







The elimination of lead(II) ions in a solution by bio-adsorption: Kinetics, equilibrium, and thermodynamics

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Abstract: In the present study, the removal capacity of Pb(II) ions was investigated using the biomass of dried cattle manure in an aqueous solution. The biomaterials were characterized using Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) techniques. The results reveal that the adsorption mechanism may be associated with the interaction between Pb(II) ions and functional groups through aggregation, coordination, ion exchange, microprecipitation, oxidation, and hydrophobicity. The bio-adsorption of the metal was analysed in discontinuous tests; the effect of temperature, pH, agitation, and adsorbent dose was evaluated. The maximum adsorption capacity was determined at pH 7.5, 18°C and 200 rpm. The bio-adsorption of Pb(II) was best fitted to the pseudo-second order model. The experimental data of the isotherm were adjusted to the models of Langmuir, Freundlich and Dubinin–Radushkevich; while Langmuir’s model related better to the experimental data forming a single layer at saturation. The rate of adsorption was rapid, reaching equilibrium after 25 min and removal of 96.8%. Thermodynamic parameters determined that the process was viable, spontaneous, and exothermic. The present study contributes mainly to demonstrating that a biomaterial prepared from bovine manure is a promising adsorbent for heavy metals such as Pb(II). It also reduces the environmental impact of this waste through the generation of greenhouse gases in countries that maintain intensive livestock. Another important aspect is the reduction of the micro- and macronutrients accumulation in soil and contamination of surface waters and aquifers by runoff and seepage during rainy periods.

Keywords: bio-adsorption, cattle manure, heavy metals, isotherm of Langmuir, thermodynamic parameters

INTRODUCTION

Contamination of water resources by heavy metals has become a global issue because of its effects on environmental health due to high toxicity [CHEN *et al.* 2020a; TEJADA-TOVAR *et al.* 2020b; VILLABONA-ORTÍZ *et al.* 2020]. Industries, such as metallurgy, mining, electroplating, textiles, and others, are responsible for effluents loaded with heavy metals and dyes, thus contaminating water and soil [KUMAR *et al.* 2020b]. Lead (Pb) is the most toxic, non-degradable, and bio-accumulative element, after arsenic (As). It comprises 0.002% of the earth’s crust, and it can be found in the

environment in its organic and inorganic forms [LEVIN *et al.* 2019]. Inorganic Pb is found in paints, exhaust gases produced by cars, electronics recycling areas, batteries, and canning industries (food leachate) [KUMAR *et al.* 2020a; ZULFIQAR *et al.* 2019]. Water and air are a key means of Pb transport into the food chain [ASSI *et al.* 2016].

Conventional technologies have been used to remove Pb ions from water: oxidation-reduction, electrochemical precipitation, adsorption, membrane separation, and ion exchange [JOSHI *et al.* 2019; SONI *et al.* 2020; ZHANG *et al.* 2020c]. All these procedures have some disadvantages, such as the high cost of

installation, prolonged period of operation, incomplete removal, and generation of large quantities of toxic sludge disposal of which is difficult [BASU *et al.* 2017b]. The Pb content in human blood has adverse effects, such as decreased cognitive abilities, postnatal development, delayed puberty, hearing competence, changes in the nervous system, kidneys, fertility, it prevents fetus development, and it is highly carcinogenic [ZAJAC *et al.* 2020]. The Environmental Protection Agency (EPA) and the World Health Organization (WHO) have established that the maximum concentration of lead in drinking water is $0.01 \text{ mg}\cdot\text{dm}^{-3}$ [ASSI *et al.* 2016].

In this context, the removal of Pb is necessary and urgent to improve water quality, protect public health, and meet the six goals of sustainable development of the United Nations for 2030 [LÁZARO-TORRES *et al.* 2020]. These constraints drew the attention of the scientific community to the development of sustainable techniques [KUMAR *et al.* 2020b]. Bio-adsorption is a branch of biotechnology, based on the use of live or dry biomass, with a sustainable development approach, to remove pollutants from water, through physical and chemical interactions [MAKSOUH *et al.* 2020]. The use of lignocellulosic biomaterials is advantageous over traditional adsorbents due to their components such as cellulose, hemicellulose, lignin and their polar functional groups such as alcohols, ketones, carboxylic groups, phenolics, and esters [SINGH *et al.* 2019].

Thus, different biomasses have been used for the disposal of Pb(II) ions, including agricultural residues and animal waste: rice husks and wood chips [CHEN *et al.* 2020b], *Spiraea blumei*, peanut shell and leaves of *Metasequoia glyptostroboides* [BOEYKENS *et al.* 2019], cow manure [ZHANG *et al.* 2020b], sawdust of *Triticum aestivum*, *Brassica napus*, *Picea glauca* and manure [KWAK *et al.* 2019], and farmyard manure [ZHI-LIANG *et al.* 2019a]. Cattle manure is used as an adsorbent because of its low cost and high availability [KWAK *et al.* 2019]. In a similar vein, the process uses adsorbents containing digested matter from sugar beet and milk products [ZHANG *et al.* 2020b].

On the other hand, the constant population growth has increased the world consumption of beef and veal; it is expected that by 2028, the demand for meat will increase by about 6 and 17% in developed and developing countries, respectively. In conjunction with this phenomenon, the generation of cattle manure will intensify, and its inadequate management could lead to serious environmental problems [OECD/FAO 2016]. Bovine manure is a by-product of the livestock industry, poor disposal of which has a negative impact on the environment, such as greenhouse gases, excess nutrients (nitrogen and phosphorus), antibiotics, pathogenic microorganisms, and endocrine inhibitors pesticides, herbicides, hormones, and phytoestrogens. This waste promotes the contamination of surface and underground water bodies by a direct effect of runoff, infiltration, leaching, and percolation, and indirectly by runoff [PINOS-RODRÍGUEZ *et al.* 2012]. Moreover, regulations for treating animal excreta that impact bodies of water, soil, and atmosphere in countries like the USA are strict and gears toward close monitoring. At the same time, in countries with intensive livestock farming, such as Chile, Argentina, Peru, Colombia, and Mexico, regulations on the management of animal excreta are scarce and confusing since only certain norms are specified on discharges of pollutants to water, downplaying the importance of emissions to air and soil,

and there are no clear restrictions on the management of manure in livestock operations [GARFI *et al.* 2016].

The bovine manure has been used in composting, co-composting, methane production, and the recovery of nitrogen production of biofuels (biogas, bioethanol, hydrogen) production of methane, alcohols, adsorbents, among other products of added value [AWASTHI *et al.* 2019]. In this sense, the present research was developed to determine isotherms, kinetics, and thermodynamic in the bio-adsorption of Pb(II) ions from a synthetic solution. The novelty of this work consists of studying new residues and characterising them as bio-adsorbent. These residues are easily available in large quantities for the removal of Pb(II) ions from liquid effluents and to extend their use.

MATERIALS AND METHODS

MATERIALS AND REAGENTS

Analytical grade lead nitrate ($\text{Pb}(\text{NO}_3)_2$) was used to prepare the synthetic solution. Sodium hydroxide (NaOH) and 99.0% LOBA-Chemie analytical grade nitric acid (HNO_3) were used to adjust the pH.

METHODS

Preparation and characterisation of biomass

Cattle manure (CM) was collected from the province of Concepción – Junín, Peru. It was dried at 60°C for 72 h, ground, and sieved using a 1 mm sieve, and it was stored in an airtight container until its use. The SEM-EDS analysis was also performed for the surface morphological characterisation of the biomass, using a Scanning Electron Microscope with 10 and 20 μm magnifications.

Adsorption tests

2^k factorial experimental model was established with the following factors and their respective levels of variation: pH (2, 4 and 7.5), temperature (291, 303, and 333 K), agitation speed (150 and 200 rpm), and a cattle manure dose (0.1, 0.15, 0.2 and 0.25 g); all experiments were conducted in triplicate according to a procedure described by ZHANG *et al.* [2020b].

Pb(II) adsorption tests were performed in batches. The residual Pb(II) concentration was determined by atomic absorption using an Atomic Absorption Spectrophotometer at 270 nm; the removal efficiency and removal capacity were calculated by Equations (1) and (2).

$$E = \frac{C_i - C_f}{C_i} 100 \quad (1)$$

$$q_e = \frac{(C_i - C_f)V}{m} \quad (2)$$

where: E = removal efficiency (%), C_i = initial concentration ($\text{mg}\cdot\text{dm}^{-3}$), C_f = final concentration ($\text{mg}\cdot\text{dm}^{-3}$), V = volume of the solution (dm^3), m = mass of the adsorbent (g), q_e = amount of adsorbate trapped in the adsorbent ($\text{mg}\cdot\text{g}^{-1}$).

The statistical analysis was evaluated with MINITAB 19, a statistical software, while choosing the following independent

variables: pH, temperature, and agitation, and dependent ones: removal capacity (% removal), and with the determining of the significant effects through the unidirectional ANOVA (analysis of variance) with a P -value < 0.05 . The analysis of variance (ANOVA) allowed to identify the most significant variable.

Bio-adsorption kinetics

The kinetic study allows to examine the evolution of the solute-adsorbent system as a function of time [AI *et al.* 2018; TEJADA-TOVAR *et al.* 2020b]. For this purpose, 0.9 g of the adsorbent was placed in contact with 300 cm³ of Pb(II) solution, at 200 rpm of agitation under the best conditions of pH and temperature determined experimentally; aliquots were taken every certain time interval (5, 10, 14, 18, 25, 35, 50, 80, 100, 120, 150 and 200 min). The remaining Pb(II) concentration in the solution was determined by atomic absorption at 217 nm. The fit of data obtained to the kinetic models is described in Table 1.

Adsorption isotherms

Adsorption isotherms are mathematical models that explain and determine how Pb(II) ions interact on the surface of the adsorbent [VELOSO *et al.* 2019]. For this purpose, the adsorbent was put into contact with 50 cm³ of solution at different concentrations (10, 20, 50, 100 and 200 mg·dm⁻³), at 200 rpm for 35 min, under the best conditions of pH, temperature and adsorbent dose obtained in the study. Experimental isotherm data were adjusted to the models of Langmuir, Freundlich, and Dubinin–Radushkevich, shown in Table 2.

Thermodynamic study

Thermodynamic parameters were determined to understand the principles of adsorption energy by the adsorbent: Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), indicators of the viability and spontaneity of the process [WEI *et al.* 2019]. These were calculated through the van't Hoff and Gibbs free energy equations described in Table 3.

Table 1. Kinetic adsorption models

Model	Equation	Parameter
Pseudo-first order	$q_t = q_e (1 - e^{-k_1 t})$	q_e = adsorption capacity at equilibrium (mg·g ⁻¹)
		q_t = adsorption capacity at time t (mg·g ⁻¹)
		k_1 = Lagergren's constant (min ⁻¹)
Pseudo-second order	$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$	k_2 = pseudo-second order constant (g ⁻¹ ·min ⁻¹)
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	α = adsorption rate (mg·g ⁻¹ ·min ⁻¹)
		β = Elovich constant related to the extent of surface coverage and activation energy in chemisorption (g·mg ⁻¹)
Intraparticle diffusion	$q_t = k_3^{1/2} t$	q_t = quantity of metal adsorbed per mass unit of adsorbent in a time t t = time (min) k_3 = intra particular diffusion constant (mg·(g·min) ⁻¹)

Source: VILLABONA-ORTIZ *et al.* [2020], modified.

Table 2. Adsorption isotherm models

Model	Equation	Parameter
Langmuir	$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{b q_{\max} C_e}$	q_{\max} = maximum amount of Pb(II) retained in the adsorbent (mg·g ⁻¹) b = Langmuir constant related to the affinity of the adsorbent for the contaminant C_e = concentration of adsorbate in the equilibrium
Freundlich	$\log q = \frac{1}{n} \log C_e + \log k_F$	n = adsorption intensity of the adsorbent according to its heterogeneity k_F = Freundlich's constant, related to the adsorption capacity of the adsorbent (mg·g ⁻¹ ·(dm ³ ·mg ⁻¹) ^{1/n})
Dubinin–Radushkevich	$q_t = q_{D-R} e^{-k_{D-R} \varepsilon^2}$ $\varepsilon = RT \cdot \ln \left(1 + \frac{1}{C_e} \right)$ $E = \frac{1}{\sqrt{2} K_{D-R}}$	ε^2 = the potential of Polanyi K_{D-R} = Dubinin–Radushkevich's constant related to adsorption energy (mol ² ·kJ ⁻²) E = the average adsorption energy per molecule of adsorbate required to transfer one mole of the ion from solution to the surface of the adsorbent (kJ·mol ⁻¹) R = gas constant (8.31 J·(mol·K) ⁻¹) T = absolute temperature

Source: WEI *et al.* [2019], modified.

Table 3. Equations of thermodynamic adsorption parameters

Model	Equation	Parameter
Van't Hoff	$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$	$\ln K$ = on the abscissa axis
		T = temperature (K) on the ordinate axis
		$\Delta H/R$ = the slope of the line $\Delta S/R$ = intercept with the ordered
Gibbs free energy	$\Delta G^\circ = \Delta H^\circ - T\Delta S$	ΔH° = increase of enthalpy
		ΔS° = increased entropy

Source: HUANG *et al.* [2020], modified.

RESULTS AND DISCUSSION

SCANNING ELECTRON MICROSCOPY

SEM analysis is an effective high-precision augmentation technology used to obtain information about the structural and morphological properties of biological materials [SARABANDI *et al.* 2020]. Figure 1a shows a porous and irregular surface of the bio-adsorbent before the Pb(II) bio-adsorption process. It has different and heterogeneous morphological structures: mixed fibre fragments, blocks with clefts, tiny embedded filaments all distributed at random, overlapping figures of the hexagonal units, considered as responsible for bio-adsorption [SARABANDI, JAFARI 2020]. These

irregular geometric features are due to the presence of polysaccharides that maintain the stability of the biological compounds which are decisive in adsorption, as reported by SARABANDI and JAFARI [2020]. The fibrous surface with heterogeneous and non-uniform structures leads to a higher adsorption capacity [SHIRANI *et al.* 2018]. According to XU *et al.* [2017], the presence of agglutination of the biomaterial was due to an incomplete digestion of lignocellulose as cows are herbivorous animals.

The SEM external surface micrographs for the adsorbent after bio-adsorption are shown in Figure 1b. The characteristics of surface and interstitial adsorption have been observed showing a structural alteration of the adsorbent by the interaction between the Pb(II) ions and the functional groups through physicochemical

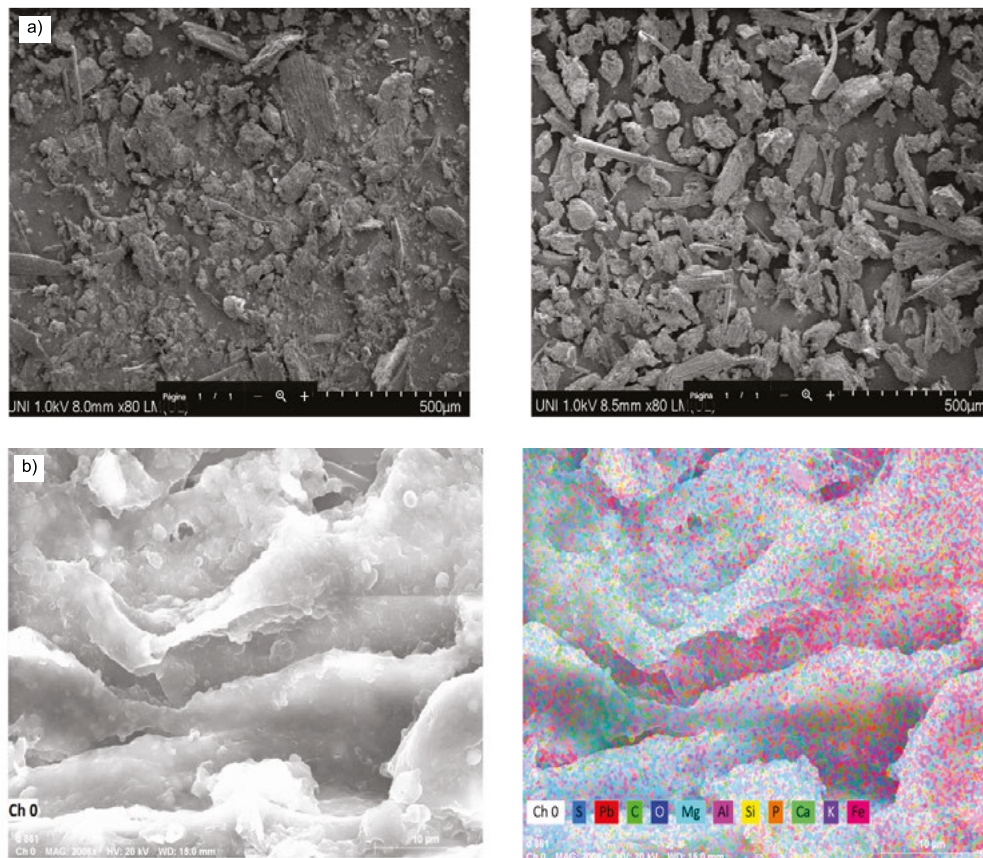


Fig. 1. Micrographs of Scanning Electron Microscopy: a) before adsorption at 500 μm , b) after adsorption at 20 μm ; source: own study

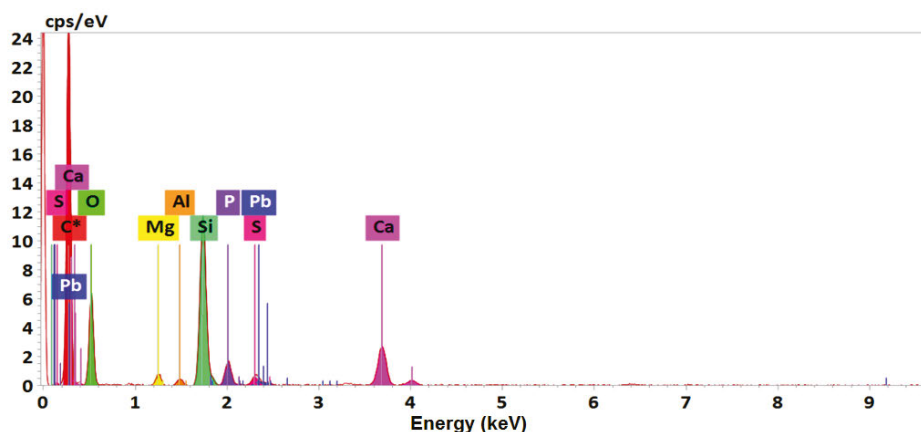


Fig. 2. Energy-dispersive X-ray spectroscopy spectrum of the adsorbent after Pb(II) removal; source: own study

mechanisms, such as aggregation, coordination, ion exchange, microprecipitation, oxidation and hydrophobicity [MUNOZ *et al.* 2017; XU *et al.* 2017]. Moreover, the coating of the contact area with lead ions is evident in the softening and filling of the surface irregularities of the bio-adsorbent material [BASU *et al.* 2017b]. Figure 2 shows results of the Energy-dispersive X-ray spectroscopy analysis of the adsorbent after bio-adsorption. It has been determined that carbon and oxygen are the elements with the highest presence in the structure of the biomaterial with 63.43% w/w and 35.78% w/w respectively; this is because they are the main components of cellulose, hemicellulose, lignin, and pectin [TEJADA-TOVAR *et al.* 2019]. The presence of these component values makes the biological material a highly specific adsorbent [ZHANG *et al.* 2020b]. Similar results have been reported that the high carbon content of the adsorbents provides an ideal porous structure for the adsorption of heavy metals [MANIRETHAN *et al.* 2019].

In a similar vein, traces of chemical elements, such as Al (0.41%), Mg (1.75%) and S (0.40%) were identified; the presence of these metallic elements is beneficial for the elimination of heavy metals, since ion exchange with their oxides would occur, a mechanism that would control the adsorption [MANIRETHAN *et al.* 2019]. In this regard, PARK *et al.* [2019] mention that the concentration of K, Ca, Mg, and Na present in the activated carbons directly influence the heavy metal adsorption kinetics. These results are similar to the Pb(II) adsorption study with activated carbon [ZHANG *et al.* 2020c]. The alteration of the adsorbent surface after the process is predominant due to physical mechanisms, such as the formation of micro-complexes and micro-precipitation of Pb(II) [TEJADA-TOVAR *et al.* 2020b].

IMPACT OF pH

pH is an important factor in adsorption and is a driver of efficiency in the removal of metal ions [IBISI, ASOLUKA 2018]. The concentration of H^+ directly influences the bio-adsorption of heavy metals on biological materials (competing with metal ions) [KUMAR *et al.* 2020b]. In this sense, Figure 3 shows that pH levels significantly influenced the removal of ions under the study.

At pH 2 and 4 there was a similar performance of 49.36% and 55.29%, respectively, while at pH 7.5 it was much higher. This phenomenon is attributed to the ionisation of H^+ , the surface charge of the adsorbent, and speciation [PARK *et al.* 2019]. At pH 7.5, the concentration of H^+ is relatively lower. It facilitates the

deprotonation of the adsorbent surface, and as a consequence, the bio-adsorption capacity is higher [TEJADA-TOVAR *et al.* 2020b]. Therefore, these unprotonated functional groups, which serve as binding sites, become easily accessible to the metal ions. This causes better sorption at high pH, since low-solubility hydroxides, such as $Pb(OH)_2$, are formed. Thus, favouring the formation of complexes and micro-precipitates is shown in Figure 1b [BASU *et al.* 2017b]. Based on the results obtained from the experiments for the adsorbent dose evaluation, the kinetic and equilibrium studies were carried out with an adsorbent dose of $3 \text{ g}\cdot\text{dm}^{-3}$.

EFFECT OF THE ADSORBENT DOSE

The ideal dosage of adsorbent is important for the efficacy of the adsorbent throughout the adsorption process [ZHANG *et al.* 2020c], as well as the availability of active adsorption sites in which to trap metal ions [GAO *et al.* 2020]. In this sense, the effect of cattle manure doses (0.1, 0.15, 0.2 and 0.25 g) on the removal of Pb(II) from the aqueous solution was evaluated at pH 7.5, 200 rpm, temperature 18°C , at $30 \text{ mg}\cdot\text{dm}^{-3}$ of Pb(II) for 35 min. The results are shown in Figure 4. When the dose increases from 0.1 to 0.25 g, the adsorption capacity of Pb(II) decreases from 13.256 to $5.919 \text{ mg}\cdot\text{g}^{-1}$, which could be due to the low availability of Pb(II) ions to fill the active sites of the bio-adsorbent [TEJADA-TOVAR *et al.* 2020b]. The above is due to the heterogeneity of cow manure, due to the structural heterogeneity reflected in Figure 1a, and due to the presence of the hydroxyl, carbonyl, amine, and unsaturated hydrocarbon groups [CHEN *et al.* 2020a].

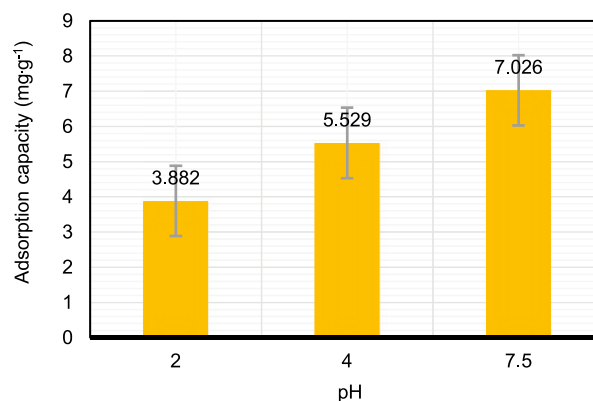


Fig. 3. Impact of pH in relation to Pb(II) ion removal; source: own study

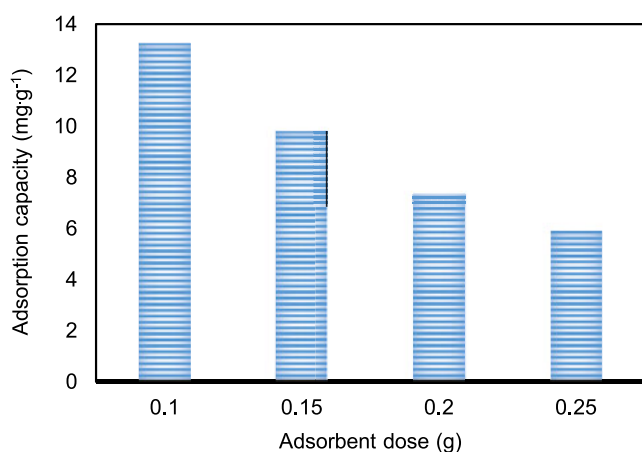


Fig. 4. Adsorbent dose effect in relation to the removal of Pb(II) ions; source: own study

The analysis of variance (Tab. 4) allowed to identify the most significant variable, determining mathematically that the effect of pH (positive slope) was crucial and essential in the process of removing the Pb(II) ions. Therefore, the H⁺ concentration is an important parameter in the adsorption of heavy metals on the adsorbent material, because H⁺ competes with metal ions [GAO *et al.* 2020; HUANG *et al.* 2019].

Likewise, variables with lesser incidence like temperature (negative slope), pH-temperature, agitation (positive slope), and temperature-agitation, all with has a *p*-value of 0.00. The information was processed through the response optimiser analysis to interpret and identify the ANOVA results (Tab. 4). The pH (7.5), temperature (18°C) and stirring speed (200 rpm) there was a higher removal of Pb(II) ions, as represented in the Pareto and response optimiser diagrams (Fig. 5).

The initial pH is a conditioning parameter of the surface charge of the adsorbent, the degree of ionisation, and the speciation of solutes [ZHANG *et al.* 2020a]. Temperature shows system energy information which shows its endothermic or exothermic character [MOGHIMI *et al.* 2020]. Additionally, the agitation speed was evaluated to reduce the thickness of the film [ADENIYI, IGHALO 2019; TAKDASTAN *et al.* 2019]. Criteria evaluated to facilitate the effect of mass transfer and determine the prudent time of the process, as shown in Figure 6.

Table 4. Analysis of variance ANOVA

Source	Sum of squares	Gf	Mean square	F-ratio	P-value
A: pH	63.1639	1	63.1639	202.79	0.0000
B: stirring rate	7.20839	1	7.20839	23.14	0.0002
C: temperature	22.3398	1	22.3398	71.72	0.0000
AB	0.00759704	1	0.00759704	0.02	0.8780
AC	12.2023	1	12.2023	39.18	0.0000
BC	6.12363	1	6.12363	19.66	0.0005
Blocks	0.641269	2	0.320635	1.03	0.3811
Total error	4.67208	15	0.311472	-	-
Total (corrected)	116.359	23	-	-	-

Explanations: Gf = degrees of freedom.

Source: own study.

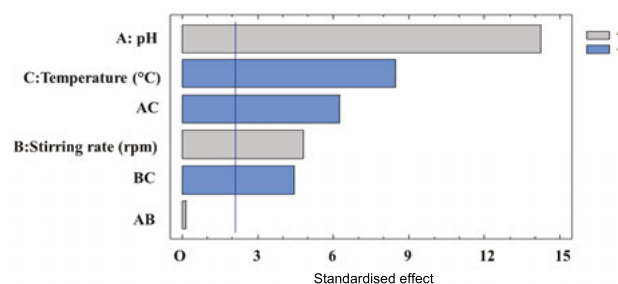


Fig. 5. Standardised effect Pareto diagram; source: own study

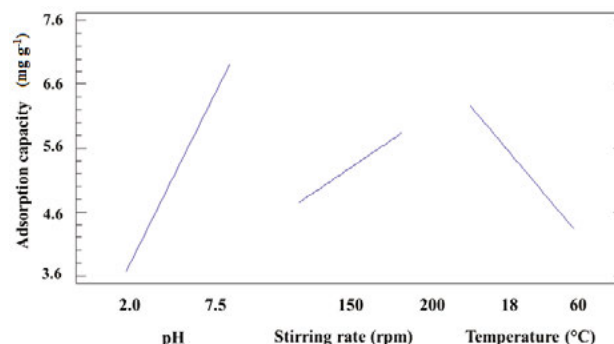


Fig. 6. pH, stirring rate and temperature effect on the removal capacity of Pb(II) ions; source: own study

ADSORPTION ISOTHERM

Adsorption isotherms represent pollutant-adsorbent interactions in aqueous media at defined pH and temperature. They are important for defining surface capacities, evaluating the effect of the initial concentration on the adsorption capacity of the metal, and designing effective adsorption systems [ZHENG *et al.* 2020]. The non-linear fit of the experimental data to the Langmuir, Freundlich, and Dubinin–Radushkevich models is shown in Figure 7; the fit parameters are summarised in Table 5.

The results reveal that Langmuir's model best describes the adsorption equilibrium of Pb(II) on cattle manure; however, Freundlich's model also performs well in fitting the data. Therefore, it can be said that the initial stages of the process

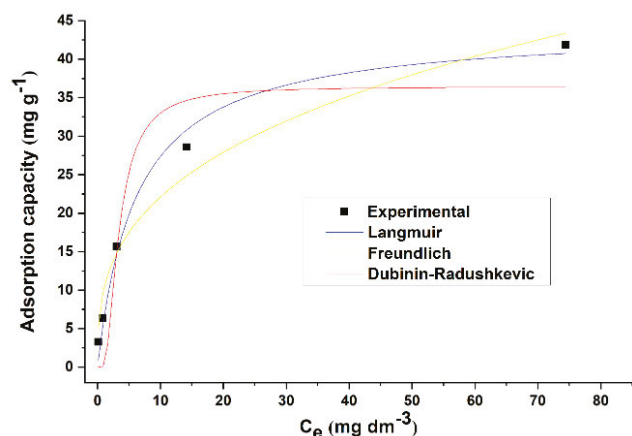


Fig. 7. Adjustment of Pb(II) equilibrium adsorption on cow manure; C_e = concentration of adsorbate in the equilibrium; source: own study

Table 5. Adjustment parameters of the Pb(II) adsorption isotherm

Model	Parameter	Value
Langmuir	q_{\max}	44.0837
	b	0.1639
	R^2	0.9816
Freundlich	k_F	10.1943
	n	2.9756
	R^2	0.9606
Dubinin-Radushkevich	q_{D-R}	36.4482
	k_{D-R}	1.4685E-6
	E	825.2072
	R^2	0.8472

Explanations: q_{\max} = maximum adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), b = Langmuir constant related to the adsorption heat ($\text{dm}^3\cdot\text{mg}^{-1}$), k_F = Freundlich's constant, related to the adsorption capacity of the adsorbent ($\text{mg}\cdot\text{g}^{-1}\cdot(\text{dm}^3\cdot\text{mg}^{-1})^{1/n}$), n = Freundlich's rate constants referred to the adsorption capacity and intensity, respectively; q_{D-R} = Dubinin-Radushkevich's adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), k_{D-R} = Dubinin-Radushkevich's rate constant ($\text{mol}^2\cdot\text{kJ}^{-2}$), E = average adsorption energy per molecule of adsorbate required to transfer one mole of the ion from the solution to the surface of the adsorbent ($\text{kJ}\cdot\text{mol}^{-1}$).

Source: own study.

occur initially through the formation of a monolayer with active sites and homogeneous adsorption energy, without any interaction between adsorbed molecules [AL-GHOUTI, DA'ANA 2020; JAMSHIDI, SHEMIRANI 2019]. At the same time, diffusion into the porous structure of the adsorbent occurs at the active adsorption sites, through the formation of multilayers.

The q_{\max} value of Langmuir's model and the n value of Freundlich's model indicate that the adsorbent has an affinity with Pb(II) ions and that the adsorption is favourable [NÚÑEZ-ZARUR *et al.* 2018]. From the value of parameter b ($\text{dm}^3\cdot\text{mg}^{-1}$), which is close to 1, it can be inferred that active adsorption centres in biomass are selective and that the ability of metals to bind to the surface depends on whether or not nearby positions are occupied [OBIKE *et al.* 2018]. A q_{\max} of Pb(II) adsorption with activated carbon from cattle manure of $49.0 \text{ mg}\cdot\text{g}^{-1}$ has been reported [KWAK

et al. 2019] and $50.41 \text{ mg}\cdot\text{g}^{-1}$ with activated carbon from stable manure [ZHI-LIANG *et al.* 2019a]. The adsorption intensity (R_L) is characterised as favourable, with a value of 0.137 [SINGH *et al.* 2019]. Dubinin-Radushkevich's model shows mean free energy of ions adsorption per sorbate (E) of $825.2072 \text{ kJ}\cdot\text{mol}^{-1}$, which is much higher than $8 \text{ kJ}\cdot\text{mol}^{-1}$. This indicates that the process is mostly controlled by chemical adsorption with strong interactions between the active sites and the Pb(II) [AJMANI *et al.* 2019].

ADSORPTION KINETICS

Adsorption kinetics studies the reaction mechanism and the extent to which the adsorbent is involved [CHEN *et al.* 2020a]. The adsorption kinetics and the fit to the pseudo-first order and pseudo-second order, Elovich, and intraparticle diffusion models are shown in Figure 8. Rapid adsorption can be observed in the initial stages, reaching in the first 5 min an adsorption capacity of $9.74 \text{ mg}\cdot\text{g}^{-1}$, and then stabilising after 25–30 min.

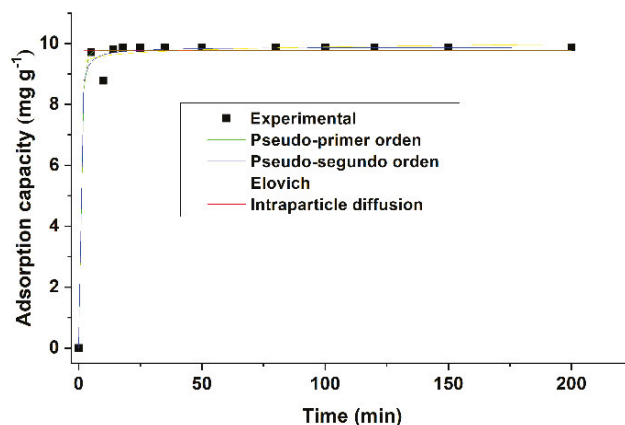


Fig. 8. Adjustment of Pb(II) ions adsorption kinetics on cow manure; source: own study

The fit of experimental data on Pb(II) ion bio-adsorption kinetics was studied, which was represented by the pseudo-first order, pseudo-second order, and Elovich models. Figure 8 and the parameters summarised in Table 6 show that the models evaluated consistently describe the experimental adsorption data; this indicates that the limiting step of the process is the chemical reaction between the ion and bio-adsorbent active centres [AMRO *et al.* 2019]. The high value of α in Elovich's model indicates the rapid removal process of Pb(II) ions, added to them the high content of carbon, oxygen, and the porous and heterogeneous structure (SEM). This could be possible because the adsorbent retains Pb(II) ions by electrostatic attraction forming complexes with the carboxyl and hydroxyl groups [BASU *et al.* 2017a]. From the adjustment to the intraparticle diffusion model, it can be said that the adsorption was carried out mainly on the external surfaces of the adsorbent in the first stage. It was due to the predominance of the diffusive phenomena from the core of the solution to the exposed surface area of the manure [MOROSANU *et al.* 2017]. Thus, the process would favour the formation of complexes in the structure of the material as shown in Figure 1b. Subsequently, over time, the active sites were occupied by Pb(II) ions diffusing into the hexagonal pores (interstitial adsorption) and reacting with the internal active sites to reach equilibrium [ZHI-LIANG *et al.* 2019b].

Table 6. Model fit parameters of Pb(II) ions bio-adsorption-kinetics

Model	Parameter	Value
Pseudo-first order	q_1	9.76
	k_1	0.996
	R^2	0.9868
Pseudo-second order	q_2	9.8792
	k_2	0.3860
	R^2	0.9893
Elovich	β	7.8392
	α	5.5029E30
	R^2	0.9898
Intraparticle diffusion	k_3	9.7622
	R^2	0.9879

Explanations: q_e = adsorption capacity at equilibrium time ($\text{mg}\cdot\text{g}^{-1}$), k_1 = pseudo-first-order kinetic rate constant (min^{-1}), k_2 = pseudo-second-order kinetic rate constant ($\text{g}^{-1}\cdot\text{min}^{-1}$), α = Elovich constant ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$), β = exponent in Elovich's equation ($\text{g}\cdot\text{mg}^{-1}$); k_3 = intraparticle diffusion rate constant, R^2 = coefficient of determination. Source: own study.

THERMODYNAMIC STUDY

The temperature in the Pb(II) removal process was examined at 18, 30, and 60°C. The equations, showed in Table 3 (Gibbs free energy), were applied to determine the thermodynamic parameters ΔG° ($\text{kJ}\cdot\text{mol}^{-1}$), ΔH° ($\text{kJ}\cdot\text{mol}^{-1}$), ΔS° ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). Results show the reliability and spontaneity of the process [GAO *et al.* 2020]. The estimated parameters are summarised in Table 7.

Table 7. Thermodynamic parameters of Pb(II) bio-adsorption

pH	Temperature (K)	ΔG°	ΔH°	ΔS°
7.5	291	-75.07	-75.07	-0.2233
	303	-84.06		
	333	-97.16		
2.0	291	-10.07	-10.07	-0.0336
	303	-17.06		
	333	-28.75		

Explanations: ΔG° = Gibbs free energy ($\text{kJ}\cdot\text{mol}^{-1}$), ΔH° = change of the enthalpy ($\text{kJ}\cdot\text{kg}^{-1}$), ΔS° = change of the entropy ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). Source: own study.

From the values of ΔG° it is established that the adsorption of Pb(II) is viable and spontaneous under the conditions evaluated. The negative value ΔH° showed that the process was exothermic by nature, qualifying it as chemical adsorption and reversible at pH 7.5 [ADENIYI, IGHALO 2019], while at pH 2.0 it was physisorption; this energy variation could justify the low adsorption capacity, due to the competition of the H^+ with the

functional groups of the adsorbent [KUMAR *et al.* 2020b]. Negative values of ΔS° identify the lowest randomness of the reaction at the solid-solution interface during the adsorption process. Therefore, these parameters define that the Pb(II) ion migrated from the liquid phase core to the surface of the material [ZHAO *et al.* 2020].

CONCLUSIONS

1. The kinetic study determined that the pseudo-second order model better correlated the experimental data.
2. Langmuir, Freundlich and Dubinin–Radushkevich models were used for the adsorption isotherms, and the Langmuir equation was better related to the experimental data at an equilibrium time of 25 min, pH 7.5, and stirring rate of 200 rpm.
3. The adsorption mechanism could be related to ion exchange and micro-precipitation, as observed in the SEM analysis, by the interaction between Pb(II) ions and functional groups through mechanisms such as aggregation, coordination, ion exchange, microprecipitation, oxidation, and hydrophobicity.
4. Thermodynamic parameters determined that the process was viable, spontaneous, and of exothermic nature.
5. The main contribution of the present work is the finding of an alternative for the recovery of cattle manure as an adsorbent based on the study results. This contributes to reducing the environmental impact of the waste on the generation of greenhouse gases in countries with intensive livestock farming. Besides, this alternative promotes reducing the accumulation of micro- and macronutrients in the soil and the contamination of surface waters and aquifers by runoff and seepage during rainy periods.

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