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Bioseparation of Pb(II) and Cd(II) from aqueous solution using cork waste biomass. Modeling and optimization of the parameters of the biosorption step.

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Abstract

In this work the ability of cork wastes to remove Cd(II) and Pb(II) from aqueous solutions has been studied. The kinetics of the biosorption system, the influence of the aqueous pH and the initial metal concentration on the metal uptake were investigated, showing a pH dependent profile. The maximum sorption for both metals was found at pH 5, independently that if the metals were in individual solutions or mixed. When a solution of the mixed metals were studied, a reduction in the Cd(II) uptake was observed showing a clear competition between the metals which was corroborated by the P-factor approach, behavior probably due to a lower attraction of this metal towards the corresponding active groups of the cork. Finally, the cork has been evaluated by FTIR and SEM in order to determine if the biosorption process modifies its chemical structure and morphology, respectively. Cork has been proved to be an efficient biomaterial useful for heavy metal separation purposes that is not altered by the process.

Keywords: Cork; Heavy metals; Kinetic; Isotherm; Biosorption.

1. Introduction

It is well known that the increase in industrial activities has intensified the environmental pollution and the deterioration of some ecosystems due to the accumulation of pollutants such as heavy metals, synthetic compounds, nuclear waste liquids, etc. Among them, the exposure to heavy metals presents a high risk to the human health, so, increasing attention is focusing on their concentration and elimination from the environment [1]. Heavy metals are dangerous and not biodegradable contaminants that tend to be accumulated in living organisms, causing various diseases and disorders. Nowadays, still there are no widely accepted methods to remove them from the contaminated sites [2,3]. Some methods like precipitation, ion exchange, electrochemical processes and/or membrane processes are commonly applied to the treatment of industrial effluents. However the application of such processes is sometimes restricted due to technical or economic constraints [4,5,2]. The search for new technologies, preferably clean technologies and cheap ones, has directed the attention to biosorption systems, which are based on metal binding capacities of various biological materials through biosorption process [6].

Biosorption can be defined as the ability of biological materials to accumulate compounds as metals and/or heavy metals from waste water through metabolically mediated or psycho-chemical pathways of uptake [7]. Biosorption take place by more than one mechanism. It consists of several quantitative and qualitatively processes according to the type of biomass, origin and processing [8]. Recent biosorption experiments have been performed by the use of by-products or the waste materials from large-scale industrial operations such as the waste from the production of wool, rice, straw, coconuts shaving, peat, waste of tea leaves, mushrooms, nutshells and waste from sugar production [3,9-14]. These biomaterials have different types of functional groups, such as carboxylic, sulfates, phosphates and amino groups, which are the binding sites for ion exchange and complex reactions related to the sorption processes. The choice of the biomass should be based on its origin, chemical composition and type in addition to the composition of the sample solution to be purified [3]. The major advantages of biosorption processes over conventional treatment methods include their low cost, high efficiency, minimization of generation of chemical and/or biological sludge, no additional nutrient requirement, regeneration of biosorbents, the possibility of metal and/or heavy metal recovery and valorization of a waste when it is the origin of the biomass.

In this sense, cork (Quecur suber L.) has been chosen in the present work as biosorbent for the elimination of the heavy metals Cd(II) and Pb(II) from aqueous solution. Cork is the outer bark of the oak tree and it is industrially used for several purposes, principally the manufacturing of wine stoppers [15,16]. The physical characteristics of the cork (elasticity, impermeability, low density…), and its chemical composition (a complex mixture of fatty acids and heavy organic alcohols ≈45% w/w, tannins ≈6% w/w, polysaccharides ≈12% w/w, lignin ≈27% w/w, alkanes, mineral content ≈5% and the most abundant element Ca 0.038-0.625% w/w), make this waste to be though as an ideal material for the biosorption of heavy metals [3,17-20].

2. Experimental

2.1. Materials and Methods

The cork was kindly provided by the wine stopper manufacturer Surochem S.L. (Girona, Spain). Cork samples of three different sizes were selected and labelled as S1, S8 and S9 (nominal diameter of 2-4 mm, 1-2 mm and 0.5-1 mm, respectively). All chemicals used were of analytical grade. A 1000 ppm stock solution of lead and 500 ppm stock solution of cadmium were prepared by diluting the required amounts of $Pb(NO_3)_2$ 99% and $Cd(NO_3)_2{\cdot}4H_2O$ 99%, in 1M of HNO_3 (all from Panreac, Spain). Others reactives used, also from Panreac (Spain), were NaOH 98%, $NaHCO_3$ 99% and Na_2CO_3 99%. All solutions were prepared using Milli-Q water.

2.2. Procedure

The uptake of Cd(II) and Pb(II) was carried out in batch experiments at 25°C, and was evaluated for the metals in individual solutions (single or individual system) or for both metals together from the same initial stock solution (binary system). The metal ion concentration in the initial solution, for both different systems, was ranged from 4.8×10^{-4} to 9.6×10^{-1} mM. Samples (0.1000 g) of cork were accurately weighed in 50 ml plastic extraction tubes, 10 cm^3 of the different aqueous metal solutions were added and the system was shaken in a rotary mixer (CE 2000 ABT-4, SBS Instruments SA, Barcelona, Spain) at 25 rpm during the desired time. For the kinetic studies, 5, 10, 15, 30, 45, 60 min, and 2, 4, 6, 12, 24 and 48 h were evaluated, to find the equilibrium time and which was selected for the biosorption studies.

After agitation, the two phases were separated by decantation and the liquid phase was filtered through 0.22 µm Millipore filters (Millex-GS, Millipore, Ireland).

The analysis of the metal concentration in the remaining aqueous solutions was carried out by an inductively coupled plasma optical emission spectrophotometer, ICP-OES (Iris Intrepid II XSP Radial, Thermo Elemental, USA). The uptake of the metal by the cork was calculated following Eq. (1).

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

where C_i corresponds to the initial concentration and C_f is the final concentration, both in the aqueous phase solution. Usually, initial metal concentrations were 0.018 mmol/l for each of the heavy metals, otherwise specified. In all the experiments, the initial and equilibrium pH were measured using an Omega300 pHmeter. The initial pH of the solutions was varied within the range 2-6, to avoid metal hydroxide precipitation. Agitation was carried out using a rotary mixer for all the experiments.

For interpretation and prediction purposes, kinetic and equilibrium sorption data were analyzed using classical empirical models [21].

Each individual test was carried out in duplicate.

2.2.1. FTIR and SEM characterization

In order to determine if any of the different steps carried out over the cork modified its morphological structure, FTIR and SEM analysis were performed. To do so, small portions of all the three sizes of the cork before and after the sorption process were studied.

For the FTIR analysis, a Nicolet Avatar 320 spectrophotometer (Nicolet Instrument Corporation, United States) was used. In this case, samples were prepared mixing 15 mg of the cork in a matrix of 300mg of KBr and pressing. The spectrum was recorded in the range of 500-4000 cm^{-1}. SEM images were obtained by using a scanning electronic microscope ZEISS EVO® MA 10 (Oberkochen, Germany) at the UAB Microscopy Service.

2.2.2. Determination of functional groups of the cork surface

It is well known the existence of a wide variety of functional groups on the surface of the cork biomass [3,18]. This variability of functional groups provides to the material different degrees of acidity which can be determined by neutralization and gives interesting characterization information of such biomaterial.

In order to determine the concentration of the acid functional groups present on the surface of the cork biomass, the Bohem method was followed which consists on a selective neutralization of the acid groups with bases of different dissociation constants [22]. To do so, around 1.0000 g of cork biomass was exactly weighed in an erlenmeyer flask, and 100 ml of 0.1 M NaOH, Na_2CO_3 or $NaHCO_3$ solution was added and placed in an orbital shaker at 25ºC for 48 hours, time enough to ensure that the biosorption equilibrium is reached. After this time, the cork was separated from the corresponding base solution, and 10 ml of each one was titrated with 0.1 M of HCl (pH of the solutions was measured permanently).

To determine the presence of the basic functional groups present on the cork surface, a similar procedure as describe above was used but now using an acidic solution. To do so, 1.0000 g of cork was put in contact with 100 ml of 0.1 M HCl solution during 48 h, after that the solution was filtrated and an aliquot of 10 ml was titrated with 0.1 M NaOH.

From the titration results obtained, the static exchange capacity (SEC or q_{sec} in mequiv/g), was calculated by using equation 2.

(2)

where C_0 is the initial concentration of NaOH, Na_2CO_3, $NaHCO_3$ or HCl (mequiv/l), C_{eq} is the equilibrium concentration of NaOH, Na_2CO_3, $NaHCO_3$ or HCl (mequiv/l), V is the volume of the initial solution in liters (0.1 L in this work) and m is the mass of cork used (1.0000 g in this study).

3. Results and Discussion

3.1. Kinetic studies

In order to determine the maximum uptake of the heavy metals on the cork, kinetic studies were run for the three different cork samples (S1, S8 and S9). To do so, individual heavy metal solutions and cork of different particle sizes were contacted during 5, 10, 15, 30 and 45 and 1, 2, 4, 6, 12, 24 and 48 h. Fig. 1 shows that in less than 6 h the maximum metal uptake is reached for all cases. As it can be expected, the highest metal biosorption percentages are found for the cork with the smallest particle size (S9). In this case, a biggest surface area is present, having available more chemical groups on the cork surface and obtaining thus a higher metal biosorption efficiency, when working with the same amount of biomaterial (0.1000 g).

Furthermore, lead shows higher uptake for cork than cadmium in all the cases, probably due to the higher interaction of Pb ions towards the carboxylic and phenol groups in the cork [17-21,23,24].

Fig. 1. Percentage of biosorption of Cd(II) and Pb(II) by three different particle sizes of cork: S9 (1–0.5 mm), S8 (1–2 mm) and S1 (2–4 mm). Initial solution 20 ppm at pH 5.

3.2. Sorption kinetics modeling

3.2.1. Pseudo-first order rate equation

In order to understand the kinetics of the sorption of Pb(II) and Cd(II) metals on solid cork, the pseudo-first order rate equation [26], also called Langergren equation, was used (Eq. 3).

(3)

where q_e and q_t are the concentration of sorbed metal ion per unit of mass of sorbent in mol/g at the equilibrium and at time t, respectively, and k is the rate constant in min^{-1}.

Straight lines were observed for all the sorption systems studied when analyzing until 60 min, corroborating the applicability of the pseudo-first order equation (see the good correlation coefficients shown in Table 1). From the slope, the k rate constant was calculated for each sorption kinetic (Table 1). The *k* values were found to be higher for the sorption of Pb(II) than for Cd(II). In addition, the values of *k* were higher for cork type S8 compared to the other two types (S1 and S9).

Table 1. Kinetic parameters for the pseudo-first order model (adjusting until minute 60).

Metal/cork system	$k \cdot 10^{-2}$ (min^{-1})	R^2
Cd_S1	2.62	0.9916
Cd_S8	2.88	0.9782
Cd_S9	2.60	0.9625
Pb_S1	3.13	0.9776
Pb_S8	3.48	0.9946
Pb_S9	3.22	0.9778

Fig. 2 shows the values of the concentration of sorbed metal, q_t, predicted by the model as well as the experimental values vs. the contacting time for Pb(II) and Cd(II). As previously commented, the correlation between both values is good for short time analysis (t < 60 min). However, it is poor for both metals for long time analysis (t> 60 min), when the system reaches the saturation what cannot be explained by the pseudo first order model and suggesting that this process is diffusion limited because of the heterogeneous characteristic of the system. In order to address this issue the Chrastil approach was applied to the analysis of the kinetic results.

Fig. 2. Experimental and calculated values, by the pseudo first order equation (until 60 min), vs. time for the sorption of Pb(II) and Cd(II) on cork for the individual systems.

3.2.2. Chrastil's diffusion model

The Chrastil's approach [26], proposed for diffusion limited systems, was applied to all the values of the kinetic study (Eq. (4)). Because the time curves depend strongly on the heterogeneous nature of the substrate-sorbate system, the effect of the cork particle size on the biosorption kinetics was also evaluated.

(4)

Where q_e and q_t are as for the previous equation, k is a rate constant proportional to the diffusion coefficient as defined by the Fick's law in l/mol min [27], q_0 is the concentration of the cork material (g cork/l), and n is a structural diffusion resistance constant with reaction order characteristics [28]. When diffusion resistance is small, n tends to 1 (for low-resistance films n = 0.9-1.0) and the reaction is of first order (see Eq. (3)). If the system is strongly limited by diffusion resistance, n is small (high-resistance structures n = 0.5-0.6).

According to Eq. (4), the parameters of the model were determined by non-linear regression analysis (Data Fit, version 8.0.32, Oakdale Engineering, PA, USA) of the experimental kinetic curves (including all times measured). The values obtained are shown in Table 2. As it can be seen, this model allows for a better prediction of the sorption kinetic for any time compared with the previous approach using the pseudo first order model. It is corroborated by the coefficient of multiple determinations R^2, Table 2, and seen in the regression curves in Fig. 3 (continuous curves).

Table 2. Kinetic parameters for the Chrastil's diffusion model.

Metal/cork system	[q_{eq}] x 10^{-5} (mol metal/g cork)	[kq_o] x 10^{-2} (g cork/mol metal·min)	n	R^2
Cd_S1	0.76	2.6	0.87	0.988
Cd_S8	0.86	2.1	0.55	0.986
Cd_S9	1.3	3.4	0.69	0.978
Pb_S1	1.3	1.8	0.53	0.983
Pb_S8	1.5	1.9	0.52	0.775
Pb_S9	1.9	3.0	0.51	0.990

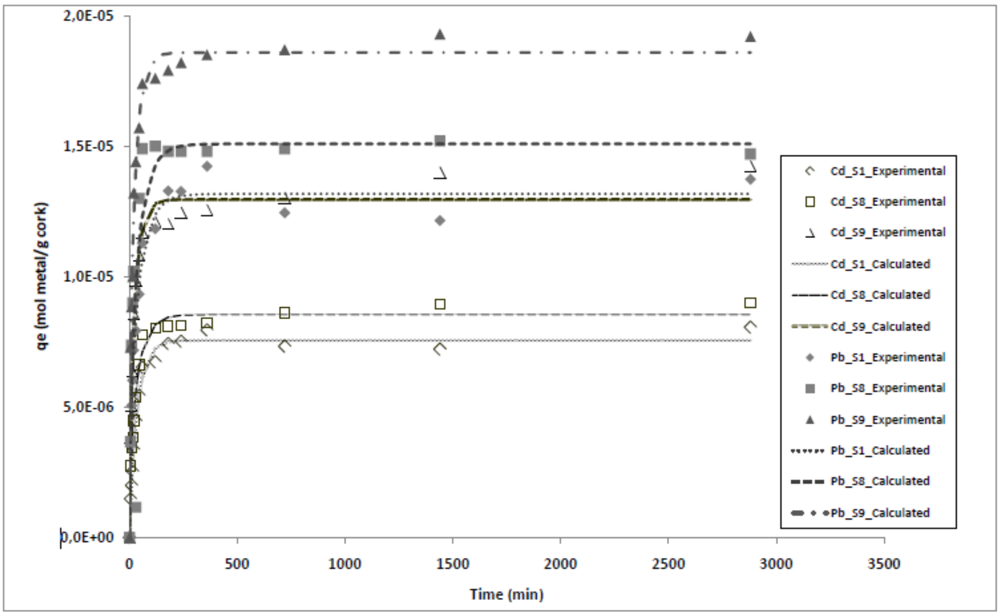

Fig. 3. Experimental and calculated values by the Chrastil's equation vs. time for the sorption of Pb(II) and Cd(II) on cork for the individual systems.

In addition, diffusion characteristics of the metal/cork system can be determined from the analysis of the resulted parameters n and k calculated from the modelization using Eq. (4). The results obtained for the diffusion resistance coefficient show values between 0.87 and 0.51 (Table 2), indicating that the sorption process of Pb and Cd on cork is significantly limited by diffusion resistance. No significant influence of the particle size on the diffusion process was noticed for Pb(II) (with n between 0.51 and 0.53). However, for the sorption of Cd(II), a significant decrease on the diffusion coefficient, from $n = 0.87$ (in cork with a particle size of 2-4 mm) to 0.69 (cork with a particle size of 0.5-1 mm) was obtained, meaning higher resistance to the diffusion of Cd(II) in the cork with the smallest particle size. However, the decrease of the particle size of the cork produces a significant increase on the rate constant for both metals studied, with values in the range from 2.3-3.4·x 10^{-2} and 1.8-3.0·x 10^{-2} g/mol min for Cd(II) and Pb(II), respectively. This behavior is due to the increase of the surface area produced when decreasing the particle size of the sorbent. In addition, from the equilibrium sorption results (q_e), it is seen that the highest metal biosorption was obtained for the cork with the smallest particle size for both metals studied. Moreover, it was found a higher metal biosorption for Pb(II) than for Cd(II) ions for each particle size of the cork tested.

3.2.3. Rate determining diffusion step

As the Chrastil model has shown, the biosorption process studied is diffusion controlled. The mechanism of mass transfer diffusion involves three consecutive steps: i) film diffusion, ii) intraparticle diffusion and iii) adsorption of the sorbate on the interior surface sites of the sorbent. The last one is considered too fast and is not treated as a rate-limiting step of the sorption process. To evaluate whether the sorption process is controlled by film diffusion or intraparticle diffusion the Reichenberg model was applied, where B_t is a mathematical function of the ratio q_t/q_e and is determined using the corresponding table for interpreting the experimental results in terms of the particle diffusion equation [29].

If the plot of B_t vs. time pass through the origin, the rate limiting step is exclusively due to intraparticle diffusion. If that is not the case, film diffusion as well as intraparticle diffusion should be taken into account. Table 3 shows the results of B_t for the uptake of both metals onto the three types of cork and for both metals showing linearity that do not pass through the origin, meaning that metal-cork sorption process is mainly governed by both, film and intraparticle diffusion.

Table 3. Lineal regression from the Reichenberg graphics of Bt vs. time for Pb(II) and Cd(II) in single systems for the three types of cork (graphics not shown).

Metal/cork system	Regression	R^2
Cd_S1	$B_t = 0.0204t - 0.1697$	0.9607
Cd_S8	$B_t = 0.0243t - 0.1311$	0.9589
Cd_S9	$B_t = 0.0217t - 0.0310$	0.9811
Pb_S1	$B_t = 0.0171t - 0.0559$	0.9607
Pb_S8	$B_t = 0.0292t + 0.0225$	0.9742
Pb_S9	$B_t = 0.0292t - 0.0224$	0.9801

3.3. FTIR and SEM characterization

Fig. 4 shows the FTIR spectra for cork S1 (similar spectra where obtained for the other two cork samples, so spectra are not shown). Comparing with previously published results, the spectra registered for our cork samples show the same bands to those of a Portuguese cork [30,31]. Also, comparing the bands between the spectra of the cork before and after theist use in the described biosorption process, for all three sizes checked, it can be seen that there are no significant differences. So, it can be said that the chemical structure of the cork is not affected by the process.

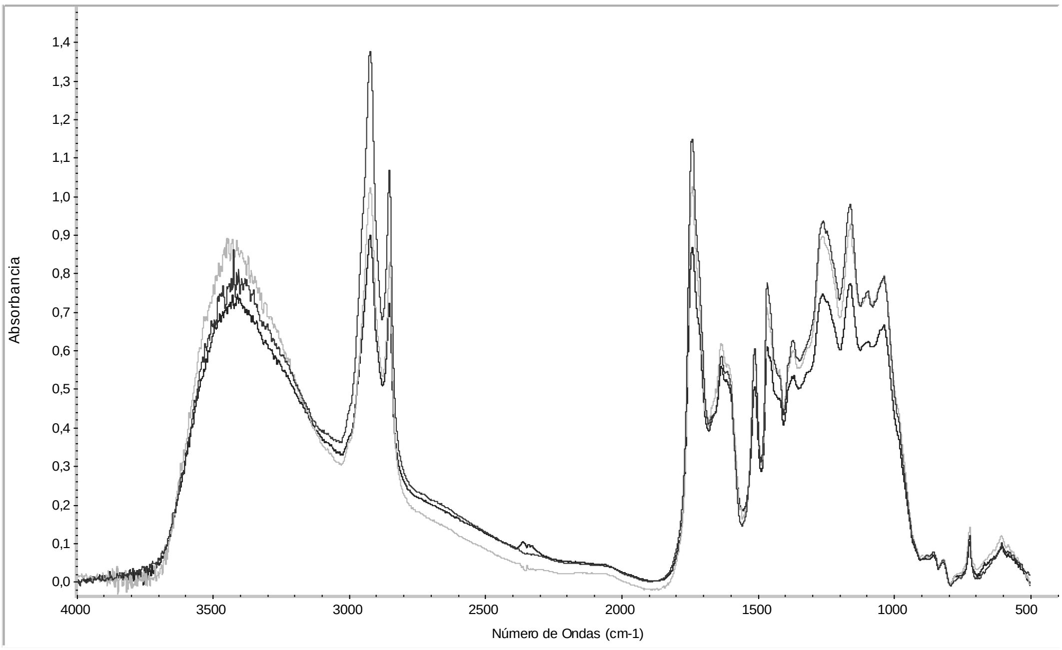

Fig. 4. FTIR spectra of the cork before and after (in duplicate) the biosorption process.

On the other hand, the SEM images of cork S8 (Fig. 5a for the cork before the biosorption process and Fig. 5b for the cork after its use) do not show differences in the morphology of the cork. Similar results were obtained for the other two sizes of the cork. It can be affirmed that the morphological structure of the cork is not affected by the metal biosorption experiments.

Both are good results for cork reuse purposes, and also for its further real application.

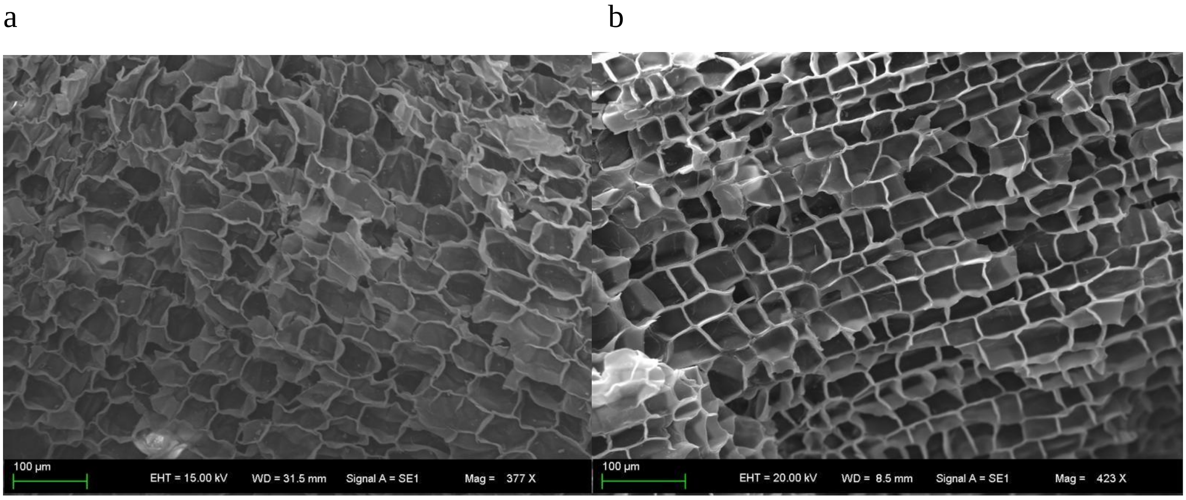

Fig. 5. SEM images of the cork before (a) and after (b) the biosorption process.

3.4. Influence of the pH on the heavy metal uptake

The metal speciation, as well as the protonation of the chemical groups of the cork surface are influenced by the pH of the aqueous solution, so, it can also modify the capacity of the cork biosorption process. With the aim of determining this influence, a number of experiments were carried out varying the pH of the initial aqueous solution from 2 to 6, using the different cork particle sizes, and for individual heavy metals solutions.

From the results seen in Fig. 6, it can be observed that the biosorption percentage for Pb(II) at pH 2.0 is 18 ± 1 % and around 5 ± 1 % for Cd(II) for any size of cork. As the pH raises it increases gradually, reaching a maximum at pH 5.0, and decreasing again when the solution is set at pH 6.0. Same behavior is observed for both metals. This could be due to the fact that at low pH, the majority of carboxylic and phenol groups in the cork are protonated**,** causing a low interaction between them and the heavy metal (under their aqueous cationic speciation form), according with an ion exchange model. On the other hand, when the pH is higher than 5, the metal ions can hydrolyze, causing even precipitation (such as hydroxides, oxides, etc.) which leads to poor biosorption. So, optimal system biosorption capacity was reached for pH 5, where the yield of biosorption obtained was 95 ± 1 % for Pb(II), and 68 ± 1 % for Cd(II) and increases when the size of the cork decreases.

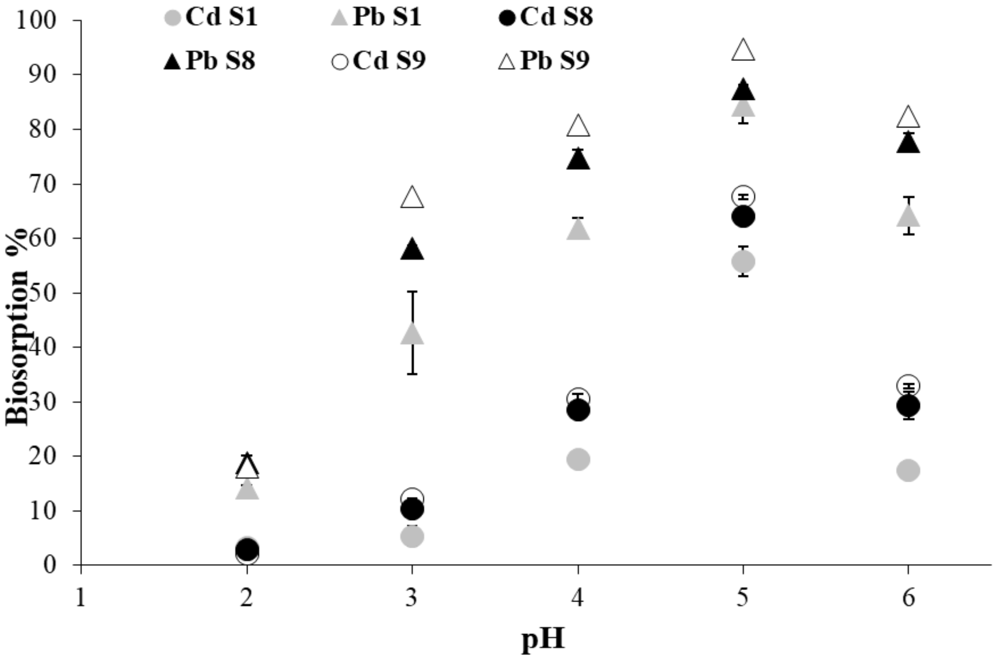

Fig. 6. Effect of the pH of the initial solution on the biosorption of Cd(II) and Pb (II).

3.5. Effect of the initial metal concentration

The effect of the metal ion concentration in the initial solution was evaluated in two different systems, metals in individual solutions and both together into the same initial aqueous solution. Corresponding results are shown in Fig. 7. It can be observed that for Cd(II) biosorption percentages are different for the same initial concentration depending on the presence of Pb(II) in the solution, demonstrating a real competition between the heavy metals studied for the functional groups of the cork surface. On the other hand, Pb(II) is not affected by the presence of Cd(II). It can also be observed that the capacity of cork biosorption is greater when solutions with low metal ion concentrations are used and capacity decreases when the concentration of the ions increases. This is probably due to the fact that at low concentrations of the metal ions, the proportional surface area available for metal biosorption is higher, allowing a better opportunity for their uptake. When metal ion concentrations are increased, the functional groups can be saturated, as the biomass quantity is maintained almost constant between all set of experiments (0.1000 g).

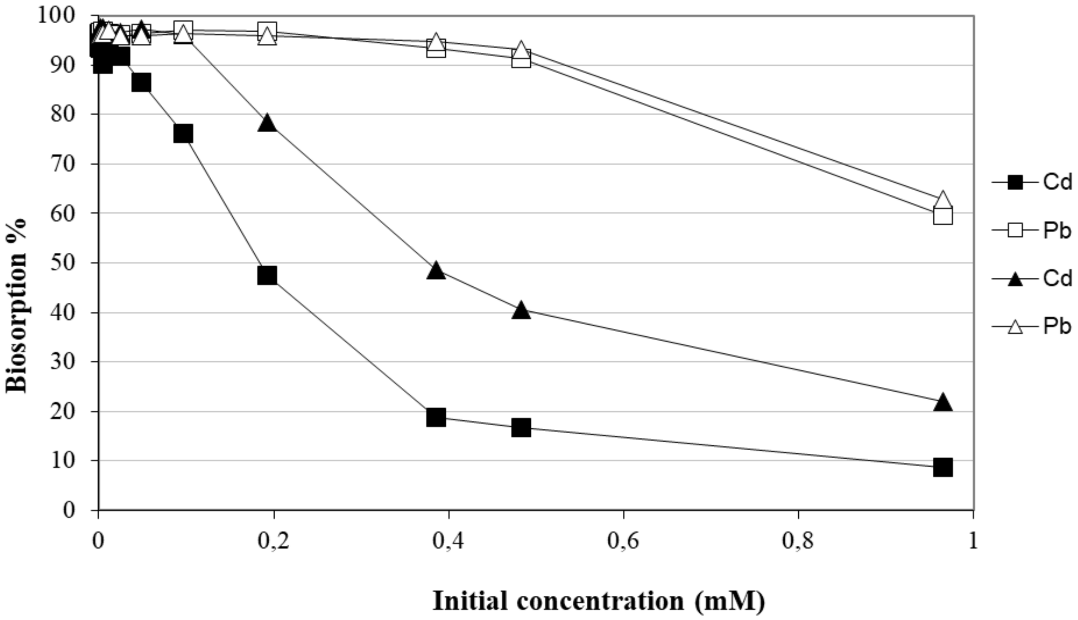

Fig. 7. Biosorption of Cd(II) and Pb(II) on cork from aqueous solutions at pH 5 for binary system (, ■) and single system (Δ,▲).

3.6. Sorption isotherms modeling

3.6.1. Single system: Freunlich and Langmuir isotherms

Freundlich and Langmuir isotherm equations were applied to model the equilibrium of the sorption of the single-component metals by the cork [1]. The constants for both models were determined by fitting the experimental data values with the linear forms of the models, represented by Eqs. (5) and (6), respectively.

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \qquad (5)$$

$$\frac{C_e}{q_e} = \frac{b}{K_L}C_e + \frac{1}{K_L} \qquad (6)$$

where C_e is the equilibrium concentration of metal in the residual solution in mol/l, q_e is the equilibrium concentration of sorbed metal ion per unit of mass of sorbent in mol/g, k_F and n are Freundlich constant, K_L=$Q_o b$ and Q_o and b are Langmuir constants, representing the saturation concentration of sorbed metal per unit of mass of sorbent in mol/g and the ratio of sorption/desorption rates in l/mol, respectively.

For both linealized models, plots of log q_e vs. log C_e (Eq. (5)) and C_e/q_e vs. C_e (Eq. (6)) are represented and the Freundlich and Langmuir constants were obtained (Table 4). From the results, it was observed that the Langmuir model fitted better than the Freundlich one for the sorption equilibrium experimental results in single systems for both metals (with R^2 higher than 0.997 for the first model). The higher value of Q_o for Pb(II) than for Cd(II) indicates that more moles of lead ions can be sorbed on the cork at the equilibrium. Moreover, because b is the ratio between sorption and desorption constants at the equilibrium the higher value of b for Cd(II) indicates that the metal molecules are more strongly bonded to the cork than the Pb(II) ones. In Fig. 8 experimental and calculated data for the Langmuir model are represented showing good correlation between them.

In addition, from the Langmuir constant found, the standard Gibb's free energy (ΔG^o) of the sorption process were evaluated using Eq (7).

$$\Delta G^o = -RT\ln b \qquad (7)$$

where b is the Langmuir equilibrium constant shown in Eq. (6), R is the universal gas constant and T is the temperature. More negative values of ΔG^o corroborate high affinity of the metal for the sorbent substrate. Results are shown in Table 4, demonstrating higher affinity for Cd(II) metal cations

Table 4. Freundlich and Langmuir constants for single and binary systems.

Single metal system				
Langmuir constants				
Metal	$Q_o \cdot 10^{-5}$ (mol/g)	$b \cdot 10^{5}$ (L/mol)	K_L (L/g)	R^2
Pb(II)	6.55	0.39	2.55	0.9972
Cd(II)	2.13	1.02	2.18	0.9985
Freundlich constants				Gibb's free energy
Metal	k_F	n	R^2	$-\Delta G^o$ (kJ/mol)
Pb(II)	0.108	1.26	0.9562	26.0
Cd(II)	0.0021	1.91	0.8737	28.4
Binary metals system (P-Factor approach)				
Metal	$Q_o \cdot 10^{-5}$ (mol/g)	$b \cdot 10^{5}$ (L/mol)	K_L (L/g)	R^2
Pb(II)	6.05	0.51	3.11	0.9992
Cd(II)	0.83	1.38	1.14	0.9976

3.6.2. Binary systems: Modified Langmuir-like models

3.6.2.1. Extended Langmuir model

Multi-metal equilibrium sorption isotherms for the two components were modeled using the extended Langmuir Eq. (8) for competitive sorption [32].

$$q_{e,i} = \frac{K_{L,i} C_{e,i}}{1 + \sum_{i=1}^{z} b_i C_{e,i}} \qquad (8)$$

where $K_{L,i}=Q_{o,i}b_i$ and $Q_{o,i}$ and b_i are the Langmuir isotherm constants relative to component i in the single systems for the z components. Fig. 8 shows the poor correlation of the calculated values by the extended Langmuir equation for Pb(II) and Cd(II) compared to the experimental values for the sorption isotherms in the binary system being greater the difference for Pb(II) than for Cd(II). However, the trend for both calculated and experimental is similar for Cd(II). The poor correlation shown by the extended Langmuir isotherm model is due to the limitation of this model which is based on the assumptions of equal sorption capacities for both metals, competition for the same binding sites and no interaction between the metal sorbates. Moreover, the values of Q_o and b are different for both metals (Table 4), corroborating, that interaction and competition between these two metals are significant and that sorption is occurring on sites that are not equally accessible to the two metals.

3.6.2.2. Modified extended Langmuir model

In order to overcome the limitations of the extended Langmuir equation, Jain and Snoeyink [33] proposed a modified competitive Langmuir model. This model was based on the fact that sorption occurs without competition and that not equal sorption capacities can be considered for all the different sorbates species. In this case, the number of sites for non-competitive sorption is assumed to be proportional to the difference between the maximum loadings of each component, $Q_{o,1}$ - $Q_{o,2}$ (where $Q_{o,1} > Q_{o,2}$) being the model for binary mixtures described by the following equations (Eqs. (9) and (10)).

$$q_{e,1} = \frac{(Q_{o,1} - Q_{o,2}) b_1 C_{e,1}}{1 + b_1 C_{e,1}} + \frac{Q_{o,2} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \quad (9)$$

$$q_{e,2} = \frac{Q_{o,2} b_2 C_{e,2}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \quad (10)$$

Where the subscripts 1 and 2 represent to Pb(II) and Cd(II) ions, respectively and the Langmuir parameters found for the single system were used for the calculations.

Fig. 8 shows the comparison between experimental and calculated data for the results of the modified extended Langmuir model. The correlation between data for the Pb(II) sorption isotherm in the binary mixture was improved by this model. However, still significant differences between the experimental and the predicted values were observed which indicates the limitation on the application of this model to the estimation of the binary mixture sorption equilibrium values studied.

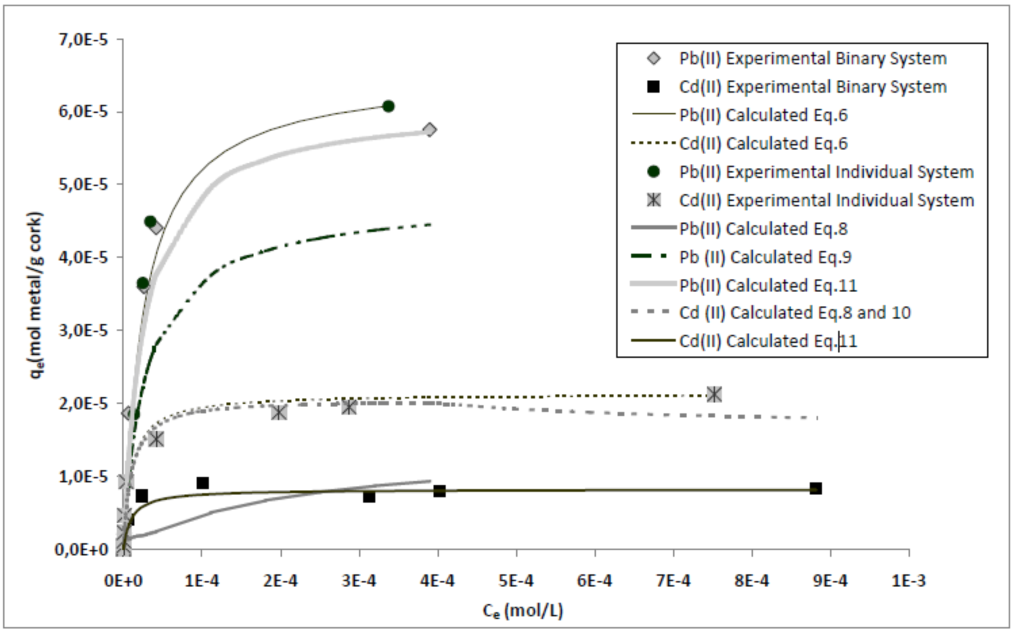

Fig. 8. Experimental and calculated sorption isotherms of Pb(II) and Cd(II) for the single and binary systems on cork, at pH 5.0, for the different models applied.

3.6.2.3. P-Factor approach based on the Langmuir model.

McKay and Al-Duri [34] developed a simplified approach based on the introduction of a factor (P-factor) to correlate the isotherms of both systems the single component and the multi component, using the Langmuir constants. For binary mixtures, the isotherm equation for each of the components is presented in Eq. (11).

$$q_{e,i} = \frac{1}{P_i} \frac{K_{L,i} C_{e,i}}{1 + \sum_{i=1}^{z} b_i C_{e,i}} \quad (11)$$

where the subscripts *i* refers to each component and *P* is the capacity factor (P-factor) calculated using Eq. (12).

$$P_i = \frac{(K_{L,i} / b_i)_{\sin gle\ system}}{(K_{L,i} / b_i)_{binary\ system}} = \frac{(Q_{o,i})_{\sin gle\ system}}{(Q_{o,i})_{binary\ system}} \qquad (12)$$

From the Langmuir constants ($K_{L,i}$ and b_i) previously calculated by fitting the experimental sorption data for each component on individual and binary systems (Table 4), the P-factors were calculated obtaining 1.072 and 2.587 for Pb(II) and Cd(II) respectively. Fig. 8 shows the good correlations between experimental and calculated data for both metals in binary mixtures when the P-factor was used. Moreover, this model shows the better fits compared with the other models applied.

3.7. Biomass titration and static exchange capacity

Taking into account that the expected functional groups of the cork biomass are carboxylates and fenolates, potentiometric titration technique was used in order to quantify the content of acid groups obtaining 1.64 mequiv g^{-1} of acid groups on the surface of the cork. It is expected that these acidic sites in the cork biomass surface are the responsible of the removal of heavy metals from aqueous solutions by an ion-exchange mechanism based on acid/base equilibrium system [7,8].

The static exchange capacity (SEC or q_{sec}) was calculated using Eq. (2) for the different acid and basic groups and expressed in terms of Na^+. The concentration of strong acidic groups corresponds to the value found when a weak base (in this case $NaHCO_3$) was used as the reagent for the titration system. To determine the concentration of strong and weak carboxylic groups, the titration is carried out with Na_2CO_3 (such results are collected in Table 5). From the difference of both values, it is possible to calculate the value of the weak acidic groups

(0.14 mequiv g^{-1}). From the titration with NaOH as reagent, the phenolic and all carboxylic groups were titrated, so the phenolic groups can be determined from the difference with the value found for Na_2CO_3 (0.99 mequiv g^{-1}). The content in basic groups, determined by titration with HCl (0.48 mequiv g^{-1}), results in a smaller amount than the acidic ones, which are by the way the responsible of the cork uptake of the metals.

The results found are in agreement to those found in other studies in the literature [17-20] what provide strong evidence to support the presence of different surface groups in cork and which are the responsible of the uptake of both metals.

4. Conclusions

From the reported results, it can be said that the biomass of cork can be used as biomaterial sorbent for the removal and recovery of heavy metals, specially Pb(II) and Cd(II) from aqueous solutions without modification of its chemical structure and morphology. Biosorption is pH-dependent showing a maximum value at pH 5 and is highly influenced by the metal ion content in the initial solution. The adsorptive sites on the cork biomass showed a higher uptake for Pb(II) ions compared to Cd(II) ions which was corroborated by the Langmuir saturation constant. Moreover, because b is the ratio between sorption and desorption constants at the equilibrium the higher value of b for Cd(II) indicates that the metal molecules are more strongly bonded to the cork than the Pb(II) ones.

The kinetic study indicate that the process mechanism occurs by both film and intraparticle diffusion. From the different sorption models applied, the P-factor approach based on the Langmuir model provided the best correlation for the metal cork system studied.

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