Biotreatment system removes selenium from refinery wastewater

Highlights of a pilot study show how a biotreatment technology significantly reduced selenium from a US crude oil refinery. Lori C. Donovan, R.E. Hanson, William Sheridan, and F. Stephen Lupton of Honeywell UOP - Industrial Wastewater Technologies explain the test results.

Laboratory and pilot testing conducted at a wastewater treatment plant located at the end of a pipe discharge location of a crude oil refinery in the western United States demonstrated that Honeywell UOP's XCEED™ SE Biotreatment technology can reduce selenium to levels in compliance with local regulations and allow discharge to a local municipal wastewater treatment plant without further treatment. The refinery needed to reduce selenium, which is present in the crude oil slate, in the final discharge from a level of approximately 200 micrograms per liter (µg/L) to less than 50 µg/L to meet the discharge requirements. The plant had previously run trials on various commercially available biological and chemical treatment technologies and subsequently evaluated the XCEED system to treat this effluent.

Laboratory bench testing and a field demo pilot test were used to validate the XCEED treatment system performance and collect data for full-scale design. For selenium treatment, the refinery sought a cost-effective, robust system that could handle influent water quality fluctuations while still achieving less than 50 µg/L total recoverable selenium in the treated effluent without post-treatment. The system had to be easy to operate with low labor and maintenance requirements, have a small footprint, and be flexible enough to scale up treatment as the refinery capacity grows.

Based on the positive results from the bench scale treatability test, an axenic onsite pilot study was conducted at the refinery site using a mobile XCEED SE biotreatment system, including inoculation, startup, and continuous forward flow. The pilot treated a slipstream of clarified water from the existing wastewater treatment plant (end of pipe) and evaluated different hydraulic test conditions.

The system removes selenium using UOP's immobilized cell biological treatment technology, which consists of a series of bioreactors and UOP's proprietary biological growth media, along with all associated process equipment, instrumentation, and laboratory equipment necessary for operation. The system was inoculated using nitrate-reducing cultures developed during the laboratory study.

Organic carbon and phosphoric acid were dosed prior to the first bioreactor to provide nutrients for biological growth. Nitrogen was not required due to nitrate present in the influent water.

The majority of the selenium present in the influent was dissolved, with selenium comprising approximately 80 percent of the dissolved selenium. The remainder of the selenium was primarily present as selenite.

Selenium removal

For all test conditions, effluent total recoverable selenium concentrations were less than the 0.05 mg/L total recoverable selenium target for discharge to the local sewer authority with two exceptions. The first exception occurred during the 24-h hydraulic retention time (HRT) after beginning forward flow. The second exception occurred after a power failure resulted in no nutrient addition to the bioreactor. After the power failure, influent nitrate concentrations increased.

Nitrate removal

Nitrate concentrations varied in the influent, with a large nitrate concentration spike occurring on day 30 due to an upset upstream. Although influent nitrate concentrations varied, the effluent nitrate concentration remained relatively stable, averaging less than 1 mg NO₃-N when upset conditions were excluded for pilot testing.

Table 1. Influent Water Quality Summary

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average</th>
<th>SD</th>
<th>SD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>influent pH (SU)</td>
<td>8.55</td>
<td>0.22</td>
<td>2.5</td>
</tr>
<tr>
<td>influent ORP (mV)</td>
<td>945</td>
<td>18</td>
<td>1.9</td>
</tr>
<tr>
<td>influent Dissolved Oxygen (mg/l)</td>
<td>3.05</td>
<td>0.20</td>
<td>6.5</td>
</tr>
<tr>
<td>influent Total Nitrate (mg/L)</td>
<td>16.7</td>
<td>0.20</td>
<td>1.2</td>
</tr>
<tr>
<td>influent Selenium, total recoverable (mg/L)</td>
<td>0.102</td>
<td>0.005</td>
<td>5.0</td>
</tr>
<tr>
<td>influent Selenium, filtered total recoverable (mg/L)</td>
<td>0.102</td>
<td>0.005</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Conclusions

Findings from the laboratory and pilot testing successfully demonstrated that Honeywell UOP's XCEED SE biotreatment technology can meet the total recoverable selenium target of 50 µg/L without the need for post-treatment, allowing the refinery to comply with local regulations. The main testing objectives that included achieving the local sewer total recoverable selenium limit, validating the design HRT treatment performance, and collecting sufficient data to optimize the design of the full-scale system were met.

- Selenium removal: Effluent total recoverable selenium concentrations were typically less than half of the 30-µg/L total recoverable selenium target with the two exceptions described above. This issue should not be a concern in the commercial system, which will be fully developed and have a larger biomass.
- Refinery wastewater quality: Pilot influent total recoverable selenium concentrations were variable. Approximately 80 percent of the influent was selenium and was present as selenite. The influent was also characterized by elevated DO and nitrate, which increase the organic carbon demand as both DO and nitrate must be removed prior to selenium reduction. The influent temperature and pH were within the range necessary for selenium reduction.
- Dissolved oxygen and nitrate removal: Variable DO in the refinery wastewater was consistently reduced to less than 0.2 mg/L in the effluent during pilot testing. Likewise, although influent nitrate concentrations varied, the effluent nitrate concentration remained relatively stable and averaged less than 1 mg NO₃-N when upset conditions were excluded for pilot testing.
- Nutrient addition: Organic carbon was added to provide an organic substrate for biological growth. Phosphoric acid was also added to provide phosphorus necessary for biological growth. A nitrogen-based nutrient was not required.
- Microbial inoculum: The pilot was inoculated with nitrate-reducing bacteria cultivated from the laboratory study, which successfully removed selenium after a short inoculation and start-up period.

Figure 1: Removal of Selenium from Refinery Wastewater in the XCEED Bioreactor

Figure 2: Removal of Nitrate from Refinery Wastewater in the XCEED Bioreactor