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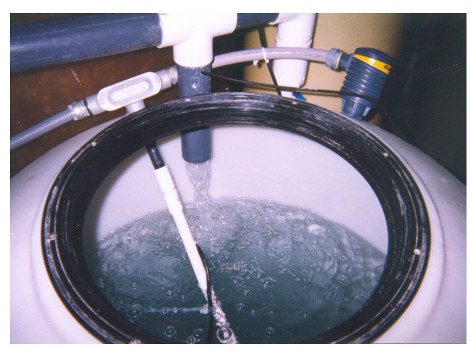
EcoMat Inc.'s Biological Denitrification Process

Innovative Technology Evaluation Report



SITE

SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

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Notice

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Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

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Hugh W. McKinnon, Director
National Risk Management Research Laboratory

Abstract

This report summarizes the findings of an evaluation of a biodenitrification (BDN) system developed by EcoMat Inc. of Hayward, California (EcoMat). This evaluation was conducted between May and December of 1999 under the U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation (SITE) Program; it was conducted in cooperation with the Kansas Department of Health and Environment (KDHE). The demonstration site was the location of a former public water supply well in Bendena, Kansas. The well water is contaminated with high levels of nitrate. Based on historical data, nitrate concentrations in the water have ranged from approximately 20 to 130 ppm, well above the regulatory limit of 10 mg/l. Low concentrations of volatile organic compounds (VOCs), particularly carbon tetrachloride (CCl_4), have been a secondary problem. The overall goal of EcoMat was to demonstrate the ability of its process to reduce the levels of nitrate in the groundwater to an acceptable concentration, thus restoring the water supply well as a drinking water source.

EcoMat's process is a two component process consisting of 1) an *ex situ* anoxic biofilter BDN system, and 2) a post-treatment system. The BDN system utilizes specific biocarriers and bacteria to treat nitrate-contaminated water, and employs a patented reactor for mixing the suspended biocarriers and retaining biocarrier within the reactors to minimize solids carryover. Methanol is added to the system as a carbon source for cell growth and for inducing metabolic processes that remove free oxygen and encourages the bacteria to consume nitrate. EcoMat's post-treatment system can be subdivided into two primary treatment parts: one part for oxidation and a second part for filtration. The oxidation treatment is intended to oxidize residual nitrite back to nitrate, oxidize any residual methanol, and destroy bacterial matter exiting the BDN system. The oxidation treatment may consist of ozonation or ultraviolet (UV) treatment, or a combination of both. Filtration usually consists of a clarifying tank and one or more filters designed to remove suspended solids generated from the BDN process.

The demonstration consisted of four separate sampling events interspersed over a 7½ month period of time. During these events EcoMat operated its system to flow between three and eight gallons per minute. During this same time period nitrate levels in the well water varied from greater than 70 mg/l to approximately 30 mg/l. For Event 1, chlorination was the only post-treatment used. Post-treatment for Event 2 consisted of clarification; sand filtration; cartridge filtration using 20µm rough filters; and UV oxidation. Post-treatment for Event 3 consisted of ozone; UV oxidation; clarification; cartridge filtration using 20µm rough filters, 5µm high efficiency filters, carbon adsorption, and 1µm polishing filters. Post-treatment for Event 4 consisted of chlorination, clarification, 5µm high efficiency filtration, air stripping, and 1µm polishing filtration.

The primary objective of the study focused on three performance estimates. The first performance estimate was to determine if the BDN portion of the process was capable of reducing combined nitrate-N/nitrite-N (total-N) to less than 10.5 mg/l. The second performance estimate included evaluation of the post-treatment for its ability to produce treated groundwater that would meet applicable drinking water standards with respect to nitrate-N, nitrite-N, and total-N, using a level of significance of 0.10. This required reducing high levels of nitrate-N to less than 10.5 mg/l, maintaining nitrite-N levels to less than 1.5 mg/l, and achieving a total-N level of less than 10.5 mg/l. When rounded to whole numbers, these performance estimates would meet the regulatory maximum contaminant limits (MCLs) of 10, 1, and 10 mg/l for nitrate-N, nitrite-N, and total-N respectively. The

Abstract (Cont'd)

third performance estimate involved evaluating the final effluents for other parameters, such as turbidity, pH, residual methanol, suspended solids, and biological material.

Results for the final system outfall indicate that when the post BDN effluent contains nitrite-N levels in excess of the regulatory limit of 1 mg/l the EcoMat post-treatment components failed to adequately and reliably reduce the nitrite-N levels to below the 1 mg/l level. The post-treatment system was varied considerably throughout the demonstration. For Event 1, chlorination was the only post-treatment used. Post-treatment for Event 2 consisted of clarification; sand filtration; cartridge filtration using 20µm rough filters; and UV oxidation. Post-treatment for Event 3 consisted of ozone; UV oxidation; clarification; cartridge filtration using 20µm rough filters, 5µm high efficiency filters, carbon adsorption, and 1µm polishing filters. Post-treatment for Event 4 consisted of chlorination, clarification, 5µm high efficiency filtration, air stripping, and 1µm polishing filtration. Comparison of samples collected immediately upstream and immediately downstream of the post-treatment systems indicated that none of the combinations used were effective for removing residual methanol. In all instances methanol levels were virtually the same or higher in final effluent exiting the post-treatment systems.

Since the post-treatment system implemented by EcoMat varied for each of the four events, data from the four events was first analyzed separately. Formal statistical analyses were used to address the first two performance estimates discussed above, using a significance level of 0.10. The overall conclusion from these tests was that:

- Events 1 and 2 were found to be successful in meeting the first two performance goals for significantly reducing levels of nitrate-N and nitrite-N after BDN and after post treatment.
- Event 3 and 4 were not shown to be successful in significantly reducing levels of nitrate-N and nitrite-N after BDN and after post treatment.

Daily dissolved oxygen (DO) field measurements indicated that the de-oxygenating step of EcoMat's BDN process may not have been optimized throughout the demonstration, and especially during Events 3 and 4. The desired DO level of partially biodenitrified (partial BDN) water in the De-oxygenating Tank is $\leq$ 1 mg/l. However, DO values below 1 mg/l were measured only during the first two events.

The effectiveness of the post-treatment systems were variable for different parameters. Comparison of samples collected immediately upstream and immediately downstream of the post-treatment systems indicated that none of the combinations used were effective for removing residual methanol to the demonstration objective of $\leq$ 1 mg/l. In all instances, downstream methanol levels were virtually the same or higher than upstream methanol levels. Methanol concentrations averages in final effluent were between 15 and 98 mg/l during the four events. the first two events appear to have had a substantial beneficial impact on solids carryover. Residual bacterial content in the final effluent, decreased significantly in Events 3 and 4, likely the result of adding "high efficiency" (5µm) and "polishing" (1µm) filters to the post-treatment system. Nevertheless, the levels of total heterotrophic and facultative anaerobe bacterial matter measured in the final effluent for all events was well above corresponding inlet water levels.

An economic analysis was also conducted for estimating the cost of implementing EcoMat's biological denitrification technology at full-scale. For a 100 gpm system, the estimated cost to treat nitrate-contaminated groundwater over a one year period is $490,000, or approximately $0.012/gal. The cost over 5, 10,or 15 years is estimated to increase to approximately$730,000 ($0.0034/gal.); $1,000,000 ($0.0024/gal.) and $1,300,000 ($0.002/gal.), respectively.

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Abbreviations and Acronyms

AQCR	Air Quality Control Regions
AQMD	Air Quality Management District
ATTIC	Alternative Treatment Technology Information Center
ARARs	Applicable or Relevant and Appropriate Requirements
BDN	Biodenitrification
cm^3	Cubic centimeter
CAA	Clean Air Act
CCl_4	Carbon tetrachloride
CERI	Center for Environmental Research Information
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CSCT	Consortium for Site Characterization Technologies
cfu	Colony forming units
CWA	Clean Water Act
DI	Deionized
DO	Dissolved oxygen
EcoMat	EcoMat Inc. of Hayward, CA
EDA	Exploratory data analysis
FA	Facultative anaerobes
FC	Fecal coliform
FS	Feasibility study
FID	Flame Ionization Detector
ft^2	Square feet
gpm	Gallons per minute
GC/MS	Gas chromatography/mass spectroscopy
G&A	General and administrative
g/cm^3	Gram per cubic centimeter
HSWA	Hazardous and Solid Waste Amendments
ICP	Inductively coupled plasma spectroscopy
ITER	Innovative Technology Evaluation Report
KDHE	Kansas Department of Health and Environment
kW/Hr	Kilowatts per hour
LDR	Land disposal restriction
LOS	Level of significance
m^3	Cubic meter
MS/MSD	Matrix spike/matrix spike duplicate
MCLs	Maximum contaminant levels
MCLGs	Maximum contaminant level goals
MDL	Method detection limit
MeOH	Methanol or methyl alcohol
mg/l	Milligrams per liter

Abbreviations and Acronyms (Cont'd)

MPN	Most probable number
NAAQS	National Ambient Air Quality Standards
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NIST	National Institutes of Standards and Technology
NOAA	National Oceanographic and Aeronautic Administration
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
NRMRL	National Risk Management Research Laboratory (EPA)
NSCEP	National Service Center for Environmental Publications
Nitrate-N	A measure of nitrate in which each mg/l of nitrate-N equates to 4.4 mg/l of nitrate
Nitrite-N	A measure of nitrite in which each mg/l of nitrite-N equates to 3.2 mg/l of nitrite
ND	Non-detectable, not detected, less than detection limit
NPDWS	National primary drinking water standards
NTU	Normal turbidity unit
OSHA	Occupational Safety and Health Administration
ORD	Office of Research and Development (EPA)
OSWER	Office of Solid Waste and Emergency Response (EPA)
OSC	On-scene coordinator
PLFA	Phospholipid fatty acids
POTW	Publicly owned treatment works
PPE	Personal protective equipment
PQL	Practical quantitation limit
POA	Project Objective Agreement
PVC	Polyvinyl chloride
PWS	Public water supply
POTW	Publicly owned treatment works
QAPP	Quality assurance project plan
RPD	Relative percent difference
RI/FS	Remedial Investigation / Feasibility Study
RPM	Remedial project manager
RCRA	Resource Conservation and Recovery Act
SAIC	Science Applications International Corporation
SARA	Superfund Amendments and Reauthorization Act
SDWA	Safe Drinking Water Act
SOP	Standard operating procedure
SW-846	Test methods for evaluating solid waste, physical/chemical methods
SWDA	Solid Waste Disposal Act
SITE	Superfund Innovative Technology Evaluation
S.U.	Standard units
TER	Technology Evaluation Report
TCH	Total culturable heterotrophs
TOC	Total organic carbon
TSCA	Toxic Substances Control Act
TSD	Treatment, storage, and disposal
THM	Trihalomethanes
µg/l	Micrograms per liter
UV	Ultraviolet
US EPA	United States Environmental Protection Agency
VOC	Volatile organic compound
WSR	Wilcoxon signed rank

Acknowledgments

This report was prepared under the direction of Dr. Ronald Lewis (retired) and Mr. Randy Parker, the EPA Technical Project Managers for this SITE demonstration at the National Risk Management Research Laboratory (NRMRL) in Cincinnati, Ohio. EPA NRMRL peer review of this report was conducted by Mr. Vicente Gallardo. Mr. Andrew Matuson of Science Applications International Corporation (SAIC) served as the SITE work assignment manager for the implementation of demonstration field activities and completion of all associated reports.

The demonstration required the combined services of several individuals from EcoMat Inc., the Kansas Department of Health Services (KDHE), the town of Bendena, KS, and SAIC. Peter Hall and Jerry Shapiro of EcoMat, Inc. served as logistical and technical contacts for the developer. Rick Bean of the KDHE was instrumental for making provisions for the treatment shed and associated utilities, and for conducting additional sampling and analysis independent of the SITE Program. Iraj Pourmirza of the KDHE Bureau of Water - Water Supply Section provided technical support regarding drinking water issues. The cooperation and efforts of these organizations and individuals are gratefully acknowledged.

This report was prepared by Joseph Tillman, Susan Blackburn, Craig Chomiak, and John Nicklas, of SAIC. Mr. Nicklas also served as the SAIC QA coordinator for data review and validation. Joseph Evans (the SAIC QA Manager), Dr. Herbert Skovronek, and James Rawe, all of SAIC, internally reviewed the report. Field sampling and data acquisition was conducted by William Carrier, Dan Patel, Steve Stavrou, and Joseph Tillman.

Cover Photographs: Clockwise from top left are **1)** "EcoLink" - synthetic polyurethane cubes, 1 cm on a side, used as biocarrier medium; **2)** Gas detector tube monitoring above overflow tank (dark tank in background is the "EcoMat Reactor" , also known as "R2"); **3)** Concrete cap for 23 ft. ID Public Water Supply Well # 1 (vent pipe visible on right side of cap); **4)** Post-BDN effluent discharging to overflow tank; **5)** Overview of biodenitrification system - Overflow tank (front), 2 m^3 EcoMat Reactor (center), and De-oxygenating Tank (far right); **6)** Portion of post-treatment system (clarifying tank at left); and **7)** Shed for housing treatment system.

Executive Summary

This report summarizes the findings of an evaluation of the EcoMat Biodenitrification (BDN) treatment process. The process was tested for treating groundwater contaminated with high levels of nitrate at the location of a former public water supply well in Bendena, Kansas. This evaluation was conducted under the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) Program.

It should be noted that BDN processes have been used for some years for treatment of wastewater and groundwater. However, the technology has been known in the past to be applied to the treatment of groundwater for drinking water purposes. Thus, the SITE Program's interest was to evaluate such an application.

Overview of Site Demonstration

The EcoMat BDN process is a type of fixed film bioremediation that uses specific biocarriers and bacteria to treat nitrate-contaminated water. Fixed film treatment allows rapid and compact treatment of nitrate with minimal byproducts. Unique to the EcoMat system is a patented mixed reactor that retains the biocarrier within the system, thus minimizing solids carryover. Methanol is added to the system as a source of carbon for cell growth and for inducing metabolic processes that remove free oxygen and encourage the bacteria to consume nitrate. Methanol is also important to assure that the nitrate conversion results in the production of nitrogen gas rather than the intermediate nitrite, which is considered to be more toxic.

EcoMat's BDN system was evaluated under the SITE Program at the location of a former public water supply well #1 (PWS) in Bendena, Kansas. The primary contaminant in the well water was nitrate. Based on historical data, nitrate concentrations in the water ranged from approximately 20 to 130 ppm, well above the regulatory limit of 10 mg/l. Low concentrations of VOCs, particularly carbon tetrachloride (CCl_4), were a secondary problem. The overall goal of EcoMat was to demonstrate the ability of its process to reduce the levels of nitrate in the extracted groundwater and restore the public water supply well as a drinking water source.

The central goal of EcoMat was to demonstrate that its system could produce groundwater from PWS Well # 1 that would be in compliance with the drinking water MCLs for nitrate-N, nitrite-N, and total-N, while at the same time meeting requirements for other parameters such as turbidity, pH, residual methanol, suspended solids, and biological material. With respect to both the BDN and post-treatment components of the system, EcoMat proposed the following three performance estimates:

- With incoming groundwater having nitrate-N of 20 mg/l or greater, and operating at a flow through rate of 3-15 gpm, the BDN unit would reduce the combined nitrate-N and nitrite-N level (total-N) in PWS Well #1 groundwater to at or below a combined concentration of 10 mg/l.
- The post treatment or polishing unit would produce treated groundwater meeting applicable drinking water standards with respect to nitrate-N (10 mg/l), nitrite-N (1 mg/l), and total-N (10 mg/l).
- Coupled with the planned or alternative post-treatment, the product water would consistently meet drinking water requirements, except for residual chlorine. Specifically it would not contain turbidity of greater than 1 NTU, detectable levels of methanol (1 mg/l), or increased levels of biological material or suspended solids, and would have a pH in the acceptable 6.5-8.5 range.

For the purposes of these evaluations, demonstration criteria were chosen that, when rounded to the nearest whole number, they would be consistent with the Kansas Department of Health and Environment (KDHE) MCL values. The KDHE MCL values for nitrate-N, nitrite-N, and total-N were 10, 1, and 10 mg/l, respectively. Thus, values less than the nitrite-N demonstration criterion of 1.5 mg/l (i.e., $\leq$ 1.49 mg/l) would reduce to 1 mg/l. Values less than the nitrate-N and total-N demonstration criterion of 10.5 mg/l (i.e., $\leq$ 10.49 mg/l) would reduce to 10 mg/l.

Conclusions from this SITE Demonstration

Since the post-treatment system implemented by EcoMat varied for each of the four events, data from the four events were first analyzed separately. Formal statistical analyses were used to address the first two performance estimates previously discussed (i.e., total-N level less than 10 mg/l, and nitrate-N and nitrite-N levels less than 10 mg/l and 1 mg/l, respectively), using a significance level of 0.10. The overall conclusion from these tests was that:

- Events 1 and 2 were determined successful in meeting the 1st and 2nd performance goals. Concentrations of total-N, nitrate-N, and nitrite-N were significantly reduced to below MCLs immediately following BDN treatment and after post treatment.
- Event 3 and 4 were determined not successful in meeting the 1st and 2nd performance goals for significantly reducing levels of total-N, nitrate-N, and nitrite-N after BDN and after post treatment.

A number of additional conclusions may be drawn from the evaluation of the EcoMat BDN and post-treatment processes as a whole, based on extensive analytical data supplemented by field measurements. These include:

- The filtration systems incorporated following the first event appear to have had a substantial beneficial impact on solids carryover. Based on laboratory and field measurements, the 5µm high efficiency and 1µm polishing filters used during the last two events produced better results for reduction of biological material, total suspended solids, and turbidity in the final effluent.
- Specific to turbidity, which has a secondary drinking water criterion of 1 Normal Turbidity Unit (NTU), average field measurement results for Events 3 and 4 final effluents were 1.2 and 0.96 NTU, respectively. These results were improved in comparison to the 1.8 NTU average value for Event 2 final effluent, in which “sand filtration” and “rough filtration” (20µm) were used; and where greatly improved in comparison to the 4.4 NTU average value for Event 1 final effluent, in which no filtration was used.
- Total suspended solids (TSS) laboratory results were similar to the turbidity field measurements. The demonstration criterion for TSS in final effluent was to be less than or equal to that of the inlet water, in which TSS was consistently measured to be below the detection limit of 5 mg/l for all four events. TSS results for Event 1 were consistently above this 5 mg/l threshold and averaged 10 mg/l. During Events 2, 3, and 4 TSS was measured above 5 mg/l in 3 of 9, 7of 9, and 7 of 8 of the final effluent samples collected, respectively. However, the average TSS value for these events was below the detection limit of 5 mg/l.
- The demonstration criterion for residual bacterial content in the final effluent was also to be less than or equal to that of the inlet water. The highest bacterial counts in final effluent occurred for Event 2. This was likely due to the fact that no disinfection (i.e., chlorine, ozone, etc.) was used and that “rough” filtration (20 µm) was the smallest filtration size used during Event 2. Residual bacterial content in the final effluent, decreased significantly in Events 3 and 4, likely the result of adding “high efficiency” (5µm) and “polishing” (1µm) filters to the post-treatment system. Nevertheless, the levels of total heterotrophic and facultative anaerobe bacterial matter measured in the final effluent for all events was well above corresponding inlet water levels.
- None of the post treatment system combinations used during the demonstration was effective in removing residual methanol to the demonstration objective of $\leq$ 1 mg/l. Methanol concentration averages in final effluent were between 15 and 98 mg/l during the four events. Methanol was actually measured on average to be higher in the final effluent samples than in post BDN samples (collected upstream of the post-treatment system) for three of the four events. This may be an anomaly attributable to ongoing methanol degradation in the post BDN samples prior to analysis. The final effluent samples were disinfected (preserved) so that further reaction was halted.
- There appears to be an inverse correlation between flow rate and nitrate removal (i.e., higher flow rate correlating to less effective nitrate removal), based on a per sample round comparison of system flow rate and Total-N concentration in final effluent. However, it was not possible to confirm that this was a cause/effect relationship because of (a) the narrow range of flows actually investigated and (b) variations in performance that occurred or became necessary due to upsets, and other operational problems.

- pH was not altered by the EcoMat BDN or post-treatment systems. For Events 1 and 2 there was a very slight increase in pH from the inlet water to the post BDN effluent. No discernable change in pH between inlet water and final effluent was measured for Event 3. For Event 4, the pH values for inlet water ranged from 8.3 - 9.2 (outside of the acceptable drinking water limits of 6.5-8.5). Final effluent pH values were slightly lower and ranged from 6.8 - 8.9.

- Daily dissolved oxygen (DO) field measurements indicated that the de-oxygenating step of EcoMat's BDN process may not have been optimized. The desired DO level of partially biodenitrified (partial BDN) water in the de-oxygenating tank is $\leq$ 1 mg/l. However, DO values below 1 mg/l were measured only during the first two events. Average DO during Events 1 and 2 were 1.1 and 1.0 mg/l, respectively. DO in partial BDN effluent during Event 3 were consistently measured above 1 mg/l and averaged 2.1 mg/l. DO in partial BDN effluent during Event 4 was also consistently measured above 1 mg/l and averaged 2.8 mg/l. Because Events 3 and 4 had poorer nitrate removal than Event 1 and 2, the inability to optimize the de-oxygenating step of the BDN process during the last two events could have negatively impacted results.

- The quality assurance analyses of critical sample data indicated adequate data quality was achieved for evaluating the EcoMat technology. With respect to data accuracy, the overall demonstration recovery average for 44 nitrate-N MS/MSD sample sets was approximately 95%. The overall demonstration recovery average for 44 nitrite-N MS/MSD sample sets was approximately 96%. With respect to data precision, the overall demonstration average relevant percent difference for those MS/MSD sets for nitrate-N and nitrite-N were 2.7 and 2.1, respectively.

- Carbon tetrachloride, which had been historically detected in PWS Well #1 water, was not detected in inlet water or final effluent samples. Thus, the effectiveness of any of the post-treatment combinations for treating this compound could not be evaluated.

- For a 100 gpm system, the estimated cost to treat nitrate-contaminated groundwater over a one year period is $490,000, or approximately $0.012/gal. The cost over 5, 10,or 15 years is estimated to increase to approximately$730,000 ($0.0034/gal.); $1,000,000 ($0.0024/gal.) and $1,300,000 ($0.002/gal.), respectively.