


Article

Coffee Pulp: A Sustainable Alternative Removal of Cr (VI) in Wastewaters

Dora Luz Gómez Aguilar ^{1,*}, Juan Pablo Rodríguez Miranda ², Javier Andrés Esteban Muñoz ¹ and Jhon Fredy Betancur P. ³ 

¹ Chemistry Department, National Pedagogical University, Bogotá 110231, Colombia

² Engineering Department, University Distrital Francisco José de Caldas (UDFJC), Bogotá 110231, Colombia

³ Manizales University, Manizales 170003, Colombia

* Correspondence: dgomez@pedagogica.edu.co; Tel.: +57-5941894

Received: 11 April 2019; Accepted: 5 June 2019; Published: 1 July 2019



Abstract: Currently, agricultural waste is proposed as a sustainable alternative in the removal of heavy metals present in industrial wastewater, to fulfill some of the goals proposed in the Sustainable Development Goals stated for the 2030 Agenda, in particular in Sections 3.9 and 6.9. Considering this context, the coffee pulp (Castilla variety) of Caldas municipality (Colombia) was used in study for the removal of one of the most toxic chemical species of chromium: Cr (VI). Therefore, the agricultural residue was subjected to a bromatological characterization, determination of the lignocellulosic composition and elucidation of characteristic organic functional groups by IR spectrophotometry. Additionally, the optimal parameters for contaminant removal were identified, regarding particle size, biomass quantity, optimum pH, stirring time, temperature, adsorption kinetics, zero charge potential (pH_{pzc}) and adsorption isotherms, to analyze the kinetic model that fitted the process, the explanation of the possible adsorption mechanism between the contaminant, the surface of the coffee pulp and the capacity of maximum adsorption, respectively. Finally, the innovation of the research is discussed considering two criteria: First, when a mixture was made in different proportions between two agricultural residues (coffee pulp and plantain pseudostem) to show if there was an increase in the removal of the contaminant under the same optimal conditions found experimentally; and the second criterion, the comparison of the maximum adsorption capacity, with the percentages of removal carried out by other authors using the pulp of unmodified coffee.

Keywords: industrial wastewater (IWW); heavy metals; coffee pulp (CP); agricultural residues; plantain pseudo stem (PP); Sustainable Development Goals (SDG); hexavalent chromium

1. Introduction

Water as one of the natural resources that promotes a sustainable development of the countries has multiple applications at the domestic, agricultural and industrial levels. In the development of this type of activity, usually the discharged pollutants type: Organic (organic waste, surfactants, fats and oils, fertilizers and pesticides, microorganisms) and inorganic (heavy metals, radionuclides). In relation to the latter, they are the ones most produced by activities such as agriculture and livestock, electronics, electroplating, painting, metallurgy, mining and tanneries [1].

In the case of inorganic contaminants, specifically heavy metals (M^{n+}), they are chemical elements with an atomic density greater than $5 \text{ g} \times \text{cm}^{-3}$, atomic mass between 63.5 and $200.6 \text{ g} \times \text{mol}^{-1}$ and atomic number greater than 20 [2], which can be chemically classified as light, heavy or metalloid and which, in terms of their toxicity, are classified as toxic (they exert a negative impact on the ecosystem, due to their high persistence and concentrations, it bioaccumulated and biomagnified) and non-toxic (essential micronutrients for life) [3]. Similarly, they are considered prior environmental

contaminants [4] and an indicator of one of the dimensions of sustainable development “Environmental Health” in the Environmental Performance Indicators (EPI), which measure the sustainability of the countries; these parameters were established by Yale University [4].

The previous one has led to the search for new alternatives in the removal of the mentioned pollutants, which may be present in the case of industrial wastewater (IWW). Among the techniques that have been used for removing these pollutants are conventional and advanced; among the conventional ones, adsorption with activated carbon and chemical precipitation are found; and between advanced technologies they are membrane as: ultrafiltration, microfiltration, nanofiltration, reverse osmosis, electrodialysis; electrocoagulation, and photocatalysis [5]. It should be added that one of the advantages of these methods is their high efficiency when the metal concentration is higher than $100 \text{ mg} \times \text{L}^{-1}$, among the disadvantages are the generation of sludge and the high cost for implementation and maintenance [5].

Therefore, since 1990 there have been proposed new methods that are less expensive in their implementation and maintenance, more efficient for removal of contaminant concentrations below $1 \text{ mg} \times \text{L}^{-1}$ to $\mu\text{g} \times \text{L}^{-1}$ [5], environmentally friendly and with less sludge production. This type of technology were known as unconventional or green, as a sustainable alternative in the treatment of these waters, among which include bioremediation (fungi, bacteria, yeast and green, brown and red algae), phytoremediation, hydrogels, fly ash and adsorption with agricultural residues [5]. Some of the heavy metals that have been investigated by some authors and, in contrast to the World Health Organization (WHO) are considered for their importance in human and environmental health correspond to: arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), tin (Sn) and titanium (Ti) [6].

Therefore, among the heavy metals mentioned, the one that has caused the greatest negative impact in the ecosystem and health, is the chromium. This chemical element of atomic number 24 and atomic density $7.19 \text{ g} \times \text{cm}^{-3}$ (at 20°C), which in addition to being used in activities such as electrolytic chrome-plating, tanning of skins, biochemical techniques (characterization of carbohydrates, marker of different cell types and proteins), production of dyes and pigments, has several oxidation states being the most stable trivalent (Cr (III)) and hexavalent (Cr (VI)) [7]; this element can be present in rocks and that at the level of minerals present in the earth's crust, there are more than 103 [8].

According to Coreño-Alonso, Tomasini & Reyna (2010) [7], compounds containing chromium with an oxidation state 3+, generally have a green color and are not considered mutagenic or carcinogenic, unlike 6+ that in addition to occurring in the yellow-orange coloration, can cause the mentioned characteristics at the level of human health. Similarly, Cr (III) is considered an essential micronutrient (as it occurs in foods such as lentils, egg yolks, nuts, chicken, red meat, among others), but can become toxic when presented in high concentrations; in comparison to Cr (VI), which can be toxic by any route of ingestion; at the level of the respiratory system causes damage to the nasal septum, deformation of the nose, bronchitis, pulmonary fibrosis, lung cancer, nasal cavity, laryngitis; in relation to the digestive system, it causes hepatitis, gastrointestinal ulcer; and on the skin, original sores, dermatitis and ulcer; it should be added that in relation to the toxicity of Cr (VI), being high, and to reduce the chemical species to a less toxic one, in this case to Cr (III), Álvarez, García & Querol (2007) [9] state that Cr (VI) must first be reduced with sodium metabisulfite to convert it to Cr (III), to then precipitate it in the form of $\text{Cr}(\text{OH})_{3(s)}$ or $\text{Cr}_2(\text{SO}_4)_{3(s)}$.

According to the previous context, in contrast to the use of clean technologies for the removal of this pollutant, present in industrial wastewaters (IWW), fungi (*Paecilomyces* sp.), Macrophytic plants (*Lemna minor*), algae bacterium (*Bostrychia calliptera-Rhodomelaceae*), biological systems and bio-adsorbents such as agricultural or lignocellulosic residues were used [10]. Regarding the latter, besides being considered as liquid or solid products obtained in agroindustrial process, which not have been an specific use in the production chain, it seeks to give an application in terms of the IWW treatment, since they have a bad disposition which has led to environmental problems such as the generation of greenhouse gases (GHG), bad odors (produced by the hydrogen sulfide $\text{H}_2\text{S}_{(g)}$)

generated and in mantles aquifers form hydrogen sulfide) and emerging pollutants in waters for human consumption [11].

It should be added that, in terms of the chemical constitution of these residues, lignin, cellulose and hemicellulose represent the highest percentage in their composition [12,13]. Therefore, one of this type of waste corresponds to the coffee pulp, which is obtained as a by-product of the pulping of the coffee bean, and which, in the context of Colombia, has been used in lombriculture [14], as a culture of edible mushrooms (*Pleurotus ostreatus*) [15].

According to the presented panorama, the present investigation had similar to objective the application of a clean technology, in this case the use of an agricultural waste (coffee pulp, Castilla variety) such as bioadsorbent, in the removal of Cr (VI) in Synthetic Residual Waters; so that this technology is implemented in industrial wastewater treatment systems (IWWTS) presenting in its activities the use of chemicals that have the contaminant described, so that their discharges comply with environmental regulations in force (that in the context of Colombia, it applies Resolution 631 of 2015 of the Ministry of Environment and Sustainable Development, MADS), as well as to comply with the goals set out in the Sustainable Development Goals Agenda 2030, in particular paragraphs 3.9 and 6.9.

2. Materials and Methods

2.1. Collection Site and Treatment of Agricultural Residues Coffee Pulp (CP) and Plantain Pseudostem (PP)

The agricultural residues corresponding to the coffee pulp (Castilla variety) and the plantain pseudostem (Dominico-Harton variety) were collected from a coffee farm “El Bosque” (Maracas lane, black broken—municipality of Neira) located at coordinates 5.140579 °N–75.484538 °W (Manizales, Colombia), which were dried at 60 °C and comminuted in a mill to a particle fixing of 0.180 mm.

2.2. Bromatological Analysis, Lignocellulosic Content and Infrared Spectrum (IR)

In the bromatological analysis, the parameters of percentage of humidity, ash, crude fiber, total protein, crude ether extract and carbohydrate were determined using the methodology reported by the AOAC (Association of Official Analytical Chemistry), while for the quantification of lignin and cellulose, the ANSI (American National Standards Institute)/ASTM standards (American Society for Testing and Materials) were used.

The IR spectrum for each agricultural residue before the removal of the Cr (VI) contaminant was carried out using an IR AFFINITY-1S equipment Shimadzu brand with the Attenuated Total Reflection ATR technique.

2.3. Quantification of Cr (VI)

To determine the concentration of Cr (VI) in the Synthetic Residual Water the reference method 3111 B standard methods (Atomic Absorption Spectrophotometry—AAS, direct flame method air-acetylene (oxidant is employed); slit 0.2 nm) with the VARIAN AA 140 spectrophotometer. We used 2.8411 g of analytical reagent of $K_2Cr_2O_7$ 99.5% purity, for the realization of a stock solution of $1000\text{ mg} \times L^{-1}$ in Cr (VI) in a volume of 1000 mL; from this, the Cr (VI) standards of concentrations of 1, 5, 10 and $15\text{ mg} \times L^{-1}$ in a volume of 25 mL were made to perform the calibration curve.

2.4. Determination of the Optimum pH of Adsorption with CP

It was prepared by 25 mL of Synthetic Residual Water of Cr (VI), at a concentration of $100\text{ mg} \times L^{-1}$, using a stock solution of $1000\text{ mg} \times L^{-1}$ Cr (VI). Then, the pH of each solution was adjusted to 1, 2, 3, 4, 5 with HNO_3 0.100 M and pH 9 with NaOH 0.100 M. Later, 0.500 g of agricultural residue (CP) was added and stirred for 60 min at 100 RPM with a magnetic stirrer at room temperature 18 °C. After this time, they were filtered on qualitative filter paper and with the supernatant determined its final

concentration by AAS. It should be noted that this experimental procedure was performed in triplicate for each pH.

2.5. Kinetic Adsorption with CP

It was prepared by a volume of 25 mL of a Synthetic Residual Water of Cr (VI) at a concentration of $100 \text{ mg} \times \text{L}^{-1}$, using a stock solution of $1000 \text{ mg} \times \text{L}^{-1}$ Cr (VI) and adjusted to the optimum pH of the contaminant adsorption determined according to number 2.4. Subsequently, 0.500 g was added of the agricultural residue (CP) and placed on 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 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.

2.6. Isotherm Adsorption with CP

It was prepared by 25 mL of a Synthetic Residual Water of Cr (VI) at different concentrations (20, 50, 100, 150, 250 and $500 \text{ mg} \times \text{L}^{-1}$), from a stock solution of $1000 \text{ mg} \times \text{L}^{-1}$, were adjusted to the optimum pH of adsorption determined according to numeral 2.4. Subsequently, they were added a mass of 0.500 g of CP with an agitation of 100 RPM and allowed to optimum contact time found in Section 2.5. It should be noted that this experimental procedure was performed in duplicate for each concentration.

2.7. Determination of the Zero Charge Point (pH_{pzc}) and Active Sites

For the determination of pH_{pzc} the mass titration method reported by Rodríguez-Estupiñan, Giraldo, Moreno-Piraján (2010) was used [16]; for this, were weighed 0.500 g; 0.600 g; 0.700 g; 0.800 g; 0.900 g and 0.100 g of agricultural residue (CP or PP); subsequently, 15 mL NaCl 0.100 M were added, they were left stirring in a magnetic stirrer at 100 RPM at a temperature of 18°C , the containers were covered for a time of 48 h and after this time the pH of each mix were read.

Regarding the determination of active sites present on the surface of coffee pulp, the Boehm methodology exposed by Boehm (1994, cited in Segovia et al., 2018) was used [17], in which we seek to quantify the concentration ($\mu\text{mol} \times \text{g}^{-1}$ o $\text{mmol} \times \text{g}^{-1}$) of the basic sites and total acids by volumetric acid base by regression. Therefore, to neutralize the total active sites of basic character, 0.100 g of agricultural residue (CP or PP) in a beaker was weighed and added 25 mL of a HCl solution 0.010 M; in relation to the neutralization of the total acid-active sites, these exclusively quantified the carboxylic, phenolic and lactonic groups, which were determined by measuring the previous amount of the residue and 25 mL of a 0.010 M NaOH solution was added.

To quantify carboxylic active sites, 0.100 g of the respective agricultural residue was weighed in beakers and 25 mL of a 0.010 M NaHCO_3 solution was added; in relation to the quantification of carboxylic and lactonic active sites, the same mass of the residues respectively was measured and 25 mL of 0.010 M Na_2CO_3 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 and after time; the base acid titration was carried out with 0.010 M HCl to titrate the aliquots of NaOH, NaHCO_3 and Na_2CO_3 and for the values of the aliquot of HCl was used NaOH 0.010 M.

2.8. Determination of the Removal Percentage with Mixtures of Lignocellulosic Residues (CP and PP)

The mixtures between lignocellulosic residues (CP and PP) were made with the purpose of determining if the percentages of Cr (VI) removal increased, with respect to the use of lignocellulosic residues in an independent way. To stop this, three mixtures were prepared, in the mixture one was used a ratio 1:1 CP and PP (0.250 g:0.250 g), the two mixtures were made in a ratio of 2:1 CP and PP (0.250 g:0.125 g) and three mixtures were made in a ratio of 3:1 CP and PP (0.250 g:0.0825 g).

Subsequently, each of the mixtures were placed in 25 mL of the solutions that had a concentration of $100 \text{ mg} \times \text{L}^{-1} \text{ Cr (VI)}$, were shaken at 100 RPM, the pH was adjusted as determined in Section 2.4 and was left in the contact time obtained according to number 2.5. Finally, they were filtered on qualitative filter paper and with the supernatant their final concentration in the AAS was determined.

3. Results and Discussion

3.1. Bromatological Analysis and Lignin and Cellulose Percentage

Table 1 presents the results of bromatological analysis, cellulose and lignin present in the coffee pulp (CP) and plantain pseudostem (PP), for each of these parameters, the respective analyzes were performed in triplicate.

Table 1. Data of bromatological analysis, cellulose and lignin in agricultural residues.

PARAMETER	AGRICULTURAL RESIDUALS		
	COFFEE PULP (CP)	PLANTAIN PSEUDOSTEM (PP)	METODOLOGY USED
% Humidity	12.40 ± 0.00	13.40 ± 0.64	AOAC 7.003/84, 930.15/90 Adapted [18] (p. 47)
% Ashes	10.43 ± 0.18	10.61 ± 0.24	AOAC 7.009/84, 942.05/90 Adapted [18] (p. 47)
% Fats and Oils (F and O)	1.85 ± 0.08	1.00 ± 0.25	AOAC 7.060/84, 920.39/90 Adapted [18] (p. 48)
% Protein	10.53 ± 0.64	3.73 ± 0.18	Kjeldahl Method-Gunning-Arnold Adapted-Griffin-1995 [19] (p. 51)
% Raw fiber	16.29 ± 0.50	16.71 ± 0.11	AOAC 7.066/84, 962.09/90 Adapted [18] (p. 48)
% Carbohydrates	48.50 ± 0.00	54.55 ± 0.00	Found between the difference of the parameters (humidity, ash, crude fiber, ether extract and total protein)
% Cellulose	29.93 ± 0.21	49.20 ± 2.65	ANSI/ASTM D1103-60 [19]
% Lignin	19.25 ± 0.16	5.49 ± 0.25	ANSI/ASTM D1106-56 [20].

When analyzing the data in Table 1, it is observed that between the two lignocellulosic residues (CP and PP) the parameter that differs most in the bromatological analysis was the protein percentage, being higher in the CP with a value of 10.53% with respect to the PP of 3.73%, which is significant, because according to the exposed by the authors mentioned in the introductory section, the CP is very used in the lombriculture, in the obtaining of edible fungi and as a raw material in the production of animal concentrates.

On the other hand, at the level of the lignocellulosic composition, the CP presented a lower cellulose value of 29.93% with respect to that of PP, which was 49.20%; while, in lignin, the highest percentage was presented by the CP of 19.25% in relation to the PP of 5.49%. These two parameters are very important since, these compounds are those that occur externally in the cell wall of the plants

and are responsible for providing the functional groups that allow carrying out the adsorption of the removal of heavy metals, in this case the Cr (VI).

3.2. Infrared (IR) Spectrum of the CP and PP

The reading of the infrared spectrum was performed in the range of the middle IR region ($400\text{--}4000\text{ cm}^{-1}$); this was done in order to observe and analyze the absorption bands characteristic of the functional groups associated with agricultural residues (CP and PP) that could intervene in the Cr (VI) bioadsorption process, as well as the lignin and cellulose chemical structure, which mainly make up the waste. Therefore, the obtained spectra are illustrated in Figures 1 and 2, respectively:

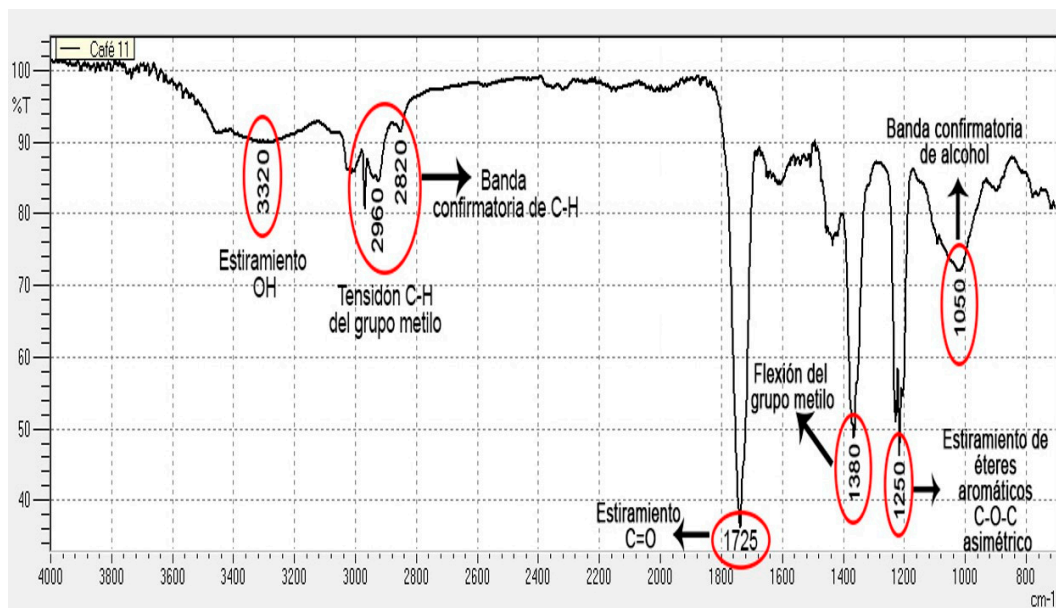


Figure 1. Infrared spectrum of the coffee pulp before the application of the bioadsorption process of chromium (Cr) (VI).

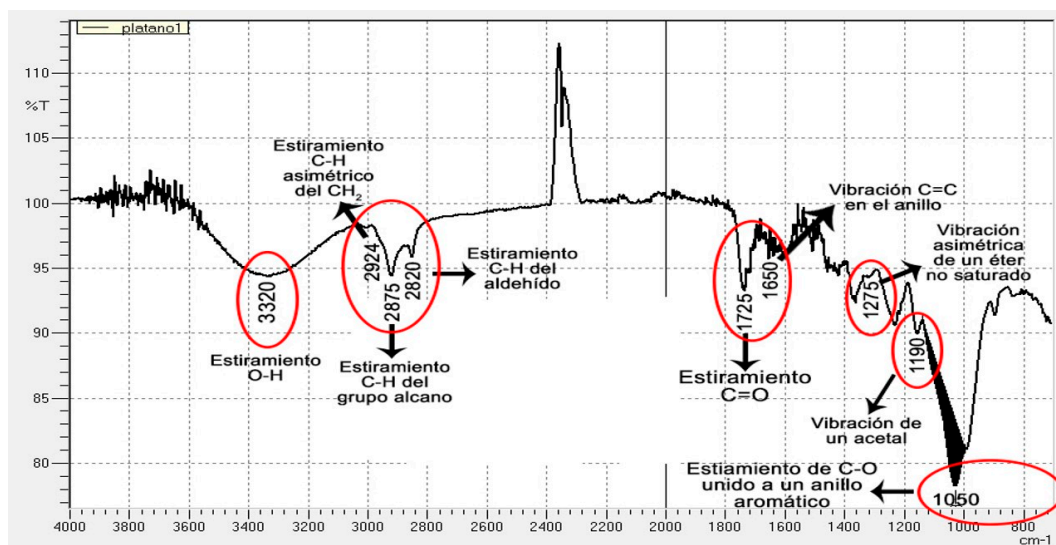


Figure 2. Infrared spectrum of the plantain pseudostem before the application of the bioadsorption process of Cr (VI).

At the level of the interpretation of the absorption bands of the infrared spectra exposed in Figures 1 and 2, concerning the residues of coffee pulp and plantain pseudostem, respectively, a broad band in common around the region can be observed of 3320 cm^{-1} , which is attributed to the stretching of the hydroxyl group (OH); similarly, a band in common is observed around $2924\text{--}2960\text{ cm}^{-1}$ associated with the symmetric stretching of the C-H bond, coming from saturated chain alkyl compounds and in the region of 2820 cm^{-1} associated with the voltage vibration coming from the CH_2 [21].

The absorption bands in common in the region of 1725 cm^{-1} are associated with the $\text{C}=\text{O}$ stretching from the carbonyl group, as well as the 1250 cm^{-1} that indicates an asymmetric stretching of the C-O-C bond associated with an aromatic ether; finally, the band presented at 1050 cm^{-1} is confirmatory for the hydroxyl group [21].

According to the elucidation of the absorption bands carried out, in relation to the chemical structure of lignin and cellulose are illustrated in Figure 3a,b respectively:

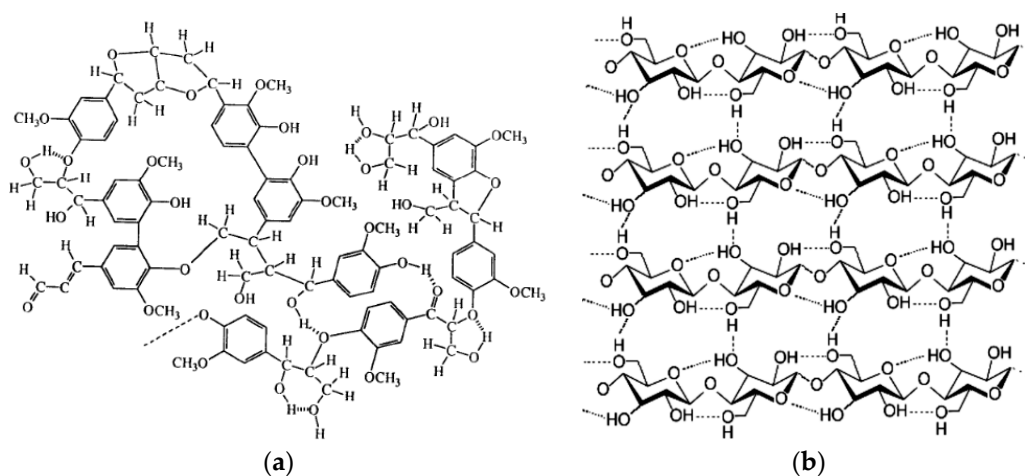


Figure 3. Chemical structures of: (a) Lignin [22]; (b) cellulose [22].

As seen in Figure 3a,b, the hydroxyl group is present in the chemical structures of lignin and cellulose, which is bound to the aromatic ring and saturated chains, respectively; in the case of the stretching of the carbonyl group, it can be inferred that it is associated with lignin, since it is attached to the aromatic rings. In the same way, the ethers are present in the chemical composition, with a structure $\text{C}=\text{C}-\text{O}-\text{R}$ attached to the aromatic ring; it should be noted that the absorption band of 1190 cm^{-1} present in the PP spectrum is associated with the vibration of an acetal, which is associated with the chemical structure of cellulose.

According to the present context, it can be inferred that according to the absorption bands characterized in relation to the functional groups, those that can probably intervene in the bioadsorption process of the contaminant, are the hydroxyl and carbonyl groups. These can be attributed to the chemical structure of lignin and cellulose, which are the major components according to the proximal analysis performed and described in Section 3.1.

3.3. Determination of Optimal pH of Adsorption in the CP

The XLSTAT software free version was used for 15 days, with the objective of observing the optimum pH of adsorption of the contaminant, in which in the “y” axis was plotted the removal percentage (this obtained between the ratio of the initial and final concentration and the initial concentration) and on the “x” axis the pH units, with which obtain the box plots graphic illustrated in Figure 4:

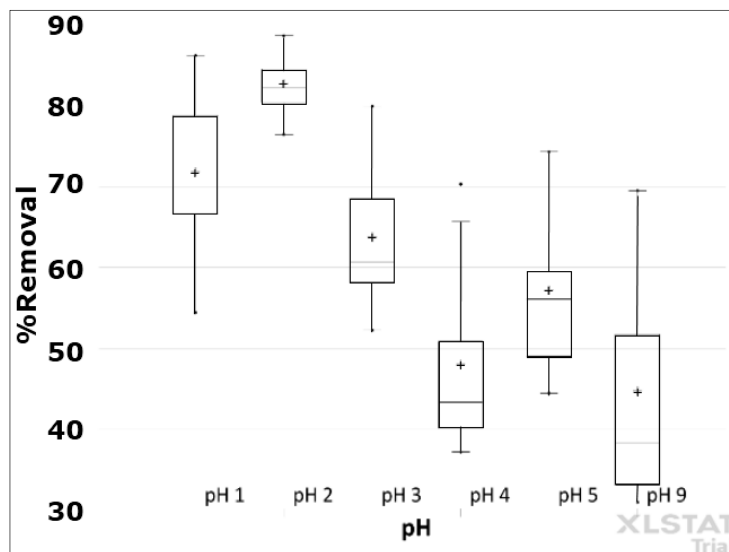


Figure 4. Box plots of Cr (VI) at different pH, obtained from XLSTAT software.

According to Figure 4, the optimum pH of adsorption of Cr (VI) was 2.0, due to the presented higher percentage of removal of contaminant.

3.4. Determination pH_{pzc} and Active Sites of the Surface of the CP

Table 2 reports the values obtained from the total active sites of acid and basic character present in the surface of the CP and the potential of zero charge pH_{pzc} .

Table 2. Quantification of the total acidic and basic groups on the surface of the coffee pulp (CP) and zero charge potential (pH_{pzc}).

Total Active Sites		pH_{pzc}
Acids ($\text{mmol} \times \text{g}^{-1}$)	Basics ($\text{mmol} \times \text{g}^{-1}$)	
0.28	0.17	3.95

In Table 2 it observed that predominantly the acid sites upon the basics on the surface of the CP, allowing establish that the pH_{pzc} of the bioadsorbent is acid and that the hydroxyl groups present in the lignin and cellulose of the CP (see Table 1 and numeral 3.2) are responsible for the adsorption of Cr (VI) in the agricultural waste, in contrast to what was exposed by Leyva (2007, cited in Moreno, 2007) [23].

On the other hand, with the above data we propose the adsorption mechanism to explain the removal of Cr (VI) in the Synthetic Residual Waters. For this, it should be noted that the optimum pH obtained for this removal according to number 3.3 was 2.0 pH units, in this condition the species of Cr (VI), according to Rollinson (1973, cited in Acosta et al., 2010) [24] is in the aqueous solution as $(\text{HCrO}_4)^-$, $(\text{Cr}_2\text{O}_7)^{2-}$, $(\text{CrO}_4)^-$ and that the pH_{pzc} was 3.95 indicating that the load of the surface of the CP is positive with respect to the optimum pH of 2.0, which is lower than the zero load point of the CP [17]; for this reason, the removal occurs by electrostatic interactions, as illustrated in Figure 5:

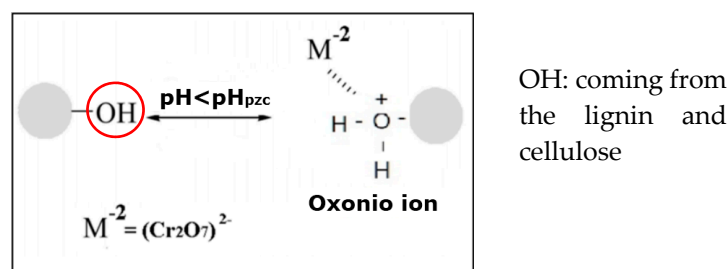


Figure 5. Cr (VI) adsorption mechanism with CP surface proposed by authors.

3.5. Adsorption Kinetics of CP

Regarding the kinetics of adsorption obtained for Cr (VI), according to the time of removal, the optimal time of adsorption of the contaminant was 105 min, because this is the highest percentage of contaminant removal and where removal indicating that it had reached equilibrium between the Cr (VI) with the functional groups of the surface of the CP is kept constant. In turn, to determine the kinetic model that best matched the behavior of the data, they applied the methods graphics zero order, first order, second order, pseudo-first order and pseudo second order, where the selection criterion for the model that best matched the process bioadsorption was given in terms of the coefficient of determination (R^2), will approach the value of one.

Therefore, it was established that the kinetic model that was most adjusted to the process of bioadsorption of Cr (VI) was the pseudo second order kinetic model of Ho and McKay, since it obtained the correlation coefficient higher compared to the zero-order models one, two and pseudo first order [25], obtaining Figure 6:

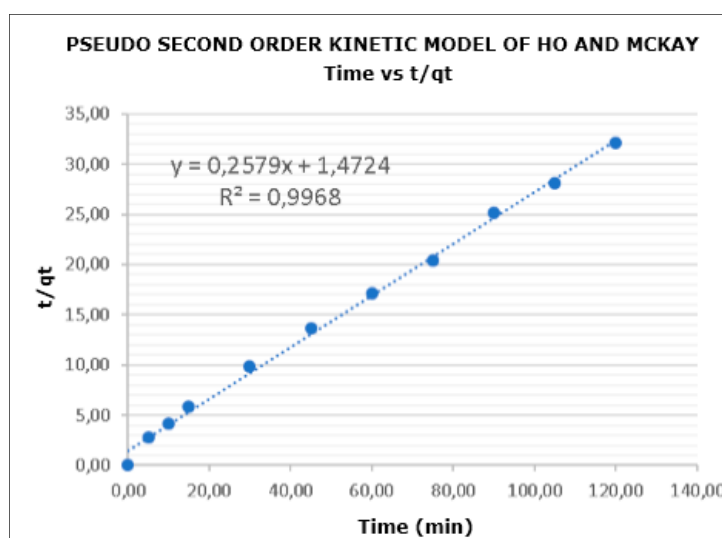


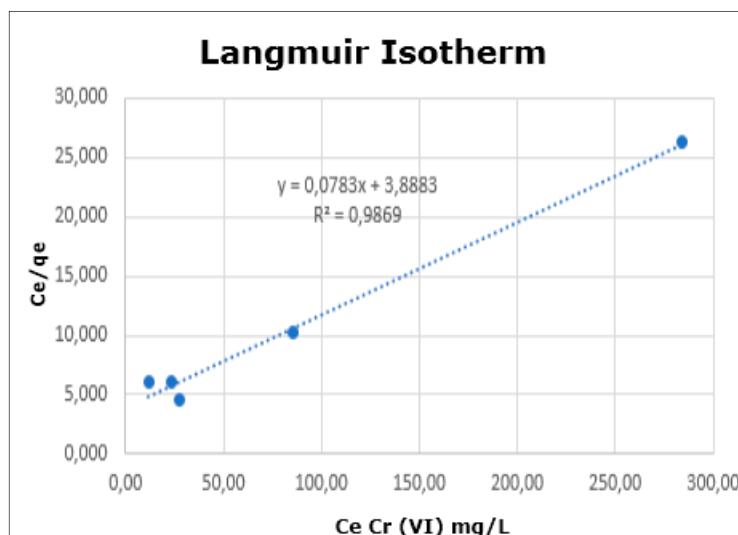
Figure 6. Pseudo second order of Ho and McKay kinetic model for the removal of Cr (VI) with CP.

3.6. Adsorption Isotherms of the CP

To identify this parameter, three mathematical models were applied (Langmuir, Freundlich and Henry), being the linearized model of Langmuir the one that was most adjusted in the removal of Cr (VI), because this was the one that presented the highest correlation coefficient in comparison to the other two models [26], according to the values shown in Table 3 and Figure 7:

Table 3. Datos de isotermas de adsorción con CP.

Adsorption Isotherms			Separation Factor (RL) Model Langmuir	Maximum Adsorption Capacity (q_{\max}) ($\text{mg} \times \text{g}^{-1}$)
Langmuir R^2	Freundlich R^2	Henry R^2		
0.9869	0.8420	0.7180	0.12–0.77	13.48

**Figure 7.** Linearized Langmuir Model for Cr (VI) with CP.

The Langmuir isotherm has three assumptions: The first indicates that the adsorption of Cr (VI) only occurs at specific sites located on the surface of the CP (see mechanism adsorption in Figure 5); the second establishes that each metal is adsorbed only on each active site of the CP surface; and the third assumption suggests that there is no interaction between adsorbed metals Cr (VI) adjacent to the surface of the CP [23].

Additionally, in Table 3 it is observed that the separation factor RL was found in a range of 0.12 to 0.77 indicating that the adsorption of Cr (VI) on the surface of the CP was favorable [27]; and finally, according to the maximum adsorption capacity of the CP (q_{\max}), it is deduced that 13.48 mg of Cr (VI) is adsorbed for each gram of agricultural residue (CP).

3.7. Mixtures of more Efficient Bio Adsorbents for the Removal of Chromium (VI) in Synthetic Wastewater

Table 4 reports the data obtained from the mixtures in different proportions between the CP and the PP.

Table 4. Results of the mixtures in different proportions between the CP and PP for the removal of Cr (VI).

Mixture	Mixture Ratio (g) Agricultural Waste (PP:CP)	Optimum pH of Adsorption (pH Units)	Vol. (mL)	% Removal
1	0.250:0.250	2.0	25	59.13
2	0.125:0.250			59.28
3	0.0825:0.250			58.86

According to the data shown in Table 4, it is observed that by varying the ratio between CP and PP to increase the removal of Cr (VI) in the Synthetic Residual Waters, there was no improvement in the percentages of removal of the contaminant, allowing inferring that this type of methodology would not be feasible to implement it in a Wastewater Treatment Plant System (WWTPS).

4. Conclusions

The coffee pulp becomes a sustainable alternative to be used as a bioadsorbent in the Wastewater Treatment Plant Systems (WWTPS) for the removal of Cr (VI), since, it is easy to acquire, its cost of implementation and maintenance would be economical, it does not generate sludge in the treatment and it is of high efficiency 87.94%. A cost level is lower compared to conventional technologies, in the case of chemical precipitation would be necessary to use a reducing agent (sodium metabisulfite) to convert the Cr (VI) to Cr (III) and then prepare it with the addition of NaOH and in the case of adsorption, the material that is most used is activated carbon, which in the market is high cost. With the above, it is proposed to promote this type of technology, so that industries that generate dumping with Cr (VI) are used to comply with both the regulations and the market that prevails in each country, so that our system of this type of pollutants continues to be negatively impacted even more negatively and to meet the goals in numbers 3.9 and 6.9 in the Sustainable Development Goals of the 2030 Agenda.

On the other hand, when comparing the data obtained from the coffee pulp for the removal of Cr (VI), with those reported by other authors using optimal conditions of adsorption, it was found that linearized models of Langmuir are those that have always been presented as a behavior of the data in the isotherms. Regarding the interpretation of the mathematical models of adsorption kinetics, the one that best fits is the behavior of the pseudo second order of Ho and McKay. While, the capacity of maximum adsorption has varied, the main difference is found in the initial dose of contaminant. The reported results are: $5.90 \text{ mg} \times \text{g}^{-1}$ [28], $44.95 \text{ mg} \times \text{g}^{-1}$ [29], $59.54 \text{ mg} \times \text{g}^{-1}$ [30] and $220 \text{ mg} \times \text{g}^{-1}$ [31], and that found in the present study was $13.48 \text{ mg} \times \text{g}^{-1}$, being observed that this result is shown among those previously reported.

Author Contributions: D.L.G.A. performed the experimental methodology, the systematization and analytical treatment of the experimental data obtained; J.P.R.M. and J.F.B.P. guided the research conducted, and revised the manuscript; J.A.E.M. and D.L.G.A. drafted the manuscript. Finally, all the authors discussed the results and contributed to the final version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: We thank the Pontificia Javeriana University, which allows us to develop the experimental work of the present investigation.

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

References

1. Srivastava, N.K.; Majumder, C.B. Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *J. Hazard. Mater.* **2008**, *151*, 1–8. [CrossRef] [PubMed]
2. Kaplan, D. Absorption and Adsorption of Heavy Metals by Microalgae. In *Handbook of Microalgal Culture: Applied Phycology and Biotechnology*, 2nd ed.; Richmond, A., Hu, Q., Eds.; John Wiley & Sons, Ltd.: Hoboken, NJ, USA; Blackwell Publishing Ltd.: Israel, Middle East, 2013; pp. 602–611.
3. Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manag.* **2011**, *92*, 407–418. [CrossRef] [PubMed]
4. Wendling, Z.A.; Emerson, J.W.; Esty, D.C.; Levy, M.A.; de Sherbinin, A.; Spiegel, N.; Pinkerton, V.; Boucher, L.; Ratté, S.; Mardel, S.; et al. *2018 Environmental Performance Index*; Yale Center for Environmental Law & Policy: New Haven, CT, USA, 2018; Available online: <https://epi.envirocenter.yale.edu/2018/report/category/hlt> (accessed on 26 March 2019).
5. Wang, J.; Chen, C. Biosorbents for heavy metals removal and their future. *J. Biotechnol. Adv.* **2009**, *27*, 195–226. [CrossRef] [PubMed]
6. Organización Mundial de la Salud (OMS) (2011). Adverse health effects of heavy metals in children. Available online: https://www.who.int/ceh/capacity/heavy_metals.pdf (accessed on 26 March 2019).
7. Coreño-Alonso, A.; Tomasini, A.; Reyna, G. Cromo: Lo bueno y lo malo, los inicios de una historia. *R. Enl. Quím.* **2010**, *2*, 14–54.
8. Barthelmy, D. Mineralogy Database. 2014. Available online: <http://webmineral.com/> (accessed on 26 March 2019).

9. Álvarez, E.; Garcia, A.; Querol, X. Adsorption of Cr (VI) from Synthetic Solutions and Electroplating Wastewaters on Amorphous Aluminium Oxide. *J. Haz. Mater.* **2007**, *142*, 191–198. [CrossRef] [PubMed]
10. Artunduaga, F. Tratamiento para la remoción de Cr (VI) presente en aguas residuales. *R. Nov.* **2015**, *1*, 66–73.
11. Vargas, Y.; Pérez, L. Use of Agro-Industrial Waste in Improving the Quality of the Environment. *R. Fac. Cienc. Básic.* **2018**, *14*, 1–14.
12. Saval, S. Aprovechamiento de residuos agroindustriales: pasado, presente y futuro. *R. Biotechn.* **2012**, *16*, 14–16.
13. Alonso, M.; Ramírez, C.; Rigal, L. Valorización de residuos agroindustriales del tequila para alimentación de rumiantes. *R. Chap. Ser. Cien. Forest. Amb.* **2012**, *18*, 449–457.
14. Blandón, G.; Dávila, M.; Rodríguez, N. Caracterización microbiológica y físico-química de la pulpa de café sola y con mucílago, en proceso de lombricompostaje. *R. Cenic.* **1999**, *50*, 5–23.
15. Rodríguez, V.; Gómez, C. Cultive Hongos Comestibles en Pulpa de Café. 2001. Available online: https://www.cenicafe.org/es/index.php/nuestras_publicaciones/avances_tecnicos/avance_tecnico_0285 (accessed on 26 March 2019).
16. Rodríguez-Estupiñán, P.; Giraldo, L.; Moreno-Piraján, J.C. Adsorción simple y competitiva de níquel y cadmio sobre carbón activado granular: Efecto del pH. *R. Afinid.* **2010**, *LXVII*, 449–454.
17. Segovia-Sandoval, S.J.; Ocampo-Pérez, R.; Berber-Mendoza, M.S.; Leyva-Ramos, R.; Jacobo-Azuara, A.; Medellín-Castillo, N.A. Alnut shell treated with citric acid and its application as biosorbent in the removal of Zn (II). *J. Wat. Proc. Engine.* **2018**, *25*, 45–53. [CrossRef]
18. Bernal, I. *Análisis de Alimentos*, 2nd ed.; Academia Colombiana de Ciencias Exactas físicas y Naturales: Bogotá, Colombia, 1998.
19. ASTM International. *ANSI/ASTM D1103-60: Method of Test for Alpha-Cellulose in Wood*; ASTM International (ASTM): West Conshohocken, PA, USA, 1960.
20. ASTM International. *ANSI/ASTM D1106-56: Standard Test Method for Acid-Insoluble Lignin in Wood*; ASTM International (ASTM): West Conshohocken, PA, USA, 2001.
21. Calderón, C. *Manual Para la Interpretación de Espectros Infrarrojos*; Universidad Nacional de Colombia: Bogotá, Colombia, 1995.
22. Rubio, S. Recuperación de celulosa en un residuo forestal mediante líquidos iónicos. In *Tesis de Maestría en Ciencia y Tecnología Ambiental*; Centro de Investigación en Materiales Avanzados: Chihuahua, México, 2016.
23. Moreno, J. *Importancia y Aplicaciones de la Adsorción en Fase Líquida. En Sólidos Porosos*; Universidad de los Andes: Bogotá, Colombia, 2007; pp. 155–207.
24. Acosta, I.; López, V.; Coronado, E.; Cárdenas, J.; Martínez, V. Remoción de Cromo (VI) en solución acuosa por la biomasa de la cáscara de tamarindo (*Tamarindus indica*). *R. Biotechn.* **2010**, *14*, 11–23.
25. Ho, Y.S.; Mckay, G. Pseudo-second order model for sorption processes. *J. Proc. Biochem.* **1999**, *34*, 451–465. [CrossRef]
26. Ayawei, N.; Ebelegi, A.N.; Wankasi, D. Modelling and Interpretation of Adsorption Isotherms. *J. Chem. Hind.* **2017**, 2017. [CrossRef]
27. Nascimento, R.F.; Lima, A.C.; Vidal, C.B.; Melo, D.Q.; Cabral Raulino, G.S. *Adsorção: Aspectos Teóricos e Aplicações Ambientais*; Universitária da Universidade Federal do Ceará (UFC): Imprensa Universitária, 2014.
28. Alemayehu, H.; Burkute, A.; Ede, A. Adsorptive removal of Pb (II) and Cr (VI) from wastewater used acid untreated coffee husk, Interlink continental. *J. Environ. Sci. Toxicol.* **2014**, *1*, 9–16.
29. Anastopoulos, I.; Karamesouti, M.; Mitropoulos, A.; Kyzas, G. A review for coffee adsorbents. *J. Mol. Liq.* **2017**, *229*, 555–565. [CrossRef]
30. Ede, A. Adsorptive removal of Cr (VI) ion from wastewater by activated coffee husk and banana peel: Comparative study. *World J. Pharm. Res.* **2014**, *4*, 212–225.
31. Ede, A.; Alemayehu, H.; Burkute, A. Adsorptive removal of Pb (II) and Cr (VI) from wastewater using acid untreated and treated coffee husks: Comparative study. *Int. J. Res. Chem. Environ.* **2014**, *4*, 26–31.

