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Human hair biogenic fiber as a biosorbent of multiple heavy metals from aqueous solutions

Abstract: Human hair natural fiber is mainly considered a waste in our society and its disposal can cause a major environmental impact. Hence, its valorization as a biosorbent of pollutants such as heavy metals is an interesting route to explore since it can reduce the amount of waste and at the same time contributes to the circular economy strategy. In this work, the ability of two kind of human hairs, used as biosorbents to remove Cr(III), Ni(II), Co(II), Mn(II), Cu(II), Zn(II), Cd(II) and Pb(II) ions from multiple-metal aqueous solutions, were examined and compared under different operating conditions. The influence of the time, pH and initial metal concentration on the metal uptake were studied. The biosorption kinetics and isotherm were also modeled observing that pseudo-second order kinetic model and Langmuir model fitted successfully experimental data. Moreover, biosorption process did not significantly modify the morphology and the chemical structure of the hair samples, which was proved by SEM and FT-IR studies. These kinetic results underline the satisfactory capacity of human hair for the biosorption of Pb(II), Cu(II) and Cr(II) (values up to 95%), pointing up the high efficacy of human hair for the removal of heavy metal ions from aqueous media.

Keywords: Hair; Biofibre; Metals; Biosorption; Kinetics; Isotherms

1. Introduction

Intensifying environment pollution and deteriorating of ecosystems anthropologically, caused by mainly industrial activities, have seriously threatened human existence and development (Wang et al., 2020). Compared with other pollutants, such as dye (Lazaridis et al., 2007), phenols (Sas et al. 2020), inorganic anions, and pesticides (which are toxic to many living lifeforms and organisms), heavy metal ions are extremely harmful to human, animals, and plants because of their toxicity, accumulation, no biodegradable nature and causing various diseases and disorders (Patnaik et al., 2004). Different methodologies, including precipitation, flotation, ion exchange, membrane-related processes, electrochemical techniques and activated carbon adsorption, have been actually established for the removal of heavy metal ions from aqueous effluents (Carolin et al., 2017). Some of these methods are often too expensive to be applied on a large scale or cost prohibitive due to having inadequate efficacy at low metal concentrations (Low, Lee and Liew 2000). So, considering the importance of the removal of heavy metal ions from aqueous effluents, it is necessary to put emphasis on searching new, clean and cheap technologies that can improve upon these methods (Qin et al., 2020). Biosorption techniques have attracted more attention in recent years, not only due to its particular use for the removal of trace levels of contaminants from industrial effluents, but also due to economic reasons (Tran et al., 2019). Biosorption can be defined as the ability of biological materials to accumulate compounds such as heavy metal ions, from effluents through metabolically mediated or physical-chemical pathways of uptake (Beni and Esmaeili, 2020). Although biosorption process is complicated, it can be simply approached as a combination of physical and chemical sorption mechanism (Davis, Volesky and Mucci, 2003) based on the strong chemical interactions between heavy metal ions and some functional groups which can be present on the biomass surface, such as carboxyl, hydroxyl, phosphate, sulfate, and amino groups that act as binders for these ions (Ahalya, Ramachandra and Kanamadi, 2003). Actually, many low-cost and commercially available biomass such as cork waste (López-Mesas et al., 2011), moss peat (Seki et al., 2006), tree leaves (Kaakani, Mortula and Abouleish, 2017), wheat (Gorgievski et al., 2013), rice (Amer, El-Gendy and El-Haggar, 2017) and sugar beet pulp (Castro et al., 2017) have been used to remove heavy metal ions. Although many kinds of biomass have been reported to remove heavy metal ions, these studies just focused on single or few metal ions mixture system (less than 3 species). Considering that multiple metal ions mixture exists abundantly in natural and aqueous effluents, understanding how biomass removes metal ions in their multiple ion mixtures is interesting and useful for practical applications and for the development of the corresponding treatment of such contaminated sites by using these biomass systems (Zhao et al., 2019).

Among many other biosorbent materials, keratinous materials contain intricate networks of stable and water-insoluble fibers with high surface areas and are biogenic abundant bioresources (Kar and Misra, 2004) (Saha et al., 2019). Particularly, keratinous-composed human hair is considered an ubiquitous waste and its accumulation can cause environmental problems. Hence, the search for alternatives that take advantages of this waste as a new raw material is interesting thus contributing to the idea of circular economy (Gupta, 2014). "For instance, human hair has been proposed for being used for several applications such as: i) fashion and cosmetic industry (test Material for hair care products, cosmetic brushes), ii) fertilizer because it is predominantly made up of nitrogen-containing proteins (Zheljazko V. D. et al., 2008), iii) reinforcement of construction materials due to high tensile strength and thermal insulation capacity (Butt, W.A., Mir, B.A. and Jha, J.N., 2016), iv) oil spill remediation (Ukotije-Ikwut P.R. et al., 2016) and v) pharmaceuticals and biomedical applications since human hair is composed of 20 essential amino acids (Lee, H. et al., 2014)". Moreover, the presence of carboxyl, amido and disulfide groups in human hair postulate this waste as a good biosorbent of several chemicals such as heavy metals although it has been rarely studied for this application (Zhang et al., 2019) (Krishnan S.S, Cancilla A. and Jervis R.E, 1988) (Tan T.C., Chia C.K. and Teo C.K., 1985). Based on these favorable aforementioned properties, the use of human hair as biosorbent could be potentially a low cost alternative for removing metal mixtures from aqueous effluents. So, human hair is presented in this work as a biosorbent for the elimination of heavy metal ions such as Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) from multiple aqueous solutions and under different operating conditions. Considering the important role of the chemical structure and the surface properties of human hair in the metal biosorption process, two different kinds of hair were employed and their biosorption effectiveness of heavy metal ions was compared. One sample is untreated human hair (**H1**), and the other is periodically bleached and dyed hair, which is considered as the treated hair (**H2**). Operational parameters affecting the biosorption process such as the contact time, the pH of the aqueous metal media, and the initial heavy metal concentration were studied in both cases. Biosorption kinetics and equilibrium isotherms were modelled.

Based on the afore mentioned considerations, the aim of this work was to study the effectiveness of human hair as a biosorbent for the removal of heavy metal ions in multiple-metal aqueous solutions and the effect of the main operational parameters on the biosorption step.

2. Experimental

2.1. Materials and methods

Human hair was collected from local barbershops. The untreated hair was from a 27-year old human (**H1**), and the treated (bleached and dyed) hair was from a 45-year old human (**H2**). The collected hair was washed with commercial 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 ºC). The hair was cut to an approximate length of 1-2 mm by using scissors. Particle size has been reduced and controlled (restricted to 1-2 mm) since, as it has been reported previously, the biosorption increase as the range of particle size becomes thinner since smaller particles give large surface areas (Shim Y. S. et al., 2003 and Amuda O.S. et al., 2007). All chemicals used were of analytical grade. Stock solutions of separate heavy metal ions, such as Cr(III), Mn(II), Co(II), Ni(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 each metal ion was first prepared. The initial multiple heavy metal aqueous solution was properly prepared by including eight metals at the concentration level required for each experiment, so, at the corresponding dilution level. Sodium hydroxide (> 98%, from Panreac, Spain) and nitric acid (> 70%, from JT-Baker, Spain) were alternatively used for the pH adjustment of the initial aqueous solution prior 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. Biosorption procedure

The biosorption step was carried out under batch operation mode at a constant temperature of 22±1 ˚C. In all sets of experiments, 0.100 g of human hair was accurately weighted in 50 mL plastic extraction tubes, and 10 mL of the multiple heavy metal aqueous solution was added. The system was properly shaken on a rotary mixer (CE 2000 ABT-4, SBS Instruments SA, Barcelona, Spain) at 25 rpm, during the desired time. After that, solid was separated from the liquid by subsequent decantation and the liquid was filtered through 0.22 μm syringe filter (CN-CA Syringe Filter, HEAION, USA). Finally, to completely separate the biomaterial, a filtration step is added. Later, the metal concentration in the remaining aqueous solutions was determined by an inductively coupled plasma optical emission spectrophotometer with mass detector, ICP-MS (XSERIES 2 ICP-MS, Thermo Scientific, USA).

The uptake of each metal ion by each sample of human hair was calculated using equation 1:

$$\%biosorption = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{(Eq. 1)}$$

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

The exchange capacity (q_t) is the concentration of biosorbed metal ion per unit of mass of biosorbent (in mmol/g) at time t, which was calculated using the equation 2:

$$q_t(mmol/g) = \frac{(C_i - C_f) \times V}{W} \qquad \text{(Eq. 2)}$$

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

The amount of metal sorbed (q_e), is the concentration of biosorbed metal ion per unit of mass of biosorbent (in mmol/g) at the equilibrium, which was obtained as follows (equation 3):

$$q_e(mmol/g) = \frac{(C_i - C_e) \times V}{W} \qquad \text{(Eq. 3)}$$

where V is the total volume of the solution (in L), W is the amount of biosorbent (in g), 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.

For the kinetics studies, the initial metal ion concentration was set at 0.18 mmol/L (for each of the heavy metal ion under study) (López-Mesas et al., 2011). The initial pH of the multiple heavy metal aqueous solution (also at 0.18 mmol/L for each heavy metal ion) was varied within the range 1.0-6.0 when determining the influence of this parameter in the biosorption process (higher pH values are not evaluated to avoid metal hydroxides precipitation). The initial heavy metal concentration was ranged from 0.5×10^{-3} to 0.5 mmol/L for the removal of heavy metals from multiple-metal system when determining the effect of initial concentration. Finally, biosorption isotherm of Pb(II) in single-metal system into human hairs was studied at different initial concentration levels (0.5×10^{-3} to 4 mmol/L mmol/L). The pH was adjusted at 4.0, unless otherwise stated.

Each test was carried out in duplicate and the average values are shown in the corresponding figures (experimental errors found were less than 2% and 5.0×10^{-5} mmol/g in the biosorption percentage and the biosorption capacity, respectively).

2.3. Hair characterization

FTIR and SEM analysis were employed to determine whether the heavy metal biosorption process has some influence in the chemical or on the morphological structure of the hair. To do so, small portions prepared from **H1** and **H2** samples, before and after the biosorption process were checked. For the FTIR analysis, a Bruker Fourier Transform Infrared Spectrometer (FTIR) (Tensor 27, Bruker, Germany) was used. In this case, samples less than 1 mg were used. The spectrum was recorded in the range of 600–4000 cm^{-1} with 16 scans and a resolution of 4 cm^{-1}. SEM images were obtained by using a scanning electronic microscope (ZEISS EVO MA 10, Oberkochen, Germany) at the UAB Microscopy Service. The sample used sputter-coating arrangement.

3. Results and discussion

3.1. Influence of the pH on the heavy metal uptake

The pH has both influences on the metal aqueous speciation and on the chemical functional groups speciation on the active sites of the hair surface (Liu et al., 2007). The effect of the initial pH on the biosorption capacity was studied in the range of pH 1.0 to 6.0 at an initial concentration of metals in solution of 0.18 mmol/L. As showed in Figure 1, in both hair systems the metal uptake was strongly dependent on the pH value of the aqueous solutions. At an initial pH value lower than 3.0, little biosorption occurred for **H1** and **H2**, and especially at pH 1.0 almost no biosorption was observed. A sharply increase in the biosorption capacity took place in the pH range between 3.0 and 5.0 for all heavy metal ions. Above pH 5.0, biosorption of all metal ions were found to be relatively constant. The low biosorption capacity at pH values below than 3.0 is attributed to the high concentration of H^+ ions. In this situation, the concentration of H^+ ions far exceeds the metal ions concentration in the solution and hence H^+ compete with them for reaching the hair surface binding sites (Olgun and Atar, 2012). So, the reduction of protons can efficiently decrease the competition between metal ions and H^+ ions on the biosorbent surface and increase the biosorption metal capacity of the hair.

(Insert Figure 1 here)

Although biosorption process for **H1** and **H2** show similar trend with the pH, there are some clear differences. For the removal of Pb(II), Cr(III) and Cu(II), **H2** is more sensitive to the pH values than **H1**. On the other hand, the biosorption capacity of **H1** to the rest of metal ions under study is low even if pH reaches 6.0. In contrast, the bleached and dyed hair (**H2**) shows a better biosorption capacity compared to **H1** for all the metal ions at pH 5.0 and 6.0 due to the presence of new active sulfonate groups and to the increase of the surface area produced during these treatments. This behavior can be explained since the sulfonate groups created on **H2** surface (after bleaching and dying process) makes it more sensitive to pH change.

3.2. Effect of the initial metal concentration

The effect of the initial metal concentration was evaluated for solutions containing multiple heavy metals, using previously optimized pH (pH = 4.0) and contact time (24 h). The initial metal ion concentration increase from 0.5×10^{-3} to 0.5 mmol/L. Corresponding results are shown in Figure 2.

Figure 2 shows that the concentrations of biosorbed metal at the equilibrium increased with the increase on the initial concentration of metal ions, which is attributed to an increase of the mass-transfer driving force. As it can be seen, the maximum biosorption capacity of **H1** and **H2** was reached for some metal ions, including Mn(II), Co(II), Ni(II), Zn(II) and Cd(II), for initial concentration above 0.05 mmol/L for **H1** and 0.2 mmol/L for **H2**. On the contrary, the biosorption capacity at equilibrium of Pb(II), Cr(III) and Cu(II) for **H1** and **H2** continuously increase with the increase of their initial concentration due to the difference of affinity between Pb(II), Cr(III) and Cu(II) in comparison with the rest of the metals. In this regard, as previously reported, significant amounts of Pb (II) were removed whereas a less amount of Cd (II) was recovered (Krishnan S.S, Cancilla A. and Jervis R.E, 1988).

(Insert Figure 2 here)

3.3. FTIR and SEM characterization

Two different hair systems (**H1** and **H2**, as indicated previously) were characterized by FTIR. As showed in Figure 3 and Table 1, IR absorption bands at 1040, 1075, 1175, and 1229 cm^{-1} all correspond to different products of cystine oxidation. The other peaks at 1241, 1454, 1518, and 1637 cm^{-1} are related to chemical groups of the typical amino acid constituents of human hair. It has been seen that there were no significant differences with other human hair reported previously in the literature (Kim and Park, 2013). In addition, the FTIR absorption bands of both human hairs samples before and after the metal biosorption are not substantially different, indicating that the main functional groups on human hair did not change during the metal biosorption process which can be an indication of a possible reuse of such biomaterial. Nevertheless, comparing **H1** and **H2**, before and after heavy metal biosorption process, only slightly differences in the profile of the bands were found in the range of 1000 to 1300 cm^{-1} (as can be seen in Figure 3b). For **H2** sample, the intensity of the peaks at 1041 and 1175 cm^{-1} of **H2** were higher, as well as the profile became sharper, compared to **H1** sample, due to the greater presence of sulfonate (R-SO_2O^-) in **H2** sample as a result of the oxidation reactions produced during bleaching and/or dyeing treatments carried out.

(Insert Figure 3 and Table 1 here)

Apart from chemical structure, the morphology of a biomass also plays an important role in the biosorption process (López-Mesas et al., 2011). So, SEM micrographs were obtained from **H1** and **H2,** before and after the heavy metal biosorption process (Figure 4). As it can be seen, the surface topography of **H1** and **H2** is slightly different (Figure 4a and 4c, respectively). The bleached and dyed hair **H2**, showed more “jagged” or “chipped” appearance, probably due to those treatments (corresponding to the bleaching and dyeing processes). The rougher surface of **H2** results in an increase of the surface area, which acts by promoting the biosorption of metals, and supports the higher biosorption capacity obtained for **H2** in front of **H1** sample (Figure 2). Furthermore, the biosorption of metals onto the human hair did not affect significantly the morphology of **H1** and **H2** as it can be seen by comparison of Figures 4a and 4b (for **H1**), and 4c and 4d (for **H2**).

(Insert Figure 4 here)

FTIR and SEM characterization results showed that **H2** sample has a bigger surface area as well as more quantity of active sulfonate groups. Consequently, biosorption capacity of **H2** is expected to be higher than for **H1** as it was obtained from the kinetic results. The fact that no morphological differences are found before and after the biosorption process, pointed up that these samples could be reusable, so it can be a practical biosorbent system for further real applications.

3.4. Kinetic studies

Kinetic studies were conducted for both different human hair samples (**H1** and **H2**) to determine the maximum uptake of each metal ions from the initial multiple heavy metal aqueous solution. Figure 5 shows the percentage of biosorption of the eight metal ions (Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)) onto **H1** and **H2** at different contact times (5, 10, 20, 30, and 45 minutes, and 1, 2, 3, 4, 6, 12, 24, 48 and 72 hours).

(Insert Figure 5 here)

From the results shown in Figure 5, it is clear that the two different hairs (**H1** and **H2**) show different biosorption capacities to the different heavy metal ions under study. In general, **H2** reaches the maximum metal uptake in less than 1 h showing better biosorption efficacy than **H1**. For **H1**, even after 48 h of contact between the hair and the heavy metal ion solutions, the system did not reach a maximum uptake value and an equilibrium state for most of the heavy metals studied. For **H1**, only Cu(II), Cr(III) and Pb(II) have high biosorption percentages over this time, around 90%. Percentages of biosorption of Cr(III), Cu(II) and Pb(II) by using **H2** sample reached over 95% in less than 30 min. The higher sorption of **H2** sample is due to the bigger surface area and more abundant accessible functional groups formed during bleaching and dyeing processes as it was demonstrated by SEM and FTIR results. Both **H1** and **H2** show better biosorption capacity to Cr(III), Cu(II) and Pb(II) compared with the rest of metal ions in aqueous solution which have an uptake capacity that increases as follow: Cd(II) > Zn(II) > Ni(II) > Co(II) > Mn(II), and getting always higher biosorption percentages when using **H2** as biosorbent. Given that the biosorption of the Cd(II), Zn(II), Ni(II), Co(II) and Mn(II) onto **H1** was very low (the percentage of biosorption lower than 40% even for longer contact time i.e. 70 h), the kinetic analysis was not considered for the sorption of these metals onto **H1** sample. These results are in agreement with the ones reported by Tan T.C. et al. (Tan T.C., Chia C.K. and Teo C.K., 1985) and Krishman S.S. et al. (Krishnan S.S, Cancilla A. and Jervis R.E, 1988) which showed that human hair has a great capacity for recovering Cr(III), Cu(II) and Pb(II) and a more limited sorption capacity for Cd(II) and Ni(II). In addition, Tan T.C. et al. also reported a profound effect of the presence of other metal ion on the sorption of the metal in a mixed metal ion system. Nevertheless, the percentage of biosorption, even for short contact times, was significative for all metal ions onto **H2** sample (Cd(II) (90%±0.06), Zn(II) (92% ±0.23), Ni(II) (75%±0.26), Co(II) (63%±0.14) and Mn(II) (49%±0.19)), and for this reason all the set of eight heavy metals were considered for modeling the kinetics of biosorption onto **H2**. In brief, it is worth to note that **H2** sample is a better biosorbent relative to **H1**.

3.5. Biosorption kinetics modeling

In order to investigate the kinetics of biosorption of heavy metals onto the hair, the pseudo-first (Ho and McKay, 1998) and pseudo-second (Ho and McKay, 1999) orders kinetic models and the Weber-Morris intraparticle diffusion model (Weber and Morris, 1963) are tested.

3.5.1. Pseudo-first order rate equation

The linear form of the pseudo-first order rate equation, also called Langergren equation is given by the equation 4:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad \text{(Eq. 4)}$$

where q_e and q_t are the concentration of biosorbed metal ion per unit of mass biosorbent (in mmol/g) at the equilibrium and at time t (min), respectively, and k_1 is the rate constant of the equation (in min^{-1}).

The plots of log(q_e-q_t) vs. t for the pseudo-first order model results in the rate rate constants (k_1), the R^2 and the q_e values given in Table 2.

(Insert Table 2 here)

Generally, the pseudo-first order equation does not fit well for the whole range of contact time, so it is applicable over the initial time of sorption process. So, the initial rapid step, where biosorption was fast, has been chosen and the experimental data of this step were fitted by the pseudo-first order model. For **H1,** the range time was less than 24 h when determining Cu(II), Cr(III) and Pb(II). For **H2,** the range time was less than 30 min for Cu(II), Cr(III) and Pb(II), and less than 1 h for the rest of the metals (Cd(II), Ni(II), Zn(II), Co(II) and Mn(II)). For both hair systems, correlation coefficients are found to be above 0.87, but the calculated q_e is not equal to experimental q_e, suggesting the insufficiency of the pseudo-first order model to fit the experimental data for the initial period of time. In order to address this issue the pseudo-second order model was applied to the analysis of the kinetic experimental results.

3.5.2. Pseudo-second order rate equation

The same experimental data were also adjusted to the pseudo-second order kinetic model which is given in the following form (equation 5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{(Eq. 5)}$$

where k_2 is the rate constant of the second-order equation (in mmol/g min), q_e and q_t are the concentration of biosorbed metal ion per unit of mass biosorbent (in mmol/g) at the equilibrium and at time t (min), respectively.

The plots of t/q_t vs. t for the pseudo-second order model results in the corresponding rate constants (k_2), the R^2 and the q_e values given in Table 2. This model is more likely to predict kinetic behavior of biosorption of heavy metal ions into hair for the whole range of contact time studied, indicating that 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 (Ho and McKay, 1999).

As can be seen from the Table 2, pseudo-second order kinetic model provides the better prediction of the biosorption kinetics for whole range of contact time studied compared with pseudo-first order kinetic model. It was corroborated by the extremely high correlation coefficients R^2 (Table 2) and the good regression curves showed in Figure 6 (continuous curves), for **H1** and **H2**, where theoretical biosorption capacity (q_t) data were calculated by the pseudo-second order model and compared with the experimental data. Moreover, the relationship between the measured and the predicted data was better for **H2** compared to **H1**. So, it seems that chemical sorption is the rate-controlling step in this biosorbate-biosorbent pair system, as the pseudo-second order model provides the best correlation of the experimental data.

(Insert Figure 6 here)

3.5.3. Weber-Morris intraparticle diffusion model

The intraparticle diffusion model proposed by Weber and Morris in 1962 has been widely applied in the determination of intraparticle diffusion rate constant, k_3, and the boundary resistance, k_d (Weber and Morris, 1963). This model is expressed as the following equation 6:

$$q_t = k_3 t^{1/2} + k_d \qquad \text{(Eq. 6)}$$

where k_3 is the intraparticle diffusion rate constant (mmol/(g min$^{1/2}$)) and k_d is the intercept that gives idea about the thickness of the boundary layer, and q_t is the concentration of biosorbed metal ion per unit of mass biosorbent (in mmol/g) at time t (min).

According to Weber and Morris, if the rate-limiting step is intraparticle diffusion, a plot of solute sorbed (q_t) against the square root of the contact time (t) should yield a straight line passing through the origin. In this case, the plot can be divided into multi-linearity correlations (Figure 7), which indicates that three steps occur during the whole biosorption process (Ofomaja, 2010) (Wu, Tseng and Juang 2009) and therefore many steps influence the sorption process. The first linear portion can be attributed to the transport of metal species from the solution to the external surface of the biosorbent through film diffusion, especially to the diffusion of the metal species on the boundary layer. The second linear portion describes the gradual biosorption where the intraparticle diffusion is rate-limiting. The third stage was attributed to the final equilibrium where the intraparticle diffusion starts to slow down due to extremely low biosorbate concentration left in solution. Moreover, the deviation of straight line from the origin indicated that the pore diffusion is not the sole rate-controlling step. Consequently, both the film diffusion and intraparticle diffusion were simultaneously operating during the biosorption process.

(Insert Figure 7 here)

3.6. Sorption isotherm modeling

Freundlich and Langmuir isotherm models (Febrianto et al., 2009) (Liu et al., 2004) were selected to fit the experimental data of biosorption of Pb (II). The linear forms of the Freundlich and Langmuir isotherms are presented by the following equations, (equation 7) and (equation 8), respectively:

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \qquad \text{(Eq. 7)}$$

$$\frac{C_e}{q_e} = \frac{b}{K_L} C_e + \frac{1}{K_L} \qquad \text{(Eq. 8)}$$

where C_e is the equilibrium concentration of the metal ion in the residual solution (in mol/L), q_e is the equilibrium concentration of the sorbed 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. Q_0 and b correspond 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 (7) and (8), log q_e versus log C_e and C_e/q_e versus C_e are calculated and compared with the experimental data, respectively. Also, all the constants and correlation coefficients obtained for each model are summarized in Table 3.

(Insert Table 3 here)

From the correlation coefficient values, it was observed that the Langmuir isotherm ($R^2 > 0.99$) fitted the data better than the Freundlich isotherm showing that the biosorption process rely on a specific sites sorption mechanism where adsorbate molecules occupy specific sites on the biosorbent. Taking on board the Langmuir equation, the saturated biosorption capacity of **H1** and **H2** at 295 K for Pb(II) were calculated: 1.70×10^{-5} and 23.2×10^{-5} mol/g, respectively.

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 the following equation (9):

$$\Delta G^0 = -RT \ln b \qquad \text{(Eq. 9)}$$

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 of **H1** and **H2** are shown in Table 3. The negative ΔG^0 values indicated that the biosorption of metals into human hair is thermodynamically feasible and of spontaneous nature.

4. Conclusions

The biosorption of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) from their multiple aqueous solutions by two different hair systems were investigated. The bleached and dyed hair (**H2**) showed better biosorption capacity than **H1** (untreated one). The biosorption capacities of the heavy metal ions followed the order Cu(II) > Pb(II) > Cr(III) > Zn(II) > Cd(II) > Ni(II) > Co(II) > Mn(II) for **H2**, and Cu(II) > Cr(III) > Pb(II) for **H1**, being not significant the biosorption of the rest of the heavy metal ions for **H1**. The operating parameters, such as the contact time, the pH of the aqueous solution and the initial metal concentration strongly affect the efficacy of removing the selected heavy metal ions under study. **H2** shows faster biosorption rate than **H1**. The optimum pH value is 4.0. For the multiple heavy metal solution, the maximum removal of Cu(II), Cr(III) and Pb(II) efficiencies are found to be higher than 90% for **H1** and higher than 95% for **H2**. Kinetic modeling of the equilibrium data shows that the biosorption of heavy metal ions onto human hair follows well the pseudo-second order kinetic and the Weber-Morris intraparticle diffusion models, which means that both chemisorption and intraparticle diffusion are the rate-controlling steps. Biosorption at equilibrium was better correlated with Langmuir isotherm model compared to Freundlich model. The calculated standard Gibb's free energy (ΔG^0) indicated the feasibility and spontaneous nature of the biosorption process. The better biosorption capacity of **H2** was attributed to the more abundant active functional groups (especially sulfonate ones) formed during bleaching and dyeing treatments and the bigger surface area relative to **H1**. So, the human hair shows satisfactory biosorption capacity, which can be enhanced with the common bleaching and dyeing treatments, and can be considered as a potential biosorbent for the removal of heavy metal ions.

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Conflict of Interest

There are no conflicts of interest associated with this publication.

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