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Chemical Modifications of Douglas Fir Bark, a Lignocellulosic By-product—Enhancement of Their Lead(II) Binding Capacities

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Chemical Modifications of Douglas Fir Bark, a Lignocellulosic By-product—Enhancement of Their Lead(II) Binding Capacities

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ABSTRACT

Chemical modification of Douglas fir bark and its subsequent utilization in adsorption of Pb^{2+} from aqueous solutions was investigated. We developed a new solvent-free approach to enhance the natural properties of bark by utilizing polyfunctional groups covalently attached at their surface. The hydroxyl groups of their polysaccharide moiety were functionalized by periodate oxidation and derivatized via reductive amination in presence of aspartic acid or 4,4′-diamino-2,2′-stilbene disulfonic acid. The degree of substitution of derivatized bark was estimated by the means

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of pH titration. Adsorption isotherms of Pb^{2+} on derivatized barks were determined and compared with the performances of crude bark. Adsorption was characterized using the noncompetitive Langmuir adsorption model in terms of affinity (b) and maximum binding capacities (q_{max}). Derivatization resulted in enhancements of both q_{max} (×4–7) and b (×1.5–10). These experimental data are discussed in the context of the Hard and Soft Acid and Base theory.

Key Words: Douglas fir bark; Chemical modifications; Biosorption; Adsorption isotherms; Langmuir; Lead.

INTRODUCTION

New valorization processes are emerging, as a consequence of the enforcement of the European legislation regulating organic waste management. In this context, biosorption has received some attention. It takes advantage of binding capacities of various biological materials for mineral pollutants, e.g., heavy metals from soil or waste waters.[1] This technique is promising for the treatment or pretreatment of industrial waste streams and natural waters, and is an alternative to conventional processes for the removal of metals, such as ion exchange. Not only is biosorption a cost-effective tool for waste water treatment, but it could also be the starting point of new ways of utilization and/or valorization of forest[2,3] or agricultural[4] by-products. It has been expected that advantage could be taken from the strong adsorption capacities displayed by barks, a low-cost forest by-product, to remove heavy metal ions from aqueous solutions.[3] Moreover, barks are commercially available in large amounts from sawmills and paper plants.

The abilities of barks to bind heavy metal ions from polluted solutions[3,5–11] and the impact of various operating factors on this phenomenon[9] have been largely described. Recently, we proposed an interpretation of the mechanisms involved in heavy metal adsorption onto coniferous barks using adsorption isotherms and Langmuir modelization.[12] This mechanism could be easily correlated to the chemical and physical characteristics of the metal ions studied. Among them, hydration enthalpy, polarizability, and the number of unpaired electrons appear strongly significant. The adsorption process also depends upon the adsorbent surface chemistry. In this respect, the sorptive properties of barks can be attributed to the contents of acidic sites, such as carboxylic and/or phenolic groups borne by pectin and tannin/lignin contents, respectively.[4,5,13] The aim of this study is to enhance the metal sorption capacities of barks (quantitative and qualitative aspects) by introduction of covalently bound weak/or strong acidic functional groups,

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such as carboxyl or sulfonyl. Chemical activations of barks has already been described. It is commonly based on treatments with acids or bases,[3,14,15] or with acid–formaldehyde.[6,9,16] Recently, chemical modifications of sawdusts were also performed by direct esterification with succinic anhydride.[17] Both acidic-formaldehyde treatment and esterification increase forest by-product binding capacities; however, the use of toxic solvents/reagents is the major drawback of theses methods.

Our specific goal is to convert a common forest by-product into a valuable biosorbent capable of high metal ion loading using an aqueous-based functionalization and derivatization method. The main objectives of the present study are first to establish the efficiency of: (i) aldehyde functionalization by periodic oxidation of the polysaccharidic moiety of bark, (ii) derivatization through reductive amination with aspartic acid and 4,4′-diamino-2,2′-stilbene disulfonic acid. In a second part, the Pb^{2+} sorption capacities of the grafted barks were fully characterized.

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MATERIAL AND METHODS

Material

Coniferous barks of the Douglas fir species were collected from a local firm located in the Limousin region (France). An industrial size fraction (particle size <7 mm) was selected, air dried at 50°C for 48 hr and then ground, sieved (particule size <200 μm), and stored for further use in an air-tight container.

All chemicals were of commercial grade in the highest purity and were used without further purification. Milli-Q deionized water (Millipore system) was used throughout all experiments.

Bark Functionalization

The first chemical step consists of aldehyde group generation. To this end, the cellulosic and hemicellulosic moieties of Douglas fir bark were oxidized by periodic acid as shown in Fig. 1. Douglas fir bark (6 g) was placed in 0.157 M $NaIO_4$ aqueous solution. In order to avoid radical-induced depolymerization reactions, the reaction was conducted in the dark in the presence of propanol-1 as radical scavenger with a 9 : 1 (v/v) $NaIO_4$/propanol-l ratio. The reaction mixture was stirred at room temperature for 7 days and then reaction was stopped by destruction of excess periodate with ethylene glycol. The oxidized product was rinsed with milli-Q water and air-dried at 50°C.

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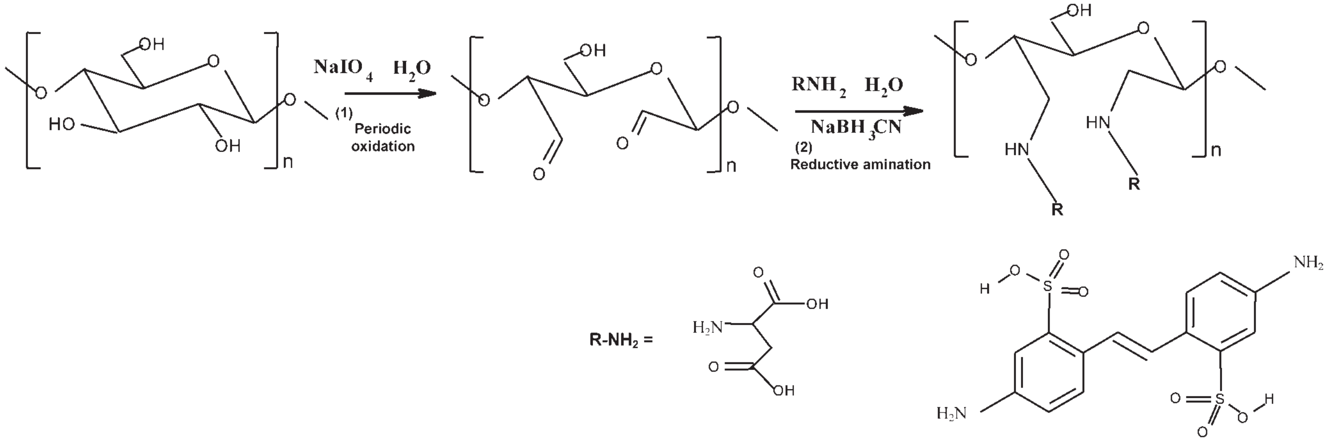

Figure 1. Functionalization and derivatization steps of the cellulosic and hemicellulosic moieties of Douglas fir bark.

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The control oxidation was carried out by assaying residual periodate according to the method of Hay et al.,[18] and modified by Painter and Larsen.[19] Aliquots from the reaction medium were added to 1 M KI/pH 7, 0.1 M KH_2PO_4 mixture (volume ratio 1 : 8) and then titrated with 0.026 M $Na_2S_2O_3$ in presence of starch. Concurrently, released formic acid was titrated by 0.1 M sodium hydroxide from aliquots after addition of ethylene glycol. A control experiment with no periodate was also carried out to titrate acidity naturally leached from bark. A measure of the content of oxidized functions e.g., aldehyde groups, was performed by a method adapted from Pommerening et al.[20] that made use of an internal Canizzaro rearrangement reaction. An excess of sodium hydroxide was added to 100 mg of oxidized bark; after stirring and heating at 70°C for 15 min, the suspension was neutralized by an equivalent amount of hydrochloric acid; then carboxylic functions were titrated with 0.1 M sodium hydroxide.

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Bark Derivatization

In a second step, 4.5 g of dialdehyde bark (DAB) were derivatized by reductive amination (Fig. 1) with 2079 mL of a 0.0257 M of aspartic or 4,4′-amino-2,2′-stilbene disulfonic acid solutions. The amount of primary amine was chosen to exceed the number of aldehyde groups borne by oxidized bark to ensure a maximum derivatization. Thus, 2 and 4 $(-NH_2)/(-CHO)$ molar ratios were used to favor the derivatization with aspartic or 4,4′,-diamino-2,2′-stilbene disulfonic acid, respectively. $NaBH_3CN$ at a concentration of 0.0257 M was used as reducing agent and pH was adjusted to 6.5; the resulting reaction mixture was stirred at room temperature for 5 days. The derivatized bark was rinsed with milli-Q water and air-dried at 50°C.

Characterization of Modified Douglas Fir Bark

pH Titration

The effect of the chemical treatment was evaluated through measurement of the acidity of the adsorbent (crude, dialdehyde, and derivatized barks) by pH titration. Typically, crude or aspartic acid-grafted barks (100 mg) or stilbene derivative-grafted bark (45 mg) were weighed into separate flasks. A total batch volume of 25 mL was made up by adding distilled water. A blank experiment with no sorbent was also performed. The batches were equilibrated for 30 min at room temperature and the solutions were titrated by 0.1 M NaOH under N_2 to avoid the trapping of air carbon dioxide.

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FT-IR Spectroscopy

Crude, dialdehyde, and derivatized barks were further characterized by infrared (IR) spectroscopy with a FT-IR Perkin–Elmer Spectrum 1000 in the frequency range 550–4000 cm^{-1}.

Study of Sorption Process Equilibrium

To follow the kinetics of metal adsorption and then select an optimum contact time, 100 mg of ground crude bark were placed in batch conditions in contact with 10 mL of 9.65 $\mathrm{meq\,L}^{-1}$ $Pb(NO_3)_2$. After an incubation time up to 250 min, the adsorbent was separated from the suspension by vacuum filtration through a sintered glass filter (porosity 3).

The biosorption experiments were carried out in batch conditions by adding 100 mg of crude or derivatized barks to 10 mL of $Pb(NO_3)_2$ solution (1.21, 2.41, 4.82, 7.23, 9.65 $\mathrm{meq\,L}^{-1}$ for crude bark; 4.82, 7.23, 9.65, 14.47, 19.3, 24.13, 28.95, 38.61 $\mathrm{meq\,L}^{-1}$ for aspartic acid-grafted bark; 14.47, 19.3, 24.13, 28.95, 38.61 $\mathrm{meq\,L}^{-1}$ for stilbene derivative-grafted bark). The initial pH of each metal solution was adjusted to 5.0 with HNO_3. The suspension was shaken at room temperature during 2 hr to ensure equilibrium. The adsorbent was finally separated from the suspension by vacuum filtration through a sintered glass filter (porosity 3).

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Metal Ion Analytical Determinations

The concentrations of residual heavy metal ions in the filtrate were determined by atomic absorption spectrometry with a Varian Spectra A-600 instrument. The amount of heavy metal ions captured by the adsorbent was calculated as the difference between initial and final concentrations of the metal ion in the solution.

RESULTS AND DISCUSSION

Bark Functionalization and Derivatization

Functionalization of bark involved the formation of dialdehyde functions in the polysaccharidic moiety by periodate ($NaIO_4$) oxidation. If this procedure is well documented in the case of purified polysaccharides, such as glycopyranosides,[21] cellulose,[22–24] or hemicellulose from the xylan family[25] as described in one of our previous paper, however, to our knowledge, no reference exists regarding the direct chemical modifications of barks in aqueous media. Our goal is to obtain a sufficiently high aldehyde functional group content and

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to keep bark degradation as low as possible. The oxidation of bark is connected to the amount of sodium periodate consumed during the reaction. Its consumption quickly tends towards a limiting value lower than 0.12 mol L^{-1} (Fig. 2) that indicates the maximal oxidation of the polysaccharidic moiety of bark. Typical aldehyde concentrations could be easily estimated according to the Canizzaro reaction.[20] In our case, it was evaluated to 6 meq g^{-1} for DAB, indicating that the operating conditions are well adapted to this industrial wood by-product. The instability of some other functional groups sometimes leads to further oxidation ("over-oxidation"). As indicated in Fig. 2, the low amount of formic acid released during periodic oxidation is a good indicator of the chemical stability of bark and then of the low degradation of the polysaccharides they contained. Thus, over-oxidation could be neglected in this case.

The apparition of the aldehyde function provided a single point of attachment of aspartic acid and 4,4′-diamino-2,2′-stilbene disulfonic acid by a reductive amination reaction involving the terminal amine group. A higher dialdehyde substitution would provide a higher derivatization density and thus enhance the binding capacity of modified bark. The amount of aspartic acid or stilbene derivative that can be loaded is a function of the concentration of the aldehyde groups generated onto the bark surface. The percentage of derivatization could be easily estimated by the means of pH titration. Figure 3 shows pH titration curves of crude and derivatized barks. The curves obtained in the case of derivatized barks present a second inflection point at pH = 9.4, which is not observed in both the crude or $NaBH_3CN$-treated dialdehyde barks (Fig. 3). This suggests the apparition of an additional functional group that may be related to secondary amine resulting from reductive amination of DAB. The number of NaOH equivalents necessary to neutralize this secondary amine function is representative of the number of aspartic acid or stilbene derivative equivalents that are associated to the DAB. The substitution degrees of bark, established as the ratio of the secondary amine to the aldehyde contents, was estimated to 9.2% and 11.7% for aspartic acid–grafted and stilbene

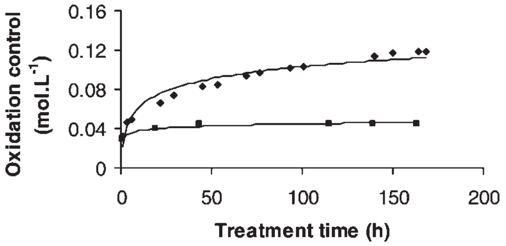

Figure 2. Sodium periodate consumed (◆) and formic acid (■) estimated in function of treatment time.

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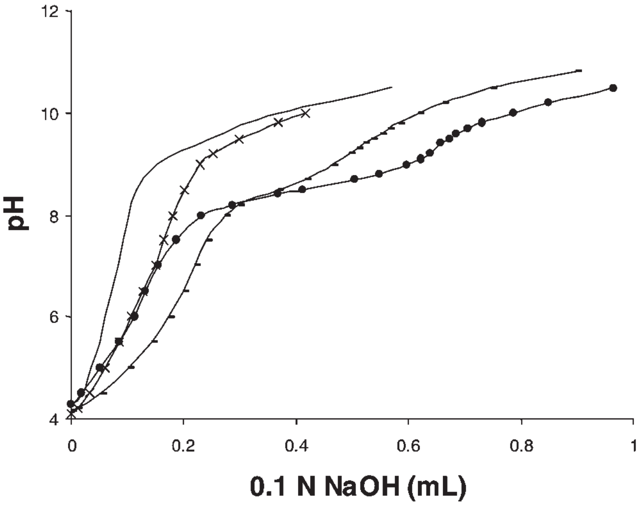

Figure 3. pH titration curves of crude (—×—, $4\,\mathrm{mg\,mL^{-1}}$), NaBH$_3$CN-DAB (–, $4\,\mathrm{mg\,mL^{-1}}$), aspartic acid (—●—, $4\,\mathrm{mg\,mL^{-1}}$) grafted and stilbene derivative (—■—, $1.8\,\mathrm{mg\,mL^{-1}}$) grafted barks.

derivative–grafted barks, respectively (Table 1). These substitution degrees are low; however, to our knowledge, no reference exist in the literature, regarding the direct reductive amination in heterogeneous conditions of solid substrates from biological origin.

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Characterization of Modified Douglas Fir Bark

The FT-IR spectra of crude, DAB, and functionalized barks are presented in Fig. 4. The spectra were examined in the frequency range 550–4000 $\mathrm{cm^{-1}}$. The aldehyde functionalization is clearly identified through the variation of

Table 1. Degree of bark derivatization.

Derivatized barks	Amino groups content ($\mathrm{meq\,g^{-1}}$ bark)	Substitution degree[a] (%)
Aspartic acid-graft	0.55	9.2
Stilbene derivative-graft	0.70	11.7

[a]DAB aldehyde content: $6\,\mathrm{meq\,g^{-1}}$ DAB.

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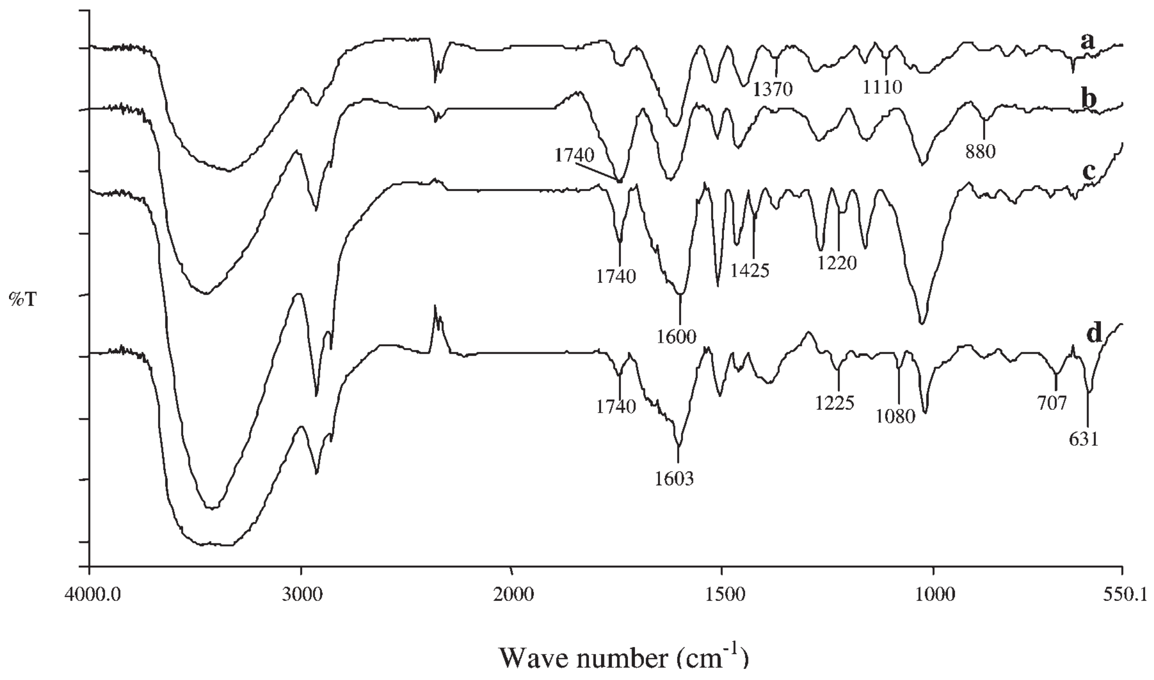

Figure 4. FT-IR spectra of (a) crude, (b) DAB, (c) aspartic acid-grafted and (d) stilbene derivative-grafted barks.

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the absorption bands at 1740 cm^{-1} (C═O stretching in aldehydes), 880 cm^{-1} (hydrated form and acetal structures of dialdehyde cellulose), 1370 cm^{-1} (CH bending of hemicelluloses and cellulose), and 1110 cm^{-1} (OH of hemicelluloses and cellulose). The derivatization is then confirmed by the decrease of the absorption band at 1740 cm^{-1} (C═O stretching in aldehydes) and by the apparition of characteristic bands originating from the grafting of the ligands:

- *Aspartic acid derivative:* 1600 cm^{-1} (COO^- stretching), 1425 cm^{-1} (COO^- stretching), 1220 cm^{-1} (C–O stretching of COOH in dicarboxylic amino-acids).
- *Stilbene derivative:* 1603 cm^{-1} (C═C stretching vibrations in aromatic groups), 1225 cm^{-1} (SO_3^-), 1080 cm^{-1} (SO_2 deformation), 707 cm^{-1} (S–O), 631 cm^{-1} (C–S stretching).

Unfortunately, the characteristic NH_2 absorption bands at 3300–3500 cm^{-1} is not observed because of the overlap with the large OH band at 3200–3600 cm^{-1}. However, the transformation could be easily and quickly monitored on the basis of FT-IR spectroscopy.

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Metal Sorption: Adsorption Isotherms

Adsorption isotherms constitute a good approach to appreciate the specific metal uptake value (q) which could be determined by the following relation:

$$q = \frac{(C_o - C_{eq})}{X} \tag{1}$$

where q is the specific metal uptake per mass unit of bark (meq g^{-1}) at the metal equilibrium concentration C_{eq} (meq L^{-1}) in the aqueous phase, C_o the initial metal concentration (meq L^{-1}), and X (g L^{-1}) the bark concentration in solution.

The amount of Pb^{2+} bound as a function of contact time between ground crude bark and the metal solution is presented in Fig. 5. The adsorption reached equilibrium within about 2 hr. Thus, a contact time of 2 hr was chosen for the determination of adsorption isotherms reported in Fig. 6 for Pb^{2+}.

As a direct characterization, the description of adsorption isortherms in shape and adsorbed quantities constitute a first and fast investigation of the binding strength of the solute onto the solid surface. In this respect, Giles[26] described a classification of adsorption isotherms that could be used in the diagnosis of adsorption mechanisms. His work gave evidences

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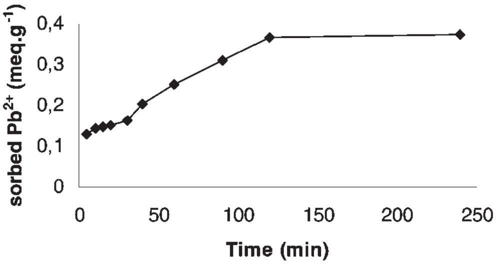

Figure 5. Adsorption kinetic of Pb^{2+} ion onto crude bark.

for the direct relation between solute adsorption mechanisms at solid surfaces and the types of adsorption isotherm obtained. The classification system divided all isotherms into four main classes according to the initial slope, and subgroups are described for each class, based on the shapes of the upper parts of the curves. The four main classes are named the S, L Langmuir type), H (high affinity), and C (constant partition) isotherms. The L curves are the best known and occur in probably the majority of cases of adsorption from dilute solution. This is observed with crude bark (Fig. 6). Here the initial curvature shows that the more substrate sites are filled the more difficult solute molecules find a vacant place. In the case of derivatized barks, the curves appear to be of the H (high affinity) type. The latter is described as a special case of the L curve, in which the solute has such a high affinity that in dilute solutions it is completely adsorbed, or, at least, there is no measurable amount remaining in solution. The initial part of the isotherm is therefore quasi-vertical. However, the plateau-shaped upper

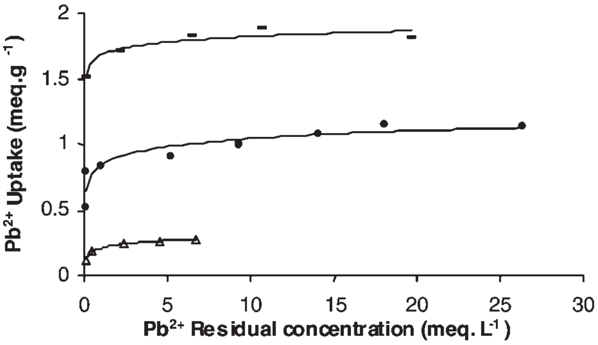

Figure 6. Lead (II) adsorption isotherms onto crude material (—△—) and derivatized barks (—●— aspartic acid, and —■— stilbene derivative).

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parts of both crude and modified bark isotherms exhibit the subgroup 2, which indicates the formation of a complete "monolayer."

Moreover, the sorption equilibrium data can be described through numerical parameters estimated from sorption isotherm models in order to evaluate and compare the specific metal uptake on a determined solid surface. The adsorption isotherms obtained from crude and derivatized barks toward Pb^{2+} were shown to fit the Langmuir model. The hypotheses for a Langmuir type isotherm is the formation of a monolayer, sorption energy independent of the sorbed solute on the neighboring sites, and a homogeneous distribution of sorption sites. The Langmuir isotherm is thus expressed by the following equation:

$$q = \frac{(q_{\max} b C_{\mathrm{eq}})}{(1 + b C_{\mathrm{eq}})} \tag{2}$$

where $q_{\max}$ (meq g^{-1}) is the maximum metal specific uptake, b (L meq^{-1}) is the Langmuir constant, and C_{eq} (meq l^{-1}) is the metal equilibrium concentration in the aqueous phase. Such parameters are of a high importance since they provide valuable information that could contribute to improve our understanding of metal uptake mechanisms onto crude and derivatized barks. The b parameter is related to the energy of adsorption. Furthermore from the initial linear part of the isotherm, b value is a direct function of the distribution coefficient K_{d} considered as the slope of a simple linear model ($q = K_{\mathrm{d}} C_{\mathrm{eq}}$), and then characterizes the affinity of the solute for the sorbent. The $q_{\max}$ and b parameters were readily obtained from our experimental data by plotting Eq. (2) in the following reciprocal form:

$$\frac{1}{q} = \frac{1}{q_{\max} b} \frac{1}{C_{\mathrm{eq}}} + \frac{1}{q_{\max}} \tag{3}$$

Figure 6 gives evidence of such a relationship between metal adsorption amounts and metal equilibrium concentrations. The Langmuir parameters, $q_{\max}$ (determined by the intercept of the straight line with the Y-axis) and b (determined from the slope of the straight line), obtained for the metal ion from the graphical interpretation are presented in Table 2. The results show that the adsorption behavior of Pb^{2+} ion onto both crude and grafted barks can be satisfactorily described by Langmuir isotherms. On the quantitative aspect, the capacities $q_{\max}$ of the derivatized barks are improved from a factor 4 in case of aspartic acid-grafted bark, to 7 in case of stilbene derivative-grafted bark if compared to crude bark. Derivatization also leads to an increase in affinity, × 10 in the case of stilbene derivative-grafted bark (Table 2).

Of interest is the fact that the functionalization of bark has a beneficial impact on their ability to bind Pb^{2+} (Table 2). This phenomenon could be

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Table 2. Saturation capacities evaluated from Langmuir isotherms for Pb^{2+} metal ion.

Bark samples	q_{max} (meq g^{-1}bark)	b (L meq^{-1})	Correlation coefficient
Crude bark	0.26	7.74	0.98
Aspartic acid-grafted bark	1.04	11.56	0.80
Stilbene derivative-grafted bark	1.81	76.77	0.89

explained by the chemical modification of bark that introduces on their surface a larger number of ion exchange sites. According to the classification of *Hard and Soft Acid and Base* established by Pearson,[27] Pb^{2+} is, in most instances, located in the borderline (vs. soft acid) of the classification and owing to the physicochemical environment, binds preferentially to softer ligands. The rules proposed by Pearson, and already discussed for inorganic ligands, are also valid for organic ligands. Among bio-organic compounds the most important donor atoms are O, N, and S. In this context, $R\text{-}CO_2^-$, which is more nucleophilic than $R\text{-}SO_3^-$, is the hardest base. Then, the borderline (vs. soft acid) Pb^{2+} may interact more easily with $R\text{-}SO_3^-$ than with $R\text{-}COO^-$. This prediction is confirmed by our results since stilbene derivative-grafted bark ($R\text{-}SO_3^-$ ligand) present a higher affinity ($b = 76.\ 77\,L\,meq^{-1}$) than aspartic acid-grafted bark ($R\text{-}COO^-$ ligand, $b = 11.\ 56\,L\,meq^{-1}$). Lastly, if these rules are of major importance for the competition of metals for natural ligands in complex biological system, they have to be moderated/modulated according to the physicochemical environment of the ligands. In this context, several factors such as the tridimensional structure (geometry and flexibility; hindrance by noncomplexing parts; position of donor atoms with respect to the size and coordination number of the cations) or the hydration properties of the ligands could interfere, making the simple hard and soft concept more difficult to use.

CONCLUSION

A method for the enhancement of lead(II) binding capacities of Douglas fir bark is proposed. This is achieved through a chemical modification of their polysaccharidic moiety in aqueous medium. We have developed a new solvent-free approach to optimize the natural properties of bark utilizing polyfunctional groups covalently attached to their surface. The hydroxyl groups of their polysaccharidic moiety were functionalized after oxidation with sodium periodate and derivatized via reductive amination in presence of aspartic acid or 4,4′-diamino-2,2′-stilbene disulfonic acid.

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The metal binding properties of Douglas fir bark were analyzed by the means of adsorption isotherms. The evaluation of both the affinity b (qualitative aspect) and the maximum capacity $q_{\max}$ (quantitative aspect) were computed according to the Langmuir model. The stilbene derivative-grafted bark (R-SO_3^- ligand) displays better capabilities than the aspartic acid one (R-COO^- ligand) toward Pb^{2+}. This behavior could be explained by the Hard and Soft Acid and Base Theory. Barks, a common by-product of the forest industry, could be easily converted, for a specific utilization, into ion exchange resins with high specificity towards a specific metal.

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