CELLULOSE CHEMISTRY AND TECHNOLOGY

KINETIC STUDY OF LEAD(II) REMOVAL FROM AQUEOUS SOLUTION ONTO LIGNIN-BASED MATERIALS

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Received March 22, 2014

In this study, the removal of lead(II) ions from aqueous solution on two types of lignin-based materials (a cellolignin obtained from chestnut wood (L1) and lignin extracted from rape (L2)) was examined from a kinetic point of view. The influence of initial lead(II) concentration and contact time was studied in batch experiments. The experimental data showed that biosorbent L2 had a higher biosorption capacity than L1, and required a shorter contact time. The kinetics of biosorption was followed based on the amount of lead(II) retained at various time intervals, and the data were analyzed using three kinetic models: pseudo-first order, pseudo-second order and intra-particle diffusion model. The results indicated that chemical interaction might to be a rate-limiting process in lead(II) removal on both biosorbents. This hypothesis was sustained by the analysis of FT-IR spectra, which showed that biosorbent L2 had more alcoholic-OH groups than L1, and they played an important role in the biosorption process.

Keywords: lignin-based materials, lead(II) ions, biosorption, kinetics, aqueous solution

INTRODUCTION

Lead is a heavy metal with a broad range of industrial applications, such as battery manufacturing, smelting, printed wiring board manufacture etc.,[1,2] and thus large amounts of industrial effluents that contain this pollutant are discharged into the environment. Water containing high concentrations of lead(II) ions can cause severe human health problems due to its toxic and carcinogenic effect,[3,4] as well as the degradation of the environment quality. Therefore, the removal of lead(II) from industrial wastewater has become an important issue in many industrialized countries. Under these conditions, the development of cost-effective removal methods is required for treating metal-containing wastewater, and this could be also important from economic considerations.[4]

The methods that are frequently used to remove heavy metals from industrial wastewater include chemical precipitation, membrane filtration, electrochemical techniques, ion exchange and adsorption on activated carbon.[5-9] However, most of these methods have several important drawbacks, such as high cost of operation, large input of chemicals, high energy consumption, incomplete removal of metal ions, especially when large volumes of wastewater are treated, or generation of high quantities of sludge.[10,11] Biosorption of heavy metals from aqueous solutions plays an important role in the water pollution control, and in recent years, the use of low-cost and efficient biosorbent materials has received considerable interest. Such biosorbents are mostly naturally abundant or are obtained from waste biomass, and some of them have excellent biosorption characteristics.[12,13] Due to cost effective sources of raw materials and their metal-binding properties, the biosorption process based on low-cost biomasses is a promising treating method of metal-containing wastewater that can be successfully used for industrial applications.[14]

Cellulose Chem. Technol., ***50*** *(2), 339-347 (2016)*

Lignin is the second most abundant natural raw material after cellulose. It is present in large quantities in the cell walls of plants, and represents the main binding agent for fibrous plant components.[15,16] Lignin is mainly obtained from black liquor, a waste discharged in large amounts by the paper industry. The data reported in the literature have shown that over 5 10^5 metric tons/year of lignin is produced worldwide by pulping, and in many cases its disposal represents a major problem from the environmental protection viewpoint.[17,18]

Chemically, lignin is considered a natural amorphous cross-linked polymer, which has an aromatic three-dimensional structure, containing numerous functional groups, such as hydroxyl, carboxyl, methoxyl and carbonyl.[16] These functional groups can interact with metal ions from aqueous solutions, making it potentially useful as a biosorbent material for removing heavy metals. Therefore, depending of the nature of the raw material and the extraction method, the number and the availability of functional groups in the structure of lignin-based materials will be different, and this will influence the efficiency of such biosorbents in the removal processes of metal ions.

In this study, the kinetics of lead(II) ions biosorption onto two types of lignin-based materials (a cellolignin obtained from chestnut wood (L1) and lignin extracted from rape (L2)) from aqueous solutions was examined. The influence of initial lead(II) concentration and contact time was studied in batch experiments. In order to establish the biosorption mechanism, the experimental results were analyzed using three kinetic models: pseudo-first order, pseudo-second order and intra-particle diffusion model. On the basis of these models, the kinetic parameters for lead(II) biosorption onto both types of lignin-based materials were calculated and discussed.

EXPERIMENTAL

Chemical reagents

All chemical reagents were of analytical grade and were used without further purification. A stock solution of lead(II) (10^{-2} mol Pb(II)/L) was prepared by dissolving lead nitrate (purchased from Reactivul Bucharest) in double distilled water. Working solutions were obtained by diluting the stock solution with double distilled water. Fresh dilutions were prepared and used for each experiment. The initial pH value of the working solutions was obtained using acetate buffer with pH = 6.0.

Biosorbents

In this study, two types of lignin-based materials were used as biosorbents for the removal of lead(II) ions from aqueous solutions. The first was a cellolignin (L1), which is a residual ligninocellulosic material resulting from furfural production from chestnut wood. This biosorbent was purchased from Tanin Sevnica-Slovenia, and was used without other physical-chemical treatment.

The second was a lignin obtained in the laboratories of the Department of Natural and Synthetic Polymers ("Gheorghe Asachi" Technical University of Iasi) from rape (L2), according to Šćiban.[19] Both types of lignin-based materials were dried in air for 6 hours at 70 ± 2 °C, ground and sieved. For the biosorption experiments, only the fraction with a particle size of 50 μm was considered, which was stored in desiccators for subsequent use. The characterization of the biosorbents has been done by FT-IR spectrometry (FTS 2000 Series (Bio-Rad) spectrometer, in 400-4000 cm^{-1} spectral domain, and 4 cm^{-1} resolution, by the KBr pellet technique) and optical microscopy (Olympus Microscope, natural and polarized light). Also, the content of some functional groups was determined from the recorded IR spectra.[20]

Biosorption experiments

The biosorption experiments were performed by the batch technique, at room temperature (20 ± 2°C), mixing samples of around 0.125 g of each type of lignin-based material with volumes of 25 mL solution of a known concentration of lead(II) (0.21-2.54 mmol/L) in 100 mL conical flasks with intermittent stirring (for 24 hours). The initial pH of the working solution was obtained by adding 5.0 mL of acetate buffer (pH = 6.0). For kinetic experiments, a constant biosorbent dose of 0.125 g was mixed with 25 mL of 0.54 mmol/L lead(II) solution at various time intervals between 5 and 180 min.

After biosorption, the biosorbents (L1 and L2) were separated through filtration, and the lead(II) concentration in the filtrate was determined spectrophotometrically with 4-(2-pyridyl-azo)-resorcinol (Digital Spectrophotometer S 104 D, λ = 530 nm, 1 cm glass cell, against a blank solution),[21] using a prepared calibration graph.

THEORETICAL BACKGROUND

Data evaluation

The biosorption capacity (q, mmol/g) of the considered lignin-based materials towards lead(II) ions from aqueous solutions was calculated from the mass balance expression:

$$q = \frac{(c_0 - c)\cdot(V/1000)}{m} \qquad (1)$$

and the percentage of lead(II) removal (R, %) can be obtained using Eq. (2):

$$R, \% = \frac{(c_0 - c)}{c_0} \cdot 100 \qquad (2)$$

where: c_0, c are the initial and equilibrium concentration of lead(II) in solution (mmol/L); V is the volume of solution (mL) and m (g) is the dry mass of biosorbent (L1 or L2) added to 25 mL of aqueous solution.

Kinetic models

The kinetics of biosorption is an important aspect that can be used to characterize the efficiency of a given biosorbent in the heavy metals removal processes. In order to determine the lead(II) uptake rate and to explain the transport of metal ions to the surface of the biosorbent, three different kinetic models (pseudo-first order, pseudo-second order and intra-particle diffusion model) were used for the mathematical description of the experimental data.

The linear form of the pseudo-first order kinetic model, based on solid capacity, can be expressed by the following relation:[22,23]

$$\log(q_e - q_t) = \log q_t - \frac{k_1}{2.303} \cdot t \qquad (3)$$

where: k_1 is the pseudo-first order rate constant (1/min); q_e and q_t are the biosorption capacity at equilibrium and at time t, respectively (mmol/g).

The pseudo-second order model is based on the hypothesis that the rate limiting step in the biosorption mechanism is the chemical interaction between metal ions from aqueous solution and functional groups from biosorbent surface. The mathematical equation of the pseudo-second order kinetic model, in the linearized form, can be written as:[23,24]

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \qquad (4)$$

where: k_2 is the rate constant of the pseudo-second order kinetic model (g/mmol min).

The intra-particle diffusion model was considered in order to evaluate the importance of the diffusion process in the biosorption of lead(II) onto the considered biosorbents. The kinetic equation of the intra-particle diffusion model is:[25,26]

$$q_t = k_{dif} \cdot t^{1/2} + c \qquad (5)$$

where: k_{diff} is the intra-particle diffusion rate constant (mmol/g min$^{1/2}$) and c is the concentration of lead(II) ions from the solution at equilibrium (mmol/L).

RESULTS AND DISCUSSION

Characterization of lignin-based materials

Optical microscopy in natural and polarized light was used for the surface analysis of both types of lignin-based materials. The microscopic images (Fig. 1), recorded at different orders of magnitude, demonstrate the roughness of the surface structure of the biosorbents, where lead(II) ions can be retained. In addition, it can be observed that the microscopic images of L1 (Fig. 1a) are brighter than the microscopic images of L2 (Fig. 1b). Considering the basic principle of optic microscopy, i.e. that the intensity of light received by the detector is higher when surface porosity is lower, the differences observed between the microscopic images from Fig. 1 suggest that biosorbent L2 is more porous than L1. This means that in the case of biosorbent L2, the intra-particle diffusion process will have a more important role in the biosorption mechanism.

The presence of different functional groups in the structure of the lignin-based materials considered has been proved by FT-IR analysis (Fig. 2). Several important peaks are observed in the spectra of both biosorbents. The broad bands at 3408 cm^{-1} and 3423 cm^{-1}, respectively, are determined by the stretching vibration of aromatic and aliphatic hydroxyl groups. The peaks at 2908 and 2935 cm^{-1} are attributed to the C–H stretching of methyl and methylene groups from the chains and the aromatic methoxy groups. The peaks at 1714 and 1610 cm^{-1} (in L1 spectra) and at 1712 and 1610 cm^{-1} (in L2 spectra) can be attributed to the conjugated carboxyl and carbonyl stretching vibrations. The band at 1323 and 1211 cm^{-1} in L1 spectra, and 1321 and 1219 cm^{-1} in L2 spectra, respectively, correspond to the syringyl ring C–O stretching vibration.[27] The relatively intense bands at 1514 and 1504 cm^{-1} indicate that in both lignin-based materials the phenolic units are abundant.[21] All these observations demonstrate that in the structure of the lignin-based materials used as biosorbents in this study, numerous functional groups (hydroxyl, carboxyl, carbonyl, etc.) are present, and they represent potentially binding sites, because they can interact with lead(II) ions during the removal process. Similar absorption bands have been observed in the FT-IR spectra recorded for lignins obtained from different sources (eucalyptus paper pulps, Kraft pine lignin, flax lignin, wild tamarind lignin)[28,29] and were used to prove the presence of functional groups (such as alcoholic and phenolic hydroxyl, carbonyl, etc.) in their structure. The intensity of the adsorption bands has been correlated with the number of functional groups in the lignin structure, and depends on the origin of lignin. In addition, the analysis of functional groups indicated that both lignin-based materials had almost the same content of total hydroxyl groups (Table 1), but in the case of biosorbent L2, the content of alcoholic hydroxyl groups was higher than in the case of L1.

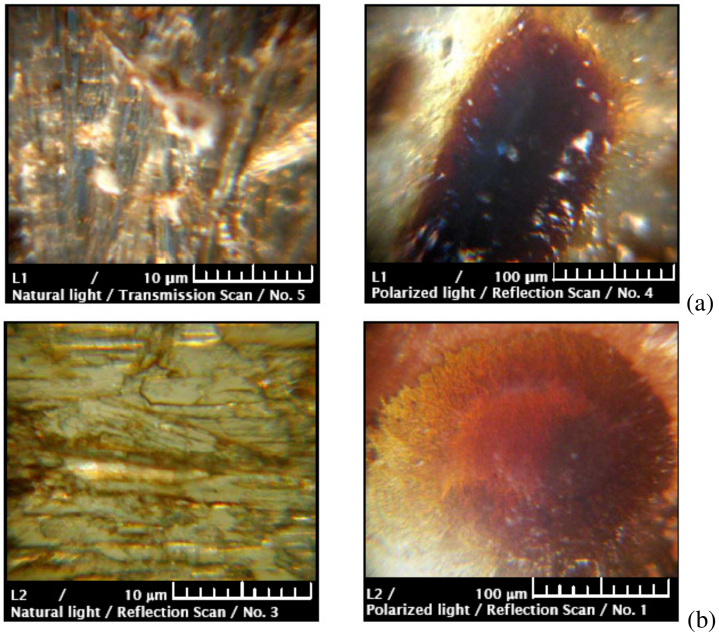


Figure 1: Microscopic images of L1 (a) and L2 (b) lignin-based materials at different magnifications

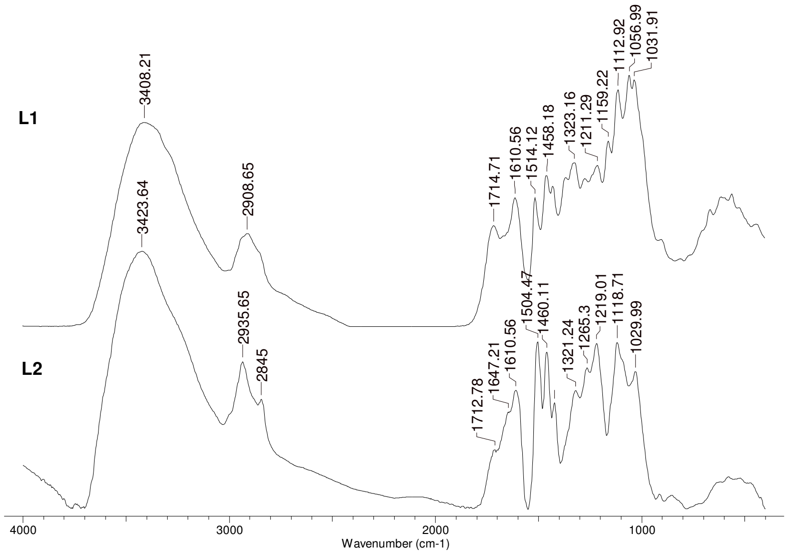


Figure 2: FT-IR spectra of L1 and L2 lignin-based materials

Table 1
Some physical-chemical characteristics of lignin-based materials (L1 and L2) used as biosorbents

Characteristic	L1	L2
Ash, %	0.53	0.63
Total OH groups, mmol/g	1.72	1.66
Alcoholic OH groups, mmol/g	0.42	0.61
Total methoxy groups, mmol/g	1.12	1.24
Total carbonyl groups, mmol/g	0.88	0.59

Biosorptive characteristics of lignin-based materials

In several previous studies,[30,31] it has been shown that both lignin-based materials can be successfully used for the removal of lead(II) ions from aqueous solution, and the efficiency of the biosorption process depends by the initial solution pH, biosorbent dose and also by the type of biosorbent. On the basis of the data presented in the studies mentioned above, we considered that the optimum experimental conditions for the biosorption of lead(II) on the lignin-based materials under study were initial pH = 6.0 (acetate buffer) and a biosorbent dose of 5 g/L, and these values were used further in the experiments.

In order to study the influence of initial lead(II) concentration on the removal efficiency on each type of lignin-based material, the experiments were performed under the optimum experimental conditions, and the obtained results are illustrated in Fig. 3.

The biosorption capacity towards lead(II) increases with an increasing initial metal ions concentration, for both biosorbents. This is mainly determined by an increase of the interaction probability between the lead(II) ions and the functional groups from the biosorbent surface, with an increase of the initial concentration of lead(II).

It can also be observed that in the studied concentration range, the L2 biosorbent has better biosorptive characteristics that L1, and this could be easily remarked at high initial metal ions concentration. For example, at an initial concentration of 2.54 mmol/L, the biosorption capacity is 0.26 mmol/g in the case of L2 and only 0.15 mmol/g when L1 is used as biosorbent. These results suggest that the biosorption of lead(II) ions from aqueous solution on the considered lignin-based materials occurs predominantly by strong interactions (probably electrostatic), and so the efficiency of the removal process mainly depends by the number and availability of surface functional groups. When the biosorbent has a high number of available functional groups (in special alcoholic hydroxyl groups) as it is the case of L2, the amount of lead(II) retained increases, and thus the biosorption process is more efficient. However, it should be noted that from an environmental protection point of view, an efficient removal of lead(II) takes place at an initial concentration of lead(II) lower than 0.24 mmol/L, when the lead(II) content in the solution obtained after phase separation is lower than the permissible limit for lead(II) discharge.[32] If the initial lead(II) concentration is higher than this value, two or more biosorption stages are required.

Biosorption kinetics

The kinetic studies are very important in the design of biosorption systems for an industrial scale process. This is because the kinetic parameters often provide useful information about the biosorption mechanism, surface properties and the efficiency of a biosorbent for metal ions, under well-defined experimental conditions.[33] In order to investigate the mechanism of lead(II) biosorption onto the considered lignin-based materials, the influence of contact time between the biosorbent (L1 and L2) and the lead(II) aqueous solution has been studied, and the obtained results have been modelled using three different kinetic models (pseudo-first order, pseudo-second order and intra-particle diffusion model).

The experimental results (Fig. 4) show that under the mentioned experimental conditions, the efficiency of lead(II) removal increases with an increase of contact time, for both types of biosorbents. The biosorption process is fast during the initial stage, in the first 30 min around 69% from initial lead(II) concentration is retained on L1, and around 79% on L2, respectively. After this initial step, the rate of the biosorption process slows down until it reaches equilibrium, which is practically obtained after 60 min in the case of L1, and 40 min in the case of L2 (Table 2).

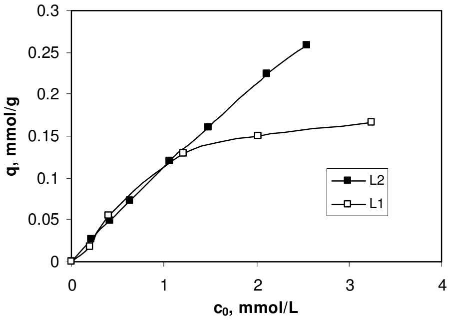


Figure 3: Influence of initial lead(II) concentration on lead removal efficiency on lignin-based materials (pH = 6.0 (acetate buffer); 5 g lignin/L; 24 hours of contact time)

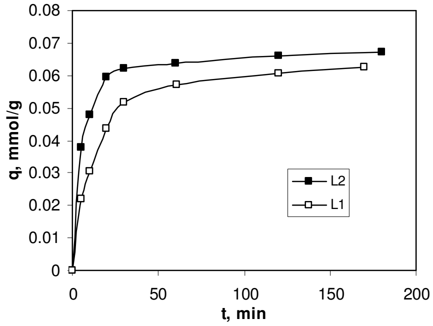
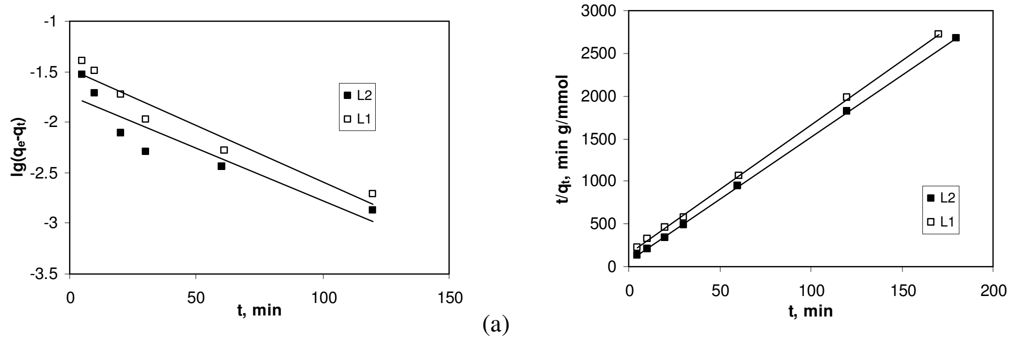


Figure 4: Influence of contact time on lead(II) biosorption by each type of lignin-based material (pH = 6.0 (acetate buffer); 5 g lignin/L; c_0 = 0.64 mmol Pb(II)/L)



(a) (b)

Figure 5: Linear representation of pseudo-first order (a) and pseudo-second order (b) kinetic models for the biosorption of lead(II) on L1 and L2 lignin-based materials

Table 2
Comparative values of q (mmol/g) obtained after 24 hours (considered maximum amount of lead(II) retained onto lignin-based materials) and after the time required to reach equilibrium

	L1	L2
$q^{24\ hours}$, mmol/g	0.0657	0.0731
$q^{equilibrium}$, mmol/g	0.0598	0.0682
$\Delta q = q^{24\ hours} - q^{equilibrium}$	0.0059	0.0049

Table 3
Kinetic parameters for the biosorption of lead(II) onto L1 and L2 lignin-based materials

Biosorbent	q_e^{exp}, mmol/g	L1	L2
		0.0625	0.0667
Pseudo-first order kinetic model	R^2	0.9351	0.8476
	q_e, mmol/g	0.0236	0.0289
	k_1, 1/min	$4.8198\ 10^{-3}$	$4.4291\ 10^{-3}$
Pseudo-second order kinetic model	R^2	0.9997	0.9998
	q_e, mmol/g	0.0662	0.0685
	k_2, g/mmol min	1.5080	3.6369

The relatively low value of the contact time required to reach equilibrium is one more argument supporting the hypothesis that the biosorption process of lead(II) on the considered lignin-based materials occurs predominantly by electrostatic (ion-exchange or superficial complexation) interactions, between positively charged metal ions (Pb^{2+}) and negatively charged functional groups from the biosorbent surface.[10,11]

The kinetic parameters of the pseudo-first order and pseudo-second order kinetic models, calculated from the linear dependences ($\lg(q_e-q_t)$ vs. t (Fig. 5a) and t/q_t vs. t (Fig. 5b), respectively), together with the correlation coefficients (R^2) are summarized in Table 3.

The obtained values show that the equilibrium biosorption capacity (q_e, mmol/g) calculated from the pseudo-first order equation is very different from the experimental values (q_e^{exp}, mmol/g), for both lignin-based materials. Therefore, the pseudo-first order kinetic model is not adequate for describing the kinetics of lead(II) biosorption onto L1 and L2 biosorbents. The high values of the correlation coefficients (R^2) and the very good correspondence between the calculated and experimental values of biosorption capacities (q_e, mmol/g) indicate that the retention of lead(II) on both types of lignin-based materials is very well represented by the pseudo-second order kinetic model.

The compatibility of the experimental data with the pseudo-second kinetic model shows that the rate limiting step may be the chemical interaction, involving ion-exchange or superficial complexation between the surface groups of the biosorbent and the lead(II) ions from the aqueous solution. In addition, the high value of the rate constant obtained in the case of lead(II) biosorption onto L2 indicates that this biosorbent has a higher number of functional groups available for interacting with metal ions, compared to L1. This observation is in agreement with the experimental results presented above (see Table 1).

According to the intra-particle diffusion model, if the intra-particle diffusion process is the rate limiting step, the plot q_t vs. $t^{1/2}$ should yield a straight line, passing through the origin.[34] The graphical representation of this dependence obtained in the case of lead(II) biosorption onto L1 and L2 biosorbents (Fig. 6) does not go through the origin, and two separated zones can be observed in both cases. Each of these zones has been analyzed separately, according to Eq. (5), and the kinetic parameters calculated from the slopes (k_{diff}) and intercepts (c) of the linear portions of the plots are summarized in Table 4.

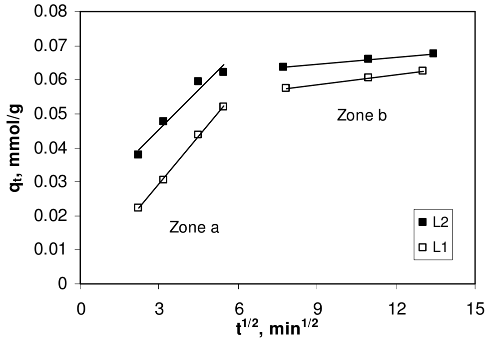


Figure 6: Intra-particle diffusion kinetics for the biosorption of lead(II) on L1 and L2 lignin-based materials

Table 4
Kinetic parameters of intra-particle diffusion model for the biosorption of lead(II) onto L1 and L2 lignin-based materials

Kinetic parameters		L1	L2
Zone a	R^2	0.9983	0.9565
	k_{diff}^a, mmol/g min$^{1/2}$	0.0093	0.0077
	c, mmol/L	0.0015	0.0024
Zone b	R^2	0.9993	0.9739
	k_{diff}^b, mmol/g min$^{1/2}$	0.0010	0.0008
	c, mmol/L	0.0495	0.0566

The deviation of the straight lines from the origin indicates that the intra-particle diffusion process is not the only rate limiting step, but that the boundary diffusion also controls the lead(II) biosorption up to a certain degree, in both cases. According to some studies,[35,36] the first zone (zone a) corresponds to the mass transfer effect (k_{diff}^{a}) taking place with boundary layer diffusion, while the second zone (zone b) can be attributed to the intra-particle diffusion (k_{diff}^{b}). The significant difference between these two zones is given by their slope. Thus, the higher slope of the first zone in comparison with the second zone, obtained for both biosorbents, suggests that the active sites are located on the biosorbent surface, and are readily accessible to the exchange ions, or at the external inter-layer surface. Hence, the experimental data indicate a limited contribution of mass transfer and boundary layer diffusion in the biosorption process of lead(II) ions onto L1 and L2 lignin-based materials, and that the intra-particle diffusion influenced the removal process up to a certain degree.

By analyzing the results obtained from kinetic modelling, it can be observed that the biosorption of lead(II) onto both types of lignin-based materials occurs through sequential equilibrium stages. There are two stages involved in the biosorption mechanism, as shown in Fig. 4. Biosorption occurs very fast at the surface in the first stage, and more slowly through intra-particle diffusion in the second stage. The ion exchange interactions from the first stage may be effective in binding the lead(II) to the biosorbent surface, while the diffusion of the metal ions to the pores of the biosorbents may be effective in the second stage.[37]

CONCLUSION

The results presented in this study indicate that both lignin-based materials (cellolignin (L1) and lignin extracted from rape (L2)) can be used as low-cost and efficient biosorbents for the removal of lead(II) ions from aqueous solution. In order to evaluate the biosorptive characteristics of the considered biosorbents, the influence of initial lead(II) concentration and contact time was examined, under the optimum experimental conditions (pH = 6.0 (acetate buffer), 5 g/L biosorbent). The experimental results showed that biosorbent L2 displayed higher biosorption capacity (0.26 mmol//g) in comparison with biosorbent L1 (0.15 mmol/g), in the studied concentration range. Also, the contact time for the maximum biosorption efficiency depends on the type of the lignin-based material, and it is close to 40 min for L2, and to 60 min for L1, respectively. These observations suggest that the biosorption process of lead(II) is controlled by chemical interactions between the metal ions and the surface functional groups of the biosorbent, and mainly depends on the number and availability for interaction of the latter.

From a kinetic point of view, the experimental data are very well fitted by the pseudo-second order kinetic model, and confirm the chemical nature of the rate limiting process. The higher value of the rate constants shows that the biosorption of lead(II) onto the considered lignin-based materials is a relatively fast process, depending on the type of biosorbent, which occurs at least in two stages: a very fast stage at the beginning, corresponding to surface biosorption, followed by a slower intra-particle diffusion process.

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