayer, due to the effective distribution of active sites on the adsorbent's surface (22). Additionally, it was determined that the Langmuir isotherm is the model that best fits the adsorption tests for lead in a batch system, indicating that the process occurs through monolayers and that the energy of each adsorption site is very similar. In the removal of Pb using coffee waste, a maximum adsorption capacity of 285.71 mg/g at 333 K was achieved, with an excellent fit to the Langmuir model, demonstrating that the process was homogeneous in nature and involved adsorption in monolayers (23). These results contradict those obtained with coffee pulp, whose data fit more favorably to the Freundlich model, revealing a lower adsorption capacity than that found in the afore mentioned study. In the removal of Cu using used coffee waste, the tests were also adjusted to the Langmuir model, yielding a maximum adsorption capacity of 11.60 mg/g, indicating that the sorption occurred on a heterogeneous surface, which became saturated in a monolayer configuration (24).

The adsorbent composed of coffee waste and clay, used for the removal of various metals, including lead, copper, cadmium, zinc, and nickel, demonstrated that equilibrium fits the Langmuir model, with adsorption capacities for copper and lead of 31.2 and 19.5 mg/g, respectively. In general, the adsorption occurred in the following order: $Cd^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+}$, which is due to the degree of hardness, depending on the charge and radius of the cations. Softer metals interact more easily with anions, explaining the observed order of adsorption (25) .When using coffee beans for the removal of Pb from aqueous solutions, an adsorption capacity of 22.5 mg/g was found at pH 5, with the experimental data fitting the Langmuir model. These results were attributed to the charging of the coffee beans' surface, which enhanced the electrostatic interaction between the beans and the cationic ions of Pb (26).

The removal of Pb from aqueous solutions was studied using activated carbon derived from coffee waste. This carbon was modified with zinc chloride to generate acidic conditions and promote polymerization reactions that lead to the formation of carboxylic groups on its surface, resulting in an increased surface area. It was confirmed that the modification of the activated carbon enhanced lead removal. The initial concentration data indicated that at 10 mg/L, the adsorption capacity is 9.65 mg/g. Furthermore, at 90 mg/L, the adsorption capacity increases to 62.5 mg/g. This increase in adsorption capacity was attributed to the driving force provided by mass transfer, with equilibrium being achieved after 2 hours. The model that best fit the experimental data was the Freundlich model, likely due to the heterogeneous distribution of active sites on the activated carbon surface. Table 7 shows the removal percentages of Cu and Pb depending on the dose of coffee pulp used.

Table 7. Removal percentage of Cu and Pb in one-component solutions

Metal	Dosage 1g	Dosage 3g	Dosage 5g
Cu	65.30%	71.00%	69.40%
Pb	30.30%	13.80%	25.40%

From Table 7, it can be deduced that the removal in both cases does not exhibit a linear dependence on the amount of sorbent used; that is, it cannot be stated that a higher dose of sorbent necessarily leads to a higher metal removal rate. It is also observed that lead has a significantly lower removal rate than copper. It has been noted that copper can form complexes with both organic and inorganic ligands present in water. For example, it forms strong complexes with OH^- and CO_3^{2-} ions and weak complexes with Cl^- and SO_4^{2-} ions. Copper complexes exhibit high stability with organic matter, binding to the organic ligands

present, which can affect the complexation of other metals in the solution (31).

Based on the premises presented, as well as the presence of OH⁻, SO_4^{2-}, F⁻, Cl⁻, and other ions—characterized not only in the leachate but also on the surface of the coffee pulp—it can be inferred that the removal rates are higher for Cu compared to Pb. Reference (24) noted that in the presence of chelating agents such as EDTA (ethylenediaminetetraacetic acid), Cu forms complexes. However, during adsorption tests, a higher Cu adsorption capacity was observed in the absence of this chelator (11.6 mg/g) than when it was present in the solution (10.52 mg/g).

In the research conducted by (27) on the removal of heavy metals, including copper and lead, it was found that the removal percentage ranged between 75% and 90%, with the optimal conditions being a pH of 5 and an adsorbent dose of 20 g/L (coffee waste). It was concluded that at concentrations lower than 10 mg/L, the adsorption rate is constant, but it increases considerably when the concentration exceeds 100 mg/L. In the study carried out by (32), which involved batch tests for the treatment of metals such as copper and lead using spent coffee waste, it was found that the amount removed depends on the dose used. The higher the amount of adsorbent material, the greater the removal of metals. It was also found that the fraction of metals removed was reduced at pH levels lower than 4 due to the competition between metals and H⁺ ions.

In the removal of lead from drinking water using coffee-based adsorbents, the effect of proteins (such as caffeine, chlorogenic acid, and extracts) present in spent coffee beans and waste was studied. These components were analyzed in the presence or absence of the adsorbents, and it was found that they have a direct relationship with the adsorption rates of lead, as they are responsible for ion exchange with the metal (33). Using defatted spent coffee beans, a maximum cadmium adsorption capacity of 6.73 mg/g was achieved through the Langmuir model, with equilibrium reached at a pH range of 7.8 to 8.9. This study concluded that the adsorbent used is an excellent metal exchanger, as the removal rate reached 100% (28). Using spent coffee beans, 85% of Cu and 87% of Pb were removed from aqueous solutions, with contact time and the amount of coffee used identified as the most important variables to achieve these removal rates. It was also evident that using a greater amount of adsorbent provided a larger surface area for ion exchange (34). In line with the previously presented research, and by comparing the removal percentages found, it was again concluded that the adsorption percentages achieved with coffee pulp are low compared to other plant-based materials or coffee waste.

One of the reasons for the low adsorption could be the low surface area of the MCP. This issue may have arisen due to factors such as the presence of ions like phosphate and sodium, a result of the chemical modification, which possibly caused clogging of the structure. The thermal activation time was likely insufficient to increase the surface area and open the pores. As a result, the MCP structure was softened, leading to the loss of aliphatic chains during the applied pretreatment, leaving only the aromatic chains of the tars, which came together and formed linear planes (35)(36). The thermal modification of the coffee pulp must be carried out at high temperatures (>600°C) and in inert atmosphere conditions through nitrogen or a similar gas since this guarantees that the surface area is increased of the adsorbent material and that the surface pores are not covered by other compounds present on it. As in the present study the coffee pulp could not be thermally modified through an inert atmosphere, but rather through carbonization at temperatures of 600°C and in the presence of oxygen, the surface area did not undergo substantial changes.

Thermodynamic parameters

The values of the Gibbs free energy, enthalpies and entropies of copper and lead in individual solutions are presented below (Table 8 and Table 9).

Table 8. Gibbs free energy (ΔG) and enthalpy (ΔH) of copper in individual solution

Dosage MCP (g)	C_i (mg/L)	C_e (mg/L)	V(l)	q_e (mg/g)	K_{eq}	$\ln K_{eq}$	ΔG^0 (kJ/mol)	DH^0 (kJ/mol)	DS^0 (kJ/mol)
1	2	0.54	0.03	0.044	2.71	0.99	-2.46	-9982.9	-33.72
3	2	0.58	0.03	0.014	2.44	0.89	-2.19	-9944.5	-33.59
5	2	0.61	0.03	0.0083	2.26	0.82	-2.012	-9916.9	-33.50

Tabla 9. Gibbs free energy (ΔG) and enthalpy (ΔH) of lead in individual solution

Dosage MCP (g)	C_i (mg/L)	C_e (mg/L)	V(l)	q_e (mg/g)	K_{eq}	$\ln K_{eq}$	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)
1	2	1.04	0.03	0.014	0.44	-0.82	2.00	3895.5	13.15
3	2	1.28	0.03	0.0022	0.17	-1.76	4.33	4242.1	14.32
5	2	1.20	0.03	0.0018	0.25	-1.40	3.42	4106.6	13.86

Regarding the first parameter, copper at all doses reacts spontaneously and is thermodynamically favorable since the ΔG values are negative. The enthalpy of the formation of copper and individual lead determined that the process occurs through chemisorption, since the values in all doses are greater than 400 kJ/mol (37), indicating a strong bond between these metals and the pores on the surface of the coffee pulp. In the case of copper, the process is exothermic because the ΔH values are negative, and for lead it is endothermic due to the positive ΔH values. In the first case, it can be concluded that the process releases energy. In the event of scaling, the energy required for the process to occur is low, constituting an efficient and possibly profitable process, as it does not require an additional energy supply.

In the case of lead, being an endothermic process, an additional energy source is required, which, could increase cost if implemented on a larger scale. An advantage of energy supply is that an increase in pore size and widening could be generated, creating more surface area on the adsorbent, leading to an increase in adsorption rates. Endothermic processes can be attributed to the increase in the mobility and diffusion of the adsorbate, as a greater number of molecules can gain enough energy to interact with the active sites on the adsorbent's surface (38) (22).

The entropy values for copper are negative, indicating greater disorder at the liquid-solid interface. This could lead to a lower affinity of the adsorbent for copper, as reflected in the study, where copper adsorption rates were lower than those for lead. The entropy values for lead were positive, favoring adsorption, as there was a greater affinity between the coffee pulp and lead.

When comparing the thermodynamic parameters from this study with others found in adsorbents of plant origin (Table 10), it becomes evident that it is not possible to generalize the spontaneity or reaction type of adsorption. Each sorbent and process has its peculiarities according to its nature, temperature used, treatment applied and types of tests performed;

However, in some studies with adsorbents derived from coffee, some similarities do appear, especially in the behavior presented by lead.

Table 10. Thermodynamic parameters of sorbents of plant origin

Adsorbente	Metal	Adsorption type	Spontaneity	Reaction type	Source
Pepper peel	Pb	Chemisorption	Spontaneous	Endothermic	[39]
Peanut shells	Cu	Chemisorption	Not Spontaneous	Endothermic	[13]
Sesame stems	Ni	Physiosorption	Spontaneous	Exothermic	[40]
	Zn	Physiosorption	Spontaneous	Endothermic	
Coffee beans	Cd	Physiosorption	Not Spontaneous	Exothermic	[14]
Activated carbon and coffee husk	Ni	Physiosorption	Not Spontaneous	Endothermic	[20]
Magnetic nanoparticles from coffee waste	Pb	Physiosorption	Spontaneous	Endothermic	[22]
Used coffee residue	Pb	Physiosorption	Spontaneous	Endothermic	[23]
Coffee and clay waste	Pb y Cu	Physiosorption	----	Exothermic	[25]
Coffee beans	Cd	Physiosorption	Not Spontaneous	Exothermic	[14]
Persimmon leaves	Pb	Chemisorption	Spontaneous	Endothermic	[41]
P. Africana leaves	Pb Cd	Chemisorption	Spontaneous	Endothermic	[38]
Tea tree husk	Pb. Cd. Cu	Chemisorption	Spontaneous	Endothermic	[42]

For example, in the study of coffee beans [14] were cadmium was removed, adsorption was physical and the reaction was exothermic and not spontaneous. In the present study with MCP, adsorption for both metals was chemical, spontaneous and exothermic in the case of copper, and non-spontaneous and endothermic in the case of lead. In the study [20] with coffee husks and activated carbon produced from spent coffee, it was concluded that the mechanism by which adsorption occurs is physical, endothermic and non-spontaneous and that temperature affects the equilibrium; At higher temperatures, the adsorption capacity tends to increse and diffusion in the pores of the adsorbents is facilitated. [22] found negative values of the Gibbs free energy at temperatures between 298 and 318K indicting that the process is favorable and spontaneous. Concerning the enthalpy and entropy, the positive values showed that the system is endothermic. These parameters allowed us to

conclude that an increase in temperature favors the adsorption of Pb with the magnetic nanoparticle with coffee waste.

In the removal of lead with used coffee waste, it was found that the reaction is spontaneous, and that the heat of adsorption allowed us to establish that the process is physical and endothermic (23).

For its part, (25), experimenting with an adsorbent material composed of coffee waste and clay, determined that the reaction with different heavy metals such as copper and lead is physical and exothermic since the values of the heat of adsorption are negative. Negative enthalpy values show that the adsorption of cadmium with coffee beans is exothermic. Gibbs free energy is positive , meaning the reaction is non-spontaneous. In relation to the entropy, its negative value indicates that the cadmium in the aqueous phase had a more chaotic distribution compared to the stability and relatively ordered state achieved on the surface of the adsorbent (14). Using activated carbon prepared from P. Africana leaves, it was found that the removal of Pb and Cd is spontaneous and thermodynamically favorable. The ΔH° values are in the range of 5-10 kJ mol^{-1} indicating a relatively weak binding between the ions and the adsorbent. The process is endothermic and chemisorption occurs. The positive values ΔS indicated an increase in randomness of the solid/liquid interface, showing a good affinity of the adsorbents for the adsorbed species (38).

Conclusions

However, for batch and column tests, 12 hours for the mixed solution, 9 hours for lead, and 15 hours for copper were determined as the optimal values. Variables such as pH and initial concentration were adjusted, resulting in different adsorption rates.

In the adsorption isotherms, the Freundlich model provides the best fit for the experimental data for each metal. However, the maximum adsorption capacities obtained from the Langmuir model are higher than those from the Freundlich model. It can be concluded that although the Freundlich model produces lower error, the adsorption capacity calculated by the Langmuir model is significantly higher, indicating that a greater amount of metal is retained on the surface of the coffee pulp. Regarding the maximum adsorption capacities (K_f and q_{max}) obtained for the different doses, the values found are low compared to others reported in the literature, indicating that the surface of the coffee pulp saturates easily. There are few active sites available to retain larger amounts of heavy metals.

The enthalpy values for copper and lead formation determined that the process occurs through chemisorption, as the values at all doses are greater than 400 kJ/mol. This indicates a strong bond between these metals and the pores on the surface of the coffee pulp. In the case of copper, the process is exothermic because the ΔH values are negative, whereas for lead, it is endothermic due to the positive ΔH values.

CRediT authorship contribution statement

Elizabeth Carvajal Florez: Data curation, Methodology, Visualization, Formal analysis, Investigation, Writing – original draft, Writing – review & editing.

Conflict of interest

The authors no declare.

Ethical implications

The authors do not have any type of ethical involvement that should be declared in the

writing and publication of this article.

Financing

References

1. Ojeda L, Lozano G, Quintero M, Whitty K, Smith C. Generación de residuos sólidos domiciliarios por periodo estacional: el caso de una ciudad mexicana. In: I Simposio Iberoamericano de Ingeniería de Residuos Castellón. 2008.

2. Kaza S, Yao L, Bhada-Tata P, van Woerden F. What a waste 2.0: a global snapshot of solid waste management to 2050. World Bank Publications; 2018.

3. Sáez A, Urdaneta JA. Manejo de residuos sólidos en América Latina y el Caribe. Omnia. 2014;20(3):121–35.

4. Hoornweg D, Bhada-Tata P. What a waste: a global review of solid waste management. 2012;

5. Costa AM, Alfaia RG de SM, Campos JC. Landfill leachate treatment in Brazil–An overview. J Environ Manage. 2019;232:110–6.

6. Pap S, Šolević Knudsen T, Radonić J, Maletić S, Igić SM, Turk Sekulić M. Utilization of fruit processing industry waste as green activated carbon for the treatment of heavy metals and chlorophenols contaminated water. J Clean Prod [Internet]. 2017 Sep [cited 2017 Aug 23];162:958–72. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0959652617312532

7. Empresas Varias de Medellín. Informe de caracterización del agua a la entrada y salida de la planta de tratamiento en el relleno sanitario La Pradera, ubicado en el municipio de Don Matias- Antioquia. Medellín; 2016.

8. Braham JE, Bressani R. Pulpa de café: composición, tecnología y utilización. CIID, Ottawa, ON, CA; 1978.

9. Elías LG. Composición Química de la Pulpa de café y otros Subproductos. Centro Internacional de Investigaciones para el Desarrollo. 1978. 19–29 p.

10. Gladis Blandón-Castaño; María Teresa Dávila-Arias; Nelson Rodríguez-Valencia. Caracterización microbiológica y físico-química de la pulpa de café sola y con mucílago, en proceso de lombricompostaje. Cenicafé. 1999;50(1):5–23.

11. Valencia U de. Apuntes de química física avanzada. Superficies sólidas: adsorción y catálisis heterógenea [Internet]. [cited 2016 Mar 29]. Available from: http://www.uv.es/tunon/pdf_doc/Superficies_Solidas_A.pdf

12. Kırbıyık Ç, Kılıç M, Çepelioğullar Ö, Pütün AE. Use of sesame stalk biomass for the removal of Ni (II) and Zn (II) from aqueous solutions. Water science and technology. 2012;66(2):231–8.

13. Ali RM, Hamad HA, Hussein MM, Malash GF. Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. Ecol Eng [Internet]. 2016;91:317–32. Available from: http://www.sciencedirect.com/science/article/pii/S0925857416301641

14. Azouaou N, Sadaoui Z, Djaafri A, Mokaddem H. Adsorption of cadmium from aqueous

solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics. J Hazard Mater [Internet]. 2010;184(1):126–34. Available from: http://www.sciencedirect.com/science/article/pii/S0304389410010307

15. Pulido Gutiérrez H, de la Vara Salazar R. Diseño de experimentos : principios estadísticos para el diseño y análisis de investigaciones. 2nd ed. McGraw-Hill, editor. 2012.

16. Bustamante-Alcántara E. Adsorción de metales pesados en resiudos de café modificados químicamente [Internet]. Universidad Autónoma de Nuevo León, México. Tesis doctoral; 2011. Available from: http://eprints.uanl.mx/2323/1/1080223849.pdf

17. Dávila-Guzmán NE, de Jesús Cerino-Córdova F, Soto-Regalado E, Rangel-Mendez JR, Díaz-Flores PE, Garza-Gonzalez MT, et al. Copper Biosorption by Spent Coffee Ground: Equilibrium, Kinetics, and Mechanism. Clean (Weinh) [Internet]. 2013;41(6):557–64. Available from: http://dx.doi.org/10.1002/clen.201200109

18. Cubides Guerrero P, Ramírez Franco JH. Adsorción de Cr VI sobre residuos de café. Revista Mutis [Internet]. 2014;4(2):18–25. Available from: http://revistas.utadeo.edu.co/index.php/mutis/article/view/953/992

19. Velásquez J. J, Quintana G, Gómez C, Echavarría Y. Adsorción de NI(II) en carbón activado de cascarilla de café. Revista Investigaciones Aplicadas [Internet]. 2008;2(1):1–6. Available from: https://revistas.upb.edu.co/index.php/investigacionesaplicadas/article/view/142/116

20. Hernández Rodiguez M, Yperman J, Carleer R, Maggen J, Dadi D, Gryglewicz G, et al. Adsorption of Ni(II) on spent coffee and coffee husk based activated carbon. J Environ Chem Eng [Internet]. 2018;6(1):1161–70. Available from: http://www.sciencedirect.com/science/article/pii/S221334371730684X

21. Alhogbi BG. Potential of coffee husk biomass waste for the adsorption of Pb(II) ion from aqueous solutions. Sustain Chem Pharm [Internet]. 2017;6:21–5. Available from: http://www.sciencedirect.com/science/article/pii/S2352554117300323

22. Edathil AA, Shittu I, Hisham Zain J, Banat F, Haija MA. Novel magnetic coffee waste nanocomposite as effective bioadsorbent for Pb(II) removal from aqueous solutions. J Environ Chem Eng [Internet]. 2018;6(2):2390–400. Available from: http://www.sciencedirect.com/science/article/pii/S2213343718301623

23. Naga Babu A, Reddy DS, Kumar GS, Ravindhranath K, Krishna Mohan G v. Removal of lead and fluoride from contaminated water using exhausted coffee grounds based bio-sorbent. J Environ Manage [Internet]. 2018;218:602–12. Available from: http://www.sciencedirect.com/science/article/pii/S0301479718304791

24. Escudero C, Gabaldón C, Marzal P, Villaescusa I. Effect of EDTA on divalent metal adsorption onto grape stalk and exhausted coffee wastes. J Hazard Mater [Internet]. 2008;152(2):476–85. Available from: http://www.sciencedirect.com/science/article/pii/S0304389407010047

25. Boonamnuayvitaya V, Chaiya C, Tanthapanichakoon W, Jarudilokkul S. Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay. Sep Purif Technol [Internet]. 2004;35(1):11–22. Available from: http://www.sciencedirect.com/science/article/pii/S1383586603001102

26. Gomez-Gonzalez R, Cerino-Córdova FJ, Garcia-León AM, Soto-Regalado E, Davila-Guzman NE, Salazar-Rabago JJ. Lead biosorption onto coffee grounds: Comparative

analysis of several optimization techniques using equilibrium adsorption models and ANN. J Taiwan Inst Chem Eng [Internet]. 2016;68:201–10. Available from: http://www.sciencedirect.com/science/article/pii/S1876107016303145

27.   Utomo HD, Hunter KA. Adsorption of heavy metals by exhausted coffee grounds as a potential treatment method for waste waters. e-Journal of Surface Science and Nanotechnology. 2006;4:504–6.

28.   Kaikake K, Hoaki K, Sunada H, Dhakal RP, Baba Y. Removal characteristics of metal ions using degreased coffee beans: Adsorption equilibrium of cadmium (II). Bioresour Technol. 2007;98(15):2787–91.

29.   Boudrahem F, Aissani-Benissad F, Aït-Amar H. Batch sorption dynamics and equilibrium for the removal of lead ions from aqueous phase using activated carbon developed from coffee residue activated with zinc chloride. J Environ Manage [Internet]. 2009;90(10):3031–9. Available from: http://www.sciencedirect.com/science/article/pii/S0301479709001108

30.   Ahsan MdA, Jabbari V, Islam MdT, Kim H, Hernandez-Viezcas JA, Lin Y, et al. Green synthesis of a highly efficient biosorbent for organic, pharmaceutical, and heavy metal pollutants removal: Engineering surface chemistry of polymeric biomass of spent coffee waste. Journal of Water Process Engineering [Internet]. 2018;25:309–19. Available from: http://www.sciencedirect.com/science/article/pii/S2214714418303635

31.   Bodek I, Lyman WJ, Reehl WF, Rosenblatt DH. Environmental inorganic chemistry: properties, processes, and estimation methods. Pergamon press New York:; 1988.

32.   Utomo HD, Hunter KA. Adsorption of Divalent Copper, Zinc, Cadmium and Lead Ions from Aqueous Solution by Waste Tea and Coffee Adsorbents. Environ Technol [Internet]. 2006 Jan 1;27(1):25–32. Available from: https://doi.org/10.1080/09593332708618619

33.   Tokimoto T, Kawasaki N, Nakamura T, Akutagawa J, Tanada S. Removal of lead ions in drinking water by coffee grounds as vegetable biomass. J Colloid Interface Sci. 2005;281(1):56–61.

34.   Impellitteri CA, Allen HE, Lagos G, McLaughlin MJ. Removal of soluble Cu and Pb by the automatic drip coffee brewing process: Application to risk assessment. Human and Ecological Risk Assessment: An International Journal [Internet]. 2000 Apr 1;6(2):313–22. Available from: https://doi.org/10.1080/10807030009380065

35.   Guo F, Li X, Liu Y, Peng K, Guo C, Rao Z. Catalytic cracking of biomass pyrolysis tar over char-supported catalysts. Energy Convers Manag [Internet]. 2018;167:81–90. Available from: http://www.sciencedirect.com/science/article/pii/S0196890418304424

36.   Valderrama Rios ML, González AM, Lora EES, Almazán del Olmo OA. Reduction of tar generated during biomass gasification: A review. Biomass Bioenergy [Internet]. 2018;108:345–70. Available from: http://www.sciencedirect.com/science/article/pii/S0961953417304026

37.   Valencia U de. Apuntes de química física avanzada. Superficies sólidas: adsorción y catálisis heterógenea [Internet]. 2016 [cited 2018 Aug 31]. Available from: https://www.uv.es/tunon/pdf_doc/Superficies_Solidas_A.pdf

38.   Elaigwu SE, Rocher V, Kyriakou G, Greenway GM. Removal of Pb2+ and Cd2+ from aqueous solution using chars from pyrolysis and microwave-assisted hydrothermal

carbonization of Prosopis africana shell. Journal of Industrial and Engineering Chemistry [Internet]. 2014;20(5):3467–73. Available from: http://www.sciencedirect.com/science/article/pii/S1226086X13006680

39.   Cruz Olivares J, Barrera Diaz CE. Proceso dinámico para la biosorción de Pb (II) de soluciones acuosas utilizando una columna empacada con cáscara de pimienta(Pimenta dioica L. Merrill). 2013;

40.   Harinath Y, Reddy DHK, Sharma LS, Seshaiah K. Development of hyperbranched polymer encapsulated magnetic adsorbent (Fe3O4@SiO2–NH2-PAA) and its application for decontamination of heavy metal ions. J Environ Chem Eng [Internet]. 2017;5(5):4994–5001. Available from: http://www.sciencedirect.com/science/article/pii/S2213343717304694

41.   Lee SY, Choi HJ. Persimmon leaf bio-waste for adsorptive removal of heavy metals from aqueous solution. J Environ Manage [Internet]. 2018;209:382–92. Available from: http://www.sciencedirect.com/science/article/pii/S0301479717312689

42.   Liu J, Hu C, Huang Q. Adsorption of Cu2+, Pb2+, and Cd2+ onto oiltea shell from water. Bioresour Technol [Internet]. 2018; Available from: http://www.sciencedirect.com/science/article/pii/S0960852418312938