Removal of Oxygen Demand and Acute Toxicity during Batch Biological Treatment of a Petroleum Refinery Effluent

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A survey of the process streams at an operating petroleum refinery showed that desalting water from the crude and splitter units had the highest concentrations of pollutants, and accounted for approximately one-third of the BOD and COD of the combined effluent. Combined effluent (234 ± 62 mg BOD/L, 510 ± 0 mg COD/L, and Microtox EC50 4.9 ± 0.4%) was treated using a laboratory-scale batch biological reactor. Ninety-three percent of BOD and 77% of COD were removed over the first 24 hours of biological treatment. Acute (Microtox) toxicity was reduced in two discrete stages; the first coinciding with BOD and COD removal and the second stage occurring after BOD and COD had been removed. A final EC50 value of 27.8% was achieved in batch tests. The two stages of toxicity removal correspond quantitatively to the toxicity removal observed during secondary and tertiary biological treatment at the petroleum refinery’s full-scale wastewater treatment plant.

Key words: refinery effluent, toxicity, biological treatment

Introduction

Water is used in a variety of operations during the separation and transformation of crude oil into gasoline, fuel oils, lubricating oils, asphalts and petrochemical feedstocks (Dold 1989). As a result, considerable quantities of wastewater are produced which contain a range of contaminants from hydrocarbons and aromatic organic compounds to heavy metals. The amount of wastewater discharged is dependent upon parameters such as the properties of the crude oil, types of processing units, final product mix, and method of treatment and disposal, and is specific to each refinery (UNEP 1987).

During the past several decades, pollution control measurements have largely been based on conventional pollutants such as oxygen-demanding materials and suspended solids that had demonstrable effects on the environment (Metcalf and Eddy 1991). In response to increasing concern surrounding effluent toxicity, mutagenicity and carcinogenicity, a considerable amount of work has been devoted to effluent characterization, and testing of specific components (Dold 1989). A num-

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ber of rigorous studies (Dorris et al. 1974; API 1978; Burks 1982; Chapman et al. 1994; Bleckmann et al. 1995) have not been able to identify the compounds or groups of compounds primarily responsible for toxicity in petroleum refinery effluents. Despite the inclusion of many specific compounds on priority pollutant lists (API 1978; Burks 1982; PACE 1985; PACE 1987; Gulyas 1995), regulations have moved toward whole effluent toxicity testing.

Several studies have examined the toxicity of refinery whole effluent. Bleckmann et al. (1995) measured the toxicity of refinery effluent to five fresh and salt water test organisms (daphnid shrimp, fathead minnow, mysid shrimp, sheepshead minnow, and Vibrio fischeri). Mysid shrimp were found to be the most sensitive, followed by Microtox (Vibrio fischeri). Sherry et al. (1997) measured the toxicity of treated effluent from three Ontario refineries using Microtox™, an assay based on the electron transport in submitochondrial particles, water flea (Daphnia magna), and rainbow trout (Oncorhynchus mykiss) bioassay. Only two assays (Microtox™ and the submitochondrial test) were sensitive enough to detect toxicity in the treated effluent. Based on these studies, and others (Aruldoss et al. 1998), it can be concluded that the Microtox test is a rapid and sensitive means to assay the toxicity of refinery effluent.

The Chevron refinery in Burnaby, B.C., processes 8000 cubic metres of crude oil daily into motor gasoline, diesel, jet fuels, asphalts, heating fuel oils, butanes, and propane. Approximately 1700 cubic metres of effluent are produced each day and are subjected to pre-treatment, primary, secondary and tertiary treatment prior to discharge to the Greater Vancouver Regional District (GVRD) sewers. As part of a longer-term strategy to obtain a direct discharge permit, a study was undertaken to assess the performance of the treatment system. This study had three main objectives: (1) to conduct a survey of various process streams to determine the relative loading from each, (2) to characterize the removal of oxygen demand and acute toxicity using lab-scale batch biological reactors, and (3) to compare these results with the operation of the full-scale wastewater treatment plant.

Materials and Methods

Source of Wastewater and Seed

Wastewater and seed were obtained from the wastewater treatment plant (WWTP) at the Chevron refinery. Prior to biological treatment, the effluent undergoes sour water stripping to remove H₂S and NH₃, oil/water separation in an API separator, dispersed air flotation for removal of emulsified oil droplets, and aeration with equalization to remove trace sulphides. The primary treated effluent is stored in holding pond #3 prior to further treatment. Since late 1996, to provide secondary and tertiary treatment of their wastewater, the refinery has been operating a WWTP that consists of a Deep Shaft Technology Inc. (DSTI™) (Fig. 1) activated sludge bioreactor followed by a dissolved air flotation clarifier and final effluent polishing biofilters. The treated effluent is routed to
the Greater Vancouver Regional District sewer system, where it receives further treatment prior to being discharged.

Samples collected at various points in the refinery (Table 1) were analyzed by Analytical Services Laboratory of Vancouver, B.C. (refer to Sample Analysis section for details). To carry out the lab-scale biological treatment portion this study, forty litres of combined petroleum refinery effluent were collected from holding pond #3 and stored in HDPE Nalgene jerry cans with minimal headspace at 4°C. Biomass was collected from the deep extraction sampling port of the DSTI, and used for seed in batch biological treatment reactors and BOD tests. Samples used to evaluate the performance of the full-scale treatment system were taken from three points: (1) the influent feed line to the deep shaft bioreator, (2) the inlet to the tertiary polishing biofilters and (3) the outlet of the tertiary polishing biofilters.

**Batch Biological Treatment**

The lab-scale batch treatability evaluation was carried out using a 15-L (13.4-L working volume) cylindrical jacketed Plexiglas batch reactor operated at 35°C and pH 8. Reactor temperature was maintained at 35°C by circulating water from a constant temperature bath (VWR Scientific, Model 1131) through the annular Plexiglas jacket encasing the reactor. Samples were collected from the sampling port at the bottom of the reactor. Building air supplied the reactor with 13 to 15 standard litres per minute (SLPM) of air. The air flow rate was measured using a digital flow meter (Matheson Gas Products, Model 8111-1424).

Before the run commenced, 14 litres of wastewater (Table 2) were warmed overnight to 35°C in the reactor. To prepare an active seed culture, two litres of biomass (6053 ± 26 mg SS/L) were aerated at 35°C overnight. Fifteen millilitres each of the following BOD nutrient solutions
Table 1. Characteristics of selected process water streams

<table>
<thead>
<tr>
<th>Substance</th>
<th>Desalting water</th>
<th>Spent caustic</th>
<th>Condensate</th>
<th>Boiler plant blowdown</th>
<th>All wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crude unit</td>
<td>Splitter</td>
<td>Alkylation</td>
<td>FCC</td>
<td>Polymerization</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.54</td>
<td>0.45</td>
<td>0.16</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Ammonia N</td>
<td>34.9</td>
<td>5.66</td>
<td>2.79</td>
<td>0.010</td>
<td>0.009</td>
</tr>
<tr>
<td>o-Phosphate</td>
<td>0.29</td>
<td>1.52</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.002</td>
</tr>
<tr>
<td>Sulphide</td>
<td>51.5</td>
<td>50.8</td>
<td>&lt;0.2</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Benzene</td>
<td>24.9</td>
<td>24.7</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>1.83</td>
<td>1.79</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Toluene</td>
<td>21.2</td>
<td>27.7</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>m-, p-Xylene</td>
<td>6.14</td>
<td>8.38</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>3.18</td>
<td>3.84</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>8.5</td>
<td>39.5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Total BOD</td>
<td>285</td>
<td>389</td>
<td>8</td>
<td>10.5</td>
<td>5</td>
</tr>
<tr>
<td>Total COD</td>
<td>921</td>
<td>1090</td>
<td>302</td>
<td>37.5</td>
<td>32</td>
</tr>
<tr>
<td>Phenols</td>
<td>1.9</td>
<td>3.7</td>
<td>0.21</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>pH</td>
<td>6</td>
<td>6</td>
<td>7</td>
<td>5.5</td>
<td>6</td>
</tr>
<tr>
<td>Average flowrate (L/min)</td>
<td>149</td>
<td>144</td>
<td>118</td>
<td>33.7</td>
<td>69.6</td>
</tr>
</tbody>
</table>
(Standard Method 5210) were added to the reactor: phosphate buffer, MgSO₄, CaCl₂, and FeCl₃ (APHA 1992). After the initial samples were collected (Table 2), aeration was initiated, and the remaining 12.3 L in the reactor were seeded with 1.12 L of biomass (6053 ± 26 mg SS/L) in order to obtain a MLSS concentration of approximately 635 mg/L. The DO in the reactor was monitored for the first 2 hours to ensure that the 13 to 15 SLPM aeration rate was sufficient to maintain the DO level above 5 mg/L.

Sample Collection and Preservation

After the reactor sampling port was purged, samples were collected and acidified to pH 2 or less with concentrated H₂SO₄ in order to arrest further biological activity. The samples were then filtered by vacuum filtration through Whatman 41 Ashless (11 cm diameter) filter paper. The resulting soluble sample fractions were stored at 4°C with minimal headspace.

Stripping Test

A stripping test was carried out in order to determine the relative contribution of stripping to COD and toxicity removal. The test was conducted in the six-litre (working volume) jacketed Plexiglas reactor. Reactor temperature was maintained at 35°C by circulating water from a constant temperature bath (VWR Scientific, Model 1131) through the annular Plexiglas jacket encasing the reactor. Samples were collected from the sampling port at the bottom of the reactor. Two aquarium pumps (Rolf C. Hagen Inc., Optima Model) supplied a total of five standard litres per minute (SLPM) of air to the reactor. The air flow rate was measured using a digital flow meter (Matheson Gas Products, Model 8111-1424). To augment agitation provided by aeration, mixing was provided by a stir bar and a magnetic stirrer (Fisher Scientific). In order to ensure abiotic conditions during this run, the pH of the wastewater was reduced to 2.

Table 2. Characteristics of wastewater used in the biological treatability study

<table>
<thead>
<tr>
<th></th>
<th>Amount</th>
<th>Rebhun and Galil 1987</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD (mg/L)</td>
<td>234 ± 62</td>
<td>268</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>510 ± 0</td>
<td>625</td>
</tr>
<tr>
<td>BOD/COD</td>
<td>0.46 ± 0.12</td>
<td>0.43</td>
</tr>
<tr>
<td>Toxicitya (EC₅₀ % v/v)</td>
<td>4.9 ± 0.4</td>
<td>— c</td>
</tr>
<tr>
<td>EPHb (C₁₀–₃₂) (mg/L)</td>
<td>17.3</td>
<td>40</td>
</tr>
<tr>
<td>Phenols (mg/L)</td>
<td>20</td>
<td>—</td>
</tr>
</tbody>
</table>

aMicrotox assay, 5-minute exposure.
bExtractable petroleum hydrocarbons.
c—; Not determined.
Sample Analysis

Wastewater quality parameters

Soluble BOD was measured according to Standard Method 5210 B, 5-day BOD test (APHA 1992). The pH of the preserved samples was adjusted to seven using concentrated NaOH prior to analysis. Biomass obtained from the WWTP was used to seed the BOD tests.

Soluble COD was measured according to Standard Method 5220 B, closed reflux, colourimetric method (APHA 1992). The pH of the preserved samples was not adjusted before testing. All samples were analyzed in triplicate, and their absorbance measured at 600 nm. A new calibration curve was prepared whenever new COD chemicals were prepared, using seven potassium phthalate standards of known COD concentration, ranging from 20 to 900 mg/L.

Suspended solids were measured according to standard method 2540 D (APHA 1992) with the exception that samples were analyzed in triplicate instead of duplicate. Solids analysis was always performed immediately after sampling.

Acute toxicity of effluent samples was determined using a Microtox™ 500 analyzer. Analyses were run using the full range test, according to standard procedures (Microbics 1992). The pH of the preserved samples was adjusted to seven using concentrated NaOH prior to analysis. The toxicity data were analyzed using Microtox™ computer software supplied by the Microbics Corporation.

Analyses for specific chemical compounds

Analytical Services Laboratories Ltd. (ASL) of Vancouver, B.C., performed the tests for the following compounds: volatile hydrocarbons (VH), benzene, toluene, ethyl benzene, xylene (BTEX), extractable petroleum hydrocarbons (EPH), phenols, oil and grease, fluoride, ammonia nitrogen, sulphide, and o-phosphate.

VH analysis was carried out according to the British Columbia Ministry of the Environment, Land and Parks (BC MELP) Method “Volatile Hydrocarbons in Water” (ASL 1999). The VH assay determines the concentration of volatile hydrocarbons of chain length C6-C10. BTEX analysis was based on U.S. EPA Methods 624/524 and 5030/8260. These procedures involved purge and trap extraction of the sample and subsequent analysis of the volatile components by capillary column gas chromatography with mass spectrometric detection (ASL 1999).

The EPH assay was carried out according to BC MELP Method for “Extractable Petroleum Hydrocarbons in Water by GC/FID,” July 1999. The procedure involved sample extraction with dichloromethane, which was thereafter transferred to toluene and analyzed by capillary column gas chromatography with flame ionization detection (ASL 1999).

Phenols were measured in accordance to Standard Method 5330 D, direct photometric method (ASL 1999; APHA 1992). Fluoride was measured using a selective ion electrode and methods adapted from Standard Method 4500-F (ASL 1999; APHA 1992). Ammonia nitrogen was mea-
sured using a selective ion electrode and methods adapted from Standard Method 4500-NH₃ (ASL 1999; APHA 1992). Phosphate was measured using methods adapted from Standard Method 4500-P (ASL 1999; APHA 1992). Sulphide was measured using the methylene blue colourimetric method adapted from Standard Method 4500-S₂ (ASL 1999; APHA 1992). Oil and grease were measured using procedures adapted from the EPA, Standard Method 5520, and the BC MELP (ASL 1999). The procedure involves an extraction of the entire water sample with hexane. This extract was then evaporated to dryness, and the residue weighed to determine oil and grease.

Data Analysis

Measured values
Replicate values for each sample were used to calculate an average and estimate an error on this latter value. Error was approximated as the 95% confidence interval. This interval was calculated with the confidence function built into the Microsoft Excel software package. This function uses a Student-t test and assumes a symmetric Gaussian distribution.

In the case of all the analyses performed, replicates actually originated from the same sample. Thus the error associated with these results is only representative of error imparted by the method of analysis itself and does not take into account errors in sampling and manipulation of the sample.

Calculated values
Error analysis was performed on BOD, COD, OUR, and Microtox™. Error on values that are the average of a series of results was estimated as the 95% confidence interval for the series.

Reported results
Values quoted in this paper are reported as the average ± the 95% confidence interval. Likewise, values plotted in graphs represent the average and the error bars represent the 95% confidence interval. All plotted values include error bars, although the data points sometimes hide the bars.

Results and Discussion

Sources of Pollutant Load at the Chevron Refinery
The results of the refinery stream survey are presented in Tables 1 and 3. The desalting water from the crude unit and splitter had the highest concentrations of pollutants, and accounted for approximately 32% of the BOD and COD of the combined effluent. The fact that greater than 100% recovery of BTEX components was measured, likely reflects losses due to volatilization of these compounds. The combined effluent grab sample from the refinery used for the biological treatment tests (Table 2) was similar to that reported in previous work (Pace 1985; Rebhum and Galil 1987).
The combined refinery wastewater initially contained 17.3 mg/L of EPH and 20 mg/L of phenols. Assuming a formula of $C_nH_{2n+2}$ for the EPH, a theoretical oxygen demand (ThOD) of 3.5 mg O$_2$ will be consumed per mg of EPH oxidized and 17.3 mg/L of EPH will exert an oxygen demand of 60.6 mg/L. Similarly, using a formula of $C_6H_6O$ for phenols, 2.4 mg O$_2$ will be consumed per mg of phenols oxidized and the initial 20 mg phenols/L will exert a ThOD of 47.6 mg/L. Combined, these two groups of compounds account for only a maximum of 46% of the initial 234 mg/L BOD and 21% of the initial 510 mg/L COD. Gulyas et al. (1995) conducted a study of the organic compounds at different stages of a refinery wastewater treatment plant, and found that the compounds detected [i.e., three iso-alkanes, traces of carboxylic acids, and acetic acid 2-(2-butoxyethoxy)-ethyl ester] did not account completely for the relatively high COD.

In lab-scale batch biological treatment, BOD and COD reduction occurred over the first 24 hours of treatment (Fig. 2). BOD and COD were reduced to final values of 16 and 116 mg/L, representing 93 and 77% removal, respectively. During this time, BOD removal in the full-scale system varied between 48 and 99%, (average 79.3% ± 14.4%) (Fig. 3). The shape of the degradation profiles was consistent with a multi-component wastewater. As predicted by the Monod equation, at high substrate concentrations ($S>>K_s$), the rate of substrate utilization for a given compound (or set of compounds) will be zero order.

### Table 3. Material balance for wastewater components from process water sampling

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mass flowrate predicted by sub-stream sampling (g/min)</th>
<th>Total mass flowrate measured in combined effluent (g/min)</th>
<th>% of total measured in captured by sampling program</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>0.19</td>
<td>0.33</td>
<td>57</td>
</tr>
<tr>
<td>Ammonia N</td>
<td>6.35</td>
<td>61.8</td>
<td>10</td>
</tr>
<tr>
<td>$o$-Phosphate</td>
<td>0.75</td>
<td>0.70</td>
<td>107</td>
</tr>
<tr>
<td>Sulphide</td>
<td>15</td>
<td>46.7</td>
<td>32</td>
</tr>
<tr>
<td>Benzene</td>
<td>7.25</td>
<td>4.47</td>
<td>162</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.53</td>
<td>0.37</td>
<td>143</td>
</tr>
<tr>
<td>Toluene</td>
<td>7.15</td>
<td>4.87</td>
<td>147</td>
</tr>
<tr>
<td>$m$-$p$-Xylene</td>
<td>2.12</td>
<td>1.84</td>
<td>115</td>
</tr>
<tr>
<td>$o$-Xylene</td>
<td>1.02</td>
<td>0.84</td>
<td>123</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>9.49</td>
<td>252</td>
<td>4</td>
</tr>
<tr>
<td>Total BOD</td>
<td>102</td>
<td>253</td>
<td>40</td>
</tr>
<tr>
<td>Total COD</td>
<td>355</td>
<td>940</td>
<td>38</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.85</td>
<td>5.74</td>
<td>15</td>
</tr>
<tr>
<td>Total water flow</td>
<td>599.3 L/min</td>
<td>1260.7 L/min</td>
<td>47.5</td>
</tr>
</tbody>
</table>
The residual COD was likely due to the presence of non-biodegradable compounds originally in the wastewater with a minor fraction due to the accumulation of soluble microbial products. Other studies on the biodegradation of refinery wastewater reported similar residual COD values. Eckenfelder (1988) compiled residual CODs from eight different biodegradation studies of petroleum and petrochemical wastewaters. The residual CODs varied from 22 to 106 mg/L (mean = 77, 95% C.I. = 22). Gulyas et al. (1995) determined the organic compounds at different stages of a refinery WWTP using GC-MS, and found that the few substances detected [i.e., three iso-alkanes, traces of carboxylic acids, and acetic acid 2-(2-butoxyethoxy)-ethyl ester], could not explain the 120 mg COD/L of
the effluent from the sedimentation tank. They concluded that this residual COD was due to humic acids, which were formed by the activated sludge process. It has also been found that certain bipolymers formed during aerobic biological wastewater treatment contain recalcitrant sugars, uronic acids, and amino acids (Hejzlar et al. 1986). Similarly, Chudoba (1985) showed that non-degradable organic by-products would accumulate in a biological treatment process.

The possibility that some of the residual COD was due to the sample preservation technique was also investigated. Since each sample was acidified after collection and then filtered prior to testing, it was hypothesized that the acidification process may have resulted in the dissolution of capsular cellular material. This would have resulted in a higher COD than if the samples had been filtered prior to acidification. Test results indicated that the preservation method did not significantly affect a sample’s COD, and the hypothesis was rejected.

Wastewater contaminants can also be removed by stripping or through sorption onto biological solids. While previous work has shown that sorption is not an important removal mechanism (Rebhun and Galil 1987; Eckenfelder 1988), air stripping is of particular concern during the biological treatment of petroleum wastewaters (Dold 1989). Results from the stripping test indicated that 3% of the COD was stripped over 52.5 hours, indicating that the primary mechanism of COD removal was biodegradation.

**Removal of Acute Toxicity during Batch Biological Treatment**

Rather than being continuously removed, as in the case of BOD and COD, toxicity appeared to be removed in discrete stages. Over the first 10 hours of biological treatment, the effluent EC_{50} increased from 4.9 ± 0.4% to 16.0 ± 3.2% (Fig. 2). This initial toxicity removal phase corresponded to removal of most of the phenols and EPH (Table 4) and all of the BTEX and methyl-t-butyl ether (results not shown). Acute toxicity remained constant until 48 hours of treatment when a second significant toxicity removal phase brought the final EC_{50} to 27.8 ± 1.6% at 72 hours. No further improvement in toxicity was observed beyond this point and the run was terminated at 120 hours. Stripping was not a significant mechanism in the removal of acute toxicity, accounting for an EC_{50} change from 4.1 ± 0.4% to 6.8 ± 0.6% over 52.5 hours.

The first stage of toxicity removal corresponded to the degradation of BOD and COD, and the second stage occurred after BOD and COD had been removed. This implies that compounds which were more resistant to biological treatment exerted the secondary toxicity. Since the second stage of toxicity removal was not associated with a further decrease in COD, the compounds contributing to toxicity were either not detectable by the COD test or they were compounds present in trace quantities. Certain toxic compounds have been designated as priority pollutants and regulated to the level of trace (µg/L) quantities (Eckenfelder 1988).

It is possible that the population of microbes that degraded the readily biodegradable compounds were not able to degrade the more recalcitrant compounds; and another population of microbes, with much slow-
er growth rates, eventually reached a level necessary for removal of the toxicity-contributing compounds. Eckenfelder (1988) found that in the treatment of petrochemical wastewaters, some toxic organics degrade very slowly in the activated sludge process. Therefore, long sludge retention times (SRT) are required to achieve acceptable toxicity reduction, in spite of the fact that BOD removal is achieved at considerably lower SRTs.

**WWTP Toxicity Monitoring Program**

A toxicity monitoring program was carried out at the refinery’s WWTP between January 26, 2000, and March 15, 2000. Over the same period, the first stage of biological treatment increased the EC$_{50}$ from $1.7 \pm 0.58$ to $14.8 \pm 3.97$, and the tertiary biofilters further increased the EC$_{50}$ value to $29.8 \pm 5.15$. These values correspond to the two stages of toxicity removal observed during batch biological treatment (Fig. 4). While these results indicate that there may be a limit to the extent of toxicity

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**Table 4.** Concentration of phenols and EPH during batch biological treatment (mg/L)

<table>
<thead>
<tr>
<th></th>
<th>Raw</th>
<th>0.5 h</th>
<th>3 h</th>
<th>10 h</th>
<th>24 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenols</td>
<td>20</td>
<td>0.34</td>
<td>0.16</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>EPH (C10–C32)</td>
<td>17.3</td>
<td>8.7</td>
<td>4</td>
<td>3.8</td>
<td>3</td>
</tr>
</tbody>
</table>

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![Fig. 4](image-url). Comparison of toxicity removal observed during the two stages of biological treatment at the Chevron WWTP (DSTI and tertiary biofilter) and during the two stages of laboratory batch biological treatment.
removal which can be realized using biological treatment, it is worth noting that the biomass used in the experimental batch runs was obtained from the high rate DSTITM bioreactor. As such, this microbial culture was comprised of fast-growing microbes selected for rapid removal of BOD and COD. Experiments using effluent from a long batch test and slow growing biomass from the biofilters will determine whether further toxicity removal can be achieved through biological treatment.

Conclusions

Desalting water from the crude and splitter units had the highest concentrations of pollutants, and accounted for approximately 32% of the BOD and COD of the combined effluent. VH and MTBE did not significantly contribute to BOD, COD, and acute toxicity. Phenols and EPH only accounted for a maximum of 46% of the initial BOD (i.e., 234 mg BOD/L) and 21% of the initial COD (i.e., 510 mg COD/L).

In lab-scale batch biological treatment, the major portion of the BOD and COD reduction occurred over the first 24 hours of treatment. Overall, BOD and COD removal were 93% and 77%, respectively. Toxicity appeared to be removed in discrete stages, with the first stage coinciding with BOD removal and the second stage occurring after BOD and COD had been removed. A final EC50 value of 27.8% was achieved in batch tests.

Comparison of the acute toxicity removal pattern in lab-scale batch biological treatment with that at the WWTP indicates that the DSTITM bioreactor at the refinery removes toxicity up to the first constant toxicity phase, followed by the removal of the more recalcitrant toxic compounds by the biofilters. Toxicity removal by the WWTP may be limited by the biodegradability of the residual material.

Acknowledgments

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