Water Technologies & Solutions
technical paper

the use of bio augmentation and ATP-based monitoring for bioactivity and stress to improve performance at a refinery WWTP

Authors: Peter E. Norman and Walter W. Tramble, SUEZ Water Technologies & Solutions

Presented at the WEF Industrial Wastewater Seminar at the New Jersey Water Environment Association Conference, Atlantic City, May 9-11, 2011.

abstract

A study was conducted in a refinery wastewater lagoon system to evaluate the use of a bio augmentation treatment program in reducing various contaminants and whole effluent toxicity. A new ATP-based monitoring technology was also evaluated for utility in measuring bioactivity and stress in the wastewater, lagoons, and effluent. The study was carried out in two phases, with higher bio augmentation dosages used in the second phase. A control period was chosen for comparison, based on similarities in water temperature and operating conditions. Results showed improvements in COD removal, bioactivity, and reductions in both the ATP stress parameter and the traditional WET results. Some evidence of a dose response correlation was observed.

keywords

Wastewater, Toxicity, Bio augmentation, Bio health, ATP, cATP, BSI, Biomass enhancement, Performance improvement, Refinery.

introduction

A North American refinery was facing challenges associated with effluent toxicity from its existing once-through aerated wastewater treatment ponds. Traditional wastewater monitoring was not revealing either the presence of toxicity nor providing clues as to its cause. A new ATP-based monitoring tool was implemented to determine if it had utility in discovering the source of the toxicity and providing actionable information. In addition, a bio augmentation program was implemented in an attempt to improve bio-activity in the ponds, improve COD removal, and reduce effluent toxicity.

The wastewater treatment plant (WWTP) comprised primary solids and oil removal followed by once through secondary treatment. The wastewater flow averaged about 1048 m^3/hr (6.6 MGD), but ranged from 750 to 1700 m^3/hr. About 40- 75% of this flow is process wastewater and the remainder is storm water and infiltration. Primary treatment comprised gravity oil and solids separation in API-style units, followed by dissolved air flotation (AFU) units. Wastewater entering these units was chemically treated with a polymer for emulsion breaking and colloidal solids coagulation, and a polymeric flocculent or coagulant aid. Performance of these units is normally acceptable with effluent Oil & Grease <25 mg/l and COD <250 mg/l.

Following primary treatment, the treated wastewater flowed to two consecutive aerated wastewater ponds for removal of residual organics and solids. The flow was once-through, with no recycle, and the treatment processes utilized were biological oxidation of organics by the microbiological populations present, as well as various physico-chemical processes found in these types of lagoons, e.g. chemical oxidation, volatilization, precipitation, and settling.

The two ponds were divided by vertical baffling into 5 "cells" (2 + 3), in an attempt to reduce short-circuiting and maximize hydraulic retention time. Total usable volume of the two ponds was estimated at 33,300 m^3 (8.8 million gallons) during the study period, giving a nominal hydraulic retention time of ~32 hours (19 – 44). These ponds were partially aerated with floating mechanical aerators. Measured oxygen (DO) in the pond 2 effluent was normally > 2mg/l. Nutrients (N, P) were supplied by process wastewater, with supplemental phosphate added when residual P fell below 0.1 mg/l. Average pH was about 7.2, ranging from 6.7 to 7.5.

Apart from the phosphate supplement and aeration, the only other additives being added to the biological treatment system was small amounts of commercial bacteria. Operators did not have a clear strategy for determining dosage and there was suspicion that addition rates were inadequate to achieve any significant biomass enhancement.

The refinery had traditionally used bio augmentation at continuous low rates and periodic shock dosing rates, but the impact of this approach was uncertain, and undocumented. Historically, industrial bio augmentation programs comprise the daily addition of relatively small quantities of product containing blends of bacteria and sometimes fungi, in either dry of liquid form, sometimes blended with various additives, such as biological nutrients. The strains of bacteria used are often bacillus and pseudomonas species, which are isolated from nature and selected for their degradation capabilities on specific types of contaminants. Typical concentrations of bacteria used are in the billions per gram of dry product and somewhat less in the liquid products.

Additives used by different manufacturers are meant to enhance growth under various WWTP operating conditions. There have been very few success stories well documented in the literature, though many industrial WWTP have claimed success in using these products for upset recovery and start-up applications. The purpose of bio augmentation is to increase the active numbers of specific strains of microorganisms suited to the bio-degradation (oxidation) of the main contaminants of concern. Under ideal steady-state conditions, a well-adapted population grows in biological treatment systems to levels adequate to remove most of the BOD_5. However, in many industrial plants with variable influent quality, non-steady-state conditions prevail, and stable well adapted populations with adequate activity levels, fail to persist. Although BOD_5 may be removed to low levels, COD and TOC removal may not meet newer, lower effluent limits, or toxicity may remain.

Wastewater performance was traditionally assessed at this refinery WWTP by tracking effluent COD, TSS, phenols, sulfides, oil and grease, and periodic whole effluent toxicity (WET). Microscopic checks on protozoan counts were also done weekly. The plant had historically always met its permit requirements, with very low effluent contaminant concentrations. e.g. Phenols and Sulfides <0.5 mg/l, Oil <10 mg/l, COD<125 mg/l, no toxicity failures. However, in 2009 there were several occasions where toxicity measurements were worse than normal, without discernible increases in the traditional water quality parameters, or changes in the microscopic checks. SUEZ was asked to help the refinery determine the cause of the problem and provide a solution. This paper discusses a two-pronged approach, the first based on improved monitoring and the second based on improved bio augmentation.

methodology

1. Improved Monitoring

The first recommendation implemented was the use of a new ATP-based monitoring test for assessing bio-activity and stress within the secondary treatment ponds and in the influent and effluent wastewater. This technology, marketed under the SUEZ name Bio Health (trademark of SUEZ; may be registered in one or more countries), has been described in detail elsewhere (Norman and Whalen, 2009). Basically, proprietary reagents are used to extract and measure total ATP from the wastewater, as well as the extra-cellular or dissolved ATP fraction, that has been released by stressed and dead microorganisms. The ability to measure all the released ATP, including chelated and adsorbed ATP, is what is unique about this technique. The data so obtained can then be used to calculate more accurate estimates of cellular-ATP, a measure of bioactivity, and stress (using a parameter called Biomass Stress Index, or BSI).

A comprehensive monitoring program was set-up and carried out from March 2009 looking at component wastewater streams, pond water and final effluent. Frequency of sampling was 3 to 5 times per week. Traditional parameters were measured using standard methods.

2. Bio augmentation

In this application, the authors attempted to document the success of otherwise of a new bio augmentation program using a combination of traditional water quality parameters and the new SUEZ Bio Health ATP test method. The treatment program implemented was based on a new powder product incorporating a blend of bacterial bacillus strains particularly good at degrading hydrocarbons, together with some enzymes and additives meant to compensate for expected low DO conditions in parts of the ponds. The treatment was started in October 2009. After an initial shock dose, on-going maintenance additions were 20 kg/week (in equal daily doses) until late January 2010, and then 47 kg/week until the end of the study in mid-March. These dosages were lower than recommended, but were chosen for economic reasons. Both the initial shock dose and maintenance dosing were divided between the two ponds. More product was added to Pond 1 than to Pond 2.

The products were not subjected to pre-acclimation or pre-growth in batch reactors, but were added "as-is" to the ponds. It is believed that pre-growth can reduce required treatment dosages and increase speed of response to bio augmentation, but that was not evaluated in this study.

One of the issues faced was that the water temperature of the pond system changed significantly from season to season. As the metabolic rate of bacteria are known to change significantly with temperature, for example halving with a 10°C decrease in temperature, this change had to be accounted for in the analysis. Thus, it was decided that the best baseline performance to use for comparison was the previous March and April (2009) when water temperatures averaged 13.3°C (55.9°F). A longer baseline was not available as the ATP monitoring only started in March 2009 and water temperatures increased significantly after April. During the first phase of bio augmentation the water temperature averaged 15.2°C (59.4°F) and during the second phase it averaged 12.6°C (54.7°F). Other important environmental conditions (pH, DO, nutrients, flow, and thus retention time) were relatively unchanged before and during the study.

Another issue complicating analysis of this trial was that several of the traditional water quality parameters were already at very low levels, such that measurable increases in removal were unlikely. Therefore, the focus for performance improvement became toxicity results, COD removal percentages and changes in cellular-ATP and biomass stress index (as indicators of bioactivity and biological stress respectively). Some oil data will also be discussed.

Samples analyzed for this analysis were:

(1) Primary treatment effluent = Pond 1 influent: Average of two samples' results from two AFUs.

(2) Pond 1 effluent

(3) Pond 2 effluent

Influent wastewater was analyzed for ATP stress by blending a fixed ratio of wastewater and pond sample. This was found to be necessary as straight influent wastewater was too toxic or lacking in biomass to get meaningful ATP data.

results

Results from three separate periods were compared:

(1) A "Baseline" period of March 2 to April 30th, 2009

(2) Phase 1 Bio augmentation from October 20th to January 25th, 2010

(3) Phase 2 Bio augmentation from January 26th to March 14th 2010.

Table 1 contains the data summary for the Baseline period. Table 2 contains baseline performance data, i.e. removals and changes in parameters.

Table 1 – Baseline Raw Data: March 2nd 2009 to April 30th 2009

Sample	cATP (ng/ml)	BSI (%)	Oil (mg/l)	COD (mg/l)	Phenol (mg/l)	Water Temperature (°C)
AFU Average (Pond Influent)		58.4	11.7	213	15	
Pond 1 Effluent	20	57.7	8.8	138	0.3	
Pond 2 Effluent	15	59.7	6.7	109	0.3	13.3

Table 2 – Baseline Performance Across Secondary System

Sample	BSI[1]	Oil	COD	Phenol
Across Pond 1	-0.7 abs. -1.2% rel.	-25%	-35%	-98%
Across Pond 2	+2.0 abs. +3.5% rel	-24%	-21%	0
Across Pond 1+2	+1.3 abs. +2.2% rel	-43%	-49%	-98%

Note: First number is absolute change; second number is relative % change in number.

Across the entire secondary system, the COD removal was 49% which is less than typically seen in a refinery, while Oil removal was 43%. These relatively low removals are due in part to relatively low loadings, cold water temperature, and once-through design. In the warmer months, COD removal approaches 60%.

Bioactivity as measured with cellular-ATP was very low also and BSI was high, compared to other data collected in paper mills and a few petro-chemical plants. Previously published data shows cATP in healthy once through lagoons in the 50- 400 ng/ml range, with BSI's <30%.

Data (not shown) from the period March 2 through October 19th, with a much warmer average water temperature of 20°C, still showed an average cATP of only 11- 15 ng/ml, with BSI around 57%. So, the low bioactivity and high relative stress were not temperature related and appear to be typical for this plant.

Raw data for the first, lower dosage, phase of bio augmentation is presented in Table 3.

Performance data for the same period and comparisons with Baseline are presented in Table 4.

Table 3 – Phase 1 Bio augmentation: October 20th 2009 to January 25th, 2010

Sample	cATP (ng/ml)	BSI (%)	Oil (mg/l)	COD (mg/l)	Phenol (mg/l)	Water Temperature (°C)
AFU Average (Pond Influent)		68.8	14.3	218	17.2	
Pond 1 Effluent	18	57.0	12.7	120	0.3	
Pond 2 Effluent	15	55.6	9.7	96	0.3	15.2

Table 4 – Phase 1 Performance Across Secondary System and Change

Sample	cATP	BSI	Oil	COD	Phenol
Across Pond 1		-17%	-11%	-45%	-98%
Across Pond 2		-2.5%	-24%	-20%	0
Across Pond 1+2		-19%	-32%	-56%	-98%
Difference vs Baseline					
Pond 1	-10%	+16%		+10%	
Pond 2	0	+6%		same	
Pond 1+2		+21%	-11%	+7%	same

Note: Table first shows change in parameter in % terms during this period. Then difference in change to the change that occurred during baseline. A positive number means performance improved by that absolute amount.

During the first part of the bio augmentation program the wastewater appeared to impart more stress on the pond biomass than during the comparative baseline period i.e. influent BSI was 69% versus 58%. This higher stress ("toxicity") occurred even though COD averaged about the same.

Table 3 shows that the cATP leaving Pond 1 was 10% lower than during the baseline period, possibly as a result of the higher influent stress. Bio augmentation did not compensate for this stress increase at these lower dosages. Pond 2 showed about the same stress level as baseline.

Table 4 shows that BSI (stress) decreased more across the ponds that they did in the baseline period (21% better reduction/performance), with most of that stress reduction in Pond 1. An improvement of 7% in overall COD removal, but 11% deterioration in Oil removal was also noted, but none of these differences were statistically significant at the 95% confidence level.

Data for the Phase 2 (higher dosage) Bio augmentation period is shown in Tables 5 and 6.

Table 5 – Phase 2 Bio augmentation: January 26th, 2010 to March 14th 2010

Sample	cATP (ng/ml)	BSI (%)	Oil (mg/l)	COD (mg/l)	Phenol (mg/l)	Water Temperature (°C)
AFU Average (Pond Influent)		53	11	234	23	
Pond 1 Effluent	28	53	10	89	0.3	
Pond 2 Effluent	23	45	5.7	80	0.3	12.6

Table 6 – Phase 2 Performance across Secondary System and Change

Sample	cATP	BSI	Oil	COD	Phenol
Across Pond 1		0	-10%	-62%	-99%
Across Pond 2		-14%	-43%	-10%	0
Across Pond 1+2		-15%	-48%	-66%	-99%
Difference vs Baseline					
Pond 1	+40%	-1%	-15%	+27%	
Pond 2	+53%	+18%	+19%	-11%	
Pond 1+2		+17%	+5%	+17%	+1%

Note: See notes to Table 4.

Tables 5 & 6 shows that bioactivity as measured by cellular ATP concentrations increased 40- 53% in both ponds, compared to levels seen during the baseline period. Pond 2 increased more than Pond 1. This may be due to delay in activation, acclimation and/or growth in the part of the daily dosage added to Pond 1, or merely the fact that Pond 2 benefits from the total dosage, whereas Pond 1 only saw the part of the dosage added there.

In addition, microorganism stress reduction improved by 17% points compared to baseline (+2% increase over both ponds) during this phase of treatment. Oil removal improved somewhat (43 up to 48%) and COD removal improved significantly (49 to 66%).

[Statistically these results held up better than the Phase 1 results. Pond 2 COD, BSI and cATP results were all statistically different to baseline at 95% confidence level.]

When data for the whole period of bio augmentation was studied, overall, changes relative to baseline were as follows:

- cATP: 8% increase in Pond 1 and up 26% in Pond 2
- BSI: 20% increase in BSI reduction across both ponds
- COD removal: 60%, or 11% better than baseline

Other analyses included looking at correlation coefficients between influent BSI and COD and pond BSI and COD. During the baseline period, there was a strong correlation (R=0.7-0 .8) between them for both parameters. However, during the bio augmentation program these correlations were reduced significantly (<0.5), and for BSI was reduced more during Phase 2, than Phase 1. This also shows the impact of the bio augmentation.

Although not as statistically robust, the COD removal improvements also showed a dose-response relationship.

COD removal was also studied during the entire period March 2 to October 19th, when the average water temperature was significantly warmer (19.7°C). The untreated COD removal averaged 59%. Thus, even with the relatively large temperature disadvantage (-7°C), the Phase 2 bio augmentation still improved COD removal by 7% compared to the warmer period.

Toxicity results were also tracked during the entire bio augmentation treatment program. **There were no final effluent toxicity exceedances during the treatment.**

In addition, very high toxicity events, as defined by BSI= 100%, were compared in secondary influent and pond data. See Table 7.

Table 7: High Stress Events (% of samples)

Period	Influent	Pond 1 or 2
Baseline	25%	25%
Bio augmentation	27%	11%

During the baseline period 25% of tested samples showed very high stress in the influent, with and equal fraction of pond samples showing high stress (if either pond showed high stress it was counted). However, during the treatment (October through March), with 20 high influent toxicity events (approximately same % as baseline), only 8 pond samples or 11% showed high stress.

discussion

Full-scale industrial wastewater treatment plant studies are inherently difficult to carry out due to paucity of data, variability in sampling and analytical methodologies across a range of technicians and variability in operations over time. In addition, it is rare to be able to use one completely equivalent system as a control over the same time period. The number of parameters that can vary are large and controlling for the one or two under study is almost impossible, especially over multi-week study periods. Bio augmentation programs by their very nature have to be conducted over relatively long periods when treating large systems like the one described in this study. Obtaining robust statistical correlations with 95% confidence levels is rare.

Bio augmentation programs are usually carried out with one of two purposes in mind:

1) Starting up a system, or recovering from an upset, to achieve target performance, in the shortest period of time, or
2) Increasing removal of one or more target organic compounds i.e. performance enhancement

In the real world of operating industrial plants, management does not have the time to carry out exhaustive, accurate scientific studies, but rather judge success on a basis of "how long did it take me to regain effluent quality?", or "Am I meeting my permit numbers for COD, BOD, phenol?", etc. On this basis, many dozens of plants have successfully used bio augmentation, without documenting statistically valid success.

This study was an attempt to gather such valid data. Without a parallel control system, an equivalent time period had to be used for comparison. Data analysis seems to confirm that water quality and operating conditions at that earlier time were relatively equivalent, making that period a suitable control. On the important parameter of final effluent COD the enhanced bio augmentation treatment did produce significantly lower COD than during the baseline (control) period.

Increases in cellular ATP and decreases in BSI (stress) also were significant and tracked the COD decrease in a logical fashion. Thus, the data obtained in this study is persuasive in showing the utility of this ATP technology for more sensitive bio-activity and stress measurements in biological wastewater treatment systems.

Results from earlier work at this plant, using the Bio-Health ATP testing, showed an early warning and good correlation with traditional whole effluent toxicity (WET) results. During this study, additional "upstream" testing was carried out to identify which component wastewater streams exhibited the highest "toxicity" characteristics. This data has not been included in this report, but reported elsewhere (Norman and Whalen, 2010). The results of this work have persuaded the refinery managers to routinely use the ATP testing to provide an early warning of wastewater toxicity. This data is then used, when certain thresholds are passed, to divert the suspicious stream to off-line ponds for gradual release later on. This practice of off-line equalization has resulted in improved management of toxicity and a far reduced incidence of WET failures.

During the first part of the study reported herein, ATP and COD data pointed to bio augmentation dosages being inadequate for the desired outcome. At this point it was decided to increase addition rates, resulting in the Phase 2 part of the study.

conclusions

1. The trial of a new bio augmentation product was successful in the objectives of increasing COD removal, increasing active biomass (as shown by cATP) and reducing stress (as shown by BSI) in the treatment ponds. This appears to have occurred through the process of adding more bacteria to the system, of a type selected for their ability to degrade the contaminants present in that wastewater.
2. Oil removal was increased over the whole system during the second phase of the trial when a higher dose was used. However, this conclusion is not statistically robust.
3. Phenol removal was already very high and little change was seen.
4. The trial validates the use of Bio Health ATP-based monitoring, showing a correlation between increased COD removal and active biomass as measured with the cellular-ATP parameter. The BSI stress parameter was also shown to decline during the trial and no effluent toxicity episodes were recorded in the final effluent.
5. A dose-response relationship appeared to exist between the bio augmentation product dose and the responses of COD removal, cATP bioactivity and BSI stress level in the ponds.

references

- Norman, P.E.; Whalen, P.A. (2009), New Method for Upset Prediction: ATP-based Biomonitoring and Statistical Control at Two Refinery Wastewater Plants. Proc. WEFTEC.
- Norman, P.E.; Whalen, P.A. (2010), The Future of Wastewater Monitoring, Hydrocarbon Engineering, October 2010.