Use of Chemically Treated Human Hair Wastes for the Removal of Heavy Metal Ions from Water

Helan Zhang [1], Fernando Carrillo-Navarrete [2,3], Montserrat López-Mesas [1] and Cristina Palet [1,*]

[1] Centre Grup de Tècniques de Separació en Química, Unitat de Química Analítica, Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain; hlzhang1126@163.com (H.Z.); montserrat.lopez.mesas@uab.cat (M.L.-M.)

[2] Institute of Textile Research and Industrial Cooperation of Terrassa (INTEXTER), Universitat Politècnica de Catalunya (UPC), Colom 15, 08222 Terrassa, Spain; fernando.carrillo@upc.edu

[3] Departament d'Enginyeria Química, ESEIAAT—Universitat Politècnica de Catalunya (UPC), Colom 1, 08222 Terrassa, Spain

[*] Correspondence: cristina.palet@uab.cat; Tel.: +0034-93-581-3475; Fax: +0034-93-581-1985

Abstract: Human hair is considered a ubiquitous waste product and its accumulation can cause environmental problems. Hence, the search for alternatives that take advantage of this waste as a new raw material is of interest, and contributes to the idea of the circular economy. In this study, chemically modified human hair was used as a low cost biosorbent for the removal of heavy metal ions from aqueous solutions. The effect of the contact time, the pH, and the biosorbent concentration on the biosorption process were investigated. Kinetic modeling indicated that the pseudo-second order kinetic equation fitted well with $R^2 > 0.999$. Furthermore, the equilibrium data fitted the Langmuir adsorption isotherm at 295 K resulting in saturation concentrations of 9.47×10^{-5}, 5.57×10^{-5}, 3.77×10^{-5}, and 3.61×10^{-5} mol/g for the sorption of Cr(III), Cu(II), Cd(II), and Pb(II), respectively. The biosorption process did not change the chemical structure and morphology of the hair, which was shown by FTIR and SEM. In addition, desorption experiments prove that 0.1 mol/L EDTA solution is an efficient eluent for the recovery of Pb(II) from the treated human hair. To summarize, treated human hair showed satisfactory biosorption capacity and can be considered as an effective biosorbent for the treatment of water with a low concentration of heavy metal ions.

Keywords: human hair; heavy metal; kinetics; isotherms; biosorption

1. Introduction

Heavy metal ions are considered extremely harmful to humans, aquatic organisms, and other life forms because of their toxicity, accumulation, and non-biodegradable nature, causing various diseases and disorders [1]. Hence, the removal of heavy metal ions from wastewater has attracted attention for the protection of public health and the environment [2]. Conventional methods for removing heavy metal ions, including chemical precipitation, flotation, ion exchange, evaporation, and membrane processes are practical and cost-effective only with high strength wastewater (which contains high concentration levels of pollutants), and they are ineffective when applied to low strength aqueous effluents with heavy metal ion concentrations less than 100 ppm [3]. Adsorption techniques currently play an important role in the removal of heavy metal ions from wastewater, offering considerable advantages, such as low-cost, availability, profitability, ease of operation, and efficiency [4,5]. Various materials have been developed as adsorbents for the removal of heavy metal ions. In particular, activated carbon is frequently used as an adsorbent due to its high surface area, high adsorption capacity, and high degree of surface reactivity [6]. However, activated carbon is

relatively expensive and is difficult to recycle by eluting the heavy metal ions because of the strong interaction between activated carbon and heavy metal ions. Waste biogenic materials are considered ideal alternative biosorbents for the removal of heavy metal ions from low strength wastewater due to their relatively good cost-effective adsorption capacity [7]. Accordingly, various biogenic materials, including chitosan derivatives [8], agricultural waste materials [9], chicken feathers [10,11], cork waste [12,13], rubber leaf powder [14], chemically modified plant waste [15], and soybean stalks [16], among others, have been proposed and applied as biosorbents to effectively remove heavy metal ions. The good biosorption properties of these biogenic materials are attributed to the presence of abundant metal binding functional groups of these materials, such as carbonyl, carboxyl, hydroxyl, sulphate, sulfur, phosphate, and amido and amino groups [17].

Among natural resources, keratinous materials can be used as biosorbents, either directly or after activation, to remove heavy metal ions due to their intricate networks characterized by high stability, insolubility in water, and high surface area containing many carboxyl, amido, and sulfur functional groups [18]. In addition, keratin is an abundant nonfood protein; in fact, it is the major component of wool, hair, horns, nails, and feathers. Moreover, keratin wastes, such as feathers, horns, nails from butchery [19], human hair from hairdressers, poor quality raw wools from sheep breeding, and some by-products from the textile industry, amount globally to more than four millions tons per year [20]. Several examples of the use of keratinous materials have been already reported, especially using modified keratinous materials. Al-Asheh et al. compared adsorption capacities between inactivated and chemically activated chicken feathers as a biosorbent for removing heavy metal ions (i.e., Cu(II) and Zn(II)) from wastewater [21]. Park et al. prepared wool and silk blend nanofibrous membranes by electrospinning, which exhibited an excellent performance as an adsorbent of heavy metal ions [22]. The Aluigi research group successfully prepared keratin-rich nanofiber mats by electrospinning wool keratin/polyamide blends. This material shows good adsorption capacity for Cu(II) ions from water, with the adsorption capacity increasing with the increase of the specific surface area of the nanofiber mats [23].

Keratinous-composed human hair is considered a ubiquitous waste product and its accumulation can cause environmental problems. Hence, the search for alternatives that take advantage of this waste as a new raw material is of interest, and contributes to the idea of circular economy. In this sense, human hair can contribute significantly in many critical areas of public importance, such as agriculture, medicine, construction materials, and pollution control [24]. In particular, the presence of carboxyl, amido, and disulfide groups in human hair suggest this waste product could be a good biosorbent of several chemicals, including heavy metals, although it has been rarely studied for this application [11]. In this regard, one of the major drawbacks is that its hydrophobic nature in native form limits the diffusion of heavy metal ions from the solution to the external surface of the human hair [**Error! Bookmark not defined.**]. To overcome this issue, disulfide bonds present in human hair can be readily oxidized to yield the corresponding cysteic acid residues, which increase the hydrophilic properties of the human hair and subsequently improve its capability to bind positively charged metal ions [25]. For this reason, oxidized human hair was chosen in the present work as a biosorbent for the removal of heavy metal ions from aqueous solutions. Environmental parameters affecting the biosorption process, such the pH value, biosorbent concentration, and contact time were studied. In addition, FT-IR and SEM analysis were conducted for the structural and morphological characterization of the biosorbent after the oxidation pretreatment and after the subsequent heavy metal biosorption process. The kinetic and isotherm data experimentally obtained were correlated with the established kinetic models (pseudo-first order, pseudo-second order, and Weber–Morris intraparticle diffusion model) and with well-known thermodynamic models (Freundlich and Langmuir). A comparison between these was performed. Finally, a desorption/regeneration test was performed in order to study the reusability of the biosorbent.

2. Experimental

2.1. Chemicals

All the chemicals used in this work were of analytical grade. Stock solutions of separate heavy metal ions, such as Cr(III), Mn(II), Ni(II), Co(II), Cu(II), Zn(II), Cd(II), and Pb(II) were prepared by dissolving their nitric salts (>99%, all from Panreac, Spain) in deionized water. A 1000 ppm stock solution of metal ions was first prepared, which was then diluted to the initial heavy metal concentration for each experiment. Sodium hydroxide (>98%, Panreac, Spain) and nitric acid (>70%, JT-Baker, Spain) were alternatively used for the pH adjustment of the initial aqueous solution prior to commencing the biosorption experiments. In all the experiments, the initial pH was measured, and usually the final pH was also checked, using an Omega 300 pH meter (Crison instruments, S.A., Spain).

2.2. Human Hair

Human hair waste (from different male individuals of approximately 13 years of age) was collected from local barbershops. The human hair samples were mixed together, washed with common laboratory detergent, rinsed several times with deionized water (purified with a milli-Q Gradient system from Millipore Corporation) and then left to dry at room temperature (22 ± 1 °C). The hair was cut to an approximate length of 1–2 mm using scissors.

2.3. Chemical Treatment of Human Hair

The treatment process of the human hair was carried out as follows: 20.0 g of the untreated human hair was weighed and soaked in 400 mL of the pretreatment reagent of known concentration (10% H_2O_2, originally at 35% in water, from Sigma-Aldrich, Germany) and at adjusted pH of 9 (pH 9.0 yields better biosorption results in comparison with others, when pH 5.0, pH 7.0 and pH 9.0 are assayed) [26]. After a given soaking time (5 h), the solution was filtered. The hair separated from the solution was washed many times with deionized water. To minimize any loss of the treated hair, at each washing step, the hair was separated by centrifugation, and the liquid was then decanted. Finally, the treated and cleaned hair was dried at room temperature.

2.4. Characterization of Human Hair

Structural characterization of the human hair was carried out to analyze any chemical change produced in the samples after the oxidative pretreatment and/or after the biosorption of heavy metals. The identification of the functional groups in the untreated and treated human hair was performed using a Fourier transform infrared (FT-IR) spectrometer (Tensor 27, Bruker, Germany). The spectra were recorded in the range of 600–4000 cm^{-1} with 16 scans and a resolution of 4 cm^{-1}. The surface morphology of the human hair samples (untreated and treated) was observed by scanning electron microscope (SEM; ZEISS EVO® MA 10, Oberkochen, Germany). The samples used the sputter-coating arrangement.

2.5. Heavy Metal Ions Biosorption Experiments

The uptake of heavy metal ions onto the hair systems was carried out by batch experiments at a constant temperature (22 ± 1 °C) on a rotary mixer (CE 2000 ABT-4, SBS Instruments SA, Barcelona, Spain) at 25 rpm. In all sets of experiments, 0.1 g of human hair (untreated or treated) was weighed in 50 mL plastic extraction tubes; the 10 mL of heavy metal ion aqueous solution was added and the final system was shaken for a certain period of time. Usually, the concentration of each heavy metal ion was 0.10 mmol/L (for multiple heavy metal system containing eight ions) and 0.18 mmol/L (in the multiple-metal system containing four ions, and also in the single-metal systems). The pH was adjusted to 4.0, unless otherwise specified. The initial pH of the multiple heavy metal aqueous solution was varied within the range 1.0 to 6.0 (higher pH values were not considered to avoid

precipitation of metal hydroxides). To study the effect of the biosorbent concentration on metal uptake, its mass was varied from 1 to 20 g/L. The effect of the initial metal ion concentration on biosorption isotherms was studied in single-metal systems with 0.1 g of treated human hair. A range of initial metal ion concentrations from 0.5×10^{-3} to 2.0 mmol/L was used. In all cases, after agitation, the two phases were separated by decantation and the liquid was filtered through 0.22 μm syringe Millipore filters (Millex-GS, Millipore, Ireland). Then, the heavy metal concentration in the remaining aqueous solution was determined by an inductively coupled plasma optical emission spectrophotometer with mass detector, ICP-MS (XSERIES 2 ICP-MS, Thermo Scientific, Bremen, Germany).

The uptake of the metal ions by human hair was calculated using Equation (1), which quantifies the biosorption efficacy:

$$\% \ biosorption = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and the final concentration of heavy metal in the aqueous phase solution, respectively (in mmol/L).

The amount of metal sorbed per unit of mass of biosorbent at time t (q_t in mmol/g) was calculated using Equation (2):

$$q_t (mmol/g) = \frac{(C_i - C_f) \times V}{W} \tag{2}$$

where V is the total volume of the solution (in L), W is the amount of biosorbent (in g), and C_i and C_f are the initial and the final concentrations of heavy metal in the aqueous solution (each given in units of mmol/L), respectively.

The amount of metal sorbed at the equilibrium per unit of mass of biosorbent (q_e in mmol/g) was obtained as follows:

$$q_e (mmol/g) = \frac{(C_i - C_e) \times V}{W} \tag{3}$$

where V is the total volume of the solution (in L), W is the amount of biosorbent (in g), and C_i and C_e are the initial and equilibrium concentrations of heavy metal in the aqueous solution (each given in units of mmol/L), respectively.

All batch biosorption experiments were carried out in duplicate and the results are reported as their average in the corresponding figures (experimental errors found were less than 2.5% and 0.0025 mmol/g in the biosorption percentage and the biosorption capacity, respectively).

2.6. Desorption, Regeneration and Reuse

Desorption experiments were performed only for the removal of Pb(II) from treated human hair samples as biosorbent. Each hair sample containing the adsorbed Pb(II) was contacted and stirred with 10 mL of 0.1 mol/L HNO₃ or 10 mL of 0.1 mol/L EDTA. After 24 h of mixing (with the rotary mixer) at room temperature (22 ± 1 °C), the aqueous and solid phases were separated by centrifugation and subsequent filtration, and the Pb(II) content of the final solution was analyzed by ICP-MS, as indicated in Section 2.5. Desorption percentage was calculated using Equation (4):

$$\% \, desorption = \frac{amount \quad of \quad Pb(II) \quad desorbed}{amount \quad of \quad Pb(II) \quad adsorbed} \times 100 \tag{4}$$

The reuse of the treated human hair in a second biosorption step, after elution of the adsorbed metal ions (with nitric acid or EDTA), requires the cleaning of the remaining eluting solution from the surface of the biomaterial. The treated human hair was washed with deionized water and dried in an oven at 40 °C overnight. These regenerated human hair samples were employed to adsorb heavy metals again.

All batch biosorption, desorption, and regeneration experiments were carried out in duplicate and the results are reported as their average in the corresponding figures (experimental errors found were less than 2% and 0.002 mmol/g, in the biosorption and desorption percentages and the biosorption capacity, respectively).

3. Results and Discussion

3.1. Comparison of Biosorption Efficacy Between Untreated and Treated Human Hair

The oxidation of human hair usually takes place with hydrogen peroxide in an acid or alkaline medium by attacking the disulfide bond of keratin. As a result of this reaction, sulfonic acid groups are formed, and hair samples are functionalized. In an alkaline medium, the oxidation process is much more effective [**Error! Bookmark not defined.**]. Moreover, during oxidation, other proteins in the human hair are also oxidized, which leads to cell membrane damage causing the cortex and the cuticle to open and separate. The objective of this pretreatment is to increase the hydrophilicity of the human hair surface and also to increase its specific surface area. The biosorption capacities of untreated and treated human hair samples for recovering eight metal ions (Cr(III), Mn(II), Ni(II), Co(II), Cu(II), Zn(II), Cd(II), and Pb(II)) were determined. The obtained results are shown in Figure 1. As seen from the figure, the metal biosorption capacity of chemically treated human hair is significantly better than that of untreated human hair. Moreover, the affinity of both types of hair for Cr(III), Cu(II), and Pb(II) is greater than that for the other metal ions, which can be explained by the stronger interactions between the functional groups of the biosorbent and these three metal ions. The metal biosorption onto the treated human hair follows in the order of Cr(III) > Pb(II) > Cu(II) > Cd(II) > Ni(II) > Co(II) > Mn(II) > Zn(II). Finally, four metal ions, namely, Cr(III), Cu(II), Cd(II), and Pb(II), were selected from those metals to study the biosorption mechanism of treated human hair in subsequent experiments.
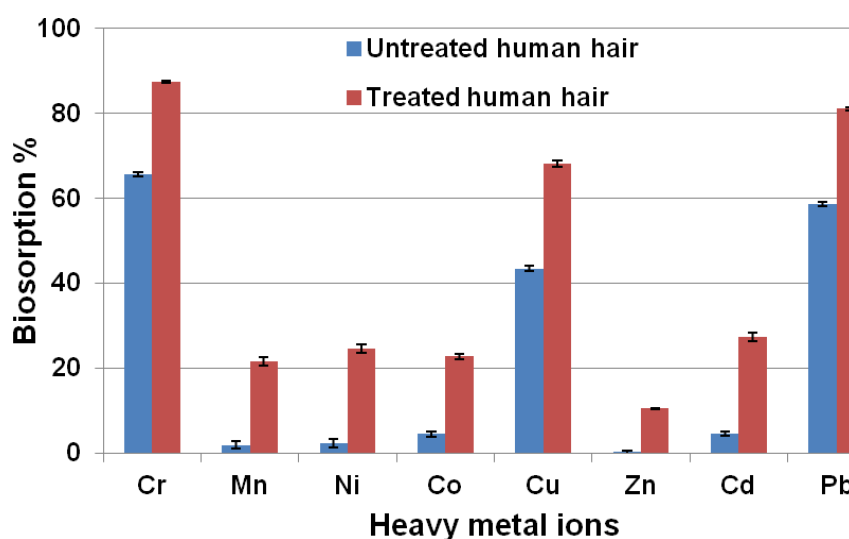

Figure 1. Comparison of biosorption between untreated and treated human hair in a multiple-metal system. The initial metal ion concentration was 0.1 mmol/L, the contact time was 24 h, the pH was 4.0, and the biosorbent was 0.1 g in 10 mL of the initial solution.

3.2. FT-IR and SEM Characterization

In order to understand how metal ions bind to the biosorbent, it is essential to identify the functional groups of its surface as these could be responsible for the metal binding. Thus, the untreated, treated, and metal loaded-treated human hairs were discriminated by FT-IR, as can be seen from the infrared spectra collected in Figure 2. The full-scan spectra of human hair (Figure 2a)

display their corresponding infrared peaks. The broad and medium intensity band ranging from 3000 to 3600 cm^{-1} is indicative of the stretches of the bonds belonging to the carboxylic acid (-COOH), alcohol (-OH), and amino acid (-NH$_2$) groups. The peaks located at 1632 cm^{-1} (amide I), 1520 cm^{-1} (amide II), and 1241 cm^{-1} (amide III) are related to typical human hair amino acids. The peaks at 1041, 1075, 1180, and 1229 cm^{-1} all correspond to different products of cystine oxidation in human hair, and their peak assignment belongs to sulfonate (S-O sym. stretch), cystine monoxide (R-SO-S-R), sulfonate (S-O asym. stretch), and cystine dioxide (R-SO2-S-R), respectively. Carefully comparing the spectra of the three different hair samples, some differences can be seen between them, as expected, due first to the oxidation process (treated human hair), and, later, to the metal biosorption (metal loaded-treated human hair), particularly in the region from 850 to 1750 cm^{-1} (see Figure 2b). The intensity of the peaks at 1041 and 1180 cm^{-1} increased after chemical pretreatment, which means that conversion of cystine to cysteic acid, cystine monoxide, and cystine dioxide, as well as to sulfonates, occurred during this treatment process. The weak broad shoulder between approximately 1000 and 1130 cm^{-1} in the untreated human hair infrared spectra is probably due to environmental factors, such as sunlight, chlorinated water, and frequent shampooing causing partial oxidation of the hair surface [27]. The FT-IR spectra from treated human hair before and after the metal biosorption are very similar, indicating that the main functional groups on treated human hair did not change during the metal biosorption process (which can be an indication of a possible reuse of such biomaterial). However, the slight differences found around 1400 cm^{-1}, and some red shift of the emission spectra (from 3277.2 cm^{-1} to 3274.8 cm^{-1}, from 1526.8 cm^{-1} to 1519.7 cm^{-1}, and from 1078.4 cm^{-1} to 1074.9 cm^{-1}), before and after the biosorption process, is probably related to the presence of the heavy metal ions on the hair surface. Based on the FT-IR spectra changes, as seen in Figure 2, some hair surface chemical functional groups (including hydroxyl, amino, carboxyl, and sulfonic acid) could act as important biosorption sites for heavy metal ions.
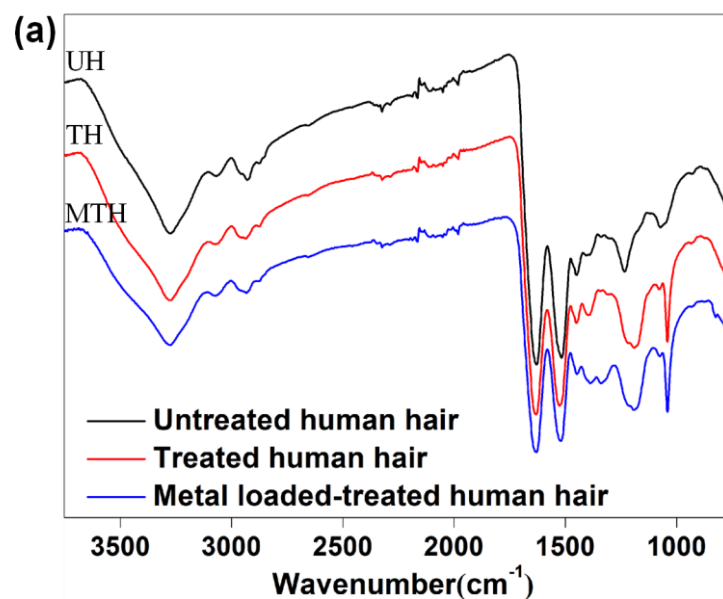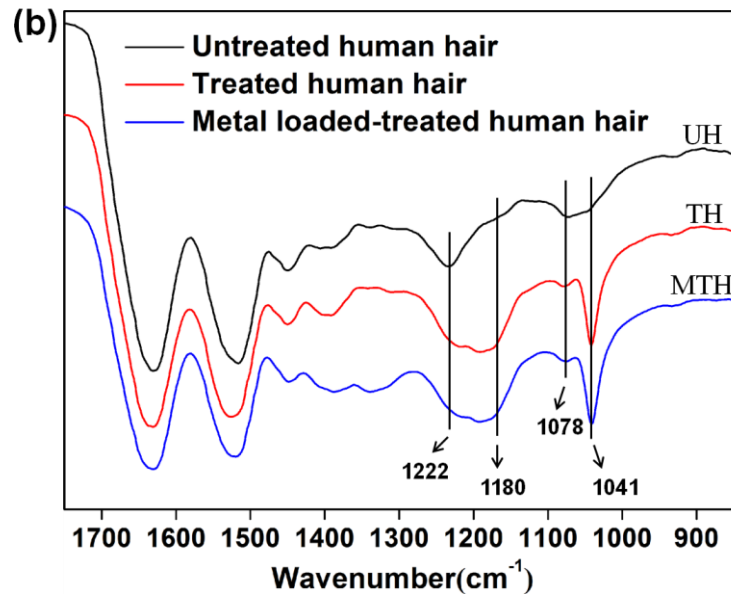
Figure 2. FT-IR spectra of human hair. UH: untreated human hair, TH: treated human hair, MTH: metal loaded-treated human hair. (**a**) Full-scan spectra, and (**b**) spectra in the range from 850 to 1750 cm^{-1}.

The scanning electron microscopy (SEM) technique was applied to address concern about the alteration of the human hair surface morphologies in the different cases of the study. Figure 3 shows the SEM micrographs of the untreated, treated, and metal-loaded treated human hair. It is observed that each cuticle scale of the human hair is uniquely shaped. Some have smooth rounded edges and others have jagged edges, overlapping each other as they ascend along the length of the fiber towards the tip (Figure 3). The surface topographies of the untreated and treated human hair are different (see Figure 3a,b for comparison): the majority of the cuticle scales of the treated human hair fibers represent a more jagged appearance, probably due to the oxidation treatment. After metal biosorption, the surface appears to be somewhat smoother compared with the hair prior to its use, suggesting that the cuticle scales are closed through biosorption, probably due to the acidic water media (see Figure 3b,c).
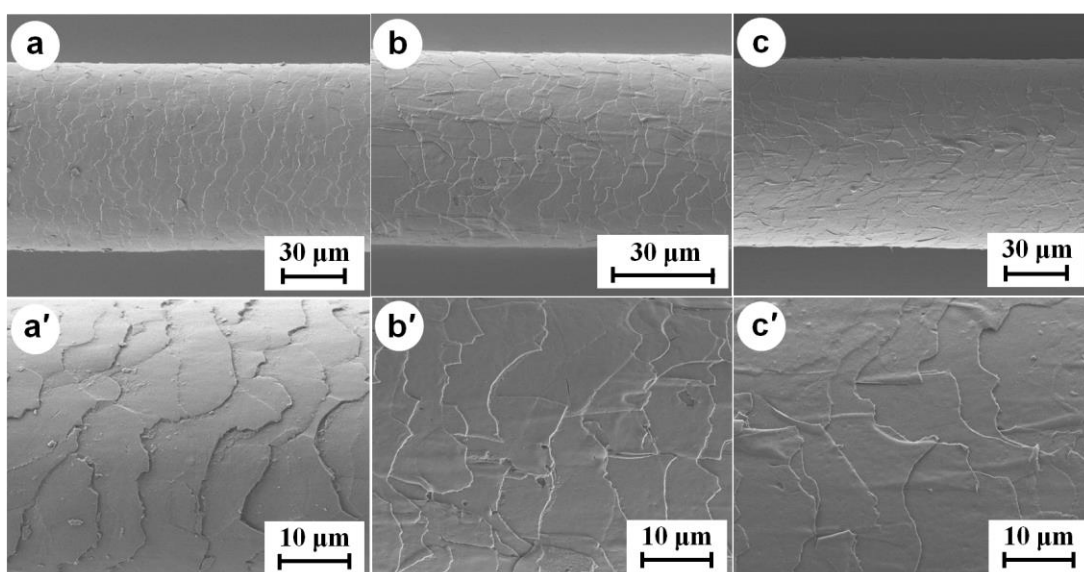

Figure 3. Scanning electron microscopy (SEM) micrographs of the human hair: (**a**) and (**a′**) correspond to the untreated human hair; (**b**) and (**b′**) correspond to the treated human hair; and (**c**) and (**c′**) correspond to the metal loaded-treated human hair.

3.3. Effect of the pH in Multiple Metal System

The pH level of the aqueous solution is an important variable for the biosorption of metal ions onto the biosorbents, due to the metal speciation and the speciation of the chemical functional groups present on the biosorbent's surface. The pH was controlled at the beginning and end of the experiments in order to evaluate any differences. The changes observed were lower than 0.3 units, and thus considered not significant.

The effect of the pH solution on the removal efficacy of the treated human hair for Cr(III), Cu(II), Cd(II), and Pb(II) was studied between pH 1.0 and 6.0 in the multiple-metal system (Figure 4). As observed from the results in Figure 4, the biosorption of metal ions increases significantly with increasing the pH. This behavior can be explained by the competition between the protons and the metal ions for the same binding site on the surface of the treated human hair. At low pH values, the surface of the biosorbent would also be surrounded by H^+ ions, which decrease the Cr(III), Cu(II), Cd(II), and Pb(II) ions interaction with binding sites of the treated human hair. As the pH increases, the basic forms of the chemical functional groups on the hair surface predominate, increasing negative charge, so metal cation biosorption increases. However, when the pH is around 5, the partial hydrolysis of metal ions (particularly for Cu; the remaining metals could occur at pH higher than 5) results in the formation of $M(OH)_n^{(m-n)}$ species affecting the biosorption hair capability. The biosorption percentage found could be related to the precipitation of the metals. Therefore, pH 4.0 was selected as the optimal condition in the subsequent experiments.
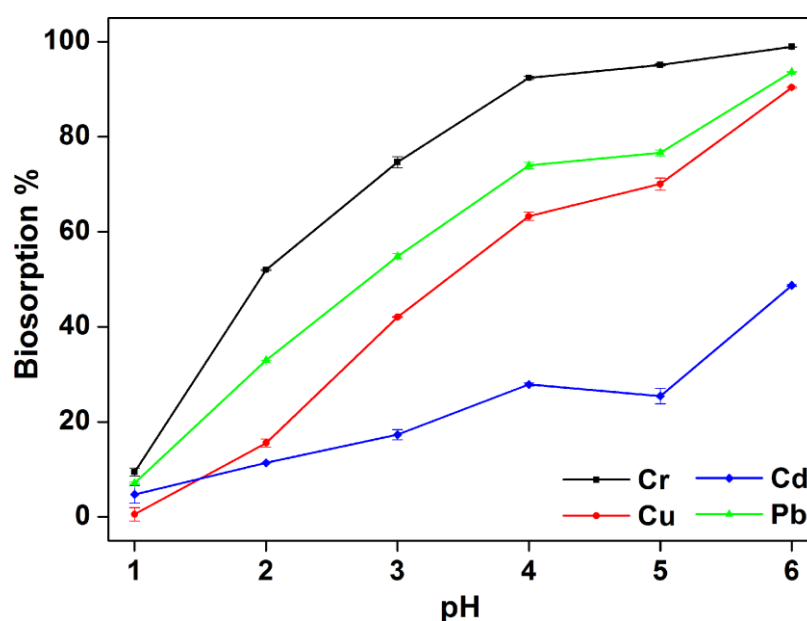

Figure 4. Effect of pH on the biosorption of the treated human hair for Cr(III), Cu(II), Cd(II), and Pb(II) in the multiple-metal system. The initial concentration was 0.18 mmol/L, the contact time was 24 h, and the biosorbent was 0.1 g in 10 mL initial solution.

3.4. Effect of Biosorbent Concentration

The effect of the biosorbent concentration on the removal efficacy of Cr(III), Cu(II), Cd(II), and Pb(II) ions was studied in the range of 1–20 g/L in a multiple-metal system (Figure 5). It was observed that the removal efficacy of the treated human hair for Cr(III), Cu(II), Cd(II), and Pb(II) ions increased with the increase of biosorbent concentration (Figure 5a). This can be explained by the increase in surface area of the biosorbent when increasing its amount, which in turn increases the binding sites. For Cr(III) and Pb(II), the sorbed metal ion (mmol) per unit weight of biosorbent significantly decreased by increasing the biosorbent concentration (Figure 5b). This can be explained due to the fact that at high biosorbent concentration, the available metal ions in the aqueous solution are insufficient to cover all the biosorbent sites due to the corroborated high affinity of these two metals (as can be seen from results collected in Figures 1 and 4). Furthermore, the metal uptakes

(mmol/g) for Cu(II) and Cd(II) are basically stable with the increase of biosorbent concentration; this means the biosorption quantity of Cu(II) and Cd(II) increases through increasing the biosorbent concentration. Thus, functional groups induced on the biosorbent hair surface have stronger affinity for Cr(III) and Pb(II) than for Cu(II) and Cd(II).
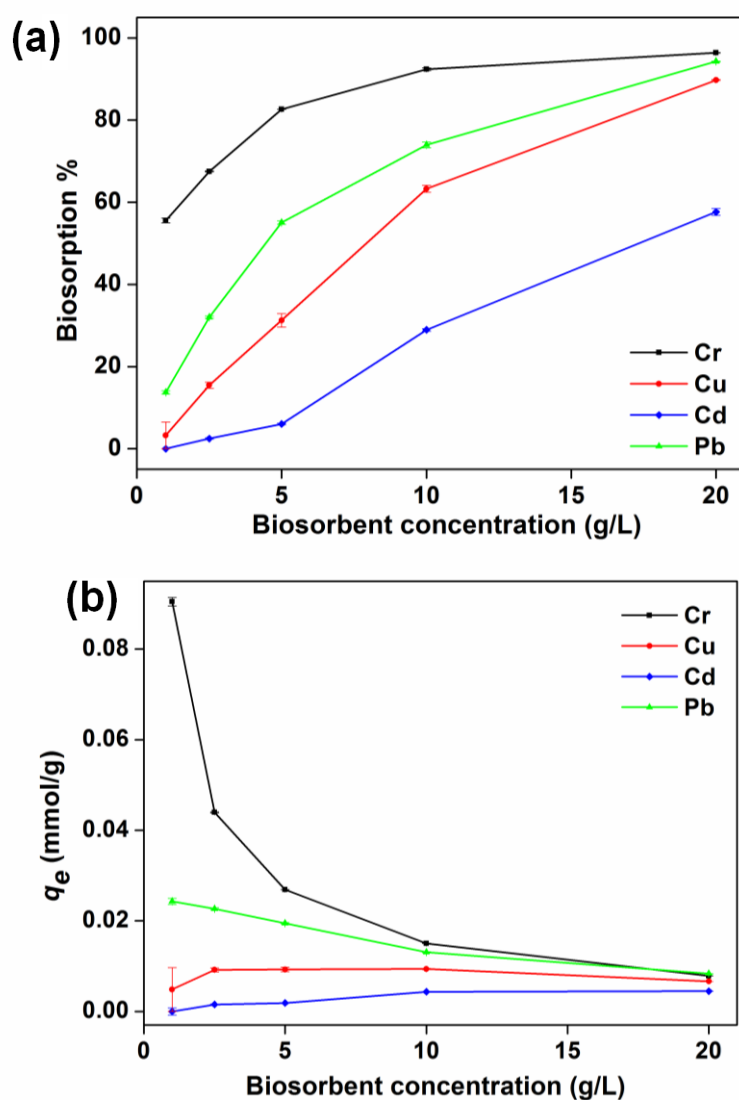
Figure 5. Effect of the biosorbent concentration on the percentage of biosorption (**a**) and on the amount of sorbed metal ion per unit weight of biosorbent (**b**) of the treated human hair for Cr(III), Cu(II), Cd(II), and Pb(II) in the multiple-metal system. The initial metal ions concentration was 0.18 mmol/L, the contact time was 24 h, and the pH of the 10 mL initial aqueous solution was 4.0.

3.5. Effect of Contact Time

Contact time with aqueous contaminated samples is an important parameter for successful usage of biosorbents in practice. Multiple- and single-metal aqueous systems (at pH = 4) of Cr(III), Cu(II), Cd(II), and Pb(II) were placed in contact with treated human hair (0.1 g) for periods of 5, 10, 20, 30, and 45 min, and 1, 2, 3, 4, 6, 12, 24, 48, and 72 h. Results plotted in Figure 6 show the biosorption capacity of treated human hair for removing Cr(III), Cu(II), Cd(II), and Pb(II) ions. Three steps can be differentiated during biosorption: the initial step with fast metal biosorption, the second step with gradual biosorption, and the third step, which can be related to the equilibrium uptake.

The first step can be related to the diffusion of metal species from the solution to the external surface of the hair, which occurred instantaneously. The second step corresponds to a gradual biosorption uptake of heavy metal ions until reaching an equilibrium (the third stage). For each metal ion, the biosorption efficacy is higher for the single-metal system than for the multiple-metal system. Among these, the percentage of biosorption for Cd(II) is outstanding, with an increase from 29% to 86%. Furthermore, the single-metal system reached the biosorption equilibrium more rapidly than the multiple-metal system (around only 30 min in the former case), which is attributed to the effect of the competition between the heavy metal ions. Therefore, the selectivity order is Cr(III) > Pb(II) > Cu(II) > Cd(II), which corresponds to biosorption efficacy in the single-metal system of 98%, 96%, 95%, and 86%, respectively.
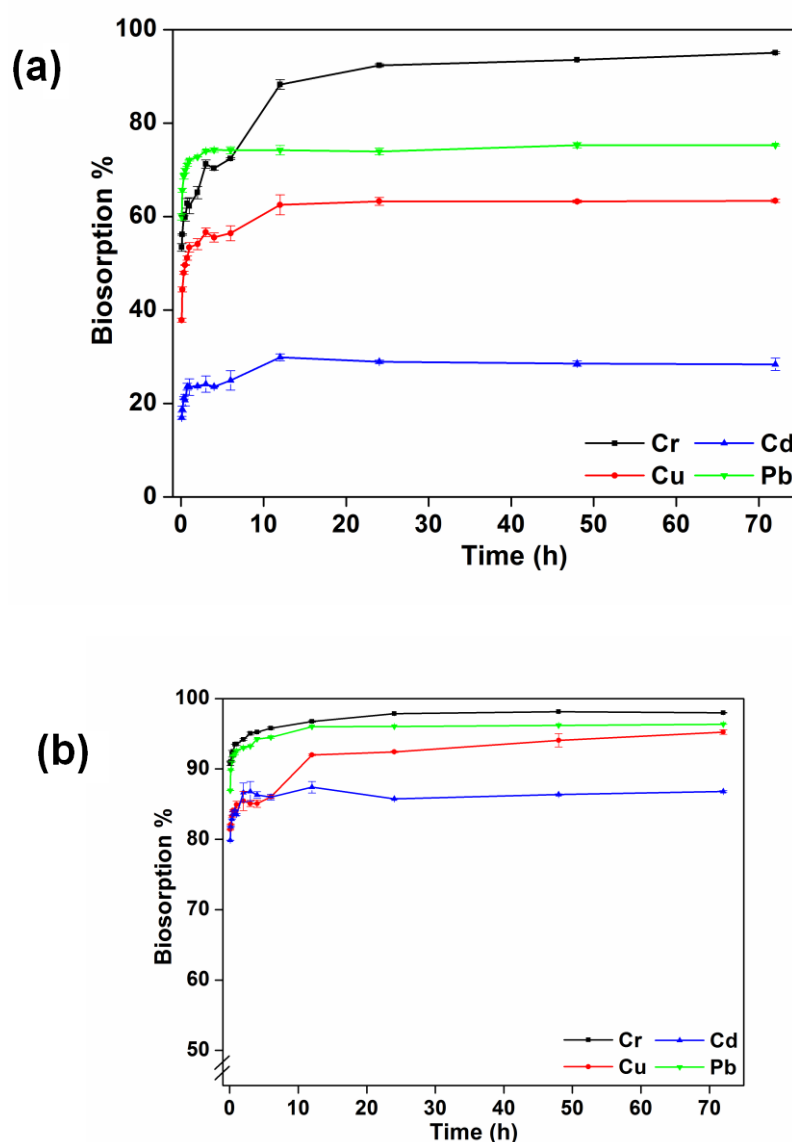

Figure 6. Percentage of biosorption of the treated human hair for Cr(III), Cu(II), Cd(II), and Pb(II) at different contact times. (**a**) Multiple-metal system, and (**b**) single-metal system. The initial metal ion concentration was 0.18mmol/L, the pH was 4.0, and the sorbent concentration was 10 g/L.

3.6. Kinetic Studies

Kinetic models have been used to model experimental data in order to investigate the mechanism of biosorption. Furthermore, it is important to determine the potential rate controlling

steps, such as mass transport, chemical reaction, and intraparticle diffusion processes, in such systems. Many attempts have been made to formulate a general expression describing the kinetics of liquid–solid phase sorption systems [28]. In the present case, the kinetic models applied to the treated human hair as a biosorbent of heavy metals in solution were the pseudo-first order equation [29], the pseudo-second order equation, and the Weber–Morris intraparticle diffusion model. These are given by Equations (5)–(7), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

$$q_t = k_3 t^{1/2} + k_d \tag{7}$$

where, q_e and q_t are the amount of biosorbed metal ions per unit of mass biosorbent (in mmol/g) at the equilibrium and at time t (min), respectively; k_1 (in min^{-1}) is the rate constant of the pseudo-first order equation; k_2 (in g/(mmol·min)) is the rate constant of the pseudo-second order equation; k_3 is the intraparticle diffusion rate constant (in mmol/(g·min$^{1/2}$)); and k_d is the intercept that relates to the thickness of the boundary layer.

　　　Experimental data were fitted to pseudo-first and pseudo-second order kinetic models and the rate corresponding constants (k), correlation coefficients (R^2), and q_e were estimated (values shown in Table 1). It is noteworthy that the pseudo-first order equation does not fit well for the whole range of time, which is generally applicable only over the initial time of the sorption processes, i.e., 30 and 60 min for the multiple- and single- metal biosorption systems, respectively [30]. Moreover, for the four metal ions in single and multiple systems, the calculated q_e did not match well with experimental data, which suggests the insufficiency of the pseudo-first order model to fit the experimental data.

　　　The pseudo-second order model is more likely to predict kinetic behavior for the whole range of time studied, which indicates that chemical sorption is the rate-controlling step [31]. Correlation coefficients were always greater than 0.999, and the values of the predicted equilibrium biosorption capacities showed a good correlation with the experimental q_e values for all four metal ions in both systems. This shows that the biosorption process perfectly complies with the pseudo-second order model. In other words, the chemical sorption due to the formation of chemical bonds between the metal and sorbent in a monolayer onto the surface is the rate-controlling step [32]. The equilibrium biosorption capacities for Cr(III), Cu(II), Cd(II), and Pb(II) were 0.0166, 0.0174, 0.0165, and 0.0174 mmol/g, respectively, in the single-metal system, and 0.0155, 0.00945, 0.00429, and 0.0133 mmol/g, respectively, in the multiple-metal system.

Table 1. Sorption kinetic constants in the multiple- and single-metal systems for Cr(III), Cu(II), Cd(II), and Pb(II) for both pseudo-first and pseudo-second order models.

Metal		Cr		Cu		Cd		Pb	
System		Single	Multiple	Single	Multiple	Single	Multiple	Single	Multiple
Pseudo first order	$k_1 \times 10^3$ (min^{-1})	9.21 [a]	4.19 [b]	6.91 [a]	15.0 [b]	26.3 [a]	12.9 [b]	26.8 [a]	27.3 [b]
	q_e (mmol/g)	0.00132	0.00655	0.00263	0.00346	0.00151	0.00190	0.00173	0.00233
	R^2	0.9327	0.7343	0.9905	0.8794	0.9136	0.8592	0.8381	0.9030
Pseudo second order	k_2 (g/mmol min)	15.4	1.51	3.83	6.75	38.2	16.2	17.8	16.6
	q_e (mmol/g)	0.0166	0.0155	0.0174	0.00945	0.0165	0.00429	0.0174	0.0133
	R^2	1.000	0.9993	0.9999	0.9999	1.000	0.9997	1.000	1.000
	k_d (mmol/g)	0.0151	0.00831	0.0145	0.00517	0.0148	0.00223	0.0157	0.0103

[a]: 30 min, [b]: 1 h.

　　　For the single-metal system, the kinetic constant values found for the pseudo-second order model (k_2) decreased in the following order: Cd (II) > Pb(II) > Cr(III) > Cu(III). This indicates that Cd

(II) was more easily and rapidly adsorbed by treated human hair than Pb(II), Cr (III), and Cu (II). In this case, the sorption rate was lower for the heavy metal with the smallest ionic radius since Cu(II) has an ionic radius of 0.069 nm compared to 0.097 nm for Cd(II), 0.119 nm for Pb(II), and 0.070 nm for Cr(III).

The pseudo-first and pseudo-second order models cannot provide information about the diffusion mechanism controlling biosorption. Thus, the Weber–Morris intraparticle diffusion model was adjusted [33]. The plots of q_t versus $t^{1/2}$ are shown in the Figure 7. Unlike some simple cases, mathematical formulations representing the diffusion and biosorption are generally solvable analytically. In this case, these plots can be divided into multi-linear correlations, which indicates that the biosorption process take place in three steps and is not controlled solely by the intraparticle diffusion mechanism. The first stage corresponds to the sharper stage, where the metal ions move from the solution to the external surface of the biosorbent, through film diffusion, or the boundary layer diffusion of the metal species [34]. The second step describes the gradual biosorption onto the surface of the treated hair, where the intraparticle diffusion is the rate-limiting [35]. The third stage corresponds to the final biosorption equilibrium where the intraparticle diffusion starts to slow down due to extremely low metal ion concentration left in the solution. The presence of these three stages in the plots (Figure 7) suggests that the film diffusion and intraparticle diffusion were simultaneously controlling the biosorption process and both are enhanced with the increase of the initial metal concentration.
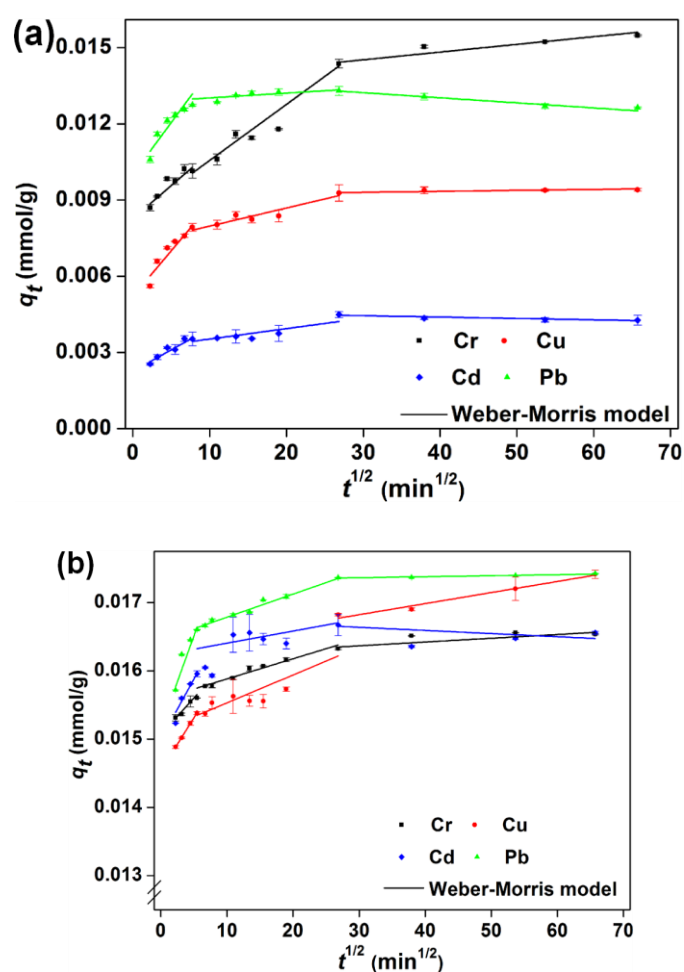

Figure 7. Weber–Morris intraparticle diffusion kinetic model applied for the metal ion biosorption onto the treated human hair, with time: (**a**) in the multiple-metal system, and (**b**) in the single-metal system.

3.7. Thermodynamic Isotherm Characterization

Sorption isotherms at equilibrium are very important data to understand the mechanism of each sorption system from a physicochemical perspective. The sorption capacity of a sorbent can be also described by the equilibrium sorption isotherm, which is characterized by some specific constants whose values provide information about the affinity between the liquid–solid sorption systems.

In the present study, two isotherm models were selected to fit the experimental data, namely, the Freundlich and Langmuir isotherm models [36]. The linear forms of the Freundlich and Langmuir isotherms are presented by Equations (8) and (9), respectively:

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{8}$$

$$\frac{C_e}{q_e} = \frac{b}{K_L}C_e + \frac{1}{K_L} \tag{9}$$

where C_e is the equilibrium concentration of the metal ion in the residual solution (in mol/L); q_e is the amount of the sorbed metal at the equilibrium per unit of mass of sorbent (in mol/g); k_F and n are Freundlich constants; and $K_L = Q_0 b$, where Q_0 and b are the Langmuir constants, corresponding to the saturation concentration of the sorbed metal ion per unit of mass of sorbent (in mol/g) and the ratio of sorption/desorption rates (in L/mol), respectively.

For both models and following Equations (8) and (9), $\log q_e$ versus $\log C_e$ and C_e/q_e versus C_e are calculated and compared with the experimental data, respectively. In addition, all the constants and correlation coefficients obtained for each model are summarized in Table 2.

Table 2. Freundlich and Langmuir isotherm constants for the biosorption of Cr(III), Cu(II), Cd(II), and Pb(II) by the treated human hair.

	Constant	Cr	Cu	Cd	Pb
Freundlich	$K_F \times 10^3$	1.56	2.87	0.546	0.247
	n	2.30	1.90	2.86	3.63
	R^2	0.8646	0.8402	0.9291	0.8607
Langmuir	$Q_0 \times 10^5$ (mol/g)	9.47	5.57	3.77	3.61
	$B \times 10^{-4}$ (L/mol)	1.07	2.06	8.64	8.04
	K_L (L/g)	1.01	1.15	3.26	2.90
	R^2	0.9912	0.9905	0.9952	1.000
	$-\Delta G^0$ (kJ/mol)	22.8	24.4	27.9	27.7

From the correlation coefficient values of both isotherm equations, it was observed that the Langmuir isotherm fitted the data better than the Freundlich isotherm, showing that the biosorption process relies on a specific site's sorption mechanism where adsorbate molecules occupy specific sites on the biosorbent. In Figure 8, experimental and calculated data for the Langmuir isotherm model are represented showing good correlation between the data. Taking on board the Langmuir equation, the saturated biosorption capacities of the treated human hair at 295 K for Cr(III), Cu(II), Cd(II), and Pb(II) were 9.47×10^{-5}, 5.57×10^{-5}, 3.77×10^{-5}, and 3.61×10^{-5} mol/g, respectively.
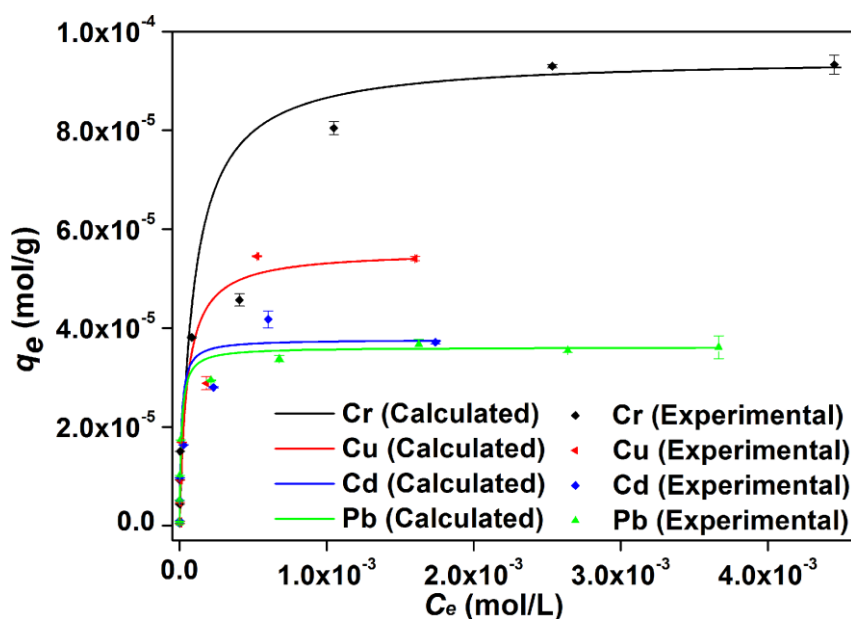
Figure 8. Experimental (·) and calculated (-) values adjusting using the Langmuir isotherm model for the sorption of Cr(III), Cu(II), Cd(II), and Pb(II) using the treated human hair.

It is worth noting that the theoretical maximum values of adsorption capacity given by the Langmuir equation (Q_o) for the treated human hair were found to decrease in the order Cr (III)> Cu(II) > Cd(II) ~Pb(II). The metals with highest absorption capacities are those with lowest ionic radius, i.e., Cu(II) and Cr(III), while Pb(II), which has the largest ionic radius (0.119 nm), shows the smallest sorption capacity. This observed trend, based on the ionic radius, may be caused by the quick saturation of adsorption sites induced by the largest ions. This behavior is in agreement with that observed for the absorption of Pb(II), Cd (II), Ni(II), and Zn(II) using natural zeolite as a sorbent, where the adsorbed amount decreased as the ionic radius increased [37].

In addition, from the estimated Langmuir sorption/desorption constant, the standard Gibb's free energy (ΔG^0) of the biosorption process can be evaluated by using Equation (10):

$$\Delta G^0 = -RT \ln b \qquad (10)$$

where *b* is the Langmuir equilibrium constant shown in Equation (8), *R* is the universal gas constant (8.314 J/mol K), and *T* is the absolute temperature (K). The standard Gibb's free energy (ΔG^0) values are shown in Table 2. The negative ΔG^0 values indicate that the biosorption of metals into human hair is thermodynamically feasible and of spontaneous nature.

3.8. Desorption, Regeneration, and Reuse Studies

Recovery of the adsorbed heavy metals and reuse of the biosorbent are of significance from the viewpoint of practical application. As indicated previously, two eluent solutions, EDTA and HNO₃, were screened for their potential to desorb Pb(II) ions from metal-adsorbed treated human hair (98% of biosorption). Both eluents can effectively desorb the heavy metal ions from the metal loaded-treated human hair, with the elution efficiency of EDTA solution being slightly better than that of the HNO₃ solution, 89% ± 1% and 85% ± 1%, respectively. EDTA may combine both acidic and complexing effects, while nitric acid only has the acidic effect to liberate the adsorbed metals, which explains the higher ability of EDTA for removing the metal. In addition, the ability of EDTA to complex heavy metals, such as lead, due to the high complex constant, is well known.

The reuse of regenerated human hair for the possible continuous removal of heavy metals was investigated. After the desorption process, the hair samples were washed several times (following two different methods of cleaning), dried in an oven at 40 °C overnight, and their performance in a second biosorption step of fresh Pb(II) aqueous sample was then checked. The results show that the metal removal percentages (in the second biosorption step) of the regenerated hair samples are

dependent on the elution methods. When using EDTA as eluent and deionized water for rinsing the used biomaterials, the Pb(II) removal percentage was 87 ± 2 %, while for samples eluted with HNO_3 the metal removal was 38 ± 4 %. Consequently, although HNO_3 is a very powerful metal eluent, it shows negative effects for the reuse of hair samples and results in a decrease of metal uptake capacity during the second application. This is probably because the acidic environment after the desorption step with nitric acid leads to the ionization state of functional groups on the biomaterial's surface, thus becoming a competitive medium for the next metal biosorption step. To confirm this concept, another set of samples were first eluted using EDTA, then rinsed with HNO_3 solution, and later washed with deionized water and dried. The biosorption capacities of the regenerated human hair samples by this method also decreased the second time (75 ± 1 %). It is clear that the desorption of metal adsorbed onto the biomaterials using HNO_3 negatively affects their reuse.

4. Conclusions

Chemically treated human hair behaved better than untreated hair in the process of removing metals from aqueous effluent. In particular, treated human hair was demonstrated to be an effective biosorbent for the removal of Cr(III), Cu(II), Cd(II), and Pb(II), and showed less effectiveness for metals such as Ni(II), Co(II), Mn(II), and Zn(II). It was observed that the operating parameters controlling the biosorption process, such as the pH of the aqueous heavy metal solution, the biosorbent concentration, and the contact time, had a significant influence on the metal uptake. In addition, treated human hair showed higher biosorption capacity when metals were applied in the single-system compared with the multiple-system solution, due to the induced competition between metal ions for the biosorbent sites. In the single system, removal efficacy of the treated human hair was found to be 86% for Cd(II), 92% for Cu(II), 96% for Pb(II), and 98% for Cr(III) when working with 10 g/L of biosorbent concentration at pH = 4.0.

According to the kinetic study, the biosorption of metal ions onto the treated human hair followed well the pseudo-second order kinetic model. Hence, physico-chemical interaction between induced functional groups (i.e., sulfonic acid groups as demonstrated by FTIR) in treated hair and metal ions is the fundamental mechanism controlling biosorption, with the film diffusion being the rate limiting step. Biosorption at equilibrium was better correlated with the Langmuir isotherm model compared to the Freundlich model, corroborating the finding that the mechanism of sorption is based on site-specific molecular sorption. The calculated standard Gibb's free energy (ΔG^0) indicated the thermodynamically feasible and spontaneous nature of the biosorption process.

Preliminary desorption experiments proved that EDTA and HNO_3 solutions were efficient eluents for the recovery of Pb(II) from the treated human hair. In particular, the treated human hair regenerated with EDTA showed the best biosorption efficiency when reused.

Taking into consideration the present findings, it can be stated that treated human hair could potentially be used as an effective and low-cost biosorbent for the removal of heavy metal ions from aqueous solution.

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