

METAL ION SORPTION TO BIRCH AND SPRUCE WOOD

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Sorption of metal ions from aqueous solutions to birch wood and spruce heartwood and sapwood has been studied. Functional groups in wood were determined by acid-base titrations. The sorption of metal ions to wood of the different tree species was investigated by a column chromatographic technique. The mechanism of sorption is mainly ion exchange by complexation of metal ions to the functional groups, e.g. carboxyl groups and phenolic hydroxyl groups, in the wood phase. By combination of the sorption experiments with four different metal ion mixtures, the following affinity order was established for spruce sapwood particles: $\text{Fe}^{3+} \gg \text{Pb}^{2+} \gg \text{Cu}^{2+} \gg \text{Fe}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+} \geq \text{Ca}^{2+} \geq \text{Sr}^{2+} \geq \text{Ba}^{2+} \gg \text{Mg}^{2+} \gg \text{K}^+ > \text{Na}^+ \approx \text{Li}^+$. For all three types of stemwood studied, the affinity orders were almost the same. The ion exchange properties of wood were comparable to those of a weakly acid cation exchanger. The affinity order obtained for the synthetic resin was quite similar to the order given above for wood. The metal sorption properties of wood materials imply that they could be a potential material for removal of metal ions from aqueous solutions.

Keywords: Wood; Sawdust; Metal ions; Affinity; Sorption; Functional groups; Protonation constants

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INTRODUCTION

A main part of terrestrial biomass consists of wood. Thus, wood sawdust is available in large amounts, is inexpensive, and possesses interesting sorption properties for metal ions. The ash content in wood is a measure of the inorganic components. For spruce and birch wood from Finland, the ash content is in the range of 0.3 to 0.4% (Saarela 2009). The concentrations of main metal ions in wood such as Ca, Mg, and K are in the range of 100 to 1000 ppm (Ivaska and Harju 1999; Saarela 2009). Most toxic trace metal ions in wood occur in concentrations below 1 ppm.

Wood and pulp contain functional groups, mainly carboxylic and phenol groups. These groups possess cation exchange properties, and the metal ions found in the wood are mainly bound to the functional groups. The ion exchange reactions of metal ions on wood take place by complexation and association to these functional groups in the pulp phase (Karhu et al. 2002). The affinity series determined for pulps show that metal ions are bound to pulps with different strength (Södö et al. 2007; Su et al 2010a,b). The stoichiometric ratio of the ion exchange reaction between divalent and monovalent cations has been determined to be ca 1:2 by Karhu (2002). This ratio has been verified in

our later work (Su et al. 2010b). Ion exchange selectivity coefficients for pairs of cations to pulps have been determined by some groups (Ohlsson 1975; Karhu 2002; Rudie 2006).

Knowledge of the metal ion binding properties to wood materials is of great importance both from industrial and environmental points of view (Gupta et al. 1970; Colodette et al. 1988; Ajmal et al. 1998; Bulut and Baysal 2006; Argun et al. 2007). Metal ions play an important role in many pulping and papermaking processes. The main problems connected with metal ions in these processes are scaling, boiler plugging, and decreased bleaching efficiency (Hartler and Liebert 1972; Dence and Reeve 1996; DeMartini and Verill 2005; Felissa et al. 2007). In addition, the impacts of metal ions in future biorefineries will be even more important (George et al. 2006). Metal ions can also create problems in pulping processes that use recycled papers as raw materials. Removal of toxic metal ions from wastewaters by using low-cost adsorbents by adsorption methods has also received more attention. A comprehensive review article has recently been published on the removal of metal ions from aqueous solutions for a large number of biosorbents (Hubbe et al. 2011).

In our work, a column chromatographic method was used to study the sorption affinity of different metal ions to wood particles. This method is an optimal tool to establish the affinity order of different metal ions to natural materials (Södo et al. 2007; Su et al. 2010a,b). A similar column method has earlier been applied to study the removal of heavy metals from aqueous solutions by using sawdust (Marin and Ayele 2003).

A comparison between the ion-exchange properties of wood, which is a natural material, with a synthetic weakly acidic cation exchanger will be made. Both materials contain carboxyl groups as the main acidic sites.

EXPERIMENTAL

Wood Samples

Two straight and healthy Norway spruce (*Picea abies*, 47-years old) and birch (*Betula pendula*, 25-years old) trees were cut in southwestern Finland. Discs were cut from the stem at approximately 2 m height above the ground. The discs were de-barked and chipped manually using a knife. Sapwood and heartwood of Norway spruce were studied separately. The chips were air-dried overnight and ground in a MF 10 Basic laboratory mill (IKA-WERKE, GMBH & Co. KG) equipped with a 1-mm screen. These wood particles were extracted in a Soxhlet apparatus with acetone:water (9:1, V/V). The extracted wood particles were then air-dried overnight to evaporate the solvent and stored in a freezer until further use. The water contents of the samples were determined in separate experiments by drying the samples in an oven at 105°C for ca. 24 hours. All results are given on oven dry (o.d.) wood basis.

Chemicals

All metal salts and the acetone used in this work were of analytical grade from Merck. The nitric acid (65%) was from Mallinckrodt Baker B.V. The commercial buffer solutions for pH calibration were citrate with pH 4.00, phosphate 7.00, and boric acid 10.00 (FF-chemical Oy). Divalent iron stock solution (0.1 M) was prepared by dissolving

FeSO₄·7H₂O in water. Stock solutions (0.1 M) of the other metal ions used for sorption experiments were prepared from their nitrate salts. Deionized water was used throughout this work (>18.2 MΩ·cm, Purelab Ultra MK2, Elga).

The sorption properties of wood materials are compared to those of a weakly acid cation exchanger, Amberlite IRC 76 (Rohm and Haas, Sigma). The resin is a cross-linked styrene-divinylbenzene copolymer with functional carboxylic groups. The particle size of the resin is within the range 16 to 50 mesh.

Instrumental Methods

Potentiometric acid-base titrations were carried out with an automatic titrator (Mettler Toledo DL 50). Concentrations of the metal ions in samples were determined by the inductively coupled plasma optical emission spectrometry (ICP-OES) technique with a Perkin Elmer Optima 5300 DV instrument. A Denver Instrument pH meter (model 15) was used for measurement of pH in the solutions.

Potentiometric Acid-Base Titration

The metal ions originally present in the wood samples were removed by washing, first with 0.01 M nitric acid solution, and then with deionized water. The sample preparation procedure has been described in more detail in our earlier papers (Su et al. 2010a,b).

Accurately weighed samples (ca. 1.5 g) were dispersed in 150 mL of a 0.1 M KNO₃ solution and kept under nitrogen atmosphere. 1.5 mL of a nitric acid solution (1 M HNO₃ + 0.1 M KNO₃) was added in order to protonate the acid groups in the wood samples. The potentiometric titrations were carried out up to pH ca. 12.5 at 25°C. After each addition of 0.1 M KOH solution, the pH value was allowed to stabilize before a new addition was made. The titration time was 10 to 14 hours, depending on the type of wood samples studied. A blank solution without wood sample was also titrated to visualize the shifts of the titration curves when the wood suspensions were titrated.

Sorption Experiments

Study of the rate of ion the exchange reactions

The kinetics of metal ion sorption to wood particles was studied with a batch technique. For this purpose, the wood samples were washed and protonated in nitric acid solution (0.01 M) for about 2 h. The suspension was then filtered and washed with deionized water. The pretreated samples were precisely weighed (ca. 4.3 g) and dispersed in 100 mL of deionized water. The initial pH of the suspension was measured. A mixture of metal ions including Pb²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Ni²⁺, Mn²⁺, Ba²⁺, Sr²⁺, Ca²⁺, Mg²⁺, Rb⁺, K⁺, Na⁺, and Li⁺ (5 mL of a 0.005 M solution with respect to each metal ion) was added to the suspensions. The pH values were recorded as the function of time.

In the study of the rate of desorption reactions, the washed sample was first treated with the above mixture of metal ions and kept overnight to reach equilibrium. The suspension was then filtered and washed with deionized water. The same amount of sample as used for the sorption experiments was dispersed in 100 mL of deionized water. 1 mL of 0.05 M nitric acid was added to the suspension, and the pH was measured as a function of time. It should be pointed out that the equivalent amount of metal ions and the

diluted nitric acid added in the experiments was less than the total capacity of acid groups of the samples.

Column chromatographic method

The affinity order of different metal ions to the wood materials was determined by a column chromatographic method. The length of the glass tube was 79 cm, and the inner diameter was 22 mm. For the sorption experiments, the suspension of wood particles was first poured into the glass column and was allowed to settle down to generate the chromatographic column (*Step 1*). The packed column was washed first with 0.01 M HNO₃ and then with deionized water (*Step 2*). The functional groups, e.g. carboxyl and phenolic hydroxyl groups, in the wood samples were also protonated in this step. In the sorption step (*Step 3*), a solution (500 mL) containing an excess of the studied metal ions, compared to the total capacity of wood, was poured through the column. Four different metal ion mixtures (Table 2) were used for loading. The pH values of the mixtures were 4.9, 4.5, 2.7, and 4.0, respectively. The concentration of each metal ion in the mixtures was 0.005 M. The metal ions that were not sorbed were washed out with deionized water. The sorbed metal ions were then eluted with a 0.005 M HNO₃ solution (*Step 4*). The eluent was collected in ca. 5 mL fractions (exactly weighed).

The concentrations of the metal ions in these fractions were determined by the ICP-OES technique. The pH of each fraction was also measured. The packed wood particles in the column were reused for four sorption experiments, and steps 2 to 4 were then repeated. The procedure of the chromatographic experiments has been described in more detail in our earlier papers (Södö et al. 2007; Su et. al. 2010a,b). The amount of wood particles packed in the glass column was ca. 18 g. The length of packed part in the column was 34 cm for birch and 53 cm for spruce wood due to different densities and swelling of the materials.

RESULTS AND DISCUSSION

Determination of Functional Groups in Wood

The data from the potentiometric acid-base titrations were treated with FITEQL software (Herbelin and Westall 1999) for characterization of the acid-base properties of the sawdust samples. The FITEQL software has been described in our previous works (Su et. al. 2010a,b). A model with four types of acid groups gave the best goodness of fit to the experimental potentiometric titration data. Table 1 shows the concentrations of the different acid groups and their protonation constants calculated with the FITEQL program.

It can be seen from Table 1 that the respective protonation constants were similar in the three wood samples studied. Two of them, R₁H⁺ and R₂H⁺, corresponded to carboxyl groups, with lgK values of ca. 4.0 and 5.7, respectively. R₁H⁺ probably can be assigned to the glucuronic acids in xylan, and R₂H⁺ probably corresponds to the galacturonic acids in pectin. The concentrations of the R₁H⁺ and R₂H⁺ acid groups were almost equal in the different wood samples. The total concentrations of the carboxylic acids were in the range of 73.9 to 79.6 µeq/g.

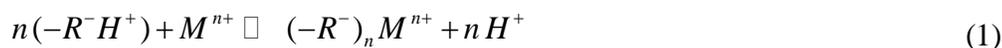
The third group probably can be assigned as a phenolic hydroxyl moiety with a lgK value of ca. 7.9. The weakest acid group ($R_4^-H^+$) was very likely a phenolic hydroxyl group in lignin. The lgK values of this group were slightly different in the birch, spruce sapwood, and spruce heartwood samples. The concentration of $R_3^-H^+$ and especially of $R_4^-H^+$ were higher in birch wood than in spruce wood. It can also be seen in Table 1 that the total concentration of acid groups in birch was higher than in spruce. The spruce heartwood contained slightly more acid groups than the spruce sapwood.

Table 1. Protonation Constants (lg K) and Concentrations ($\mu\text{eq/g}$) of Acid Groups in Three Different Types of Wood

	Birch		Spruce sapwood		Spruce heartwood	
	lg K	Concentration $\mu\text{eq/g}$	lg K	Concentration $\mu\text{eq/g}$	lg K	Concentration $\mu\text{eq/g}$
$R_1^-H^+$	4.0	56.9	3.9	55.8	4.0	59.8
$R_2^-H^+$	5.7	18.8	5.7	18.1	5.7	19.8
$R_3^-H^+$	7.9	18.8	7.9	14.9	7.9	16.9
$R_4^-H^+$	10.2	81.2	10.0	44.9	10.1	49.9
Total		176		134		146

Study of Equilibration Time

The sorption and desorption reaction of metal ions with wood can be expressed by the following general equation (1),



where $-R^-$ denotes the anionic groups in the wood and M^{n+} the metal ions in the sorption experiments. When metal ions are sorbed to the wood particles by ion-exchange, the hydrogen ions are released from the solid phase to the aqueous phase. The reaction (1) is shifted to the right, and the pH value of the suspension decreases (Fig. 1a).

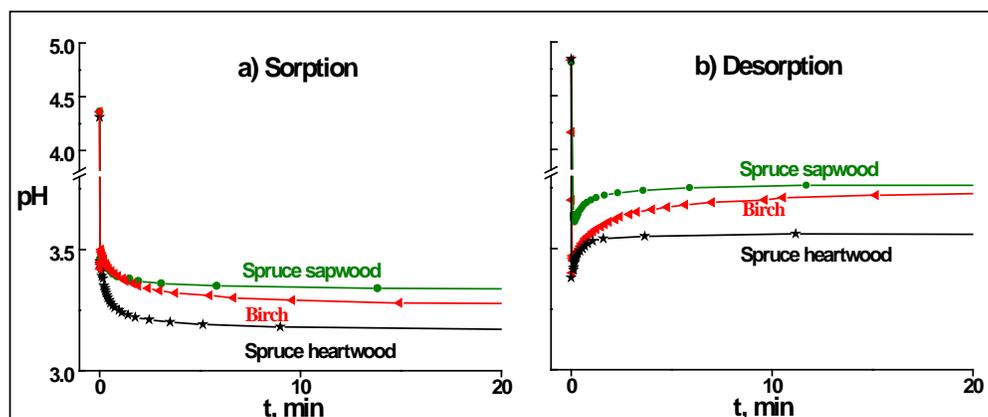


Fig. 1. Equilibrium time for a) sorption and b) desorption of metal ions to wood particles

During desorption, the bound metal ions are replaced by hydrogen ions, and the concentration of free hydrogen ions in the aqueous solution decreases. Reaction (1) shifts to the left and the pH value of the suspension increases (Fig. 1b).

The sorption/desorption reaction times of metal ions to the three types of wood particles are shown in Fig. 1. The pH of the sample suspension is plotted as a function of time during the sorption respective desorption experiment. It can be seen from the figure that equilibrium was reached within ca. 20 min for wood particles of both birch and spruce. This is a satisfactory reaction rate for the column chromatographic experiments.

Column Chromatographic Experiments

Sorption of Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Rb^+ , K^+ , Na^+ , and Li^+

The elution (desorption) curves obtained with mixture 1 (Table 2) are given in Fig. 2. The pH profile of the eluate and the concentration of respective metal ions in each fraction are shown in Fig. 2. As can be seen in the figure, the pH of the eluate started to decrease simultaneously when the metal ions were eluted, and it finally decreased to the pH of the eluent (0.005 M HNO_3), when all metal ions had come out from the column.

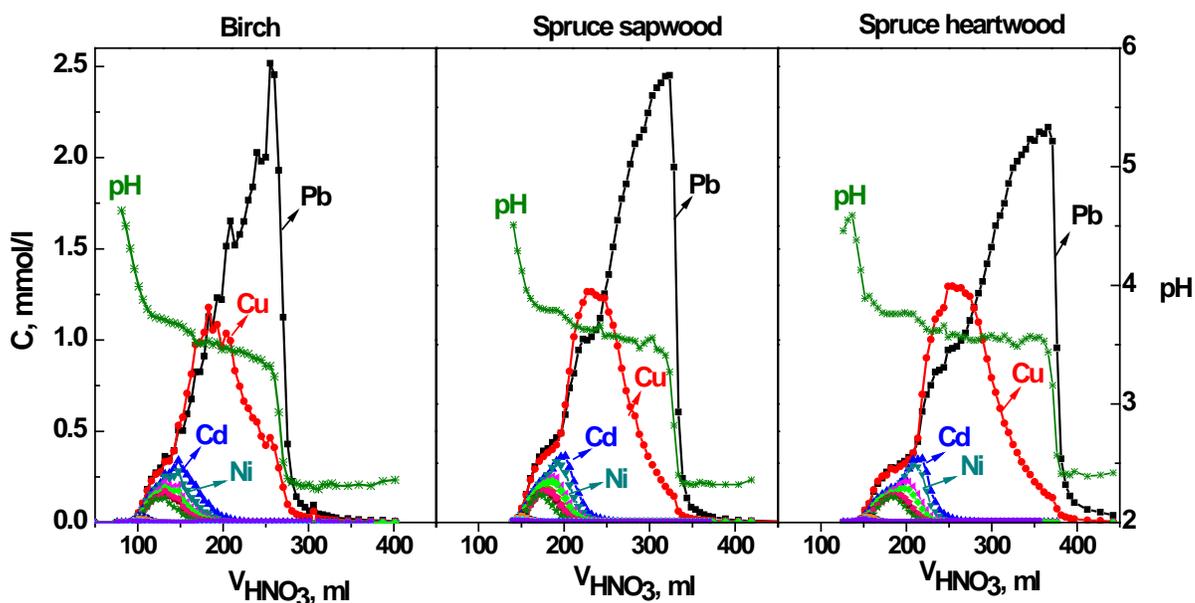


Fig. 2. Concentrations of metal ions and pH in the collected fractions as function of the elution volume (Mixture 1, Table 2)

The sorption of lead and copper ions clearly differed from that of the other metal ions present in the mixture. For all the three types of wood particles, lead had the highest sorption capacity and was the last element to be eluted from the column. This means that the binding strength between functional groups and lead was strongest of all the metal ions in the mixture studied. Copper ions were also strongly bound to the wood particles. For other metal ions in mixture 1, the differences in the binding strength were relatively

small, and their elution curves overlapped each other with the scale of the y-axis used in the figure.

The concentrations of alkali metal ions in the eluted fractions were below the detection limits of the analytical method used, indicating that they were only very weakly sorbed in this experiment. In order to obtain a better resolution of the sorption strengths of the other metal ions, the next sorption experiment (mixture 2) was performed without lead and copper ions.

Sorption of Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Rb^+ , K^+ , Na^+ , and Li^+

The elution curves obtained with mixture 2 (Table 2) are shown in Fig. 3. For these mixtures, a clear difference in the binding strength of the metal ions in the mixture (Cd^{2+} , Zn^{2+} , and Ni^{2+} etc.) can be observed. The functional groups in wood exhibited a higher binding affinity to cadmium compared to zinc and nickel. In this experiment Mn^{2+} , Sr^{2+} , and Ca^{2+} were bound to wood particles with about equal strength. The alkali metal ions were very weakly bound and were eluted first out from the column.

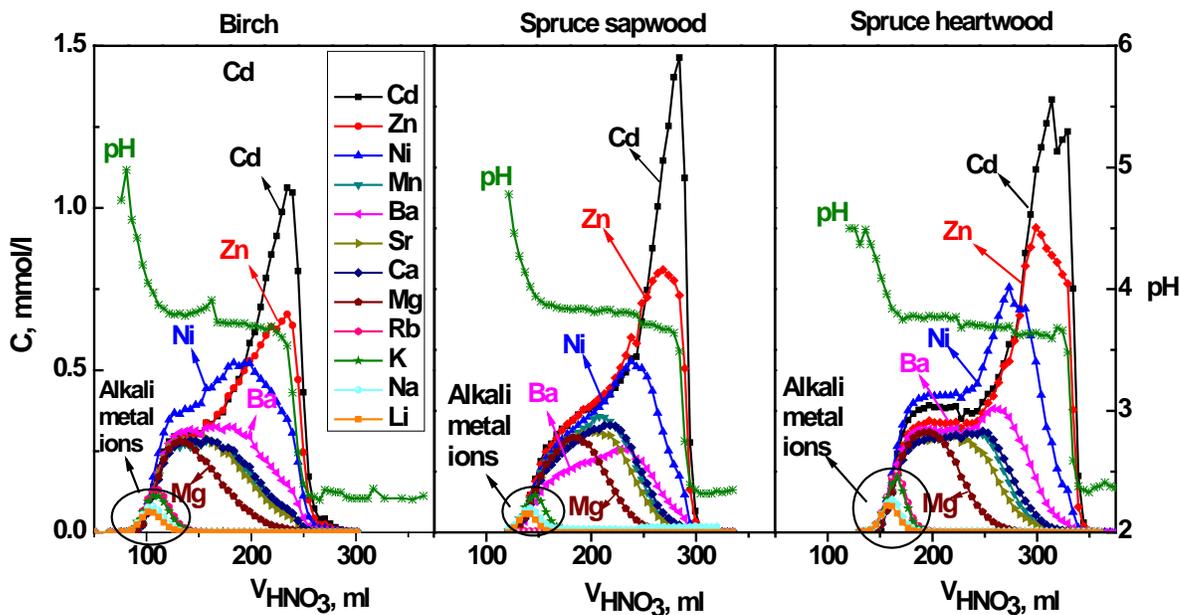


Fig. 3. Concentrations of metal ions and pH in the collected fractions as function of the elution volume (Mixture 2, Table 2)

Sorption of Fe^{3+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Rb^+ , K^+ , Na^+ , and Li^+

Trivalent iron was included in the mixture of metal ions (mixture 3, Table 2) to study its sorption behavior (Fig. 4). Fe^{3+} was very strongly sorbed to wood particles and therefore strongly decreased the sorption of the other metal ions present in the mixture. The elution profile of Fe^{3+} differed clearly from the elution curves for the other metal ions. Elution of Fe^{3+} started before the other metal ions and showed strong tailing at the end of the chromatogram. This may be due to formation of trivalent iron hydroxide and

other precipitates on the wood particles. They were difficult to remove even when a large volume of nitric acid (0.005 M) was used. For spruce heartwood, two peaks were observed on the elution curves for iron, and the minimum of the two peaks occurred at the same elution volume as the peak maximum of lead.

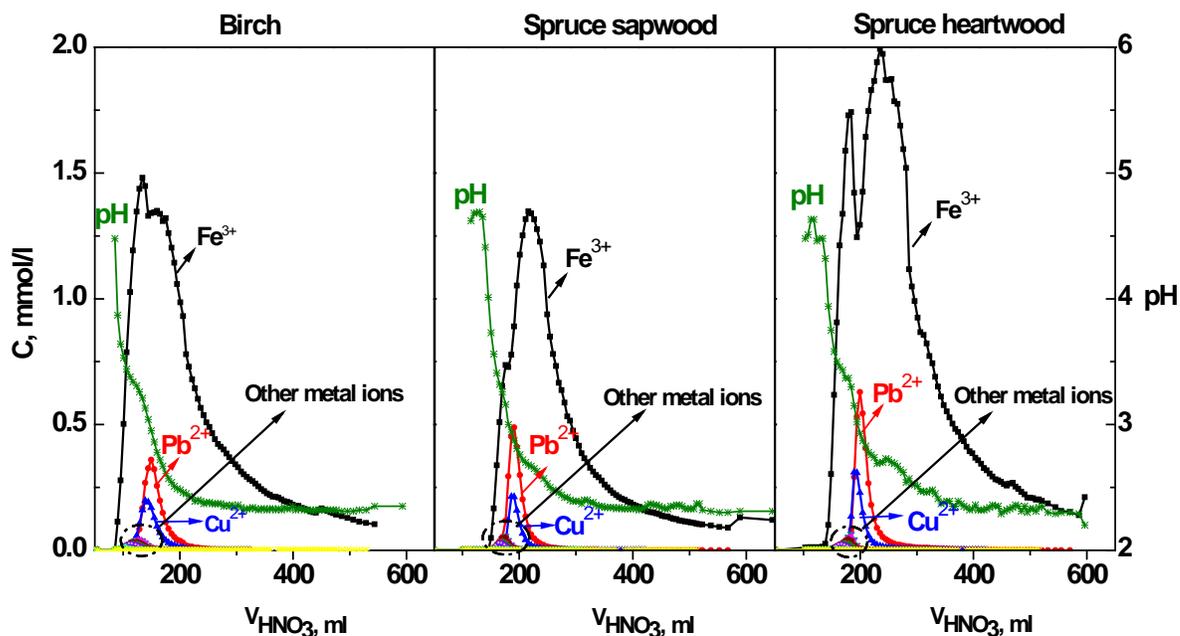


Fig. 4. Concentrations of metal ions and pH in the collected fractions as function of the elution volume (Mixture 3, Table 2)

Sorption of Fe^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Rb^{+} , K^{+} , Na^{+} , and Li^{+}

In this experiment, divalent iron was used instead of trivalent iron (Mixture 4, Table 2). Only spruce sapwood was studied. The elution curves obtained are shown in Fig. 5. It can be seen that the binding strength of Fe^{2+} was much lower than those of Pb^{2+} and Cu^{2+} . For the desorption of Fe^{2+} , a tailing was also observed, and still after elution with 700 mL of nitric acid, all iron was not completely removed from the column. Part of the divalent iron was probably oxidized to trivalent iron during the sorption experiment, which will result in precipitation of trivalent iron salts on the wood particles (Södö et al. 2007). The quantitative data for the sorption of metal ions in all the experiments are summarized in Table 2.

Comparison of metal ion sorption to different wood types

The binding affinity of metal ions to wood particles depends on the functional groups in wood phase and also on the operating conditions, e.g. pH and concentrations of other metal ions present in the two-phase system. Table 2 summarizes the contributions (in percentage) of each metal ion to the operating capacities obtained in different experiments for the studied wood samples.

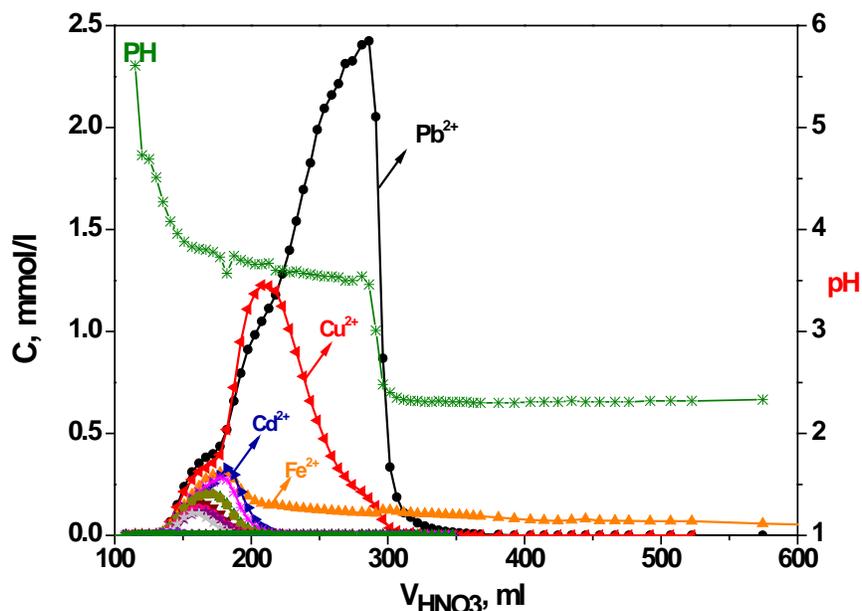


Fig. 5. Concentrations of metal ions and pH in the collected fractions as function of the elution volume with spruce sapwood (Mix. 4, Table 2)

The operating capacities of wood particles are expressed as the sum of the concentration of each metal ion in all the eluted fractions, given in $\mu\text{eq/g}$. The operation capacities of wood obtained in different sorption experiments are also listed in Table 2. From this table, the concentration (expressed as $\mu\text{eq/g}$) of each metal ion sorbed to wood particles in the different experiments can be calculated. For example, in experiments with mixture 2, twelve metal ions were studied. Cadmium ions dominated the sorption and contributed to 22 to 25% of the total sorption of metal ions. The concentrations of cadmium sorbed to birch, spruce sapwood, and heartwood were 8.5, 9.9, and 12.0 $\mu\text{eq/g}$, respectively. Zinc was sorbed at 18 to 21% (7.0, 8.2, and 9.8 $\mu\text{eq/g}$, respectively), nickel at 14 to 17% (6.5, 5.7, and 8.6 $\mu\text{eq/g}$, respectively), and barium at 8 to 11% (4.1, 3.0, and 5.0 $\mu\text{eq/g}$, respectively).

Among the metal ions studied, trivalent iron shows the highest adsorption capacity to wood particles (mixture 3, Table 2). The presence of Fe^{3+} strongly decreased the sorption of other metal ions, implying that Fe^{3+} occupies most functional sites in wood. When Fe^{3+} is excluded from the metal ion mixture (mixture 1), more than 50% of functional groups are bound by Pb^{2+} , and more than 25% by Cu^{2+} . These two metal ions in turn decreased the sorption of other metal ions present in mixture 2 (Table 2). For instance, the binding percentage of Cd^{2+} on birch decreased from ca. 22% to ca. 5% and zinc decreased from ca. 18% to ca. 4% (mixture 1 and mixture 2, Table 2). It can be seen that the operating capacity obtained with mixture 1 was higher than that obtained with mixture 2, where the metal ions with stronger binding strength, e.g. Pb^{2+} and Cu^{2+} , were excluded. We found that the operating capacities of wood particles changed only slightly after several sorption-desorption cycles; thus the wood particles can be reused after

regeneration and can be regarded as a potential material for removing metal ions from wastewater.

Table 2. Sorption Percentage (%) of Each Metal Ion in Sorption Experiments

$$\text{Sorption percentage} = \frac{\text{Concentration of each metal ion sorbed to sample } (\mu\text{eq/g})}{\text{Total concentration of metal ions sorbed to sample } (\mu\text{eq/g})} \times 100\%$$

Metal ions	Birch			Spruce sapwood				Spruce heartwood		
	Mix.1	Mix.2	Mix.3	Mix.1	Mix.2	Mix.3	Mix.4	Mix.1	Mix.2	Mix.3
Fe ³⁺	×	×	91.5	×	×	91.6	×	×	×	95.0
Fe ²⁺	×	×	×	×	×	×	6.5	×	×	×
Pb ²⁺	51.0	×	3.9	54.5	×	4.6	25.1	53.6	×	5.4
Cu ²⁺	27.5	×	2.1	26.9	×	1.7	11.2	28.9	×	2.3
Cd ²⁺	4.8	22.3	0.4	4.1	25.0	0.4	1.6	3.8	24.3	0.4
Zn ²⁺	3.6	18.2	0.4	3.4	20.8	0.3	1.4	3.3	19.8	0.3
Ni ²⁺	2.8	17.1	0.3	2.5	14.3	0.3	1.0	2.4	17.4	0.3
Mn ²⁺	2.1	8.1	0.2	1.7	8.9	0.2	0.6	1.6	7.7	0.2
Ba ²⁺	2.5	10.8	0.3	2.3	7.5	0.3	1.0	2.0	10.1	0.3
Sr ²⁺	2.0	7.9	0.2	1.5	7.9	0.2	0.6	1.4	6.7	0.2
Ca ²⁺	1.9	8.4	0.2	1.6	8.7	0.2	0.5	1.4	7.7	0.2
Mg ²⁺	1.4	5.6	0.2	1.2	5.8	0.2	0.4	1.1	4.7	0.2
Rb ⁺	0.1	0.6	BDL	BDL	×	BDL	×	0.1	0.5	BDL
K ⁺	0.1	0.5	BDL	BDL	0.4	BDL	BDL	0.1	0.5	BDL
Na ⁺	0.1	0.3	BDL	BDL	0.3	BDL	BDL	0.1	0.3	BDL
Li ⁺	0.1	0.2	BDL	BDL	0.2	BDL	BDL	0.2	0.2	BDL
Operating capacity (μeq/g)	42.9	38.3	40.6	48.4	39.6	35.6	44.6	53.1	49.4	60.0

-BDL= Below detection limit

-X = Metal ion is not included in the mixture

-Mixture 1 (Mix 1): Pb²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Ni²⁺, Mn²⁺, Ba²⁺, Sr²⁺, Ca²⁺, Mg²⁺, Rb⁺, K⁺, Na⁺, and Li⁺

-Mixture 2 (Mix. 2): Cd²⁺, Zn²⁺, Ni²⁺, Mn²⁺, Ba²⁺, Sr²⁺, Ca²⁺, Mg²⁺, Rb⁺, K⁺, Na⁺, and Li⁺

-Mixture 3 (Mix. 3): Fe³⁺, Pb²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Ni²⁺, Mn²⁺, Ba²⁺, Sr²⁺, Ca²⁺, Mg²⁺, Rb⁺, K⁺, Na⁺, and Li⁺

-Mixture 4 (Mix. 4): Fe²⁺, Pb²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Ni²⁺, Mn²⁺, Ba²⁺, Sr²⁺, Ca²⁺, Mg²⁺, Rb⁺, K⁺, Na⁺, and Li⁺

The affinity order of metal ion binding to wood particles can be established from Table 2. By combination of several sorption experiments, the following orders were obtained:

For birch wood: Fe³⁺ >> Pb²⁺ >> Cu²⁺ >> Cd²⁺ > Zn²⁺ > Ni²⁺ > Ba²⁺ > Mn²⁺ ≥ Ca²⁺ ≥ Sr²⁺ > Mg²⁺ >> Rb⁺ ≥ K⁺ ≥ Na⁺ ≈ Li⁺.

For spruce sapwood: Fe³⁺ >> Pb²⁺ >> Cu²⁺ >> Fe²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ > Mn²⁺ ≥ Ca²⁺ ≥ Sr²⁺ ≥ Ba²⁺ >> Mg²⁺ >> K⁺ > Na⁺ ≈ Li⁺.

For spruce heartwood: Fe³⁺ >> Pb²⁺ >> Cu²⁺ >> Cd²⁺ > Zn²⁺ > Ni²⁺ > Ba²⁺ > Ca²⁺ ≈ Mn²⁺ ≥ Sr²⁺ > Mg²⁺ >> Rb⁺ ≥ K⁺ ≥ Na⁺ ≈ Li⁺.

Transition metal ions were more strongly bound to wood, compared to the groups of alkaline earth metal ions and alkali metal ions.

Sorption of Metal Ions by a Weakly Acidic Cation Exchanger

In this section, the sorption properties of a synthetic weakly acidic cation exchanger (Amberlite IRC 76) are studied and compared with those of wood. This synthetic resin contains, as well as wood, carboxyl groups as potential sites of adsorption. Due to this higher capacity of the weakly acidic cation exchanger, a much smaller column (30 cm length, 7 mm width) could be used. The sorption/desorption experiments were done according to a similar procedure as for wood particles using three different metal ion mixtures for loading of the resin.

The sorption of alkaline earth metal ions to the weakly acidic cation exchanger is shown in Fig. 6. The affinity order $Ba > Sr > Ca > Mg$ obtained for the synthetic resin is quite similar to that obtained for the wood samples, only the order of Sr and Ca is exchanged. For the synthetic resin the elution curves for the alkaline earth metal ions were more separated, and the equivalents of respective metal ions bound were distinctly different. In total 1.0 meq of metal ions were bound per g of resin in this experiment, which was clearly below the total capacity of ca. 11 meq/g, and the pH of the metal ion loading solution was 5.2.

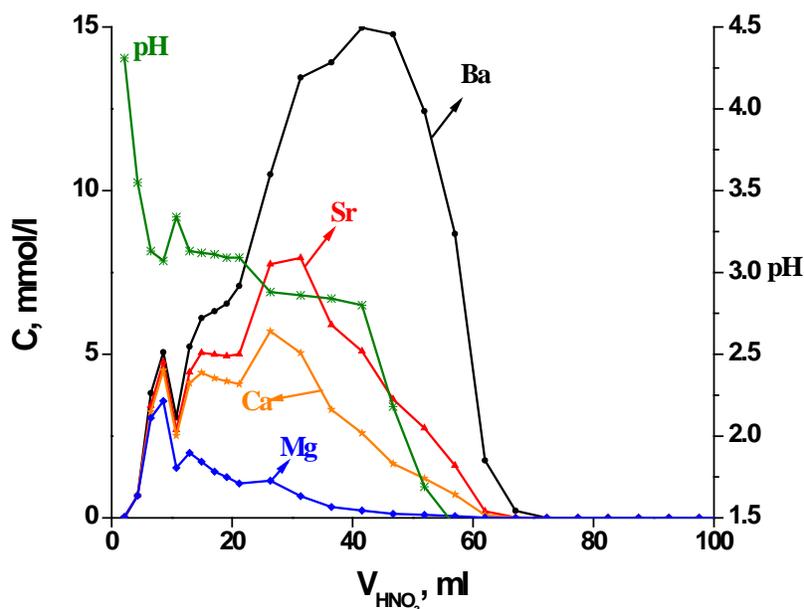


Fig. 6. Concentrations of alkaline earth metal ions and pH in the collected fractions as function of the elution volume with weakly acidic cation exchanger

Figure 7 presents the elution curves for a metal ion mixture containing Pb, Cu, Cd, Zn, Ni, Mn, Ba, Sr, Ca, Mg, Rb, K, Na, and Li ions. Pb, Cu, and Cd were clearly the most strongly bound to the weakly acidic cation exchanger. In total 2.7 meq/g of metal ions were bound to the resin, or ca. 25 % of the total capacity. 1.9 meq/g of lead ions were bound. The pH of the loading solution in this experiment was clearly below the log

K_{HA} value (5.3 to 6.1) (Dorfner 1991) of the carboxyl groups. This means that less than 1% of the carboxyl groups were dissociated at pH = 3.2, which was the pH of the loading solution in this sorption experiment.

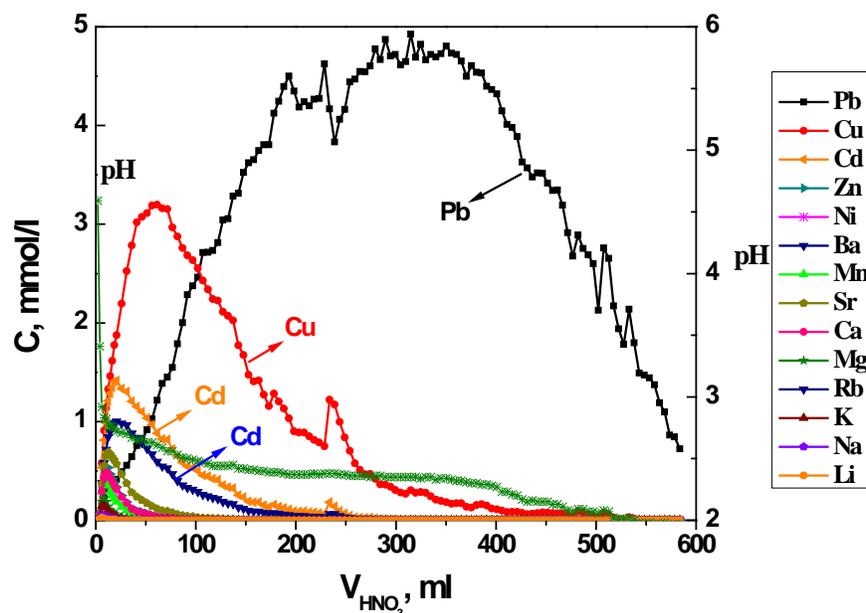


Fig. 7. Concentrations of metal ions and pH in the collected fractions as function of the elution volume with weakly acidic cation exchanger

The elution curves obtained for the three different metal ion mixtures with the synthetic resin show both similarities and differences compared to the sorption data obtained for the wood samples in this work. By combining the results from experiments with three different metal ion mixtures, the following affinity order can be obtained for sorption of metal ions to the weakly acidic cation exchanger:



By comparing the above order with the affinity series determined for wood samples in the present work, it can be seen that the alkaline earth metal ions Ba, Sr, and Ca were bound more strongly than Ni and Zn to the synthetic resin.

The differences in affinities for the two types of materials are probably best explained by their different content of different types of functional groups. The synthetic resin contains only carboxyl groups. The wood materials also have phenolic groups (Table 1), which probably increases the relative affinity to transition metal ions Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , and Ni^{2+} , compared to alkaline earth metal ions. Also, the large difference in concentration of functional groups (total capacity) can affect the sorption properties.

The total cation capacity of the synthetic resin is ca. 11 meq/g, or much higher than that of spruce wood (ca 0.15 meq/g). For spruce bark an almost 10 times higher total

capacity of 1.0 meq/g has been determined (Su et al. 2012). The operating capacities for spruce bark in sorption experiments performed in the pH range 2.7 to 4.9 were at maximum 0.40 meq/g. Brown algae (*Pilayella littoralis*) are a very effective biosorbent, for which the operating cation exchange capacity of 2.24 meq/g has been reported (Lill et al. 2011).

CONCLUSIONS

1. In the column chromatographic experiments, the metal ions were competitively sorbed to the functional groups in wood. Ion exchange by complexation of metal ions to the solid wood phase is the major binding mechanism in the sorption.
2. There were only small differences in the sorption capacity between the different types of wood particles studied. By combination of the results from the sorption experiments with the four metal ion mixtures, the following affinity sequence was obtained for spruce sapwood: $\text{Fe}^{3+} \gg \text{Pb}^{2+} \gg \text{Cu}^{2+} \gg \text{Fe}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+} \geq \text{Ca}^{2+} \geq \text{Sr}^{2+} \geq \text{Ba}^{2+} \gg \text{Mg}^{2+} \gg \text{K}^+ > \text{Na}^+ \approx \text{Li}^+$. The affinity order is almost the same as for birch and for spruce heartwood.
3. A weakly acid cation exchanger, with carboxyl groups as functional groups, showed somewhat different affinity order for metal ions compared to wood samples.
4. The results from the sorption/desorption experiments showed that the wood particles can be used several times after regeneration with diluted acid. Therefore, the wood particles can be considered as a potential material for removal of metal ions from wastewater.

ACKNOWLEDGMENTS

This work is a part of the activities at Åbo Akademi Process Chemistry Centre within the Finnish Center of Excellence Program (2000-2011) by the Academy of Finland. Financial support from the Research Institute of Åbo Akademi Foundation is also gratefully acknowledged.

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Article submitted: February 13, 2012; Peer review completed: March 16, 2012; Revised version received and accepted: March 22, 2012; Published: March 27, 2012.