Design of a Fixed-Bed Column with Vegetal Biomass and Its Recycling for Cr (VI) Treatment

Uriel Fernando Carreño Sayago 1,*, Yineth Piñeros Castro 2 and Laura Rosa Conde Rivera 3

1 Engineering Faculty, Fundación Universitaria Los Libertadores, Bogotá 111221, Colombia
2 Sustainable Processes and Products Area, Universidad Jorge Tadeo Lozano, Bogotá 110311, Colombia
3 Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Bogotá 111321, Colombia

* Correspondence: ufcarreno@libertadores.edu.co

Abstract: The aim of this work is to design a fixed-bed column with vegetal biomass of *Eichhornia crassipes* and the process of recycling it for treatment via the adsorption of water loaded with chromium (VI). In the first stage, the relationship between the fixed-bed density and the microparticle density is calculated, giving a model for the design of the fixed bed. Using this model, two systems for the treatment of Cr (VI)-contaminated water were designed and built. The vegetable biomass at three particle diameters of 0.212 mm, 0.30 mm and 0.45 mm was evaluated in the removal of Cr (VI) from water using the designed fixed-bed systems, giving the best removal of Cr (VI) with the lowest size particles and allowing the validation of the proposed model with the Thomas model. The incorporation of iron into the biomass allowed for the treatment of near 2.0 L of polluted solution, removing around 90% of Cr (VI), while it was only possible to treat nearly 1.5 L when using raw biomass, removing around 80% of Cr (VI). The recycling of the biomass was achieved via the elution of Cr (VI) with EDTA, permitting the reuse of the material for more than five treatment cycles.

Keywords: *E. crassipes*; chromium (VI); fixed bed; biomass; recycling

1. Introduction

The treatment of industrial wastewater must be an imperative goal in all organizations that release pollutants in their effluents. These are loaded with colorants, fats, and toxic metals, among other elements, causing serious environmental and social impacts on water bodies in an almost irreversible way [1]. One of the most concerning toxic metals is chromium in the state (VI), dangerous to nature and human health due to its capacity to alter the genome of cells [2–5].

Numerous pieces of research have been performed using adsorbent materials, such as cellulose, to remove toxic metals, intending to find an ideal water treatment that is economical and highly efficient [6]. *Eichhornia crassipes* is an aquatic plant, abundant in ecosystems contaminated with organic matter that is discarded as waste in Latin America [7]. Dry and crushed biomass, especially the roots of this plant, has been used to build treatment systems to remove Cr (VI) from water on a pilot scale, obtaining promising results [8]. This plant contains a large amount of cellulose and hemicellulose of 80% [9]. Cellulose has hydroxyl groups (OH) where a chemical exchange of toxic metals takes place, favoring metal removal [10]. Furthermore, the addition of iron chloride to the biomass generates its gradual oxidation with Fe0, charging it negatively and allowing the formation of chelate complexes between toxic metal ions and the oxidized sites [11].

To assess the performance of the adsorbent material, experiments using an adsorbent fixed bed and the continuous feeding of pollutant solution to obtain rupture curves, under specific operating conditions, are carried out. The experimental arrangement is similar to the ones used in industry. The behavior depends on the adsorption kinetics, adsorption capacity, and hydraulic factors. Whenever possible, these tests should be carried out on
a pilot scale [12,13] to assess the technical and economical feasibility of the process, as well as to determine the optimal operating parameters for the design of the system at an industrial scale [14,15]. The experimental adjustment and calibration of the continuous treatment systems under certain pollutant loads and flows are performed simultaneously with performance simulation using mathematical models, suitable for industrial system designs [16,17]. The mass balance has been used successfully to predict rupture curves, calibrate the input load, and meet discharge standards, being the main way to model and define the designs of treatment systems [18,19].

To improve the sustainability of the adsorption treatment system, it is imperative to incorporate elution stages to recover the adsorption capability of the adsorbent and reuse it in several treatments. An elution agent that could be used to remove chromium from biomass is ethylenediaminetetraacetic acid (C$_{10}$H$_{16}$N$_2$O$_8$), EDTA, which forms chelating complexes with heavy metals, such as Cr (VI) [20,21].

The aim of this work is the development of a continuous flow system for the treatment of water contaminated with Cr (VI) through biomass of E. crassipes (EC) and modified biomass incorporating iron chloride (ECFe). A model for the design of the treatment system, which satisfies the material balance, is proposed through the relationship between the density of the treatment bed and the density of the microparticle. Thus, two designed treatment systems are evaluated that use biomass at different particle diameters. The fresh and spent biomass are characterized through scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS) to verify the loading of the biomass with the pollutant. Finally, the reuse of biomass is evaluated by incorporating elution stages with EDTA.

2. Materials and Methods

2.1. E. Crassipes Acquisition and Conditioning

Samples of discarded dead E. crassipes plants from a wetland located in the municipality of Mosquera, on the outskirts of Bogotá D.C., were collected. Subsequently, the EC was washed with water, using all of the plant (stem, leaves and roots). Then, it was dried at 70 °C for 48 h to remove moisture and ground to a diameter of 0.212 mm. The pulverized biomass was sieved through a set of standardized meshes to obtain different particle sizes.

2.2. Preparation of Cr (VI) Solutions

A 1000 (mg/L) Cr (VI) stock solution was prepared with distilled water using potassium dichromate. This stock solution was used to prepare the test solutions of 100 and 400 Cr (VI) mg/L.

2.3. Obtaining Iron-Modified Biomass

The crushed E. crassipes biomass was mixed with an iron chloride solution at a biomass-to-solution ratio of 10:1 (w/w). The solution was prepared based on [22].

2.4. Development of Fixed-Bed Column

A fixed-bed column (Figure 1) was built with recycled polyethylene terephthalate (PET) bottles that were cut at the base area to create three compartments connected in series, with a maximum diameter of 4 cm and a height of 6 cm. Holes in the lid located at the bottom of each compartment were opened to control the flow, and a mesh was placed so that the biomass did not pass through. Each compartment was loaded with 16.5 g of adsorbent E. crassipes material.

A continuous flow of Cr (VI) aqueous solutions with pH 6 was fed continuously into the compartment located at the top of the system, at a flow rate of 25 mL/min. Samples of the effluent solution were taken at the bottom of the system at different times to follow the evolution of the Cr (VI) concentration. All of the tests were carried out in duplicate, calculating the average between the Cr (VI) concentrations at each time.
2.5. Process Experiments

To establish the best relationship between the density of the adsorbent bed and the density of the microparticle, an experiment was carried out using three microparticle sizes, namely 0.212 mm, 0.300 mm and 0.450 mm, which were obtained by sieving the dry and crushed biomass through a set of standardized meshes (40, 50, 60 and 70 meshes).

For this experiment, Cr (VI) aqueous solutions of 400 mg/L and 100 mg/L were used to feed the fixed-bed column, with 80 mL occupied by the biomass in the system.

2.6. Cr (VI) Measurement

The Cr (VI) concentration in water was quantified through the diphenyl carbazide method, following the American Public Health Association (APHA) procedure for standard tests (standard methods for the examination of water and wastewater).

A 100 µL aliquot of the sample was placed in an Eppendorf tube (200 µL), adding diphenyl carbazide solution (0.5% P/V acetone) and 900 µL of phosphate buffer (pH 2). The homogenized sample was placed in a quartz measurement cell and the absorbance of the solution at 540 nm was measured in an Evolution 300 Spectrophotometer (Universidad Jorge Tadeo Lozano, Bogotá D.C., Colombia). Each sample was analyzed in triplicate.

2.7. Elution Assays with EDTA

After the biomass saturation of each treatment, the feed of Cr (VI) solution was suspended, the remaining solution in the fixed bed was allowed to drain, and the biomass was kept in the fixed-bed column. Subsequently, an EDTA solution (0.1 g/mL) was allowed to flow through the biomass bed during 20 min at a flow rate of 15 mL/min.

2.8. Biomass Characterization

The biomass samples were analized in a scanning electron microscope integrated to an X-ray energy-dispersion spectroscopy microanalysis system (SEM-EDS, Universidad de los Andes, Bogotá D.C., Colombia). EDS is an efficient technique for the qualitative and quantitative analysis of elements’ contents in organic samples.

Figure 1. Treatment system configuration.
2.9. Model Evaluation

Mathematical modeling was used to describe the behavior of the rupture curves, which helps to understand and scale the system. Three different column adsorption models, Yoon-Nelson, Thomas and Bohart, were fitted to the data of the breakthrough curves to explain the biosorption process of Cr (VI) by EC-Na and EC-X in the fixed-bed configuration.

The Thomas model was used to estimate the maximum adsorption capacity and predict the rupture curves, assuming a second-order kinetic of reversible reactions, and the Langmuir isotherm [23]. This is one of the most representative models in the literature, and was also used to validate the proposed model.

The Yoon-Nelson model assumes that the adsorption rate decreases proportionally to the adsorbate removal and adsorbent breakdown curve, without considering information such as the adsorbate properties, adsorbent type, and adsorption column specifications [23].

The Bohart equation that describes the relationship between \( \frac{C}{C_0} \) and \( t \) in a continuous system has been widely used to describe and quantify other types of systems. This model assumes that the sorption rate is proportional to the residual capacity of the solid and to the concentration of the retained species, and is used to describe the initial part of the rupture curve. Table 1 shows the different adsorption models.

| Model               | Equation                                                                 |
|---------------------|---------------------------------------------------------------------------|
| Thomas model        | \( \ln \left( \frac{C}{C_0} \right) - 1 = \frac{K_{th} \times q \times m}{Q} - K_{th} \times C_0 \times T_b \) |
| Yoon model          | \( \frac{C}{C_0} = \frac{1}{1 + \exp \left( -K_{yn}(y - T_b) \right)} \)     |
| Bohart model        | \( T_b = \frac{N_o}{Q} \cdot Z - 1 \ln \frac{1}{1 + \frac{1}{K_{bo} \times C_0}} \ln \left( \frac{C_0}{C} - 1 \right) \) |

\( C_0 \): initial concentration of Cr (VI); \( C \): final Cr (VI); \( V \): volume; \( K_{th} \): Thomas constant (mL/mg · min); \( q \): adsorption capacity (mg Cr/g biomass); \( m \): mass of biomass in column (g); \( Q \): flow rate through the column (mL/min); \( T_b \): time of rupture (min); \( K_{yn} \): Yoon and Nelson constant (1/h), \( q \): dynamic capacity (mg/dm\(^3\)); \( Z \): bed height (cm); \( U \): linear flow rate (cm/min); and \( K_{bo} \): Bohart constant (1/h).

3. Results

Analysis of SEM: The evaluation of SEM (Universidad de los Andes, Bogotá D.C., Colombia) shows the characterization of the aquatic plant \( E. crassipes \), observing large amounts of carbon and oxygen, and the other elements evaluated showed traces, resulting in robustness and similar characteristics to those found in [24].

Figure 2 shows a characteristic image of the biomass of EC, where a porosity with a rough surface texture is observed.

Table 2 shows the physicochemical characterization of the EC sample, obtained through EDS.

| Element       | Weight | Percentage % |
|---------------|--------|--------------|
| Carbon        | 42.64  | 52.67        |
| Oxygen        | 44.15  | 40.94        |
| Sodium        | 2.13   | 1.37         |
| Manganese     | 0.31   | 0.19         |
| Potassium     | 1.45   | 0.55         |
| Calcium       | 2.16   | 0.80         |

In the microphotography of Figure 2b, different colored dots can be seen that represent the elements in the samples: blue dots represent carbon, yellow dots represent oxygen, and green dots represent the places where chromium (VI) lodged.

In Figure 3, different colored dots can be seen that represent the elements in the samples: green dots represent carbon, red dots represent oxygen, and yellow dots represent...
the places where iron lodged. Similar observations show that iron remains attached to the biomass of EC to help the chemisorption process [22].

![Figure 2](image1.png)

**Figure 2.** Biomass before (a) Cr (VI) adsorption; biomass of EC with Cr (VI) in (b).

![Figure 3](image2.png)

**Figure 3.** Micrograph of ECFe (a) fresh biomass (b) after Cr (VI) adsorption.

Additionally, in the micrograph (Figure 3b) of ECFe with Cr (VI), it is possible to confirm this information because you can see points of different colors that represent the elements in the samples: yellow points represent iron, red points represent oxygen, green points represent carbon, and purple points represent the places where chromium (VI) is present.

The use of iron (Fe) (III) chloride in vegetable cellulose has been used for the treatment of organic and inorganic contaminants. The (Fe) (III) reacts with hydratable hydroxyl cellulose, forming iron hydroxides (FeOOH); these are responsible for the cation exchange with heavy metals. The metal ions enter the interior of *E. crassipes* with FeOOH, exchanging with protons of hydroxyl groups. The ionic interaction was mainly responsible for the adsorption of As (III), As (VI) and Cr (IV). Figure 4 shows the reaction of cellulose with iron chloride (FeCl), forming iron hydroxides (FeOH) [22,23], represented in Figure 4.
Additionally, in the micrograph (Figure 3b) of ECFe with Cr (VI), it is possible to confirm this information because you can see points of different colors that represent the elements in the samples: yellow points represent iron, red points represent oxygen, green points represent carbon, and purple points represent the places where chromium (VI) is present.

The use of iron (Fe) (III) chloride in vegetable cellulose has been used for the treatment of organic and inorganic contaminants. The (Fe) (III) reacts with hydratable hydroxyl cellulose, forming iron hydroxides (FeOOH); these are responsible for the cation exchange with heavy metals. The metal ions enter the interior of E. crassipes with FeOOH, exchanging with protons of hydroxyl groups. The ionic interaction was mainly responsible for the adsorption of As (III), As (VI) and Cr (IV). Figure 4 shows the reaction of cellulose with iron chloride (FeCl), forming iron hydroxides (FeOH) [22, 23], represented in Figure 4.

Table 3 shows the characterization of the elements, and it can be observed that 8% of the weight in the sample was iron.

Table 3. Physicochemical characterization of the ECFe sample.

| Element | Weight | Percentage % |
|---------|--------|--------------|
| Carbon  | 31.64  | 46.67        |
| Oxygen  | 39.15  | 42.34        |
| Iron    | 26.13  | 8.37         |

When reacting with cellulose, iron chloride (FeCl₃) progressively oxidizes it, creating more active sites for heavy metal adsorption [22]. Chlorine reacts with the hydrogen in the biomass, creating (HCl) compounds; this is the reason why this biomass of ECFe tends to be acidic [23].

The elimination of metal ion species by Fe was explained by their adsorption on the surface of the corrosion of the biomass of the original Fe particles. Therefore, when contacting a solution, Fe (0) gradually oxidizes plant cellulose, allowing the ions of different heavy metals to form internal sphere complexes with oxidized sites [25].

The pollutant Cr (VI), in the form of dichromate (Cr₂O₇⁻), has a complex chemical structure; when it meets the biomass of ECFe there are reactions of the (H⁺) of the biomass together with the oxygens of the structure of chromium (VI), reducing it to Cr (III) and chromium oxide (Cr₂O₃) through two mechanisms. The first mechanism consists of direct reduction, in which the Cr (VI) was reduced to Cr (III) in the aqueous phase through contact with the electron donor groups present in the biomass, such as (OH) [26] (see Figure 5).

Figure 5 is a representation of the reduction of Cr (VI).

The second mechanism is indirect reduction, in which three stages are identified: (1) the binding of the anionic species of Cr (VI), with the functional groups present on the surface of the biomass being positively charged; (2) the reduction from Cr (VI) to Cr (III) via the adjacent electron donor groups; and, finally, (3) the release of Cr (III) ions in the aqueous phase due to the repulsion between the positively charged groups and the Cr (III) ions, or by the complexation of Cr (III) with adjacent groups capable of binding Cr. In conclusion, the mechanism of the removal of Cr (VI) by biomaterials is a combined mechanism between adsorption and reduction [27, 28]. In Figure 6, the process of the adsorption of Cr (III) by iron-modified cellulose can be seen.

Through Figure 6, it is shown that when reacting with the cellulose, the iron chloride, FeCl₃, progressively oxidizes it, creating active sites for the adsorption of heavy metals; the chlorine reacts with the hydrogen of the biomass, creating compounds (HCl). The representative weight of iron in this ECf biomass is 8.3% (see Table 3).

Table 4 shows the physicochemical characterization of the ECFe sample with Cr (VI).
The relationship between cellulose ECFe and Cr (VI) is shown in Table 4, with weights of 7.4 for Cr (VI) and 7.9 for Fe. The chemical reaction is represented through the following:

\[
[3(C_6H_{10}O_6)] \cdot 4\text{FeOOH} + \text{Cr}_2\text{O}_7^{2-} \rightarrow [3(C_6H_{10}O_6)] \cdot 4\text{FeOOH} \cdot \text{Cr}_2 + 7\text{H}_2\text{O}
\]

where \([3(C_6H_{10}O_6)] \cdot 4\text{FeOOH}\) represents the ECFe biomass and \(\text{Cr}_2\text{O}_7^{2-}\) represents Cr (VI); it can be seen from both Figures 5 and 6 that three parts of glucose react with dichromate.

Before the process of recycling the biomass with EDTA, microphotography was performed with the goal of knowing about the biomass modification. Figure 7 shows the biomass before the process of elution with EDTA.

**Figure 5.** Representation of Cr (VI) reduction to Cr (III).

**Figure 6.** Representation of Cr (VI) adsorption.

**Table 4.** Physicochemical characterization of the ECFe sample after treatment.

| Element     | Weight | Percentages % |
|-------------|--------|---------------|
| Carbon      | 37.6   | 50.67         |
| Oxygen      | 30.3   | 38.94         |
| Chromium    | 17.13  | 7.4           |
| Iron        | 12.23  | 7.9           |

The relationship between cellulose ECFe and Cr (VI) is shown in Table 4, with weights of 7.4 for Cr (VI) and 7.9 for Fe. The chemical reaction is represented through the following:

\[
[3(C_6H_{10}O_6)] \cdot 4\text{FeOOH} + \text{Cr}_2\text{O}_7^{2-} \rightarrow [3(C_6H_{10}O_6)] \cdot 4\text{FeOOH} \cdot \text{Cr}_2 + 7\text{H}_2\text{O}
\]

where \([3(C_6H_{10}O_6)] \cdot 4\text{FeOOH}\) represents the ECFe biomass and \(\text{Cr}_2\text{O}_7^{2-}\) represents Cr (VI); it can be seen from both Figures 5 and 6 that three parts of glucose react with dichromate.

Before the process of recycling the biomass with EDTA, microphotography was performed with the goal of knowing about the biomass modification. Figure 7 shows the biomass before the process of elution with EDTA.

**Figure 7.** Micrograph of EC after the recycling process.
Figure 7 shows how EDTA delayed the Cr (VI) in the water; this sample is in the first process of elution with EDTA. Table 5 shows the physicochemical characterization of the EC sample after the recycling process.

**Table 5.** Physicochemical characterization of the ECFe sample after treatment.

| Element       | Weight | Percentages % |
|---------------|--------|---------------|
| Carbon        | 53.86  | 60.96         |
| Oxygen        | 45.62  | 38.76         |
| Chromium      | 0.25   | 0.14          |

Table 5 shows how the Cr (VI) is in form of 0.14%, showing the elimination with EDTA and the efficiency of this eluyent chemistry.

**Mass balance in the biofilter.** The biofilter is a treatment system in which biochemical diffusion processes occur inside it (see Figure 8).

In the process of the treatment represented in Figure 8, water contaminated with Cr (VI) is imperative for the adjusted design to be able to remove a significant amount of contamination. Important goals of the process are the retention, adsorption, and velocity of entering of system.

Adsorption is a special process in a treatment system with an adsorbent and biomass; the cationic interchange between the biomass of the EC and the Cr (VI) is represented through the following differential equation:

\[
\text{Adsorption} = \rho_b \frac{\partial q}{\partial t} \quad (1)
\]

where \( \partial q \) is the ability of the biomass to adsorb to remove heavy metals, determined by the load of milligrams of heavy metals above the grams of biomass used.

\[
\rho_b = \frac{M}{V} \quad (2)
\]
The density, \( \rho_b \), of the bed of the adsorptions is a principle parameter of the design; due to the relationship between it and the biomass use under the volume of this, it must have a value under 0.7 gr/mL with the goal of having better space, for the contaminant is lodged through the particle and favors adsorption [13]. The relationship between the density of the bed of treatment, \( \rho_b \), and the density of the micro particle of this biomass, \( \rho_p \), is represented through the following:

\[
\varepsilon = 1 - \frac{\rho_b}{\rho_p} \tag{3}
\]

where \( \rho_p \) is determined by the following:

\[
\rho_p = \frac{mp}{V_p} \tag{4}
\]

The mass of the microparticle is its weight, and the volume of the microparticle is obtained through the following:

\[
V_p = \frac{4\pi r^3}{3} \tag{5}
\]

where \( r \) is the radius of the biomass microparticles used in the treatment process [29], which is related to the densities and established that the relationship between \( \rho_b / \rho_p \) should be less than 0.5; in other terms, \( \varepsilon \) values greater than 0.6.

To comply with this design parameter of treatment processes through chemisorption, it is essential to use particle diameters less than 0.212 mm; with this diameter there would be a direct relationship with the pollutant particle.

The retention or accumulation in the treatment process is dependent on the relationship between the densities and the concentration of the pollutant that enters the treatment system:

\[
Acu = \varepsilon \times \frac{\partial C(VI)}{\partial t} \tag{6}
\]

where \( \partial C(VI) \) is the entry of the pollutant into the treatment system in terms of its initial concentration. The input to the treatment system is represented by the design speed and the amount of the pollutant that the treatment system can treat:

\[
Input = \frac{\partial Cr(VI)}{\partial t} \tag{7}
\]

With these equations the general balance of matter will be completed, which is summarized in Equation (7):

\[
\varepsilon \times \frac{\partial Cr(VI)}{\partial t} = \frac{\partial Cr(VI)}{\partial t} - \frac{M}{V} \times \frac{\partial q}{\partial t} \tag{8}
\]

Through Equation (8), the most important design parameters when treating water in adsorbent-based treatment processes could be adjusted, leaving Equation (9):

\[
V \times \varepsilon \times Co = Q \times Tb \times Co - Mq \tag{9}
\]

where \( V = \) system volume (mL), \( \varepsilon = \) ratio between densities, \( Co = \) initial concentration of Cr (VI) (mg/mL), \( Q = \) design flow (mL/min), \( Tb = \) break time (min), \( M = \) biomass used (g), and \( q = \) adsorption capacity of the biomass used (mg/g).

Depending on the most important parameters when building a treatment system, Equation (9) could be used in order to model and validate the best form of treatment; for example, the necessary amount of biomass to be used to treat a certain amount of initial pollutant was used in the present investigation to establish the adsorption capacity in these initial conditions of treatment.
Equation (10) can be used to determine the adsorption capacity:

\[ q = \frac{Q T b C_o}{M} - \frac{\varepsilon V C_o}{M} \]  

(10)

To solve this equation, preliminary experiments will have to be carried out in order to establish the relationship between the densities (\(\varepsilon\)); the capacity to retain chromium (VI) via the biomass of EC will be established later.

In the development of the fixed-bed column Equation (3) was used, with the goal of determining the relationships between densities.

When a desorption-elution process is involved for the reuse of biomass, Equation (10) would be as follows:

\[ q_T = \sum_{j=1}^{n} \left[ \frac{Q T b j C_o}{M} - \frac{Q T b j C_j}{M} - \frac{\varepsilon V C_o}{M} \right] \]  

(11)

where Q = design flow (mL/min), Tbj = break time of use number j (min), Co = initial concentration of Cr (VI) (mg/mL), C = final concentration Cr (VI) in the treated solution (mg/mL), \(\varepsilon\) = porosity, M = amount of biomass used (g), and \(q_T\) = total adsorption capacity of the biomass used (mg/g).

This model, Equation (11), is designed to determine the adsorption capacity when different elution processes have been carried out; it will be used to determine the new adsorption capacity and is one of the contributions of the present investigation. Result of process adsorption: Using Equation (3), we proceeded to develop the initial conditions of the treatment bed of fixed columns with dry and crushed material of EC and ECFe with the three diameter settings. Figure 9 shows the biomass yields of ECFe, with initial concentrations of 400 mg/L and 100 mg/L, respectively. These results are given by the average of the three pieces of data obtained in the experiment and have the bars of mistake product of standard deviation.

In the particle diameters via the treatment of water contaminated with Cr (VI), the best results were those with a diameter of 0.212 mm, treating around of 2 L of water; results with this particle diameter were reported by the authors of [12].

In the treatment processes with diameters of 0.3 mm and 0.425 mm, their removals were below that of a diameter of 0.25 mm; it has been evidenced that the smaller the particle, the better the contact with the contaminant, processes that were seen to be of equal magnitude in the treatment of EC (Figure 10).
In this process, remotions lower than those of ECFe were given, due to the fact that iron oxide, the organic material of cellulose, created more hydroxyl groups. The most significant diameter was 0.25 mm, though the diameters almost gave the same results in the processing of initial amounts of 100 mg/L.

Using these parameters, we proceeded to consider the relationship of the density of the bed of contact and the density of particles.

With these parameters, the density of particles to the same volume of particles with diameters of 0.25 mm is given:

\[ \rho_p = \frac{0.008 \text{ mg}}{0.00418 \text{ mm}} = 1.91 \text{ mg/mm} \]

The bed of treatment has the following relationship between these two densities [13]:

\[ \varepsilon = 1 - \frac{0.67}{1.91} = 0.64 \]

The densities were related and it was established that the relationship between them should be less than 0.5; in other terms, \( \varepsilon \) values greater than 0.6. Table 6 shows all of the parameters used in the experiment.

| Diameter (mm) | Bed Volume (mL) | Bed Mass (g) | Bed Density (g/mL) | Microparticle Volume (mm) | Mass of Particles (mg) | Particle Density (mg/mm) | \( \varepsilon \) |
|---------------|----------------|-------------|-------------------|--------------------------|------------------------|--------------------------|-----------|
| 0.25          | 80             | 50          | 0.67              | 0.008                    | 0.00418                | 1.91                     | 0.7       |
| 0.35          | 82             | 50          | 0.69              | 0.014                    | 0.018                  | 1.26                     | 0.5       |
| 0.425         | 84             | 50          | 0.7               | 0.0335                   | 0.028                  | 0.83                     | 0.3       |

According to Table 5, the relationships between these densities are some parameter fundamentals in the design of a system with an adsorbent bed. It is necessary for the density of the bed to have free space, with the objective of assimilating the contaminate, and the density of particles must have a direct relationship with the contaminate. Both types of biomass had the same results in terms of density.

Equation (10) was utilized to establish the capacity of adsorption in the process of treatment in bed adsorptions:

\[ q = \frac{150 \times 15 \times 0.4}{50} - \frac{0.7 \times 80 \times 0.4}{50} \]
where \( q \): capacity of adsorption, \( C_0 \): 0.4 mg/mL, \( M \): (ECFe) 50 g, \( T_b \): time rupture (min): 150 min, and \( Q \): caudal (mL/min).

In the treatment with ECFe, it was established that there was a treatment of 2.0 L with a rupture time of 150 min. A new adsorption capacity of 17.6 mg/g was obtained. In the treatment with EC, the graph can establish that there was a treatment of 1.5 L with a rupture time of 70 min, its adsorption capacity being 8.0 mg/g. Through this equation, acquiring a new interpretation of biomass being involved in the retention of heavy metals is possible; with the aim of establishing the viability of this equation, it was validated through the Thomas model.

**Mathematical models of adsorption.** Through the Thomas model, Equation (10) was validated and the comportment of the process of treatment was established. The Thomas model is used to estimate the maximum adsorption capacity and predict the breakdown curves; assuming the kinetics of second-order reversible reactions and the Langmuir isotherm [29–34], the representative equation is Equation (11).

The graphical representation is shown in Figure 10 of the fit to this mathematical model, where the Thomas constants of all the experimental processes are shown, of the initial 400 and 100 mg/L of Cr (VI), both for the EC and ECFe biomass. Two graphs were obtained for each biomass, and from each of these the adsorption constant was obtained.

Considering the results of Figures 9 and 10 of the adsorption process, for both the EC and ECFe biomass, there were interesting adjustments to this mathematical model of Thomas, with all of the \( R^2 \) being above 95%. Evidencing an adjustment to Langmuir’s isotherm and second-order kinetics, it could also be argued, in all processes, that there was a diffusivity in a monolayer of the biomass of EC and ECFe. This validated Equation (10), and, with the graph, it can determine that the adsorption capacity (\( q \)) and capacity of adsorption of the equation of the design were significant; therefore, both capacities were almost the same.

Table 7 shows the parameters of the equations of Thomas and the equation of the design.

**Table 7. Comparison of the parameters of the Thomas model and design model.**

|        | EC     | \( K_{th} \) | \( q \) (Thomas) | \( q \) Design |
|--------|--------|--------------|------------------|---------------|
| 400 mg/L | Iron   | 0.0537       | 17.9             | 17.6          |
| 400 mg/L | 0.10   | 8.33         |                   | 8             |

The table appreciated that the validations of the equation of the design were representative and adjusted.

Tables 6 and 7 show the summary of the Bohart, Yoon, and Thomas model counts, where they were the best representative adjustments of the different removals of Cr (VI) by the EC and ECFe biomass. In Table 8, the summary of the EC experiment is shown, where the counts found through the equations of the graphs in Figure 11 obtained averages around 0.048 (mL/mg min), this being their speed of Cr (VI) removal in the biofilter; in [30], the kinetics of *E. crassipes* were the same.

**Table 8. Summary of the experiments obtained with EC material.**

|        | EC     | Bohart | Yoon   | Thomas |
|--------|--------|--------|--------|--------|
| 400 mg/L | K      | 0.048  | 0.039  | 0.048  |
| 400 mg/L | \( R^2 \) | 0.9542 | 0.9444 | 0.954  |
| 100 mg/L | K      | 0.047  | 0.039  | 0.047  |
| 100 mg/L | \( R^2 \) | 0.89   | 0.89   | 0.96   |
It is seen in Table 9 that the Thomas constant obtained results in its adsorption rate of 0.068, demonstrating that this biomass adsorbs at a higher rate than the biomass of EC [31–36].

Table 9. Summary of the experiments obtained with ECFe material.

|         | ECFe  | Bohart | Yoon | Thomas |
|---------|-------|--------|------|--------|
| 400 mg/L| K     | 0.061  | 0.05 | 0.061  |
| 400 mg/L| R²    | 0.90   | 0.9444| 0.966  |
| 100 mg/L| K     | 0.060  | 0.039 | 0.060  |
| 100 mg/L| R²    | 0.89   | 0.89  | 0.94   |

Recycling process. The results concerning the elutions with EDTA are represented in Figure 11.

The original ECFe biomass capacity is 17.6 mg/g, and after the elution in the second process of treatment the capacity was 14.2 mg/g. Though being less, the process was significant; the third process was also important, with a capacity of 9.2 mg/g, finishing the process of the elutions with a capacity of 3 mg/g. It has one summation with Equation (10), validating all of the variables, this equation remains Equation (11):

\[ q(\text{ECFe}) = 17.6 + 14.2 + 9.2 + 3 + 2.8 = 46.8 \text{ mg/g} \]  

(12)

The EC biomass capacity was originally 8 mg/g, and after the elution in the second process of treatment the capacity was 6.5 mg/g; after the third and quarter process it was 5.6 for both, finishing the process of elutions with 4.2 mg/g. With Equation (11):

\[ q(\text{EC}) = 8 + 6.5 + 5.6 + 5.6 + 4.2 = 29.9 \text{ mg/g} \]  

(13)

The process of recycling with EDTA was very important due to it increasing the removals of the Cr (VI); in the ECFe biomass it has achieved reuse in more than four processes, increasing the process of treatment 2.7 times. In the case of EC the process increases 3.6 times.

Through Equation (11) and with different bibliographic references, representative data were obtained to feed this equation, determining the capacities of each of these biomasses together with the new capacities determining the desorption power of the different eluents shown and summarized in Table 10.
For the EDTA eluent and with Equation (10), satisfactory results were evidenced by removing Al (II), reaching almost 150% of its adsorption capacity, corroborating what was presented in the present investigation; additionally, the EDTA reagent obtained interesting yields in recycling cassava biomass, increasing up to 40 mg/g. The authors of [37] used the biomass of Phanera vahlii to remove Cr (VI), obtaining results of 30 mg/g, and with NaOH they reached capacities in the reuse process of this biomass up to 62 mg/g, reaching almost double of its total capacity. The authors of [40] also used NaOH for desorption processes with green-synthesized nanocrystalline chlorapatite biomass, achieving results of 75% more. The eluent HCl is also a good chemical agent to use in desorption processes, since it reached more than 100% in the reuse of biochar alginate for Cr (VI), but it is not so significant with A. barbadensis Miller biomass to remove Ni (II), and in [39] significant results were also obtained to remove Pb (II) with pine cone shell biomass. With the chemical agent HNO₃, interesting contaminant recycling processes were obtained, since more than 100% of the adsorption capacity of the biomass used in this process was used [41].

Mathematical models in recycling processes. The continuous desorption process with its fit to the Thomas model for ECFe biomass always shows the fit of this model with significance, because this type of model fits representatively to desorption processes with good performance [6]. It can also verify that with values of qt it is close to the experimental values of Equation (10) designed and presented in this research, indicating the validity of this equation again, where it reflects the maximum capacity obtained.

Table 11 shows a summary of the experiments obtained with ECFe material in the process of desorption.

## Table 10. Researchers of the process of desorption.

| Reference | Biomass | Contaminate Treated | Recycling | Capacity (mg/g) with Equation (11) |
|-----------|---------|---------------------|-----------|----------------------------------|
| Present article | ECFe | Cr (VI) | EDTA | 16 | 46 |
| Present article | EC | Cr (VI) | EDTA | 11 | 29 |
| [37] | Phanera vahlii | Cr (VI) | NaOH | 30 | 62 |
| [38] | A. barbadensis Miller | Ni (II) | HCl | 14 | 20 |
| [39] | Brown algae | Al (III) | EDTA | 12 | 30 |
| [40] | Green synthesized nanocrystalline chlorapatite | Cr (VI) | NaOH | 20 | 35 |
| [41] | Graphite | Cr (VI) | HNO₃ | 20 | 52 |
| [42] | Biochar alginate | Cr (VI) | HCl | 30 | 62 |
| [43] | Pine cone shell | Pb (II) | HCl | 22 | 30 |
| [44] | Brown algae | Cu (II) | CaCl₂ | 14 | 54 |
| [45] | Cassava | Cr (VI) | EDTA | 14 | 40 |

## Table 11. Summary of the experiments obtained with ECFe material in the process of recycling.

| Cycle | Model | Parameter | 1 | 2 | 3 | 4 |
|-------|-------|-----------|---|---|---|---|
|       | Thomas | R²       | 0.99 | 0.99 | 0.98 | 0.97 |
|       |       | kt       | 0.048 | 0.044 | 0.036 | 0.033 |
|       |       | qt       | 14.2 | 9.2 | 3.0 | 2.8 |
|       | Bohart | R²       | 0.88 | 0.98 | 0.97 | 0.9 |
|       |       | kb       | 0.962 | 0.854 | 0.804 | 0.77 |
|       | Yoon  | R²       | 0.9 | 0.8 | 0.94 | 0.93 |
|       |       | ky       | 0.944 | 0.88 | 0.80 | 0.75 |
In Table 12 the EC biomass had a different behavior, and in its second and third cycle it adjusted to the Yoon model and later to the Bohart model.

Table 12. Summary of the experiments obtained with material EC in the process of recycling.

| Cycle | Model | Parameter | 1     | 2     | 3     | 4     |
|-------|-------|-----------|-------|-------|-------|-------|
|       |       | R²        | 0.91  | 0.90  | 0.85  | 0.85  |
|       | Thomas| kt        | 0.038 | 0.034 | 0.025 | 0.022 |
|       |       | qt        | 6.5   | 5.6   | 5.6   | 4.2   |
|       |       | kb        | 0.862 | 0.854 | 0.77  | 0.66  |
|       | Bohart| R²        | 0.99  | 0.99  | 0.98  | 0.97  |
|       |       | qt        | 6.5   | 5.6   | 5.6   | 4.2   |
|       | Yoon  | R²        | 0.88  | 0.9   | 0.91  | 0.92  |
|       |       | ky        | 0.844 | 0.80  | 0.77  | 0.63  |

This behavior is due to the alkalinization of the biomass, and this process makes the biomass a little more unstable. The values of qt, although evidencing a resemblance, were not so representative due to the little adjustment that there was with respect to the Thomas model.

4. Discussion

ECFe biomass is an alternative for treating polluted waters thanks to its high Cr (VI) adsorption capacity and the possibility of a high number of reuses via elution with EDTA, with the benefit of low processing costs.

The relationship between the density of the bed and the density of particles is an important parameter in the design of fixed-bed adsorption systems. It is necessary for the density of the bed to have free space, allowing the assimilation of the contaminant. The density of the particle must have a relationship with the contaminant: the density of the fixed bed being above 0.7 mg/mL and the microparticle being 0.212 mm in diameter.

Depending on the most important parameters, Equation (9) can be used to model and validate the best treatment.

Two treatment systems were designed and tested using recycled PET containers (600 and 1000 mL), where Cr (VI) removal and desorption were carried out.

Thanks to its high Cr (VI) adsorption capacity, integrated with its high number of reuses by elution with EDTA and low production costs, the proposed system can become a tool that helps sustainability, leading to the compliance of the norms of discharges from the productive sector of tanneries, allowing the preservation of the water resources surrounding these production sites.

5. Conclusions

The proposed model can be used for designing adsorption treatment systems to remove pollutants from water. The designed system allowed for the removal of Cr (VI), demonstrating a beneficial effect of iron incorporation into biomass, bringing a removal capacity of 17 mg/g for ECFe and 8 mg/g for EC. The ECFe biomass treated almost 2.0 L of pollutant solution, removing around 90% of Cr (VI), while the treatment with raw EC treated nearly 1.5 L, removing around 80% of Cr (VI). The better performance of ECFe is attributed to the increase in sites for Cr (VI) adsorption due to the oxidation of the biomass with Fe⁰. The usage of elution stages of Cr (VI) with EDTA has a significant effect on the adsorption capability recovery of the biomass, such that it can be recycled and reused in the adsorption process more than four times with ECFe, and 2.7 times with EC.

Author Contributions: U.F.C.S. proposed the mathematical model, designed and built the treatment systems, executed the experimental design, and analyzed and interpreted the micrographs as well as the adsorption results. Y.P.C. proposed the experimental design and evaluated the adsorption results, while L.R.C.R. evaluated the Cr (VI) adsorption results and analyzed the mathematical model. All authors have read and agreed to the published version of the manuscript.
Funding: The “Universidad los Libertadores” funded this research through an internal call.

Data Availability Statement: The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Acknowledgments: In this section, you can acknowledge any support given which is not covered by the author contribution or funding sections. This may include administrative and technical support, or donations in kind (e.g., materials used for experiments).

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

References

1. Taka, A.L.; Klink, M.J.; Mbianda, X.Y.; Naidoo, E.B. Chitosan nanocomposites for water treatment by fixed-bed continuous flow column adsorption: A review. *Carbohydr. Polym.* 2020, 255, 117398. [CrossRef] [PubMed]

2. Yang, X.; Liu, Z.; Jiang, Y.; Li, F.; Xue, B.; Dong, Z.; Ding, M.; Chen, R.; Yang, Q.; An, T.; et al. Micro-structure, surface properties and adsorption capacity of ball-milled cellulose biomass derived biochar based mineral composites synthesized via carbon-bed pyrolysis. *Appl. Clay Sci.* 2020, 199, 105877. [CrossRef]

3. Yoshinaga, M.; Ninomiya, H.; Al Hossain, M.A.; Sudo, M.; Akhand, A.A.; Alim, A.; Khalequzzaman, M.; Iida, M.; Tajima, I.; et al. A comprehensive study including monitoring, assessment of health effects and development of a remediation method for chromium pollution. *Chemosphere* 2018, 201, 667–675. [CrossRef] [PubMed]

4. Ferreira, L.M.; Cunha-Oliveira, T.; Sobral, M.C.; Abreu, P.L.; Alpoim, M.C.; Urbano, A.M. Impact of carcinogenic chromium on the cellular response to proteotoxic stress. *Int. J. Mol. Sci.* 2019, 20, 4901. [CrossRef] [PubMed]

5. Sayago, U.F.C. Design of a sustainable development process between phytoremediation and production of bioethanol with *Eichhornia crassipes*. *Environ. Monit. Assess.* 2019, 191, 221. [CrossRef] [PubMed]

6. Bhatti, H.N.; Mahmood, Z.; Kausar, A.; Yakout, S.M.; Shair, O.H.; Iqbal, M. Biocomposites of polypyrrole, polyaniline and sodium alginate with cellululosic biomass: Adsorption-desorption, kinetics and thermodynamic studies for the removal of 2, 4-dichlorophenol. *Int. J. Biol. Macromol.* 2020, 153, 146–157. [CrossRef] [PubMed]

7. Carreño-Sayago, U.F.C.; Castro, Y.P.; Rivera, L.R.C.; Mariaca, A.G. Estimation of equilibrium times and maximum capacity of adsorption of heavy metals by E. crassipes. *Appl. Water Sci.* 2019, 9, 399–411. [CrossRef]

8. Sayago, U.F.C. Design and development of a biotreatment of *E. crassipes* for the decontamination of water with Chromium (VI). *Sci. Rep.* 2021, 11, 9326. [CrossRef] [PubMed]

9. Sayago, U.F.C.; Castro, Y.P.; Rivera, L.R.C.; Mariaca, A.G. Estimation of equilibrium times and maximum capacity of adsorption of heavy metals by *E. crassipes*. *Environ. Monit. Assess.* 2019, 192, 141. [CrossRef] [PubMed]

10. Yi, Z.J.; Yao, J.; Chen, H.L.; Wang, F.; Yuan, Z.M.; Liu, X. Uranium biosorption from aqueous solution onto *Eichhornia crassipes*. *J. Environ. Radioact.* 2016, 154, 43–51. [CrossRef] [PubMed]

11. Al-Ghouti, M.A.; Al-Absi, R.S. Mechanistic understanding of the adsorption and thermodynamic aspects of cationic methylene blue dye onto cellululosic olive stones biomass from wastewater. *Sci. Rep.* 2020, 10, 15928. [CrossRef]

12. Abdulrazak, S.; Hussaini, K.; Sani, H.M. Evaluation of removal efficiency of heavy metals by low-cost activated carbon prepared from African palm fruit. *Appl. Water Sci.* 2017, 7, 3151–3155. [CrossRef]

13. Deng, L.; Geng, M.; Zhu, D.; Zhou, W.; Langdon, A.; Wu, H.; Yu, Y.; Zhu, Z.; Wang, Y. Effect of chemical and biological degumming on the adsorption of heavy metal by cellulose xanthogenate prepared from *Eichhornia crassipes*. *Bioresour. Technol.* 2012, 107, 41–45. [CrossRef]

14. Zhou, Y.; Fu, S.; Zhang, L.; Zhan, H.; Levit, M.V. Use of carboxylated cellulose nanofibrils-filled magnetic chitosan hydrogel beads as adsorbents for Pb (II). *Carbohydr. Polym.* 2014, 101, 75–82. [CrossRef]

15. Kumar, V.; Singh, J.; Kumar, P. Regression models for removal of heavy metals by water hyacinth (Eichhornia crassipes) from wastewater of pulp and paper processing industry. *Environ. Sustain.* 2020, 3, 35–44. [CrossRef]

16. Purnomo, R.O. Delignifikasi Adsorben Dari Batang Eceng Gondok (*Eichhornia crassipes*). *Metode Batch. Diploma Thesis, Universitas Negeri Malang, Malang, Indonesia, 2018.*

17. Gaballah, M.S.; Ismail, K.; Aboagye, D.; Ismail, M.M.; Sobhi, M.; Stefanakis, A.I. Effect of design and operational parameters on the adsorption of heavy metal by cellulose xanthogenate prepared from *Eichhornia Crassipes*. *Int. J. Mol. Sci.* 2019, 20, 3152–3155. [CrossRef] [PubMed]

18. Mitra, T.; Singh, B.; Bar, N.; Das, S.K. Removal of Pb (II) ions from aqueous solution using water hyacinth root by fixed-bed and column and ANN modeling. *J. Hazard. Mater.* 2014, 273, 94–103. [CrossRef] [PubMed]

19. Aydına, S.; Nura, H.M.; Traorea, A.M.; Yıldırım, E.; Emik, S. Fixed bed column adsorption of vanadium from water using amino-functional polymeric adsorbent. *J. Desalination Water Treat.* 2021, 144, 155–159. [CrossRef]

20. Worch, E. Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling; Walter de Gruyter: Berlin, Germany, 2012.
22. Benítez, L.T.; Tovar, C.T.; Bolívar, W.M.; Ortiz, Á.V. Estudio de modificación química y física de biomasa (Citrus sinensis y Musa paradisica) para la adsorción de metales pesados en solución. Rev. Luna Azul 2014, 39, 124–142. [CrossRef]

23. Cañizares-Villanueva, R.O. Biorremediación de metales pesados mediante el uso de biomasa microbiana. Rev. Latinoam. Microbiol. -Méx. 2000, 42, 131–143.

24. Shim, Y.S.; Kim, Y.K.; Kong, S.H.; Rhee, S.W.; Lee, W.K. The adsorption characteristics of heavy metals by various particle sizes of MSWI bottom ash. Waste Manag. 2003, 23, 851–857. [CrossRef]

25. Júnior, W.N.; Silva, M.G.C.; Vieira, M.G.A. Competitiva fixed-bed biosorption of Ag (I) and Cu (II) ions on Sargassum filipendula seaweed waste. J. Water Process Eng. 2020, 36, 101294. [CrossRef]

26. Lin, S.; Yang, H.; Na, Z.; Lin, K. A novel biodegradable arsenic adsorbent by immobilization of iron oxyhydroxide (FeOOH) on the root powder of long-root Eichhornia crassipes. Chemosphere 2018, 192, 258–266. [CrossRef]

27. Wei, Y.; Fang, Z.; Zheng, L.; Tsang, E.P. Biosynthesized iron nanoparticles in aqueous extracts of Eichhornia crassipes and its mechanism in the hexavalent chromium removal. Appl. Surf. Sci. 2017, 399, 322–329. [CrossRef]

28. Hokkanen, S.; Repo, E.; Lou, S.; Sillanpää, M. Removal of arsenic (V) by magnetic nanoparticle activated microfibrillated cellulose. Chem. Eng. J. 2014, 260, 886–894. [CrossRef]

29. Dhankhar, R.; Hooda, A. Fungal biosorption—an alternative to meet the challenges of heavy metal pollution in aqueous solutions. Environ. Technol. 2011, 32, 467–491. [CrossRef]

30. Park, D.; Yun, Y.S.; Park, J.M. Mechanisms of the removal of hexavalent chromium by biomaterials or biomaterial-based activated carbons. J. Hazard. Mater. 2006, 137, 1254–1257. [CrossRef]

31. Park, D.; Yun, Y.S.; Jo, J.H.; Park, J.M. Mechanism of hexavalent chromium removal by dead fungal biomass of Aspergillus niger. Water Res. 2005, 39, 533–540. [CrossRef]

32. Chatterjee, A.; Abraham, J. Desorption of heavy metals from metal loaded sorbents and e-wastes: A review. Biotechnol. Lett. 2019, 41, 319–333. [CrossRef]

33. Chen, S.; Yue, Q.; Gao, B.; Li, Q.; Xu, X.; Fu, K. Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: A fixed-bed column study. Bioresour. Technol. 2012, 113, 114–120. [CrossRef] [PubMed]

34. Yan, H.; Yang, L.; Yang, Z.; Yang, H.; Li, A.; Cheng, R. Preparation of chitosan/poly (acrylic acid) magnetic composite microspheres and applications in the removal of copper (II) ions from aqueous solutions. J. Hazard. Mater. 2012, 229, 371–380. [CrossRef] [PubMed]

35. Anirudhan, T.S.; Shainy, F. Adsorption behaviour of 2-mercaptobenzamide modified itaconic acid-grafted-magnetite nanocellulose composite for cadmium (II) from aqueous solutions. J. Ind. Eng. Chem. 2015, 32, 157–166. [CrossRef]

36. Golie, W.M.; Upadhyayula, S. Continuous fixed-bed column study for the removal of nitrate from water using chitosan/alumina composite. J. Water Process Eng. 2016, 12, 58–65. [CrossRef]

37. Tejada-Tovar, C.N.; Villabona-Ortiz, A.; Alvarez-Bajaria, G.; Granados-Conde, C. Influencia de la altura del lecho sobre el comportamiento dinámico de columna de lecho fijo en la biosorcióin de mercurio. TecnoLógicas 2019, 20, 71–81. [CrossRef]

38. Singh, J.; Kumar, V.; Kumar, P. Kinetics and prediction modeling of heavy metal phyto remediation from glass industry effluent by water hyacinth (Eichhornia crassipes). Int. J. Environ. Sci. Technol. 2021, 19, 5481–5492. [CrossRef]

39. Saralegui, A.B.; Willson, V.; Caracciolo, N.; Piol, M.N.; Boeykens, S.P. Macrophyte biomass productivity for heavy metal adsorption. J. Environ. Manag. 2021, 289, 112398. [CrossRef]

40. Ajmani, A.; Shahnaz, T.; Subbия, S.; Narayanasamy, S. Hexavalent chromium adsorption on virgin, biochar, and chemically modified carbons prepared from Phanera vahlii fruit biomass: Equilibrium, kinetics, and thermodynamics approach. Environ. Sci. Pollut. Res. 2019, 26, 32137–32150. [CrossRef]

41. Gupta, S.; Jain, A.K. Biosorption of Ni (II) from aqueous solutions and real industrial wastewater using modified A. barbadensis Miller leaves residue powder in a lab scale continuous fixed bed column. Clean. Eng. Technol. 2021, 5, 100349. [CrossRef]

42. De Sá Costa, H.P.; da Silva, M.G.C.; Vieira, M.G.A. Fixed bed biosorption and ionic exchange of aluminum by brown algae residual biomass. J. Water Process Eng. 2021, 42, 102117. [CrossRef]

43. Han, X.; Zhang, Y.; Zheng, C.; Yu, X.; Li, S.; Wei, W. Enhanced Cr (VI) removal from water using a green synthesized nanocrystalline chlorapatite: Physicochemical interpretations and fixed-bed column mathematical model study. Chemosphere 2021, 264, 128421. [CrossRef] [PubMed]

44. Ghasemabadi, S.M.; Baghdađi, M.; Safari, E.; Ghazban, F. Investigation of continuous adsorption of Pb (II), As (III), Cd (II), and Cr (VI) using a mixture of magnetic graphite oxide and sand as a medium in a fixed-bed column. J. Environ. Chem. Eng. 2018, 6, 4840–4849. [CrossRef]

45. Jiang, X.; An, Q.D.; Xiao, Z.Y.; Zhai, S.R.; Shi, Z. Versatile core/shell-like alginateopolyethyleneimine composites for efficient removal of multiple heavy metal ions (Pb2+, Cu2+, CrO42–): Batch and fixed-bed studies. Mater. Res. Bull. 2019, 118, 110526. [CrossRef]