## DENITRIFICATION OF HIGH-STRENGTH INDUSTRIAL WASTEWATERS

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This report presents a comparison, in condensed form, of the findings of two M.S. theses resulting from the research project: "High-Rate Autotrophic Denitrification of Simulated Industrial Wastewater" by B.J.B. Ross (December 1989) and "Heterotrophic Denitrification of Simulated High-Strength Industrial Wastewater" by Srikanth Krishnamachari (May 1990).

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#### INTRODUCTION

Industries producing highly concentrated nitrogenous waste streams include chemical fertilizers, munitions, nuclear fuel processing, and semiconductor manufacturing, among others. Regenerant streams from ion exchangers used to remove contaminants from drinking or process waters may also present problems in treatment and disposal of strong nitrogenous wastes. Biological nitrification and denitrification have been applied to tertiary treatment of low-strength municipal wastewaters, with nitrogen concentrations typically < 50 mg/L. Limited studies have shown the potential of these processes to treat nitrogen concentrations > 1,000 mg/L efficiently, particularly in the absence of significant amounts of biodegradable organic matter.

Previous studies (Collins <u>et al</u>. 1988 a,b) have shown that fixed-biofilm reactors were capable of completely nitrifying between 500 and 1,000 mg NH<sub>4</sub><sup>+</sup>-N/L in a semiconductor waste, providing an economically viable alternative to air stripping. Denitrification could be used as a second stage process in a complete removal system for wastes of this type, or alone for treatment of wastes containing nitrate and/or nitrite-N. Denitrification may be carried out heterotrophically by common facultative bacteria, for example species of <u>Pseudomonas</u>, <u>Alcaligenes</u>, <u>Paracoccus</u>, <u>Bacillus</u>, <u>Propionibacterium</u>, etc. These organisms metabolize organic compounds for carbon and energy. Much less well-known are the various autotrophic denitrifying bacteria. Different species are capable of deriving energy from oxidation of hydrogen, reduced iron and sulfur ions, etc. for the incorporation of inorganic carbon. Examples of sulfur oxidizers are <u>Thiosphaera</u> <u>pantotropha</u>, <u>Thiomicrospira denitrificans</u>, and <u>Thiobacillus denitrificans</u> (Ross 1989). Both heterotrophic and autotrophic denitrifying bacteria use nitrate as a terminal electron acceptor to facilitate the oxidation of substrate. The intermediate

and final products of this process are given in the following general sequence from more oxidized to more reduced:

Certain species of bacteria may be more or less able to use each of the intermediates to oxidize substrate. Environmental conditions may also affect how completely the reduction may be carried out, resulting in accumulation of certain intermediate compounds.

Comparison of the stoichiometry of heterotrophic and autotrophic denitrification reveals that, whereas the heterotrophs are net alkalinity producers, autotrophic denitrifiers consume alkalinity (are net producers of acidity) in much the same way as nitrifying bacteria. Following are calculated stoichiometries for the two systems:

Autotrophic (Ross 1989):

 $NO_3^- + 0.79 S_2O_3^- + 0.27 HCO_3 + 0.20 H_2O = 0.05 C_5H_7O_2N + 0.47N_2 + 1.56 SO_4^- + 0.28 H^+$ 

Heterotrophic (McCarty et al. 1969):

 $NO_3^{-} + 1.08 CH_3OH + H^{+} = 0.065 C_5H_7O_2N + 0.47 N_2 + 0.76 C_{02} + 2.44 H_2O$ 

The purpose of this study was to determine the upper concentration and loading rate limitations of both heterotrophic denitrification using methanol as carbon and energy source and autotrophic denitrification using bicarbonate carbon and thiosulfate as electron donor. Studies were carried out in benchscale attached film expanded bed (AFEB) and upflow sludge blanket (USB) reactors. Therefore, comparisons were made between different microbial populations and between two high-rate biological reactor configurations.

#### **Research Objectives**

The overall goal of the study was to demonstrate the feasibility of denitrification of concentrated waste streams having NO<sub>3</sub><sup>-</sup> -N concentrations in excess of 500 mg/L. Specific objectives were as follows:

- Determine the maximum nitrate concentration which could be treated without significant loss of efficiency.
- Determine the maximum volumetric loading and removal rates achievable.
- Establish the stoichiometric chemical requirements for high-rate denitrification under the experimental conditions.
- Compare results of heterotrophic denitrification with methanol to autotrophic denitrification with thiosulfate.
- Compare the performance of two high-rate reactors, the attached film expanded bed (AFEB) and the upflow sludge blanket (USB).

#### MATERIALS AND METHODS

#### **Experimental Apparatus**

Bench-scale AFEB and USB reactors were constructed for these experiments. One AFEB and one USB were tested simultaneously under heterotrophic and autotrophic conditions; thus, a total of four reactors were used. Each had a total volume of approximately 2.5 L, 30 to 40 percent of which was occupied by denitrifying biomass under the operating conditions of the study. These reactor configurations were chosen due to their demonstrated capacity for high loading and conversion rates in a variety of applications. Extremely high

biomass densities and high cell residence times coupled with low hydraulic residence times make them ideal candidates for any anaerobic or anoxic treatment system. Energy requirements of these systems are relatively low, and solids may be handled efficiently, perhaps obviating the need for secondary clarification.

AFEB systems have been fully described elsewhere (Schraa and Jewell 1984). The essential elements of this system are that it is a fixed biofilm process employing small, lightweight, inert support media which are suspended in an upward flowing recycle stream taken from the reactor above the bed. Diatomaceous earth particles (~ 0.2 - 0.6 mm diameter) were used in this research. The bed was expanded approximately 15 to 20 percent by the recycle flow. The light support media are easy to fluidize slightly in this manner, resulting in greater biomass densities than a typical fluidized bed reactor. A schematic diagram of the experimental AFEB system is shown in Figure 1. The reactors were constructed from an acrylonitrile plastic Imhoff settling cone attached to an upper segment of plexiglass tubing. A funnel was placed in the reactor to allow for gas capture and to provide a water seal to the level of the effluent overflow port.

The USB reactors do not employ any biofilm support media, nor in this case was there any provision for effluent recycle. The biomass forms a "blanket" of sludge which will exhibit flocculant or granular properties depending on the operating conditions of the system. Influent was introduced into the reactor at the bottom, and mixing was accomplished with a magnetic stirrer set at low speed. A stir bar in a cage was balanced in the rounded bottom portion of the reactor vessel. The mixing system was intended to slowly and continuously agitate the sludge blanket just enough to enhance granulation and contact of biomass with substrate, but did not always perform satisfactorily. The USB reactors were made

of glass and as indicated in the process schematic diagram (Figure 2), were fitted with an outer collar to collect effluent overflowing the center section. A funnel in the inner part served the same purpose as in the AFEB.

#### Nitrogen Substrates

This study was meant to determine limits on the technology in terms of nitrate concentrations, volumetric conversion rates, treatment efficiencies, and actual stoichiometry in the absence of any other inhibitions or interferences. Thus, synthetic substrates were made up to provide for the growth needs of heterotrophic and autotrophic bacteria. Recipes for the synthetic wastes are given in Table I for a nitrate-N concentration of 500 mg/L. This concentration was adjusted as desired.

#### **Analytical Procedures**

Total and volatile suspended solids, pH, alkalinity, and COD (closed reflux culture tube procedure) were analyzed according to Standard Methods (APHA <u>et</u> <u>al</u>. 1985). Nitrate, nitrite, and sulfate were measured with a Dionex 2000 i/SP ion chromatograph following Standard Methods. Thiosulfate was determined by titration with iodine (Pierce and Hanisch 1948). Attached biomass was quantified as volatile solids by procedures described by Clarkson (1986).

#### Inoculation, Start-up, and Reporting of Results

Inoculum for both sets of experiments was obtained from return sludge of the Ponca City, Oklahoma, activated sludge municipal wastewater treatment

plant. The sample was divided and fed methanol or thiosulfate once per day for two weeks to encourage the growth of heterotrophic and autotrophic denitrifying bacteria, respectively. After two weeks of inoculum development, the AFEB and USB reactors were seeded by filling to about two-thirds volume and initiating continuous feeding. Initial conditions were NO3<sup>-</sup> -N concentrations between 250 and 500 mg/L and hydraulic residence times (HRT) of 6 hours. As washout of biomass occurred during the initial start-up period, small amounts of fresh inoculum from the semi-continuous seed reactors were added to replace the loss. The autotrophic USB developed a granular appearance, in place of the light, flocculant initial growth, after about six weeks. The autotrophic AFEB also became fully coated with biofilm and increased in bed volume between 350 to 450 mL within the same time period. The heterotrophic AFEB volume grew from 420 to 700 mL in seven to eight weeks. Due in part to uneven performance of the mixing system, the heterotrophic USB required about 12 weeks for development of a distinct sludge blanket with a clear blanket/supernatant interface. Truly granular sludge was not observed in this reactor; however, the appearance of the blanket was characterized by tight floc formation.

Start-up was deemed complete when the reactors exhibited significant biomass development and a stable response in terms of treatment efficiency. Experimental data were taken from that point onward. Each data point represents the mean of at least three individual samples taken after daily monitoring indicated that a steady-state condition had been reached. In this study, steadystate conditions were considered to have been achieved when no significant change in removal efficiency or other key parameters could be observed over a span of at least 10 hydraulic residence times.

All feed concentrations, loading rates, and conversion rates are expressed in terms of "nitrogen equivalent" (<u>e.g.</u> mg N<sub>e</sub>/L). This represents the total of

nitrate-N and nitrite-N, the soluble oxidized nitrogen forms present in a given sample. Small amounts of nitrite were found in most influent and effluent samples. At the highest loading rates, particularly in the heterotrophic systems, high concentrations of nitrite accumulated in the effluent. Thus, conversion efficiency in terms of  $N_e$  concentration may be relatively low when very little nitrate remained after treatment. It is felt that this was due to particular bacterial species' inability to reduce nitrite under the experimental conditions.

#### **RESULTS AND DISCUSSION**

The experimental strategy for each of the reactor systems consisted of two series of tests conducted in sequence. The first series was designed to determine an upper limit on substrate nitrogen concentration, while the second series was intended to determine the maximum loading and removal rates achievable by increasing loading rates (decreasing HRT) at substrate concentrations somewhat below the previously determined upper limit.

#### **Constant HRT/Variable Concentration Experiments**

At the conclusion of the start-up phase, both AFEB reactors were operated at approximately 3.5 hr HRT, and both USB reactors at approximately 6 hr HRT. These feed rates were maintained throughout phase one of the experiments, while feed concentrations were increased stepwise until a significant decrease in treatment efficiency was observed. Initial target concentrations were 750 mg N<sub>e</sub>/L in the autotrophic AFEB, 700 mg N<sub>e</sub>/L in the heterotrophic AFEB, 275 mg N<sub>e</sub>/L in the autotrophic USB, and 200 mg N<sub>e</sub>/L in the heterotrophic USB. Results of these experiments are summarized in Tables II and III for the AFEB and USB

reactors, respectively.

AFEB reactors. Data from Table II are plotted in Figures 3 and 4 to show the effect of influent nitrogen concentration on treatment efficiency and  $N_e$ reduction in the AFEB reactors. The plots reveal a clear break in the response curve for autotrophic denitrification at about 1,000 mg N<sub>e</sub>/L. This breakdown in efficiency probably comes about as a result of product formation (e.g. sulfate buildup) rather than as a direct function of influent nitrate loading. The break point for heterotrophic denitrification is not quite as well defined, but Figure 4 shows the upper concentration limit to be in the range of 1,400 to 1,500 mg N<sub>e</sub>/L for near complete efficiency. In terms of volumetric loading rate, these upper limits equate to about 7 and 11 kg N<sub>e</sub>/m<sup>3</sup> • d for the autotrophic and heterotrophic AFEB systems, respectively.

USB reactors. Results of the USB experiments from Table III are plotted in Figures 5 and 6 and show a similar response. The autotrophic system again begins to experience difficulty at about 1,000 mg N<sub>e</sub>/L feed concentration. The heterotrophic USB, while lagging noticeably behind the autotrophic reactor throughout the range of values tested, again breaks down at influent concentrations close to 1,400 mg N<sub>e</sub>/L.

#### **Constant Concentration/Variable HRT Experiments**

Based on the results of the first series of tests, feed concentrations were selected for each reactor in order to test the effects of increasing loading rate on system performance. This was accomplished by increasing the pumping rate of substrate through the reactors, thus decreasing the HRT incrementally until the pattern of response could be ascertained. The autotrophic AFEB reactor was operated at 750 mg N<sub>e</sub>/L, while the heterotrophic AFEB received 925 mg N<sub>e</sub>/L due

to the higher limiting value found in phase one experiments. Both USB reactors were fed at 500 mg N<sub>e</sub>/L. Even though the pattern of limiting concentration values was similar in the USB tests to the AFEB values, all feed concentrations over 500 mg N<sub>e</sub>/L resulted in treatment efficiencies less than 80 percent in the heterotrophic USB. Results of this second phase of testing are summarized in Tables IV and V for the AFEB and USB reactors, respectively.

AFEB reactors. Data from Table IV are plotted in Figure 7. The heterotrophic reactor shows a linear relationship of decreasing treatment efficiency with increasing loading rate. Conversion efficiency dropped below 90 percent at all loading rates over 10 kg N<sub>e</sub>/m<sup>3</sup> • d. However, the loss of efficiency was gradual with increasing loading such that 50 percent removal efficiency was still observed at a volumetric loading in excess of 40 kg N<sub>e</sub>/m<sup>3</sup> • d. At this operating condition, the heterotrophic AFEB was converting methanol substrate at a rate of 69 kg COD/m<sup>3</sup> • d, a rate comparable to the highest reported for biological treatment processes (Clarkson 1986).

The autotrophic AFEB demonstrated near 100 percent conversion efficiency throughout the entire range of loadings tested. Failure actually occurred as a result of physical upset of the expanded bed from excessive biogas production, which tended to carry media to the surface of the reactor. The biological capacity of the reactor had not been reached at 17.5 kg/m<sup>3</sup> • d, the highest loading rate test completed.

**USB reactors.** Data from Table V, plotted in Figure 8, again indicate a dramatic difference in response between the two bacterial populations. The heterotrophic system shows a much lower treatment efficiency throughout the range of experimental loadings than the autotrophic system. The heterotrophic response is linear, as in the AFEB, but efficiencies are much lower. Response of the autotrophic USB is very similar to the AFEB, and in this case the system was

pushed far enough to observe the loading rate limitation on efficiency. This break point clearly occurred between influent loadings of 15 and 20 kg  $N_e/m^3 \cdot d$ .

#### **General Results**

Stoichiometric parameters for chemical consumption and product formation were in accord with predicted values for all of the systems except that the autotrophic bacteria exhibited a lower than expected ratio of Ne reduced to alkalinity consumed, in comparison with the calculated stoichiometry presented earlier. Specific removal rates were calculated for the AFEB reactors based on the attached biofilm volatile solids in each reactor. Attached autotrophic biomass averaged 25 kg VS/m<sup>3</sup> of settled bed volume, and the specific removal rate in this case ranged from 0.21 to 0.67 kg Ne/kg VS • d. In the heterotrophic system, attached biomass averaged 82 kg VS/m<sup>3</sup>. With this extremely high biofilm concentration, specific activity may be assumed to be low, and in fact was measured as 0.09 to 0.14 kg  $N_e/kg VS \bullet d$ . On the basis of organic removal, the rate for the heterotrophic AFEB was between 0.31 and 0.43 kg COD/kg VS • d. Low specific activities are generally associated with long cell residence times in biological systems characterized by high biomass concentrations in the reactor and low effluent volatile suspended solids. Effluent VSS in these experiments averaged 47 mg/L in the autotrophic AFEB, 59 mg/L in the autotrophic USB, 46 mg/L in the heterotrophic AFEB, and 94 mg/L in the heterotrophic USB.

#### Discussion

In order to view the results of this research in proper perspective, they must be assessed in comparison to other studies conducted under comparable

conditions. Table VI is a summary of results obtained by other investigators. It should be noted that most experiments were conducted with feed concentrations ranging from 500 to 1,500 mg N<sub>e</sub>/L. One autotrophic study is reported, and certain heterotrophic systems used organic substrates other than methanol. Reactor types represented include static filters or packed bed reactors (PBR), upflow sludge blankets (USB), one complete-mix continuous stirred tank reactor (CSTR), and fluidized bed reactors (FBR).

In the temperature range of this study (~  $20-25^{\circ}$ C) the highest documented volumetric removal rate is 12.1 kg N<sub>e</sub>/m<sup>3</sup> • d, comparable to results obtained in this study with the heterotrophic AFEB. However, both the autotrophic AFEB and USB reactor systems significantly exceeded this rate. Part of the effect may be attributable to the fact that most other studies were conducted on real process waste streams containing impurities which could inhibit the denitrification process. The extremely positive effect of elevated temperature on reaction rates can be seen by comparing the results of Bosman <u>et al</u>. (1978) at 20 and 38°C. Denitrification rates could thus be enhanced significantly when treating warm process wastes.

#### CONCLUSIONS

These experiments have demonstrated the feasibility of applying high-rate biological treatment technology to denitrification of solutions over a concentration range of 500 to > 1,500 mg N<sub>e</sub>/L. Specific conclusions which can be drawn from this study include the following:

• The autotrophic AFEB achieved 99 percent nitrogen removal at loadings up to at least 17.5 kg/m<sup>3</sup> • d, feed concentration = 760 mg N<sub>e</sub>/L, and HRT = 1.1 hr.

- Upper limit of autotrophic AFEB loading was not reached due to physical upset from excessive biogas production.
- The autotrophic USB demonstrated that granular sludge development is achievable with this bacterial population.
- The autotrophic USB achieved 96 percent nitrogen removal efficiency at loadings up to 14.3 kg N<sub>e</sub>/m<sup>3</sup> d, feed concentration = 500 mg N<sub>e</sub>/L, and HRT = 0.8 hr.
- Upper limit of autotrophic USB loading was encountered at between 15 and 20 kg  $N_e/m^3$  d, before treatment efficiency dropped below 99 percent.
- The autotrophic bacteria showed a definite limiting feed concentration for complete conversion efficiency at about 1,000 mg  $N_e/L$ .
- The heterotrophic AFEB achieved 91 percent removal efficiency at a loading of 11.7 kg  $N_e/m^3$  d, feed concentration = 1670 mg  $N_e/L$ , and HRT = 3.4 hr.
- The maximum removal rate in the heterotrophic AFEB was noted at a loading of 42 kg  $N_e/m^3$  d. Conversion rate at this condition was 22 kg  $N_e/m^3$  d, which corresponds to an organic conversion rate of 69 kg  $COD/m^3$  d.
- Heterotrophic bacteria tolerated higher feed concentrations of nitrogen than the autotrophs before significant reductions in treatment efficiency occurred.
- Both the heterotrophic AFEB and USB reactors, in contrast to the autotrophic units, showed a linear response of treatment efficiency to loading rate.
- Accumulation of nitrite was noted when treatment efficiency dropped at higher loading rates, particularly in the heterotrophic systems.

• The heterotrophic USB performed relatively poorly, achieving a maximum conversion rate of only 4.5 kg  $N_e/m^3$  • d. This may have been related to poor sludge granulation or to problems with the mixing system in addition to any biological factors.

Three of the four systems tested therefore demonstrated superior potential for use in a number of industrial waste treatment applications. It is felt that the autotrophic systems are particularly well suited to industrial situations, provided that dilution of very strong wastes can be accomplished to bring the feed concentrations into the completely treatable range.

#### BIBLIOGRAPHY

- APHA, AWWA, and WPCF, <u>Standard Methods for the Examination of Water and</u> <u>Waste- water</u>, 16th edition (1985).
- Blaszczyk, M., E. Galka, E. Sakowicz, and R. Mycielski, "Denitrification of High Concentrations of Nitrites and Nitrates in Synthetic Medium with Different Sources of Organic Carbon, III: Methanol,", <u>Acta Microbiol. Polon</u>., 34, 195-206 (1985).
- Bode, H., C.F. Seyfried, and A. Kraft, "High-rate Denitrification of Concentrated Nitrate Wastewater, <u>Water Sci. Technol.</u>, 19, 163-174 (1987).
- Bosman, J., A.A. Eberhard, and C.I. Baskir, "Denitrification of a Concentrated Nitrogenous Industrial Effluent Using Packed Column and Fluidized Bed Reactors," <u>Prog. Water Technol.</u>, 12, 667-680 (1978).
- Clarkson, W.W., "Fermentation of Particulate Organic Matter to Methane in a Thermophilic Anaerobic Attached Film Expanded Bed Reactor," Ph.D. Thesis, Cornell University (1986).
- Claus, G. and H.J. Kutzner, "Physiology and Kinetics of Autotrophic
   Denitrification by <u>Thiobacillus denitrificans</u>, <u>Appl. Microbiol. Biotechnol.</u>,
   22, 283-288 (1985).
- Collins, A.G., W.W. Clarkson, and S.A. Florio, "Nitrification of a Strong Industrial Waste Using Aerobic Expanded Bed Reactors," <u>Proc. Industr. Wastes</u> <u>Symposia</u>, Session 15, 61st Ann. Conf. of the WPCF, Dallas (1988a).
- Collins, A.G., W.W. Clarkson, and M. Vrona, "Fixed-film Biological Nitrification of a Strong Industrial Waste," <u>J. Water Pollut. Control. Fed.</u>, 60, 499-504 (1988b).
- Jewell, W.J. and R.J. Cummings, "Denitrification of Concentrated Nitrate Wastewaters," J. Water Pollut. Control Fed., 47, 2281-2291 (1975).

- Klapwijk, A., J.C.M. van der Hoeven, and G. Lettinga, "Biological Denitrification in an Upflow Sludge Blanket Reactor," <u>Water Research</u>, 15, 1-6 (1981).
- McCarty, P.L., L. Beck, and P.S. Amant, "Biological Denitrification of Wastewaters by Addition of Organic Materials," <u>Proc. 24th Industr. Waste Conf.</u>, Purdue Univ. Ext. Serv., 135, 1271-1285 (1969).
- Miyaji, Y. and K. Kato, "Biological Treatment of Industrial Wastes Water by Using Nitrate as an Oxygen Source," <u>Water Research</u>, 9, 95-101 (1975).
- Pierce, W.C. and E.W. Hanisch, <u>Quantitative Analysis</u>, Wiley, New York (1948).
- Ross, B.J.B., "High-rate Autotrophic Denitrification of Simulated Industrial Wastewater," M.S. Thesis, Oklahoma State University (1989).
- Schraa, G. and W.J. Jewell, "High Rate Conversions of Soluble Organics with a Thermophilic Anaerobic Attached Film Expanded Bed," <u>J. Water Pollut.</u> <u>Control Fed.</u>, 56, 226-232 (1984).

#### APPENDIX

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### Table I. Synthetic Industrial Wastewater Recipes (made up with tap water)

Autotrophic Denitrification (500 mg NO <sub>3</sub> -N/L)	
Ingredients	Concentration (g/L)
Potassium Nitrate, KNO3	3.60
Sodium Thiosulfate, Na2S2O3	7.20
Sodium Bicarbonate, NaHCO3	3.60
Mono Potassium Phosphate, KH <sub>2</sub> PO <sub>4</sub>	0.10
Ferrous Sulfate, FeSO <sub>4</sub>	0.01

## Heterotrophic Denitrification (500 mg NO<sub>3</sub><sup>-</sup>-N/L)

Ingredients	Concentration (g/L).
Potassium Nitrate, KNO <sub>3</sub>	3.60
Methanol, CH <sub>3</sub> OH	1.50
Mono Potassium Phosphate, KH <sub>2</sub> PO <sub>4</sub>	0.035
Magnesium Sulfate, MgSO <sub>4</sub>	0.004
Ferrous Sulfate, FeSO <sub>4</sub>	0.002

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Infl. Conc. mg Ne/L	_Ne_Co mg/L	nsumed%	Exp.Bed Vol. mL	HRT hour	Attached Biomass kg VS/m <sup>3</sup>	Gas Collected L/d	Loading Rate kg Ne/m <sup>3</sup> •d	Removal Rate kg Ne/m <sup>3</sup> •d
Heterotro	ohic React	<u>or:</u>						
689	688	99.9	900	3.1	55	3.1	5.36	5.35
986	926	93.9	1000	3.4	••• <del>••</del>		6.90	6.48
1004	999	99.5	1000	3.4	82	6.1	7.03	6.99
1495	1412	94.4	1000	3.4			10.47	9.88
1671	1516	90.7	1000	3.4	83	9.4	11.70	10.61
1748	1211	69.3	1000	3.4	80		12.24	8.48
Autotrophi	ic Reactor	:						
741	738	99.6	875	3.4	23	5.8	5.42	5.40
882	879	99.7	1000	3.8	27		5.65	5.63
1041	1026	98.6	1000	3.8	21	6.9	6.66	6.57
1242	828	66.7	1000	3.8			7.95	5.30

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Table II. Summary of AFEB Reactors at Constant HRT and Variable Feed Concentration

Infl.	Ne Cons	Sumed	Gas	Loading	Removal	
Conc. mg Ne/L	mg/L	X	Collected L/d	Rate kg Ne∕m <sup>3</sup> ∙d	Rate kg Ne∕m <sup>3</sup> ∙d	
Heterotroph	ic Reactor:					
199	199	100		0.80	0.80	
291	290	99.7		1.16	1.16	
402	401	99.8		1.61	1.61	
592	409	69.1		2.37	1.64	
782	597	76.3		3.13	2.39	
1030	792	76.9	2.4	4.12	3.17	
1308	885	67.7	3.1	5.23	3.54	
1485	664	44.7	1.6	5.94	2.66	
Autotrophic	Reactor:					
277	265	95.3	3.4	1.11	1.05	
496	487	97.9	6.9	1.98	1.96	
758	756	99.7		3.03	3.02	
801	761	95.0	7.5	3.20	3.05	
939	923	98.3	7.8	3.76	3.69	
1086	864	79.6		4.34	3.46	

Table	e III.	Summary of	F USB	Reactors	at	Constant	6	Hour	HRT	and	Variable	Feed	Concentration
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Infl. Conc.	_Ne Cor	isumed	Exp.Bed Vol.	HRT	Attached Biomass <sub>o</sub>	Gas Collected	Loading Rate	Removal Rate
mg Ne/L	ng∕L	%	ml.	hour	kg VS∕m <sup>3</sup>	L/d	kg Ne∕m³∙d	kg Ne∕m <sup>3</sup> ∙d
Heterotro	ophic React	on:						
934	880	94.2	1000	3.4			6.54	6.16
943	796	84.4	1000	2.3	81	7.1	9.90	8.36
912	737	86.3	1000	1.7	82		12.77	11.02
941	675	71.7	900	1.0		14.0	21.96	15.74
904	472	52.2	600	0.5			42.19	22.02
Autotroph	ic Reactor	<u>`:</u>						
741	738	99.6	875	3.3	23	5.3	5.42	5.40
//1	767	99.5	900	1.7	21	8.3	10.96	10.91
747	740	99.1	850	1.3	20	11.7	13.53	13.41
173	763	98.7	850	1.1			17.46	17.23

Table IV. Summary of AFEB Reactors at Constant Feed Concentration and Variable HRT

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		<b></b>				
Infl. Conc.	<u>Ne</u> Con	sumed	HRT	Gas Collected	Loading Rate	Removal Rate
mg Ne/L	mg/L	0/ /0	hour	L/d	kg Ne∕m <sup>3</sup> ∙d	kg Ne∕m <sup>3</sup> ∙d
Heterotropi	nic Reactor:					
513	373	72.7	6		2.05	1.49
504	363	72.0	4	1.8	3.02	2.18
520	286	55.0	3		4.16	2.29
522	281	53.8	1.5	4.0	8.35	4.49
498	133	26.7	1		11.95	3.19
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Autotrophic	Reactor:					
510	491	96.3	6		2.04	1.96
476	470	98.7	3	7.5	3.81	3.76
486	469	96.5	2		5.83	5.62
490	468	95.5	1.25	24.6	9.41	8.98
497	476	96.2	0.8	40.9	14.30	13.72
492	157	36.2	0.6	18.5	20.10	6.40

# Table V. Summary of USB Reactors at Constant Feed Concentration and Variable HRT

Reactor	HRT hr	Concentration mg N/L	Removal Rate kg N/m <sup>3</sup> ·d	Substrate	Reference
PBR	0.24	3500	5.6	Methanol	(Jewell and Cummings, 1975)
PBR		970	5.6	Thiosulfate	(Claus and Kutzner, 1985)
PBR	2.4	1000	12.1	Methanol	(Blaszczyk <u>et.al.</u> , 1985)
USB		500	12.0	Fusel Oil	(Klapwijk <u>et al</u> ., 1981)
USB		900	7.2	Methanol	(Miyaji and Kato, 1975)
CSTR		1220	14.7 (32,C)	Methanol	(Bode <u>et al</u> ., 1978)
FBR		1450	10.6 (20,C)	Molasses	(Bosman <u>et al</u> ., 1978)
FBR		1450	38.4 (38,C)	Molasses	(Bosman <u>et al.</u> , 1978)

Table VI. Concentrated Nitrate Removal Rates in Previous Studies

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Figure 1. Schematic of the bench-scale experimental AFEB systems.



Figure 2. Schematic of the bench-scale experimental USB systems.



Figure 3. Treatment efficiency as a function of influent nitrogen concentration in AFEB reactors operated at constant 3.5 hour HRT.





Figure 5. Treatment efficiency as a function of influent nitrogen concentration in USB reactors operated at constant 6 hour HRT.



operated at constant 6 hour HRT.



Figure 7. Treatment efficiency as a function of loading rate in AFEB reactors operated at constant feed concentrations (Heterotrophic = 925 mg Ne/L, Autotrophic = 750 mg Ne/L).



Figure 8. Treatment efficiency as a function of loading rate in USB reactors operated at constant feed concentration of 500 mg Ne/L.

# DENITRIFICATION OF HIGH-STRENGTH INDUSTRIAL WASTEWATERS

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