Refinery Wastewater Operations: Challenges Created from the Processing of Opportunity Crudes

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Abstract

Experience has shown that low molecular weight volatile organic acids play a role in both filamentous and non-filamentous bulking events in refinery wastewater systems. The work presented here tracks the progression of these acids as they go through the various primary and secondary systems of a refinery. This work also identifies a method that can easily be implemented at refineries to track the amount of volatile organic acids entering the waste treatment system. The results collected, along with microscopic observations of the activated sludge suggests a method to predict potential sludge bulking. The work presented here also suggests a method to identify which crudes have the highest potential to increase volatile organic acid loading to the wastewater system.

Keywords: Refinery, Organic acids, Zoogloea, Sludge Bulking.

Introduction

Low-cost Opportunity Crudes give modern refineries a feedstock which is often discounted with respect to benchmark crudes. These crudes give refiners substantially better margins, which improve overall profitability and generate greater returns to their shareholders. Some of these opportunity crudes are significantly discounted because they contain various contaminants that impact corrosion, fouling, and catalyst damage in various process units within the refinery.

In order to process some crudes containing specific contaminants and/or form tenacious emulsions with water during desalting processes, additional organic acids are added to both lower the pH of the water and pull the salts and other contaminants into the water phase. In some cases this pH reduction also aids in breaking emulsions during desalter operations and improves the quality of the water processed at the wastewater plant.

As discussed above, opportunity crudes can potentially create processing challenges and they may, under certain conditions present challenges to wastewater operations. These challenges include the need for significant improvement in primary treatment to control oil and oily solids carryover into the aeration basins. Other issues that have been observed are poor sludge settling in clarifiers due to filamentous bacteria growth and/or non-filamentous sludge bulking. The most common filamentous bacteria types observed during bulking events at refineries are those that
prefer environments containing low molecular weight organic acids and alcohols and/or those filamentous bacteria that prefer low dissolved oxygen conditions. This same type of environment also promotes the growth of amorphous Zoogloea which leads to non-filamentous bulking events.

The refinery studied experienced non-filamentous bulking issues related to significant growth of amorphous Zoogloea prior to the investigation. These studies were initiated to identify the conditions leading up to these bulking events.

**Materials and Methods**

**Sample Collection and Preparation:**

Samples were collected at the Equalization (EQ) Tank influent and effluent, the Dissolved Air Flotation (DAF) effluent, Aeration Basin, and at the clarifier effluent as shown in Figure 2. The samples were placed immediately into ice after collection to prevent any potential biodegradation.

The samples were brought to our laboratories for processing. Upon arrival, the samples were immediately centrifuged at 9250 rpm (14,636 xg) for 15 minutes in a Thermo Scientific Sorvall Legend XTR refrigerated centrifuge at a temperature of 4°C. The supernatant was then placed in a syringe and filtered through a sterile 0.45µm syringe filter into sterile centrifuged tubes. The samples were kept in a refrigerator until analyzed.

**Analytical Methods:**

Organic acids were identified and quantified using proprietary methods on a Dionex™ ICS5000 Ion Chromatograph.

Organic acids were also identified using the Hach™ Volatile Acids Method 10240 (DOC316.53.01259). This esterification method uses the TNTplus™ 872 reagents and reports volatile acids in the range of 50 to 2,500 mg/L as acetic acid.

Aeration Basin samples were examined using an Olympus CX41 Phase Contrast Microscope. Photomicrographs were captured using a Nikon Digital Sight DS-Fi1 camera.

**Results and Discussion**

The work described in this paper was initiated due to events surrounding non-filamentous bulking observed during the processing of certain crudes at a Gulf Coast refinery. Previous work, at other refineries, suggested that bulking due to amorphous Zoogloea was related to high levels of organic acids, especially acetic acid being present in wastewater entering the refinery aeration basins. The literature also suggested that the events being observed at oil refineries dealing with amorphous Zoogloea bulking issues are due to a selective advantage Zoogloea have for the organic acids entering the waste plant1. The photomicrograph on the left in Figure 1 shows the presence of amorphous Zoogloea during a bulking event at the refinery. This event was the
impetus for an initial organic acid study conducted at the refinery. The photograph on the right in Figure 1 was taken during the initial organic acid study.

The organic acid characterization studies were conducted with weekly samples collected during a five week period. Table 1 shows the results generated for the EQ Tank influent sample point using ion chromatography.

Table 1

<table>
<thead>
<tr>
<th>Organic Acid</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic</td>
<td>55</td>
<td>11</td>
<td>137</td>
<td>134</td>
<td>69</td>
<td>81</td>
</tr>
<tr>
<td>Acetic</td>
<td>100</td>
<td>32</td>
<td>69</td>
<td>74</td>
<td>90</td>
<td>73</td>
</tr>
<tr>
<td>Propionic</td>
<td>30</td>
<td>10</td>
<td>33</td>
<td>18</td>
<td>27</td>
<td>24</td>
</tr>
<tr>
<td>Formic</td>
<td>BDL</td>
<td>1</td>
<td>BDL</td>
<td>BDL</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Butyric</td>
<td>ND</td>
<td>3</td>
<td>9</td>
<td>BDL</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Valeric</td>
<td>ND</td>
<td>ND</td>
<td>6</td>
<td>BDL</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

ND - Not Detected
BDL - Below Detection Limit

Glycolic acid in these samples was introduced into a desalter at this refinery for acidification and metals removal purposes. All the other acids have their origin in the processed crude, at the time of sample collection. Figure 2 below shows the fate of volatile organic acids through primary and secondary wastewater treatment. The values reported are for week #3 of the study. Similar results were observed for each of the other weeks in this study.

Figure 1: Microscopic Floc Examination
The investigation clearly shows that significant biological activity was occurring in the EQ tank with reduction of organic acids as they pass through the EQ tank. Reduction in organic acids has been observed in prior work at other refineries but not documented to this extent. As expected, the volatile organic acids are completely removed in the secondary system. The results of the study clearly showed low levels of organic acids entering the aeration basin. This could explain the lack of amorphous Zoogloea observed in the samples and is documented in the photomicrograph in Figure 1.

While the organic acid data could prove valuable in predicting potential conditions for bulking in the secondary clarifiers, organic acid analysis using ion chromatography in a refinery environment would not be practical. An easier method that could be conducted by wastewater operators on site would be ideal.

To this end, the use of the Hach™ TNTplus™ 872 method for volatile organic acids was evaluated. The test can be conducted on site with readily available test equipment. The test reports values as mg/L of acetic acid with a concentration range from 50 to 2,500 mg/L as acetic acid.

The Hach™ method was evaluated in conjunction with ion chromatography to determine the accuracy of the TNTplus™ 872 method, as a substitute for ion chromatography in field testing. Comparably, this study was also conducted over a five week period. To minimize testing, samples were collected at only the EQ tank Influent and the DAF Effluent. Tables 2 and 3 show the results obtained by ion chromatography and the Hach TNTplus™ 872 method. Note that the Hach™ method reports the organic acids as acetic acid only.
Results show that the sum of the organic acids generated by ion chromatography is not equal to the total value generated by the Hach™ TNTplus™ 872 test. This is particularly evident when the samples contain higher levels of propionic, butyric, valeric, and citric acids. When these acids are present at higher concentrations, the Hach™ TNTplus™ 972 test tends to under-report those values. It was observed however, that conversion of the organic acids into acetic acid equivalents brought those concentrations more in line with the values reported by the Hach™ test. The conversion of each acid was accomplished by converting the organic acid value to its molar equivalent and multiplying that value by the molecular weight of acetic acid. No changes to the acetic acid concentration were made. The results of these calculations appear in Tables 4 and 5.

As shown in Tables 4 and 5, acetic acid equivalents of the individual organic acids are within 20% of most of the values reported by the Hach™ TNTplus™ 872 test. Based on these calculations, the Hach TNTplus™ 872 test is a usable field method to estimate the organic acid loading to a refinery wastewater system.

Figure 3 below shows the levels of amorphous Zoogloea present in two of the samples collected during the second round of organic acid testing. As shown, the amorphous Zoogloea on the third
week of the study appeared at low to undetectable levels. However, at week 5, there is an increase in the presence of amorphous *Zoogloea* associated with the flocs. These observations coincide with lower levels of organic acids in the DAF effluent (found at weeks 1 and 2) with increasing concentrations of organic acids (during weeks 4 and 5) as shown by the Hach TNTplus™ 872 test (Table 5). More organic acid data, along with microscopic observations, are required to conclusively predict potential bulking events at specific organic acid concentrations.

![Low Levels of Amorphous Zoogloea Week# 3](image1)

![Increasing Levels of Amorphous Zoogloea Week# 5](image2)

**Figure 3: Microscopic Floc Examination during Second Organic Acid Study**

The weekly sampling conducted during these studies show that the amounts of organic acids varied widely during these studies (see Table 2 above). Fortunately, access to the crude slate information was available in order to compare the results of Table 2 with the crudes being processed. Table 6 contains these comparisons.

<table>
<thead>
<tr>
<th>Week #</th>
<th>Crude Slate</th>
<th>Acetic</th>
<th>Propionic</th>
<th>Butyric</th>
<th>Valeric</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>58% Crude A</td>
<td>42% Crude B</td>
<td>82</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>30% Crude C</td>
<td>45% Crude B</td>
<td>65</td>
<td>26</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>26.9% Crude C</td>
<td>21.5% Crude B</td>
<td>51.5% Crude E</td>
<td>84</td>
<td>39</td>
</tr>
<tr>
<td>4</td>
<td>38% Crude F</td>
<td>62% Crude E</td>
<td>203</td>
<td>29</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>60% Crude G</td>
<td>27% Crude E</td>
<td>13% Crude B</td>
<td>208</td>
<td>28</td>
</tr>
</tbody>
</table>

As shown in Table 6, there is a high variation in organics acids entering waste treatment as the crude slate changes from week to week. From the table it appears that the biggest contributors to organic acids during sampling were Crudes F and G. Crude E could also be a contributor to
higher organic acid loading. These data reflect a small sample of the organic acids reaching waste treatment during our sampling period. Variations in organic acids from different crude shipments are likely, and could potentially warrant monitoring of organic acids at the waste plant, to predict whether conditions exist to cause sludge bulking.

**Conclusion**

The work presented here profiles the volatile organic acid composition of wastewater passing through primary treatment and into the aeration basins of the refinery studied. This work also shows that the Hach™ TNTplus™ 872 test for volatile organic acids can be useful for daily monitoring of these organic acids at the refinery. The test appears to correlate relatively well with ion chromatography data when that data is converted to acetic acid equivalents.

This study also showed that the variation in organic acid concentration plays a role in non-filamentous bulking events due to selective growth of amorphous Zoogloea. While we would have preferred a stronger correlation, more data must be collected along with microscopic observations to show conclusively that specific organic acid concentrations trigger bulking events.

Note that not all bulking events involving organic acids will involve amorphous Zoogloea. The types of crudes processed at refineries also play a role in the presence of Zoogloea. Our experience has shown that refineries processing heavy Canadian, Venezuelan, and some shale crudes show a higher propensity of having bulking issues related to amorphous Zoogloea.

**References**

2. Hach TNTplus™ 872 test method 10240. DOC316.53.01259.