Retention of 2,4,6-trinitrotoluen (TNT) and heavy metals from industrial waste water by using the low cost adsorbent pine bark in a batch experiment

E. Nehrenheim*, M. Odlare* and Bert Allard**

*School of Sustainable Development of Society and Technology, Mälardalen University, P.O. Box 882, SE-721 23 Västerås, SWEDEN (E-mail: emma.nehrenheim@mdh.se; monica.odlare@mdh.se)
**School of Science and Technology, Örebro University, SE-701 82 Örebro, SWEDEN (E-mail: bert.allard@oru.se)

Abstract Pine bark is a low cost sorbent originating from the forest industry. In recent years, it has been found to show promise as an adsorbent for metals and organic substances in contaminated water, especially landfill leachates and storm water. This study aims to investigate if pine bark can replace commercial adsorbents such as active carbon. An industrial effluent, collected from a treatment plant of a demilitarization factory, was diluted to form concentration ranges of contaminants and shaken with pine bark for 24 hours. Metals (e.g. Pb, Zn, Cd, As and Ni) and explosives, e.g. 2,4,6-trinitrotoluene, TNT, were analysed before and after treatment. The aim of the experiment was twofold; firstly, it was to investigate whether metals are efficiently removed in the presence of explosives and secondly, if adsorption of explosive substances to pine bark was possible. Langmuir and Freundlich isotherms were used to describe the adsorption process where this was possible. It was found that metal uptake was possible in the presence of TNT and other explosive contaminants. The uptake of TNT was satisfactory with up to 80 % of the TNT adsorbed by pine bark.

Keywords TNT, pine bark, adsorption, heavy metals

INTRODUCTION
Explosives production and demilitarization activities generate explosives contaminated water, often in combination with one or several heavy metals. Recently, several laboratory studies and field studies have indicated that energetic compounds, such as explosives, are toxic at relatively low concentrations to a number of organisms including microorganisms (Odlare et al, 2008), plants, invertebrates (Simini et al., 1995), vertebrates and humans (Bruns-Nagel et al., 2000; Beltz et al., 2001). 2,4,6-trinitrotoluene (TNT) and is listed as potential human carcinogen in the USA.

Water treatment is often an expensive and time-demanding process for industries, municipal plants and households. Therefore, new technologies developed in recent years have focused on finding cost-efficient and low maintenance treatment methods for many commonly occurring substances. Recently developed and evaluated treatment technologies, developed for explosives reduction in wastewater are e.g. photochemical degradation (Kröger and Fels, 2007), solvent extractions (Chen et al, 2007), degradation with iron (Barreto-Rodrigues et al., 2009) and adsorption (An et al., 2009). At the industry studied in the present paper, active carbon has been used as adsorbent for several years with good result. However, the active carbon treatment generates a heavily contaminated active carbon sludge which today must be sent off site for destruction. One of new adsorption technology that has not yet been tested for explosives is the use of low cost adsorbents, which are essentially porous materials, either natural or originating as by-products of industrial processes. The materials have been evaluated for other contaminants worldwide. Some examples of materials include clays, ashes, slags, zeolite and various...
different fibres from agricultural activities (Johansson Westholm and Färm, 2004). Hydraulic flow rate, sorbent/solution ratio, pH and concentrations of contaminants are examples of important parameters that determine the effectiveness of the treatment with such materials (Nehrenheim et al, 2008).

Pine bark, a by-product of the forest industry is one material that has proven effective in removing many contaminants in water. It has been evaluated primarily for its promising capacity to adsorb heavy metals from contaminated effluents such as storm water (Färm, 2003) and landfill leachate (Kietlinska and Renman, 2005; Nehrenheim et al 2005; Nehrenheim et al, 2008). In many of these cases, close to 100 % of the metals in solution were captured by the pine bark. Apart from heavy metals, pine bark has been investigated for its capacity to remove other contaminants such as pentachlorophenol from industrial wastewater (Bras et al, 2005; Edgehill and Lu, 1998) and uranium from aqueous systems (Freer et al 1989). Ratola et al. (2003) found that pine bark retained 80.6 % and 93.6 % of lindane and heptachlor, respectively. Pine bark is organic and can be biologically degraded as oppose to many other adsorbent materials evaluated, which makes the whole treatment process gentle to the environment. This makes the material interesting for treatment of industrial effluents containing explosives.

Nammo Vingåkersverken is an old ammunition factory, re-constructed for demilitarization purposes. The processes on site are primarily focusing on the dismantling of ammunition and reuse of the ammunition parts. Nammo Vingåkersverken has a re-use or re-circulation rate of more than 90 % of the ammunition mass received by the factory. The remaining 10 % is primarily residual explosive contaminated material, primarily water and sludge, from the melt out processes and process water treatment. There is a close to zero tolerance level of any discharge from the factory. The recipient is a lake that is used as a drinking water source.

The aim of the present study was to investigate metal and explosives, mainly 2,4,6-trinitrotoluen (TNT), uptake from an industrial effluent at the factory. The potential of pine bark to adsorb both metals and explosive substances was evaluated in a batch experiment where pine bark was shaken together with an industrial effluent collected from a demilitarization factory treatment plant. The most alarming pollutants in the effluent were represented by high concentrations of TNT and zinc (Zn). Therefore, these substances have the main focus of the study.

THEORY
Two established mathematical approaches are predominately used to evaluate TNT adsorption to low cost sorbents; The Langmuir adsorption isotherm and the Freundlich adsorption isotherm. By transforming the mathematical expressions, the constants of the isotherms can be derived from sorption batch experiments such as the one described in the present study. Where it was possible, data was fitted to the isotherms. The results might be difficult to interpret due to competition of other ions in the water, but they can be considered valuable as a comparison to other substances or materials.

Sorption
Sorption is a broad term, describing transfer processes of substances or solids, between particles or grains and the gases or liquids that surround them. Sorption includes adsorption and absorption which basically means attraction to the grains or particles, or
desorption which is the opposite, a release towards the surrounding environment. Absorption is simpler, being the incorporation of a substance in one state into a different state (Gustavsson et al., 2004).

**Langmuir adsorption isotherm**

The Langmuir isotherm has been used by many researchers to model potential sorption of contaminants to particulate media such as soil. The isotherm was originally developed for sorption of gas and vapour onto particles (Langmuir, 1916; Dullien, 1979) and it has been found to give varying results when used for metal sorption onto particles in water treatment systems (Al-Asheh and Duvnjak, 1998; Al-Asheh et al., 2000; Jang et al., 2005). The Langmuir isotherm assumes a homogenous sorbent surface, and equally active sorption sites (Cucrovic et al., 2001). The Langmuir isotherm can be expressed as;

\[
\frac{Q_e}{Q} = \frac{bC_e}{1 + bC_e}
\]

where \( C_e \) (mg·L\(^{-1}\)) is the equilibrium adsorbate concentration, \( Q_e \) (mg·g\(^{-1}\)) is the mass of adsorbate per mass of adsorbent at equilibrium and \( Q \) (mg·g\(^{-1}\)) is the maximum mass adsorbed at saturation conditions per mass unit of adsorbent. \( b \) (L·mg\(^{-1}\)) is an empirical constant with units that are the inverse of concentration \( C_e \). The Langmuir adsorption maximum \( Q \) is calculated from the slope obtained by plotting \( Q_e \) against \( Q_e/C_e \). \( Q \) is the upper limit of \( Q_e \). Converting the Langmuir equation to a linear form allows the calculation of \( b \) and \( Q \).

**Freundlich adsorption isotherm**

The Freundlich isotherm is based on an exponential distribution of sorption sites and energies (Curcovic et al., 2001). It considers monolayer coverage and assumes a heterogeneous balance distribution of the sorption sites (Al-Asheh et al., 2000). The Freundlich isotherm is given by:

\[
Q_e = kC_e^{n/1}
\]

where \( k \) (mg·g\(^{-1}\)·(L·mg\(^{-1}\))) and \( n/1 \) are the empirical Freundlich constants.

**MATERIALS AND METHODS**

**The industrial effluent**

The dominant explosive in the industrial effluent is TNT. Trace concentrations of other explosives can also be found. Chemically, TNT is a toluene molecule with nitro-groups attached to its ring structure. Nitro aromatic compounds of this kind do not occur naturally in the environment and most microorganisms are therefore not adapted to degrade and mineralize these substances. The persistence of TNT and several other explosives stems from the fact that the nitro groups are symmetrically arranged to cover the ring structure. This generates a very stable structure that is extremely resistant to microbial degradation.
Table 1
Metal and TNT concentrations in the effluent treated in the pine bark batch experiment and zero charge concentrations of metals in pine bark (Nehrenheim and Gustavsson, 2008)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Waste water pollution (µgL⁻¹)</th>
<th>Zero charge concentration in pine bark (mg·kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>290</td>
<td>n.a.</td>
</tr>
<tr>
<td>As</td>
<td>3.2</td>
<td>0.11</td>
</tr>
<tr>
<td>Ba</td>
<td>9.2</td>
<td>n.a.</td>
</tr>
<tr>
<td>Cd</td>
<td>2.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Co</td>
<td>2.5</td>
<td>0.25</td>
</tr>
<tr>
<td>Cr</td>
<td>3.7</td>
<td>1.8</td>
</tr>
<tr>
<td>Cu</td>
<td>22.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Hg</td>
<td>0.0</td>
<td>n.a.</td>
</tr>
<tr>
<td>Mn</td>
<td>95.8</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ni</td>
<td>1.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Pb</td>
<td>7.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Zn</td>
<td>3970</td>
<td>83</td>
</tr>
<tr>
<td>TNT</td>
<td>29.5*</td>
<td></td>
</tr>
</tbody>
</table>

Besides explosives, the effluent contains metals which have been released from the metal shells of ammunition parts. The most commonly occurring heavy metals in the samples of the process water are arsenic, copper, lead, zinc, cadmium and chromium. Some heavy metals are essential for living organisms (e.g. copper and zinc) although excessive levels can be detrimental. In contrast, cadmium, chromium, and lead serve no vital function in organisms and are toxic to most (Duffius, 2002). Table 1 shows the concentrations of analyzed metals found in a first screening of the sampled process water. The water treatment process currently used (adsorption by active carbon followed by a biological treatment step) reduces the concentrations of all metals and explosives in the effluent. Moreover, Table 1 gives the zero charge concentrations of the pine bark, i.e. the known concentrations of ions in pine bark before treatment (Nehrenheim and Gustavsson, 2008).

**Pine bark**

In choosing a suitable filter material for the treatment of the effluent, six criteria were identified, which were all met by pine bark; (1) Availability close to the factory site to avoid long transportation, (2) Recognition world wide, (3) Cost efficiency, (4) Low operation demands, (5) Potential for local handling after filtration, either by biological treatment or incineration and (6) No pre-treatment of the material, neither time demanding separation of particles nor chemical treatment to enhance uptake.

Pine bark is a by-product from a global industry, namely manufacturing pulp and paper, cellulose and other woods products. The physico-chemical properties of slag and pine bark have been described by Nehrenheim and Gustafsson (2008). The material is a commercial product supplied by Zugol AB in Falun, Sweden. The forestry by-product pine bark (*Pinus silvestris*) consists of approximately 85-90 % dried and granulated pine bark and 10-15 % wood fibres. 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%). The porosity of the material has been determined to be 34-49 % and the apparent density ranges from 0.6-0.9 g·cm⁻³. The pine bark in this study had an apparent density of 0.69 g·cm⁻³. Table 1 gives the zero charge concentrations of heavy metals (Nehrenheim and Gustavsson, 2008). The sorption mechanisms to pine bark are expected to differ from other materials, being mainly controlled by complexation with humic material on
the sorption sites. Pine bark (the same product as in this study) has been subject for investigation regarding its risk for leaching background concentrations of contaminants in previous studies by Ribé et al (2009). This study showed that even though there was a toxic effect from the pine bark on the eco-toxicological test organisms, this effect was related to pH rather than the release of hazardous compounds.

**Sampling**

*Effluent sampling.* Contaminated effluent was collected from the treatment plant at the factory site, directly before the active carbon batch filtration step (see Fig. 1). Three replicate samples of 5 L effluent were collected from the surface of the large sedimentation basins and brought to the laboratory. The sampled effluent was then mixed in a one batch and immediately frozen in plastic bottles without further preservation. The experiment took place within a few days.

**Batch experiment**

*Preparation of concentration gradients.* Solutions for the batch experiment were prepared by diluting the effluent collected at Vingåkersverken to reach concentrations of 0, 0.2, 0.4, 0.6, 0.8 and 1 times the original concentration in the effluent (see Table 1 for original concentrations). All the solutions had similar pH, between 6.95 and 7.56.

*Experiment design.* Three replicates of each of the five concentrations and the control (de-ionized water) were prepared in shaking flasks of 500 ml volume. 200 ml of solution in each flask were mixed with 3 grams of pine bark. Thereafter, the solutions were shaken with pine bark for 24 hours in order to ensure equilibrium between solution and pine bark (Nehrenheim et al, 2010). The experiment was conducted in room temperature (22°C). After centrifugation and filtration, samples of the initial solutions and leachate from the experiment were analysed for concentrations of metals and explosives by authorised laboratories in Sweden.

**Chemical analyses**

The metal samples were extracted with HNO₃ and analysed by means of ICP-MS. All samples were preserved with HNO₃ supra-pure and frozen 4 days prior to the analyses. Samples of explosives were extracted with acetonitrile and analysed by means of HPLC with Diode Array detector, using a LiCrospher 100 RP18 15 cm tube.

**RESULTS AND DISCUSSION**

The metals As, Pb, Cd, Cr and Zn were found in concentrations (see Table 1) that correspond well to strongly polluted landfill leachate in Sweden (Öman et al., 2000). Most alarming was the high concentration of Zn. Therefore, in the presentation of the results, we focus on these metals.
Fig. 1 shows that metal uptake from about 70 to 100% for Zn, Pb and Cd. In the non-diluted effluent, the uptake was not sufficient for all metals, especially As and Cr. All values after treatment were however far below US EPA maximum concentration levels (MCL) (2003). Analysed concentrations (min-max) after treatment were 16-791 µg·L⁻¹ for Zn; 0.8-1.6 µg·L⁻¹ for Pb; <limit of quantitation (LOQ) – 4.3 µg·L⁻¹ for Cr; <LOQ – 0.66 µg·L⁻¹ for Cd; and <LOQ – 3.2 µg·L⁻¹ for As.

Competition for sorption sites is suggested as the main reason for the limited uptake of metals at the highest concentrations but the differences in chemical states of the metals in solution may also influence the sorption behaviour. The pine bark concentration added to the effluent solutions corresponds to the concentration of active carbon, currently used as an adsorbent at the effluent treatment plant. By increasing the mass of pine bark added to each batch in future studies, more sorption sites will be available, so that a larger proportion of the metals can be expected to be adsorbed. To fulfil the aims of low maintenance in the treatment method, no separation of small particles was conducted on the pine bark used. Therefore, the treatment efficiency could be further enhanced by using smaller particles of the adsorbent. According to Langmuir (1997), particles smaller than about 1 µm have a significant percentage of their atoms on their surface, which gives them an extremely high sorption capacity due to their unsatisfied surface charge which is related to their colloidal behaviour. This argues for an evaluation of the materials in finer grains.

The main heavy metal pollutant in the process waste water was Zn (Table 1). Langmuir and Freundlich isotherms were fitted to the adsorption data of Zn. Good fits were obtained for Zn (see Fig. 2). The model constants and Pearson correlation coefficients are given in Table 2. For Zn, the Freundlich isotherm gives higher correlation coefficients than the Langmuir isotherm.
Uptake of TNT

TNT was present in the non-diluted effluent at concentrations of 29.5 mg·L\(^{-1}\). In the diluted batches, the percentage uptake was high, approaching 80 %, whereas pine bark in the non-diluted effluent batch reduced TNT concentrations by only 50 %. As discussed earlier, it is suggested that an increased concentration of pine bark in the batches together with separation of finer grains, should further optimize the uptake. The percentage uptake of TNT by pine bark at the various initial concentrations (C\(_0\)) is shown in the left-hand part of Fig. 3.

Langmuir and Freundlich isotherms were fitted to the adsorption data. The model constants and Pearson correlation coefficients are given in Table 2. A reasonably good fit was achieved for TNT uptake to pine bark (see Fig. 3). At the highest equilibrium concentration, 15 mg·L\(^{-1}\), fit was not as good. Apart from experimental error, one explanation for this might be that competition for surface sites occurred in the system when the equilibrium concentration increased. Adsorption of TNT occurs simultaneously with the heavy metal ions. Further studies, with spiked solutions containing only individual substances would be necessary to model multi-solute effects.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>Langmuir isotherm</th>
<th></th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q ) (µg·g(^{-1}))</td>
<td>( b ) (L·µg(^{-1}))</td>
<td>Pearson correlation, ( r )</td>
</tr>
<tr>
<td>Zn</td>
<td>213</td>
<td>0.014</td>
<td>0.96</td>
</tr>
<tr>
<td>TNT</td>
<td>1.68 (mg·g(^{-1}))</td>
<td>0.19 (L·mg(^{-1}))</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Figure 2 Langmuir isotherm (whole line), Freundlich isotherm (dotted line) fitting for adsorption of Zn data (▲) to pine bark
Based on the Langmuir and Freundlich models, it is possible to estimate the bed life for a packed bed reactor. The estimation was conducted based on the determined apparent density, 0.69 g·cm⁻³. In the model, we have assumed a contact time of at least 24 hours, corresponding to the experiment. It is however possible that this time could be significantly decreased, which will be assayed in further experiments. Moreover, it is assumed that the waste water is equally distributed in the packed bed reactor. Fig. 4 gives the estimated capacity of a packed bed reactor as a function of the equilibrium (or influent) concentration based on the Freundlich and Langmuir isotherm model parameters.

**CONCLUSIONS**

The present study has been focused on finding a low cost and environmentally friendly alternative to adsorption of TNT and heavy metals with active carbon. We conclude that using low cost adsorbent pine bark to treat demilitarisation process effluents is possible. The metal and explosives uptake by pine bark was reasonably high, despite the small
amount of adsorbent and the complex effluent matrix. This makes it interesting to further investigate this low cost filter technique for industrial effluent treatment applications.

Adsorption equilibrium was calculated for Zn and TNT which showed that data could be fitted to Langmuir and Freundlich equations. We presented an estimation of the number of TNT contaminated bed volumes of waste that can be treated by a packed bed reactor based upon these equations.

In order to enhance the adsorption process, the concentration of pine bark could be increased to achieve a complete purification of the industrial effluent. Alternatively, the material can be crushed or separated so that the particles are smaller. Before exchanging active carbon for pine bark on-site, the effectiveness of the adsorption process to pine bark must be optimized to leave negligible levels of metals and explosives in the process water that continues towards the biological treatment step.

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