TVA HYBRID BIOREACTORS: Cost Saving Processes for Destruction of Water and Air Contaminants

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Summary

The Tennessee Valley Authority (TVA) has developed and patented Hybrid Bioreactors that simultaneously destroy water and air contaminants with dramatic savings over existing treatment methods. Contaminants destroyed include a wide variety of chlorinated solvents and VOCs such as TCE, DCE, methylene chloride, MTBE, BTEX, and fuel components. The new bioreactors can be used in a variety of applications ranging from site restoration to industrial compliance. Cost comparisons show that Hybrid Bioreactors achieve dramatic savings over water treatment methods used at Superfund sites. For chlorinated solvent removal, water decontamination costs using Hybrid Bioreactors are generally less than one-tenth of costs reported by EPA and DOE at Superfund sites. Furthermore, Hybrid Bioreactor decontamination costs for BTEX, fuel components, and other VOCs are generally only one-tenth those for chlorinated solvents. Air stripping merely transfers water contaminants to the atmosphere, and carbon adsorption only transfers the contaminants to another medium; removal and disposal of the contaminants are still necessary. Thermal oxidation generates NO_x, CO, and toxic by products, releasing them to the atmosphere. However, TVA's Hybrid Bioreactors destroy both water and air contaminants in a single step and generate no contaminated off gases or other secondary waste streams. TVA is currently demonstrating a 300-cubic-foot mobile Hybrid Bioreactor in Muscle Shoals, Alabama, to develop design information for commercial deployment. Further information is available at: http://www.tva.com/environment/envservices/alw biofilter.htm and at http://www.tva.com/environment/envservices/alw_pubs.htm#biofilter.

Body

Industrial operations today release large quantities of toxic materials to the environment, and improper use and handling of hazardous materials in the past have resulted in widespread contamination of soils and groundwater with pollutants such as trichloroethylene (TCE), benzene-toluene-ethyl benzene-xylenes (BTEX), methyl tertiary butyl ether (MTBE), and other volatile organic compounds (VOCs). Traditional cleanup methods such as scrubbing, stripping, and adsorption merely transfer pollutants to other media—removal or separation of the pollutants from these media and subsequent disposal of the pollutants is still necessary. Incineration can generate other toxic by products, releasing them to the atmosphere. Aerobic biofilters (gas treatment) and bioreactors (liquid treatment) can convert toxic pollutants to non-toxic products and are generally more economical than traditional clean up methods at low contaminant concentrations. In bioreactors and biofilters, contaminated streams are passed through packing containing microorganisms which degrade or mineralize the pollutants into harmless compounds such as carbon dioxide and water. In many cases, bioreactors and biofilters provide cost-saving, environmentally friendly alternatives to traditional pollution control or remediation technologies.

In many biological treatment processes of economic importance, the microorganisms directly consume the target contaminants, and the contaminated stream can be passed continuously through the process to achieve continuous biodegradation of the target contaminants. In other words, the microorganisms directly metabolize the contaminants as sources of food and growth. Such biodegradation processes will hereinafter be referred to as direct-metabolic (D-M) processes. Contaminants easily destroyed by D-M processes include a wide variety of VOCs such as methyl ethyl ketone, toluene, xylene, benzene, styrene, and methylene chloride as well as other compounds such as carbon disulfide, hydrogen sulfide, ammonia, and odor-causing compounds. However, certain contaminants, particularly chlorinated solvents like TCE, are not metabolized directly by naturally occurring aerobic microorganisms and thus cannot sustain the microorganisms as sources of food. In such cases, certain alternate carbon (food) sources, or primary substrates, can be supplied that the microorganisms directly metabolize, and in so doing, the microorganisms generate enzymes capable of degrading certain target contaminants that cannot be directly metabolized. In other words, the contaminants targeted for destruction are indirectly degraded by enzymes generated when the microorganisms directly metabolize another compound—a process known as

cometabolism. Hereinafter, such biodegradation processes shall be referred to as cometabolic (C-M) processes. The primary substrates can themselves be contaminants such as toluene, or they can be relatively innocuous compounds such as methane or propane.

TVA has developed and demonstrated several biofiltration processes (gas treatment) which economically destroy a wide variety of air contaminants released from a broad cross section of industries and clean up operations. In a project funded by the U.S. Army Environmental Center, a field demonstration was conducted of a biofiltration process (Figure 1) that efficiently and economically destroys TCE, dichloroethylene (DCE), methylene chloride, and other contaminants in air streams generated by air stripping of contaminated groundwater or industrial operations such as degreasing. The demonstration was conducted at Anniston Army Depot (ANAD), Anniston, Alabama during 1997-1999 at a groundwater air stripping site. This biofiltration process (Figure 1) requires use of a primary substrate to induce enzymatic degradation of TCE, as the microorganisms do not directly consume TCE. To achieve economical TCE destruction, the primary substrate—propane in this process—is intermittently removed from the system and alternated with periods of the waste stream feed—TCE contaminated air. This biofiltration process utilizes novel, patented processing schemes that dramatically improve process efficiency and economics. Although this biofiltration process is cost-effective for remediating contaminated air, considerable interest has been expressed in liquid-treatment bioreactor processes that would avoid air stripping altogether and decontaminate the water directly in a single step to save costs and simplify operation.

Hybrid Bioreactors and Cost Savings

In response to stakeholder interest, TVA conducted bench-scale tests that culminated in development and patenting of new liquid-treatment bioreactor processes (Figure 2) that economically destroy contaminants directly in groundwater or wastewater. The new bioreactor design eliminates an air stripping first step and thus saves capital and operating and maintenance (O&M) costs. More importantly, these new processes destroy the water contaminants <u>and</u> preclude their release as vapor-phase contaminants, whereas air stripping merely transfers water contaminants to the atmosphere. These new patented processes were termed "Hybrid Bioreactors" because they combine certain elements of traditional gas-phase biotrickling filter processes and traditional liquid-phase bioreactor processes. Flow of the contaminated water can be single-pass or recycled, continuous or batch. Unlike conventional aerobic bioreactors of this type, the patented process schemes employed in the new Hybrid Bioreactors preclude release of vapor-phase contaminants.

Testing of the new Hybrid Bioreactor process scheme was carried out in continuous-operation process equipment to directly detoxify TCE-contaminated water (0.5 to 20 mg/L TCE). After 4 months of operation and manipulation of critical process parameters, the single-stage Hybrid Bioreactor surpassed the performance of the two-stage, air stripper-biofilter process demonstrated at ANAD. At that stage of development, a Hybrid Bioreactor half the size of the ANAD gas-phase biofilter alone could accomplish that which required both the air stripper and the gas-phase biofilter in the ANAD demonstration. The Hybrid Bioreactor's smaller size and elimination of air stripping translate into substantial savings in capital and O&M costs. The higher performance of the Hybrid Bioreactor is a result of degrading TCE directly in the contaminated water and employment of patented processing schemes that preclude release of vapor phase contaminants. Favorable results with the C-M (cometabolic) Hybrid Bioreactor led to expansion of the test program to address a variety of applications and contaminants.

A similar D-M (direct metabolic) Hybrid Bioreactor was constructed and tested for detoxification of water contaminated with compounds that can be directly metabolized by aerobic microorganisms, benzene and toluene (4 mg/L of each). In less than 5 months of testing, the contaminated water rate had been increased 13-fold without sacrifice in performance (100% destruction of benzene and toluene). A 13-fold increase in water rate without reduction in performance translates into a 13-fold reduction in the size (and costs) required for the bioreactor at a given water rate. So far, the size and consequent costs required for a commercial D-M Hybrid Bioreactor have been reduced to within the same range as that required for air stripping alone, which only transfers water contaminants to vapor phase for release to the atmosphere;



FIGURE 1. TCE Biofilter process demonstrated at ANAD

FIGURE 2. Hybrid Bioreactor process

carbon adsorption, incineration, or some other removal method must then be employed to mitigate the contaminated air. Hybrid Bioreactors both remove and destroy the water contaminants in a single step with substantial savings and without impacting the environment. D-M Hybrid Bioreactor size and costs are generally only about one-tenth of those for C-M Hybrid Bioreactors because the contaminants are directly consumed by the microbes and do not require a primary substrate to induce cometabolic enzymatic degradation, as is the case with contaminants like TCE. Demonstration of a 300-cubic-foot mobile Hybrid Bioreactor is currently underway at TVA's Constructed Wetlands Complex in Muscle Shoals, Alabama to further optimize process parameters and develop information for scale-up to larger operations.

Treatment costs using Hybrid Bioreactors are dramatically less than those reported at Superfund sites. Cost comparisons between Hybrid Bioreactors and water treatment technologies used at Superfund sites (EPA Report 542-R-00-013, February 2001; DOE websites <u>http://www.em.doe.gov/techneed/hy12.html</u> and <u>http://www.em.doe.gov/techneed/hy15.html</u>) show that Hybrid Bioreactors enjoy a remarkable economic and environmental advantage, as shown in Figures 3 and 4. Using C-M Hybrid Bioreactors (e.g. TCE), estimated treatment costs were less than one-fourth of treatment costs reported at all 17 sites using multiple treatment systems (Figure 3). C-M Hybrid Bioreactor costs were less than one-tenth of the costs reported at 75% of these sites. At the 11 sites using only air stripping (which releases the contaminants in vapor phase), Figure 4, C-M Hybrid Bioreactor estimated costs were less than one-half of reported costs at 8 of these sites. The economic advantage using D-M Hybrid Bioreactors. For D-M Hybrid Bioreactors, estimated costs were less than those reported for air stripping alone (Figure 4).



FIGURE 3. Hybrid cost savings over multiple treatment systems used at Superfund sites



FIGURE 4. Hybrid cost savings over air stripping systems used at Superfund sites

Process Equipment and Operation

The process equipment for the C-M Hybrid Bioreactor consisted of a 304 stainless steel cylindrical vessel four inches in diameter and ten feet long. The bioreactor was filled with eight feet of packing consisting of one-half-inch ceramic saddles supported by a 304 stainless steel screen. The C-M Hybrid process was operated analogously to the TCE Biofilter process demonstrated at ANAD except that the contaminated stream was water containing TCE rather than air containing TCE. Process operation consisted of continuous alternation between a waste stream cycle (initially 2 hours) and a separate propane feeding cycle (initially 4 hours) to avoid intermingling of the TCE and propane, which competitively inhibits TCE degradation. The TCE-contaminated water was fed to the top void area of the bioreactor (Figure 2) and allowed to flow by gravity through the packing and out of the bottom of the bioreactor on a single-pass basis. Air was fed cocurrent to water flow. In the subsequent feeding cycle, propane gas was fed into the bioreactor cocurrent to air flow on an intermittent basis and was consumed by the microorganisms.

The process equipment for the D-M Hybrid Bioreactor was the same as that for the C-M Hybrid, except the packing consisted of 0.5-inch diameter lava rock. In the D-M Hybrid, pollutant degradation is accomplished by direct metabolism, so the primary substrate (propane) feeding cycle as described for the C-M Hybrid does not exist. Operation of the D-M Hybrid was essentially the same as that of the C-M Hybrid during the waste stream operation except that the water contaminants were benzene (4 mg/L) and toluene (4 mg/L). D-M processes are generally much more efficient than cometabolic processes because the bioreactor is receiving the waste stream continuously without interruptions for the primary substrate feeding cycle. This, coupled with direct consumption of the pollutants, yields higher degradation rates and efficiencies and lower costs.

Results

To facilitate better understanding of the results, definition of certain process operating variables or performance parameters follows:

- Load, mg/day-L Influent mass rate of contaminant per unit volume of packing (milligrams fed per day per liter of packing volume)
- <u>Degradation efficiency</u>, <u>%</u> Percent of contaminant removed from the water that was degraded in the bioreactor
- <u>Elimination efficiency, %</u> Percent of influent contaminant that was removed from the water <u>and</u> degraded in the bioreactor
- <u>Degradation rate, mg/day-L</u> Mass rate of contaminant degraded in the bioreactor per unit volume of packing (milligrams degraded per day per liter of packing volume)
- <u>Hybrid-to-biofilter size ratio</u> size of a single-stage Hybrid Bioreactor relative to the size of the ANAD TCE Biofilter alone that will match the maximum performance level achieved in the two-stage stripper/biofilter process used in the ANAD field demonstration. Since biofilter/bioreactor capital and O&M costs are mostly a function of size, this size ratio yields a comparison of Hybrid Bioreactor costs relative to the costs for the gas-phase biofilter alone, which would also require a prior air stripping step (added cost) to accomplish that which the Hybrid Bioreactor can accomplish in a single step.

Improvement in C-M Hybrid Bioreactor performance as the test program progressed is illustrated in Figure 5, which shows that performance improved dramatically during the first month of startup. Within approximately one month, degradation efficiency had increased to nearly 100%, indicating nearly zero vapor-phase TCE losses from the bioreactor. When degradation efficiency is 100%, all of the TCE that is removed from the water is degraded in the bioreactor and none is released in vapor phase. Degradation efficiency reached 100% approximately 2 months after startup. Thereafter, even with large increases in TCE load, the TCE degradation rate and elimination efficiency continued to improve while degradation efficiency remained at 100%. Less than 4 months after startup, the performance of the single-stage Hybrid Bioreactor had surpassed that of the maximum level achieved in the ANAD two-stage biofilter-stripper process, indicating that the size and thus cost required for a Hybrid Bioreactor of equal performance would be less than that of the gas-phase biofilter alone, which also requires an air stripper.

Figure 6 compares the effect of load (L) on performance of the ANAD stripper-biofilter with that of the Hybrid Bioreactor. With increase in TCE load, the slope of the degradation rate curve for the gas-phase biofilter decreases from that of the load line. The load line is simply the degradation rate (R) plotted against load (L) for the hypothetical case in which all of the contaminant fed to the bioreactor is degraded, the elimination efficiency is therefore 100%, and the degradation rate is therefore equal to the load (R = L, R/L = 1). For the gas-phase biofilter, the slope of the degradation rate and in decrease in the elimination efficiency (E) because E = 100(R/L). In contrast, the slope of the degradation rate curve for the C-M Hybrid Bioreactor remained nearly the same as the load line R = L, indicating that nearly all of the TCE fed to the bioreactor was degraded. Within the load ranges tested in the gas-phase biofilter, the performance limits of the Hybrid Bioreactor was degraded. Within the load ranges tested in the gas-phase biofilter, the performance limits of the Hybrid Bioreactor was degraded. Within the load ranges tested in the gas-phase biofilter, the performance limits of the Hybrid Bioreactor was degraded. Within the load ranges tested in the gas-phase biofilter, the performance limits of the Hybrid Bioreactor was degraded. Within the load ranges tested in the gas-phase biofilter, the performance limits of the Hybrid Bioreactor.



FIGURE 5. Rapid improvement in C-M Hybrid Bioreactor performance over time



FIGURE 6. C-M Hybrid Bioreactor surpasses performance of ANAD Biofilter-Stripper Process

Figure 7 shows the effect of increase in load and degradation rate on the size required for a Hybrid Bioreactor to match performance with that of the maximum achieved in the two-stage, stripper-biofilter process demonstrated at ANAD. As these results show, the performance of the Hybrid Bioreactor has substantially exceeded that of the gas-phase biofilter, allowing use of a Hybrid Bioreactor substantially smaller and less costly than the gas-phase biofilter alone to accomplish the same as that which required both air stripping and gas-phase biofiltration at ANAD.

As performance improved, it became apparent that the waste stream cycle time could be increased and the feed cycle time could be decreased to further improve performance and reduce size and costs. Figure 8 compares performance of the 2:4 process scheme with performance after increasing the waste stream cycle time to 3 hours and reducing the feed cycle time to 3 hours (3:3 process scheme) as a function of water rate at an influent TCE concentration of approximately 5 mg/L. Results obtained with the 3:3 scheme exhibited the same relationships between the water rate and the elimination and degradation efficiencies as were obtained with the 2:4 scheme. With increase in water rate, the TCE elimination efficiency decreased, as expected due to decrease in the contact time between the contaminated water and the microorganisms, but the reduction in elimination efficiency was small relative to the decrease in bioreactor size. With increase in water rate, degradation efficiency remained at virtually 100%, indicating virtually zero vapor-phase TCE losses from the bioreactor. These results show that when very high elimination efficiencies (e.g. > 99.8%) are unnecessary, the 3:3 scheme was clearly superior to that of the 2:4 scheme, in that a specific bioreactor will handle a higher water rate at the same elimination efficiency, or a specific water rate will require a smaller bioreactor at the same elimination efficiency. On the other hand, the 2:4 scheme may be superior when very high elimination efficiencies are required to meet required discharge concentrations. From another perspective, bioreactor size and costs increase with increase in the elimination efficiency required for the bioreactor, as would be expected, in that longer contact times between the contaminated water and the microorganisms are needed to remove larger proportions of the contaminants.





FIGURE 7. Reducing size (costs) of C-M Hybrid Bioreactor to less than ANAD Biofilter alone



Figure 9 illustrates the dramatic improvement in performance of the D-M Hybrid Bioreactor as growth and establishment of biomass progressed. As performance improved, the water rate was increased, which increased the VOC (food) load and in turn further increased biomass levels. As water rate was increased and performance improved, elimination efficiency of both benzene and toluene reached 100% with degradation rate equal to load, and the size required for the D-M Hybrid Bioreactor for a given elimination efficiency decreased from over 100 to less than 10 cubic feet per gallon-per-minute of water flow. In all tests with the D-M Hybrid Bioreactor at steady state conditions, toluene degradation efficiency was 100%, indicating zero toluene vapor-phase losses from the bioreactor. Benzene degradation efficiency ranged from 99.97% to 100.00%, indicating zero or virtually zero vapor-phase benzene losses from the bioreactor. A degradation efficiency of 99.97% means that only 0.03% of the contaminants removed from the water are released as vapor phase from the water are released as vapor-phase to the atmosphere.

Figure 10 shows that detoxification of water containing directly consumable VOCs can be accomplished in bioreactors one-tenth or less the size (capital and O&M costs) of that required for detoxifying water contaminated with TCE. Further improvements in process performance have been achieved since the data in Figure 10 were collected. At the current stage of development, the D-M Hybrid Bioreactor has achieved 98% benzene and toluene destruction with 5 cubic feet of packing per gallon-per-minute of continuous water flow at influent concentrations of 2.5 mg/L each. With 10 cubic feet of packing per gallon-per-minute of continuous water flow, the D-M Hybrid has achieved 100% benzene and toluene destruction at influent concentrations of 5 mg/L each. The C-M Hybrid Bioreactor has achieved 97% destruction of TCE with approximately 40 cubic feet of packing per gallon-per-minute of continuous water flow at an influent concentration of 1.6 mg/L. With 150 cubic feet of packing per gallon-per-minute of



FIGURE 9. Rapid improvement in D-M Hybrid Bioreactor performance over time



FIGURE 10. D-M Hybrid Bioreactor size (costs) only 10% those of C-M Hybrid Bioreactor

continuous water flow, the C-M Hybrid has achieved greater than 99.9% TCE destruction at an influent concentration of 6 mg/L. In recent tests with the C-M bioreactor in which MTBE was introduced as a contaminant along with the TCE, MTBE destruction efficiencies have been approximately the same as those achieved for TCE, and TCE destruction efficiencies are at least as high as those obtained without addition of MTBE. For lower influent contaminant concentrations and/or less stringent contaminant removal requirements, the size and consequent costs of both the D-M and the C-M Hybrid Bioreactors can be reduced substantially. In short, the designs, sizes, and capital and O&M costs for Hybrid Bioreactors are functions of the contaminant species present, the concentrations of the contaminants, the degree of contaminant removal required to meet discharge regulations, and the flow rate of the contaminated water stream. Thus, the designs, sizes, and costs for Hybrid Bioreactors are site specific, as is the case with other pollution control and remediation technologies.

Conclusions

Hybrid Bioreactors were highly successful in detoxifying TCE- or benzene/toluene-contaminated water in a single step without air stripping and with zero or virtually zero vapor phase losses. With increase in load or water rate, degradation rate increased and the size and cost decreased dramatically with relatively slight decrease in elimination efficiency. The high performance achieved in the Hybrid Bioreactors resulted from degradation of the contaminants directly in the contaminated water and employment of patented process schemes to eliminate vapor-phase loss of contaminants from the bioreactors. Economic comparisons show that Hybrid Bioreactors enjoy remarkable economic and environmental advantages over other water treatment technologies, with treatment costs generally less than one-tenth those reported at Superfund sites. Designs and costs for Hybrid Bioreactors are site specific, as is the case with other technologies, and are functions of the contaminant species present, the concentrations of the contaminants, the degree of contaminant removal required to meet discharge regulations, and the flow rate of the contaminated water stream. Advantages of Hybrid Bioreactors include:

- Dramatic cost savings over existing technologies
- Decontaminates both water <u>and</u> air in a single step
- Removes <u>and</u> destroys the contaminants
- Handles a wide range of contaminants
- Does not generate contaminated off gases
- Does not generate secondary waste streams
- Simple, automatic, remote process operation requiring minimal labor

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