The influence of dissolved organic carbon on sorption of heavy metals on urea-treated pine bark

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ABSTRACT

A previous study showed considerably higher metal adsorption by urea-treated pine bark (UTB) compared to non-treated bark (NTB) at metal adsorption from their individual relatively concentrated solutions. Comparison of the sorption characteristics of the two pine barks at low but environmentally relevant metal concentrations, and investigation of the influence of pH and dissolved organic carbon (DOC) on the sorption process are the aims of the present study. Sorption of Cu^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} on pine bark of the species *Pinus sylvestris* was measured in multi-metal solutions in the presence and absence of DOC. In the absence of DOC, UTB gave lower residual metal concentrations (2–7 μg/l for copper, 1–5 μg/l for nickel, <0.05 μg/l for zinc and lead) in the range of initial concentrations up to 0.7 mg/l, compared to NTB (6–15 μg/l for copper, 2–24 μg/l for nickel, 2–9 μg/l for zinc, 2–3 μg/l for lead). In the presence of DOC, sorption of Zn, Ni and Pb decreased by up to 75% depending on the DOC concentration. Metal sorption on UTB is less sensitive to pH and more adsorbed metal ions are retained compared to NTB. The potential use of urea-treated bark for treatment of waste water containing DOC and low concentrations of metals is discussed.

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1. Introduction

Pine bark is a low-cost sorbent widely used to remove heavy metals from waste waters. Its ability to sorb heavy metals from solutions containing individual metal species has been extensively studied and described in the scientific literature [1–4]. In general, these experiments were usually carried out using rather concentrated metal solutions (tens-to-hundreds mg/l) prepared in deionised water. This creates, to some extent, ideal conditions for sorption, which are, in most cases, far removed from those found in real waste waters, since almost no competing processes occur during metal sorption in such experiments. In many cases, the pH was not adjusted during the metal adsorption process, nor was its value measured after sorption. Only the initial pH was known. Furthermore, metal concentrations in the mixtures were commonly of the order of tens-to-hundreds of mg/l [1,5,6], which is suitable for an initial screening of sorption properties, but not for evaluation of sorption at the lower metal concentrations. The approach adopted in this paper is therefore more applied. Sorption of copper, nickel, zinc and lead was measured in low-concentration (below 1 mg/l)

multi-metal solutions, which are more relevant for Scandinavian effluents. For example, landfill leachates in Sweden have very low concentrations of heavy metals—tens of μg/l [7], still there is a demand from the local authorities to further reduce concentrations to meet discharge permits.

The efficiency of metal removal by adsorbents is commonly expressed as the percentage of metal adsorbed. This is a very convenient measure of sorption when the aim is to compare the performance of several adsorbents. However, this parameter does not say anything about actual metal concentrations in solution, resulting from sorption, which is important in the evaluation of the performance of treatment facilities. Instead, in the present paper, we use the residual concentration to assess sorption efficiency, because discharge limits for metals are set by authorities as concentrations (μg/l), as are guideline values and environmentally quality standards developed for the protection of aquatic life in for example Sweden [8], Canada [9] and the Netherlands [10].

In a previous on-site study, pine bark was found to be the most appropriate reactive filter material for treatment of low strength landfill leachate [11] of 4 different filter materials tested. However, metal retention was less than expected from previous laboratory experiments and significant leaching of Cu was observed when the concentration of leachate decreased. One important reason for this was probably the presence of organic material (measured as DOC) because subsequent experiments have shown that the presence of DOC significantly reduces metal adsorption to pine bark [12]. Dissolved organic carbon (DOC) is one of the factors known to signifi-

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Nomenclature

C_0	initial heavy metal concentration (mg/l)
C_e	equilibrium heavy metal concentration (mg/l)
C_{des}	concentration of a heavy metal in the leaching solution (mg/l)
V	volume of the heavy metal solution used in the experiment (l)
V_{des}	volume of deionised water for desorption (l)
m_0	heavy metal content in the initial solution (mg)
m_{des}	amount of heavy metal desorbed from bark (mg)
m_{ads}	amount of metal taken up by bark (mg)
m_{resid}	amount of heavy metal retained by the bark after desorption (mg)

cantly reduce heavy metal removal in waste water treatment plants [13]. According to Vogl and Heumann [14], copper, nickel and zinc in the waste water are largely complexed with humic substances. The distribution coefficient of heavy metals between solid matrix and landfill leachate decreases by a factor of 2–6, due to complex formation, especially for Ni [15]. The same effect of DOC on solubility of heavy metals in freshwater was observed by Vesely et al. [16].

Dissolved organic carbon is also to a large extent responsible for enhanced leaching of already adsorbed metals from sorbents, sediments and soil [17,18] since DOC is poorly adsorbed by solid materials and thus moves with water flow [19]. DOC–metal complexes increase the mobility of heavy metals [15,20] and their availability for uptake by plant roots [21,22]. The reality in Sweden is that metal concentrations in landfill leachate are so low, that the presence of dissolved organics to a large extent prevents efficient sorption of the metals by sorbents (pine bark, blast furnace slag). Adsorbed metals are washed out from the filter material because the stability of metal–FA/HA complexes is usually higher than metal–bark complexes. Variations in inlet metal and DOC concentrations, for example during snow melt, require the application of stable adsorbents that can better retain bound metals [11].

Urea-treated pine bark has been shown to be a good candidate for that, since it has better adsorption potential because of higher adsorption ability and lower desorption ability at high metal concentrations than non-treated pine bark. Functional analysis, as well as kinetic studies and adsorption isotherms of copper, nickel, zinc and lead ions from individual solutions with metal concentrations of 10–300 mg/l in the absence of dissolved organic materials showed faster and stronger sorption of metals on urea-treated pine bark than untreated bark, while metal retention was also several times more effective (unpublished data).

Some authors suggest using membrane [23,24] or sorption [25,26] techniques to remove humic substances together with complexed heavy metals. Publications studying sorption of heavy metals in the presence of DOC by low-cost sorbents are very scarce [27–29]. No investigations have been reported on the sorption of heavy metal–humic acid complexes on cellulose-rich materials.

The aim of the present research is therefore to investigate the sorption efficiency of urea-treated and non-treated pine bark, with respect to the removal of heavy metal ions from low-concentration solutions in the presence of humic acids (HA), as a function of the concentration of HA and the pH during sorption.

2. Materials and methods

2.1. Materials

The pine bark material Zugol® (Zugol AB, Falun, Sweden) from the species *Pinus sylvestris* was used for experiments "as supplied"

without sieving. The particle size distribution provided by the producer is the following: <0.25 mm—7.5%; >0.25 mm < 5.0 mm—76.2%; >5.0 mm—16.3%.

Two gram bark samples were used for treatment and sorption. Bark samples were loaded into 100 ml of the treatment solution – 5% urea solution – at pH 6 or 9. After 2 h of shaking in shaking machine, the pH was checked and adjusted to the desired value using Meterohm 744. This procedure was repeated again after 2 h and then again after 12 h. After 24 h of treatment, bark samples were separated from the solutions by filtration, intensively washed with water and left to dry at 20 °C.

Some bark samples were treated with NaOH solution without the presence of urea to get pH 9 according to the same procedure described above.

Bark samples labelled in the present paper as "non-treated bark" were just shaken with 100 ml of tap water during 24 h without any pH control. They were then filtered off, washed and air-dried.

2.2. Copper, nickel, zinc and lead sorption by pine bark from multi-metal solutions

Sorption of copper, nickel, zinc and lead was investigated in batch experiments to measure, the lowest achievable concentration of the metals in the solution after reaction with the filter material (i.e. the residual concentration). Four mixtures of the metals with equal concentrations of each metal ion in the range 56–670 μg/l, which are environmentally relevant according to [7], were prepared in tap water. Our preliminary experiment has also shown that sorption of one metal is not affected by the presence of others, when they are present in concentrations of a few mg/l and lower.

Sorption experiments were carried out with samples of non-treated pine bark and samples treated with urea solution at pH 6 and 9 and NaOH at pH 9. The initial pH of the solutions was 4 and the solution volume was 100 ml.

After shaking the metal solutions with bark samples for 2 h in shaking machine, liquid was separated from bark by filtering on paper filter (Quantitative filter paper (acid washed), Quality 00R, Munktell Filter AB, Sweden) and the residual concentration of the metal was determined using an atomic absorption spectrophotometer (AAS Vario 6, Analitik Jena) with atomisation in a graphite furnace. Detection limits were assumed to be 10 times larger than the values provided by the manufacturer, in order to ensure the reliability of measured metal concentrations (Cu(II)—0.19 μg/l, Ni—0.3 μg/l, Zn—0.03 μg/l, Pb—0.8 μg/l). Standard calibration solutions were prepared from the commercially available standard stock solution 'Spectrascan' (Technolab A/S). All measured concentrations were within the range of values of the calibration curves.

2.3. Heavy metal sorption by pine bark from multi-metal solutions in the presence of DOC

DOC solution was prepared by mixing 5 g of humic acid sodium salt (Aldrich, technical grade) with 1 l of deionised water. After 5 days of storage at 4 °C the concentrated solution was filtered through a 0.45 μm filter. Measurement of DOC in the stock solution was performed at the Department of Limnology, Evolutionary Biology Centre, Uppsala University, using a Shimadzu TOC-5000 IR-spectrophotometer with ASI-5000a autosampler. The TOC/DOC equivalency was then determined based on TOC measurement of the DOC-analysed stock solution using Dr Lange ISIS 9000 (MDA photometer). The required concentrations of DOC (10, 50, 100, 150 and 200 mg/l) were obtained by diluting the stock solution.

Sorption was measured in multi-metal solutions with concentrations of each metal in the range 0.5–0.8 mg/l. DOC stock solution was added to the metal solution to obtain the required concentration of DOC in the range from 10 to 200 mg/l. The mixtures were then left for 48 h to reach equilibrium for metal complexation with humic acid. The pH was then adjusted to 4.

Urea-treated and non-treated bark samples of the same weight were utilised for sorption experiments. After sorption in 100 ml metal solutions for 2 h, liquid was separated from bark by filtration on paper filter, and the pH of the solutions and the concentrations of the metals were measured immediately with an AAS Vario 6 (Analitik Jena) with flame atomisation. As explained earlier, detection limits were assumed to be 10 times larger than the values provided by the manufacturer (Cu(II)—0.03 mg/l, Ni—0.04 mg/l, Zn—0.014 mg/l, Pb—0.13 mg/l).

2.4. Heavy metal sorption by pine bark from multi-metal solutions in the presence of DOC at different pH values

Heavy metal sorption on non-treated and urea-treated bark samples was measured at a fixed pH in the range 4–9. Bark samples were treated with urea solution as described above. 100 ml of multi-metal solutions with concentrations of each metal in the range 0.5–0.7 mg/l were used in these experiments. The DOC concentration in the solutions for present and subsequent sorption experiments was 50 mg/l. This value was chosen as it represents the average value of 10 landfill leachates studied in Sweden [7]. The experiment was carried out with magnetic stirring, constant pH measurement and manual pH adjustment.

Metal complexation with humic acids was allowed during 48 h in several flasks at the pH values chosen for further sorption. In the case of metal complexation at pH 8 and 9, the metals were in contact with humic acids at pH 7 during the first 24 h to avoid precipitation in the form of hydroxides. The pH was then increased to the desired value. After 2 h of sorption, liquid was separated from bark by paper filtration and the concentration of the metals was measured.

2.5. The influence of bark treatment time on heavy metal sorption by pine bark from multi-metal solutions in the presence of DOC

Another set of experiments on metal sorption by pine bark treated with 5% urea solution at pH 6 was carried out with treatment times of 2, 3 and 5 days. During the first 24 h of bark treatment, the pH was adjusted as described above. Subsequently, the pH of the treatment solution was checked and adjusted if needed every 24 h. Bark samples were then separated from the solutions by filtration, intensively washed and left to air-dry.

Non-treated pine bark samples were treated with tap water for the same time as urea-treated bark without any pH control or adjustment.

Sorption of metals on bark samples treated with urea solution and non-treated bark samples was measured for 2 h in multi-metal solutions with concentrations in the range of 0.5–0.7 mg/l in the presence of 50 mg/l DOC and at a fixed pH of 7.

2.6. Heavy metal desorption from pine bark

Non-treated and urea-treated (treatment time 24 h at pH 6) bark samples after metal sorption during 2 h were used for the experiment. 20 ml of deionised water was added to 2 g of each dry bark sample. Flasks were then placed into a rotating machine for 24 h. Liquid was then filtered from the bark and analysed for copper and nickel content.

2.7. Data treatment

Percentage of metals adsorbed by bark was calculated as:

$$A(\%) = \frac{C_0 - C_e}{C_0} \times 100,$$

where C_0 and C_e are the initial and equilibrium heavy metal concentrations (mg/l).

The percentage of metals desorbed from bark was calculated from:

$$D(\%) = \frac{m_{des}}{m_{ads}} \times 100 = \frac{C_{des} \cdot V_{des}}{(C_0 - C_e) \cdot V} \times 100,$$

where C_{des} is the concentration of a heavy metal in the leaching solution (mg/l), V_{des} is the volume of deionised water for desorption (l), m_{des} is the amount of heavy metal desorbed from bark (mg), V is the volume of the heavy metal solution used in the experiment (l) and m_{ads} is the amount of metal taken up by bark (mg).

Total sorption efficiency, R, can be derived from:

$$R(\%) = \frac{m_{resid}}{m_0} \times 100 = \frac{m_{ads} - m_{des}}{m_0} \times 100$$

$$= \frac{(C_0 - C_e) \cdot V - C_{des} \cdot V_{des}}{C_0 \cdot V} \times 100,$$

where m_{resid} is the amount of heavy metal retained by the bark after desorption (mg) and m_0 is the heavy metal content in the initial solution (mg).

Statistical analysis was performed on some of the data. ANOVA followed by post hoc testing using Tukey's HSD test at $p \leq 0.05$ was carried out on untransformed values. The normality of data was confirmed using graphical techniques and homogeneity of variances was confirmed by the Brown Forsythe test. All statistical analysis was carried out using Statistica 7.1., Statsoft Inc., USA.

2.8. Retrieval of environmental quality standards or guideline values

Guideline values were collected from Canadian [9], Dutch [10] and Swedish [8] legislation to enable comparisons of residual concentrations after sorption and desired environmental concentrations in freshwater ecosystems. The values retrieved are presented in Table 1.

Table 1
Reference values for Cu, Ni, Pb, Zn in µg/l in freshwater.

Metal	SEPA-Class 3[a]	CCME[b]	MPC[d]	NC[e]
Copper (Cu)	3	2[c]	1.5	0.45
Lead (Pb)	1	1[c]	11	0.26
Nickel (Ni)	15	25[c]	5.1	3.3
Zinc (Zn)	20	30	9.4	2.9

[a] Data obtained from [8]. Metal levels as levels in filtered samples after acid-conservation. Classified in 5 classes, Class 3: effects may occur. Concentration shown is lowest value of Class 3.

[b] Data obtained from [9]. Values should protect all forms of aquatic life and all aspects of the aquatic life cycle including the most sensitive life stages of the most sensitive species over long term. Metal levels as total concentration after acid digestion.

[c] Exact values depend on hardness of water. Lowest value presented.

[d] Data obtained from [10]. MPC—Maximum Permissible Concentration. The values can only be exceeded during short term to protect ecosystems. Metal levels as dissolved concentration.

[e] Data obtained from [10]. NC—Negligible Concentration. The values should not be exceeded in the long run to protect ecosystems. Metal levels as dissolved concentration.

Table 2
Initial, residual concentrations and % sorbed of metals after sorption to non-treated pine bark, urea-treated pine bark treated at pH 6 or pH 9 and pine bark treated at pH 9 by alkali solution.

Metal	Treated pine bark	N of multi-metal solution							
		1		2		3		4	
		C_{init}, µg/l	C_{resid}, µg/l (%)	C_{init}, µg/l	C_{resid}, µg/l (%)	C_{init}, µg/l	C_{resid}, µg/l (%)	C_{init}, µg/l	C_{resid}, µg/l (%)
Cu	NTB	76	7 (90)	100	6 (94)	195	6 (97)	670	15 (98)
	UTB6		7 (91)	100	4 (96)	195	5 (97)	670	7 (99)
	UTB 9		4 (95)	100	3 (97)	195	5 (98)	670	4 (99)
	pH 9		3 (95)	100	3 (97)	195	4 (98)	670	4 (99)
Ni	NTB	61	2 (97)	187	2 (99)	331	3 (99)	638	24 (96)
	UTB 6		2 (97)	187	2 (99)	331	1 (99)	638	5 (99)
	UTB 9		2 (97)	187	1 (99)	331	2 (99)	638	4 (99)
	pH 9		2 (97)	187	3 (98)	331	2 (99)	638	8 (99)
Zn	NTB	66	2 (89)	164	5 (97)	310	5 (98)	495	9 (98)
	UTB 6		<0.03* (100)	164	<0.03* (100)	310	<0.03* (100)	495	<0.03* (100)
	UTB 9		<0.03* (100)	164	<0.03* (100)	310	<0.03* (100)	495	<0.03* (100)
	pH 9		<0.03* (100)	164	<0.03* (100)	310	<0.03* (100)	495	<0.03* (100)
Pb	NTB	56	2 (97)	103	3 (97)	249	2 (99)	554	3 (99)
	UTB 6		<0.8* (100)	103	<0.8* (100)	249	<0.8* (100)	554	<0.8* (100)
	UTB 9		<0.8* (100)	103	<0.8* (100)	249	<0.8* (100)	554	<0.8* (100)
	pH 9		<0.8* (100)	103	<0.8* (100)	249	<0.8* (100)	554	<0.8* (100)

Sorption experiments were conducted for 2 h in solutions containing a mixture of Cu, Ni, Pb and Zn at increasing concentrations ranging from 0.056 to 0.67 mg/l.
NTB—Non-treated pine bark; UTB 6, UTB 9—pine bark treated by urea solution at pH 6 and 9 respectively; pH9—pine bark treated at pH 9 by alkali solution.
* Concentration below detection limit of AAS with atomisation in graphite furnace.

3. Results and discussions

3.1. Sorption of heavy metals from multi-metal solutions, not containing DOC

Comparing non-treated and urea-treated pine bark in a previous unpublished study it has been shown that the adsorption processes most closely followed pseudo-second order reaction kinetics and can be adequately described by both Freundlich and Langmuir isotherms. Maximum adsorption capacities were 7.5, 8.3, 5.1 and 67.3 mg/g for Cu(II), Ni(II), Zn(II) and Pb(II) respectively for non-treated bark and 12.1, 11.7, 9.9 and 104.1 mg/g for urea-treated bark.

In this study, the efficiency of heavy metals removal by both non-treated and pre-treated bark from low-concentration metal solutions was 90–100% depending on the initial concentration of metals (Table 2). This can be generally considered as a high removal rate, and the presence of one metal does not influence sorption of others. Pre-treated bark always yielded lower residual concentrations than non-treated bark (Table 2). The removal efficiency of the metals, measured as residual concentration, was also rather stable in the studied range of metal concentrations (Table 2). Treatment by urea solution at pH 6 resulted in slightly lower sorption efficiency compared to treatment at pH 9. Zinc and lead ions were removed almost completely and were not detected after sorption onto treated bark samples. In the case of sorption onto non-treated bark samples, the lowest residual concentration was approximately 2 µg/l for both metals, and it increased gradually with an increase in initial metal concentration. Surprisingly, nickel was removed somewhat better than copper at low initial metal concentrations. Residual concentrations for nickel were 1–2 µg/l in the range of initial concentrations between 50 and 200 µg/l, while for copper the corresponding values were 3–7 µg/l across the whole range of studied concentrations. However, it must be noted that for sorption onto non-treated bark, the residual concentration of nickel increases rapidly as the initial concentration increases.

Sorption on treated pine bark was rather similar at pH 6 and 9. From a practical point of view, treatment of bark by urea solution at the lower pH value is easier to achieve. Thus, bark treated by urea at pH 6 was used for further experiments.

Based on the guideline values presented in Table 1, it is clear that Zn concentrations can be reduced to values below the no ecotoxicological effect values regardless of bark pre-treatment, while Pb and Ni concentrations can be reduced below all environmental effect values at all tested concentrations with urea-treated bark, but not with non-treated bark. Cu concentrations cannot be reduced below any of the guideline values.

3.2. Sorption of heavy metals from multi-metal solutions in the presence of DOC

These experiments were carried out to define the sensitivity of heavy metal sorption on non-treated and urea-treated bark to the presence of different concentrations of DOC.

The experiments showed that increasing concentrations of dissolved organic carbon significantly decrease the sorption of metals on pine bark (Fig. 1). Similar results were obtained by Nehrenheim et al. [12] for non-treated pine bark.

Even though heavy metal sorption was significantly suppressed in the presence of DOC, residual concentrations of all consid-
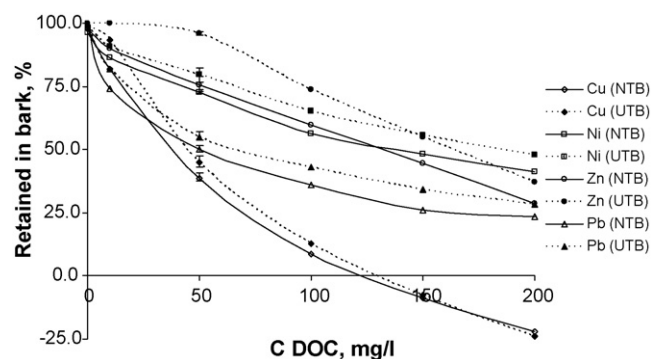
Fig. 1. The influence of DOC on the percentage of adsorbed metals by non-treated pine bark or urea-treated pine bark at different concentrations of DOC. Urea-treated pine bark was produced by incubating pine bark in 5% urea at pH 6.0 for 24 h. Sorption experiment at different concentrations of DOC was conducted in a metal solution containing 0.71 mg/l Cu, 0.71 mg/l Ni, 0.52 mg/l Zn and 0.74 mg/l Pb for 2 h at pH 5.5 (initial pH 4).
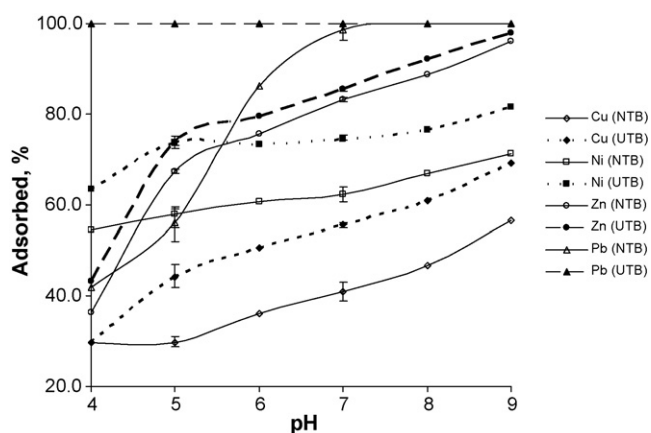
Fig. 2. The influence of sorption pH on the percentage of adsorbed metals by non-treated and urea-treated pine bark. Urea-treated pine bark was produced by incubating pine bark in 5% urea at pH 6.0 for 24 h. Sorption experiment at different pH values was conducted in a metal solution containing 50 mg/l DOC, 0.68 mg/l Cu, 0.56 mg/l Ni, 0.51 mg/l Zn and 0.61 mg/l Pb for 2 h.

ered metals were still lower after sorption on urea-treated pine bark, with values ranging from 10 to 60 μg/l. Larger differences due to bark treatment were observed at lower DOC concentrations.

Among the metals considered, sorption of copper ions was most sensitive to the presence of DOC. The residual concentration of copper increased rapidly with the increase of DOC concentration. Desorption of copper from bark was observed at C_{DOC} > ca. 120 mg/l. The source of copper released into solution was the pine bark itself because it contains small amounts of heavy metals – 6.6 μg/g of Cu(II), 0.84 μg/g of Ni(II), 13.2 μg/g of Zn(II) and 4.6 μg/g of Pb(II) – defined by washing out of the metals from pine bark with 1 M HNO$_3$ followed by measurement using AAS. This is probably due to the strong complexation of Cu^{2+} with humic substances. The same behavior was observed by Nehrenheim et al. [12], although the DOC concentration at which sorption shifted to desorption was lower (ca. 80 mg/l), which may be explained by the smaller metal concentrations used in the latter sorption experiments.

Sorption of zinc onto urea-treated bark was insensitive to the presence of DOC. The uptake of Zn^{2+} was almost 100% in the range of DOC concentrations up to 50 mg/l. Surprisingly, in the presence of DOC, sorption of Ni^{2+} was much higher than Pb^{2+}. The opposite was the case in sorption experiments without DOC.

The initial pH value was 4, but pH of solutions after metal sorption onto pine bark was higher. Measurements of pH drift during sorption showed that pH increased rather quickly, reaching its final value within 0.5 h. The pH increase was higher for sorption onto urea-treated bark than for non-treated pine bark. In fact, in reality almost all sorption processes were carried out at pH ca. 5
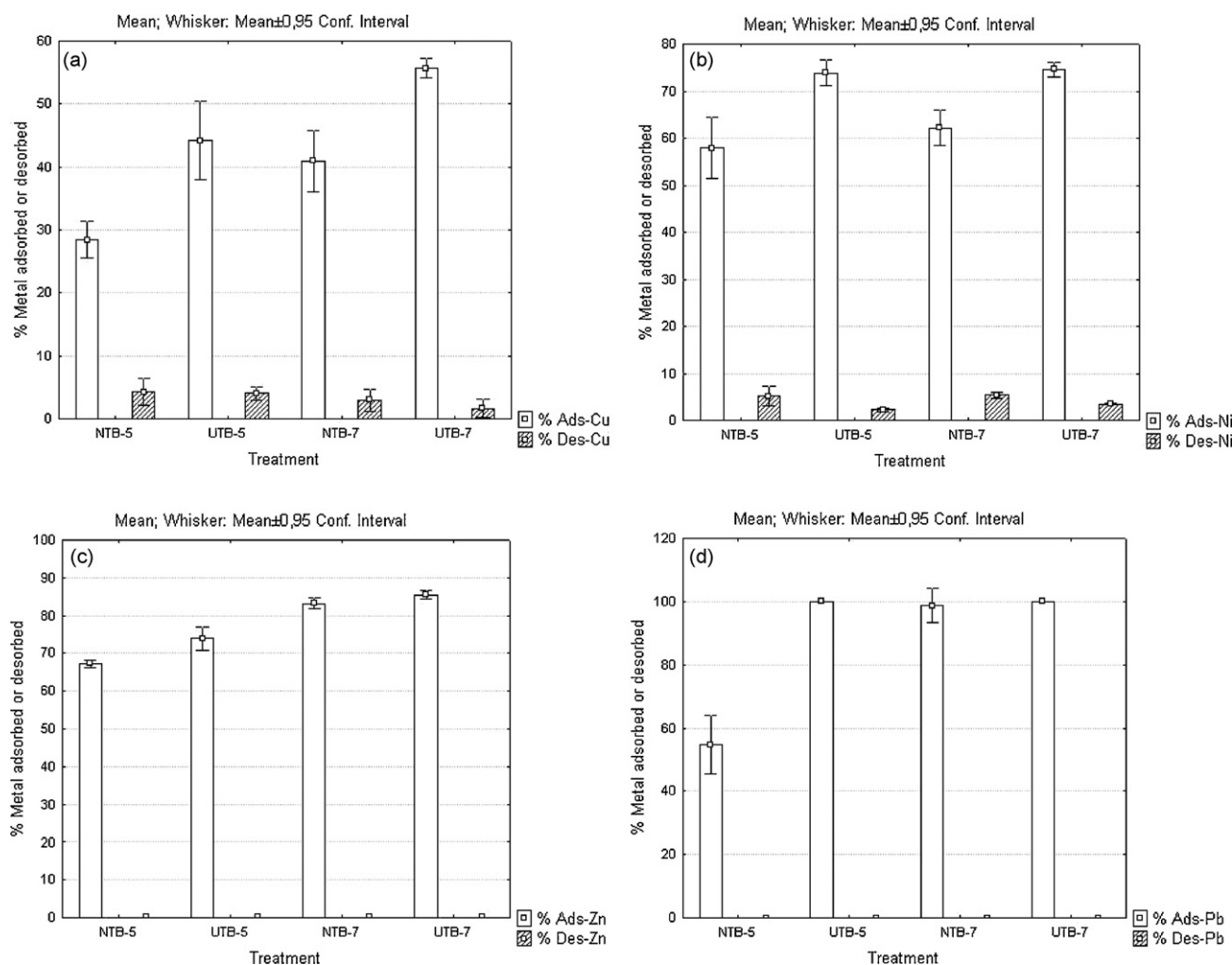

Fig. 3. Percentage metals (a—Cu, b—Ni, c—Zn, d—Pb) adsorbed and desorbed by non-treated and urea-treated pine bark at pH 5 and 7. Mean values with Confidence Interval presented. Adsorption was conducted at pH 5 or 7 with a metal solution containing all 4 metals each at 0.5–0.7 mg/l for 2 h. NTB corresponds to non-treated bark, UTB corresponds to urea-treated bark. The pine bark was treated with 5% urea at pH 6.0 for 24 h prior to adsorption experiment.

for non-treated bark and ca. 5.5 for urea-treated bark. Gaballah and Kilbertus [30] reported that heavy metal sorption is strongly affected by solution pH. Greater reductions of metal concentrations in treated solutions were achieved at higher pH.

3.3. Heavy metal sorption onto pine bark as a function of pH and duration of pre-treatment

Fig. 2 shows the influence of pH on the sorption of copper, nickel, zinc and lead to non-treated and urea-treated pine bark samples in multi-metal solutions in the presence of DOC. Several similar experiments have been performed confirming the general influence of pH on metal adsorption (data not shown). In Fig. 3a–d the percentage adsorbed metals at pH 5 and 7 is presented from a replicated experiment. These pH values were chosen as they are reasonable to get in practical applications.

Compared to non-treated bark, urea-treated bark showed stronger adsorption across the whole range of pH values, except for Pb which showed 100% adsorption in both cases. Sorption of metals increased with an increase of pH. Sorption of nickel was only weakly dependent on pH, while sorption of lead onto urea-treated bark did not depend on pH at all. Urea-treated bark was less sensitive to pH during metal sorption, compared to non-treated bark samples. The residual concentration of zinc decreased very quickly between pH 4 and 5, and thereafter decreased more slowly. The results obtained for Zn confirm observations of Kalbitz and Wennrich [31] who showed that (i) dissolved organic matter (DOM) plays a minor role in mobilising heavy metals at pH < 4.5 because highly protonated DOM is less capable of forming complexes with heavy metals, and (ii) mobilisation of Zn is pH-dependent but not DOM-dependent due to the low stability of its organic complexes.

Only copper displayed some decrease of residual concentration as the time of chemical treatment of pine bark with urea solution increased (Fig. 4). Treatment of pine bark with urea for a relatively short time (1 day) probably produces mild degradation and depolymerisation of polyphenolic compounds of bark, thereby removing relatively easily soluble substances and creating new active centers for metal chelation. However, longer bark treatment may not be so favorable for metal sorption. Deeper bark degradation may produce more water-soluble compounds, which will be released into the treatment solution. Some of these soluble substances contain nitrogen. This means that nitrogen from urea is utilised to solubilise some components of bark and is not retained by bark in a polycondensation reaction. Further work is in progress to elucidate the chemical mechanisms behind the increase sorption potential of urea-treated pine bark.

3.4. Heavy metals desorption

Results are presented in Fig. 3a–d. Desorption was negligible (less than 0.1%) for Pb and Zn and was therefore also independent of pH and the type of bark used. For Cu and Ni, metal desorption
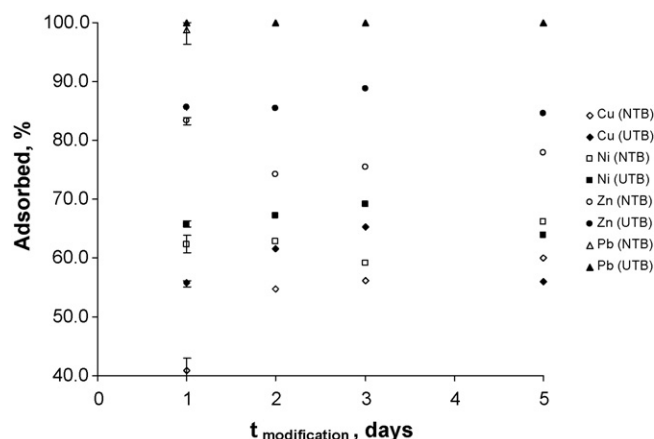

Fig. 4. The influence of treatment time on the percentage of adsorbed metals by non-treated and urea-treated pine bark. Urea-treated pine bark was produced by incubating pine bark in 5% urea at pH 6.0 for 1, 2, 3 or 5 days. Sorption experiments using pine bark with different treatment times was conducted in metal solution containing 50 mg/l DOC, 0.68 mg/l Cu, 0.56 mg/l Ni, 0.51 mg/l Zn and 0.61 mg/l Pb at pH 7 for 2 h. NTB corresponds to non-treated bark, UTB corresponds to urea-treated bark.

was lower for urea-treated bark. The extent of desorption of Cu and Ni was also dependent on pH during sorption (Fig. 3). Preliminary blank experiments revealed no leaching of the metals from both non-treated and urea-treated bark samples.

3.5. Influence of DOC on retention of metals taking adsorption–desorption processes into account

Table 3 shows the total efficiency of heavy metal removal by non-treated and urea-treated pine bark samples from the solutions containing dissolved organic carbon, taking into consideration the efficiency of metal adsorption and the percentage of the metal desorbed in leaching experiments. The results are compared with previous unpublished results obtained in the sorption–desorption experiments from concentrated solutions without DOC (Table 3). It can be seen that, despite only a small improvement in sorption efficiency and a slightly better retention of the metals in desorption tests, the total amount of heavy metals taken up by urea-treated bark is substantially larger than for non-treated pine bark samples. This is particularly important for nickel, which has been shown to be poorly retained in the effluent from a constructed wetland for treatment of landfill leachate [32].

3.6. Comparison with other studies and implications for use in on-site applications

For practical applications, it would of course be advantageous to use non-treated pine bark to reduce the cost of materials. However, a material that has both a high adsorption potential and

Table 3
Total efficiency (%) of metal retention by non-treated and urea-treated pine bark, taking into account adsorption–desorption processes.

pH during sorption		Cu		Ni		Zn		Pb	
		NTB	UTB-6	NTB	UTB-6	NTB	UTB-6	NTB	UTB-6
With DOC[a]	5	27	42	55	72	67	73	55	100
	7	40	55	59	72	83	86	99	100
Without DOC[a]	5	92	93	84	87	78	97	93	100
	7	92	93	89	90	100	100	100	100
Without DOC[b]	6	36	67	7	24	10	28	60	93

[a] Initial concentration of the metals was in the range of 0.5–0.7 mg/l and DOC concentration was 50 mg/l.
[b] Initial concentration of the metals (except Pb) was 200 mg/l; concentration of Pb was 300 mg/l.

lower desorption potential should be environmentally advantageous. This would justify a slightly higher cost. In contrast, to previous pre-treatment methods using the highly toxic and carcinogenic substance formaldehyde [33] urea does not have any known toxic effects. However, urea is a nitrogenous compound and if used in excess amounts, it might cause eutrophication in surface water. However, this does not seem likely in this application.

It is not straightforward to compare the results of the reported batch experiments with published results from column experiments using reactive filter material with waste water containing low concentrations of metals and organic material [12,34]. Nevertheless, some reflections can be made. The retention of metals is clearly dependent on the filter material chosen and one material is not optimal for all metals and all types of waste waters. For example, Kietlinska and Renman [34] used a laboratory column filled with polonite® mixed with peat and fed with a Swedish landfill leachate containing metals and organic material (measured as TOC) in the concentration ranges presented here. They found that the Cu concentration was reduced by 67%, Ni by 2% and Zn by 86% (Pb was not analysed). However, removal of Ni by adsorption to Blast Furnance Slag (BFS) mixed with peat was 19%. In an on-site study performed by Nehrenheim et al. [11], non-treated pine bark was found to be the most efficient material for sorption. However, leaching was observed as the strength of the leachate decreased. This underpins the importance of combining studies of adsorption with desorption under varying waste water concentrations to ensure the use of a stable reactive filter. A suitable filter technology solution should most likely also contain different materials or a combination of technologies for optimal retention of metals with different properties in different types of waste waters. Studies along these lines are presently in progress.

4. Conclusions

In the absence of dissolved organic carbon, sorption efficiency of copper, nickel, zinc and lead on urea-treated pine bark (*P. sylvestris*) in multi-metal solutions (at initial concentrations of up to ca 0.5 mg/l for each metal) decreases in the following order: Pb–Zn > Ni > Cu. For non-treated bark, the metal binding affinity decreases in the order: Pb > Zn > Cu > Ni. Heavy metals adsorption is significantly stronger on urea-treated pine bark than non-treated bark. Compared to non-treated bark, urea-treated bark removes metals from solutions to residual concentrations that are rather constant across a wider range of initial concentrations.

The presence of dissolved organic substances significantly reduces heavy metal sorption onto pine bark. The order of sorption efficiency of the considered metals decreases in the order: Zn > Ni > Pb > Cu. Sorption of copper is the most sensitive to DOC content, while Zn is the least sensitive. In the presence of DOC, sorption of heavy metals was still slightly stronger on urea-treated bark than non-treated bark, although the difference in residual concentrations was much smaller. Metals adsorbed by urea-treated bark are retained on the sorbent noticeably better compared to non-treated bark.

Bark treated with urea did not contribute to the DOC content in treated solutions, while non-treated pine bark released small amounts of dissolved organics during the sorption experiments.

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