Development of an integrated approach for the removal of tributyltin (TBT) from waterways and harbors: Prevention, treatment and reuse of TBT contaminated sediments.

Task 3551 - Remediation of Sediments: Treatment of the Aqueous Phase

Full-scale Filtrate Water Treatment

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EXECUTIVE SUMMARY

Within the framework of the EU project TBT - Clean LIFE02 ENV/B/00341, several sediment remediation techniques were examined on TBT contaminated sediments. The TBT Clean project was supervised by an environmental consultant (ERM) and carried out by the Port of Antwerp, APEC, two private contractors (ENVISAN and DEC) and a research lab (ERC).

Several techniques for the remediation of TBT contaminated sediment were tested on lab-, pilot- and full-scale. All remediation techniques had one thing in common, that an aqueous phase, containing TBT was generated. In the case of sediment chemical washing, the aim was in fact to transfer the TBT contamination from the solid to the aqueous phase. ENVISAN performed some full-scale experiments on the filtrate water coming from the sediment dewatering following the chemical washing or prior to the thermal treatment.

Because it is reported that TBT is highly attracted to suspended or fixed particulate matter in water, an adsorption process was considered to be the most efficient and the less expensive technique. Full-scale tests with activated carbon, a non-selective absorber, were performed at the ENVISAN treatment centre in Gent. These tests showed a complete removal of TBT form the aqueous phase, at different preconceived pH values, ranging from 7 to 11.
1. GENERAL INTRODUCTION

During recent decades, tri-butyltin (TBT) has frequently been used as paint additive to prevent biofouling and algae growth on ship hulls. As the ship moves through the water, TBT is very slowly released from the polymer matrix of the paint layer by a process of self-polishing. The highly toxic effect of TBT on settling water organisms prevents them from sticking on the ship hulls.

Because of the slow release and its strong tendency to adsorb onto sediments, TBT is detected in significant concentrations in sediments along busy maritime traffic routes and in port and harbour docks (Alzieu, 1991). Due to the chemical characteristics of the organotin compounds, sediment has acted as a sink for these chemicals. Average concentrations of 50 to 1,000 µg/kg Dry Weight (DW) were detected at the Port of Antwerp.

Furthermore, even higher TBT concentrations can be detected in ship repair yards. Because the effectiveness and durability of the paint coats are limited, the old paints must be removed in regular intervals to be replaced by a new layer of antifouling paint (Evans et al., 1975). The depainting and paint coating is done in the dry-docks at ship repair sites. Historically, the wastewater coming from these activities, possibly loaded with paint flakes containing TBT, has been discharged in the harbour. A sampling campaign in the vicinity of the wet and dry docks of the Antwerp Ship Repair site, gave TBT concentrations up to more than 90,000 µg TBT/kg DW.

Three types of TBT contamination in the sediment can be identified (Reed, 2002). Firstly, the larger paint flakes that can be found close to the ship repair sites. This is the contamination that causes the extremely high TBT concentrations and also large variations in the sediment at the Antwerp Ship Repair site. Secondly, there are the small paint particles derived from the high pressure hosing of the ship hulls and finally the TBT that is slowly released and adsorbed to the sediment.

Therefore, sediment has become a reservoir for possible remobilization of TBT in the environment either through diffusion out of the sediment or release during resuspension of the contaminated sediment (Harris et al., 1996). From a toxicological point of view, TBT is a very harmful chemical because of its potential biocidal properties and adverse effects on non-target organisms. Effects of TBT on the aquatic fauna, even at low concentrations, are e.g. slower growth rate, sex mutation and sterility and cell deformations. In general TBT appears to have a hormone disturbing effect and is highly toxic for shellfish and other sea organisms. Besides, it is supposed that TBT can also have a negative influence on the immune system of bigger mammals, such as dolphins. Therefore, a world-wide ban has been placed on the use of TBT in ship paints and on the relocation of dredged material, contaminated with TBT, in open sea. Since 1st of January 2003, this prohibition has seriously affected highly industrialised ports.
In addition to the stringent legislation on the primary release via TBT containing anti-fouling paints, the development of an effective remediation method to treat historically contaminated sediment is equally important.

The only applicable real scale treatment for TBT contaminated dredged sediment for the moment is the disposal in controlled landfills after prior dewatering. Within the framework of an EU project (TBT – CLEAN LIFE02 ENV/B/000341), various sediment remediation techniques were being examined. The choice of the different remediation techniques was always based on the fact that the degradation of TBT and the remediation of TBT contaminated sediment is influenced and can be enhanced by factors such as pH, temperature, sunlight (UV), oxygen concentration, the possibility to concentrate the TBT contamination and the transfer from the solid to the aqueous phase.

Several techniques for the remediation of TBT contaminated sediment were tested on lab-, pilot- and full-scale. When TBT contaminated sediment could be treated or a part of it could be treated, the volume that needs to be disposed in dumpsites would be reduced. Moreover, cleaned sediments could than be used as secondary materials, if complying with the reuse criteria.

For all the remediation techniques that were examined, an aqueous phase was generated that contained a certain TBT concentration. Due to the very low toxic levels for aquatic organisms, a treatment of the aqueous phase, in the framework of the remediation of TBT contaminated sediments, is thus also very important.

The TBT-Clean project is supervised by an environmental consultant (ERM) and carried out by the Port of Antwerp, APEC, two dredging companies (ENVISAN and DEC) and a research lab ERC. ENVISAN examined several techniques for the remediation of the TBT contaminated sediment on lab-, pilot- and/or full-scale.
2. FULL-SCALE FILTRATE WATER TREATMENT

2.1. Introduction

In the framework of the TBT – Clean project, a lot of remediation techniques for the TBT containing sediments were examined. All remediation techniques had one thing in common, that an aqueous phase was generated. For a few of these techniques, such as thermal treatment (see TASK 3550 : Remediation of Sediments - Treatment of the Solid Phase : Full-scale Thermal Treatment) and chemical washing (see TASK 3550 : Remediation of Sediments - Treatment of the Solid Phase : Sediment Chemical Washing), a sediment dewatering step was incorporated, generating a large amount of TBT containing filtrate water. Due to the very low toxic levels for aquatic organisms, a treatment of the filtrate water is thus also very important.

It is reported in TASK 3544 : Sveenring of Technologies that TBT is susceptible to oxidation and photo-degradation. Radicals react at the tin-carbon bond, and remove one butyl-group each time. This can be accelerated by UV-radiation (see lab-scale tests performed by ERC in the framework of TASK 3551 : Remediation of Sediments - Treatment of the Aqueous Phase). However, because TBT is highly attracted to suspended or fixed particulate matter in water, an adsorption process may prove to be the most efficient and the least expensive means to reduce / remove TBT from the aqueous phase. Activated carbon is a material that adsorbs soluble organic matter very well, thus also TBT. Although activated carbon is not a selective adsorber, the organic load was rather limited, because of the low organic contamination (COD) in the filtrate water from the sediment dewatering.

It is furthermore reported that the degradation of TBT in the aqueous phase, under the same conditions as in sediments, is almost 4 times higher than in sediments. The explanation is the fact that contaminants in the water phase are easier accessible. Also the removal or degradation of TBT from the aqueous phase is far more easier compared to the removal or degradation of TBT from the solid phase.

2.2. Task Objective

As mentioned in TASK 3544 : Screening of Technologies, the degradation of TBT and the remediation of TBT contaminated sediment can be enhanced by pH, temperature, sunlight (UV), oxygen concentration, the possibility to concentrate the TBT contamination and the transfer from the solid phase to the aqueous phase. Besides, the release of TBT from the solid phase to the aqueous phase is influenced by factors such as pH and salinity. Therefore, a TBT containing aqueous phase is generated during a lot of the examined remediation techniques, especially those techniques incorporating a sediment dewatering by means of chamber filter presses, with lime as dewatering agent.

The task objective was to remove TBT from the aqueous phase by means of an activated carbon filtration. This was based on the strong tendency of TBT to adsorb to particulate organic matter (Fent, 1996).
2.3. Lab-scale experiments

Lab-scale experiments concerning the treatment of the aqueous phase, by means of adsorption to activated carbon (AC), were carried out by ERC. Filtrate water from the sediment dewatering with lime was used for the lab-scale tests. Batch shaking experiments showed an efficient adsorption of organotins onto the activated carbon.

Preliminary tests with granular activated carbon, gave a very slow (± 4h) TBT removal at high pH (> 12) and a very efficient (> 99%) and rapid (in less then 1h) removal at a pH ranging from 7 to 9. The pH of the filtrate water is thus an influencing factor in view of the TBT removal by filtration in an activated carbon filter.

Figure 1: TBT removal in a batch shaking set-up with activated carbon at different pH

In Figure 1, it is also shown that the available adsorption surface (or contact time) is an important factor, influencing the TBT removal. Therefore some additional lab-scale tests were conducted, in which the same amount of activated carbon (AC) was added, however crushed. The results of these additional lab-scale tests are shown in Table 1. The Table clearly shows the importance of a good contact between the filtrate water and the activated carbon. With crushed activated carbon, a complete TBT removal was achieved after one hour, even at a pH > 12.

Table 1: TBT concentration after 1h shaking in a batch shaking set-up

<table>
<thead>
<tr>
<th>Added Activated Carbon (AC) (g/l)</th>
<th>pH</th>
<th>TBT conc. (µg/l) after 1h</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 g/l - granular</td>
<td>&gt; 12</td>
<td>6.24</td>
</tr>
<tr>
<td>2 g/l - granular</td>
<td>9</td>
<td>0.088</td>
</tr>
<tr>
<td>2 g/l - granular</td>
<td>7</td>
<td>0.044</td>
</tr>
<tr>
<td>2 g/l - crushed</td>
<td>&gt; 12</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>2 g/l - crushed</td>
<td>7</td>
<td>&lt; DL</td>
</tr>
</tbody>
</table>
2.4. Treatment scheme

Based on the results of the lab-scale experiments, a treatment scheme, incorporating an Activated Carbon (AC) filtration was envisaged. The treatment scheme is shown below (see Figure 2). The filtrate water stock was pumped into a first pH adjustment tank. In this tank, the pH of the filtrate water was adapted to the prescribed value by means of a pH control and the addition of H$_2$SO$_4$ (96%). Testruns were executed in a pH range from 7 to 11.

![Figure 2: Treatment scheme for the remediation of TBT containing filtrate water in an activated carbon filter](image_url)

After the pH control, the filtrate water was pumped to an Activated Carbon (AC) filter at 10 m$^3$/h. Activated carbon is very efficient adsorbing material for the removal of a wide range of organic compounds and is generally utilised to remove low concentrations of non-degraded organic compounds. The principle of the activated carbon filtration is based on the high adsorbing capacity, because of the high internal surface of the activated carbon. The activated carbon filter was designed for a filtrate water flow of 10 m$^3$/h and an assured hydraulic retention time of 20 minutes.

The activated carbon filter was fed on top and the filtrate water percolated downstream. From the bottom of the filter, the filtrate water was pumped to a second pH adjustment tank. The latter was needed for the testruns at high pH, to be able to discharge the cleaned water at a pH between 6 and 9.
2.5. Full-scale experimental set-up

For the full-scale experiments, the pH of the filtrate water was controlled respectively at pH 7, 8, 9, 10 & 11 in a first pH adjustment tank with a retention time of about 15 minutes (see Photo 1). The pH adjustment tank was provided with a mixing pump, a pH – control and a dosage of H₂SO₄ (96%).

![Photo 1: pH adjustment tanks used for the full-scale filtrate water experiments](image1.jpg)

After the pH adjustment, the filtrate water was directly pumped to an Activated Carbon (AC) filter (see Photo 2). In general, a necessary step prior to activated carbon filtration is the removal of all particulate material, e.g. by means of a sandfiltration, in order to exclude the possibility of clogging. For the full-scale filtrate water experiments, the preceding sandfiltration was not foreseen, since the amount of suspended solids (on a 0.45 µm filter) in the filtrate water from the sediment dewatering is very low, normally below 20 mg/l.

![Photo 2: Activated Carbon filter used for the full-scale filtrate water experiments](image2.jpg)
The effluent of the activated carbon filter was not directly discharged because of the experiments conducted at high pH. Therefore the effluent was lead into a second pH adjustment tank in which the pH was adjusted between 6 and 9, which are the imposed discharge limits.

2.6. Experimental data & discussions

2.6.1. Introduction

The filtrate water, originating from the full-scale sediment dewatering with lime as dewatering agent, conducted to prepare the sediment cakes for the full-scale thermal treatment (see TASK 3550: Remediation of Sediments – Treatment of the Aqueous Phase: Full-scale Thermal Treatment), was stored to be able to perform the full-scale filtrate water experiments. The filtrate water was sampled at the end of the dewatering tests to perform the lab-scale filtrate water test. The TBT concentration in the filtrate water was about 9.8 µg/l.

During the full-scale filtrate water treatment tests, samples were taken again and a TBT concentration of only ± 6.5 µg/l was detected. During the storage time of about two months, between the full-scale sediment dewatering tests and the full-scale filtrate water treatment tests, the TBT was thus decreased with 34%. This was probably due to the storage of the filtrate water in open air and to the fact that TBT compounds are susceptible to photo-degradation. Under influence of sunlight, hydroxyl radicals are produced and these radicals react at the tin-carbon bond.

2.6.2. Full-scale filtrate water tests

In preparation for the full-scale filtrate water treatment tests, the buffer capacity of the filtrate water was detected. Sulfuric acid (H₂SO₄, 96%) was used to determine the filtration curve. The sulfuric acid was diluted in order to have a solution of 1 meq/ml (0.5 M H₂SO₄). The diluted acid solution was added gradually to 1 lit. of filtrate water and pH was noted during the titration. The titration curve is shown in Figure 3. Based on this figure, one could determine the amount of acid that was needed to adjust the pH of the filtrate water to a certain value (see Table 2).

<table>
<thead>
<tr>
<th>pH value</th>
<th>meq/l acid (H₂SO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 11</td>
<td>17 meq/l</td>
</tr>
<tr>
<td>pH 10</td>
<td>22 meq/l</td>
</tr>
<tr>
<td>pH 9</td>
<td>25 meq/l</td>
</tr>
<tr>
<td>pH 8</td>
<td>27 meq/l</td>
</tr>
<tr>
<td>pH 7</td>
<td>28 meq/l</td>
</tr>
</tbody>
</table>
During the full-scale filtrate water treatment tests, the pH was controlled at the preconceived value. The influent and effluent of the activated carbon filter was sampled, by taking several subsamples during each testrun. In Table 3, the TBT concentrations in the influent and effluent samples are shown. The results showed a very efficient TBT removal in an activated carbon filter. The TBT concentrations in the effluent were below detection limit for each testrun at the preconceived pH value. The activated carbon filter was fed on top and was operated in order to assure a retention time of 20 minutes. Because of the large specific surface of the activated carbon and the close contact between the filtrate water and the activated carbon, TBT was completely removed, which confirmed reported data in literature of > 99% removal.

Table 3: TBT concentration in the influent and effluent of the activated carbon filter for different preconceived pH values

<table>
<thead>
<tr>
<th>pH</th>
<th>INFLUENT</th>
<th>EFFLUENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 7</td>
<td>6.2</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>pH = 8</td>
<td>6.3</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>pH = 9</td>
<td>6.5</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>pH = 10</td>
<td>6.4</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>pH = 11</td>
<td>6.5</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

Besides the effect on TBT, also the effect on other important parameters such as COD and Total nitrogen (Ntot) was followed. It is well known that activated carbon is a non-selective adsorber. Therefore, besides TBT, also COD is partially removed in an activated carbon filter. In Table 4, the COD concentrations in the influent and effluent samples of the activated carbon filter are shown.
Table 4: COD concentration in the influent and effluent of the activated carbon filter for different preconceived pH values

<table>
<thead>
<tr>
<th>pH</th>
<th>CODtot (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>INFLUENT</td>
</tr>
<tr>
<td>pH = 7</td>
<td>128</td>
</tr>
<tr>
<td>pH = 8</td>
<td>142</td>
</tr>
<tr>
<td>pH = 9</td>
<td>166</td>
</tr>
<tr>
<td>pH = 10</td>
<td>146</td>
</tr>
<tr>
<td>pH = 11</td>
<td>134</td>
</tr>
</tbody>
</table>

Table 4 shows a COD removal in the activated carbon filter of about 67% in average, with a maximum removal of 80% at pH 8. It is known that the efficiency of an activated carbon filter is decreasing with an increasing pH. This was indeed confirmed in the full-scale water treatment tests.

During the full-scale filtrate water treatment tests, the COD concentration in the influent of the activated carbon filter was always higher than 125 mg/l, which is often prescribed as discharge limit. After treatment in an activated carbon filter, the COD concentrations in the effluent were, even at high pH, always below this 125 mg/l.

Since activated carbon is a non-selective adsorber, all organic compounds can be adsorbed. The organic load of the activated carbon was thus higher than the TBT – load. However, since the COD concentration in the filtrate water, which is an overall measure for the organic compounds, was rather low, the overall load of the activated carbon is low. Based on the figures of Table 4, one can estimate that 3.200 m³ of filtrate water can be treated with 1 ton of activated carbon.

In Table 5, the Total Nitrogen (Ntot) concentrations in the influent and effluent samples of the activated carbon filter are shown. The Ntot concentration in the filtrate water (influent) was rather low. A part of the Ntot concentration might have disappeared during the storage period of about two months, between the full-scale sediment dewatering tests and the full-scale filtrate water treatment tests. Because of the high pH of the filtrate water, ammonia nitrogen ((NH₄⁺ – N), which is included in the Ntot measurement and counts for, in average, 85% of the Ntot concentration, might have partially stripped out of the filtrate water.

The figures in Table 5 show a rather limited removal of Ntot. This was because ammonia nitrogen (NH₄⁺ – N) is not adsorbed on activated carbon and about 85% of the Ntot was NH₄⁺ – N. The low concentration of the Ntot that was removed, was mainly organic nitrogen.
Table 5: Ntot concentration in the influent and effluent of the activated carbon filter for different preconceived pH values

<table>
<thead>
<tr>
<th>pH</th>
<th>IN</th>
<th>OUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>26</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>24</td>
<td>17</td>
</tr>
<tr>
<td>9</td>
<td>26</td>
<td>13</td>
</tr>
<tr>
<td>10</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>19</td>
<td>16</td>
</tr>
</tbody>
</table>

The suspended solids in the filtrate water were not determined, because the concentration in the filtrate water was always very low, much lower than the usual discharge limit of 60 mg/l. Besides, during the storage period of the filtrate water, a settlement of suspended solids might have occurred. It is known that the amount of suspended solids in the influent of an activated carbon filter should be as low as possible to avoid clogging. In the effluent of an activated carbon filter, the suspended solids concentration is generally below 5 mg/l.

Also Ptot was not analysed, because this is also a parameter that doesn’t cause any problem, certainly not because of the very low amount of suspended solids in the filtrate water and in the effluent of the activated carbon filter.
3. FINAL CONCLUSIONS

The task objective was to remove TBT from the aqueous phase by means of an activated carbon filtration. This was based on the strong tendency of TBT to adsorb to particulate organic matter. Lab-scale experiments concerning the treatment of the aqueous phase, by means of adsorption to activated carbon (AC), were carried out by ERC. Filtrate water from the sediment dewatering with lime was used for the lab-scale tests. Batch shaking experiments showed a very efficient (> 99%) adsorption of organotins onto the added activated carbon at a pH ranging between 7 and 9. Further lab-scale tests also showed the importance of the available adsorption surface (or contact time) and thus the good contact between the filtrate water and the activated carbon for the removal of TBT.

Full-scale filtrate water treatment tests were executed in which the pH was adjusted and the assured hydraulic retention time in the activated carbon filter was 20 minutes.

The filtrate water was fed on top of the filter and percolated, thus in close contact with the activated carbon, downwards. The full-scale filtrate water treatment tests confirmed the results of the lab-scale experiments. A complete removal of TBT was detected for all the preconceived pH values. Besides, also the COD concentration was removed for 67% in average. After treatment in an activated carbon filter, the COD concentration was always below 125 mg/l, which is a general discharge limit.
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