



## Leaching of contaminants from untreated pine bark in a batch study: Chemical analysis and ecotoxicological evaluation

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### ABSTRACT

Low cost sorbents have been widely studied in recent years in the search for filter materials that retain contaminants from water. One promising, low cost material is pine bark, a by-product from the forest industry. Many studies have shown that pine bark has great potential for the treatment of metals and organic substances, as a replacement for other commercial sorbents such as active carbon. However, some potential problems are introduced through the use of natural materials and by-products. One such problem that must be addressed is the possibility of leaching of contaminants from the filter material, especially in the initial filtration step or during flushes of lightly contaminated water, e.g. during rainfall for on-site treatment of storm water or landfill leachate. The aim of this preliminary study was therefore to identify potential risks and limitations of using pine bark as a filter material. Leachate from a standardized batch test was analysed for metals, dissolved organic carbon (DOC) and phenols. In addition to these chemical analyses, an ecotoxicological test was conducted using the test organism *Daphnia magna*. The results showed significant leaching of DOC and some metals. Only a small fraction of the DOC was present as phenols. The leachate was however found to be toxic to the test organism without pH adjustment, and the EC<sub>50</sub> was established at an approximate leachate concentration of 40%. This was concluded to be related to the low pH in the eluate, since no toxicity was observed after pH adjustment before the toxicity tests.

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### 1. Introduction

In recent years, low cost sorbents have been extensively studied by many researchers because of their promising ability to remove metals, nutrients (e.g. phosphorous) and organic compounds from contaminated water. There are many advantages with this technology, including low cost and low maintenance and space requirements [1,2]. Pine bark, a by-product from the forest industry, is particularly effective in removing metals from solution [3–6], storm water run off [7] and landfill leachate [1]. In addition to retaining metals, pine bark has also been shown to efficiently remove phosphorous [8], lindane [9], pentachlorophenol [10,11] and uranium [12] from water. However, one important problem with using pine bark as a filter is the release, or desorption, of contaminants from the unused filter material, particularly during the initial filtration phase. Some researchers have noted a discoloration of the leachate from treatment with pine bark and attributed this

to the leaching of phenols and organic acids from the material [13]. Phenol is produced during bacterial decomposition of organic material. Pure phenol shows acute toxicity to freshwater invertebrates, such as *Daphnia magna*, at concentrations ranging from 7 mg/l to 200 mg/l [14]. In addition to the release of organic substances, desorption of metals may also have negative effects on the surrounding environment [7]. An evaluation of these potential problems in using pine bark as a filter material is needed in order to ensure optimal performance of the technology and to maximize the environmental benefits. It is difficult to characterize and predict the toxicity of leachates solely by chemical analysis, since they contain a complex mixture of pollutants [15]. It is therefore advisable to assess the efficiency and safety of any new water treatment method in ecotoxicological tests. In this way, any synergistic or interactive effects resulting from the complex matrix of pollutants can be detected.

The aim of the present study was to investigate the release of potentially hazardous substances from pine bark. A leaching test was performed to determine the release of several metals, dissolved organic carbon (DOC) and phenol. Toxicity of the leachate to *D. magna* was measured in acute toxicity tests, with and without pH adjustment of the leachate.

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## 2. Methods and materials

### 2.1. Sorption on pine bark

The bark from pine (*Pinus silvestris*) used in the study originates from the timber industry and is a natural product which was used with no pre-treatment. The everyday use of the material is absorption of liquids from accidents, i.e. oil or gasoline. The bark is a commercial product supplied by Zugol AB in Falun, Sweden. According to the suppliers, pine bark has a particle diameter  $\varnothing$  of <0.25 mm (7.5%), 0.25–5.0 mm (76.2%) and >5 mm (16.3%). The material consists of 85–90% pine bark and 10–15% cellulose. Its properties have been described in more detail by Nehrenheim et al. [16] and Nehrenheim and Gustafsson [3].

### 2.2. Leaching experiment

Two leaching tests were conducted according to Swedish standard [17], with minor modifications regarding the filter grain size, one without and one with subsequent pH adjustment. The pine bark was delivered by the production company and used immediately after opening the bag. Small grains were not separated since our aim was to evaluate untreated material in the form in which it would be used in practice. Samples of pine bark were weighed as received into 1 l Duran borosilicate bottles and deionised water (pH 7) was added to attain a liquid to solid ratio in the bottles of 10 l/kg. As the dry matter content ratio of the pine bark was 60.7%, 148 g of undried sample material was used with 842 ml of deionised water to establish the required liquid to solid ratio (900 ml leachant/90 g dry mass of sample). The first test was run with duplicate samples. The second leaching test (with subsequent pH adjustment) was run with triplicate samples. Bottles were prepared and put on a roller table (10 rpm) for 24 h. The solids were then separated from the leachate by sieving and centrifugation, followed by filtration on a 0.45- $\mu$ m membrane filter (Whatman). The fraction of the total organic carbon, TOC, that passed through a 0.45- $\mu$ m filter was defined as dissolved organic carbon, DOC. All sampling and preservation of leachate samples used for the DOC, phenol and metal analyses were performed according to Swedish standard [18]. On completion of the leaching, unpreserved leachate samples were used immediately for the toxicity tests. In the second round of leaching tests the pH of the undiluted leachate samples was adjusted by the addition of 0.1 M NaOH to render the samples slightly alkaline prior to the toxicity tests.

### 2.3. Chemical analysis

DOC content in the filtered leachates was determined spectrophotometrically with a Dr Lange ISIS 9000 (MDA Photometer) with Dr Lange LCK 381 (60–735 mg/l TOC range) reagents. Total phenols were determined spectrophotometrically using a Dr Lange ISIS 9000 (MDA Photometer) with Dr Lange LCK 345 and 346 reagents (0.05–5 mg/l and 5–200 mg/l phenol range, respectively). For the lower range of phenol concentrations (LCK 345; 0.05–5.00 mg/l) total phenols were analysed photometrically through complexation with 4-nitroaniline. For the higher range of phenol concentration (LCK 346; 5–50 mg/l) total phenols (defined as ortho- and meta-substituted phenols) were determined spectrophotometrically through complexation with 4-aminoantipyrine. In the second round of leaching tests phenol concentrations of the leachate samples were measured prior to any pH adjustments.

The metal concentrations of the leachates of the first round of leaching tests were determined by ICP-MS and ICP-AES at the accredited laboratory Analytica, according to US EPA standard procedures [19,20].

pH was measured with a Metrohm 744 (Metrohm), calibrated with Merck/Riedel de Haën buffer solutions.

### 2.4. Toxicity tests

#### 2.4.1. Toxicity test without pH adjusted leachates

*D. magna* was used as a test organism to assess acute aquatic toxicity of leachate samples according to Swedish standard [21], using Daphtoxkit™ *magna* Straus (MicroBioTests Inc., Belgium). The test makes use of test organisms obtained from ephippia instead of parthenogenic females, but a comparison of the Daphtoxkit™ and conventional *D. magna* assays have shown a high correlation between the systems [22]. The toxkit method has been used in several investigations of the toxicity of landfill leachate and storm water in the region [1] and a comparison with the toxicity of effluents is therefore possible.

Each leachate sample was diluted to give final leachate concentrations of 6.25%, 12.5%, 25%, 50% and 100%. Each concentration of the dilution series was tested with four replicate sample wells, each containing five test organisms, together with a control for each dilution series. The ecotoxicity tests were performed within 72 h of the leaching test. The test organisms were exposed to the leachate solutions for a total of 48 h, to establish 24 h and 48 h median effect concentrations, EC<sub>50</sub> values, for each leachate sample. When parthenogenic daphnid neonates born in a stock culture are used in a toxicity test they can take up food (which provides them with an energetic reserve and, hence, precludes mortality by starvation) until they are collected for the assay. In order to provide the neonates hatched from ephippia with food prior to the test they are fed with a suspension of *Spirulina* algae for 2 h in the hatching dish, before the transfer to the test vessels. At termination of the tests, oxygen concentrations were measured in the test solutions to exclude oxygen deprivation as a cause of organism mortality. The validity of the tests was assessed according to ISO 6341. The toxicity of the reference substance K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is assessed on a biannual basis.

#### 2.4.2. Toxicity tests with pH-adjusted leachates

The toxicity of pH-adjusted leachate was conducted as above with the exception of pH adjustment of the leachates. The pH of the filtered leachates was measured and adjusted to slightly alkaline by the addition of 0.1 M NaOH prior to the commencement of the toxicity tests.

### 2.5. Data analysis

The results from the toxicity tests with leachates without any pH adjustment were fitted to a sigmoid function (Eq. (1)) by the least-squares method using the software programme SigmaPlot 4.0® (by Windows):

$$y = \frac{I_{\max} - I_{\min}}{1 + e^{-(x-x^0)/b}} \quad (1)$$

where  $b^{-1}$  is the 'hill slope' of the function and  $x^0$  is the EC<sub>50</sub> value. The  $I_{\max}$  value is the highest immobility detected and the  $I_{\min}$  value is the lowest. The  $R^2$  value of the fits, for data at both 24 h and 48 h, was >0.99.

## 3. Results and discussion

Pine bark has a complex chemical structure consisting of both extractable and non-extractable components, of which the non-extractable can adsorb cationic polyelectrolytes [8]. Metals are thought to sorb to pine bark by ion exchange at a multitude of ionic sites, both cationic and anionic, with metal ions replacing adjacent hydroxyl groups to form a chelate [23–25]. For example, Cu-ions

**Table 1**  
Metal concentrations and pH in the leachate

Metal	Concentration	Leachate samples	US EPA MCL <sup>a</sup>	EU MAC-EQS <sup>b</sup>
Ca	mg/l	0.82	–	–
Fe	mg/l	0.12	0.3	–
K	mg/l	9.3	–	–
Mg	mg/l	0.29	–	–
Na	mg/l	3.6	–	–
S	mg/l	0.29	–	–
Al	μg/l	650	50–200 <sup>c</sup>	–
As	μg/l	<1	10	–
Ba	μg/l	50	2000	–
Cd	μg/l	<0.05	5	0.45–1.5 <sup>d</sup>
Co	μg/l	<0.2	–	–
Cr	μg/l	<0.9	100	–
Cu	μg/l	13	1300	–
Hg	μg/l	<0.02	2	0.07
Mn	μg/l	68	50 <sup>c</sup>	–
Ni	μg/l	0.84	–	20
Pb	μg/l	0.81	15	7.2
Zn	μg/l	16	5000	–
pH		4.6		

<sup>a</sup> Maximum contaminant level (MCL): The highest level of a contaminant allowed in drinking water. MCLs are enforceable standards. Ref. [29].

<sup>b</sup> European Union Proposal for Maximum Allowed Concentration Environmental Quality Standards (MAC-EQS) applicable to water. Ref. [30].

<sup>c</sup> National Secondary Drinking Water Standards, which are non-enforceable guidelines regulating contaminants that may cause cosmetic or aesthetic effects in drinking water. Ref. [31].

<sup>d</sup> Depending on water hardness (<40–200 mg/l CaCO<sub>3</sub>).

have been suggested to interact with phenolic groups present in lignins and tannins whereas Pb-ions are attracted to carboxylic acid groups in polysaccharides [26].

### 3.1. Metal desorption

Metals desorbed from the filter material were found in the leachate from the experiment (Table 1), including Cu, Pb, Zn and Ni, which are considered as pollutants in landfill leachate and storm water runoff [1]. These metals could contaminate an effluent during the start-up process of an on-site facility for water treatment. Background metal analyses, therefore, play a significant part in the evaluation of the suitability of pine bark as a filter material.

### 3.2. Changes of pH during leaching and toxicity tests

In the first leaching test pH decreased from neutral to 4.6. In the second leaching test the pH changed from neutral to 5.0. After adjustment with 0.1 M NaOH pH was 7.4. pH was measured in the test vessels (with dilution series of leachate) at the start of the toxicity test for the second leaching test and was found to be 7.5 (S.D. ± 0.2). At the end of the test (after 48 h exposure) pH was 7.3 (S.D. ± 0.3).

### 3.3. Desorption of phenols and other DOC

The DOC concentration in the leachate from pine bark was 69 mg/l (S.D. ± 0.62). Organic material was released from the pine bark due to modification or microbial degradation of complex polymers such as cellulose, lignin and proteins. Phenols were measured to 4.4 mg/l (S.D. ± 0.35), and represented 7% of the DOC. The remaining DOC probably comprised other monomer units such as organic acids and sugars. The formation of organic acids is likely to be responsible for the drop in pH in the undiluted leachate.

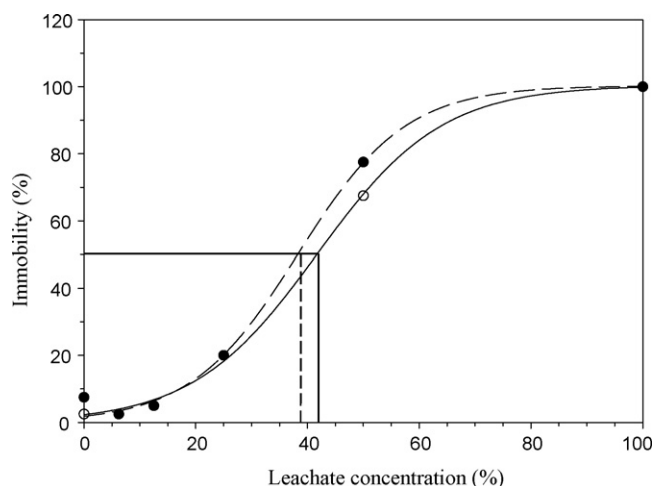
In parallel studies, conducted according to the same experimental protocol but with storm water instead of deionised water, data showed that significantly more phenols were released (13%) when

the pine bark was leached with storm water. The storm water was collected in a brook in central Västerås and contained low concentrations of metals and salts. One explanation for this could be that storm water contains a larger number of microorganisms, which attack the pine bark. Another explanation could be the presence of salts and metals in the storm water, since these ions can form complexes with the organic material, which may promote DOC desorption. Nehrenheim et al. [27] found that solutions of larger salt concentration increased the leaching of DOC. DOC concentrations measured by Nehrenheim et al. [27] were in the range of 23–104 mg/l, which is approximately 30% higher than in our study.

### 3.4. Toxicity tests

The toxicity tests were valid according to ISO 6341 since oxygen concentrations were larger than 2 mg/l after 48 h of testing and no more than 10% of the control organisms were immobilized after 48 h. In the first toxicity test, the average EC<sub>50</sub> values for *D. magna* were 41.8% and 38.3% after 24 h and 48 h (Fig. 1). The data fitted very well ( $R^2 > 0.99$ ) to the sigmoid curve which tended to be symmetrical around the EC<sub>50</sub> values [28,29].

All the metals analysed in the leachate samples were detected at concentrations below US EPA Maximum Contaminant Levels (MCLs) [29] and European Union Maximum Allowed Contamination Environmental Quality Standards [30]. Manganese and aluminium exceeded the US EPA National Secondary Drinking Water Standards [31], but these standards are non-enforceable guidelines (as opposed to the MCLs, which are enforceable standards), regulating contaminants that may cause cosmetic or aesthetic effects in drinking water. The concentrations of manganese and aluminium detected in the leachates were, however, lower than reported toxicity limits for the two metals [32,33]. Phenol concentrations were also well below reported EC<sub>50</sub> values [14]. The low pH (4.6) was probably a significant factor for the high immobility of the test organisms in the undiluted leachate. This could explain the strong correlation between the 24 h and 48 h dose–response relationship shown in Fig. 1, since the pH effect overshadowed the other potentially toxic effects. The pH-adjusted leachate samples showed no toxicity in the 24 or 48 h *D. magna* acute toxicity test. Since pH adjustments were conducted after the



**Fig. 1.** Immobility (%) of *Daphnia magna* (mean) after 24 h (white symbols) and 48 h (filled symbols) exposed to solutions of filtered pine bark leachate without any pH adjustment. Duplicate leachate samples from the same batch of pine bark were diluted to final concentrations of 6.25%, 12.5%, 25%, 50% and 100% of the initial leachate. EC<sub>50</sub> concentrations for 24 h and 48 h exposures are shown.

leaching test and the phenol concentration not significantly different than in the first test, some assumptions can be made. The phenol or heavy metal concentrations are not responsible for the toxicity alone or by synergetic effects. However, the lower pH in the first test could possibly affect the availability of the substances in the leachate and thereby give additional affects to the pH value itself.

In most applied systems, the effluent in need of treatment would have a certain buffering capacity towards pH changes. In such systems, metals in solution could be expected to be less toxic, given their low solubility at higher pH. Nehrenheim et al. [1] investigated the toxicity of treated and untreated water from a landfill and found no toxicity of the pine bark leachate. The toxicity was assessed as bioluminescence inhibition of the bacterium *Vibrio fischeri* (Microtox® comparison test) and as growth inhibition of the green algae *Pseudokirchneriella subcapitata*. The pH in their study was above 7.3 on all sampling occasions. Both pH and ionic strength were significantly lower after the leaching tests in our study without pH-adjustment. Together with the results from the toxicity tests with pH adjusted leachate samples, this support the hypothesis that pH was the primary cause of toxicity.

#### 4. Conclusions

The leaching of the pine bark filter showed that desorption of metals occurs. The duration of this desorption process is difficult to predict.

Phenols represent only a small part, 7%, of the released DOC, but these concentrations could be significant for the total toxicity if synergistic effects with other contaminants occur. The presence of organic acids also represents a potential risk for recipient ecosystems, by significantly lowering the pH.

24 h and 48 h EC<sub>50</sub> values for acute toxicity of leachates without pH adjustment to *D. magna* could be determined by using the least-squares method. All the test organisms were immobilised in the batch test with 100% of the leachate concentration.

The pH adjusted leachate samples showed no toxicity to *D. magna* during 24 h or 48 h exposure.

The results from the present study imply that some treatment of the first bed volumes, such as recirculation of the effluent in the filter, rinsing or chemical stabilisation of the pine bark, could be necessary in an on-site application for natural systems. There could also be a risk of hazardous effects during heavy rainfalls if the materials are used in natural, on-site systems.

To avoid the release of organic acids and desorbed metals from the filter material into the recipient water treatment facilities could be designed to ensure buffering of the first effluent. Another method of avoiding the release of organic material and desorbed metals is through chemical stabilisation of the pine bark prior to usage. Different successful methods for pre-treatment of slag and pine bark have been explored by researchers with the aims of increasing uptake rate, sorbent saturation concentration or decrease desorption of soluble substances, i.e. phenols. Examples of chemical pre-treatments for pine bark are formaldehyde, sulphuric acid [34,35] or hydrochloric acid [36]. More recently Fenton's reagent has been used to stabilise pine bark [37].

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