Thermophilic Aerobic Treatment of High Strength Organic Production Wastes and Waste Activated Sludge from a Pharmaceutical Manufacturer: Bench-Scale Test Results and Full-Scale Design Issues

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ABSTRACT

A pharmaceutical intermediate manufacturer currently generates dilute process wastes, high organic strength liquid process wastes and waste biological sludge some of which are treated on-site while the remainder are hauled off-site for additional treatment and disposal. The high organic strength waste streams are generated from batch processes and contain a variety of solvents such as methanol, acetone, methylene chloride, MIBK, and toluene. The COD range of the high strength waste is 40,000 mg/L – 500,000 mg/L. There is also a high inorganic salt content associated with the high strength wastes that includes chloride, sulfate, and sodium ions at concentrations of 2,000 – 170,000 mg/L measured as non-volatile dissolved solids (NVDS). The high strength waste is currently sent to onsite storage tanks prior to being trucked off-site to a nearby treatment and disposal facility. With production expected to increase in the coming years and the new pharmaceutical effluent guidelines taking effect in 2001, capital improvements would be needed to treat the additional loading to the existing WTP. Plant and corporate personnel wanted to evaluate thermophilic treatment of the high strength wastes (maximum 5,000 lb/day COD) and excess biological sludge (maximum 375 lb/day COD) for its potential to lower the COD loading to the existing WTP, minimize off-site disposal, lower WTP plant operating costs, and keep the WTP in compliance with the new pharmaceutical effluent guidelines. This paper discusses the approach utilized to evaluate the performance of the thermophilic treatment process on the target wastes along with presentation of the results and the implications of the results on the full-scale design of the system.

KEYWORDS

Thermophilic Aerobic Treatment, High Organic Strength Pharmaceutical Waste, Waste Activated Sludge

BACKGROUND

A pharmaceutical intermediate manufacturer currently generates dilute process wastes, high organic strength liquid process wastes and waste biological sludge some of which are treated on-site while the remainder are hauled off-site for additional treatment and disposal. The dilute process wastewaters are treated in an existing activated sludge pretreatment plant consisting of equalization, neutralization, biological treatment, gravity clarification, and carbon polishing prior to discharge to the local public-owned treatment works (POTW). The excess biological solids produced in the activated sludge system are thickened using a gravity table unit prior to being hauled off-site to a near-by waste treatment and disposal facility.

The high organic strength waste streams are generated from batch processes and contain a variety of solvents such as methanol, acetone, methylene chloride, MIBK, and toluene. The COD range of the high strength waste is 40,000 mg/L – 500,000 mg/L. There is also a high inorganic salt content associated with the high strength wastes that includes chloride, sulfate, and sodium ions at concentrations of 2,000 – 170,000 mg/L measured as non-volatile dissolved solids (NVDS). The high strength waste is currently sent to onsite storage tanks prior to being trucked off-site to a nearby treatment and disposal facility. With production expected to increase in the coming years and the new pharmaceutical effluent guidelines taking effect in 2001, capital improvements would be needed to treat the additional loading to the existing WTP. Also, operating costs would increase for the management and disposal of the additional high strength wastes trucked off-site and the increase in dewatering and disposal of the excess biological sludge. Plant and corporate personnel wanted to evaluate thermophilic treatment of the high strength wastes (maximum 5,000 lb/day COD) and excess biological sludge (maximum 375 lb/day COD) for its potential to lower the COD loading to the existing WTP, minimize off-site disposal, lower WTP plant operating costs, and keep the WTP in compliance with the new pharmaceutical effluent guidelines. This paper discusses the approach utilized to evaluate the performance of the thermophilic treatment process on the target wastes along with presentation of the results and the implications of the results on the full-scale design of the system.

PROJECT APROACH

A preliminary economic benefits analysis was performed which included the installation of a modified thermophilic treatment system designed to convert 90% of the COD load from the high strength process wastes and waste activated sludge into carbon dioxide and water. Based on the favorable economic benefits analysis, continuous flow bench-scale testing of a combination of the high strength process wastes and the waste activated sludge was performed from June 2, 1999 to October 29, 1999. The key objectives of the bench-scale work were as follows.

- Confirm that the modified thermophilic treatment process could biologically degrade the highly variable process wastewaters.
- Quantify both effluent and off-gas quality of the modified thermophilic treatment process under average and maximum COD loading conditions.
- Evaluate the impact of the effluent from the modified thermophilic treatment system on the biological treatment performance of the existing activated sludge system with regard to COD removal and nitrification.
- Evaluate the impact of the modified thermophilic treatment system effluent on the COD removal capabilities of the existing carbon polishing system.

BENCH-SCALE TEST DESCRIPTION

Continuous Flow Testing

To initiate the testing, a 10-liter (L), plastic, reactor vessel was seeded with thermophilic biomass from an existing, full-scale, modified thermophilic treatment system (see Figure 1). The bench reactor was aerated using compressed oxygen and diffused air to maintain the reactor dissolved oxygen level >1 mg/L. Mixing was accomplished via an overhead mechanical mixer. The reactor was heated in a water bath designed to maintain the reactor temperature between 45 ^{o}C – 48 ^{o}C. The reactor was continuously feed a mixture of waste activated sludge and various grab samples of production wastes volumetrically proportioned to account for the variability in production of the numerous products made at the facility. Nitrogen and phosphorous were added to the feed as required to prevent nutrient limitations on the biomass.

Daily reactor maintenance included measuring the volume of wastewater fed the reactor and centrifuging a fixed volume of reactor contents. The centrate was decanted, sampled, and discarded while the concentrated solids were returned to the reactor. Water was added to correct for volume lost due to evaporation.

Reactor monitoring included periodic grab sampling to analyze for pH, COD (including solids), total suspended solids (TSS), and volatile suspended solids (VSS). Reactor influent and effluent monitoring included, COD, soluble COD (SCOD), TSS, total dissolved solids (TDS), NVDS, ammonia-nitrogen (NH_3-N), phosphate-phosphorous (PO_4-P), total Kjeldahlnitrogen (TKN), alkalinity, and pH. In addition, the influent and effluent were periodically tested for BOD_5, carbonaceous BOD_5, volatiles and semi-volatiles. Reactor off-gas samples were also collected at the end of the average and maximum COD loading runs and analyzed for volatiles and NH_4.

Batch Testing

At the end of both average and maximum COD loading runs on the continuous flow reactor, batch respirometer and carbon isotherm tests were performed using effluent processed from the thermophilic reactor. Samples used for respirometry were filtered through a 0.02 µm ceramic ultrafilter to simulate the full-scale treatment system. Effluent used for the carbon isotherm testing was collected as decant from the centrifuge.

The batch respirometer tests, which measure biological oxygen uptake as a function of time, were designed to evaluate the impact of the thermophilic system effluent on the ability of the existing activated sludge system biomass to remove organics and nitrify. Each respirometer test utilized an 8-unit respirometer manufactured by Challenge Environmental Systems, Inc. The basic principle of operation of the respirometer is that known quantities of wastewater and active aerobic microorganisms are added to each reactor unit. Each reactor is completely closed-off to the atmosphere. As biodegradation of the target waste constituents begins, the carbon dioxide generated during the aerobic metabolism of the organics is removed via a caustic scrubber from the reactor headspace thus creating a pressure drop in the unit which is detected via a manometer. The pressure drop is counteracted by the input of oxygen which is generated at an electrolytic cell and directed through a flow measuring cell which meters in the precise increments of oxygen to each reactor as needed. The amount of oxygen delivered to each reactor is collected and stored during the test and is later downloaded into a spreadsheet for analysis.

A typical test setup for evaluating the impact of the thermophilic reactor effluent on the organic removal capability of the existing activated sludge biomass is given in Table 1. The biomass used to seed each reactor was taken directly from the full-scale activated sludge plant the day of testing. The target initial seed concentration was 120 mg/L VSS. All reactor units were placed in a waterbath operated at 25 ^oC and were mixed via individual magnetic stir bars. The six reactors utilized in this test included an activated sludge seed blank, a normal activated sludge feed control with an initial COD of 200 mg/L, and a effluent sample from the thermophilic bench reactor at an initial COD of 200 mg/L. The remaining three respirometer reactors were setup with normal activated sludge waste feed at 200 mg/L COD plus an average, 2X, and 4X volumetric loading, respectively of thermophilic bench reactor effluent. Diammonium phosphate and phosphate buffer were added to each reactor to provide excess nutrients and insure pH stability throughout the test. A 0.18% sodium sulfate solution was used as dilution water to maintain background salt levels similar to the original biomass seed environment. Reactor volume was 250 milliliters. Each reactor was sampled for initial and final COD and pH. Oxygen uptake was monitored continuously throughout the test. Test duration was 45 hours.

A typical test setup for evaluating the impact of the thermophilic reactor effluent on the nitrification capability of the existing activated sludge biomass is given in Table 2. The biomass used to seed each reactor was a concentrated nitrifier population obtained from Sybron Chemicals. The target initial seed dosage was recommended by Sybron to be 0.6 mls nitrifiers per 200 mg/L NH_3-N. All reactor units were placed in a waterbath operated at 25 ^oC and were mixed via individual magnetic stir bars. The seven reactors utilized in this test included a nitrifier seed blank, three reactors loaded with nitrifiers at three different initial NH_3-N levels (50 mg/L, 150 mg/L, and 250 mg/L), and three reactors loaded with a peak thermophilic reactor effluent loading plus three different initial NH_3-N levels (50 mg/L, 150 mg/L, and 250 mg/L). Diammonium phosphate was added as the NH_3-N source. Sodium carbonate and phosphate were added to each reactor to provide a carbon source for the nitrifiers and insure pH stability throughout the test, respectively. A 0.3% sodium sulfate solution was used as dilution water to maintain background salt levels similar to the original nitrifier seed environment. Reactor volume was 250 milliliters. Each reactor was sampled for initial and final NH_3-N, and pH along with final NO_3-N. Oxygen uptake was monitored continuously throughout the test. Test duration was 67 hours.

The carbon isotherm tests were designed to evaluate the ability of the existing carbon system to remove the residual COD from the thermophilic system in the event the COD passes through the WTP without further removal. Testing was performed using 100 ml sample volumes of centrifuged effluent from the bench thermophilic reactor (ultrafiltered effluent was not available for this testing). Five different carbon doses were tested: 0, 10, 100, 1,000, and 5,000 mg/L). The carbon selected to do the testing was the exact same carbon utilized at the facility. Each sample was put into covered 500-ml glass flasks and placed on a low agitation shaker for 20 hours at 25 ^{o}C. After 20 hours on the shaker, the samples were allowed to settle for 30 minutes prior to being sampled for final pH and soluble COD.

BENCH-SCALE TEST RESULTS

Wastewater Characteristics

The pharmaceutical intermediates manufacturing facility produces a wide variety of products that result in several discrete, high strength waste streams with varying characteristics. The influent to the thermophilic bench reactor was varied throughout the entire test to mimic the current production schedule and activated sludge wasting rates at the plant. The waste characteristics of the individual waste streams are given in Table 3 while the characteristics of the feed to the thermophilic bench reactor throughout the test are listed in Table 4. Particular attention was given to the overall COD and NVDS of the combined feed to the bench reactor. COD ranged from 18,000 mg/L – 103,800 mg/L and NVDS varied from 900 mg/L –52,800. Both flow rate and salt levels for the feed were adjusted throughout the test to maintain target COD loading rates and prevent salt levels within the reactor from changing more than +/- 400 mg/L/day.

Continuous Flow Test Results

Bench reactor operation was initiated June 4, 1998 using biomass from an existing full-scale thermophilic system operating at a COD loading rate of 200 mg/L/hr and having a background NVDS level of 20,000 mg/L. The initial biomass level in the bench reactor was 6,650 mg/L VSS. The initial COD loading rate for acclimation was 50 mg/L/hr. Loading rates were slowly increased over the following 6 weeks to achieve the target design average loading of 200 mg/L/hr. Reactor NVDS levels were 14,000 mg/L – 22,500 mg/L during the same time period. The reactor continued to operate at a 200 mg/L/hr-loading rate for 2 weeks in order to collect influent and effluent samples for analytical and respirometric impact testing (see Table 5 for results).

After sampling, COD loading rates were increased over the following two weeks to achieve the maximum design loading rate condition of 300 mg/L/hr. This loading rate was achieved on August 27, 1998 and was maintained for the remainder of the project. From October 15, 1998 to October 31, 1998, the bench feed was spiked with methanol, acetone, methylene chloride, MIBK, and toluene (see Waste Combination 10 - Spiked in Table 4 and Table 5) to simulate worse case solvent loading to the reactor. Final influent, effluent and off-gas sampling was performed at the end of October 1998 to complete the test.

Overall bench–scale reactor test results are presented in Figure 2, Figure 3, Figure 4, and Table 5. Figure 2 tracks the Feed COD, Reactor COD, and the Effluent Soluble COD concentrations throughout the test. Figure 3 is a COD mass balance around the reactor. These results show that with a highly variable wastewater, the thermophilic reactor was able to achieve 87% COD destruction during the average design COD loading rate period and 85% removal during the maximum loading rate period. BOD removal efficiency was >99% at the target COD design loading of 200 mg/L/hr and >97% at the maximum COD design loading of 300 mg/L/hr (see Table 5). Table 5 is a summary of the influent, effluent, and off-gas results from the thermophilic reactor collected at the end of both the average and maximum design COD loading runs. These results confirm >95% - 99% removal of the target organics of concern as listed in Table 5. The off-gas results, however, do indicate that some residual volatile organics are being stripped from the reactor. COD and specific organics removal in the full-scale system is expected to be higher with the inclusion of a chemical treatment step designed to convert the excess biological solids and recalcitrant organics from the thermophilic reactor into a biodegradable substrate that can be fed back to the thermophilic reactor for final treatment. In addition, regular use of an ultrafilter to process effluent from the thermophilic reactor will keep all the biomass in the reactor and allow for the acclimation and ultimate biodegradation of residual organics. In addition, reactor off-gas collection and treatment will be included in the final system design.

Additional bench-scale results tracking the reactor mixed-liquor suspended solids concentrations in the reactor are given in Figure 4. These results show a gradual increase in suspended solids over the testing period. The thermophilic biological sludge production rate was calculated to be <0.08 mg VSS produced per mg of COD removed. In addition the differential between the TSS and VSS curves in Figure 4 remained constant throughout the test indicating little to no accumulation of inorganic suspended solids in the reactor. Use of chemical treatment in the full-scale system will eliminate the generation of excess organic solids from the system and will solubilize a majority of the inorganic solids thus eliminating the need for sludge dewatering equipment and minimizing the cost for sludge processing and off-site disposal.

Batch Testing Results

Typical results for batch respirometer tests evaluating the impact of ultrafiltered thermophilic reactor effluent on the existing activated sludge treatment performance are given in Figure 5 and Table 6. The thermophilic effluent used for this test was obtained during the end of the maximum COD loading run (300 mg/L/hr) and would represent a worse case impact on the existing plant biomass. Figure 5 is a plot of cumulative oxygen uptake versus time for each respirometer reactor. Table 1 outlines the test setup. Review of the results in Figure 5 indicates that the AFC effluent can be biodegraded by the existing activated sludge biomass and that no negative effect in performance is observed under normal volumetric loading and 2X volumetric loading conditions. A slight inhibition is observed when the thermophilic effluent volumetric load is 4X the expected average loading. Table 6 presents the initial and final COD measurements for the test. Comparison of the COD removed in each respirometer reactor to the cumulative oxygen uptake indicates a reasonable oxygen balance verifying that the COD removal is a result of biological treatment.

Typical results for batch respirometer tests evaluating the impact of ultrafiltered thermophilic reactor effluent on the nitrification performance are given in Figure 6 and Table 7. The thermophilic effluent used for this test was obtained during the end of the maximum COD loading run (300 mg/L/hr) and was dosed at a level to yield a worse case background thermophilic COD contribution that the nitrifiers would see in the full-scale activated sludge system. Each reactor was supplemented with the appropriate NH_3-N dosage to represent a low, average, and high concentration range of NH_3-N levels contributed by the thermophilic system. Table 2 outlines the test setup. Figure 6 is a plot of cumulative oxygen uptake versus time for each respirometer reactor. Review of the results in Figure 6 indicates that the thermophilic bench reactor effluent under maximum COD loading conditions and maximum COD contribution to the activated sludge system has little impact on nitrification at NH_3-N levels upto 250 mg/L. Although the impact of the thermophilic effluent was negligible, oxygen uptake rates (slope of each curve) did decrease with increasing initial NH_3-N concentration indicating growth inhibition was present due to NH_3-N. Table 7 presents the initial and final NH_3-N results along with the final NO_3-N readings for each reactor. Comparison of the NH_3-N removal times 4.3 (theoretical oxygen demand to convert NH_3-N to NO_3-N) to the cumulative oxygen uptake for each respirometer reactor yields a reasonable oxygen balance verifying that the NH_3-N conversion is a result of biological nitrification. In addition, the NH_3-N removed is comparable in all reactors to the NO_3-N produced at the end of the test providing further validation for the test

In addition, carbon isotherm testing of the thermophilic effluent (after centrifuging/removing 95% of the suspended solids) was performed using the same carbon currently used to polish the effluent from the full-scale activated sludge system. This testing was performed to verify that the thermophilic effluent soluble COD could be removed via carbon if it passed directly through the activated sludge system. Results of the isotherm test are given in Table 8. Initial soluble COD of the effluent was 2,354 mg/L. The equilibrium soluble COD level was calculated to be 1,000 mg/L indicating that >57% of the soluble COD can be removed in the existing carbon system.

CONCLUSIONS

In general, the treatment performance of the thermophilic biological treatment system at the bench-scale level on the high concentration pharmaceutical wastewater was very successful. The major conclusions drawn from the testing are listed below.

- The high strength wastewaters generated at the pharmaceutical manufacturing facility in combination with the waste activated sludge are readily biodegradable under thermophilic aerobic test conditions. The bench system results showed 87% COD destruction during the average COD loading rate conditions of 200 mg/L/hr and 85% removal during the maximum loading condition of 300 mg/L/hr. BOD removal efficiency was >99% at 200 mg/L/hr and >97% at the maximum COD design loading of 300 mg/L/hr. Specific organic removal ranged from >95% - 99% at maximum loading.
- Volatile organic parameters of concern were measured in the off-gas indicating that some air stripping was occurring in the bioreactor. Off-gas collection and treatment is required in the full-scale system.
- Biomass sludge generation rate for the entire test was 0.08 mg VSS Produced per mg COD Removed. Sludge yield will decrease with the incorporation of a chemical treatment step as part of the full-scale system.
- Batch respirometric tests showed that the thermophilic reactor effluent after ultrafiltration through a 0.02 membrane and under maximum design COD load conditions will not inhibit the biological organic and nitrifying treatment capability of the existing activated sludge system.
- Batch carbon isotherm tests showed that activated carbon treatment of the thermophilic effluent could remove an additional 57% of the soluble COD if going untreated through the existing activated sludge system.

FULL-SCALE DESIGN ISSUES

A block-flow diagram integrating the proposed treatment system of equalization, thermophilic bioreactor, ultrafiltration, and chemical treatment into the existing activated sludge system is given in Figure 8. The basis of design for flow and organic loading is 9,900-gpd maximum flow and 5,375 lb/day COD, respectively. Materials of construction for the high strength system need to withstand 65 ^{o}C temperatures and maximum sulfate and chlorides levels 1% - 3% and 0.6% - 1.4% by weight, respectively. The high strength waste equalization system needs to balance the highly variable COD/NVDS load, address an explosive off-gas environment and have off-gas treatment. The thermophilic reactor and aeration equipment will be sized to treat an average COD load of 200 mg/L/hr with a maximum COD loading of 300 mg/L/hr. Chemical treatment will be sized to treat tow times the excess sludge production based on the 0.08 mg VSS produced per mg COD removed measured during the treatability testing. In addition, the chemical treatment unit will be designed to capture/chemically treat excess foam generated by the thermophilic reactor. The ultrafilter will be sized using a minimum flux rate of 50 gfd based on bench test results and previous experience with similar waste streams. Overall system performance is expected to destroy 90% of the influent COD with no organic sludge production. Design/build system costs are estimated at $2.5M - $3.0M with annual operating cost estimated at $240,000/yr. The project is currently waiting approval by the client for capital funding.