

Article

Removal of Zn(II) in Synthetic Wastewater Using Agricultural Wastes

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Received: 30 September 2020; Accepted: 28 October 2020; Published: 3 November 2020



Abstract: In the present investigation, results obtained from the process of the biosorption of Zn(II) in synthetic wastewaters are presented, using three agricultural wastes (coffee pulp, banana pseudo-stem, and corncob). Firstly, the percentage of lignin and cellulose for each material was determined. Then, using the free software XLSTAT, the waste with the highest removal for this metal was selected and, after this, the optimum pH, kinetics, adsorption isotherm, and point of zero charge (pH_{pzc}) were found. Finally, a comparison with other lignocellulosic materials derived from banana, corn, and coffee crops was carried out. According to the results obtained, coffee pulp was the material that showed a high removal compared to the other two (63.58%), for which the optimum pH was 5.0 units. The kinetic model, which was adjusted to the process of biosorption, was the pseudo second order of Ho and McKay, which in turn presented an isotherm of Langmuir's linearized model where the maximum adsorption capacity with that waste was $13.53 \text{ mg} \times \text{g}^{-1}$, obtained with a particle size of 180 μm , contact time of 90 min at 100 RPM, temperature of 25 °C, and pH_{pzc} 3.95 units. Lastly, the authors state that this type of agricultural waste can be used as a green technology in the treatment of wastewater, particularly in the removal of the aforementioned pollutant, in order to fulfill goals 3.9 and 6.9 of the Sustainable Development Goals of the 2030 Agenda; to the level of challenge of the research, the authors propose for the future to carry out the implementation of this type of waste, without chemical modification, in the treatment of wastewater for the removal of the mentioned pollutant in a pilot study with different wastewaters and industries.

Keywords: biosorption; banana pseudo-stem (BP); coffee pulp (CP); corncob (CC); zinc

1. Introduction

The World Health Organization (WHO) has cataloged thirteen heavy metals as toxic, among which is Zn [1]. This metal, of atomic number 30, with oxidation states -2 , 0 , $+1$, $+2$, and $+3$ [2,3], has multiple applications at the industrial and laboratory level, among which are car parts, electronic equipment, light machine tools, metal coating, glass manufacturing, matches, glues, paint manufacturing, varnishes, ceramics, medications, sunscreen, deodorants, electrodeposition, toys, and batteries [4,5]. When the concentrations of this element are high, it can generate health problems, entering through three exposure routes (inhalation, ingestion, and contact). The first is the most recurrent, which leads to generating the symptoms of metal smoke fever disease, among which are fever, stomach cramps, skin irritation, vomiting, nausea, anemia, ataxia, and convulsions [5–7]. According to the report by

Simon-Hettich et al. (2001, p.19) [6], for some workers in a galvanizing plant exposed to concentrations between 77 and 150 mg Zn $\times$ m⁻³ of this pollutant from 15 to 30 min, it resulted in some other symptoms than the aforementioned, in addition to dose-related inflammation, increasing polynuclear lymphocytes in the broncho alveolar lavage fluid, and a marked increase in cytokines. Therefore, in the wastewater discharge generated in industrial processes that incorporates said metal, its final disposal is carried out without a treatment process, which can affect surface water sources or supply areas for a certain population, as well as the ecosystem. In the case of Colombia, the regulations that apply to wastewater discharge correspond to Resolution 631 of 2015 of the Environment and Sustainable Development Ministry (ESDM), which establishes that the maximum permissible limit for Zn is 3 mg $\times$ L⁻¹ in articles 8, 10, 11, 12, and 13 [8]. Some Wastewater Treatment Systems (WWTS) for the removal of said contaminant have employed conventional technologies such as chemical precipitation, ion exchange, and activated carbon [9,10]; due to the fact that these methods generate a considerable amount of activated sludge, plant maintenance costs are high (in the case of chemical precipitation) and activated carbon is a sorbent material of high cost in comparison to the other techniques that have been investigated.

In this sense, currently clean technologies for the purification of said matrices have been proposed and investigated and involve the use of phytoremediation, bioremediation, hydrogels, biopolymers, fly ash, and biosorption with agricultural wastes. Among the advantages of this type of method are the low cost, being friendly to the environment, not generating sludge, and having a reuse cycle [11,12]. In this order of ideas, in this research we used three agricultural wastes: coffee pulp (CP), banana pseudo-stem (BP), and corncob (CC) from farms of Caldas (Colombia) as a sustainable alternative to the removal of Zn(II) in synthetic wastewater to accomplish the goals of SDG 3.9 (“by 2030, reduce significantly the number of deaths and illnesses caused by soil, water and air pollution”) [13] and 6.9 (“by 2030, improve water quality by reducing discharges and reduction in untreated water”) [14]. For this, there were two phases of the investigation: the quantification of lignin and cellulose and the elucidation of organic functional groups using infrared spectrophotometry for the three wastes. In the second phase, a statistical comparison was performed to determine the lignocellulosic material more efficiently, and then determine the optimal biosorption variables with the waste selected, corresponding to time contact (min), the optimum pH, the kinetics, the isotherms biosorption and the pHPzc. Finally, a comparison was made of the maximum adsorption capacity based on the removal of Zn(II) between wastes from crops of banana, coffee, and corn (modified and not chemically modified). In terms of the challenges of this type of research, in which it is proposed to use agro-industrial wastes as biosorbents of inorganic contaminants (such as heavy metals and particularly Zn(II)) in untreated water, this involves the implementation of a pilot study with industries that implement this type of technology to minimize the pollution load. Lastly, the novelty of this research is the use of agricultural waste (without chemical modifications), different from the current applications of this type of by-product (among which are animal feed, energy production, biofuels), in the treatment of untreated water that incorporates heavy metals [11]. As advantages of the research, it is established that the use of this type of waste will allow that they are not disposed of directly in the soils (due to the fact that, by anaerobic degradation of the microbial type, they could cause emissions of greenhouse gases and contamination in subway waters). Finally, in terms of the disadvantages, it is necessary to carry out the desorption of the Zn(II) with respect to the agricultural wastes, since, if this process is not carried out, the sorbent materials would be contaminated by this type of metal.

2. Materials and Methods

2.1. Collection Site and Physical Treatment of CP, BP, and CC

The selection of the fresh samples (CP, BP, and CC) was performed in a zigzag [15] and they were collected from various sites on coffee farms from the department of Caldas (Colombia). The lignocellulosic wastes of CP (Castillo variety) and BP (Dominico Harton variety) were obtained

from El Bosque farm (vereda Maracas, Quebrada Negra—municipal Neira) and the BP (Criollo variety) from the vereda Guacaica (municipal Neira).

The collected masses of CP and CC were 10.0 and 30.0 Kg for BP; for this last, transverse cuts were made to obtain a thickness of 3.0 cm. Subsequently, the CP and the BP were dried in a parabolic solar dryer for a period of 7 to 15 days, which was carried out directly on the corresponding farms. Regarding the CC, unlike the two mentioned residues, it was only obtained after the shelving process; once the samples were partially dehydrated with a mass of approximately 2.0 Kg, they were again dried at a temperature of 60 °C until a constant mass was obtained. Once the samples were dry, they were triturated to a particle size of 180 µm, given that the literature references sizes range from 75 to 251 µm [16].

2.2. Cellulose and Lignin Content in the Three Residues and Analysis IR

For the determination of the lignocellulosic content, the techniques ANSI (American National Standards Institute, Washington, DC, USA)/ASTM (American Society for Testing and Materials, West Conshohocken, Pennsylvania) were used. On the other hand, the Shimadzu-brand AFFINITY-1S IR spectrophotometer was used for the three residue spectrum analyses, before the Zn (II) removal process was conducted, using the Attenuated Total Reflection (ATR) technique.

2.3. Quantification of Zn(II)

For the determination of the concentration of Zn(II) in Synthetic Wastewater (SWW), the reference method 3111 B of standard methods was used (Atomic Absorption Spectrophotometry-AAS, direct method of air-acetylene flame) with a VARIAN AA 140 kit, for which ZnSO₄ (analytical reagent) was used to find the calibration curve.

2.4. Determination of the Optimum pH of Adsorption of Zn(II)

SWW of 25 mL of Zn(II) with an initial concentration of $100 \text{ mg} \times \text{L}^{-1}$ was prepared, to which was added 0.500 g of CP, BP, and CC [17–19], and it was adjusted to a pH between 1, 2, 3, 4, and 5 with HNO₃ 1M in triplicate for each pH. Higher pHs were not used, since, when alkalizing the Zn(II) dissolutions, it precipitates as Zn(OH)₂ according to Segovia et al., (2018) [5]. In turn, these dissolutions were stirred for 90 min at 100 RPM after they were filtered with filter paper to determine the final concentration.

2.5. Determination of the Adsorption Kinetics for Zn(II)

This determination was only performed with the most efficient biosorbent obtained from Section 2.4 when comparing each of the removal percentages at different pHs using the free software XLSTAT. SWW of 25 mL of Zn(II) was prepared in triplicate at a concentration of $100 \text{ mg} \times \text{L}^{-1}$. The dissolutions were adjusted to the optimum pH determined in Section 2.4 and a mass of 0.500 g of the most efficient biosorbent was added with an agitation of 100 RPM, then they were left for different contact times (5, 10, 15, 30, 45, 60, 75, 90, 105, and 120 min) and filtered on filter paper qualitatively to determine the final concentration.

2.6. Determination of the Adsorption Isotherm for Zn(II)

SWW of 25 mL Zn(II) was prepared in triplicate at different concentrations (20, 50, 100, 150, 250 and $500 \text{ mg} \times \text{L}^{-1}$), adjusted to the optimum pH determined in Section 2.4 with a mass of 0.500 g of the more efficient biosorbent, with an agitation of 100 RPM and the optimum time determined in Section 2.5 for this metal.

2.7. Determination of the Point of Zero Charge (pH_{pzc}) for the Efficient Biosorbent

For this case, the methodology described in Gomez et al. (2020) [12] was used for the determination of the pH_{pzc} for the efficient biosorbent chosen for the removal of Zn(II) in the SWW. From this, a possible explanation was given for the mechanism of adsorption that could occur in the biosorption process.

3. Results and Discussion

The results obtained for the three agricultural wastes by each procedure were performed in triplicate and are presented according to the methodology described in Sections 2.1–2.7.

3.1. Lignocelulosic Content for CP, BP, and CC and Elucidation of Organic Functional Groups by Infrared Spectrophotometry (IR)

Table 1 presents the obtained results for the content of cellulose and lignin in the coffee pulp (CP), banana pseudo-stem (BP), and corncob (CC), and their respective comparative literature:

Table 1. Lignin and cellulose content in CP, BP, and CC.

Agricultural Waste	Parameter	Value of This Study	Comparison Interval		Bibliographic Reference
			Years	Value	
CP	% Lignin	19.25 ± 0.16	2017–2020	12.20–36.89	[12,20]
	% Cellulose	29.93 ± 0.21		16.50–63.00	
BP	% Lignin	5.49 ± 0.25	2009–2014	5.00–37.30	[21]
	% Cellulose	49.24 ± 2.65		31.27–65.00	
CC	% Lignin	12.23 ± 0.11	2008–2018	7.39–15.80	[22]
	% Cellulose	47.50 ± 0.60		32.30–57.00	

%Lignin: ANSI/ASTM D1106-56 [23]; %Cellulose: ANSI/ASTM D1103-60 [24].

In Table 1, a comparison was made related to the percentage of lignin and cellulose present in each agricultural waste (CP, BP, and CC) with a theoretical interval, where this was obtained from publications of various authors, among which it was observed that the data obtained in the present investigation are included within them for each lignocelulosic material. On the other hand, it is important to clarify that, for a more rigorous comparative analysis of these wastes, it would be important for the authors in the articles to specify the variety used in the agricultural wastes.

In this sense, it was also deduced from Table 1 that the percentage of lignin was higher in the CP, followed by the CC and finally the BP; in relation to the percentage of cellulose, it was greater in the BP, followed by the CC and finally the CP. The aforementioned characterization was important, since these compounds are found on the external part of the cell wall of these materials [25] and have functional groups that are responsible for carrying out interactions with the contaminant for their respective removal under optimal adsorption conditions such as temperature, particle size, amount of biomass, pH, stirring time, initial concentration of the contaminant, and volume of wastewater [26].

On the other hand, the elucidation of the functional groups present for each agricultural waste (CP, BP, and CC) was carried out using IR spectrophotometry with the ATR technique of Total Attenuated Reflection, obtaining the spectra shown in Figures 1–3, respectively.

According to the spectra illustrated in Figures 1–3, it was observed that a band at 3320 to 3344 cm^{−1} appeared in the three agricultural wastes, indicating the presence of the OH group. Additionally, to confirm the presence of the alcohol, specifically the primary alcohol, a tension band C-O bonded to an aromatic ring around 1012 to 1050 cm^{−1} is evidenced in the three agricultural wastes; these bands could be attributed mainly to the presence of lignin, because in its composition it has aromatic rings. Additionally the spectra confirmed the presence of hydroxyl groups in the cellulose, since it has primary and secondary alcohols. Moreover, another band of interest is presented around 1725 cm^{−1},

which corresponds to the presence of the carbonyl group of the aldehyde and its confirmation band C-H around 2820 cm^{-1} , which confirmed the presence of this functional group in lignin. Finally, at around 1250 cm^{-1} was presented the presence of a band of an asymmetric stretch of aromatic ethers C-O-C present in the molecule of lignin [27].

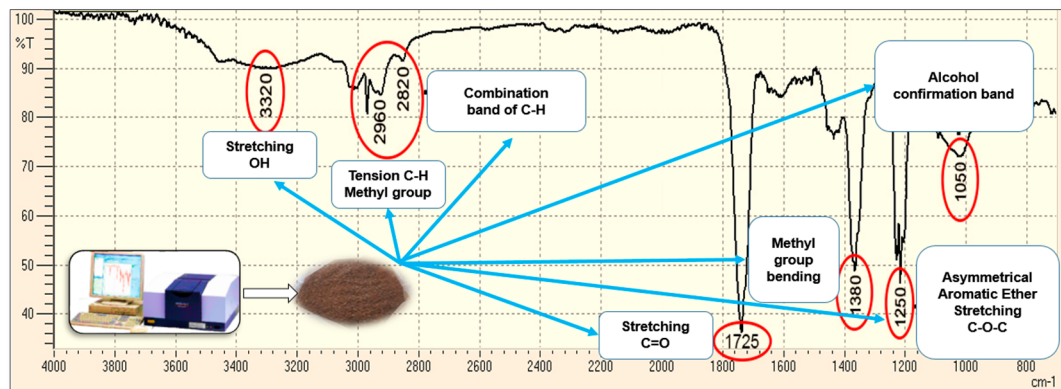


Figure 1. IR spectrum of the coffee pulp taken in a Shimadzu brand IR AFFINITY-1S equipment with the ATR technique of Total Attenuated Reflection.

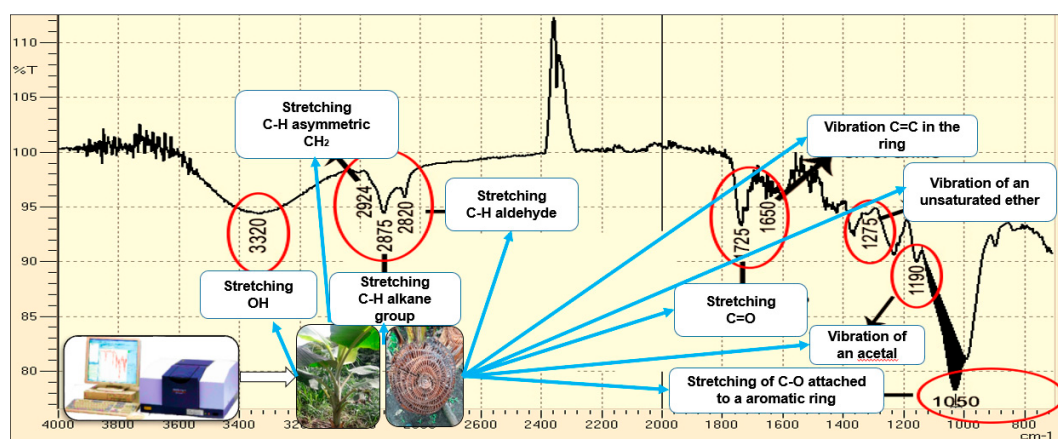


Figure 2. IR spectrum of the banana pseudo-stem taken on Shimadzu brand IR AFFINITY-1S equipment with the ATR technique of Total Attenuated Reflection.

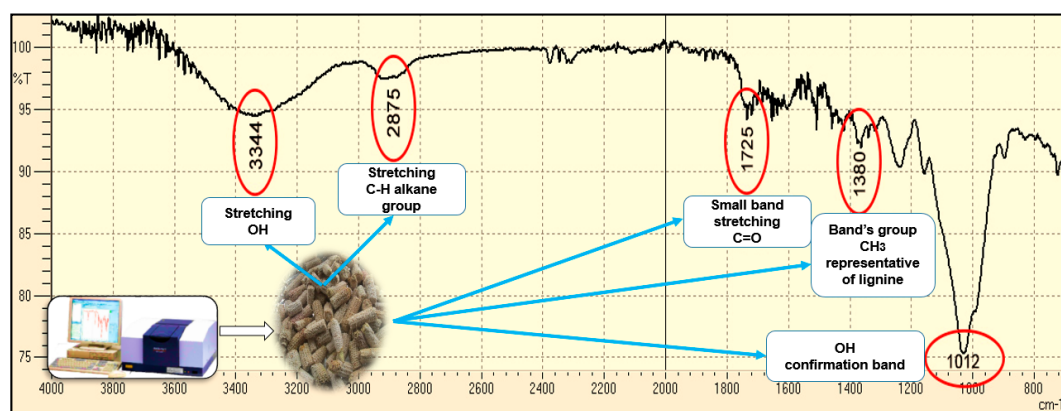


Figure 3. IR spectra of the corncob taken on an IR AFFINITY-1S equipment Shimadzu brand with the ATR technique of Total Attenuated Reflection.

In relation to these analyses, the presence of three functional groups present in the chemical structures of lignin and cellulose was concluded, such as the OH group, the carbonyl group, and the presence of an ether.

3.2. Determination of the Most Efficient Biosorbent for the Removal of Zn(II)

For the determination of the most efficient biosorbent for the removal of Zn(II), the free software XLSTAT was used, performing a boxplot and a scattergram (see Figures 4 and 5, respectively) for the three agricultural wastes (CP, BP, and CC). According to these, it was observed that, of the three wastes, the most efficient in the removal of Zn(II) in SWW corresponded to the CP.

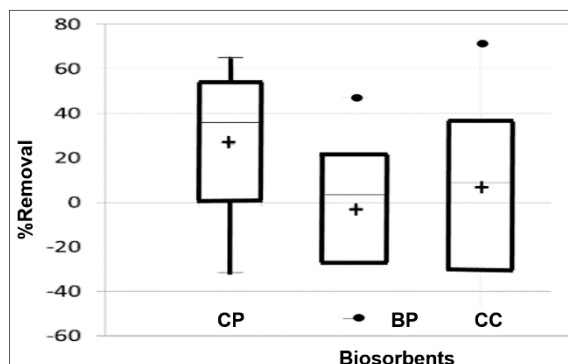


Figure 4. Box plot of the three agricultural wastes.

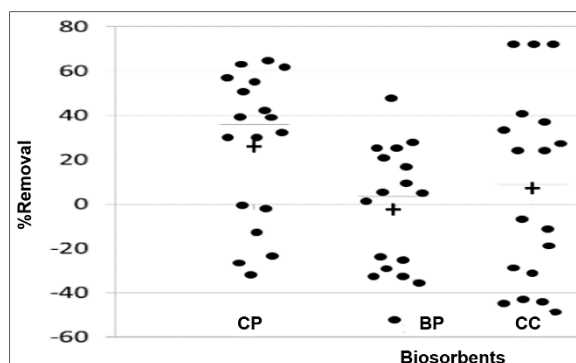


Figure 5. Scattergram of the three agricultural wastes.

3.3. Determination of Optimum pH of Zn(II) with CP

The removal percentages were obtained for the CP, as indicated in Section 3.2, at pH 1 (−27.25%), pH 2 (−1.39%), pH 3 (31.05%), pH 4 (40.06%), and pH 5 (63.56%). These results were plotted (see Figure 6) and it was observed that the optimum pH was 5.00 units, in terms of a size of a particle of 180 μm , 0.500 g of biomass, a temperature of 20 $^{\circ}\text{C}$, stirring for 60 min, and 100 RPM.

According to Segovia et al., (2018) [5], regarding the optimum pH exhibited it is clear that the chemical species of zinc in aqueous solution corresponds to Zn(II) at pHs above 7.0 unit; according to the Pourbaix diagram, the zinc precipitated as $\text{Zn}(\text{OH})_2$.

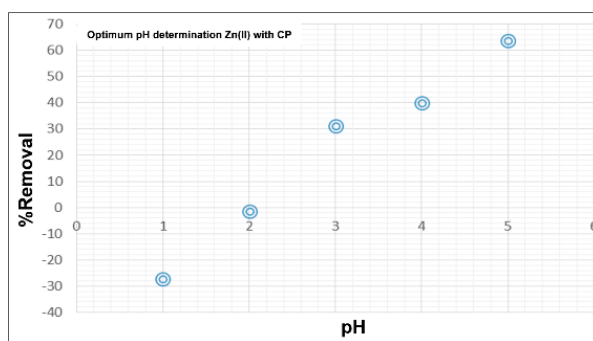


Figure 6. Determination of the optimum pH in the removal of Zn(II) with CP.

3.4. Kinetics and Adsorption Isotherm

According to the results of the Table 2, the kinetic model adjusted to the biosorption process of Zn(II) in the SWW was the pseudo second order of Ho and McKay with an equilibrium time of 90 min and removal percentage of 63.78%, under the optimal conditions set forth in Section 3.3 (see Figure 7). Similarly, the isotherm model that best fit the behavior of the data corresponded to Langmuir's linearized model (it was obtained by applying $\frac{dq}{dt} = K (qe - qt)^2$), with respect to the other two models applied (see Table 3), allowing us to establish three assumptions for the adsorption phenomenon. The first indicates that the adsorption of the Zn(II) pollutant occurs only in specific active sites (functional groups exposed in Section 3.1) located on the surface of the CP, the second establishes that each metal is adsorbed only on each active site, and the third assumption suggests that there is no interaction between the adsorbed metal adjacent on the CP surface [28].

Table 2. Kinetic orders applied to the biosorption process, r^2 , and kinetic parameters.

Order Kinetic	Kinetic Parameters	r^2
0	t vs. C	0.3035
1	t vs. Log C	0.3767
2	t vs. $\frac{1}{C}$	0.4489
Pseudo-first order	t vs. Log (qe - qt)	0.3093
Pseudo-second order	t vs. $\frac{t}{qt}$	0.9997

t: time; C: Concentration Zn(II); qe: concentration Zn(II) in the equilibrium; qt: concentration Zn(II) in a specific time; %Removal = $\frac{\text{initial C} - \text{final C}}{\text{initial C}} \times 100$.

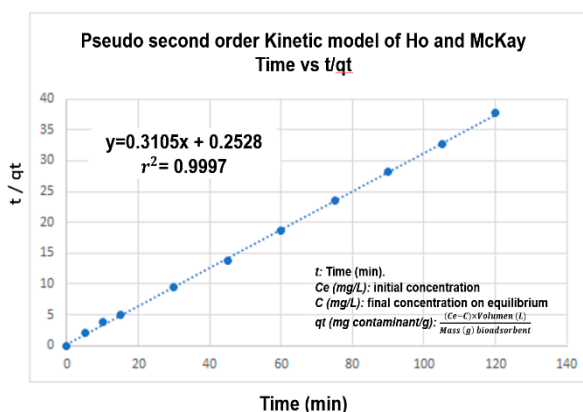


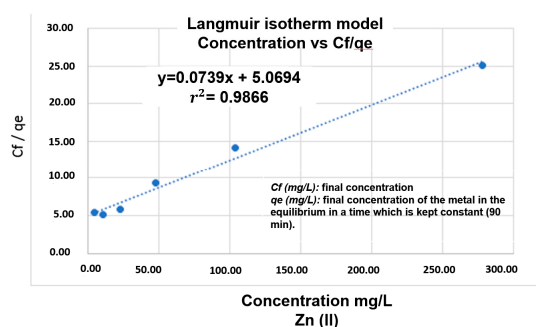
Figure 7. Adsorption kinetics for Zn(II) with CP.

Table 3. Adsorption isotherms applied to the biosorption process.

Adsorption Isotherms	Langmuir	Freundlich	Henry
r^2	0.9866	0.9516	0.8079

The equations that were applied to obtain the adsorption isotherms were taken from Ayawey et al., (2017) [29].

In turn, with the adsorption isotherm obtained (see Figure 8) under the conditions described above, CP presented a maximum capacity of adsorption of $13.53 \text{ mg} \times \text{g}^{-1}$ for this metal. In relation to this value, a bibliographic review was performed to carry out a comparative analysis with the wastes derived from the crops of coffee, banana, and corn (modified and not chemically modified) based on the maximum adsorption capacity for the removal of Zn(II). Therefore, Tables 3 and 4, respectively, report the consolidated values.

**Figure 8.** Adsorption isotherm for Zn(II) with CP.**Table 4.** Maximum adsorption capacity in agricultural wastes without chemical modification used for Zn(II) biosorption.

Lignocellulosic Material	Characteristics				Adsorption Isotherm	Adsorption Kinetics	Author
	Water Type	pH	Maximum Adsorption Capacity ($\text{mg} \times \text{g}^{-1}$)	% Efficiency			
Coffee Pulp	Synthetic	5.0	13.53	63.78	Langmuir	Pseudo second order	Present study
Coffee waste	Synthetic	5.0	4.40	44.00	Langmuir	Pseudo second order	[30]
Banana peels	Synthetic	2.0–6.0	NE	90.00	Langmuir	Pseudo second order	[31]
Banana waste	Synthetic	2.0–3.0	NE	>90.00	Langmuir	Pseudo second order	[32]
Banana pseudo-stem	Synthetic	6.0	0.94	97.24	Langmuir	Pseudo second order	[33]
Stigmas/Corn Silk	Synthetic	5.0	13.98	NE	Langmuir	Pseudo second order	[34]
Corn cob	Synthetic	7.0	30.30	50.00	Langmuir	Pseudo second order	[35]

As observed in Table 4, the wastes that have been studied for the removal of Zn(II) without chemical modification derived from the crops of corn (*Zea mays*), banana (*Musa paradisiaca*), and coffee (*Coffea*) were found for the first, cob, stigma, and silk; for the second, the pseudo-stem and waste; for the latter, waste and pulp. These biosorbents were applied in SWW where the optimum pH ranged between 2.0 and 7.0 units, with maximum adsorption capacities ranging from 0.94 to $13.98 \text{ mg} \times \text{g}^{-1}$ and removal percentages between 44% and 97.24%; the isotherm and adsorption kinetics models applied were Langmuir and pseudo second order, respectively. Additionally, it was evidenced that the CP is more efficient and presented a greater maximum adsorption capacity with respect to

coffee residues; meanwhile, the CC presented the highest maximum adsorption capacity of the three agricultural wastes.

Likewise, Table 5 shows the wastes that have been studied for the removal of Zn(II) with chemical modification; we found the coffee and corn wastes. These biosorbents have been applied in SWW, where the optimum pH ranged between 5.10 and 7.0 units, with maximum adsorption capacities ranging from 19.61 to 79.21 $\text{mg} \times \text{g}^{-1}$; among the chemical modifications made were the activation of active sites with inorganic chemical compounds (acids and salts); finally, the isotherm and adsorption kinetics models that were applied are Langmuir and pseudo second order, respectively. Compared to the wastes without chemical modification, an increase in the maximum adsorption capacities was observed for the metal studied.

Table 5. Maximum adsorption capacity of coffee wastes with chemical modification used for the biosorption of Zn(II).

Lignocellulosic Material	Characteristics					Adsorption Isotherm	Adsorption Kinetics	Author
	Water Type	pH	Maximum Adsorption Capacity ($\text{mg} \times \text{g}^{-1}$)	% Efficiency	Modification			
Coffee waste	Synthetic	5.1	19.61	NE	ZnCl ₂ and KOH activated with CO ₂	Langmuir	Pseudo second order	[36]
Corn cob	Synthetic	7.0	79.21	NE	H ₃ PO ₄	Langmuir	Pseudo second order	[37]

NE: not specified.

3.5. Determination of Point of Zero Charge (pHpzc) for the CP

From the results shown in Table 6, it was observed that the optimum pH determined for the biosorption of Zn(II), in this case for CP, which was the more efficient of the three lignocellulosic materials, is greater than the point of zero charge. According to this, Leyva (2007) [38] states that when this type of relationship is present, the surface of the biosorbent could be negatively charged, presenting electrostatic interactions between the surface and the attraction of the cationic chemical species, as mentioned in Sections 3.3 and 3.5. Therefore, the electrostatic interactions that occur there would be between the deprotonized hydroxyl groups coming from the lignin and cellulose of the CP and the metal ion [12].

Table 6. Point of zero charge for the CP and its relation with the optimum pH.

Optimum pH for CP	pHpzc	Chemical Species in Aqueous Solution	Conclusion
5.0	3.95	Zn ²⁺ [5]	pH > pHpzc The surface of the biosorbent is negatively charged.

In Figure 9, the possible mechanism of adsorption proposed is illustrated.

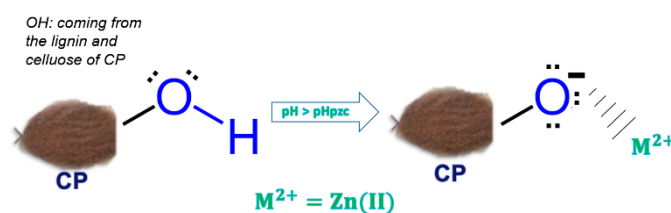


Figure 9. Adsorption mechanism proposed in Zn(II) biosorption with CP.

4. Conclusions

At the level of the adsorption parameters, we obtained that the optimum pH for the removal of Zn(II) with coffee pulp was 5.0 pH units. The kinetic adsorption model that was the best adjusted was that of the pseudo second order of Ho and McKay, with an isotherm of Langmuir's linearized model and pH_{pzc} 3.95 units. The removal of Zn(II) with coffee pulp was 63.78%. The maximum adsorption capacity was 13.53 mg × g⁻¹ using a particle size of 180 µm, a contact time of 90 min, and 100 RPM in synthetic wastewater.

Regarding the bibliographic review carried out for wastes from coffee, banana, and corn that have not been modified or chemically modified, it is important to highlight that more research is needed with these wastes for the removal of Zn(II), such as coffee grounds and corn stubble. Finally, the implication of the present research is that this type of agricultural waste, such as coffee pulp, can be used for the removal of Zn(II) in a pilot study with industries, to contribute to achieving goal 3.9 of objective 3 "Health and Well-being" and goal 6.9 of objective 6 "Clean Water and Sanitation" of the SDG Agenda 2030.

Author Contributions: Performed the experimental methodology, systematization, and analytical treatment of the experimental data obtained, D.L.G.A.; guided the research conducted, J.P.R.M., R.I.M.A., and M.X.A.M.; drafted the manuscript, J.A.E.M. and D.L.G.A.; translated the article and reviewed the writing and citation of the bibliographic references, J.P.R.M., R.I.M.A., and M.X.A.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: We thank Crispin Celis (head of the chemistry department) and Oscar Rodríguez (Pontificia Universidad Javeriana) for all the support and encouragement they gave us during the time we spent undertaking this research work.

Conflicts of Interest: The authors declare no conflict of interest.

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