Removal of ecotoxicity and COD from tank truck cleaning wastewater
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ABSTRACT
Tank truck cleaning (TTC) activities generate highly complex wastewater. In a previous study, we found that a significant ecotoxic effect was still present in biologically treated TTC wastewater. The aim of the present study was therefore to investigate the removal of acute toxicity from TTC wastewater by a sequence of technologies routinely applied for industrial wastewater. Acute toxicity was assayed with the widely applied and standardized Vibrio fischeri bioluminescence inhibition test. During a 5-month period, raw wastewater was grab-sampled from a full-scale TTC company and treated by the different unit operations on a laboratory scale. Chemical pretreatment of the wastewater by coagulation with FeCl₃ removed approx. 38% of the influent chemical oxygen demand (COD) and reduced the bioluminescence inhibition by 8%. Biological treatment with activated sludge subsequently removed another 77% of the remaining COD. This treatment step also reduced the bioluminescence inhibition but the removal efficiency varied strongly from 5 to 92% for the different samples. Powdered activated carbon almost completely removed the remaining COD and inhibition in all samples. The results suggest that conventional technologies did not suffice for complete removal of toxicity from TTC wastewater, and that advanced wastewater treatment technologies such as activated carbon are required for a satisfactory detoxification.

Key words | activated carbon, activated sludge, coagulation, industrial wastewater, Water Framework Directive, whole effluent toxicity

INTRODUCTION
Currently, water quality standards and wastewater discharge limits in the European Union are mostly based on a limited number of chemical parameters (e.g. Vlarem II 1995 for the region of Flanders). The aim of The European Water Framework Directive (2000/60/EC) is to obtain water bodies with a ‘good’ biological quality. The biological or ecological impact of complex industrial effluent discharges however, cannot be estimated using chemical assays only, but should be measured using whole effluent toxicity (WET) tests (e.g. OSPAR 2005).

A typical example of a complex industrial effluent is the water originating from tank truck cleaning (TTC) activities. The TTC process mainly involves the cleaning of tank truck interiors. The wide range of transported cargo, ranging from food products to hazardous chemicals, results in wastewater with a highly variable composition. In a previous study, we found that a significant residual toxicity was still present in biologically treated TTC effluent (De Schepper et al. 2010).

The aim of the present study was therefore to investigate the removal of acute toxicity from TTC wastewater by a sequence of key unit operations applied during the treatment of industrial wastewater, i.e. chemical coagulation, activated sludge treatment and sorption by activated carbon. The treatments steps were performed on a laboratory scale, in order to assess the full toxicity removal potential of these technologies. In addition, we intended to compare the response of the fast Vibrio fischeri bioluminescence inhibition test (applying a 30 min contact time) with the standard 72 h algal growth inhibition test, as the latter was found to be significantly more sensitive in previous work with TTC effluent (De Schepper et al. 2010).
METHODS

Sampling

The full-scale TTC wastewater treatment plant consists of the following steps: oil separation, primary coagulation and sedimentation, aerobic activated sludge treatment and secondary sedimentation, and finally tertiary coagulation and flotation (for the removal of suspended solids). The wastewater is temporarily buffered in equalization tanks before primary treatment, and before biotreatment. We collected five raw wastewater samples from the equalization tank before primary treatment. The grab samples were taken once a month during a 5-month period. The samples were kept cool (at 4°C) in the dark before analysis.

Laboratory-scale treatment

In the laboratory, the samples were sequentially subjected to (1) chemical coagulation with Fe(III), (2) aerobic biological treatment with activated sludge and (3) sorption with activated carbon.

The chemical coagulation experiments consisted of two phases. In a first phase, the coagulation was performed in 500 mL glass beakers using a range of Fe(III) doses. The raw wastewater samples were first acidified with sulfuric acid to a pH value of 3–4. Increasing concentrations of FeCl₃, from 0 to 250 mg Fe/L were then added while the samples were intensively mixed (200 rpm, using a Lovibond jar-tester). Subsequently, the mixing rate was lowered (to 25 rpm), and the pH was increased again with sodium hydroxide (1 mol/L) to approx. 8.0–8.2. In the final step the coagulated samples were allowed to settle for half an hour.

In the second phase, we repeated the coagulation for each wastewater sample on 3 L batches using only two Fe(III) doses. The selected coagulant doses were based on the results from the first phase, and consisted of a ‘low’ (20 mg/L) and a ‘high’ (150 mg/L) Fe(III) dose. The samples that were chemically treated in this second phase, were subsequently fed to endogenously respiring activated sludge originating from the full-scale wastewater treatment plant, in order to simulate biological treatment. The duplicate laboratory-scale bioreactors were operated in a batch-wise fashion, where 250 mL of pretreated wastewater was added to 500 mL of activated sludge. The biotreatment experiments were performed three consecutive times for each sample. The end of the biological reaction was detected by respiration measurements using an automated respirometer, as low and constant final respiration rates (about 2 mg O₂/g MLSS.h, MLSS being the mixed liquor suspended solids content of the activated sludge) indicated that no biodegradable material was left. Samples for chemical oxygen demand (COD) and for inhibition measurements were taken within 1 min after mixing of the wastewater with the sludge, and at the end of each experiment.

Finally, powdered activated carbon (PAC, Norit SA 2) was added to the biologically treated effluent samples. Activated carbon (at 10 g/L) was added to 100 mL filtered effluent in shake flasks. After a contact time of approx. 20 h on a rotary shaker (at room temperature), the activated carbon was separated from the liquid phase by filtration over a 0.45 μm glass fiber filter.

Analyses

Turbidity was measured using a portable turbidimeter (Hach model 2100P), and expressed as nephelometric turbidity units (NTU). COD and soluble COD (sCOD, i.e. COD analysis after filtration over a 0.45 μm glass fiber filter) were determined using micro-COD tubes according to Hach reactor digestion method 8,000. MLSS was measured gravimetrically after three consecutive centrifugation/washing cycles to remove the dissolved salts, and drying overnight at 105°C.

Ecotoxicity tests

The acute toxicity before and after each unit operation was assayed with the V. fischeri bioluminescence inhibition test (according to ISO 11348-1:1998). In brief, specific volumes of the test samples were combined with a luminescent bacterial suspension and incubated at 15°C during 30 min. The decrease in luminescence was measured after the 30 min exposure time, taking into account a correction factor for the luminescence intensity change of control samples. Bioluminescence was measured with a portable tube luminometer (Berthold Technologies Junior LB 9509). The wastewater concentration applied in most assays was 50 vol%, using a sodium chloride solution (20 g/L) to dilute the samples. The effective concentration of a test sample causing a 50% decrease in light production (EC50) was determined for selected samples only, using a dilution series from 6 to 50% in a sodium chloride solution (20 g/L). The calculation of the EC50 value was performed by linear regression of the relative loss of light (gamma value) as a function of the sample concentration (in vol%), on a log-log scale, according to the ISO protocol. Finally,
toxicity units (TU) were calculated as 100% divided by the EC50.

The toxicity of wastewater samples after activated sludge treatment, and after activated carbon treatment was also investigated with the 72 h algal growth inhibition test (EC50 determination according to OECD 201 using *Pseudokirchneriella subcapitata*).

**RESULTS AND DISCUSSION**

**The raw wastewater**

The COD of the untreated wastewater ranged from 3,032 to 6,990 mg/L with an average of 5,485 mg/L (Table 1). The wastewater influent caused a significant reduction in bacterial bioluminescence, with average inhibition values of 92% for the unfiltered and 88% for the filtered samples. A higher coefficient of variation (CV, calculated as the relative standard deviation) was observed for the COD values than for the inhibition data (Table 1). The results furthermore indicate that the majority of the toxicity was caused by the dissolved fraction of the wastewater pollutants, as only about 4% of the inhibition was removed by filtration.

**Chemical coagulation**

The average initial turbidity of the raw wastewater was 1,380 ± 650 NTU. The samples were treated with increasing concentrations of the chemical coagulant FeCl₃. Concentrations of Fe(III) as low as 20 mg/L decreased the turbidity by more than 80% (results not shown). Higher Fe(III) doses resulted in a clear supernatant with a turbidity of less than 10 NTU.

Figure 1 shows the effect of low and high Fe(III) doses on the COD and bioluminescence inhibition, for the five wastewater samples. The variable efficiency of chemical coagulation with TTC wastewater was illustrated by COD removal ratios ranging from 5 to 40% at low Fe(III) doses, and from 13 to 53% at high Fe(III) doses (Figure 1). Inhibition removal efficiencies also varied strongly, from 0 to 10% at low Fe(III) doses, and from 0 to 33% at high Fe(III) doses. Interestingly, the bioluminescence inhibition in samples 3 and 5 did not change significantly by coagulation, although the COD concentration decreased by more than 40% (Figure 1).

In comparison to our results, treatment of pulp and paper effluents, industrial landfill leachate and reclaimed municipal effluents with either ferric chloride or aluminum salts significantly removed the bioluminescence inhibition (Stephenson & Duff 1996; Petala *et al.* 2006; Gotvajn *et al.* 2009). Fe(III) concentrations above 1 g/L and aluminum sulfate (alum) at concentrations above 300 mg/L on the other hand resulted in an increased toxicity (Stephenson & Duff 1996; Al-Mutairi 2006). We did not observe these inhibitory effects (Figure 1), most probably because of the lower coagulant doses applied.

**Biological treatment with activated sludge**

Following the coagulation step, the wastewater samples were fed to parallel activated sludge systems. Figure 2
summarizes the effect of the biological treatment on COD removal and bioluminescence inhibition.

The residual scOD after activated sludge treatment ranged from 430 to 1,180 mg/L with an average of 720 mg/L. This corresponds to scOD removal efficiencies ranging from 69 to 83% with an average of 77%. The final scOD values measured in the present study are comparable to the scOD values obtained after activated sludge treatment in the full-scale installation.

Biological treatment also decreased the bioluminescence inhibition, with an average efficiency of 64%. The removal efficiency however was extremely variable, ranging from 5 to 92% (Figure 2). The results suggest that the toxicity in samples 1 to 4 was generally caused by biodegradable compounds. In contrast, the poor removal of inhibition observed for sample 5 indicates that the toxicity in that sample resulted from the non-biodegradable COD fraction present in the wastewater. Low (20 mg/L) or high (150 mg/L) Fe(III) doses applied in the preceding coagulation step had no significant effect on the efficiency of the activated sludge treatment (results not shown).

In general, biological treatment is considered to play a central role in the reduction of water ecotoxicity. In agreement with our results, a number of researchers report a significant decrease in bioluminescence inhibition after activated sludge treatment of both domestic and industrial wastewaters (Chandra et al. 2004; Hernando et al. 2004; Araújo et al. 2005; OSPAR 2005; Katsoyiannis & Samara 2007; Reginatto et al. 2009; Rosa et al. 2010; Ma et al. 2011).

Bacterial bioluminescence inhibition vs. algal growth inhibition

The bioluminescence inhibition caused by the biologically treated samples was below 50% for the first four samples (Figure 2), resulting in TU values below 2. The average TU value for sample 5 was 8.6 (95% confidence interval 7.0–10.6).

The ecotoxicity of the biotreated samples was also analyzed with the 72 h algal growth inhibition assay using Pseudokirchneriella subcapitata. The TU values ranged from 610 to 5,470, confirming the very high algal growth inhibition reported for the same type of wastewater in an earlier study (De Schepper et al. 2010).

Table 2 provides an overview of published WET data for effluents from various municipal and industrial activated sludge treatment plants. The results from the bioluminescence inhibition and Daphnia sp. mobility inhibition tests for TTC effluents are low and very comparable to most of the data reported in other studies. The algal growth inhibition values however are orders of magnitude higher (Table 2). These observations point out that the effect of TTC effluent in this particular case is a specific rather than a general ecotoxicity, e.g. caused by herbicidal compounds (Hernando et al. 2004; Vermeirssen et al. 2010). De Schepper et al. (2010) applied a novel treatment plant modeling supported toxicity identification procedure to deduce that the herbicide acetochlor was indeed a major toxicant in the effluent.

Although the V. fischeri bioluminescence inhibition test is a useful and reliable tool to rapidly monitor ecotoxicity removal from industrial wastewater (Araújo et al. 2005), our results clearly illustrate the importance of the application of a battery of tests to estimate the ecotoxicological impact of complex effluents (Manusadžianas et al. 2003; OSPAR 2005; Rosa et al. 2010).

Activated carbon treatment

The residual scOD after addition of powdered activated carbon (at 10 g/L) to the biotreated effluents ranged from 51 to 155 mg/L, corresponding to an average scOD removal efficiency of 88%. Likewise, the bioluminescence inhibition was very low after PAC treatment (average inhibition of
The algal growth inhibition after PAC addition ranged from 23 to 82 TU, corresponding to a reduction of more than 95%.

Activated carbon treatment is an established technology for the removal of a wide range of recalcitrant and/or toxic compounds from (waste)water (e.g. Bundschuh et al. 2011). It is important to note that the PAC doses used in the present study are orders of magnitude higher than the typical doses applied in industrial wastewater (20–500 mg/L; Çeçen & Aktas 2012), as we mainly wanted to screen the effect of carbon treatment. In further research, the PAC dosage for the removal of the acute ecotoxicity from TTC wastewater will be investigated in more realistic detail.

CONCLUSIONS

The findings from the present study suggest that conventional technologies such as coagulation and biological treatment did not suffice for complete removal of ecotoxicity from TTC wastewater. In view of the goals of the Water Framework Directive, advanced wastewater treatment technologies such as activated carbon treatment may be required for a satisfactory detoxification of TTC effluents.

The response of the rapid V. fischeri bioluminescence inhibition assay to the biotreated wastewater did not correspond with the highly sensitive 72-h algal growth inhibition test, indicating that the bacterial test alone may not be suitable for effluent quality monitoring.

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