

## Article

# Computational Simulation of Filters Used in the Removal of Heavy Metals Using Rice Husks

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**Abstract:** The biofiltration technique is of great importance for the removal of heavy metals. In the present work, a laboratory-scale biofilter was modeled using rice husk as a filter material. The Wolborska model was used to know the dimensions necessary for the biofilter to function. The Langmuir and Freundlich isotherms were performed to quantify the filter adsorption process, showing that the Langmuir isotherms are the ones that present the highest correlation coefficient and best represent the removal process of Cd (II), Cu (II) and Cr (VI). According to the Langmuir isotherms, the maximum operating temperature allowed for this model was chosen, which was 303.15 K, because it presents the maximum removal of heavy metals. Regarding the pH variations for Cd (II) and Cu (II), the maximum removal was presented with a pH = 9.0 and for Cr (VI) with a pH = 3.0 the maximum removal was presented. According to the rupture curves, the blocking times were obtained for each height: for Cd (II) the highest  $t_b$  for  $h = 0.55$ , Cu (II) the highest  $t_b$  for  $h = 0.40$  and for Cr (VI) the highest  $t_b$  for  $h = 0.40$ .

**Keywords:** bio filter; Wolborska; lignocellulosic material; pH; Langmuir; Freundlich



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## 1. Introduction

Environmental pollution is one of the most serious problems that affects society in the 21st century. Among these difficulties, water contamination by heavy metals is one of the current problems that originates from several human activities, such as wearing to geological process; mining; and industries such as microelectronics, electroplating, battery manufacturing, dyes, chemical products and pharmaceutical products [1–3]. The heavy metals are one of the main pollutants of water, being highly toxic for human beings. It is well-known that the most abundant heavy metals in water are mercury (Hg) [4], nickel (Ni) [5], copper (Cu) [6], plumb (Pb) [7] and chromium (Cr) [8]. Various technologies have been used for the removal of metal ions, among which the following stand out: chemical precipitation, chemical coagulation, oxidation, reduction, ion exchange, filtration, ultra-filtration, nanofiltration, adsorption (activated carbon, zeolites, silica gel), technologies membrane (reverse osmosis), electrochemical treatment (electrodialysis and electrocoagulation) and application of artificial wetlands (some stabilization), among others, resulting in many cases ineffective and expensive [9,10]. Consequently, it is important to develop new technologies for the detoxification of said effluents and chemical stabilization of the compound [11]. This is the reason for the development of new technologies based on national raw materials is a pending task for researchers from developing countries like Colombia.

In Colombia, because of its different climates, there is a great variety of possible materials with potential applications as lignocellulosic material. Among the most used materials is banana skin, which has been employed to remove metals such as Cu (II), Zn (II), Co (II), Ni (II) and Pb (II) [12] with 49.14% efficiency; other natural material used is the coffee rusk, that is employed in process for removing Cu (II), Zn (II) and Cd (II) [13] with

58.45% efficiency. Additionally, using sheep's wool, uranium has been removed [14] and with the rice husk, metals like Cd (II), Zn (II), Co (II), Ni (II), Mn (II) and Hg (II) [15] can be removed with 62.85% efficiency; additionally, using the rice husk, there are heavy metal removal reports such as Cd (II), Cu (II), Cr (VI), Pb (II), Zn (II) and As (III) with adsorption capacities between 72.80% and 99.30% [16]. In most previous reports, an additional process of the material is required. Generally, a chemical process is conducted to activate the material, leaving impurities that generate a subsequent contamination [17].

Modeling and simulation processes are a very useful tool because, regard independently of the complexity of the bio filter system, it can be modeled considering most of the variables for reaching an efficient operation. Within the theoretical studies, it is found that the mathematical modeling of a heavy metal adsorption system can evaluate the dynamics regarding the ways that metals adhere to the lignocellulosic material [18]. Additionally, it was found that with a vertical flow filter, a dynamic simulation can be performed to evaluate the transport and destination of heavy metals in wastewater. For modeling systems that remove heavy metals, the following characteristics are considered: volume of residual water, temperature, concentration of heavy metals, contact time and flow [19]. Moreover, it is required to consider an initial concentration, contact time [20], porosity, depth, filtration rate, loss of load, geometry, inlet and outlet pressure and the characteristics of the affluent [21]. Furthermore, the pH is considered as a fundamental variable, because at high values, the negative sites increase and at low values, the formation of hydroxylated ions decreases as well as the adsorption of heavy metals [22]. Employing a statistical model is proposed for the analysis of adsorption; they found that for the filtering process, a controlled temperature must be maintained, avoiding the deterioration of the system used as a filter [23]; and the efficiency of a filter depends on the characteristics and properties of interactions between the filter and the substance or element that will be retained.

Contaminants are not only found in water; for example, Kalawik et al., [24] reported that heavy metals such as Hg, Cd, Pb, As and Ni have been found in foods such as sushi, the concentrations of heavy metals found are high enough to affect the health of people who eat these foods. Traces of Pb, Cu, Cd and Hg have also been found in meat sold for human consumption [25]. Other studies show how heavy metals such as Cd, Pb and As have been the most detected in foods such as vegetables and fruits, presenting a great risk to humans. Due to the large presence of heavy metals both in water and in food, the need arises to propose alternatives for the removal of heavy metals. The alternative that arises in this case is a bio-filter made from easily accessible materials that contribute to a circular economy, such as rice husk, which allows the removal of metals such as Cr (VI), Cd (II) and Cu (II) from water. In this work, kinetic models were used for modelling the effectiveness of rice husk as a material used in a filter for the removal of Cr (VI), Cd (II) and Cu (II) in batch processes. The outline of this document is the following: In Section 2, we give the model, the bio filter design, and the explication of selection of lignocellulosic material. In Section 3, isotherms and breaking curves for each heavy metal are presented. Finally, conclusions are given in Section 4.

## 2. Materials and Methods

This section will explain the model used for the bio filter, the design of the bio filter and the explanation of the selection of the material and the characteristics of the rice husk to be used in the removal of metals such as Cr (VI), Cd (II) and Cu (II).

### 2.1. Model

The Wolborska Model [26] is defined as follows:

$$\ln \frac{C}{C_0} = \frac{\beta_a C_0}{N_0} t - \frac{\beta_a z}{U_0} \quad (1)$$

where  $C_o$  is initial solute concentration (mg/L),  $C$  is effluent solute concentration (mg/L),  $N_o$  is the saturation concentration (mg/L),  $\beta_a$  is the kinetic mass transfer coefficient ( $\text{min}^{-1}$ ),  $Z$  is the depth of the column (cm) and  $U_o$  is the surface speed (cm/min). [27].

## 2.2. Isotherms

For the adsorption process of the bio filter, it was quantified by performing the Langmuir and Freundlich isotherms. Using the Langmuir model, several assumptions are made: (a) the surface is considered homogeneous, (b) it has a saturation point at which no more metals can be absorbed, (c) the heat of adsorption is independent of the degree of coating, and (d) all the sites are equivalent and the energy of the absorbed molecules is independent of the presence of other molecules [28]. The Langmuir isotherm is based on the hypothesis that all active adsorption centers are equivalent and that the ability of a molecule to bind to the surface is independent of whether there are nearby positions occupied; adsorption is restricted to a monolayer and is represented by the following equation:

$$Q_e = Q_{max} \frac{bC_e}{1 + bC_e} \quad (2)$$

where  $Q_e$  is the quantity of metal adsorbed on the surface of the biosorbent (mg/g),  $C_e$  is the amount of metal present in the solution at equilibrium condition (mg/L),  $Q_{max}$  is the maximum adsorption capacity of the biosorbent (mg/g) and  $b$  is Langmuir constant representing the affinity (sorption/desorption) of binding sites (L/mg).

As most surfaces are heterogeneous, there are multiple sites available for adsorption, that is, the heat of adsorption varies from site to site. The Freundlich isotherm, which is expressed according to the following equation:

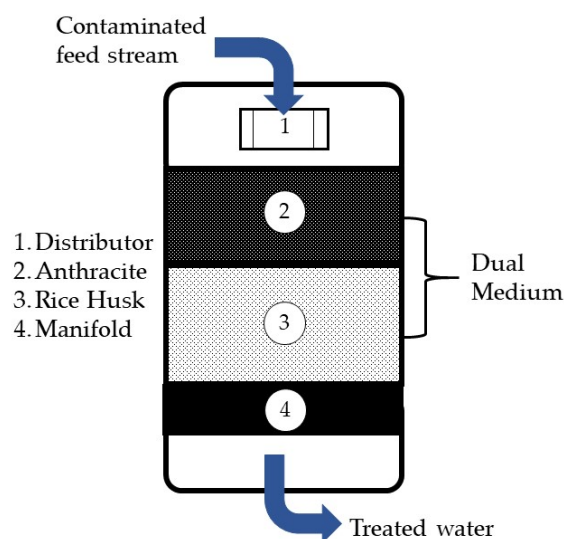
$$\log(Q_e) = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where  $Q_e$  is the quantity of metal adsorbed on the surface of the biosorbent (mg/g),  $C_e$  is the amount of metal present in the solution at equilibrium condition (mg/L),  $K_f$  is a constant indicative of the adsorption capacity of the adsorbent and  $n$  is a constant indicative of the adsorption intensity (restricted to values greater than unity, a range between 2 and 10 represents a good adsorption intensity) [29].

## 2.3. Design of the Bio Filter

The design is based on a dual medium bio filter that has two filter media; one medium allows to remain larger particles and the other medium is used for maintaining smaller particles. The objective of the double media is to eliminate large suspension solids, using sand as a filtering medium and to eliminate heavy metals of small size with various materials, in this case, lignocellulosic materials. Figure 1 shows the structure of the bio filter. In this figure, parts of the system are schematically represented and described as follows: The distributor is responsible for distributing the flow of water that will enter the filter. The dual media is responsible for retaining waste and heavy metals. Finally, the water that has been filtered with the help of the dual medium is collected in the collector.

The bio filter is in the form of a cylinder to avoid dead areas and allow the water circulates efficiently. From the total filter height, 70% corresponds to the dual medium (40% rice husk and 30% anthracite). The distributor 14%, the manifold 6% and the part where the treated solution circulates corresponds to 10%. Moreover, the bio filter has a cross-sectional area of input and output taking values of 0.28274 and 0.12566  $\text{m}^2$ , respectively. The surface speed is approximately 0.3 cm/s. The lignocellulosic material is in a fixed bed adsorption column and the contaminated fluid passes through the bed of the adsorbent.



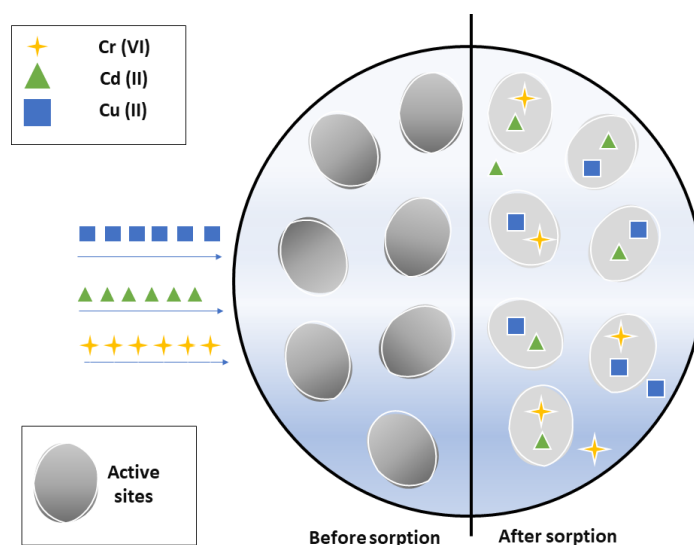
**Figure 1.** Structure of the bio filter.

According to CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act), the limit of concentrations for the metals to be studied is shown in Table 1.

**Table 1.** Permitted concentration limit [30].

Metal	Co ( $\frac{\text{mg}}{\text{g}}$ )
Cr (VI)	0.01
Cd (II)	0.005
Cu (II)	1.3

Figure 2 shows a diagram of how the process would be before and after absorption by the rice husk, in which the active sites are represented in gray in which heavy metals are trapped. The heavy metals Cd (II), Cr (VI) and Cu (II) are represented by stars, triangles and squares, respectively, some of them are outside the active sites and that not all are trapped and some that remain free. To be absorbed by the rice husk, processes such as: redox reaction, surprise and ion exchange take place.



**Figure 2.** The figure aims to describe the mechanism of absorption of heavy metals.

The initial concentrations for the metals varied in the following ranges: 0.85 and 10.85 mg/g for Cd (II), 0.92 and 32.1 mg/g for Cu (II) and 0.55 and 25 mg/g for Cr (SAW). The values exceed the permitted limits shown in Table 1, which is why it is interesting to carry out this type of study that seeks to reduce the concentration of heavy metals.

### 3. Results

For each metal, the isotherms depending on the temperature and the pH shows in this section. For obtaining the isotherms, the Brunauer–Demming–Demming–Teller classification (BBDT) is taken into account [31]. In addition, the rupture curve that is related to the kinetic equation used to model the operation of the bio filter are developed.

#### 3.1. Selection of Lignocellulosic Material

Using lignocellulosic materials, smaller solids can be removed, since it has a small pore size and can trap them. Among the lignocellulosic materials most used for the filtration process are sheep's wool, banana peel, coffee peel, orange peel, lemon peel, sugar cane residues and rice peel. Sheep wool has been used to remove metals such as Cu (II), Pb (II) and Cd (II), obtaining a high removal capacity when treating the wool with NaOH and Na<sub>2</sub>S [32]. The banana peel that has been used for the removal of Cu (II), Cd (II), Pb (II), Zn (II), Ni (II) and Co(II) with an adsorption order of Pb(II) > Ni (II) > Zn(II) > Cu(II) > Co(II), which represents a good alternative because it is a product that occurs in approximately 130 countries, to use the banana peel as an adsorbent activation treatment is required [33]. The coffee husk has been used for removal processes of Cu (II), Pb (II), Cr (VI), Ni (II) and Zn (II), coffee is considered as a possible material since it is abundant in many parts of the world; for example, in 2004, it was considered as the most valuable product exported by developing countries and due to its properties it could be used as adsorbent material [34–37]. Orange peel has been used for the removal of metals such as Cu (II), Cd (II), Pb (II), Zn (II) and Ni (II); orange peel is proposed since it is one of the main waste products of the soft drink industries; for use as an adsorbent it requires a special treatment with CS<sub>2</sub> so that its (OH)<sup>−</sup> sites can be activated and remove heavy metals [38,39]. With the lemon peel to remove Pb (II), to use the lemon peel a treatment with citric acid must be done. Using sugarcane, the removal capacity for Pb (II), Cd (II) and Cr (VI) has been studied showing efficiencies of 86%, 64% and 62%, respectively; for the use of sugarcane a chemical treatment is required [40]. Finally, the rice husk to be used to remove metals such as Cd (II), Cr (VI), Cr (III), Cu (II), Mn (II) and Fe (II) [41–43], for use the rice husk in adsorption processes, chemical treatments are not required with a simple washing can be used.

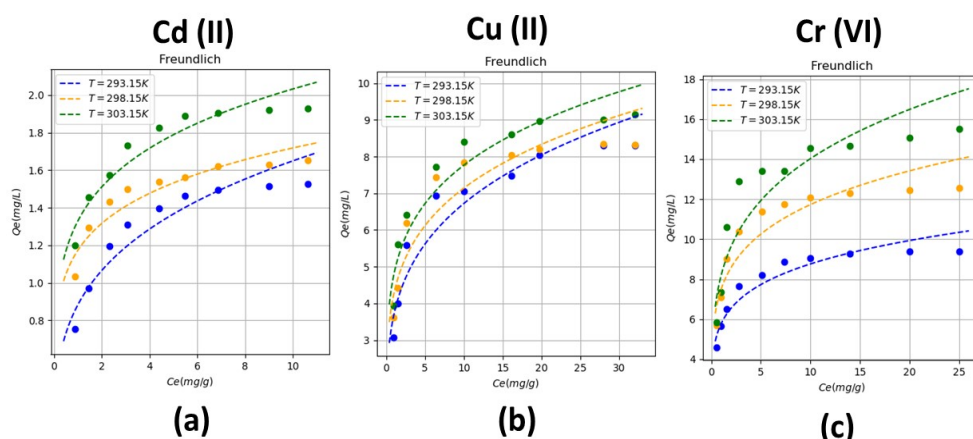
According to the studies conducted, it has been found that rice husk is a material widely used in heavy metal removal processes that demonstrates efficiency and facility in its application. This natural material is described as a viable alternative, economical and accessible to solve pollution problems of heavy metal affluent. Experimentally, the rice husk not requires an activation process to be used as a feasible material for the bio-adsorption process [43]. To use rice husk for the bio filter, the following physical-chemical properties are employed, and values are included in Table 2. For rice husk, the acid sites are more than basic sites. The acidic sites, because of their charge allow the actions to be attracted by the lignocellulosic material and be removed efficiently. The rice husk that is proposed as adsorbent material in the dual medium would not present any additional treatment if it were to be conducted experimentally, since with a simple washing the rice husk could be used as filter material. Additionally, no component was used to maximize specific area and pores.

**Table 2.** Texture and physicochemical properties [44].

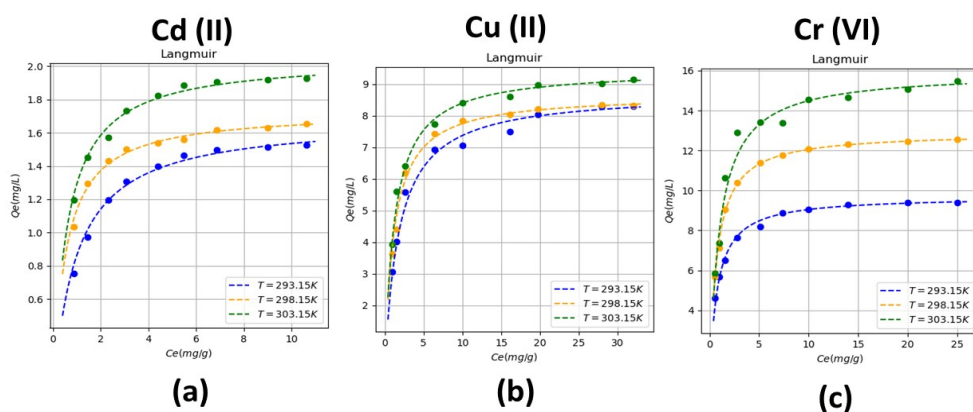
Property	Value
Specific area (m <sup>2</sup> /g)	1219
Pore volume (cm <sup>3</sup> /g)	0.59
Average pore diameter (nm)	2.23
Acid sites (meq/g)	0.70
Basic sites (meq/g)	0.28

### 3.2. Isotherm Varying Temperature

Figures 3 and 4 show Freundlich and Langmuir isotherms, respectively. In the isotherms, the temperature was varied 293.15 K (blue), 298.15 K (yellow) and 303.15 K (green) for Cd (II), Cu (II) and Cr (VI), respectively. For the isotherms, the constants corresponding to each type were calculated, as well as the correlation coefficient with which it is observed that isotherm best defines the adsorption process as shown in Table 3. The isotherm that best describes the proposed bio-filter process is the Langmuir isotherm, because comparing the correlation coefficients, those of Langmuir are better (Table 3 shows that the Langmuir coefficients compared to those of Freundlich are much higher, showing that it is the type of isotherm that best defines the adsorption process of the metals Cd (II), Cu (II) and Cr (VI), as also shown in Figure 4). In works reported experimentally for Cd (II), Cu (II) and Cr (VI), the isotherms that have been used to describe the adsorption process are those of Langmuir [30,41,45–47].



**Figure 3.** Isotherm of Freundlich at different temperatures (T) T = 303.15 K (green), T = 298.15 K (yellow) and T = 293.15 K (blue) for (a) Cd (II), (b) Cu (II) and (c) Cr (VI).



**Figure 4.** Isotherm of Langmuir at different temperatures (T) T = 303.15 K (green), T = 298.15 K (yellow) and T = 293.15 K (blue) for (a) Cd (II), (b) Cu (II) and (c) Cr (VI).



**Table 3.** Langmuir and Freundlich parameters.

Metal	Temperature	Freundlich			Langmuir		
		$K_f (\frac{L}{mg})$	$n$	$R^2$	$b(\frac{L}{mg})$	$q_{max}(\frac{mg}{g})$	$R^2$
Cd (II)	293.15 K	0.88293	3.68459	0.90350	1.05644	1.68010	0.99910
	298.15 K	1.17351	6.0386	0.87090	1.91261	1.73070	0.99980
	303.15 K	1.32962	5.42593	0.91110	1.70654	2.04960	0.99950
Cu (II)	293.15 K	3.70432	3.86249	0.91110	0.53886	8.74125	0.99870
	298.15 K	4.27891	4.49438	0.87770	0.83732	8.67302	0.99980
	303.15 K	4.80424	4.79386	0.89330	0.78222	9.46969	0.99970
Cr (VI)	293.15 K	5.77766	5.52791	0.91600	1.38389	9.69932	0.99990
	298.15 K	7.50673	5.15995	0.86850	1.42463	12.90322	1
	303.15 K	8.19726	4.28816	0.84310	1.01290	15.92356	0.99920

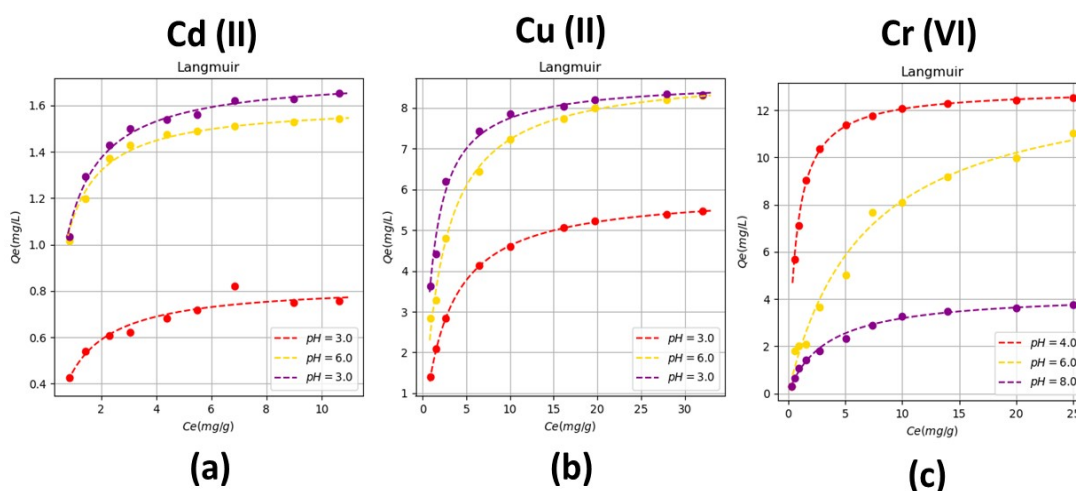
The efficiencies for each metal at different temperatures are presented below in Table 4.

**Table 4.** Efficiencies of each metal varying temperature.

Heavy Metal	Temperature (K)		
	293.15	298.15	303.15
Cd (II)	68.7%	86.21%	86.21%
Cu (II)	67.11%	89.49%	89.49%
Cr (VI)	59%	66.37%	73.75%

### 3.3. Isotherm Varying pH

Figure 5 shows the Langmuir isotherms, taking pH values of 3.0, 6.0 and 9.0, for Cd (II) and Cu (II), for Cr (VI) pH values of 4.0, 6.0 and 8.0. Only the Langmuir isotherms are shown since according to Table 5 and the previous Figures they are the isotherms that best describe the adsorption of heavy metals on the rice husk. It is very important to take this variable into account in the aqueous medium. For values of  $pH > 4.5$ , cations are absorbed and at pH values between 1.5 and 4, anions are removed. Type I isotherms, as in the figure, is limited by the completion of a single monolayer of adsorbate at the adsorbent surface. Adsorption in all other types do not reach a limit corresponding to the completion of a monolayer.

**Figure 5.** Isotherm of Langmuir at different pH values (a) Cd (II), (b) Cu (II) and (c) Cr (VI) at 298.15 K.

**Table 5.** Langmuir and Freundlich parameters for the isotherms varying the pH.

Metal	pH	Freundlich			Langmuir		
		$K_f (\frac{L}{mg})$	n	$R^2$	$b (\frac{L}{mg})$	$q_{max} (\frac{mg}{g})$	$R^2$
Cd (II)	3.0	0.47864	4.37445	0.90680	1.22282	0.83015	0.99280
	6.0	1.13099	6.51041	0.86450	2.27412	1.60720	0.99980
	9.0	1.17351	6.03864	0.87090	1.91261	1.73070	0.99980
Cu (II)	3.0	1.77588	2.75406	0.93340	0.34604	5.95592	0.99990
	6.0	3.19280	3.25097	0.94230	0.43626	8.88099	0.99980
	9.0	4.27891	4.49438	0.87770	0.83732	8.67302	0.99980
Cr (VI)	4.0	7.50673	5.15995	0.86850	1.42463	12.90322	1
	6.0	2.12208	1.85288	0.96440	0.14996	13.60544	0.96740
	8.0	1.05580	2.23964	0.95960	0.29829	4.25531	0.99770

Table 5 shows the Langmuir and Freundlich parameters for the isotherms varying the pH. According to the correlation coefficients, the isotherm that best describes the process is Langmuir's, the same as for isotherms varying in temperature. In the case of Cd (II) and Cu (II) with increasing pH,  $q_{max}$  increases, showing that at a basic pH the removal of these metals is favored. In the case of Cr (VI) the maximum of  $q_{max}$  is presented for pH = 4.0 since Cr (VI) can behave as Cr (III) under certain conditions of temperature and pH. Regarding the parameter b that indicates the affinity of the rice husk sites, a pH = 9.0 is favored for Cd (II) and Cu (II) and for Cr (VI) with a pH = 4.0.

Carrying out the calculations, it was found that, for the temperature established by Table 3 and the different pH values. Table 6 shows the efficiencies obtained.

**Table 6.** Efficiencies of each metal varying pH.

Heavy Metal	pH		
	3.0	6.0	9.0
Cd (II)	83.21%	86.21%	86.21%
Cu (II)	67.11%	89.49%	89.49%
pH	4.0	6.0	8.0
Cr (VI)	92.18%	81.12%	36.87%

In studies conducted, it was found that, for Cr (VI) at pH = 5.0, percentages of 96% are calculated. In the case of Cd (II), the pH value for an efficient elimination is given with a value close to 5.5 and for the case of Cu (II) with a pH of 4.5, there is a range between approximately 60% and 90% efficiency [42]. Comparing the results obtained with those reported in the literature, it is observed that the efficiencies obtained are lower. This behavior is because the rice husk proposed as a filtering medium only requires a wash to be used in the filter, preventing a subsequent contamination. For example, there are reports showing efficiencies of 99% using rice husk [16]. The high efficiency is attributed to the use of an acid for the activation of the lignocellulosic material, which causes the material to be removed but the water leaves with acid residues. Table 7 shows the values of the final concentrations of the materials based on the efficiencies shown in Table 6.

**Table 7.** Final concentrations of the heavy metal in rice husk.

Heavy Metal	Concentrations after Filtering (mg/g)
Cd (II)	9.35
Cu (II)	28.72
Cr (VI)	23.02



### 3.4. Efficiency Comparison

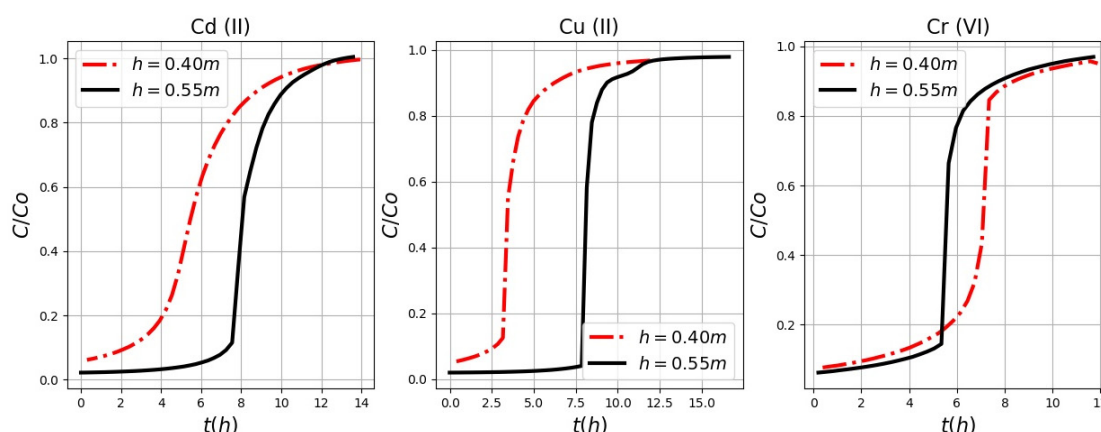
Table 8 is shown below, in which the efficiencies obtained in this work are compared with those reported in the literature for different lignocellulosic materials such as coffee, orange peel, sheep wool and banana peel. Showing that for Cd (II) there are higher efficiencies using orange peel, sheep wool and banana peel which is since these materials are chemically modified to improve their removal efficiencies, with a disadvantage that they generate secondary compounds that contaminate again. In the case of Cu (II) compared to the other four lignocellulosic materials, the rice husk has less efficiency, indicating that for this metal, other types of materials would be more effective, but one of the bases for modeling the filter with rice husk is that this material does not require activation processes and can be used with a simple wash. Finally, for Cr (VI) the highest efficiency was presented for the rice husk, showing that it manages to trap Cr better than the other lignocellulosic materials.

**Table 8.** Comparison of efficiencies of rice husk with other lignocellulosic materials.

Heavy Metal	Hice Rusk	Coffee [34,48]	Orange Peel [49–51]	Sheep Wool [51,52]	Banana Peel [53–55]
Cd (II)	86.21%	83.5%	90%	87%	89%
Cu (II)	89.49%	97%	91%	85%	72%
Cr (VI)	92.18%	86.66%	87.6%	90%	88%

### 3.5. Breaking Curve

Figure 6 shows the rupture curves that were plotted for the lignocellulosic material at a temperature of 303.15 K, for Cd (II) (a) and Cu (II) (b), with pH = 9.0; for the case of Cr (VI), at T = 303.15 K and pH = 4.0. Figure 6 presents two height values,  $h = 0.40$  and  $h = 0.55$  m, showing that, for the case of 0.40 m, the area of material transferred is much smaller than for 0.55 m, for Cd (II) and Cu (II); nevertheless, for Cr (VI), the behavior is in opposition. For the rupture curves, there are characteristic parameters such as the breaking time ( $t_b$ ), that is in the range 0.01 at 0.5 for  $C/C_0$ . At this time, useful capacity of the bed is reached, while the saturation time ( $t_s$ ) that is in the range 0.95 at 0.99 for  $C/C_0$ , indicates the time for having the total capacity of the bed is reached. The values of  $t_b$  for Cd (II), Cu (II) and Cr (VI) shows in Table 9.



**Figure 6.** Breaking curves varying height  $h = 0.40$  m (points and line) and  $h = 0.55$  m (solid line) (a) Cd (II) with T = 303.15 K and pH = 9.0 (b) Cu (II) with T = 303.15 K and pH = 9.0 and (c) Cr (VI) with T = 303.15 K and pH = 4.0.

**Table 9.**  $t_b$  varying height for Cd (II), Cu (II) and Cr (VI).

Heavy Metal	Height (h)	$t_b$ (h)
Cd (II)	0.40	5
	0.55	8
Cu (II)	0.40	7.68
	0.55	3.48
Cr (VI)	0.40	7.8
	0.55	5.61

#### 4. Discussion

Varying the temperature, taking the Langmuir isotherm as a reference, it indicates that the adsorption process occurs when a monolayer of the absorbed metal is formed, reaching a saturation point until a quantity of the metal is absorbed. In addition, it indicates that there is an interaction between the molecules adsorbed on the surface of the rice husk, the interactions happen by mechanism such as ion exchange. It is also observed that adsorption occurs at specific active sites that are located on the surface of the rice husk as shown in the filter's operating scheme (Figure 2). Regarding the coefficients that describe the behavior of the Langmuir isotherm, we have  $b$  that represents the affinity of the binding sites, which for each metal presents its maximum value at room temperature (298.15 K) and  $q_{max}$  is the maximum capacity of adsorption of the bio sorbent, which increases with the temperature value showing that up to 303.15 K the bio-filter works correctly, This is due to the fact that at the reported temperatures (293.15, 298.15 and 303.15 K) the lignocellulosic material (rice husk) does not deteriorate and does not lose its absorption capacity, if the temperature were increased, there could be inconveniences in terms of to the functioning of the bio-filter that could be evidenced in its adsorption capacity.

According to the isotherms varying the pH, these isotherms describe adsorption processes with microporous solids, which have a very fine porous structure as rice husk. These results indicate that there is a formation of a layer composed of the heavy metal removed, which in this case can be Cd (II), Cu (II) or Cr (VI), which occurs in adsorption. The pH values that favor removal are higher than 4.5; for Cd (II) and Cu (II), this behavior is observed. On the other hand, for Cr (VI) absorption is favored at pH values lower than 4, this is since Cr (VI) has different valences and in some cases, it behaves like Cr (III).

According to the rupture curves it is obtained that the capacity at the breaking point increases with the increase in height. The cycle time exhibits typical values between 2 and 24 h; after this time, the lignocellulosic material stops filtering with the same efficiency. These results indicate that useful height values may be 0.55 m for Cu (II) and Cd (II). If the height values are reduced, the effect of the axial dispersion phenomenon in the mass transfer predominates; therefore, the metal ions do not have enough time to diffuse throughout the mass of the adsorbent. With a major height, the surface area of the adsorbent contains more binding sites for adsorption. In this type of filter, the water flows through a bed of gravel and sand for long distances, which increases the probability of the solid has contact with other suspended particles, and with the medium formed on the surface of the gravel granule or sand, being thus retained between the filtering material. Later, heavy metals are suspended in the lignocellulosic material. The metal ions must have enough time to be removed and thus improve the adsorption capacity of the lignocellulosic material which in this case is the rice husk. Therefore, the higher height favors the removal of heavy metals. For the study of the Cu (II) removal in a theoretical way, different bed heights were evaluated, finding that the bed height can only determine the total sorption capacity of a fixed bed, which is directly related to the length of service time. This implies that the bed height is one of the main operational factors that control the effluent concentrations of target contaminants in practical field applications [56].

For Cr (VI), the removal is less efficient, since a smaller height should be used compared with Cd (II) and Cu (II). The chromium may be retained in the following forms: adsorbed (Cr (VI) and Cr (III)), precipitated and bioaccumulated in the support, in the cell membrane and in the metabolites produced by microorganisms [57]. Therefore, in the case of Cr (VI) it is not enough only to make changes in the height, they must be considered in the other forms that Cr (VI) can be presented since it decomposes in several ways.

## 5. Conclusions

The application of bio-adsorption in the purification of waters polluted by heavy metals presents a great potential, since lignocellulosic materials can be obtained in large quantities, are cheap and can selectively remove Cd (II), Cu (II) and Cr (VI) of aqueous solutions. The results obtained allow to conclude that rice husk is a good alternative for the implementation of filters with the capacity to remove Cd (II), Cu (II) and Cr (VI) with efficiencies of 83.21%, 67.11% and 92.18%, respectively, for certain values of the height of the filter, temperature and pH. At higher height values, the rupture curves show that the removal process occurs over a longer period and therefore the process is more efficient. Except for Cr (VI) which, depending on the interactions with the medium, can be converted into Cr (III) and presents a different behavior than for Cd (II) and Cu (II).

### Perspectives

The simulation of the bio-filter using the Thomas model, Bohart-Adams model and Yoon-Nelson model is anticipated as future work. The above, in order to compare the operating parameters of the filter A, possible real-world applications would be in the tributaries near the mining areas in Colombia in regions such as Cordoba, Antioquia or Norte de Santander, which have, as a product or heavy metal by-product, Cd (II), Cu (II) and Cr (VI). It is proposed to use in these regions because they are the ones with the highest concentration of heavy metals in the country.

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