Using Coffee Pulp as Bioadsorbent for the Removal of Manganese (Mn (II)) from Synthetic Wastewater

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Abstract: This research focuses on the removal of contaminants from wastewaters as a matter of great interest in the field of water pollution. The first decades of the 21st century have brought numerous approaches for the development of cheaper and more effective adsorbents capable of eliminating heavy metals. The study aims to examine the way coffee pulp (Castilla variety from Caldas, Colombia) was used as a bioadsorbent for the removal of Mn (II) from synthetic wastewater to fulfill goals 3 and 6 proposed in the Sustainable Development Goals stated for the 2030 Agenda, particularly in Sections 3.9 and 6.9. In order to achieve this objective, the agricultural residue was subjected to bromatological characterization, determination of the lignocellulosic composition, and identification of characteristic organic functional groups through IR spectrophotometry, using the ATR (attenuated total reflection) technique. Additionally, the optimal parameters for contaminant removal were identified, regarding the biomass quantity, the optimum pH, the stirring time, the adsorption kinetics, the zero charge potential (pHpzc), the adsorption isotherms, and the explanation of the possible adsorption mechanisms between the contaminant, the surface of the coffee pulp, and the capacity of maximum adsorption. The results show that lignocellulosic material presented a cellulose content of 29.93 ± 0.21% and a lignin content of 19.25 ± 0.16%. The optimum parameters found were as follows: Particle size of 180 µm, contact time from 90 min to 100 RPM, optimum pH of 4.0 pH units, room temperature; the kinetic model adjusted to the bioadsorption process was Ho and McKay’s pseudo-second-order, under an isotherm of the Langmuir model, for which the removal presented was 53.40%, with a maximum adsorption capacity of 8.01 mg × g⁻¹. Finally, the novelty of the reported research consists of using coffee pulp as a bioadsorbent without chemical modification, for the removal of heavy metals, in this case Mn (II), in industrial wastewater, which would be another application of this coffee by-product.

Keywords: coffee pulp (CP); synthetic wastewater (SW); bioadsorbent; sustainable development goals (SDGs); manganese

1. Introduction

Water is one of the natural resources that has boosted the development of countries at the economic, social, and environmental levels, in line with the aspects of sustainable development [1]. Due to their advancement, they have used the water resource in domestic and industrial applications where organic, inorganic, and microbiological substances are usually discharged [2,3]. Wastewaters from industries usually contain a high amount of toxic metal ions and pose a high risk to the environment and human beings. In the case of unpurified Industrial Wastewater (IW), inorganic substances that are mostly found
correspond to heavy metals ($M^{n+}$), which have become one of the environmental problems affecting the ecosystem, particularly to water sources, where they are discharged without prior treatment, because one of the characteristics of these pollutants is the tendency to bio-accumulate and bio-magnify their high persistence and toxicity. According to Domenéch and Peral (2008) [4], the sequence of flows of some metal ion pollutants to the hydrosphere, from highest to lowest emission, corresponds to: $\text{Mn} > \text{Zn} > \text{Cr} > \text{Pb} > \text{Ni} \approx \text{Cu} > \text{Se} > \text{Sb} > \text{Mo} > \text{Cd} > \text{Hg}$. Therefore, in the treatment for the removal of inorganic pollutants in wastewaters, conventional and non-advanced techniques are used [3], as well as alternative or green technologies. From these, the latter are being adopted as sustainable alternatives in wastewater treatment [3,5] and bioadsorption using agricultural by-products has attracted attention as an effective and economic method for metal ions removal, manganese being the one considered as risky for its ecosystem and health repercussions. Manganese (Mn) is a transition metal of atomic number 25, atomic density $7.43 \, \text{g} \times \text{cm}^{-3}$ (20 °C), and atomic mass 54.93 g mol$^{-1}$, which is classified as a heavy metal according to the aforementioned characteristics [6]; it can also be found in eleven oxidation states ranging from $-3$ to $+7$, with the most common colors $+2$ (pink), $+4$ (brown), and $+7$ (violet) [7,8]. The World Health Organization (WHO) considers this substance as one of the thirteen toxic metals in environmental and human health [6].

The number of minerals in the Earth’s crust that have manganese in its chemical composition is approximately 748 [9], the most common being pyrolusite ($\text{MnO}_2$), psilomelane (Ba, $\text{H}_2\text{O}_2\text{Mn}_3\text{O}_{10}$, and rhodochrosite ($\text{MnCO}_3$) [7]. On the other hand, among the industrial applications that use compounds containing this chemical element are the production of steel, food supplement for animals, fertilizer additives, ceramics, steel industry, manufacturing of dry batteries, chemical uses, ferro-manganese alloys, glass bleaching, obtaining manganese salts, paints, and varnishes, among others [7]. Regarding the effect of manganese on the human body, at the biochemical level, it is a trace element that helps bone growth, digestion, reproduction, lactation, immune response, blood glucose homeostasis, regulation of adenosine triphosphate (ATP), synthesis of vitamin B1, and components of metalloenzymes such as arginase, glutamine dismutase, and others [7,10]. Moreover, the Food and Agriculture Organization of the United Nations has pointed out that manganese is used in plants as a major contributor to various biological systems including photosynthesis, respiration, and nitrogen assimilation. It is also involved in pollen germination, pollen tube growth, root cell elongation, and resistance to root pathogens [11].

The Agency for Toxic Substances and Disease Registry (ATSDR), a federal public health agency within the United States Department of Health and Human Services, states that although manganese plays an essential role in the human body, such as those mentioned above, emissions of manganese in the air, water (lakes, rivers, groundwater), and soil are due to anthropogenic activities (production of iron and steel alloys, coke furnaces, burning of gasoline additives, use of pesticides, burning of coal or oil, mining, among others), where exposure concentrations correspond to $4 \times 10^{-3}$ parts of Mn per mg $\times$ L$^{-1}$ of water; $2 \times 10^{-5}$ parts Mn per mg $\times$ m$^{-3}$ of air; and 40–900 mg Mn $\times$ Kg$^{-1}$ of soil, leading to health consequences [12]. According to Jimenez (2003) [7], people exposed to compounds containing this chemical exceeding a concentration of 5 mg $\times$ m$^{-3}$ can suffer severe nervous and digestive disorders; in children, exposure to high Mn levels may result in decreased attention, memory loss, low-level cognitive impairment, significantly lower scores on the IQ test, verbal learning, as well as abnormal babies development [12]. Exposure to high levels of manganese compounds can lead to a disabling syndrome of neurological effects referred to as manganism. This Parkinson’s-like central nervous system (CNS)-like neurological-fulminant clinical syndrome is usually suffered by some miners or workers exposed to excessive Mn levels [12,13]. This topic has also been explored in previous studies: Sadek et al. (2003) [14] describe the case of a 30-year-old man who had the symptoms of manganism because he was exposed to manganese and steel alloys; likewise, Igbal et al. (2012) [15] report a clinical case associated with manganese poisoning in drug-addicted people from Eastern Europe and the Baltic states who have intravenously injected self-prepared methcathinone hydrochloride (ephedrone), which is synthesized from pseudoephedrine hydrochloride using potassium permanganate (KMnO$_4$)
as a potent oxidant. Finally, Verhoeven et al. (2011) [16] reported the case of a 49-year old man who was referred for evaluation of acute paranoid psychotic behavior. He was a metalworker diagnosed with manganese intoxication, because his manganese serum level was 52 to 97 nmol × L$^{-1}$ (range: 7 to 20 nmol × L$^{-1}$).

In Colombia, prevention of occupational exposures to chemicals at levels that can cause illness or disease like manganism depends upon having exposure limits, methods for measuring exposures, and means for limiting exposures to levels within the established limits. The exposure standards are defined by Decree 2566 of 2009 [17]; likewise, in this country, industrial wastewater and its effluents are discharged into surface bodies; however, resolution 631 of 2015 of Ministry of Environment and Sustainable Development (MESD) does not provide regulations or parameter limits of effluent to be discharged into inland waters. Unlike Colombia, some countries in South America present the Industrial Wastewater discharge characteristics and limits for Mn: 2.0–2.5 mg × L$^{-1}$ for Mexico [18], 2.0 mg × L$^{-1}$ for Guayaquil [19], and 4.0 mg × L$^{-1}$ for Peru [20]; in Central America: 0.5–1.0 mg × L$^{-1}$ for Dominican Republic [21]; in the European continent: Madrid and Bangladesh establish 2.0 and 1.0 mg × L$^{-1}$ respectively [22,23]; in Asia, 1.5 mg × L$^{-1}$ for Nepal [24]; and Africa: 0.2 mg × L$^{-1}$ for the Republic of Mauritius [25]. Based on the information described above, the aim of this study was to implement and evaluate a clean and sustainable technology, corresponding to the use of a lignocellulosic material (coffee pulp, Castilla variety) as a bioadsorbent in the removal of Mn (II) from synthetic wastewater (SW). The study is of great importance to industries that use chemical compounds containing manganese in their chemical composition and discharge their unpurified wastewater into water sources; due to this alternative, it helps them avoid problems in the ecosystem and diseases such as manganism; it also seeks to accomplish the targets of Sustainable Development Goals (SDGs) 3 and 6, particularly 3.9 (“Significantly reduce the number of illnesses and deaths caused by water, soil and air pollution and by hazardous chemicals, by 2030”) [26] and 6.9 (“Improve water quality by reducing discharges, discharge of hazardous chemicals and products, pollution, and reduction of untreated water and its reuse worldwide by 2030”) [27]. Therefore, the challenge to which this research entails is the implementation of a future pilot system with industries that use this type of clean technology, such as coffee pulp, to carry out the removal of manganese in Wastewater Treatment Systems that present these discharges, thus minimizing the pollutant load of this metal.

2. Materials and Methods

2.1. Physical Treatment of Coffee Pulp (CP) and Collection Site

The agricultural residue corresponding to the coffee pulp (Castilla variety) was collected in the coffee farm El Bosque (Maracas, Quebrada Negra—municipality of Neira, Colombia), which is located at coordinates 5.140579° N–75.484538° W.

Therefore, the treatment carried out to the sampled lignocellulosic material corresponded to a pre-drying in a parabolic solar dryer directly on the farm in a time of 7 to 15 days; subsequently, the partially dehydrated sample was dried at 60 °C on a Binder stove for a time of 6 days and proceeded to the crushing stage by using a Thomas Wiley-branded mill, at a particle size of 180 µm [28].

2.2. Bromatological Analysis, Lignocellulosic Content, and IR Spectrum Reading on CP

The bromatological analysis performed on the CP determined the humidity, ash, raw fiber, total protein, raw ethereal extract, and carbohydrates, through the analytical techniques reported by the AOAC (Association of Official Analytical Chemistry), while the lignocellulosic content was analyzed according to standards established by ANSI (American National Standards Institute)/ASTM (American Society for Testing and Materials).

The Shimadzu-brand AFFINITY-1S IR spectrophotometer was used for the coffee pulp IR spectrum analysis, before the Mn (II) removal process was done, by using the Attenuated Total Reflection (ATR) technique.
2.3. Quantification of Mn (II)

The method used as a reference for the determination of the Mn (II) concentration present in synthetic wastewater (SW) was the 3111 B of standard methods (Atomic Absorption Spectrophotometry—AAS, by direct aspiration of sample into an air-acetylene flame; slit: 0.2 nm) with the VARIAN AA 140 spectrophotometer. Therefore, a mass of 3.0918 g of analytical reagent of MnSO₄·H₂O, 99.5% in purity, was taken for the realization of a stock dissolution of 1000 mg × L⁻¹ in Mn (II) at a volume of 1000 mL; then, Mn (II) patterns of concentrations 1, 2, 3, and 4 mg × L⁻¹ were made at a volume of 25 mL to perform the calibration curve.

2.4. Determination of the Optimum pH of Adsorption of Mn (II) with CP

Synthetic wastewater of Mn (II) of a volume of 25 mL was prepared at a concentration of 100 mg × L⁻¹, using a stock solution of 1000 mg × L⁻¹ Mn (II). Subsequently, the pH of each solution was adjusted to 1, 2, 3 and 4 with HNO₃ 1 M (no higher pH was used, as, when alkalining, Mn (IV) precipitated). Then, 0.500 g of agricultural waste (CP) [29] was added and stirred for 1 h at 100 RPM with a magnetic stirrer at room temperature 18 °C. After some time, they were filtered into qualitative filter paper and the final concentration was determined by AAS with the supernatant. It is relevant to mention that this experimental procedure was performed three times for each pH.

2.5. CP Adsorption Kinetics

In the adsorption system, contact time plays a vital role, irrespective of the other experimental parameters that affect the adsorption kinetics. Synthetic wastewater of Mn (II) of a volume of 25 mL was prepared at a concentration of 100 mg × L⁻¹, using a stock solution of 1000 mg × L⁻¹ Mn (II), which was adjusted to the optimum pH of adsorption of the pollutant determined according to Section 2.4. Subsequently, 0.500 g of agricultural waste (CP) was added and placed in a magnetic stirrer at 100 RPM at different contact times (5, 10, 15, 30, 45, 60, 75, 90, 105, and 120 min). Subsequently, they were filtered on qualitative filter paper and the final concentration in the AAS was determined using the methodology described in Section 2.3. This experimental procedure was performed two times for each contact time.

2.6. CP Adsorption Isotherm

Synthetic wastewater of Mn (II) of a volume of 25 mL was prepared at different concentrations (20, 50, 100, 150, 250, and 500 mg × L⁻¹), from a stock dissolution of 1000 mg × L⁻¹ Mn (II), which was adjusted to the optimum pH of adsorption according to Section 2.4. Subsequently, 0.500 g of CP was added and stirred at 100 RPM. It was left at the optimum contact time found in Section 2.5. Subsequently, they were filtered on qualitative filter paper and, with the supernatant, their final concentration in the AAS was determined using the methodology described in Section 2.3. It should be noted that this experimental procedure was performed in duplicate for each contact time.

2.7. Determination of Point of Zero Charge (pHpzc) and Active Sites of the CP

the mass titration method reported by Rodríguez et al. (2010) [30] was used for the determination of pHpzc; to do this, 0.500, 0.600, 0.700, 0.800, 0.900, and 1.000 g of the CP were weighed; subsequently, 15 mL NaCl 0.100 M was added and left in a magnetic stirrer at 100 RPM at a temperature of 18 °C. Finally, the containers were covered for a time of 48 h and the pH of each mixture was read.

Regarding the determination of active sites present on the surface of coffee pulp, the Boehm methodology, proposed by Boehm (1994, cited in Segovia et al., 2018) [31], was used to quantify the concentration (µmol × g⁻¹ or mmol × g⁻¹) of the total basic and acidic sites with the volumetric acid base regression procedure. Therefore, to neutralize the total acidic active sites (where only carboxylic, phenolic, and lactonic groups are quantified), 0.100 g of the CP was weighed and placed in a beaker, and 25 mL of a NaOH 0.010 M solution was added; in relation to the neutralization of basic total active
sites, they were determined by measuring the previous amount of lignocellulosic residue and adding 25 mL of an HCl 0.010 M solution.

To quantify carboxylic active sites, 0.100 g of the agricultural residue was weighed and placed into a beaker and 25 mL of a 0.010 M NaHCO₃ solution was added; in relation to the quantification of carboxylic and lactonic active sites, the same mass of the residues was measured and 25 mL of 0.010 M Na₂CO₃ solution was added; finally, the concentration of active phenolic sites was obtained by subtraction of the total acidic active sites and the sum of the carboxylic and lactonic sites. Finally, tests were left in a thermostat bath at 25 °C for seven days; after this period time, the base acid titration was carried out with 0.010 M HCl to titrate the aliquots of NaOH, NaHCO₃, and Na₂CO₃; and NaOH 0.010 M was used for the values of the aliquot of HCl.

3. Results and Discussion

The results obtained for the CP by each procedure were made in triplicate, and are presented according to the methodology described in Sections 2.1–2.7.

3.1. Bromatological Analysis and Lignocellulosic Content

Table 1 presents the results obtained from the bromatological analysis, and the cellulose and lignin present in the coffee pulp, some literature review reports, and the analytical method follow for the parameters determination.

| Parameters            | Result % m/m | Bibliographic Reports | Interval | Methodology Used |
|-----------------------|--------------|-----------------------|----------|------------------|
| % Total Carbohydrates | 48.50 ± 0.00 | 69.31 DNR *           | DNR      | 48.50-69.31     ** |
| % Ash                 | 10.43 ± 0.18 | 6.66 DNR              | 5.43     | 4.99-8.90       |
| % Cellulose           | 29.93 ± 0.21 | DNR                  | 43.28    | 18.65-63.00     |
| % Raw Fiber           | 16.29 ± 0.50 | 11.43 DNR             | 20.23    | 11.43-20.23     |
| % Fats and Oils       | 1.85 ± 0.08  | 1.60 DNR              | 3.48     | 1.60-3.48       |
| % Humidity            | 12.40 ± 0.00 | 74.83 DNR             | 10.09    | 10.09-74.83     |
| % Lignin              | 19.25 ± 0.16 | DNR                  | 36.89    | 12.20-36.89     |
| % Total Protein       | 10.53 ± 0.64 | 11.00 DNR             | 11.20    | 8.00-14.03      |

* DNR: Does not report; ** Difference in parameters humidity, ash, crude fiber, ethereal extract, and total protein; a AOAC 7.009/84, 942.05/90 Adapted; b ANSI/ASTM D1103-60; c AOAC 7.066/84, 962.09/90; d AOAC 7.060/84, 920.39/90 Adapted; e AOAC 7.003/84, 930.15/90 Adapted; f ANSI/ASTM D1106-56; g Method Kjeldahl–Gunning–Arnold Adapted Griffin 1995.

When comparing the bromatological results to those reported by other authors, it is observed that at the total protein level, the percentages were very similar to those obtained by Blandón et al. (1999) [32] and Aristizábal, Chacón, and Cardona (2017) [36]; it is for this reason that CP is used as a raw material in the production of animal food, soil vermiculture, and for the cultivation of edible fungi (Pleurotus ostreatus) [36,40], while the results of carbohydrates, lignin, and cellulose have certain differences.

It should be noted that the parameters of protein, carbohydrates, lignin, and cellulose are very important, as these compounds have functional groups responsible for the adsorption affinity of heavy metals [41] and are responsible for adsorption of Mn (II) ions in the solution.

3.2. Infrared (IR) Spectrum of the CP

Figure 1 illustrates the IR spectrum obtained from the CP, which was read in the middle IR.
with a mass of 0.250 g of CP, temperature of 18°C.

3.3. Optimum pH Determination

Figure 2 illustrates the different pHs vs. % removal and Figure 3 shows the Box plots obtained with the free XLSTAT software to report the data obtained from the different pHs from 1 to 4 units.

According to Figures 2 and 3, it was concluded that the optimum bioadsorption pH for Mn (II), with a mass of 0.250 g of CP, temperature of 18 °C, 100 RPM, and contact time of 60 min, was 4.0 pH units, with a removal percentage of 43.88%.
On the other hand, to improve the removal of the Mn (II) with the CP, two improvement actions were taken: The first consisted of maintaining the constant mass of 0.500 g and increasing the contact time up to 2 h; the second consisted of increasing the mass of the bioadsorbent using 0.500 g and 1.000 g of the CP, without varying the parameters of temperature, particle size, agitation, metal concentration, and contact time. When comparing the two improvement actions, it was observed that there was a more significant removal of the pollutant, increasing the mass of the bioadsorbent. Thus, it was evidenced that with 0.500 g of CP, the removal of Mn (II) was 53.40%, and with 1.000 g, the removal was 65.59%.

3.4. Adsorption Kinetics Determination

Table 3 shows the data in the determination of the kinetic model in which the Mn (II) bioadsorption process was adjusted, and the mathematical treatment was performed to clarify its adjustment.

Based on the results illustrated in Table 3 and Figure 4, the Mn (II) bioadsorption process using the CP was adjusted to the pseudo-second-order model of Ho and McKay, obtaining a linear correlation coefficient of 0.9934, which was obtained by applying \( \frac{d\hat{q}}{dt} = K (q_e - q_t)^2 \).

Therefore, it can be established that in a maximum contact time of 90 min with a mass of 0.500 g of coffee pulp, pH of 4.0 pH units, agitation of 100 RPM, room temperature of 20 °C, and particle size of 180 µm, there is a Mn (II) removal of 53.40%.
Table 3. Experimental results in the determination of the kinetic model with different contact times of the Mn (II) removal process with CP.

| Contact Time (min.) | C (mg × L⁻¹) | (Ce–C) (mg × L⁻¹) | qt (mg × g⁻¹) | (qe–qt) | t/qt |
|---------------------|--------------|--------------------|---------------|---------|------|
| 0                   | 100.00       | 0.00               | 0.00          | 46.60   | 0.00 |
| 5                   | 55.16        | 44.84              | 2.24          | 44.35   | 2.23 |
| 10                  | 48.36        | 51.64              | 2.58          | 44.01   | 3.87 |
| 15                  | 46.27        | 53.73              | 2.69          | 43.91   | 5.58 |
| 30                  | 44.47        | 55.53              | 2.78          | 43.82   | 10.80|
| 45                  | 45.37        | 54.63              | 2.73          | 43.86   | 16.48|
| 60                  | 39.89        | 60.11              | 3.01          | 43.59   | 19.96|
| 75                  | 38.32        | 61.68              | 3.08          | 43.51   | 24.32|
| 90                  | 46.60        | 53.40              | 2.67          | 43.93   | 33.71|
| 105                 | 46.68        | 53.32              | 2.67          | 43.93   | 39.39|
| 120                 | 46.56        | 53.44              | 2.67          | 43.92   | 44.91|

Ce (mg × L⁻¹): Initial concentration; C (mg × L⁻¹): Final concentration on equilibrium; qt (mg contaminant × g⁻¹): (Ce–C) × Volume (L) / Bioadsorbent mass (g); qe (mg × L⁻¹): Final concentration of the metal in the equilibrium in a time of 90 min (which is kept constant); t: Time (min).

Figure 4. Ho and McKay pseudo-second-order model for adsorption of Mn (II) with CP.

3.5. Adsorption Isotherm Determination

Table 4 shows the data obtained in the determination of the adsorption isotherm model to which the Mn (II) bioadsorption process was adjusted:

The values presented in Table 4 and Figure 5 allowed the researchers to realize that the Mn (II) bioadsorption process with the CP was adjusted to the linearized version of the Langmuir model, according to Ayawei et al. (2017) [44], as its linear correlation coefficient was 0.9941. The result indicates that the adsorption of Mn (II) occurs only at specific sites on the surface of the CP and, in turn, that there is no lateral interaction between the adsorbed Mn (II) cations. Finally, the results made it possible to establish that the maximum adsorption capacity of the CP for Mn (II) removal was 8.01 mg × g⁻¹.
was 3.95; the number of acid groups present in the bioadsorbent is greater than that of the basic groups. The presence of hydroxyl groups present in the CP lignin and cellulose (see Table 1).

The cation.

Based on this data, it is possible to infer two possible Mn (II) adsorption mechanisms: (a) Adsorption mechanism 1: According to Hallberg and Johnson (2005) [46], the present specie of manganese at pH 4.0 is Mn (II); as this pH was higher than (pHpzc), it can be concluded that the surface of the bioadsorbent is negative, allowing us to infer that electrostatic interactions attract the cation.

Table 4. Experimental results of Langmuir Isotherm with CP.

| Concentration Mn (II) (mg × L⁻¹) | Absorbances (Maximum Absorption Wavelength: 279.5 nm; Slit: 0.2 nm) | Average Absorbance | Final Concentration Mn (II) (mg × L⁻¹) |
|---------------------------------|---------------------------------------------------------------|-------------------|--------------------------------------|
| 20                              | 0.150                                                         | 0.150             | 5.22                                 |
| 50                              | 0.420                                                         | 0.420             | 15.30                                |
| 100                             | 0.290                                                         | 0.290             | 39.85                                |
| 150                             | 0.410                                                         | 0.430             | 70.41                                |
| 250                             | 0.390                                                         | 0.390             | 145.43                               |
| 500                             | 0.400                                                         | 0.390             | 361.12                               |

Figure 5. Linearized Langmuir isotherm model for the Mn (II) bioadsorption process with the CP.

On the other hand, Jamaica (2019) [45] developed a study with the CP, making a chemical modification and using H₃PO₄ 85% m/v with pyrolysis at 400 °C, in synthetic wastewater. The results suggest that the adsorption process revealed as optimum variables for the adsorption: Bioadsorbent dose rate of 20 g × L⁻¹, 100 RPM, room temperature, pH 1.0 units, time of 70 min, kinetic model of pseudo-second-order and Langmuir isotherm (with a maximum capacity of adsorption (q max.) of 7.59 mg × g⁻¹), and a removal percentage increased by 10%, compared to the unchanged CP.

3.6. Determination of the Zero Charge Point (pHpzc) and Active Sites of CP Surface

The results obtained in the determination of (pHpzc) and the active sites of the lignocellulosic material are shown in Table 5:

Table 5. Zero charge potential (pHpzc) results and bioadsorbent active sites.

| Acid Groups (mmol × g⁻¹) | Basic Groups (mmol × g⁻¹) | pHpzc  |
|--------------------------|---------------------------|--------|
| 0.280                    | 0.170                     | 3.95   |

In relation to the reported data in Table 5, we can observe that the pHpzc of the bioadsorbent was 3.95; the number of acid groups present in the bioadsorbent is greater than that of the basic groups. This is due to the presence of hydroxyl groups present in the CP lignin and cellulose (see Table 1). Based on this data, it is possible to infer two possible Mn (II) adsorption mechanisms:
(b) Adsorption mechanism 2: As the CP has a high protein value (see Table 1), it is possible to detect a resonance state of the amide groups. The negative charge of this group would allow electrostatic interaction between the surface of the bioadsorbent and the Mn (II) [47].

Concerning the data obtained, it is recommended to take some actions in order to increase the efficiency of the CP for the removal of Mn (II):

1. Use masses greater than 1.000 g of coffee pulp (Castle variety), keeping the constant volume of 25 mL of the ARS, particle size of 180 µm, contact time of 90 min, agitation of 100 RPM, temperature of 20 °C, and pH 4.0 to obtain removals above 65.59%. This is because, if we increase the mass of the bioadsorbent, the electrostatic interactions will increase too, due to the increase in the number of hydroxyl-type functional groups with Mn (II) cations.

2. Perform chemical modifications to the CP using pyrolysis or the addition method with different acids such as phosphoric, sulfuric, citrus, and oxalic acid. These methods will allow the changing of the chemical composition of the lignocellulosic material, causing the presence of more functional groups that can be ionizing by the pH effect.

4. Conclusions

This research study was carried out performing two phases: First, the bromatological analysis, the quantification of lignin and cellulose, and the analysis of functional groups by IR spectrophotometry were carried out. Based on data obtained, it is possible to conclude that coffee pulp (Castilla variety) from Caldas (Colombia) presented 10.53% protein, 29.93 ± 0.21% cellulose, and 19.25 ± 0.16% lignin. The IR spectrum suggested that the most representative bands were the hydroxyl groups.

In the second stage, the findings of the procedures and analyses carried out lead to the following conclusions: The CP presented a maximum adsorption capacity of 8.01 mg × g⁻¹ at an optimal pH of 4.0 pH units, 100 RPM, 20 °C, a particle size of 180 µm, a biomass of 0.500 g, and a contact time of 90 min; the obtained efficiency was 53.40%. Results were adjusted to Ho and McKay’s pseudo-second-order kinetics model, and the Langmuir isotherm model was the most appropriate for fitting the experimental data.

Moreover, when comparing the data obtained in this research study on the removal of Mn (II) from synthetic wastewater by using coffee pulp (CP) with the literature review regarding the biosorption process of Mn (II) present in wastewater, it was observed that not enough literature is listed for reference on the coffee processing by-products such as pulp, husk, sliver silk, and mucilage for the removal of this heavy metal, with and without chemical modification. Considering the above context, it may be said that further research is needed on the abovementioned coffee by-products, in particular, the CP, with and without chemical modification, to determine its efficiency, applicability, and affinity for manganese removal from real and/or synthetic wastewater.

Finally, the broad implication of the present research is that Coffee pulp as an adsorbent can be fruitfully used for the removal of Mn (II) from Industrial wastewater (IW) to avoid adverse health effects in humans like manganism, abnormal growth of babies, mood disorders, and other psychiatric changes. Moreover, this study contributes to achieving objective No. 3 Health and Welfare and objective No. 6 of Clean Water and Sanitation from the Sustainable Development Goals of the 2030 Agenda.

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

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