Treatment of heavily contaminated storm water from an industrial site area by filtration through an adsorbent barrier with pine bark *(Pinus Silvestris)*, polonite and active carbon in a comparison study

E. Nehrenheim*, V. Ribe*, P. Carlsson**, P. Eneroth*** and M. Odlare*

*Mälardalen University. Box 883. SE-72123 Västerås. +4621-101484. *emma.nehrenheim@mdh.se*
**Structor Miljöteknik. Smedjegatan 34. SE-63230 Eskilstuna. +4616-100761. +4670-6356232. *peter.carlsson@structor.se*
***Flexiclean, Growhouse, Isafjordsgatan 39B, SE-164 40 Kista, +4670-713 70 98, *peder.eneroth@flexiclean.eu*

Abstract: This study aims to evaluate a simple and robust filtration method for separation of heavy metals from storm water. The storm water, collected at a metals manufacturing site, is heavily contaminated with heavy metals. A first analysis showed exceptionally high concentrations of Zn, which was present in concentrations exceeding 200 mgL^{-1}. The basic idea is to filter the water as it flows out of the industry area through a passive barrier in the storm water well pipeline. Pine bark was in this study compared to two other materials; polonite and the conventional adsorbent active carbon. The forestry by-product pine bark *(Pinus silvestris)* consists of approximately 85-90 % dried and granulated pine bark and 10-15 % wood fibres. Polonite is a manufactured product originating from the cretaceous rock opoka. A laboratory experiment was set up, where the storm water from the industrial site was filtered through all three filter materials in a pilot-scale model of the proposed installation. The filter cartridge model could be filled with approximately 2.2 L filter material. 3 L of the storm water was poured through the material through natural percolation, approximately 0.35 $Lmin^{-1}$. Treated and untreated storm water was analyzed for heavy metals, suspended solids, electric conductivity and pH. Active carbon showed the highest level of adsorption, with nearly 100 % of all metals adsorbing to the filter. However, significant concentrations of As was desorbed from the material into the filtered water. Pine bark retained 90 % of the metals, even the Zn which was present in high concentrations. Polonite could only adsorb 70 % of the heavy metals and released Cr from the material.
Keywords: water treatment, heavy metals, filtration, desorption, ecotoxicity test

INTRODUCTION

In Sweden, the release of hazardous substances to the environment from industrial parks is heavily restricted due to legislation. The activities of industries in Sweden are therefore generally considered to be clean and relatively safe to the environment. This applies, however, mainly to the production and manufacturing processes, transportation and waste management. Leaching of contaminants from erosion of materials during rainfalls as well as discharges during loading and unloading is a frequently overlooked environmental hazard. Today, there is awareness within the metal industry of the potentially adverse effects of releasing heavy metals from back yards to the storm water piping system. Historically, storm water in these pipes were either discharged directly into the recipient without treatment or sent to the wastewater treatment plant, which is not at all adapted to separate heavy metals from the water.

A first analysis of a water sample collected from the site in mid Sweden showed exceptionally high concentrations of especially zinc, Zn, which was present in concentrations exceeding 200 mgL^{-1}. This study aims to assess the efficiency of some very simple and robust filtration methods for separation of heavy metals in storm water. The basic idea is to filter the water as it flows out of the industrial area through a passive barrier in the storm water well pipeline. The equipment used for this filtration is a simple installation containing an adsorbent material in a filter cartridge which the water runs through. Today, the supplier of this facility is using pine bark as an adsorbent for moderately contaminated storm water from trafficated areas. The advantages with pine bark are many, as it is a waste material it can be recycled into a new life cycle step and previous studies have proposed the use of pine bark for capturing heavy metals (Montes et al. 2003, Nehrenheim and Gustavsson, 2009). There are, however, some disadvantages with using pine bark for water treatment, one of which is the discoloration due to release of organic substances from the material (Genc-Fuhrman et al. 2007, Nehrenheim et al. 2010) and varying equilibrium times, causing desorption back to the effluent (Nehrenheim et al, 2009). Pine bark was in this study compared with two other materials; polonite (Kietlinska et al. 2005) and the conventional adsorbent active carbon. Additionally, a complimentary adsorbent was investigated for combined use with pine bark, i.e. a material that could compensate for the adverse effects of water treatment with pine bark, such as pH reduction.

MATERIALS AND METHODS

The forestry by-product pine bark *(Pinus silvestris)* consists of approximately 85-90 % dried and granulated pine bark and 10-15 % wood fibres. According to the suppliers, pine bark has a particle diameter Ø of < 0.25 mm (7.5%). 0.25-5.0 mm (76.2%) and >5 mm (16.3%). Polonite is a manufactured product originating from the cretaceous rock opoka (Brogowski and Renman 2004). The major components of Polonite are SiO_2 (39.4%), CaO (42%), Al_2O_3 (4.3%) and Fe_2O_3 (2%) (Brogowski and Renman, 2004). Polonite was selected since it is silica and calcium rich and is well known for adsorbing phosphorous efficiently (Brogowski and Renman, 2004).

Pre-treatment of adsorbents

All three adsorbents were pre-treated with one bed volume of de-ionized water prior to the experiment. Had the materials been used unwashed, the risk of misleading results is large due to contamination of the filtered water, biochemical reactions on the surface during manufacturing, packing and transport which could affect the treatment result. Previous studies (Ribe et al. 2009) have shown that for instance the pine bark can release organic contaminants during the start-up phase but that this initial flush effect decreases already after the passing of a few bed volumes of water.

Experimental design

A laboratory experiment was set up, where the storm water from the industrial site was filtered through the three different filter materials in a pilot-scale model of the proposed installation. The filter cartridge model could accommodate approximately 2.2 L filter material. 3 L of the storm water was added at a flow rate possible with the materials hydraulic conductivity. The three liters of water passed through the filter within approximately nine minutes.

RESULTS AND DISCUSSIONS

Analysis of the contaminated storm water

The total concentrations of heavy metals (free ions and particle bound) in the storm water collected at the industrial site are given in table 1, together with some of the physicochemical parameters of the storm water. Table 1 also presents the guideline values from the Swedish EPA (Environment

Protection Agency). Most noteworthy are the elevated levels of Zn in the storm water, which represents a hazard to the recipient water course. Cr (chromium), Cu (copper), Pb (lead), Ni (nickel) and Cd (cadmium) were also detected at levels exceeding the guideline values. The concentration of petroleum compounds was low. Typically for storm water, the pH was neutral and the concentration of suspended solids (SS) was moderately high in comparison with the Swedish guideline values.

Table 1. Contaminants in the untreated storm water collected at the industry site

ement	onc. (μgL^{-1})	ideline value (Swedish EP gL^{-1})
[illegible]	[illegible]	
[illegible]	[illegible]4	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]		
[illegible]	100	
l index		0
[illegible]	[illegible]	[illegible]
cond. (mS/m)	5	[illegible]
(mg L^{-1})	0	-50

Treatment effect

The contaminated storm water was treated by filtration through the three filter materials; pine bark, polonite and conventional active carbon. Figure 1 shows the relative retention of heavy metals in the different filter materials.

The most alarming contaminant in the storm water from the industrial site was, as already mentioned, the extremely high concentrations of Zn. Even though the filter materials could remove approximately 70 %, 90 % and close to 100 % (polonite, pine bark and active carbon, respectively) (see Figure 1) none of the materials could capture sufficient amounts of Zn to guarantee the guideline values for Zn (60 $\mu g\ L^{-1}$). However, taking the experimental set up and it development potential into further thoughts, one can argue that the method (i.e. filtration with pine bark) has large potential for separation of Zn. However, the water was poured through the material in a downwards flow rate, which can lead to channeling within the filter materials. Moreover, a larger part of the particles in the storm water could pass the filter, i.e. the treated storm water had a concentration of suspended solids (SS) of up to 80 mgL^{-1} which means that adsorption onto the particles could have occurred, enabling the transportation of contaminants through the filter material without being adsorbed to the surfaces or diffused into the micro pores. By designing a filter solution which can capture a larger part of SS, this problem could be solved. Pine bark was the material that treated Zn most efficiently, considering total concentrations.

Further experiments analyzing the dissolved organic carbon, DOC, in order to ensure that the storm water has not been contaminated with organic material ought to be performed. If high concentrations of organic substances were present in the storm water, it could explain the remaining Zn concentration in the water after treatment (Nehrenheim et al. 2008). If not, the remaining Zn could be treated with the right optimization measure, e.g. increased retention time or a secondary treatment.

All three materials affected pH significantly. Pine bark lowered pH from 7.4 to 4.0. The acidic leachate could of course lead to an increased risk for the recipient but regarding the adsorption mechanisms, it could be argued that pine bark still is more preferable since this talk for a low risk of weak adsorption mechanisms such as precipitation on the outer part of the boundary layers of the particles. Precipitation is the weakest type of adsorption mechanism and thereby the risk of desorption of the adsorbed ions back to solution is at greatest risk (Gustavsson, 2004). In the pine bark filter, it is more likely that various forms of metal complexation to surface functional groups (Nehrenheim and Gustavsson, 2008; Nehrenheim, 2009) (Nehrenheim, 2009). In the polonite filter, on the other hand, the pH increase implies precipitation as the mechanism for separation and this filter could therefore be argued to be less reliable to use on site due to the increased risk of flush effects. Most preferable could be a mixture of the both materials in the filter or even, if possible from an application point of view, a two step filter box where polonite works like a polishing and pH stabilizing step following the the pine bark treatment. Another alternative could be using blast furnace slag, a by-product from the steel manufacturing industry, which has been tested in an earlier study (Nehrenheim, 2008). However, blast furnace slag has not been known to increase pH significantly and the treatment effect has been moderate compared to pine bark.

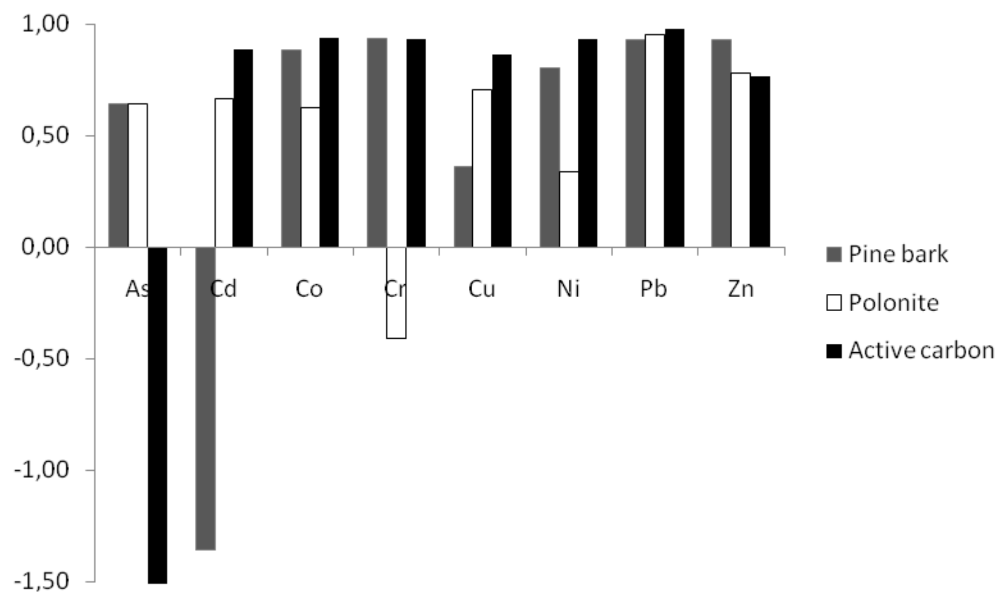

Figure 1 Relative treatment effect on the metal contaminated storm water of the three tested materials. Active carbon desorbed significant amounts of As, Polonite Cr and Pine bark Cd.

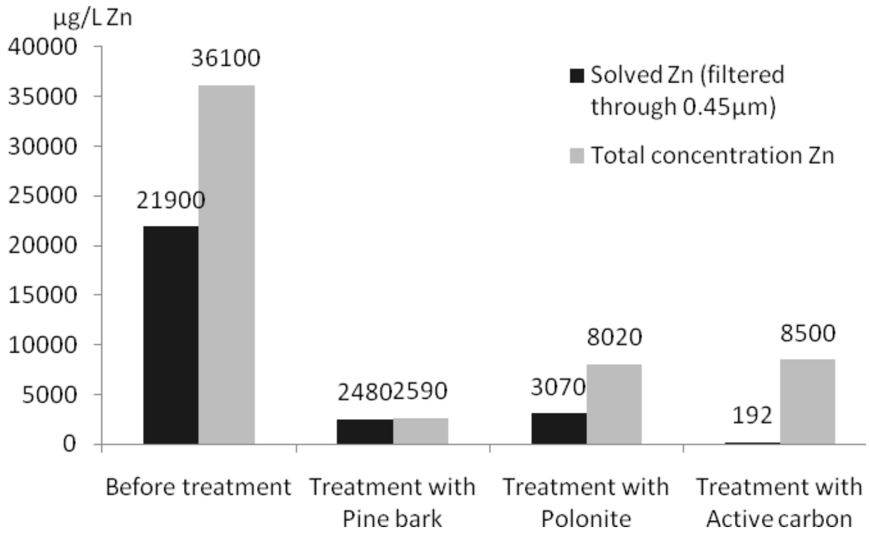

Figure 2 Concentrations of Zn in the untreated and treated storm water after filtration through pine bark, polonite and active carbon.

Leaching of substances

The experiment also showed that the materials can discharge substances during the treatment, which is in accordance with previous knowledge about the materials (Nehrenheim et al. 2008; Ribé et al., 2009). Previous leaching experiments has not shown signs of desorption of Cd from pine bark. In those studies, other metals were desorbing from the material (Ribé et al. 2009). Discharge, i.e. desorption of ions from the particle specific surface sites, could be explained by the massive amounts of Zn, leading to an ion-exchange process on the particles of the pine bark. The more commonly discussed problem in the literature is the discoloration of the treated water due to discharge of organic substances, e.g. tannins and phenols (Bailey et al 1998, Nehrenheim 2009) from the pine bark. According to Bailey et al (1998), the discharge of metals occurs at low metal concentrations before treatment, i.e. the force of chemical equilibrium is responsible for the transportation of ions in and out of the particle boundary layers, which was also discussed in previous studies (Nehrenheim, 2009). This study seem to indicate that, worringly, both low concentrations and very high concentrations of ions in the untreated water could cause the risk of discharges, and different ions are released depending upon how they are bound to the particle surface. Especially, caution should be undertaken when using passive filters with solely pine bark for treatment of waters with great variations in the concentrations of metal ions.

The ion-exchange process could be responsible for desorption of the metalloid As leaching from active carbon. The leaching of As from active carbon could be considered alarming, since the desorbed concentrations are as high as 123 µg L^{-1} (measured as difference between inlet and outlet concentrations). As leaching from active carbon has been reported before, for instance in a very extensive study by Gandy and Maas (2004) where coal and cocoa nut-shell based active carbon used in granulated active carbon filters discharged significant amount of As and another metal;

antimony (Sb). In this study, however, few of the active carbon materials were desorbing As in concentrations exceeding the 10 μg L^{-1} drinking water limit values set up by the US EPA. In that study on the other hand, no forcing of desorption was conducted that could be comparable to the massive Zn ions added in the present study, i.e. no ion exchange process was added.

CONCLUSIONS

From this preliminary experiment where three filter materials were compared we conclude that:

1. All three materials could in little time adsorb high amounts of heavy metals
2. The experimental set-up, similar to the real application, was sufficient for metal removal
3. For solved fractions of Zn, active carbon was more efficient
4. Significant amounts of As leached from active carbon through ion exchange when Zn was added.
5. Pine bark could capture more of the particle bound fractions of Zn than the other materials, even though the uptake of SS was not significantly different in the three materials. The leaching of Cd through ion exchange was however worrying.
6. A secondary step or a two step filtration would be necessary in order to guarantee the treatment effect as well as a stabilized pH.

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