REVIEW

Heavy metals removal in aqueous environments using bark as a biosorbent

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Abstract Tree bark is among the widely available and low-cost sorbents for metal adsorption in aqueous environments. A state-of-the-art review is compiled carrying out a comprehensive literature search on the biosorption of heavy metals in solution onto different bark species, including a characterization of bark structure and chemistry. The results indicate that biosorption has been gaining importance for bark valorization purposes. Promising heavy metal uptake values have already been attained using different bark species. These values are comparable to those obtained with commercial activated carbons. Bark has a cost advantage over activated carbon and can be used without any pretreatment. Thus, bark offers a green alternative to remove heavy metals from industrial waters. A brief survey of the chemical composition and structure of different bark species is presented. Suggestions are made to improve screening of bark species for specific heavy metal ions sorption.

Keywords Bark · Adsorption · Heavy metal · Water effluents · Low-cost sorbents

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Introduction

Tree barks are among the most abundant bioresources in the world. They are usually available following forestry operations and industrial processes. Statistics on bark production are scarce, and the production is usually estimated indirectly from total round wood production. Bark constitutes between 9 and 15 % of stem volume (Harkin and Rowe 1971). A rule-of-thumb factor of 0.13 applied to wood production was proposed to estimate total bark volume (Corder 1976). In 2008, about 1.542 million m^3 of round woods were produced worldwide that generated approximately 200 million m^3 of bark (FAO 2011).

Bark is usually treated as a waste stream in timber processing, and its disposal is a major concern because of the high volumes involved. Bark is either left in the forest after tree felling or used as a fuel by the forest industry. Large and concentrated amounts of bark are to be found at the premises of the forest-processing industry, both in high-capacity mills such as pulp mills and primary wood-processing mills and in the small-sized wood-processing units. When biomass-fueled furnaces are not in place, bark disposal is often a problem.

Solid waste management methods vary between countries and depend on economical reasons and market availability. Landfill is the cheapest option in countries with available areas such as the USA, while incineration is the choice when real estate is expensive, as it is the case in Japan. Recycling is the option in countries with organized and reliable markets such as Switzerland (Wigginton et al. 2012).

Incineration is not economically viable as bark has relatively low calorific value and considerable water content, e.g., bark has about half the calorific value per unit mass than fuel oils (Gaballah and Kilbertus 1998).

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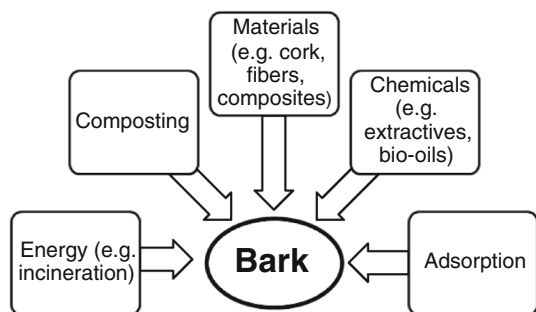Int. J. Environ. Sci. Technol. (2015) 12:391–404

Fig. 1 Main platforms for bark utilization

Environmental concerns regarding soil and air quality are also at stake when considering the burning of bark.

In recent years, there has been a renewed interest in biomass utilization as a raw material for production of chemicals, materials and energy, and studies have been developed focusing on the concept of biorefineries, i.e., to use biomass more efficiently by extracting valuable chemicals and materials (Tuck et al. 2012). Under this biorefineries concept, bark offers many possibilities because of its complex chemical composition and structure. The main utilization possibilities of bark are summarized in Fig. 1. The more traditional routes of energy generation by incineration or other thermochemical processes (such as charcoal production or pyrolysis), or by composting, are complemented with an increased use for materials production using either the whole bark or only fractions (e.g., cork and fibers) as well as for chemicals by extraction of soluble materials or by chemical modification. Recently, the adsorption approach has also been gaining support applying bark as an adsorption substrate for the removal of pollutants, namely of heavy metals, from liquid streams.

Metal adsorption on bark is a monolayer or multilayer accumulation of metal(s) from a liquid solution on the surface of bark in equilibrium. The term "heavy metal" is not defined distinctly in the literature: Certain authors consider heavy metals as metal and semi-metals that cause toxicity, while others use parameters such as density, atomic mass or atomic number for their differentiation (Naja et al. 2009). In this review, the term heavy metal includes all metals except group I and group II elements of the periodic table.

Heavy metal removal from waters is a crucial issue for human health. Heavy metals are not biodegradable and accumulate in living organisms causing various diseases (Bailey et al. 1999). Heavy metal contamination occurs in the effluents of many industries, but the important contributors are iron and steel production, mining and mineral processing, painting and photography, and metal

processing and finishing (electroplating) industries (Gaballah and Kilbertus 1998).

Treatments of industrial effluents for heavy metal removal include precipitation, adsorption on ion-exchange resins or adsorption with activated carbons. Precipitation is not as effective as adsorption, and the need to treat large volumes of sludge after the precipitation induces a further problem. Ion-exchange resins and activated carbon are very effective for heavy metal treatments, but they are expensive.

Biosorption is an option to tackle this problem. Biosorbents are highly efficient as heavy metal adsorbents and often require little processing. They are abundant in nature as waste materials or by-products and have a low cost (Bailey et al. 1999; Saka et al. 2012). They also have advantages over treatment systems based on living biomass (e.g., phytoremediation or microbial treatments) since they do not need nutrient supply or maintenance of healthy microbial populations, and they allow the recovery of metals (Park et al. 2010). Various biomass types were already tested for heavy metal adsorption including fungal biomass, bacterial biomass, algae, peat, wood, bark, leaves, pulp, exhausted coffee, among others (Naja et al. 2009; Kumar 2006; Pujol et al. 2013).

The utilization of bark in heavy metal adsorption is a promising research line as different bark species have shown high capacity to remove metal ions from aqueous solutions. Abundant, renewable and low-cost barks appear as excellent alternatives to ion-exchange resins and activated carbon for industrial applications. Other important advantages of barks are their adsorption capacity at low metal concentrations (below 100 ppm) (Vazquez et al. 2002) and their reductive ability which is important in chromium (VI) removal (Fiol et al. 2003; Aoyama et al. 2004; Şen et al. 2012).

The density and floatability of bark are also to be considered in adsorption. The low density of bark components such as cork makes it float in pond treatments, and therefore, metal removal efficiency of bark may be reduced. However, this problem can be solved by using packed column systems.

The metal recovery after adsorption can easily be made with acid washing of the bark (Horsfall et al. 2006) and retrieving of metals from the concentrate using electrolytic techniques. Incineration or landfill options can also be considered since the adsorbent has low cost (Naja et al. 2009).

There are few references that characterize the specific bark adsorbents and their heavy metal adsorption features (Bailey et al. 1999; Kumar 2006). However, knowledge on the anatomical and chemical characteristics of barks, and

Fig. 2 Schematic diagram of bark: young bark with periderm and epidermis (*above*) and older bark with a rhytidome (*below*) (Pereira 2012a)

on the adsorption process and mechanism, will allow a bark screening for higher adsorption efficiency and thereby contribute to bark valorization within the bioadsorption platform.

The aim of the present paper is to survey the past research in this matter and make a state-of-the-art review on metal sorption by different bark species, taking in background their anatomical structure chemistry.

Bark

Structure

Bark includes all the tissues outside the vascular cambium and constitutes the external region of tree stems and branches (Fig. 2). Bark is structurally heterogeneous and includes the phloem (with inner functional region for conduction and an outer non-functional region), the periderm (with phelloderm, phellogen and phellem) and the rhytidome. Bark may also be divided into inner bark (including the conducting phloem) and outer bark (non-conducting phloem, periderm and rhytidome).

Two meristems play the major role in bark formation: the vascular cambium that forms the phloem, and the phellogen that produces the phellem (cork) and the phelloderm, together building up the periderm.

The periderm is most often short-lived in most tree species. With aging, the rhytidome is formed including various superposed periderms and phloem tissues between them. However, in a few species such as the cork oak (*Quercus suber*), only one periderm is active throughout

Fig. 3 Bark of *Q. cerris* with a thick rhytidome (*above*) and bark of *Q. suber* with only one periderm (*below*)

the life of the tree and no rhytidome is formed (Pereira 2007). Figure 3 shows an example of a bark with a thick rhytidome (from *Quercus cerris*) and a bark with only one periderm (from *Q. suber*).

The bark thickness is closely related to tree species. It increases with age, and it is also variable along the tree trunk. In general, bark thickness increases with increasing stem diameter, but climatic and nutritional conditions and silvicultural practices may alter the final bark thickness.

Phloem percentage also depends on tree species and on growth conditions. In some species, the phloem is very thin and only comprises a few millimeters, but in other species, its thickness is at cm scale. Only a small part of the phloem is physiologically functional for conduction in trees.

The cells forming the structure of phloem are sieve elements, axial and radial parenchyma, fibers, sclereids and secretory cells. Sieve elements function for water and organic material transfer, while axial parenchyma cells function for organic material storage and radial parenchyma cells for transport and storage. Fibers and sclereids are sclerenchyma cells that function as a mechanical support. The phloem is usually more complex in hardwoods (broad-leaved trees) than in softwoods (needle-leaved trees) in

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Table 1 Range of chemical composition of barks, wood and leaves (Pereira 2012b)

	Barks (%)	Wood (%)	Leaves (%)
Ash	2–15	>1	2–7
Extractives	5–30	1–10	15–50
Lignin	20–30	20–35	10–15
Cellulose	20–40	40–60	15–35
Hemicelluloses	20–30	15–30	10–15
Suberin/cutin	2–45	–	1–4

Table 2 Chemical compositions of barks from a hardwood (*Betula pendula*) and a softwood (*P. sylvestris*) barks (Miranda et al. 2012, 2013)

	Betula pendula (%)	*Pinus sylvestris* (%)
Ash	2.9	4.6
Extractives	17.6	18.8
Lignin	27.9	33.7
Holocellulose	49.8	37.6
Suberin	5.9	1.6

terms of cell arrangement and cell components. The proportions of cell types also differ between bark species.

Chemical composition

The chemical composition of bark differs from other biomass resources (Table 1). Bark is considerably more heterogeneous than wood with regard to proportion of the main components as well as their composition. Chemical differences also exist between hardwood and softwood barks as exemplified in Table 2 for birch and pine barks (Miranda et al. 2012, 2013).

In general, bark contains high amounts of inorganic material that is determined as ash. The most common elements in the inorganic fraction are calcium, magnesium and potassium, in this order.

The non-structural components that may be solubilized by appropriate solvents, the so-called extractives, appear also in large amounts in different bark species and usually show a considerable diversity in terms of chemical families and molecules. The extractives of bark include in general 3–5 times more hydrophilic compounds than lipophilic compounds (Harkin and Rowe 1971).

The presence of suberin as a structural component of the phellem cells is another important chemical feature of bark. Suberin is a macromolecule with structural functions in the cell wall that is chemically characterized by an interesterified polymer of glycerol to long-chain carboxylic hydroxy acids and diacids. Suberin is a main component of the cork cell wall, e.g., about 40 % of *Q. suber* cork,

varying between 23 and 54 % (Pereira 2007, 2013). Suberin is not found in woods, and in the barks, it is included only in the phellem. Therefore, the relative amounts of the different anatomical tissues in the bark, namely the proportion of the cork tissue in the periderm and in the rhytidome, will result in differences in the chemical composition of the whole bark. Depending on the species, suberin may represent between 2 and 45 % of the structural chemical components of barks.

Lignin composition seems to be highly variable, but it must be noted that studies on bark lignins are scarce and mainly whole bark was studied. However, bark is heterogeneous and its components may have different lignin compositions. For instance, the cork lignins from *Q. suber*, *Q. cerris* and *B. pendula* barks have a composition similar to those of softwood lignins (Marques et al. 2005, Marques and Pereira 2013).

Cellulose content of bark is lower than that of wood, while hemicelluloses content is nearly equal (Table 1). The major hemicelluloses in softwood and hardwood barks are galactoglucomannans and arabino-4-*O*-methyl-glucuronoxylan, respectively, and are similar to those found in the corresponding woods (Rowell 2012).

The different bark cells have different wall structures: Parenchyma cells and sieve elements have thin primary cell walls dominated by cellulose; fibers and sclereids have thick cell walls with high proportion of lignin; and cork cells have secondary walls dominated by suberin.

Heavy metals adsorption on bark

Among tree biomass components, bark has shown the highest capacity for heavy metal sorption followed by cones, needles and wood. For instance, Al-Asheh and Duvnjak (1997) found Cd^{2+} uptake rates of 9.2, 7.5 and 7.1 μg/mg for pine bark, cones, and needles, respectively. Shin et al. (2007) compared Cd^{2+} uptakes of juniper wood and bark and concluded that bark had 3–4 times higher adsorption capacity than wood. Boving et al. (2008) studied various agricultural wastes including bark in relation to Cu^{2+} adsorption and concluded that bark was the most effective filtration media from all the adsorbents tested.

Shin (2005) found higher Cd^{2+} adsorption in bark than in wood in *Juniperus monosperma* and explained it by the contribution of calcium oxalate to adsorption as confirmed by X-ray diffraction. Bark contains calcium oxalate monohydrate crystals, while this structure is generally absent in wood (Fig. 4).

Heavy metals adsorption on biomass is defined as a physicochemical process in which three factors seem to play an important role, i.e., adsorption system-related, metal-related and adsorbent-related factors.
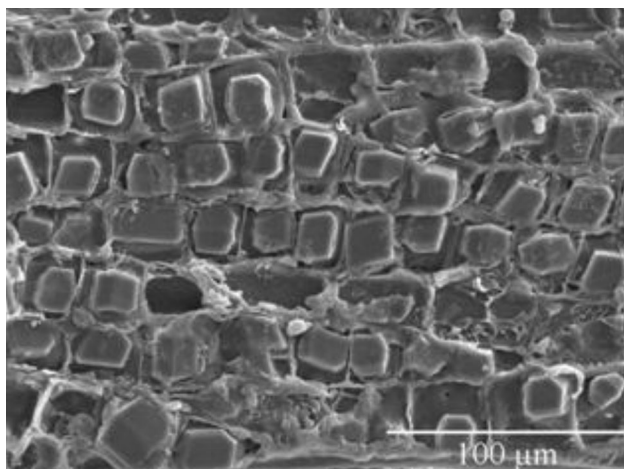
Fig. 4 Calcium oxalate crystals in teak bark

Adsorption system

The pH, temperature and adsorption time are the most important adsorption system parameters.

The pH can influence metal adsorption in three ways. First, the state of active sites can change with pH; at lower pH, the active sites are protonated and a competition starts between metal ions and protons for the active sites. Second, extreme pH values can alter the surface of the adsorbent. Third, the metal speciation in solution is pH dependent, and at higher pH values, metal hydroxide complexes and precipitates can be formed (Naja et al. 2009). Metal adsorption onto bark normally occurs under slightly acidic conditions and within the first minutes of contact time (Martin-Dupont et al. 2002).

Temperature can also alter the adsorption results. With temperature increase, the adsorption of metals increases, although the effect of temperature is small in the 4–25 °C range (Martin-Dupont et al. 2002). Ghodbane et al. (2008) showed that maximum cadmium (II) uptake capacity of *Eucalyptus* bark increased from 14.53 to 16.47 mg/g when the temperature increased from 20 to 50 °C. Higher temperatures can change the structure of the adsorbent, and the adsorption capacity may be reduced (Naja et al. 2009). The effect of structural change was observed in cork granules of *Q. cerris*, and lower adsorption capacity was found for 200–350 °C heat-treated cork granules (Şen et al. 2012).

Metal

Metal-related factors are sorption type, i.e., non-competitive sorption or competitive sorption, polarizability, cation

hydration enthalpy and number of unpaired electrons (Martin-Dupont et al. 2002).

The bigger ions are more polarizable than smaller ions because their electrons are less retained since their distance to the nucleus is larger. These electrons can, consequently, be more easily separated from the atom and bind the adsorption sites onto the bark (Martin-Dupont et al. 2002).

The polarizability does not consider aqueous environments contrary to hydration enthalpy. The more the ion is hydrated, the stronger is the hydration enthalpy and the weaker is the binding to bark. If the hydration energy is smaller, the cation can more easily lose water ligands to bind the adsorbent. According to the study of Martin-Dupont et al. (2002), the highest polarizable intermediate cations ($Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$) had the lower hydration enthalpy ($Ni^{2+} > Cu^{2+} > Zn^{2+} > Pb^{2+}$). Therefore, the theoretical binding affinity or Langmuir b constant is expected to be in the following order: $Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$. Nevertheless, in the study of Martin-Dupont et al. (2002), "b" Langmuir values followed the order $Pb^{2+} \ggg Cr^{3+} > Ni^{2+} > Zn^{2+} > Cu^{2+}$ with the affinity values 4.65, 0.53, 0.44, 0.41 and 0.38, respectively. Cr^{3+}, a hard cation, has the second bigger ionic radius after Pb^{2+}, but it had the biggest hydration enthalpy of all five cations. Hence, the number of unpaired electrons, 3 unpaired electrons in the case of Cr^{3+} and 2 unpaired electrons in the case of Ni^{2+}, play an important role in sorption by increasing their binding ability in spite of their higher hydration enthalpies.

The metal cations in solution may compete with other ions for the adsorption sites. When there is only one metal available, the adsorption is non-competitive, but in treatments of industrial effluents, there are many metals available for the adsorption that may suppress each other (competitive adsorption) (Gloaguen and Morvan 1997). In contrast, Hanzlik et al. (2004) reported that copper and silver were adsorbed better when both existed in solution and total metal uptake was higher than in single metal ion solutions. The synergistic effect was also reported for the simultaneous sorption of Cr(VI) and Cu(II) onto grape stalks (Pujol et al. 2013). Li and Li (2003) reported that spruce bark showed a selectivity order of Cd < Cu < Pb in multielement complex adsorption. Escudero et al. (2013) reported the same selectivity order after studying the adsorption of these metal ions onto grape stalks.

When the hydration energy is smaller, the cation can more easily lose water ligands to bind the adsorbent. Larger ions are more polarizable than smaller ions because part of their electrons is less retained. The more polarizable the metal is, the easier is the adsorption.

The number of unpaired electrons also influences the adsorption. Martin-Dupont et al. (2002) showed that Cr(III)

had a higher affinity to bind to bark than cations with lower hydration enthalpy because of its unpaired electrons.

Adsorbent

Adsorbent-related factors are a consequence of the anatomical and chemical properties of barks. It is important to note that the quantity of the adsorbent also alters the adsorption by changing the adsorption capacity.

The different cell types in bark may be important in adsorption due to their different chemical compositions. The difference between phloem and rhytidome particularly affects adsorption. However, the heterogeneity of bark structure has seldom been taken into account.

Only in one research (Aoyama et al. 2004), the inner and outer barks of *Cryptomeria japonica* were tested separately for heavy metal adsorption and concluded that adsorption capacity was higher in the outer bark (rhytidome) than in the inner bark (phloem): At the same experimental conditions, Cr(VI) uptake values of inner bark and outer bark were 23.0 and 28.4 mg/g, respectively. However, more studies are needed before making a generalization on the adsorption differences between the differentiated parts of bark.

Scanning electron microscopy (SEM) images of *Q. suber* cork before and after Cd(II) and Pb(II) treatments did not show any difference in cork morphology (López-Mesas et al. 2011). The SEM-EDX results of Cr^{6+}-laden cork-enriched rhytidome granules of *Q. cerris* showed that the metal ions were homogeneously adsorbed by different cell types of the rhytidome (Şen et al. 2012).

Rowell (2006) reported that adsorptive sites of the lignocellulosic materials increase only slightly with grinding of the material and concluded that heavy metal sorption by lignocellulosic materials does not depend on particle size. Therefore, the differences in adsorption performance may result mainly from chemical differences in bark cell wall components such as crystal-bearing cells in bark (Shin 2005).

Chemical composition differences between bark and other biomass may play an important role in heavy metal adsorption, particularly the higher inorganic (ash) and extractive contents of bark.

The ash content of barks was often ignored in heavy metal adsorption studies, even if the mineral content may affect ionic interaction between the metal and the bark structure and contribute to ion-exchange mechanism. Escudero et al. (2008a) confirmed that potassium ions release from Yohimbe bark during copper (II) adsorption.

Extractives have often been considered in heavy metal adsorption onto the bark (Martin-Dupont et al. 2006). Extractives have advantages in heavy metal treatments:

Some extractives such as flavonoids (particularly the B ring) can complex with metals in water (Vazquez et al. 2002), while tannins and pectins are considered as active ion-exchange compounds with their carboxylic and phenolic groups providing active sites for metal binding (Gloaguen and Morvan 1997). Netzahuatl-Muñoz et al. (2012) reported the involvement of phenolic groups of lignin and tannins present in *Cupressus lusitanica* bark in the Cr(III) adsorption. This was evidenced by changes observed in the FTIR spectrum, in particular the disappearance of the band associated with OH bending at $1,318\ cm^{-1}$ and the decrease in intensity of the bands corresponding to aromatic rings stretching at $1,517\ cm^{-1}$. On the other hand, extractives may develop coloring problems in water by leaching of compounds such as hydrolyzable tannins that may be toxic to the aquatic life (Aoyama and Tsuda 2001).

To avoid the release of soluble tannins and small molecular weight phenolics from the bark into the water, which would cause coloring and contamination, several treatments were tested. Haussard et al. (2003) treated the bark with microorganisms or with copper or chromium solution, and Oh and Tshabalala (2007) consolidated bark pine into pellets using citric acid as cross-linking agent before removing Cd(II), Cu(II), Zn(II) and Ni(II). Treatment with acidified formaldehyde was also applied, the rationale being the reaction of formaldehyde with the phenolic hydroxyl groups leading to polymerization by cross-linking of formaldehyde with the soluble tannins and other phenolics making up an insoluble phenol–formaldehyde copolymer. Freer et al. (1989) showed that the uranium adsorption capacity of *Pinus radiata* bark improved with acidified formaldehyde treatments. Vazquez et al. (2002) used this acidified formaldehyde treatment to *Pinus pinaster* bark for cadmium and mercury removal, after optimizing the treatment conditions. Sarin and Pant (2006) treated *Eucalyptus globulus* bark for absorption of chromium and found that the phenol–formaldehyde copolymer preserved high capacity of support toward the adsorption of cations.

Treatment of bark with ammonia solutions or amino-containing groups like urea is an alternative of formaldehyde treatments. In these treatments, it is aimed to increase metal adsorption of bark and reduce tannin release to the solution. Khokhotva (2010) treated *Pinus sylvestris* bark with 5 % urea solution and compared the adsorption results with those of untreated bark: Higher adsorption values of Cu(II), Ni(II), Zn(II) and Pb(II) were obtained with urea-treated bark. Three possible reasons suggested by the author for this increased sorption were as follows: dissolution of polyphenols resulting in a better accessibility to the lignin moieties which play a leading role in sorption of

metals; neutralization of strong acid (carboxyl) groups of pine bark that results in the inhibition of cation-exchange processes and avoidance of the acidification of the water treated; formation of nitrogen-containing groups on the bark surface due to the urea interaction with carbonyl and carboxyl groups that contributes to the formation of additional active centers of metal binding.

Freer et al. (1989) showed that the uranium adsorption capacity of *P. radiata* bark improved with acidified formaldehyde treatments. The acid type is important in these treatments, i.e., nitric acid/formaldehyde treatment resulted better than sulfuric acid/formaldehyde treatment (Freer et al. 1989). Martin-Dupont et al. (2004) used peroxide functionalization followed by 4,4′-diamino-2,2′-stilbene disulfonic acid derivatization in the presence of aspartic acid with Douglas fir bark. However, the toxicity of formaldehyde and lower adsorption capacities after the treatment must also be taken into account in such treatments (Palma et al. 2003; Martin-Dupont et al. 2004). Recently, Matsumoto et al. (2013) developed a filter paper mixing cedar bark (70 %) with virgin pulp (7 %) and polyester (15 %) to prevent secondary contamination of water and to achieve the same oxometallic and gold adsorption values as obtained with cedar bark.

Lignin was always regarded as mainly responsible for heavy metal adsorption onto the bark along with tannins and pectins (Martin-Dupont et al. 2006; Rowell 2006; Şen et al. 2012). Some cations show different selectivity to bark components: Cu(II) was bound to phenolic groups of lignins and tannins, while Pb(II) was bound to carboxylic groups in polysaccharides (Martin-Dupont et al. 2006). Şen et al. (2012) indicated that Cr(VI) reacts with polysaccharides of cork as well as with lignin and suberin. A NMR study of cork showed that carbohydrate moieties of cork produced metal complexations (Villaescusa et al. 2002). Heat-modified lignin also reacted with chromium (Şen et al. 2012).

Suberin is also involved in heavy metal adsorption. Psareva et al. (2005) suggested the importance of acidic monomers of suberin in heavy metal adsorption. Şen et al. (2012) analyzed untreated and Cr(VI)-treated *Q. cerris* cork samples with FT-IR spectroscopy and concluded that Cr(VI) was adsorbed onto suberin. A different monomeric composition of suberins may also affect the adsorption: For instance, Şen et al. (2010) showed that *Q. cerris* suberin is formed primarily by ω-hydroxyacids (90 %) and α,ω-diacids (8 %), while *Q. suber* suberin is constituted by ω-hydroxyacids (36 %) and α,ω-diacids (62 %). Further, the location of cork in the bark may affect its adsorption values because of chemical composition differences between outer, center and inner cork layers (Jové et al. 2011).

Surface acidic groups in the barks are considered to play an important role in heavy metal adsorption by ion-exchange mechanism. Chubar et al. (2004a, b) showed that metal cations bind to carboxylic groups in cork. A total acidic group content of 1.64 meq/g (López-Mesas et al. 2011) and 1.88 mmol/g (Olivella et al. 2011) was detected on the cork surface. *Q. cerris* cork had lower total acidic (1.55 mmol/g) but higher strong acidic groups (0.85–0.73 mmol/g) than *Q. suber* cork. Phenolic hydroxyl groups as well as weak acidic groups were also higher in *Q. suber* cork (Olivella et al. 2011). Psareva et al. (2005) treated cork with hydrochloric acid solution and increased uranium adsorption due to increase in strong and weak acidic groups.

The pH at which the adsorbent surface charge is equal to zero is defined as the point of zero charge (pHpzc). The pHpzc gives information on the ionization of functional groups and their interaction with metal species in solution. In solutions with pH higher than pHpzc, the sorbent surface is negatively charged and could interact with positive metal species, while at pH lower than pHpzc, the solid surface is positively charged (Fiol and Villaescusa 2009). Positively charged (pHpzc = 6.8 for *Pausinystalia yohimbe*) or negatively charged (pHpzc = 4.4 for *Q. cerris*, pH_{pzc} = 3.6 for *Q. suber*) bark surfaces were found in interaction with Cu^{2+} or with Cr^{6+} (Fiol and Villaescusa 2009; Şen et al. 2012).

Mechanism, models and determination of adsorption

The ion-exchange or complex formation mechanisms are often used to explain metal binding onto barks (Martin-Dupont et al. 2002; Vazquez et al. 2002; Escudero et al. 2008a; Nurchi et al. 2010). In the ion-exchange mechanism, metal cations exchange with deprotonated groups on the adsorbent surface. Some functional groups of bark, such as hydroxyl and carboxyl groups, loose the associated proton and behave as an acid, while other groups, such as carbonyl, behave as a base because of their electronegative oxygen atom (Brás et al. 2004).

The carboxylic acid group is the main functional group involved in metal adsorption by biomass, followed by the hydroxyl group, aromatic rings and amine group which together make approximately 85 % of the total groups involved in adsorption (Nurchi et al. 2010).

Adsorption isotherms are used to describe the adsorption process of metal ions, to predict adsorption parameters and to compare quantitatively adsorbent performances (Foo and Hameed 2010). Generally, Langmuir or Freundlich adsorption isotherm models are used to calculate metal adsorption as a function of equilibrium concentration of the metal ion in solution without considering pH or the other ions in the system (Naja et al. 2009). However, other models have been proposed to describe adsorption.

The empirical model of Freundlich isotherm can be applied to non-ideal sorption on heterogeneous surfaces as

well as to multilayer sorption. It assumes that the stronger binding sites are occupied first and that binding strength decreases with increasing site occupation. The following equation is used to define the Freundlich isotherm:

$$M_q = KM^{1/n}$$

where the constant K is related to maximum binding capacity and constant n is related to binding strength. The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. It is often criticized for lacking of a fundamental thermodynamic basis since it does not reduce to Henry's law at low concentrations (Ho et al. 2002).

The Langmuir model is probably the best known and the most widely applied sorption isotherm. It is based on the assumption that adsorption is a chemical phenomenon and that the sorption is restricted to a monolayer, all sorption sites are uniform, there is only one adsorbent, one sorbet molecule reacts with one active site, and there is no interaction between the sorbed species (Naja et al. 2009). The Langmuir isotherm is defined by the following equation:

$$q_e = \frac{q_{max} b C_f}{1 + b C_f}$$

where q is the amount of metal adsorbed (mg/g, mmol/g, meq/g), q_{max} is the maximum metal uptake by the adsorbent, b is the Langmuir constant and C_f is the final (equilibrium) concentration of the metal. The b parameter reflects the affinity (the lower the b value, the higher the affinity) of the adsorbent for the metal. The Langmuir model is useful in metal adsorption studies because it gives the q_{max} and b information. Generally, higher q_{max} and lower b values are sought in adsorbents. Also, the equation shows that at low sorbate concentrations, it effectively reduces to a linear isotherm and thus follows Henry's law. Alternatively, at high sorbate concentrations, it predicts a constant monolayer sorption capacity.

Sips isotherm is a combination of the Langmuir and Freundlich models and is expected to describe heterogeneous surfaces much better. At low sorbate concentrations, it reduces to a Freundlich isotherm, while at high sorbate concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The model can be written as follows:

$$q_e = \frac{q_m a_s C_e^{1/n}}{1 + a_s C_e^{1/n}}$$

where q_m is the monolayer adsorption capacity (mg/g) and a_s is the Sips constant related to energy of adsorption (Foo and Hameed 2010).

The Redlich–Peterson isotherm also incorporates features of both Langmuir and Freundlich equations. It may be used to represent adsorption equilibria over a wide concentration range. It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$$

where K_R (l/g) and a_R (l/mg) are Redlich–Peterson isotherm constants and β lies between 0 and 1.

At low concentrations, this equation approximates to a linear isotherm, and at high concentrations, its behavior approaches that of the Freundlich isotherm and of the Langmuir isotherm when $\beta = 1$. However, the equation cannot be linearized for easy estimation of isotherm parameters because of the three unknown parameters contained in the equation. Therefore, a minimization procedure is performed to maximize the correlation coefficient R^2 between the theoretical data for q_e predicted from the linearized equation and the experimental data.

The Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation (Aharoni and Ungarish 1977). It is applied in the following form:

$$q_e = \frac{RT}{b} \ln(K_T C_e)$$

where K_T is the equilibrium binding constant (l/g), b is related to heat of adsorption (J/mol), R is the gas constant ($8.314 \times 10 - 3$ kJ/K mol) and T is the absolute temperature (K).

The Dubinin–Radushkevich isotherm assumes that the characteristic sorption curve is related to the porous structure of the sorbent. The equation applied is given as follows:

$$q_e = q_D \exp\left(-B_D \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]\right)^2$$

where q_D is the Dubinin–Radushkevich isotherm constant (mmol/g); q_e is the solid-phase metal ion concentration at equilibrium (mmol/g); R is the universal gas constant [8.314 J/(mol K)]; T is the absolute temperature (K); the Dubinin–Radushkevich isotherm constant (β_D) is related to the mean free energy of sorption (E, kJ/mol) of the sorbate, and the related energy can be computed using the following relationship.

$$E = 1 \div \sqrt{2B_D}$$

In most sorption studies reported in the literature, the authors use some of the available isotherm models and calculate the isotherm parameters using different regression methods. In general, different function errors

are used to decide on the model which best fits the experimental data, i.e., by comparison of R^2 (linear regression) or sum square residuals (SSR) (nonlinear regression) or others. Recently, Poch and Villaescusa (2012) compared the results obtained using different function errors and demonstrated that the orthogonal distance regression (ODR) method gives the most accurate estimates of the Langmuir isotherm parameters among the different methods when the experimental data have an error.

The metal uptake by bark may be determined with batch adsorption essays or using packed columns (Miralles et al. 2008; Escudero et al. 2008b, 2013). Batch experiments are generally conducted in laboratory conditions, and upflow or downflow packed bed tests are used to predict industrial utilization possibilities of the adsorbents. In batch experiments, the metal adsorption is determined by introducing the metal solutions onto bark and calculating the difference between initial and final metal concentrations of the filtrates. The column experiments generally give higher adsorption results than the batch tests (Palma et al. 2003).

Flame atomic absorption spectroscopy (FAAS) is generally applied for the determination of metal concentration, but inductively coupled plasma atomic emission spectroscopy (ICP-AES) and different spectrophotometric methods are also commonly used. Fourier transform infrared spectroscopy (FT-IR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), nuclear magnetic resonance spectroscopy (NMR), electron spin resonance spectroscopy (ESR) or potentiometric titration methods are applied to determine the active sites of the adsorbent (Park et al. 2010; Nurchi et al. 2010). Metal localizations and their bindings on the adsorbent surface are evaluated with scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDX), X-ray absorption spectroscopy (XAS) or X-ray photoelectron spectroscopy (XPS) (Nurchi et al. 2010).

Overview of adsorption studies

Barks and metals tested

Although heavy metal adsorption studies have been conducted as early as the 1920s, new biosorbents including bark were tested only after the 1970s. It is noteworthy that bark adsorption tests with bark as adsorbent gained importance between 1970 and 1980 (Fig. 5). One of the oldest publications on bark adsorption was the study of Masri et al. (1974). In that study, Douglas fir and black oak barks were treated with mercury solutions and the
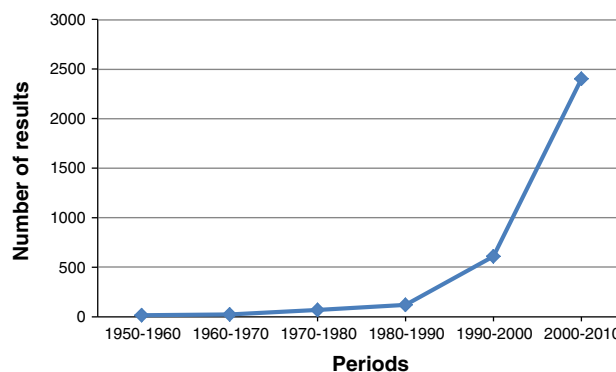
Fig. 5 Number of search results using *bark*, *adsorption* and *heavy metal* keywords on bark adsorption with heavy metals based on Google Scholar Data
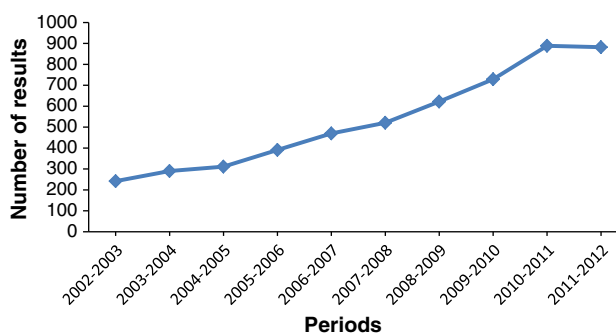
Fig. 6 Number of search results (2 years of averages) using *bark*, *adsorption* and *heavy* metal keywords on bark adsorption with heavy metals in the last 10 years based on Google Scholar Data

adsorption quantities were 100 mg Hg/g for Douglas fir bark and 400 mg Hg/g for black oak bark.

From that period on, research publications increased substantially, especially between the periods 1990–2000 and 2000–2010. The large number of research publications in the last 10 years is indicative of the interest in bark valorization and on the use of biosorbents for water treatments (Figs. 5, 6).

Google Trends analysis in 2011 and Google Insights for Search between years 2004 and 2012 showed that bark was studied mostly in USA, Canada, Australia and UK, while adsorption was searched in South Korea, India, Malaysia and Thailand. The keyword heavy metal was searched mostly in India, USA, Canada and Brazil. Nurchi and Villaescusa (2008) reported increasing interest on the use of agricultural biomass in the emerging countries of India, Brazil, Turkey, Argentina and Nigeria. These results are indicative of current problems (e.g., bark in large timber-producing countries such as the USA) and of the industrialization process (metal effluents in India).

Table 3 Research on softwood barks as biosorbents: metal cations and corresponding q_{max} (mmol/g) values

Species	Metal cations, q_{max} (mmol/g)									References
	Cd^{2+}	Cr^{3+}	Cr^{6+}	Cu^{2+}	Fe^{2+}	Hg^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	
Abies sachalinensis	0.06			0.07					0.05	Seki et al. (1997)
Chamaecyparis obtusa	0.10			0.08					0.09	Seki et al. (1997)
Cryptomeria japonica			1.38							Aoyama et al. (2004)
Juniperus monosperma	0.09									Shin et al. (2007)
Larix gmelinii var. *japonica*	0.09			0.10					0.08	Seki et al. (1997)
Larix leptolepis			0.30							Aoyama and Tsuda (2001)
	0.08			0.08					0.07	Seki et al. (1997)
Picea abies		0.07		0.12			0.09	0.16	0.10	Martin-Dupont et al. (2006)
	0.14			0.15					0.12	Seki et al. (1997)
Picea glehnii	0.11			0.12					0.11	Seki et al. (1997)
Picea jeozensis	0.11			0.11					0.11	Seki et al. (1997)
Pinus brutia								0.37		Gundogdu et al. (2009).
Pinus densiflora	0.09			0.07					0.07	Seki et al. (1997)
Pinus pinaster	0.07	0.37						0.02		Kumar (2006)
Pinus ponderosa	0.45			0.89			0.46		0.81	Oh and Tshabalala (2007)
Pinus radiata						0.47				Palma et al. (2003)
Pinus strobus	0.08			0.09					0.06	Seki et al. (1997)
		0.03		0.04			0.03	0.05	0.03	Martin-Dupont et al. (2006)
Pinus thunberghii	0.06			0.10					0.08	Seki et al. (1997)
Pseudotsuga menziesii						0.50				Masri et al. (1974)
		0.03		0.06			0.06	0.06	0.06	Martin-Dupont et al. (2006)
Sciadopitys verticillata	0.09			0.12					0.10	Seki et al. (1997)
Sequoia sempervirens						1.25				Kumar (2006)
Taxus cuspidata	0.13			0.12					0.12	Seki et al. (1997)
Thujopsis dolabrata var. *hondae*	0.12			0.09					0.09	Seki et al. (1997)

In the last four decades, more than 60 research studies were reported on the biosorption of heavy metals with barks. More than 40 bark species were tested (mainly softwood barks), and over 10 heavy metals were studied (Tables 3, 4). The adsorption tests were conducted mainly using locally available low-cost tree barks.

Copper and cadmium are the most studied metals, followed by zinc and chromium. Lead and nickel were also studied to some extent. Nurchi and Villaescusa (2008) reported that these six metals account for 90 % of the adsorption studies with agricultural biomass. Studies with iron and mercury are rare, and there is only one study with uranium and vanadium.

Critical evaluation aspects

Several authors have tested barks of different species for heavy metal adsorption. However, most of them ignored bark origin, structure and chemistry which might be important aspects regarding adsorption performance.

Some authors neglected using scientific names of the bark species they tested, and in some cases, dubious common names were used such as black oak, redwood or eucalypt bark. This is a drawback for comparing adsorption performances of different bark species for specific metals.

The heterogeneity of the bark structure was also often ignored in the heavy metal adsorption tests. In most cases, whole samples (phloem and rhytidome milled together) were used in the batch adsorption tests.

The metal solutions were usually prepared in the laboratory, but industrial effluents were also tested. For instance, Sarin and Pant (2006) studied chromium adsorption with *E. globulus* bark from an industrial effluent. They obtained higher adsorption efficiency with the industrial effluent than with a pure solution: Freundlich K_f and n values of Cr(VI) adsorption were 21.7–6.7 mg/g and

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Table 4 Research on hardwood barks as biosorbents: metal cations and corresponding q_{max} (mmol/g) values

Species	Metal cations, q_{max} (mmol/g)									References
	Cd^{2+}	Cr^{3+}	Cr^{6+}	Cu^{2+}	Fe^{2+}	Hg^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	
Afzelia africana			0.19	0.40	0.16		0.16	0.2		Gloaguen and Morvan (1997)
Castanea sativa		0.08		0.24			0.06	0.16	0.10	Martin-Dupont et al. (2006)
Harwickia binata	0.30									Kumar (2006)
Eucalyptus (*globulus*)	0.13									Ghodbane et al. (2008)
Pausinystalia yohimbe				0.15			0.15			Villaescusa et al. (2000)
			0.82							Fiol et al. (2003)
Quercus cerris cork			0.41							Sen et al. (2012)
Quercus pedunculata		0.05		0.09			0.06	0.08	0.06	Martin-Dupont et al. (2006)
Quercus suber cork				0.05			0.07			Villaescusa et al. (2000)
			0.32							Fiol et al. (2003)
			0.32				0.17		0.38	Chubar et al. (2004a)
Quercus (*velutina*)						2				Masri et al. (1974)
Tectona grandis			0.26	0.49	0.24		0.19	0.22		Gloaguen and Morvan (1997)

Scientific names in parentheses indicate probable species; in the corresponding references, the species was not mentioned

9.8–4.6 for industrial effluent and pure solution, respectively.

Chemical composition of the barks used for adsorption was generally not studied although bark species with higher lignin or tannin contents were usually used. Martin-Dupont et al. (2006) studied the chemical composition of the barks to analyze Cu^{2+} and Pb^{2+} interactions with bark-active groups.

In metal removing studies with bark, important parameters seem to be metal uptake values, maximum uptake and metal uptake affinity of the adsorbent. The metal uptake values varied between 50 and 99 % (Gaballah and Kilbertus 1998). These values can be altered by changing the sorption parameters and therefore are not adsorbent specific. Metal adsorption models are therefore used to describe the adsorption process. Langmuir parameters of maximum uptake (q_{max}) and metal uptake affinity (b) have often been used although some authors also used the Freundlich model. Other types of models were not encountered to describe bark sorption.

The values of q_{max} and b are related to the adsorbents. In barks, the highest q_{max} values were usually obtained with mercury (400 mg/g), followed by chromium (71.9 mg/g). However, the mg/g unit may mislead the real effectiveness of the adsorbents because it does not consider the atomic mass of the metals (Nurchi and Villaescusa 2012). Therefore, q_{max} values with different barks were compared using mmol/g units (Table 3, 4).

Bark had equal or even more metal uptake capacity than activated carbon (Seki et al. 1997; Aoyama and Tsuda 2001). For instance, Cd^{2+} removal values were for *Abies sachalinensis* 6.7 mg/g, *Taxus cuspidata* 14.4 mg/g, activated carbon (granular) 7.3 mg/g and activated carbon (powder) 7.1 mg/g (Table 3). Likewise, Cu^{2+} adsorption of activated carbon varied between 5.8 and 6.5 mg/g, while Zn^{2+} adsorption was 5.7 and 2.5 mg/g for granular and powder forms, respectively. Higher values were attained with different bark species (Table 3).

Among the low-cost biosorbents, lignin, chitosan and cotton have shown higher metal uptake capacities than bark. The uptake values were 1,587 mg Pb/g lignin, 796 mg Pb/g chitosan, 1,123 mg Hg/g chitosan and 1,000 mg Hg/g cross-linked polyethylenimine (CPEI) cotton (Bailey et al. 1999).

Different bark granulometries ranging from 150 μm (Gundogdu et al. 2009) to 4 mm (Jauberty et al. 2011; López-Mesas et al. 2011) were used in batch adsorption tests. For the batch tests, usually smaller granulometries were used, but in column tests, larger particles were preferred to prevent clogging of the column (Jauberty et al. 2011). The adsorption was higher with smaller particles because of the higher surface area, but the adsorption might also have been favored by the mineral content of smaller particles. Miranda et al. (2012, 2013) reported that smaller bark particles have higher mineral contents than bigger particles in pine, eucalypt, birch and spruce barks.

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Conclusion and prospects

There has been an increasing interest over the last decades in using barks and other biomasses for heavy metals removal treatments. Overall, bark shows a high adsorption capacity of metals, often comparable to that of activated carbon.

Copper and cadmium were the most studied metals, followed by zinc and chromium. Barks of *Pinus ponderosa*, *C. japonica* and *Quercus velutina* showed the highest potential in the removal of copper, chromium and mercury, respectively.

Special attention should be given to the heterogeneity of bark, and the adsorption assays should better explore this structural complexity and its associated chemical composition. There is also a need for mechanistic studies that include nature of binding sites, coordination chemistry, oxidation states and the speciation of metals.

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