Valorization of keratin biofibers for removing heavy metals from aqueous solutions

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Abstract: Four common waste keratin biofibers (human hair, dog hair, chicken feathers and degreased wool) have been used as biosorbents for the removal of heavy metal ions from aqueous solutions. Different parameters of the biosorption processes were optimized in batch systems. For multiple-metal system, consisting on a mixture of eight metal ions (Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)) , the total metal biosorption increased following the order: degreased wool > chicken feathers> human hair > dog hair. From the kinetic models tested, the pseudo-second order provided better results. Furthermore, biosorption isotherms of Pb(II) with the different keratin biofibers fitted properly Langmuir model. Surface morphology of the biosorbents were analyzed

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before and after the sorption by FTIR and SEM. The keratin biofibers tested are potentially good sorbents of metal ions, being the degreased wool and chicken feathers the more efficient ones.

Keywords: Sorption, waste reduction, kinetic study, environmental sustainability, keratin, heavy metal.

1. Introduction

In the last decade, particular attention has been paid to the application of biotechnology for heavy metal pollution control [1-8] as an alternative to conventional techniques such as chemical precipitation, membrane filtration, electrochemical treatment, solvent extraction, ion exchange, evaporation and adsorption on activated carbon [9-13]. In this sense, biosorption has been postulated as an alternative process based on the removal of metal or metalloid species from solution by various certain natural materials of biological origin [14, 15]. Particularly, waste biogenic materials are considered ideal alternatives for the removal of heavy metals from low strength wastewater due to their low cost and high sorption efficiency [16, 17]. Among the various biosorbents, cellulosic waste materials are the most abundant biosorbents for the removal of heavy metals, which include agricultural waste materials [18, 19] and waste products from timber industry [20]. Chitin is the second most abundant as has shown excellent biosorbent properties for the removal of heavy metals [21]. Brown algae also exhibit an excellent sorption uptake over a wide variety of metals [22, 23], such as brown seaweeds applied for antimony oxyanions biosorption [24]. In addition, keratinous material such as wool [6, 7], feather [5,25], hair [8] and horn are also relatively abundant and inexpensive materials that are generated in large quantity and can be effectively used to remove heavy metals due to their high content in carboxyl, hydroxyl, amino and sulfur-containing functional groups [26]. So, due to their ability to sorb heavy metals from aqueous solutions, native or processed keratinous materials have been used for the treatment of heavy metal pollution. Studies on wool keratin for removing mixtures of metals such as Ni(II), Cu(II), Zn(II), Cd(II),

Hg(II) and Pb(II) has been previously reported in the literature [27]. Another form of keratin, human hair, has been used for binding various heavy metals [28] such as Hg(II), Ag(I), Pb(II), Cd(II), Cu(II), Cr(VI), Ni(II), Cr(III). Alternatively to wool and hair, a more abundant and cheap keratin waste, such as chicken feathers, has also been proposed as a biosorbent of copper, zinc, lead, chromium, mercury and uranium [29, 30].

As far as the authors know, there is not a comparative study between different keratin-based biosorbents (human hair, dog hair, wool and chicken feathers) using a multiple-metal aqueous solution to evaluate both the efficacy of each biosorbent and the competitive interaction between ions such as Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) during the biosorption step. Hence, the aim of this work is to assess and compare the performance of the human hair, dog hair, chicken feather and degreased wool for the removal of heavy metals from multiple-metal aqueous solutions, studying the influence of the operating conditions such as the solution pH, the biosorbent dosage and the contact time on the sorption process. The experimental kinetic data were evaluated by applying the pseudo-first and pseudo-second order kinetic models.

2. Experimental

2.1. Chemicals

All the chemicals used in this work were of analytical grade. Stock solutions of individual 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. Sodium hydroxide (> 98%, from Panreac, Spain) and nitric acid (>

70%, from JT-Baker, Spain) were used for pH adjustment of the initial aqueous solution prior the biosorption experiments. EDTA (Ethylenediaminetetraacetic acid, >99 % from Sigma-Aldrich)

2.2. Biosorbents

All the different samples were washed with commercial detergent, rinsed several times with deionized water and then left to dry at room temperature (22±1 ºC).

The native hair sample was kindly provided by a local hairdressing (in Terrassa city). It consisted in a mixture of hairs of four teenagers and was selected from a previous study were up to 32 different hair samples from different ages were evaluated for heavy metals removal [31]. The hair was cut to an approximate length of 5 mm by using scissors and a fraction of the total mass was used in the batch biosorption experiments.

One dog hair sample was obtained from a local dog grooming service. After washing, an electrical grinding machine was used to make the dog hair much looser than the initial one. The loose dog hair was used in the batch biosorption experiments.

Chicken feathers and degreased wool yarns were kindly provided by a regional poultry farm and textile company, respectively. After washing, feathers and wool were directly used in the batch 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)

2.3. Characterization of biosorbents

Structural characterization of these four keratinous materials was carried out to analyze any chemical change produced in the samples after the biosorption of heavy metals. The identification of the functional groups on the keratin biofibers was performed by using Fourier transform infrared spectrometer (FT-IR) (Tensor 27, Bruker, Germany). The spectrum was recorded in the range of 600–4000 cm^{-1} with 16 scans and a resolution of 4 cm^{-1}. On the other hand, their surface morphology was observed by Scanning electron microscope (SEM ZEISS EVO® MA 10, Oberkochen, Germany). In this case, the samples were prepared by using sputter-coating arrangement.

2.4. Batch biosorption experiments

The biosorption step for removing heavy metal ions from the aqueous solution by using biosorbent (human hair, dog hair, chicken feather and degreased wool) was carried out under batch operation mode at a constant temperature of 22±1 ˚C. In all sets of experiments, 0.100 g of biosorbent was accurately weighted in 50 mL plastic extraction tubes, and 10 mL of 0.10 mmol/L for each metal of the multiple-metal aqueous solution was added at pH 4.0. 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 (usually 24 h, to ensure that equilibrium is reached). After that, the two phases were separated by decantation and the liquid was filtered through 0.22 μm Millipore filters (Millex-GS, Millipore, Ireland). Finally, after the filtration step, the metal concentration in the remaining aqueous solutions was determined by an Inductively Coupled Plasma Mass Spectrometry, ICP-MS (XSERIES 2 ICP-MS, Thermo Scientific, USA).

The percentage of biosorption of each metal ion by each biofibre was calculated using equation 1.:

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

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

In a similar way, the effect of the pH on the biosorption of heavy metals was analyzed in the pH range from 1.0 to 6.0 in the multiple-metal aqueous solution (higher pH values were not evaluated to avoid metal hydroxides precipitation), at 0.18 mmol/L for each metal. To study the effect of the biosorbent amount on metal uptake, its mass was varied from 0.01 to 0.2 g. For the kinetic studies, the multiple-metal aqueous solution or a single one (Pb(II)) at pH 4.0 were analyzed from 5 minutes up to 72 hours. The experiments were performed as previously described.

The metal uptake (q_t) is the concentration of each biosorbed metal ion per unit of mass of the biosorbent used (in mmol/g) at time *t*, which was calculated using equation 2.

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

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

2.5. Desorption, regeneration and reuse

Desorption experiments were performed just for the case of Pb(II), after the corresponding biosorption step by using these four keratin biofibers, and after the proper centrifugation and filtration steps (by Millipore filters), as indicated in the previous section. For that purpose, each biosorbent material containing the sorbed Pb(II) was contacted and stirred with 10 mL of 0.1 mol/L HNO_3 or 10 mL of 0.1 mol/L EDTA , separately. After 24 h of stirring at room temperature (22±1 ˚C), the aqueous and the solid phases were properly separated (by centrifugation and filtration as usual), and the Pb(II) content of the final and the initial aqueous solutions were analyzed by ICP-MS, as indicated. Desorption percentage was calculated using equation 3.

$$\%\ desorption = \frac{amount\ \ of\ \ Pb(II)\ \ desorbed}{amount\ \ of\ \ Pb(II)\ \ biosorbed} x100 \qquad (3)$$

The reuse of these four keratin biofibers in a second biosorption step, requires the desorption, or elution, of the previous sorbed metal ions using HNO_3 or EDTA. For that reusing purpose, two methods were proposed to regenerate the biomaterials after the metal elution step. So, on one hand, deionized water was used to regenerate the biosorbent surface that was previously eluted either with H^+ or EDTA. In this case, the removal of metal ions was accomplished either by ionic exchange with the protons from HNO_3 or by formation of a complex with $EDTA^-$, respectively. On the other hand, particularly in the case that EDTA has been used as eluent, a two steps method was used to regenerate the biosorbent that consisted of a first rinsing with HNO_3 solution and subsequent rinsing with deionized water.

Furthermore, the biosorbents properly regenerated by using both methods were dried in an oven at 40 ˚C. The different regenerated keratin biomaterial samples properly obtained were employed to biosorb Pb(II) again.

All batch biosorption, desorption and regeneration experiments were carried out in duplicates.

3. Results and discussion

The keratin biogenic materials including human hair, dog hair, chicken feathers and degreased wool were evaluated as biosorbents for the removal of heavy metals from a multiple-metal aqueous solution containing eight metal ions (Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)). The results are shown in Figure 1. The four biofibers show different biosorption capacities for the different metal ions. In general, the biofibers exhibit better biosorption capacities for Cr(III), Cu(II) and Pb(II) compared with the rest of metal ions present in the initial aqueous solution, which have uptake capacities that decrease as follow: Cd(II) > Zn(II) > Ni(II) ≈ Co(II) > Mn(II). This behavior can be explained by the different affinity of metal ions for the metal binding donor atoms present in all the biosorbents (related to the chemical groups such as hydroxyl, amino, carboxyl and sulfur).

Comparing the different behavior of the four biosorbents (Figure 1), thei biosorption (in terms of total amount of metals biosorbed), followed the order: degreased wool > chicken feathers > human hair > dog hair. Besides some environmental factors, such as sunlight, chlorinated water and frequent shampooing that could cause partial oxidation of the keratin biomaterial surface, differences in the keratin chemical structure should be

took into account to explain its different biosorption capacities over the selected metal ions (see results from Figure 1). For example, wool keratin has different amino acid composition higher molecular weight and more sites for S-S cross linking than feather keratin [32]. So, these differences have resulted in the better biosorption of the wool compared with other keratin biofibers.

Figure 1

3.2. FT-IR and SEM Characterization

The FT-IR analysis is carried out to identify the functional groups in the different biosorbents that might be involved in the biosorption process. A comparison of FT-IR spectra of these four biosorbents before and after the biosorption step is shown in Figure 2 (a)-(d) (in the later case, the biosorbents analyzed were those used in the previous experiment, corresponding to Figure 1). The wave numbers and approximate assignments of the vibrational modes for the FT-IR spectra are listed in Table 1 [33, 34].

Figure 2

Table 1

The FT-IR spectra of the biofibers before and after the biosorption step are very similar, which indicates that the main functional groups on the biosorbents did not change significantly during the biosorption process. The finding can be an indication of the

possible reuse of such biofibers. Nevetherless, the four metal-loaded biosorbents show small differences in the FT-IR spectra with the original ones. For instance, the peak at 1072.1 cm^{-1} corresponding to the cystine monoxide (R-SO-S-R) of human hair has a small shift to 1071.6 cm^{-1} after the metal biosorption process. The same changes also happened to the other three keratin biosorbents. Moreover, more slightly shifts of the peaks are found in other functional groups which can be seen in the spectra collected in Figure 2 (a)-(d). However, this small shifts are not sufficiently indicative of the involvement of the main functional groups (hydroxyl, amino, carboxyl and sulfur-containing functional groups) in the biosorption since the changes observed in the spectra could also be correlated with the extent of the sorption.

The surface morphologies of the four keratin biofibers under study were observed by Scanning Electron Microscope (SEM) before and after the metal biosorption process (corresponding SEM images are shown in Figure 3 (a)-(d)). As can be seen, there are no significant differences on the surface morphology of the four biosorbents before and after their use. This result suggests that the four biosorbents are relatively stable under the biosorption process, which is favorable in terms of their reuse. The surface morphologies of the human and dog hair and wool are very similar, which appears to be quite similar after the biosorption process. This suggest that the cuticle scales did not suffer from degradation during the biosorption step (see Figure 3 (a2), (b2) and (d2) and compared with Figure 3 (a1), (b1) and (d1), respectively). In the case of the chicken feathers rough appearance after biosorption process is seen (Figure 3 (c2) compared with (c1)), probably due to their degradation, under the acidic conditions of the metal aqueous solution. The

greater degradation of the chicken feather sample may be caused by their lower cystine content that contributes to their lower stability compared with the other biosorbents. In addition, it is noteworthy that chicken feathers expose higher surface area with the same amount of biomaterial (0.1 g in all cases) compared with the other three keratin biofibers under study, which lead to a relatively good biosorption.

Figure 3

3.3. Effect of the initial pH

The initial aqueous pH is a key parameter in metal biosorption process [35]. As usual, batch biosorption experiments were carried out in the pH range of 1.0 to 6.0 in a multiple-metal system containing the four metals with higher affinity to keratin, such as Cr(III), Cu(II), Cd(II) and Pb(II) (Figure 4 (a)-(d)). The biosorption of metal ions increases significantly with the increase of the aqueous pH value. At lower pH values, metal ions had to compete with a large number of protons for the binding sites on the biosorbent surface. Therefore, the biosorption capacities of the metal ions are very low for all four biosorbents under high acidic conditions. As pH increased, the concentration of proton decreases, and the positive metal ions can be easily sorbed by the available binding sites on the biosorbent surface. Above pH 4.0, biosorption of metal ions was found to be relatively constant up to pH 5.0. The higher biosorption values found over pH 5.0 are probably due to the metal speciation, so, with the partial hydrolysis of the metal ions under study. Therefore, the pH 4.0 was selected as optimal condition in the subsequent experiments.

Figure 4

3.4. Effect of biosorbent dosage

The removal of heavy metal ions depends on the amount of biosorbent [36]. Hence, the effect of biosorbent dosage on the biosorption of multiple-metal aqueous solution (Cr(III), Cu(II), Cd(II) and Pb(II) with a concentration of 0.18 mmol of each metal ion/L) for the different keratin biofibers was studied and the results are shown in Figure 5 (a)-(d). The biosorption percentage of metal ions increases with the increase of biosorbent dosage, due to the increase of the total surface area that results in a greater number of available metal binding sites [37]. There is a slight sharper increase in the biosorption percentage when increasing the biosorbent dosage for Pb(II) ions compared with the other metal ions present in the initial aqueous solution (being Cr(III), and Cu(II) closer, and Cd(II) the lowest one). This behavior can be explained due to the different affinity of each heavy metal ion for the keratin support [38].

Figure 5

3.5. Effect of the contact time

Multiple-metal aqueous system of Cr(III), Cu(II), Cd(II) and Pb(II) and single-metal aqueous system of Pb(II) (both at pH 4.0) were contacted with the keratin biofibers (0.1 g of each one) during 5, 10, 20, 30, 45 minutes, and 1, 2, 3, 4, 6, 12, 24, 48 and 72 hours. Results plotted in Figure 6 (a)-(d) show the biosorption percentage in each biosorbent case

Figure 6

Firstly, it was observed that in all cases the biosorption percentage of metal ions increases with the increase of the time until the equilibrium is reached. As seen from the results, the different biosorbents under study require different time interval to reach such equilibrium. In general, the biosorption of metal ions consisted in two steps: an initial rapid step, where the rate of biosorption is quite high, and a second slower step where the equilibrium uptake is achieved. Moreover, the biosorption process of the multiple-metal system (Cr(III), Cu(II), Cd(II) and Pb(II)) by the four biofibers is different and also depending on the metal sorbed. The biosorption percentage of Cr(III), Cu(II) and Pb(II) by human hair and dog hair increases gradually when increasing contact time, reaching nearly equilibrium at around 24 h. For the degreased wool only 6 h are needed to reach the equilibrium. In the case of the chicken feathers, the removal of Cu(II) and Pb(II) ions increases sharply with time, and reaches the equilibrium after 30 minutes, being necessary 48 h for Cr(III). Biosorption of Cu(II) and Pb(II) is higher than Cr(III) and Cd(II) regardless the biosorbent used. All the biosorbents show low removal of Cd(II), even at long time of the biosorption process, and the maximum of biosorption percentage is about 20%. So, in the subsequent kinetic analysis Cd(II) was not considered for the biosorption modeling step.

3.6. Biosorption kinetics modeling

The linearized pseudo-first (Equation 4) and second (Equation 5) order kinetic

models have been most widely used for the sorption of a sorbate from an aqueous solution [39-43]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

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 and k_2 (in min^{-1}) are the rate constants. The k_1, k_2 and q_e values are calculated from each fitting and are given in Table 2.

Table 2

The results indicate that the pseudo-first order equation does not fit well over the entire range of contact time investigated, which is generally applicable only over the initial time of the sorption process [44]. The calculated q_e by this model differs significantly of those measured experimentally, which is suggesting the insufficiency of the pseudo-first order model to fit the experimental data. An exception was noted for the Cr(III)/human hair system, where the pseudo-first order equation fits well in the whole range of time with high coefficient of determination (0,9472), and the calculated q_e is close to experimental one (just slightly smaller). The reason for these slightly differences in the q_e values of the Cr(III)/human hair system is that there is a time lag, possibly due

to the boundary layer at the surface of the biosorbent or the external resistance at the surface controlling the beginning of the sorption process [45].

In contrast, except for the biosorption of Cr(III) by human hair, the pseudo-second kinetic model showed the best fit to the experimental data with the highest coefficients of determination (R^2 >0.95). In addition, as shown in Table 2, most of the pseudo-second order calculated q_e values agree with the experimental data. Thus, these results suggest that the rate limiting step might be the chemical sorption. Chemical sorption could occur by the functional groups on the biosorbent surface with the metal ions as valence forces through sharing or exchange electrons.

According to the kinetic studies, the Cr(III)/human hair system was found to fit better to the pseudo-first order equation, while the rest of the metal/ biosorbent systems fit better to the pseudo-second order equation. For all the metal/biosorbent systems, the theoretical biosorption (q_t) data calculated by the agreeable kinetic models and the experimental ones are shown in the Figure 7, where it can be seen the close prediction of the models to the experimental data.

Figure 7

3.7. Biosorption isotherm modeling

The equilibrium sorption studies were performed to provide the maximum metal adsorption capacities of the biosorbents. Hence, the biosorption of Pb(II) by human hair, dog hair, chicken feathers and degreased wool were determined experimentally, and the results were fit to the known Freundlich and Langmuir isotherm models (Equations 6 and

7, respectively).

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \qquad (6)$$

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 adsorbed metal per unit of mass of sorbent (in mol/g), k_F and n are Freundlich constants related to the sorption capacity.

$$\frac{C_e}{q_e} = \frac{b}{K_L} C_e + \frac{1}{K_L} \qquad (7)$$

where K_L is the equilibrium adsorption constant which is related to the affinity of the binding sites, $K_L = Q_0 b$, Q_0 (mol/g) is the saturation concentration of the sorbed metal ion per unit of mass of sorbent and b is the ratio of sorption/desorption rates (L/mol).

The Freundlich and Langmuir parameters for the four biomaterials under study, with the respective coefficients of determination R^2, are shown in Table 3. It was observed that the equilibrium data are better represented by the Langmuir isotherm equation with high coefficient of determination (R^2 >0.98) in all cases when compared to the Freundlich equation. In addition, the Langmuir plots, represented in Figure 8, and the good agreement with the corresponding experimental data suggest that the biosorption occurs by sorption in specific sites. Moreover, from the results, it can be concluded that chicken feathers are the best biosorbent for the removal of Pb(II) among the four biosorbents studied. Since

the maximum biosorption capacities of the four biosorbents (see Table 3) follows the order chicken feathers (3.87×10^{-5} mol/g) > degreased wool (3.40×10^{-5} mol/g) > human hair (2.43×10^{-5} mol/g) > dog hair (2.07×10^{-5} mol/g) for Pb(II) at 295K. These values are lower than the maximum biosorption capacity of Pb(II) reported by Kong et al. [46] for keratin waste-hide waste biosorbent that were between 1.06×10^{-4} - 1.56×10^{-4} mol/g. Compared with conventional sorbents such as bentonite and activated carbon with reported maximum sorption capacities of Pb(II) of 3.13×10^{-5} [47] and 3.22×10^{-5} [48], respectively, the biosorption capacity of the four keratin biofibers was found to be comparable.

Table 3

Figure 8

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 (8)

$$\Delta G^0 = -RT \ln b \qquad (8)$$

where b is the Langmuir equilibrium constant shown in equation (7), 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 also shown in Table 3. The negative ΔG^0 values indicates that the biosorption of metals into these four keratin biomaterials is thermodynamically feasible and of spontaneous nature.

3.8. Desorption, regeneration and reuse studies

Recovery of the sorbed heavy metals and reuse of the biosorbent are of significance for practical applications [49]. Desorption results for all the Pb(II) loaded keratin biofibers by using EDTA or HNO_3 solutions as eluents are collected in Table 4. For the native human hair, the elution efficiency with HNO_3 solution is higher than the one with EDTA, being 76% and 48%, respectively. On the contrary, the recovery of Pb(II) from degreased wool with EDTA is much better than that with HNO_3. In the case of chicken feathers, EDTA and HNO_3 have the same elution efficiency for Pb(II) reaching values around 100%.

The reuse of the regenerated keratin biofibers for the continuous removal of heavy metals has been here investigated. For that purpose, as indicated, two regeneration methods were also checked: one rinsing with deionized water, the other rinsing with HNO_3 firstly and then with deionized water (this just in the case that EDTA is used as eluent). After regeneration, the samples were used again to biosorb Pb(II) ions from aqueous solution. It was found that the elution with EDTA and subsequent regeneration with HNO_3/deionized water of these four biosorbents allow their reuse for a second biosorption step of metal ions. Furthermore, the results also indicate that the biosorption capacities of these four biosorbents decrease compared with the first time. The human and dog hairs are deprived of half of their biosorption capacities, and the biosorption capacities of chicken feathers and degreased wool also decreased from 97% to 72%.

Table 4

4. Conclusions

Human hair, dog hair, chicken feathers and degreased wool have been used successfully for the removal of heavy metals from aqueous solution since these keratin biofibers contain carbonyl, hydroxyl, amino and sulfur groups that act as biosorption sites for metal ions. It was demonstrated that biosorption was affected by various parameters such as the pH of the initial aqueous solution, and the contact time, mainly.

The four keratin biofibers exhibit better biosorption for Cr(III), Cu(II) and Pb(II) compared with the rest of metal ions present in the initial multiple-metal aqueous solution, which have an uptake that decrease as follow: Cd(II) > Zn(II) > Ni(II) ≈ Co(II) > Mn(II). For a multiple-metal mixture consisting in Cr(III), Cu(II), Cd(II) and Pb(II) the aqueous pH is found to be a critical parameter in the biosorption processes for both the metal ion and the binding site speciation, with an optimum pH being 4.0 in most of the cases. In addition, the increase in the biosorbent dosage leads to a small increase in the metal removal, so it was a not significant parameter in the studied range. In general, the experimental biosorption data fits well the pseudo-second order kinetic model which indicates that chemical sorption is the basic mechanism governing the process (except for Cr(III)/human hair, which fits to the pseudo-first order).

Sorption isotherm of Pb(II) into the four biomaterials fit very well the Langmuir isotherm equation, confirming the mechanism of sorption in specific sites. The maximum biosorption capacities of Pb(II) at 22±1 ˚C were 2.43×10^{-5}, 2.07×10^{-5}, 3.87×10^{-5}, and 3.40×10^{-5} mol/g for human hair, dog hair, chicken feathers and degreased wool, respectively. The calculated standard Gibb's free energy (ΔG^{0}) for all the four

biomaterials indicates the thermodynamically feasible and spontaneous nature of the biosorption process.

In addition, it was demonstrated that biofibers loaded with Pb(II) can be regenerated with EDTA, even though their subsequently biosorption decreases compared to the first time.

Taking into consideration present findings, these four keratin biofibers, being cheap and easily available materials, could be an alternative to more costly adsorbents used for heavy metals removal in wastewater treatment processes.

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TABLES

Table 1. FT-IR spectral bands assignments for human hair, dog hair, chicken feathers and degreased wool, before their use.

Assignments	Wave numbers(cm^{-1})			
	Human hair	Dog hair	Chicken feathers	Degreased wool
NH stretching	3280	3273	3268	3272
C-H stretching, $-CH_3$ and $-CH_2-$ asymmetric	2957	2957	2961	2961
and symmetric modes	2924	2926	2922	2930
Amide I, 80% C=O stretch and small contribution from NH bend	1630	1629	1624	1629
Amide II, C-N stretching/N-H bending	1517	1516	1534	1515
Amide III, complex vibration contains N-H bending, C-N stretching, C=O stretching, and O=C=N bending	1233	1232	1235	1234
Cystine	1180 - 1030			

Table 2. Biosorption kinetic constants for the biosorption of Cr(III), Cu(II), Cd(II) and Pb(II) by human hair, dog hair, chicken feathers and degreased wool.

Biosorbent	Metal	Experimental	Pseudo-first order			Pseudo-second order		
		$*q_{max}\times10^2$ (mmol/g)	$k_1\times10^3$ (min^{-1})	$q_e\times10^2$ (mmol/g)	R^2	k_2(g/mmol min)	$q_e\times10^2$ (mmol/g)	R^2
Human hair	Cr/multiple	1.278	8045.1[f]	1.177	0.9472	0.108	1.425	0.9983
	Cu/multiple	1.118	2.53[e]	0.671	0.9817	1.059	1.115	0.9962
	Pb/multiple	1.231	15.89[a]	0.937	0.8660	0.884	1.207	0.9937
Dog hair	Cr/multiple	0.689	3.87[b]	5.88	0.8596	0.670	0.673	0.9714
	Cu/multiple	0.883	6.72[b]	0.408	0.9364	1.83	0.886	0.9973
	Pb/multiple	1.064	3.8[b]	1.034	0.9199	0.285	1.137	0.9848
Chicken feathers	Cr/multiple	1.196	0.909[f]	0.972	0.9395	0.309	1.209	0.9599
	Cu/multiple	1.390	37.47[c]	0.543	0.8354	5.69	1.38	0.9997
	Pb/multiple	1.481	1,60	0.05	0.3196	365.4	1.474	0.9999
Degreased wool	Cr/multiple	1.457	10.59[c]	1.347	0.9017	0.718	1.466	0.9985
	Cu/multiple	1.505	28.17[c]	1.088	0.9414	6.307	1.489	0.9999
	Pb/multiple	1.366	8.41[c]	1.298	0.9593	0.883	1.389	0.9999

a): 30 min, b): 45 min, c) 1 h, d): 3 h, e): 6 h, f): 72 h

$*q_{max}$ is the maximum concentration of metal per unit of mass of biosorbent at equilibrium determined experimentally.

Table 3. Freundlich and Langmuir isotherms constants for the biosorption of Pb(II) by human hair, dog hair, chicken feathers and degreased wool.

	constant	Human hair	Dog hair	Chicken feathers	Degreased wool
Freundlich	$K_F \times 10^4$	4.89	3.50	8.38	9.00
	n	2.51	2.34	2.52	2.46
	R^2	0.7574	0.8498	0.6766	0.6526
Langmuir	$Q_0 \times 10^5$ (mol/g)	2.43	2.07	3.87	3.40
	$b \times 10^{-4}$ (L/mol)	4.48	0.916	8.84	12.1
	K_L (L/g)	1.09	0.189	3.42	4.12
	R^2	0.9990	0.9899	0.9998	0.9999
	$-\Delta G^0$ (kJ/mol)	26.3	22.4	27.9	28.7

Table 4. The elution of biosorbed Pb(II) by using EDTA and HNO_3 solutions.

Biosorbent	Metal biosorbed (%)	Pb(II) elution efficiency (%) using EDTA (0.1 M)	Pb(II) elution efficiency (%) using HNO_3 (0.1 M)
Human hair	80 ± 1	48 ± 1	76 ± 1
Dog hair	89 ± 2	62 ± 2	61 ± 1
Chicken feather	98 ± 1	100 ± 2	100 ± 1
Degreased wool	97 ± 1	88 ± 4	67 ± 1

FIGURE CAPTIONS

Figure 1. Biosorption of human hair, dog hair, chicken feather and degreased wool for Cr(III), Mn(II), Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Pb(II) in multiple-metal aqueous system. Initial metal concentration of 0.1 mmol of each metal ion/L, contact time of 24 h, initial pH of 4.0, and 0.1 g of biosorbent in 10 mL of initial solution.

Figure. 2. FT-IR spectra of human hair (a), dog hair (b), chicken feathers (c) and degreased wool (d): fiber alone (below) and metal loaded fiber (above)

Figure 3. Scanning electron microscopy (SEM) micrographs of the biosorbents: (a1) and (a2) correspond to the human hair and metal loaded human hair; (b1) and (b2) correspond to the dog hair and metal loaded dog hair; (c1) and (c2) correspond to the chicken feathers and metal loaded chicken feathers; and (d1) and (d2) correspond to the degreased wool and metal loaded degreased wool.

Figure 4. Effect of the initial pH on the biosorption of Cr(III), Cu(II), Cd(II) and Pb(II) by human hair (a), dog hair (b), chicken feathers (c), and degreased wool (d) from the multiple-metal system.

Figure 5. Percentage of biosorption for Cr(III), Cu(II), Cd(II) and Pb(II) in multiple-metal system by human hair (a), dog hair (b), chicken feathers (c) and degreased wool (d) with different amounts of biosorbents. Initial metal ions concentration of 0.18 mmol of each metal/L, contact time of 24 h, and initial pH of 4.0, in 10 mL of initial aqueous solution.

Figure 6. Biosorption percentage of Cr(III), Cu(II), Cd(II) and Pb(II) by human hair (a), dog hair (b), chicken feathers (c) and degreased wool (d) from multiple-metal system at different contact time. Initial metal ions concentration of 0.18 mmol/L of metal, pH 4.0, and 0.1 g of biosorbent.

Figure 7. Experimental (.) and calculated (-) values fitting to the kinetic model equation: (a) human hair, (b) dog hair, (c) chicken feathers and (d) degreased wool.

Figure 8. Experimental (.) and calculated (-) values adjusted by using the Langmuir isotherm model for the biosorption of Pb(II) by using human hair, dog hair, chicken feathers and degreased wool.

FIGURES

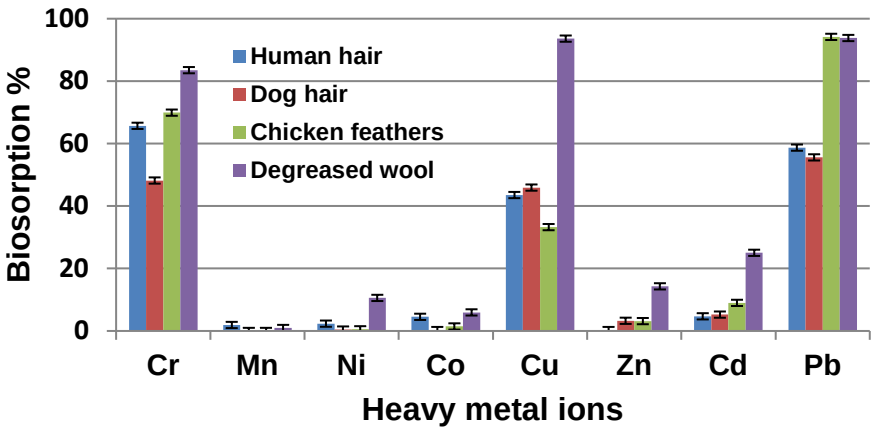

Figure 1

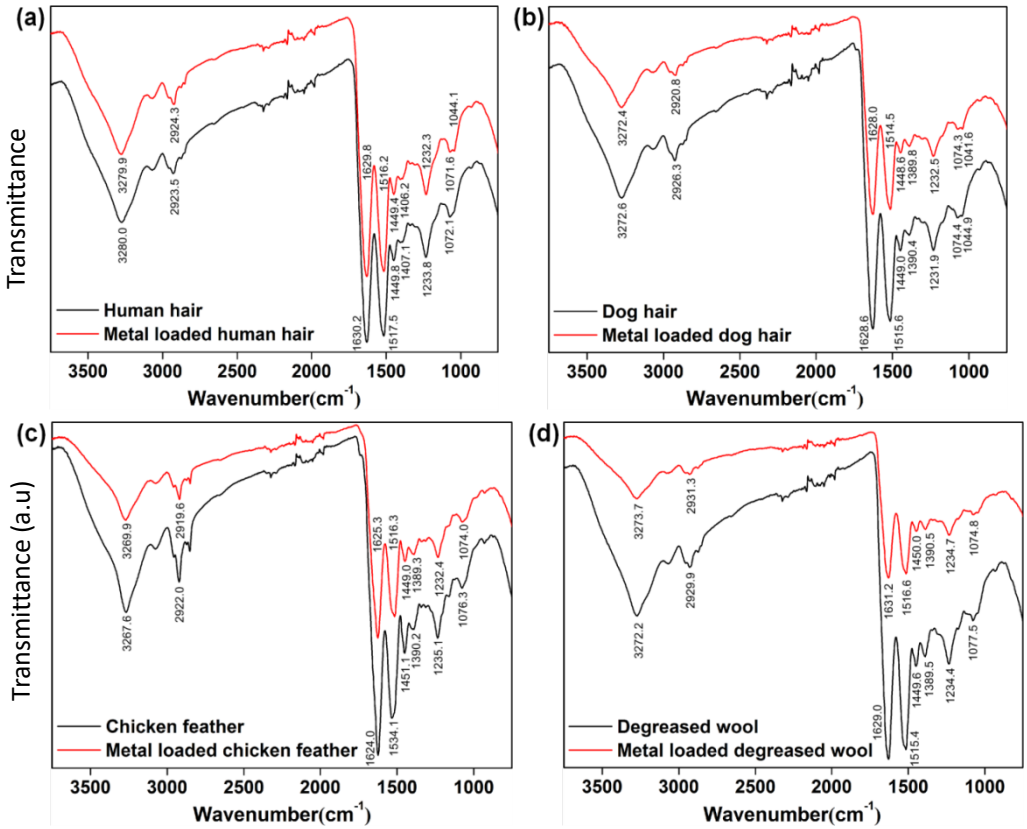
(a)
Transmittance
3279.9
3280.0
2924.3
2923.5
1629.8
1516.2
1449.4
1406.2
1407.1
1449.8
1232.3
1233.8
1071.6
1072.1
1044.1
1630.2
1517.5
Human hair
Metal loaded human hair
3500
3000
2500
2000
1500
1000
Wavenumber(cm-1)
(b)
3272.4
3272.6
2920.8
2926.3
1628.0
1514.5
1448.6
1389.8
1232.5
1074.3
1041.6
1074.4
1044.9
1449.0
1390.4
1231.9
1628.6
1515.6
Dog hair
Metal loaded dog hair
3500
3000
2500
2000
1500
1000
Wavenumber(cm-1)
(c)
Transmittance (a.u)
3269.9
3267.6
2919.6
2922.0
1625.3
1516.3
1449.0
1388.3
1232.4
1074.0
1076.3
1451.1
1390.2
1235.1
1624.0
1534.1
Chicken feather
Metal loaded chicken feather
3500
3000
2500
2000
1500
1000
Wavenumber(cm-1)
(d)
3273.7
3272.2
2931.3
2929.9
1450.0
1390.5
1234.7
1074.8
1631.2
1516.6
1077.5
1449.6
1389.5
1234.4
1629.0
1515.4
Degreased wool
Metal loaded degreased wool
3500
3000
2500
2000
1500
1000
Wavenumber(cm-1)

Figure 2

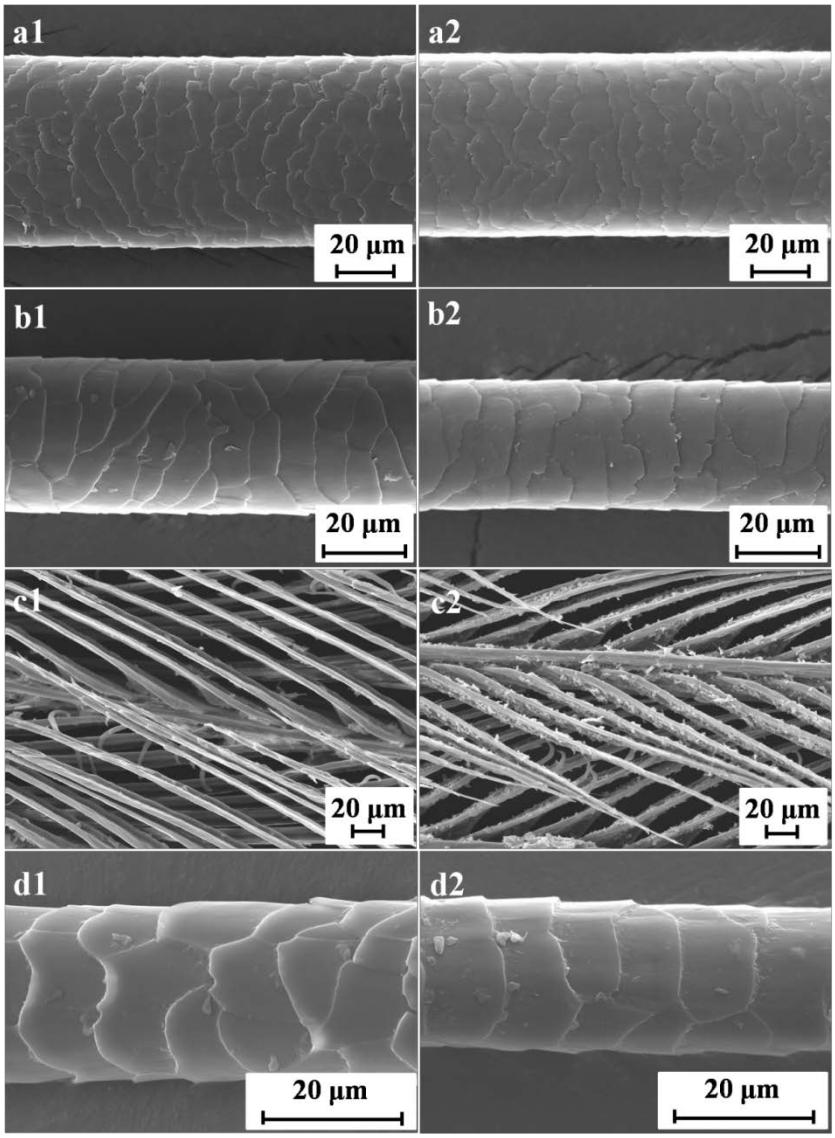

Figure 3

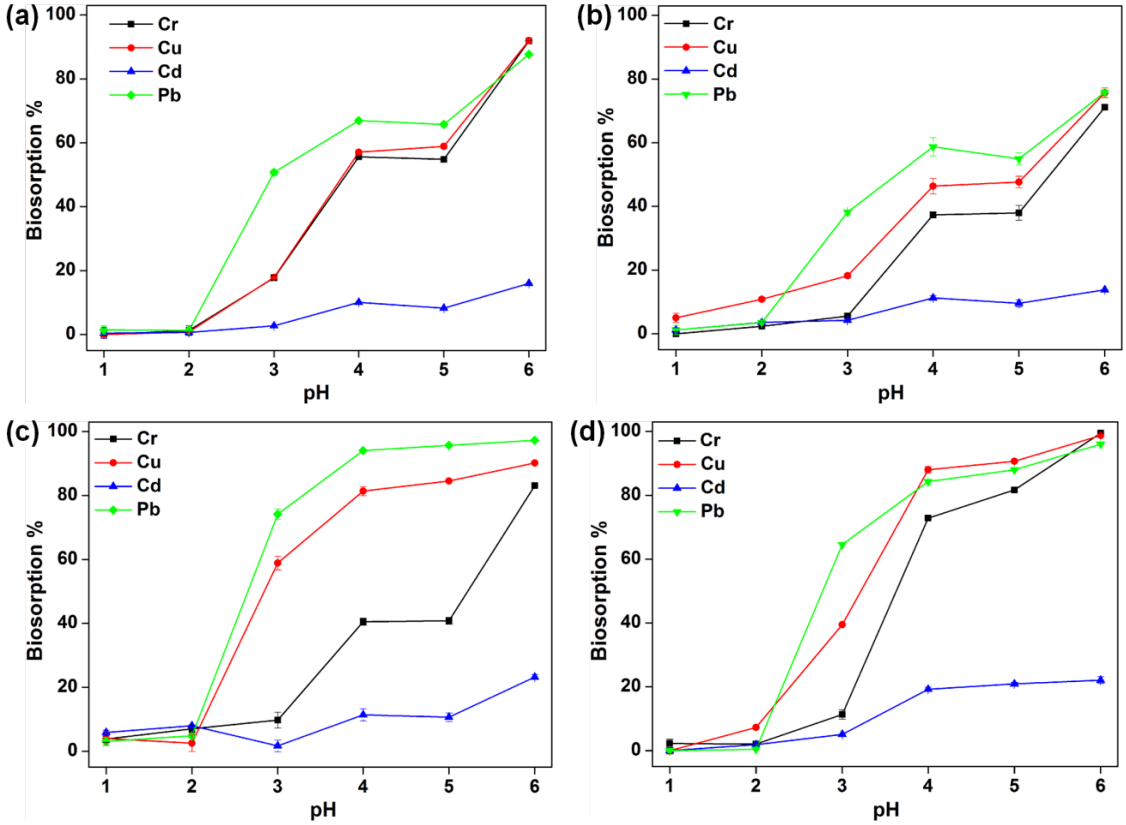

Figure 4

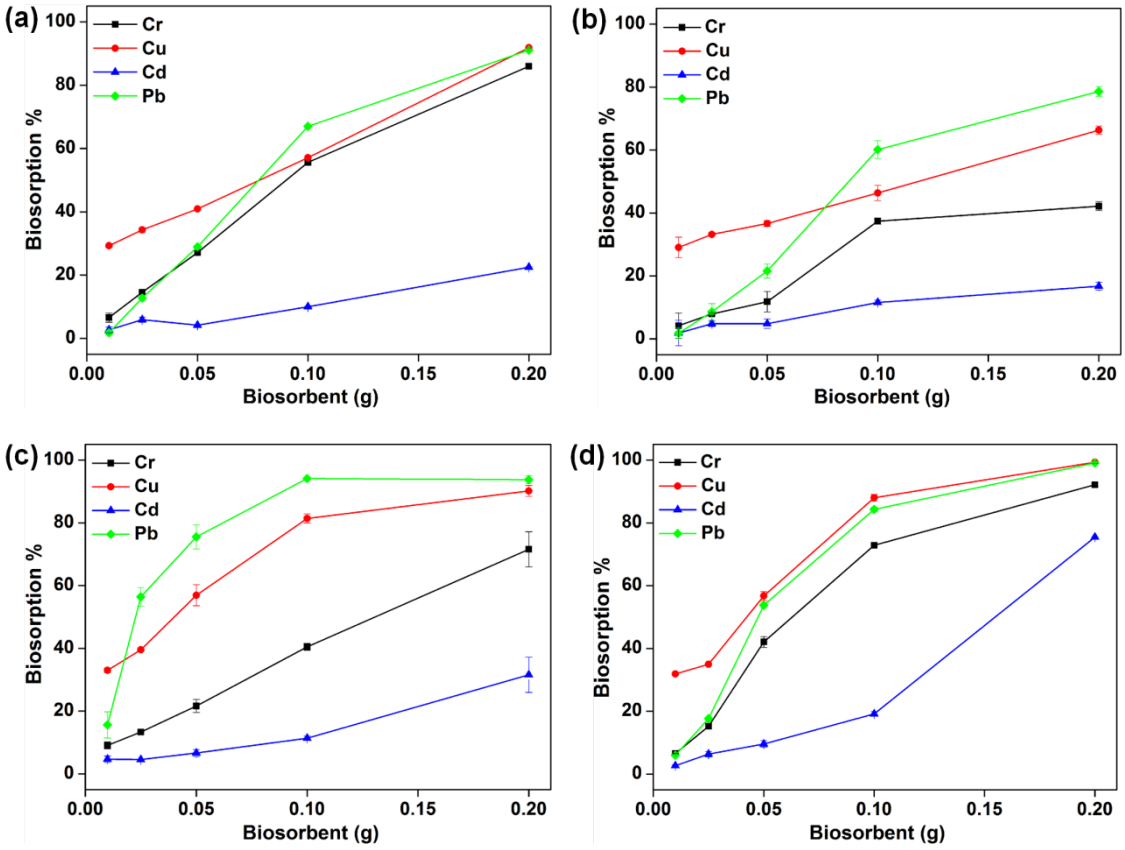
(a)
(b)
(c)
(d)
Cr
Cu
Cd
Pb
Biosorption %
Biosorbent (g)
0
20
40
60
80
100
0.00
0.05
0.10
0.15
0.20

Figure 5

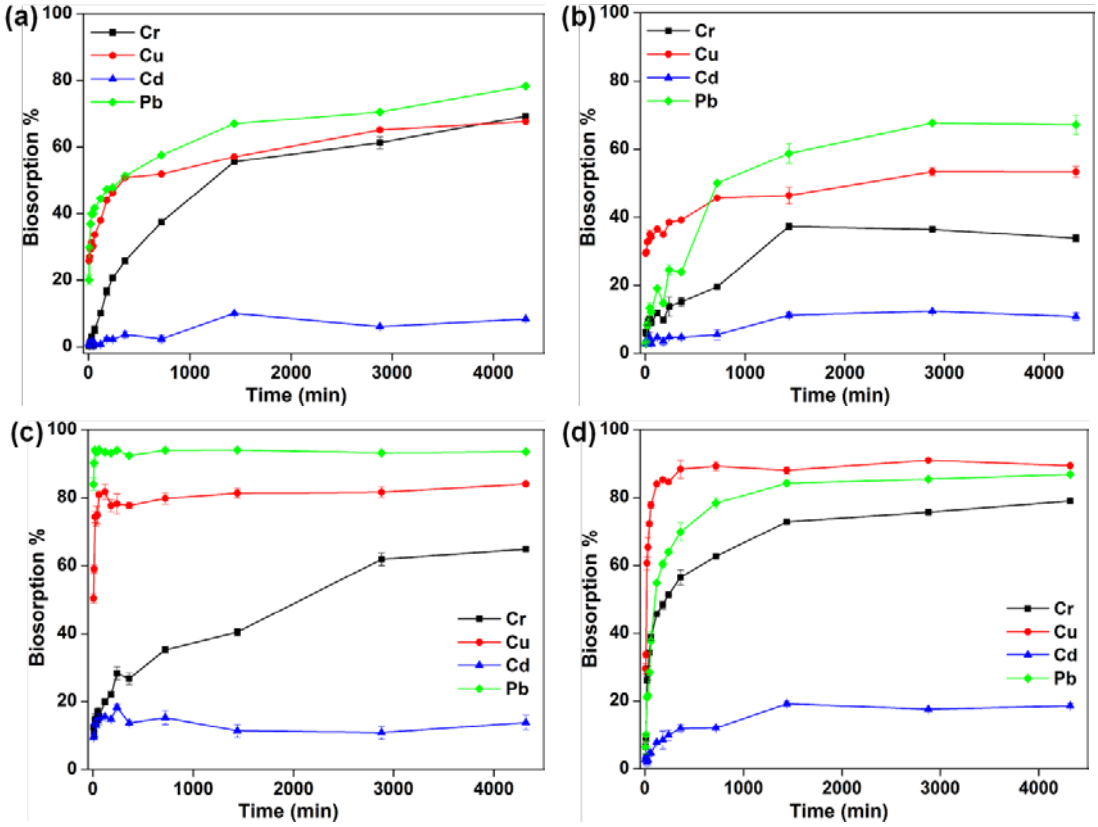
(a)
(b)
(c)
(d)
Cr
Cu
Cd
Pb
Biosorption %
Time (min)
0
20
40
60
80
100
0
1000
2000
3000
4000

Figure 6

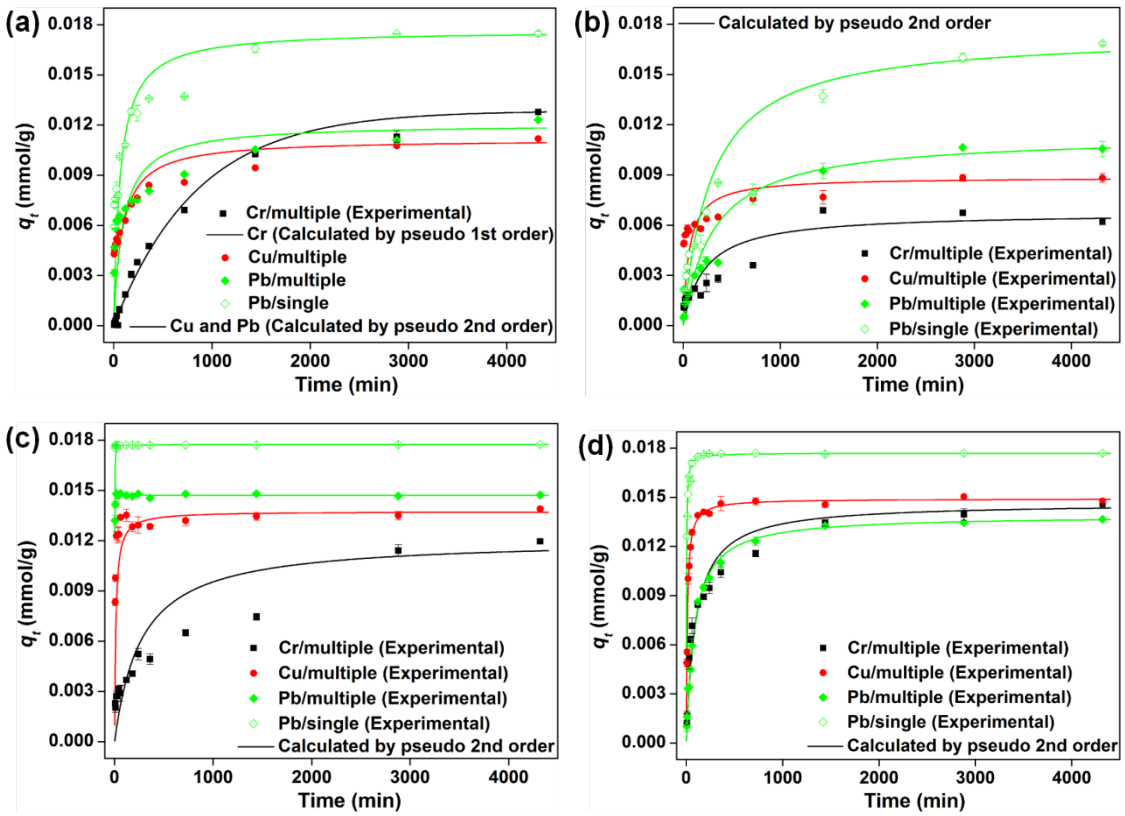
(a)
(b)
(c)
(d)
q_t (mmol/g)
Time (min)
Cr/multiple (Experimental)
Cr (Calculated by pseudo 1st order)
Cu/multiple
Pb/multiple
Pb/single
Cu and Pb (Calculated by pseudo 2nd order)
Calculated by pseudo 2nd order
Cu/multiple (Experimental)
Pb/multiple (Experimental)
Pb/single (Experimental)

Figure 7

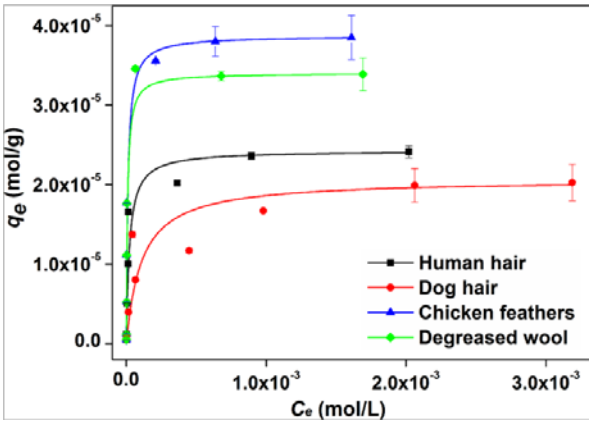
4.0x10-5
3.0x10-5
2.0x10-5
1.0x10-5
0.0
qe (mol/g)
0.0
1.0x10-3
2.0x10-3
3.0x10-3
Ce (mol/L)
Human hair
Dog hair
Chicken feathers
Degreased wool

Figure 8