Design and Start-up of an Advanced Thermophilic Treatment System for High Strength Wastewater from a Pharmaceutical Plant

Walter J. Wujcik, Ph.D., P.E., DEE
PMC Technologies, Inc.
835 Springdale Drive, Suite 201
Exton, PA 19341

Alan F. Rozich, Ph.D., P.E., DEE and Christian D. Hahn, PMC Technologies, Inc.

ABSTRACT

Development of a new product at a pharmaceutical plant would result in additional wastewater, including some low-volume, high strength process wastewaters. At full production capacity, the organic loading from the additional 100,000 gallons per day (gpd) of process wastewater (three waste streams, and an allowance for bad batch flows) would exceed 40,000 pounds chemical oxygen demand (COD) per day. This additional organic loading was greater than the capacity of the nearby wastewater treatment plant (WWTP) where the pharmaceutical plant currently discharges its existing wastewaters. The additional wastewater would require extensive pretreatment to be discharged to the nearby WWTP. The pretreatment system had to be available in twelve months as production of the new product was to begin in one year.

This paper presents the results of the bench/pilot testing performed on the process wastewater, design of the pretreatment system, and the start-up and initial performance of the pretreatment system. Descriptions are provided for unique features of the design, the chemical treatment system and the ultrafilter.

KEYWORDS

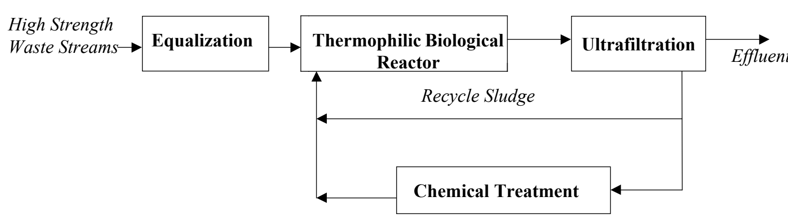
Biological treatment, thermophilic process, pharmaceutical wastes, start-up

INTRODUCTION

Expansion at a mid-Atlantic pharmaceutical plant would generate additional wastewater, including some low-volume, high strength wastes. The facility was concerned with the cost-effective treatment and disposal of these wastes, which are generated from several processes. Treatment and disposal of these wastes can be expensive. The AFC^{SM} technology treats waste streams containing high strength organic compounds and organic sludges. AFC^{SM}'s main attribute is its ability to convert high strength and potentially toxic organics, both dissolved and suspended particulate, to carbon dioxide and water. AFC^{SM} eliminates the potential long-term liability risks and minimizes the costs associated with off-site disposal because it is a complete oxidation option.

The AFC^{SM} process is a combination of single-stage thermophilic aerobic biological treatment, side stream chemical treatment, and efficient solids separation. Waste materials are fed to a self-heating thermophilic bioreactor for treatment. Effluent from this reactor is conveyed to a solids separator. Ultrafiltration is the preferred solids separation process for full-scale AFC^{SM} systems. A portion of the concentrated solids is returned directly to the thermophilic reactor, while the remaining portion goes to chemical treatment. The chemical treatment step partially solubilizes the excess biosolids before they are returned to the thermophilic reactor for further digestion and destruction. Figure 1 is a process schematic.

Figure 1 – AFC^{SM} Process Flow Diagram



The AFC^{SM} system demonstrated during bench/pilot-testing that it could effectively pretreat the new wastewater stream at the design (300 mg/L-hr COD) loading. The bench reactor COD removal efficiency was 85 - 90% during the period it was fed the design COD loading. This removal efficiency was obtained without the use of an ultrafilter. The full-scale AFC^{SM} system, with daily use of an ultrafilter, will achieve greater than 90% COD removal efficiency. A decision was made to proceed with full-scale design and construction of an AFC^{SM} pretreatment system. The AFC^{SM} system was to be completed and operational to coincide with the start-up of the additional production capacity.

BENCH/PILOT TESTING

Bench/pilot testing performed using a proprietary, thermophilic treatment process (AFC^{SM}) showed that the new wastewater was biodegradable and the AFC^{SM} process could achieve the necessary effluent quality for discharge to the nearby WWTP. Results of the bench testing and respirometric tests using unacclimated AFC^{SM} seed and the concentrated waste streams showed that a thermophilic biomass could degrade the waste streams.

Bench/pilot testing was conducted over a three-month period that encompassed the testing objectives (acclimation and application feasibility). A 10.0-liter (L) plastic reactor was seeded with thermophilic biomass from an existing full-scale AFC^{SM} system. The bench reactor was aerated using diffused air and compressed oxygen to maintain a dissolved oxygen concentration greater than 2 mg/L. Mixing was accomplished via a mechanical mixer. The reactor was heated in a water bath designed to maintain the reactor temperature between 45^{o}C and 48^{o}C. The bench-scale reactor was set up with continuous feed of the target waste streams. Evaporation loss was measured daily and recorded. Tap water was used as make up water. Excess nitrogen (N) and phosphorous (P) (greater than the required COD:N:P ratio of 200:5:1), which are essential for biomass growth, were added, as required, to prevent nutrient limitations. Sulfuric acid and sodium hydroxide were used, as needed, to maintain the reactor pH between 7.0 and 7.5.

The volume of wastewater feed added to the reactor was measured and recorded on a daily basis. In addition, a fixed volume of reactor contents was removed daily and centrifuged. The centrate was sampled and discarded as effluent, while the concentrated solids were returned back to the reactor.

The bench/pilot AFC^{SM} reactor was started with seed from an existing, full-scale AFC system (21 June 2001). Initial reactor COD loading of 30 mg COD/L-hr was gradually increased to 300 mg COD/L-hr over two months. The system was operated at the design loading rate of 300 mg COD/L-hr for one month.

Grab samples were collected during the bench-scale testing and characterized to determine total COD (COD), total suspended solids (TSS), volatile suspended solids (VSS), total dissolved solids (TDS), non-volatile dissolved solids (NVDS) and the pH. Effluent from the bench-scale test was sampled for a number of standard parameters (COD, soluble COD (SCOD), TSS, ammonia-nitrogen (NH_3-N) and phosphate-phosphorous (PO_4-P)). The results of the bench/pilot testing indicated that the pharmaceutical wastes can be readily treated biologically in a thermophilic reactor operated at a 4-day hydraulic retention time (HRT), 40-day sludge retention time (SRT), and a COD loading rate averaging 290 mg/L-hr.

Chemical treatment of biomass was evaluated in a second bench/pilot test that was initiated on 11 February 2002. Two reactors were operated, one served as a thermophilic control, while the AFC^{SM} reactor incorporated chemical treatment of biomass. A portion (600 to 800 mLs) of the biomass was removed from the AFC^{SM} reactor, heated to 65^{o}C, and treated with sulfuric acid (lowering the pH to 3) and hydrogen peroxide. This chemically treated biomass was returned to the reactor at the rate of 200 mLs per day, resulting in a SRT of 40 days. The chemical treatment evaluation showed that the

AFC[SM] reactor (with chemical treatment) had better COD, TSS, and VSS treatment performance when compared to the thermophilic control (no chemical treatment) reactor.

Respirometric test procedures were used to validate whether or not waste destruction of the chemically treated material had occurred due to biological activity. The test was run utilizing AFC[SM] bench reactor biomass as seed, with various loadings of the combined wastes in the individual reactors. The respirometric test was performed using a respirometer manufactured by Challenge Environmental Systems, Inc. The respirometer is designed to measure oxygen uptake due to biological activity in the individual reactors. The Challenge AER-200 system consists of biological reaction vessels (reactors), a cell base containing eight flow measuring cells, an oxygen generation unit, and a computer.

The basic principle of system operation is as follows: test samples and active aerobic microorganisms are added to each reaction vessel, the oxygen flow-measuring cells measure oxygen demand in precisely controlled incremental volumes, the oxygen generation unit supplies oxygen to the reaction vessels, and the computer stores the data as oxygen flow, volume, and rate. The data is stored in a format suitable for direct input to a spreadsheet for graphing and analysis.

Results showed that the combined pharmaceutical wastes were readily biodegradable by the bench/pilot reactor biomass. Increasing the COD loading resulted in an increase in oxygen uptake, indicating no biomass growth inhibition. The individual wastes (including “bad batches”) were also biodegraded by the thermophilic biomass with no sign of growth inhibition.

DESIGN

The pretreatment system was designed to take advantage of the rapid biodegradation rates associated with aerobic systems and the low sludge yields of thermophilic systems. The system is designed to treat an average flow of 100,000 gpd (peak flow of 112,000 gpd) and an average (and peak) load of 40,000 lbs./day COD. The treatment system consists of equalization, thermophilic aerobic treatment, ultrafiltration, and chemical sludge treatment. Table 1 shows the design influent conditions for the pretreatment system.

Table 1 – Design Influent Conditions for AFC[SM] Thermophilic Pretreatment System

Parameter	Product A	Product B[1]	Bad Batch[2]	Combined[3]	Peak[4]
Flow, gpd	67,440	30,000	2,428	99,868	112,000
pH, S.U.	3.0 – 3.5	9.0 – 10.0	2.0 – 3.0		
BOD, lbs/d	13,855	2,821	526	17,202	17,202
BOD, mg/L	24,642	11,280	26,000	20,660	18,423
COD, lbs/d	32,452	5,404	1,518	39,374	39,374
COD, mg/L	57,718	21,608	75,000	47,290	42,168
TOC, lbs/d	7,323	1,832	546	9,701	9,701
TOC, mg/L	13,024	7,325	27,000	11,651	10,389
SO_4, lbs/d	1,681	120	284	2,085	2,085
SO_4, mg/L	2,990	480	14,300	2,054	2,233
TSS, lbs/d	5,380	3,200	1,296	9,876	9,876
TSS, mg/L	9,569	12,794	64,000	11,862	10,577

NOTES:

1. **Based on 40% of load at original flow rate.**
2. **Occurs three times per year.**
3. **Bad batch processed over a 7-day period.**
4. **Based on maximum lbs/day regardless of flow. At reduced flow rates, mg/L load is limited to 20% increase above design.**

The three process wastewaters are combined in the 226,000-gallon capacity equalization tank to reach the target COD concentration, 47,290 mg/L. From the equalization tank, the wastewater is pumped to the 576,000-gallon capacity thermophilic reactor for biological destruction of the organic contaminants in the wastewater. pH control with sulfuric acid and sodium hydroxide is used on both the equalization tank and thermophilic reactor to maintain the pH between 7.0 and 8.5 standard units (s.u.). The mixed liquor in the reactor is continuously recirculated through the ceramic membrane ultrafiltration system. This system separates the treated wastewater from the suspended solids. The permeate stream is discharged to the local WWTP. Discharge limits are presented in Table 2. The solids-laden stream is primarily directed back to the reactor. A portion of the solids-laden stream is directed to the 57,000-gallon capacity chemical treatment tank.

Table 2 – Effluent Limitations for Advanced Thermophilic Treatment System

Parameter	Average Limit, lbs/day	Maximum Limit, lbs/day
BOD5	8,000	12,000
COD	11,000	16,500
TOC	5,000	8,000
SO4	10,000	15,000
TSS	3,000	5,000
Ammonia	700	-

A ceramic membrane ultrafiltration system is used for mixed liquor solids separation. The ultrafilter separates the solids from the treated liquid. The permeate stream is discharged to the nearby WWTP and the solids laden stream is recirculated back to the thermophilic reactor. The ultrafiltration system is equipped with an operator initiated automatic cleaning system.

The chemical treatment system includes the chemical treatment tank and equipment. The equipment includes a jet mixing system, pH controller, steam injection, temperature controller, level control system, and transfer pump. A slipstream (2 to 5 percent of the thermophilic reactor volume) of mixed liquor is treated continuously in the Chemical Treatment Tank. In the tank, the pH is maintained at 4.0 with the addition of sulfuric acid, and the biomass is hydrolyzed by the addition of hydrogen peroxide and steam. After treatment, the sludge is slowly pumped back to the reactor. Chemical treatment of the sludge provides the following:

- Organic sludge control
- Partial inorganic sludge control via solubilzation
- Foam control
- Partial recalcitrant organic control (make more biodegradable)
- Recycle/reuse of nitrogen and phosphorous

The chemical treatment tank also collects and treats any foam from the thermophilic reactor.

SYSTEM START-UP AND PERFORMANCE

The AFC^{SM} wastewater pretreatment system underwent a gradual start-up. A plan was developed to provide the procedures and benchmarks for start-up. The start-up plan, shown in Table 3, outlined a 10-week program to get the AFC^{SM} system through to interim loading conditions and initiate discharge of effluent to the WWTP. This paper briefly describes the initial start-up events (start-up was initiated on 28 October 2002) and the progress to date.

The AFC^{SM} reactor was seeded with 50,000 gallons of biomass from an existing AFC^{SM} system in New Jersey. To reach the minimum reactor volume needed to activate the jet aeration system, 30,000 gallons of wastewater and an additional 50,000 gallons of potable water were also added to the reactor. The AFC^{SM} system startup progressed quicker than the anticipated startup schedule. This situation was primarily due to the higher influent COD concentration (up to double the design value). As production ramps up, the COD concentration should decrease to design levels. The AFC^{SM} system initiated discharge to the WWTP the week of 28 December 2002. Continuous chemical treatment was started 6 February 2003. The following discussion describes technical performance and operating issues for the first seven months of operation.

Figure 2 depicts the AFC^{SM} reactor COD loading in mg/L-hr and reactor temperature for the first six months of operation. COD loadings rates have generally increased, and have averaged 150 mg COD/L-hr. The loading rate has exhibited wide variability, primarily the result of production adjustments during the new product introduction at the pharmaceutical plant. Reactor temperature has steadily increased with increases in COD loading and has remained stable throughout the harsh winter months and variability in the loading rate. Current reactor temperatures are approximately 60^{o}C (140^{o}F) at approximately 50 – 60% of design organic (COD) loading.

Since going on-line in autumn 2002, the AFC^{SM} system has performed exceptionally well. The system has met the BOD, COD, TOC, SO_4, TSS, and ammonia limits. The influent wastewater flow has been at half the design rate, while the organic concentration (as measured by COD) and solids loading has been up to twice the anticipated design values.

COD treatment efficiency (as measured by influent and effluent COD concentrations) has been approximately 95%. Figure 3 shows a plot of both the influent and effluent COD concentrations around the AFC^{SM} reactor versus time. These results show that influent COD has ranged from 30,000 to 100,000 mg/L, averaging 55,600 mg/L. Plant effluent (permeate) values have ranged from 1,500 to 6,600 mg/L, averaging 3,400 mg/L.

Testing has also been performed to measure the levels of pharmaceutical products A and B in the treatment system effluent (permeate). Product B has not been detected in the effluent. Product A was initially detected at a few parts per million (ppm) in the effluent, but has not been detected in the effluent since chemical treatment has started.

Chemical treatment was initiated 3 months (February 2003) after startup to recycle nutrients and micronutrients, to help control foaming, and to control organic sludge production. The initial start for the chemical treatment system was to be when the AFC^{SM} reactor VSS level reached 25,000 mg/L. The actual start was delayed by three weeks due to unforeseen circumstances. The initial hydrogen peroxide dosage was set at half the design rate to determine if a rate lower than observed during bench/pilot testing could successfully control solids.

The VSS level has risen to 60,000 mg/L by May 2003. The chemical treatment process, while controlling the rate of increase in VSS concentration, has not been able to decrease the VSS concentration. There are several reasons for this situation. They are listed and discussed below:

- The influent solids (TSS and VSS) levels are 2X higher than the basis of design.
- The influent solids have included significantly more "bad batches" than design conditions due to problems in production.
- The initial design was to include a separate "bad batch" equalization tank which was eliminated during value engineering
- The chemical treatment step was initiated late due to mechanical issues.
- Initial low oxidant (hydrogen peroxide) dosage in the chemical treatment process.

- Low dissolved oxygen (DO) content in the thermophilic aerobic reactor due to mechanical issues.
- No solids (inorganic) blowdown to effluent stream as called for in design.

The AFC^{SM} system was designed for an average solids (TSS) influent concentration of approximately 11,800 mg/L (9,600 mg/L VSS). This design anticipated three "bad batches" of the new pharmaceutical product per year. The initial months of the new product manufacture has resulted in a significantly larger number of "bad batches". Instead of the anticipated three per year, there has been an average of one "bad batch" per week. This situation has resulted in an average TSS influent concentration of 18,300 mg/L (17,100 mg/L VSS). In addition, the "bad batch" solids have not been processed to the same extent as the normal production solids, and as such, are not as easily treated.

The chemical treatment step was started later than recommended due to mechanical/construction issues associated with most start-ups and unavailability of plant personnel. The later start coupled with a series of bad batches hitting the system allowed the reactor solids to accumulate to a higher level. The initial hydrogen peroxide dose was set at half the design dosage. The lower dose was tried to determine the minimum acceptable dose to control organic solids. Hydrogen peroxide is the most expensive chemical used in the chemical treatment process. The initial dose was determined to be inadequate after a one-month trial. The design dose is currently being used to control solids.

The chemically treated solids are processed in the thermophilic aerobic reactor. The reactor must be supplied with sufficient oxygen to process the influent wastewater and the returned chemically treated sludge. The reactor DO was running less than 1.5 mg/L three months after initiation of chemical treatment. Mechanical problems with the blowers prevented the sufficient oxygen to the reactor. The problems were resolved after a few months of operation and the reactor DO is currently consistently above 2.0 mg/L.

An additional reason for solids accumulation in the AFC^{SM} reactor was the lack of solids blowdown to the effluent stream. The chemical treatment process is very effective in the control of organic solids. It is not as effective for inorganic solids control. The AFC^{SM} treatment system effluent was designed to include a blowdown of solids (to control inorganics). No solids blowdown has occurred. This situation has resulted in an accumulation of solids in the reactor.

The chemical treatment system is currently being optimized in order to maximize the throughput to regain control of the reactor organic solids level based on an increase in the number of bad batches hitting the system. The plant is currently evaluating ways to minimize bad batches. To date, no solids have been wasted from the system while treating over 2,000,000 lbs of COD.

SUMMARY

Expansion at a pharmaceutical plant in a small town resulted in the production of high strength wastewaters. The wastewater would have to be treated on-site to meet pretreatment requirements or be hauled off-site for treatment (at considerable expense). A review of treatment and disposal technologies showed that an AFC^{SM} treatment system could cost effectively pretreat this wastewater. Based on successful bench/pilot testing results, design of an AFC^{SM} system to treat the new production wastewater was initiated and completed. Construction of the AFC^{SM} system commenced in April 2002 and was completed by October 2002. The AFC^{SM} system start-up was commenced in October 2002. The system is designed to treat 40,000 lbs. COD/day. The major highlights of the project to date are as follows:

- The AFC^{SM} process easily treats the pharmaceutical wastes. Over 2,000,000 pounds of COD have been treated by early May 2003.
- The effluent from the treatment system has consistently met all discharge requirements.
- COD removal (based on the influent and effluent COD concentrations) has been 95% since the system start-up.
- Pharmaceutical products (A and B) have not been detected in effluent (permeate) samples collected during reactor operation.
- No sludge has been wasted from the system during the first seven months of operation.
- The system influent solids level has been significantly higher than design conditions. This situation should be rectified as the production operations become more dependable.

ACKNOWLEDGEMENTS

This project was constructed by USFilter's Industrial Wastewater Division, located in Warrendale, Pennsylvania.

REFERENCES

Rozich, A. F. and A. F. Gaudy, Jr. (1992) *Design and Operation of Activated Sludge Processes Using Respirometry,* Lewis Publishers, Inc., Chelsea, Michigan.

Rozich, A. F. and K. Bordacs. "Use of Thermophilic Biological Aerobic Treatment for Industrial Waste Treatment." Presented at the World Water Congress in Berlin, Germany, October 2001.