COLUMNAR DENITRIFICATION OF A
MUNITIONS WASTE

by

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INTRODUCTION

The presence of nitrates in water supplies contributes to the enrichment of the nation's lakes and estuaries (1, 2, 3) and can cause a blood disease in infants called methemoglobinemia (4). For these reasons and as a part of the general interest in improving the environment, it has become necessary to consider possible ways of preventing the release of nitrates into streams and lakes.

Biological denitrification has been found to be an effective means of removing nitrates from water (5, 6). Although many studies have been made using this method, most have involved the removal of nitrates from secondary sewage effluents by modified activated sludge systems. Little work has been done on the removal of nitrates from industrial effluents, and no references could be found on columnar denitrification of an industrial waste. In addition, most work has involved the use of a synthetic carbon source, such as methanol, with little emphasis on utilizing another waste high in carbon and low in nitrates as a carbon source. However, among the wastes produced by munitions manufacturing are one which is high in carbon and low in nitrates and one which is high in nitrates and low in carbon. It would appear these wastes could be treated simultaneously. Wastes of these types are obtained from the Radford Army Ammunition Plant. The carbon waste was taken from the "Water Dry Process" (a solvent recovery process), and the nitrate waste was taken from the nitroglycerin waste line.

This investigation was designed to study the feasibility of treating the two industrial wastes, one high in nitrates and low in organic matter, the other high in organic matter and low in nitrates, in a denitrification unit. The experiments were also designed to provide information concerning rapid denitrification in a columnar unit. The wastes were mixed and subjected to both batch and columnar denitrification processes during the course of the study.

LITERATURE REVIEW

Nitrogen is a colorless, odorless, tasteless gas which comprises 78 percent of the atmosphere. The chemistry of nitrogen is very complex, primarily because nitrogen can assume a wide variety of valence states as illustrated in Figure I. Adding to the complexity of nitrogen chemistry are the many roles nitrogen plays in both the organic and inorganic worlds (further illustrated in Figure 1 (7).

In natural waters nitrogen is found in only four of its seven valence states. Gaseous nitrogen can be dissolved in water in a manner described by Henry's Law. Ammonia, which is formed primarily from the breakdown of urea and the biological decomposition of plant and animal matter, is found in significant concentrations in many waste waters. Nitrite is seldom found in significant concentrations in natural waters but is present as an interim compound in both nitrification and denitrification. Nitrate is present in varying concentrations in many waste waters. Nitrate nitrogen is the end product of nitrification and, therefore, the principal nitrogen constituent of highly nitrified sewage effluents. It is also common in many industrial and agricultural waste flows. A summary of the various nitrogen compounds and their interrelationships is illustrated by Sawyer in Figure 2 (7).

The literature contains many references to suggested schemes for nitrogen removal. A brief summary of possible nitrogen removal methods is outlined in Table I (5).

All of the chemical processes shown in Table I, with the exception of breakpoint chlorination, are applicable to the removal of nitrate

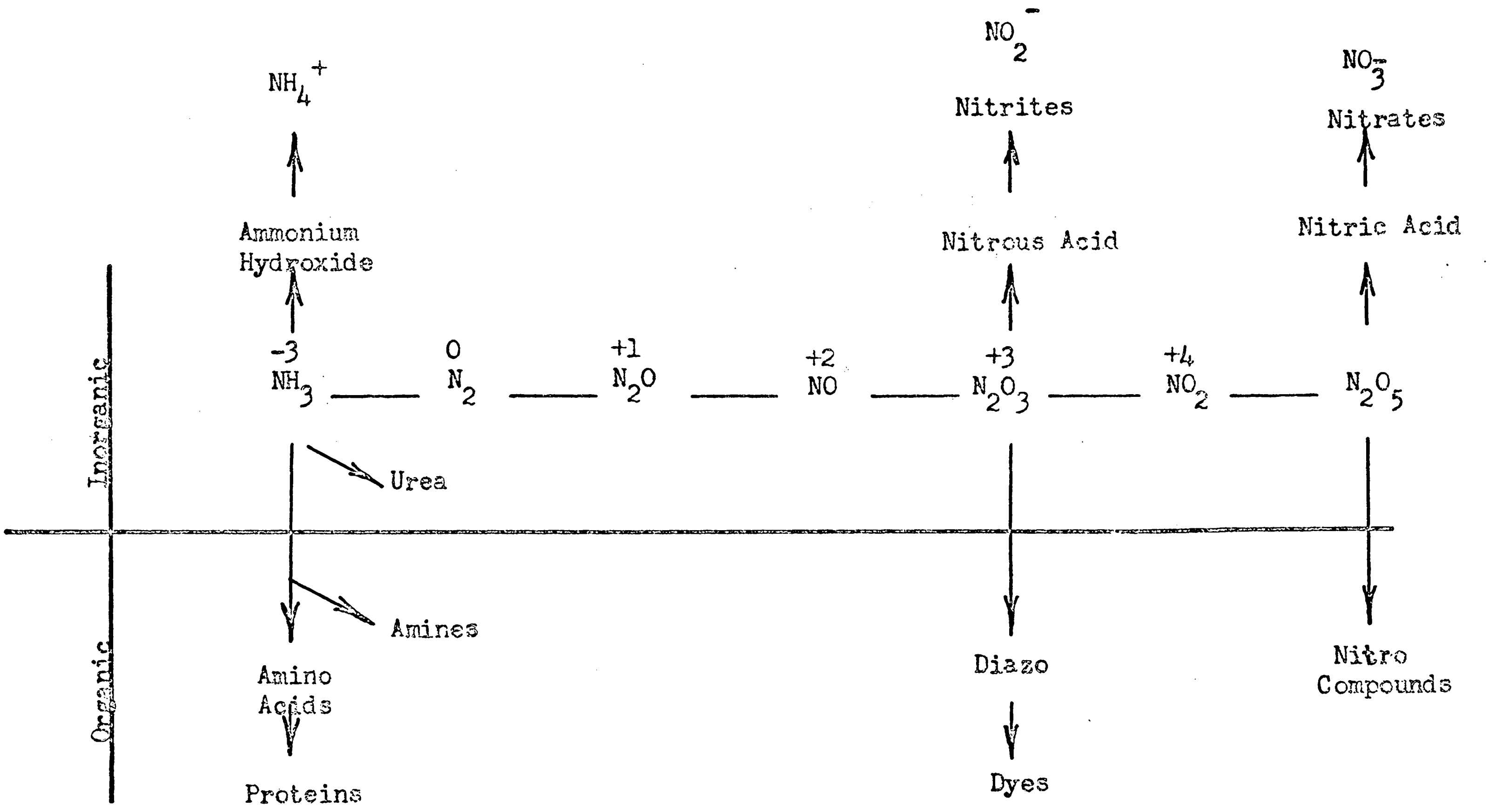


Figure 1: Chemistry of Seven Valence States of Nitrogen (7)

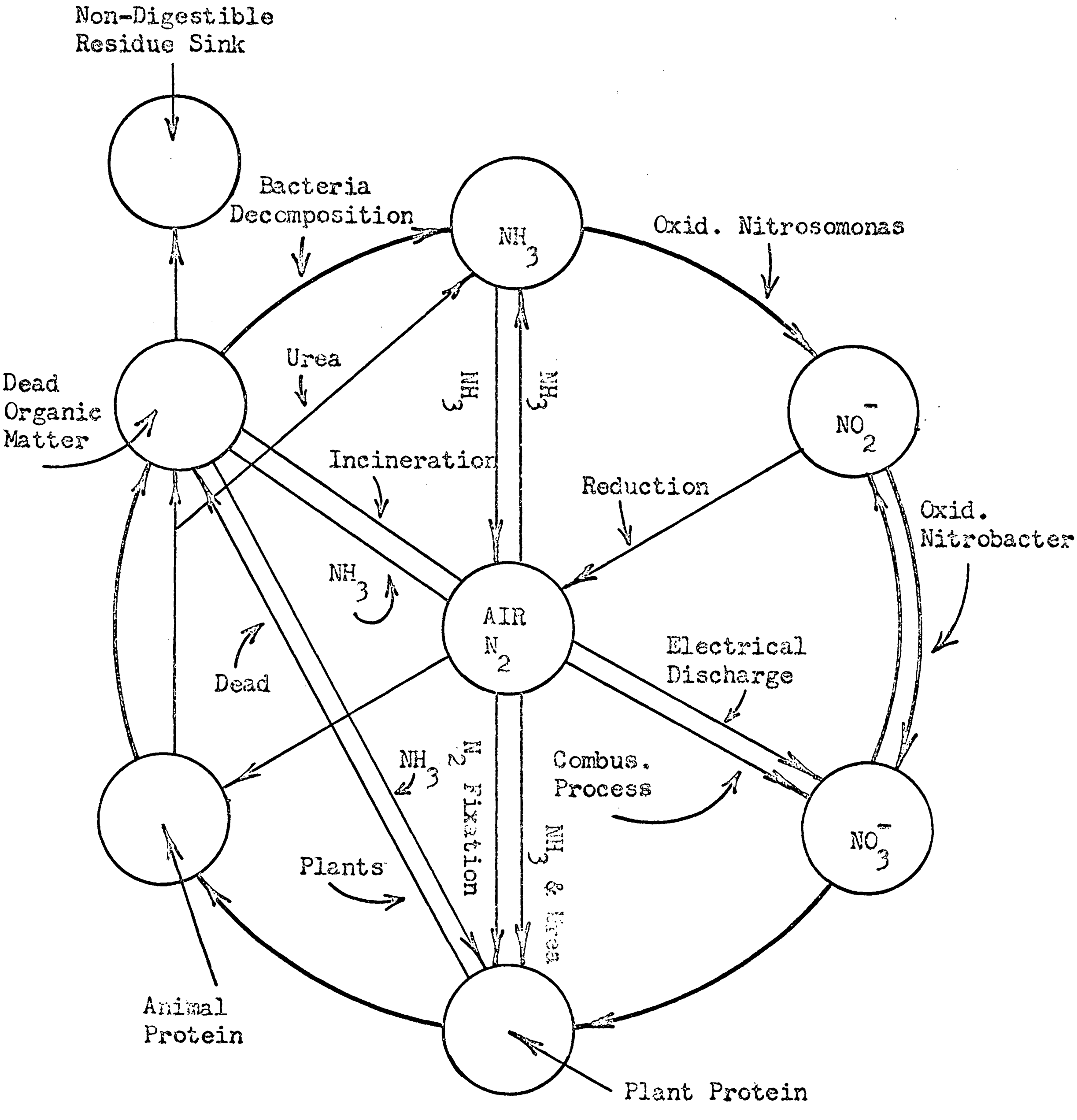


Figure 2: The Nitrogen Wheel (7)

nitrogen from wastewater flows. In the case of breakpoint chlorination, the nitrogen present in the waste must be in the form of ammonia in order for chlorine oxidation to be effective in removal. Ion exchange resins can be very effective in the removal of nitrogen compounds from waters. The type of resins necessary are dictated by the ionic form of nitrogen present. For the removal of ammonia, a cationic exchange resin must be used, while anionic resins are needed to remove nitrite and nitrate. Although resins are effective, there are three serious disadvantages to their use: the possibility of organic fouling, the high cost of resin regeneration, and the need to dispose of a concentrated chemical brine resulting from regeneration procedures. Electrodialysis is very effective but is associated with such problems as high power consumption, membrane clogging, and production of a concentrated chemical brine which demands careful and often expensive disposal techniques.

Nitrate removal can be accomplished by all of the physical processes shown in Table I except ammonia stripping and land application. The leaching of nitrates from soils, which causes contamination of groundwater, makes land application of high nitrate waste a questionable practice. Reverse osmosis or hyperfiltration can be used for removal of all dissolved salts, including nitrates, from solution, but serious operating problems may result from the fouling of membranes by organic matter or slightly soluble salts. Reverse osmosis also creates a concentrated chemical brine with associated disposal difficulties. Distillation is effective in removing substances from solution, but the economic feasibility of distillation is highly questionable.

The process of biological nitrogen removal falls under two headings,

TABLE I

Suggested Nitrogen Removal Processes
(Seidel) (5)

Biological	Chemical	Physical
Biological treatment (modified secondary)	Ion exchange	Ammonia stripping
Anaerobic denitrification	Electrodialysis	Reverse osmosis
Algae harvesting	Breakpoint Chlorination *	Land application

* Added by Dave Tucker

assimilatory nitrogen removal or dissimilatory nitrogen removal. The former involves the assimilation of nitrogen compounds into cell mass which is, in turn, wasted from the treatment system. In the latter case, nitrate and nitrite are used by the microorganisms as carbon acceptors in the oxidation of organic matter (8).

Assimilatory nitrogen removal can be achieved using conventional secondary treatment designs. Carbon limitation in normal domestic waste and most industrial waste results in nitrogen compounds left unassimilated after the carbon source has been exhausted. To overcome the carbon deficiency of these wastes, the addition of carbohydrates or similar materials as a supplemental source of food and energy is required (9). With methanol used as a food source, the assimilation of ammonia in conventional biological treatment units is expressed by McCarty by the following two equations:

Energy reaction

$$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$$

Synthesis

$$5CH_3OH + NH_3 + 5/2O_2 \rightarrow C_5H_7NO_2 + 8H_2O \quad (10)$$

The stoichiometric amount of methanol needed for the assimilation of one pound of ammonia is 12.95 pounds. The additional energy required by the biological population depends upon the mean cell residence time (θ_c) described by Lawrence et al. (11) A typical ratio of methanol required for energy to that required for synthesis is 1:3 (8). This method of nitrogen removal is unattractive because of the excessive cost associated with (1) the addition of methanol to the waste in the necessary quantity, (2) the construction of sufficiently large aeration tanks to support the necessary biological populations, and (3) the disposal of the resulting cell mass.

Nitrogen removal from wastewater may be accomplished by the harvesting of algae. Like the biological process mentioned above, algae harvesting is assimilatory in nature. Algae harvesting differs from the biological system with respect to the carbon and energy source. In the case of a biological system, a heterotrophic population of organisms uses an organic carbon source for energy and synthesis. In algae harvesting, an autotrophic population of organisms uses sunlight as an energy source and carbon dioxide as a carbon source (8). The growth of cell tissue in such a system is described in the following equation by Stumm (12).

$$106CO_2 + 81H_2O + 16NO_3^- + HPO_4^= + 18H^+ + \text{sunlight} \rightarrow C_{106}H_{181}O_{45}N_{16}P + 150\ O_2$$

Although algae harvesting is theoretically feasible, where there are large amounts of nitrate, it may be necessary to supplement the carbon dioxide to achieve complete nitrogen removal (12). Large land requirements and the cost associated with the harvesting and disposal of the algae created in the process are drawbacks to the method of algae harvesting (8).

Unlike assimilatory nitrogen removal, dissimilatory nitrogen removal or anaerobic denitrification uses nitrate as the terminal electron acceptor in the biological system. Instead of tying up nitrogen in cell mass, the microorganisms reduce nitrate from its positive five valence state to elemental nitrogen with a valence state of zero. The elemental nitrogen is then released to the atmosphere or carried from the treatment unit dissolved in the effluent. The half reactions describing anaerobic denitrification are given in Table II (13).

TABLE II

Half Reactions for the Reduction of Nitrate and Nitrite (13)

$\frac{1}{2}\ NO_3^- + H^+ + e^- \rightarrow \frac{1}{2}\ H_2O + \frac{1}{2}\ NO_2^-$

$1/3\ NO_2^- + H^+ + e^- \rightarrow 1/3\ H_2O + 1/6\ N_2 + 1/3\ OH^-$

$1/5\ NO_3^- + H^+ + e^- \rightarrow 2/5\ H_2O + 1/10\ N_2 + 1/5\ OH^-$

Many facultative microorganisms have the ability to reduce either nitrate or nitrite. Some organisms carry the reaction from nitrate to nitrite only. A second group can then carry the reaction from nitrite to elemental nitrogen. Still others have the ability of carrying nitrate to elemental nitrogen. The genera capable of denitrification include *Micrococcus*, *Denitrobacillus*, *Pseudomonas*, *Spirillum*, *Bacillus*, *Achromobacter* *Clostridium*, and some autotrophs including *Thiobacillus denitrificans* and *T. thioparus* (14, 15).

A search of the literature reveals several differing views regarding the specific pathways utilized by microorganisms in denitrification. McKinney proposed the pathway outlined in Table III (16). Delwiche postulated that denitrification proceeds in a manner described in Table IV (14).

Allen and Van Niel advanced the hypothesis that the formation of two organic complexes are involved in the denitrification process. (Table V) (17)

The only clear concensus among these three authors is the initial reduction step from nitrate to nitrite. All agree that nitrite is an intermediate in denitrification.

There is also much debate regarding the specific terminal enzymes involved in nitrate reduction. Taniguchi proposed a pathway identical to the reduction of oxygen with the exception that nitrate reductase replaces cytochrome oxidase (18). Carlson contends that the reduction of nitrates is distinguished by the presence of one or more cytochromes as electron carriers in the process (19). The pink color typical of denitrifying bacteria is also attributed to cytochromes. Sacks observed absorption peaks at 552 millimicrons and 522 millimicrons in *Pseudomonas denitricans*

TABLE III

Proposed Pathway for Anaerobic Denitrification (16)

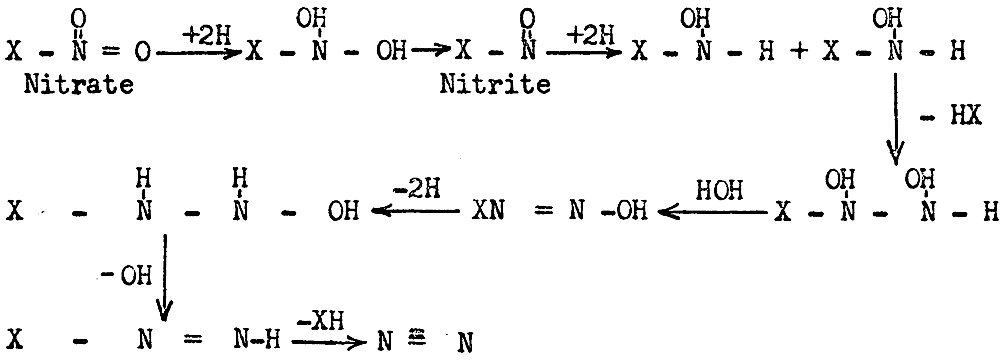


TABLE IV

Proposed Pathways for Anaerobic Denitrification (14)

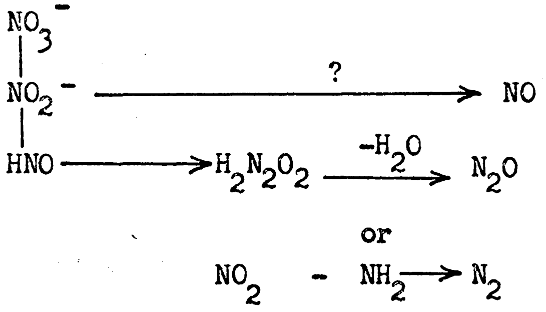
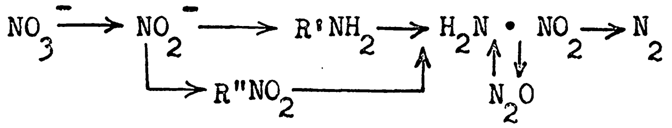


TABLE V

Proposed Pathways for Anaerobic Denitrification (17)



typical of cytochrome "C". These peaks disappeared upon aeration and reappeared in the absence of oxygen. Nitrate and nitrite also caused the absorption peaks to fade (20). Fewson and Nickolas proposed the system of electron transport described in Table VI (21). McKinney proposed still another electron transport scheme which is outlined in Table VII.

For nitrate reduction to proceed, an anaerobic environment is necessary. The exact degree of inhibition exerted by oxygen on the nitrate reduction process is not clearly known. One view holds that oxygen is a powerful inhibitor of denitrification due to the competitive advantage oxygen has over nitrate as an electron acceptor (14). Other authors contend that the inhibition is of the non-competitive type due to the large difference in the reaction rates of nitrate and oxygen utilization (22). Whichever theory is true, the fact remains that oxygen present in any significant concentrations inhibits nitrate reduction. Oxygen tensions as low as one to four percent were found to suppress denitrification by ninety percent (20).

In waste treatment applications utilizing anaerobic denitrification, it is often necessary to supplement the amount of organic carbon present in the waste. If this supplemental carbon is not present, there will be insufficient oxidizable matter to consume the nitrate. Many sources of organic carbon have been successfully used in denitrification processes. Among the carbon sources used are methanol, acetate, ethanol, acetone, and organic carbon stored in the cell mass during aerobic treatment of domestic sewage (23). The most often mentioned organic carbon source is methanol, although the use of molasses is now being mentioned (24). Sawyer has pointed out the advantages derived from using a high organic carbon waste

TABLE VI

Proposed Electron Transport System for Nitrate Reduction (21)

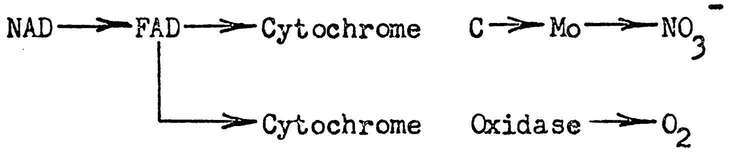
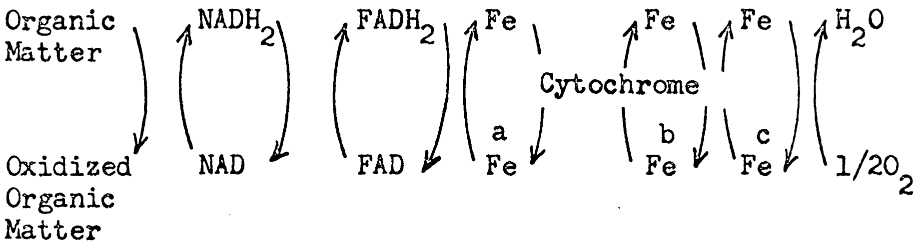


TABLE VII

Proposed Electron Transport System for Nitrate Reduction (16)



that is low in nitrogen such as a brewery waste as a carbon source (25). Aside from the economic benefits derived from using a free carbon source, there is an added benefit obtained by conserving our natural gas, the principle raw material in methanol production.

McCarty et al. developed a series of equations describing the denitrification process with methanol as the carbon source. The equations are presented in Table VIII. The equations in Table VIII govern the theoretical amount of methanol consumed for specific concentrations of nitrate and nitrite. If methanol were added in concentrations dictated by these equations, denitrification would not go to completion. An additional amount of methanol would be needed to compensate for the organic carbon assimilated into cell mass during denitrification. Because of this additional organic carbon requirement, McCarty developed the concept of the consumptive ratio (Cr). Cr is defined as the actual amount of a specific carbon source needed for denitrification divided by the stoichiometric amount as determined by the equations given in Table VIII. Consumptive ratios for several organic carbon sources are given in Table IX (23).

Since denitrification must proceed in an anaerobic environment, additional organic carbon must be present in amounts sufficient to deplete any oxygen present in the influent waste. This carbon demand is described by the equation $O_2 + 2/3\ CH_3OH \rightarrow 2/3\ CO_2 + 1/3\ H_2O$. McCarty also applies a consumptive ratio equal to that for denitrification to that carbon required for deoxygenation (23).

After the consumptive ratio has been established for a specific carbon source, it is possible to arrive at the amount of biomass produced. For methanol, using a consumptive ratio of 1.3 and a typical empirical

TABLE VIII

Nitrate Reduction Reactions Using Methanol (23)

$NO_3^- + 1/3\ CH_3OH \rightarrow NO_2^- + 1/3\ CO_2 + 2/3\ H_2O$

$NO_2^- + 1/2\ CH_3OH \rightarrow 1/2\ N_2 + 1/2\ CO_2 + 1/2\ H_2O + OH^-$

$NO_3^- + 5/6\ CH_3OH \rightarrow 1/2\ N_2 + 5/6\ CO_2 + 7/6\ H_2O + OH^-$

TABLE IX

Consumptive Ratios by McCarty (23)

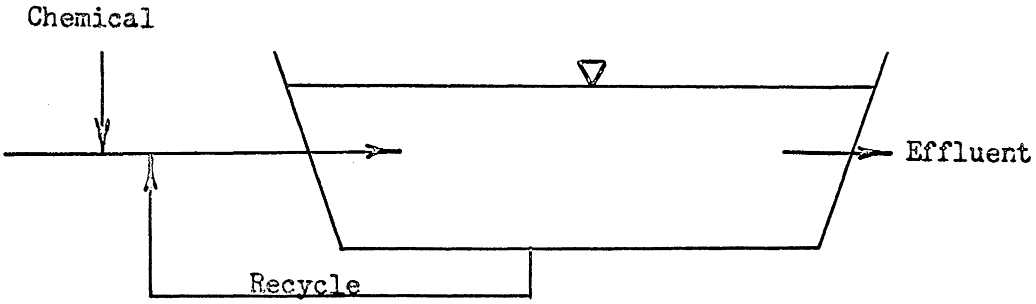
Organic Carbon Source	Consumptive Ratio
Sugar	1.65
Acetate	1.31
Methanol	1.3
Ethanol	1.47
Acetone	1.22

formulation of $C_5H_7O_2N$ for biomass, McCarty established the equations presented in Table X (23). It can be seen from the equations given in Table X that 10 mg/l nitrate-nitrogen consumes 24.7 mg/l methanol while producing 5.25 mg/l of biomass that contains 0.65 mg/l organic-nitrogen and that 10 mg/l nitrite-nitrogen consumes 15.3 mg/l methanol in the production of 3.22 mg/l of biomass containing 0.4 mg/l organic nitrogen. Further, 10 mg/l of dissolved oxygen will consume 9.3 mg/l methanol and 0.35 mg/l nitrate-nitrogen in the production of 2.0 mg/l of biomass containing 0.25 mg/l organic-nitrogen (23).

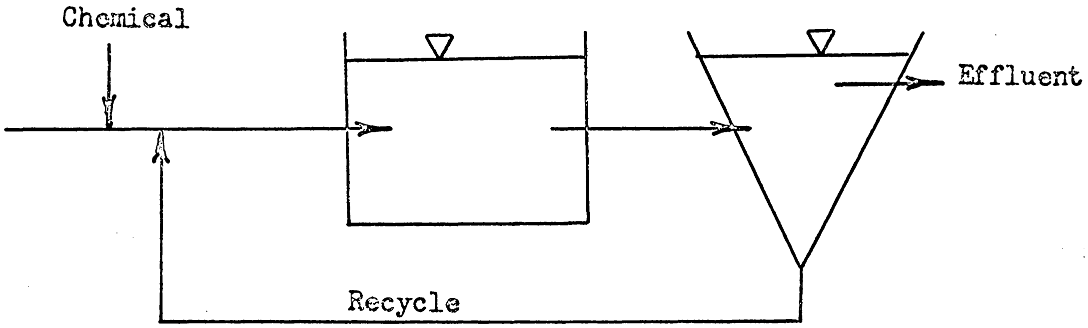
Like most biological treatment techniques, there are several process designs which may be used for denitrification. Figure 3 presents three different process designs capable of denitrification.

In the anaerobic pond, the mean cell residence time and the hydraulic detention time are identical. Because of this fact, it is necessary for the bacterial reproduction rate to be equal to or greater than the hydraulic detention time. If this criterion is not met, the bacterial population will be washed out of the system resulting in system failure (11). Studies indicate that the detention time necessary for treatment in anaerobic ponds is on the order of days instead of the hours needed for other treatment process designs which will be discussed later (26).

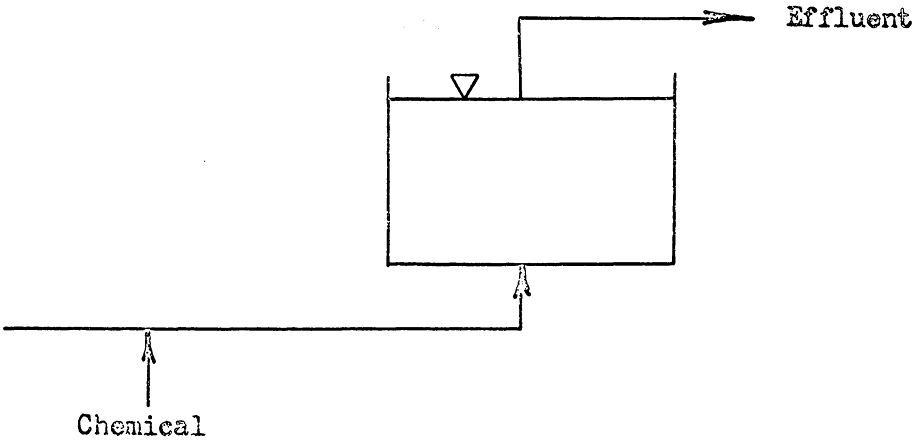
Using a covered anaerobic pond, Pafford et al. found that a waste of 20 mg/l nitrate-nitrogen could be reduced to less than 2 mg/l total nitrogen with a 15 day detention time at 14°C. With temperatures of 20°C and 22°C, the pond could produce the same results in 8.2 days. When the detention time was shortened to five days, the effluent total nitrogen concentration increased to 4 mg/l. Using an uncovered pond, the same



Anaerobic Pond



Anaerobic Activated Sludge



Anaerobic Filter

Figure 3: Anaerobic Process Designs for Denitrification (23)

TABLE X

Complete Denitrification Equations by McCarty (23)

Overall nitrate removal:

$$NO_3^- + 1.08\ CH_3OH + H^+ \rightarrow 0.065\ C_5H_7O_2N + 0.48\ N_2 + 0.47CO_2 + 1.7H_2O$$

Overall deoxygenation:

$$O_2 + 0.93CH_3OH + 0.056NO_3^- + 0.056H^+ \rightarrow 0.056C_5H_7O_2N + 0.65CO_2 + 1.69H_2O$$

investigator was unable to reduce the total nitrogen to less than 2 mg/l regardless of the detention time. Methanol was used as the carbon source in all of the above studies. (26)

The disadvantages expected from the use of an anaerobic pond include: a large land requirement, the possibility of algae blooms and wind mixing in uncovered ponds, and the high cost involved in covering a large anaerobic pond. (26, 8)

To make it possible for the mean cell residence time to be independent of the hydraulic detention time, a modification of the activated sludge design can be used for denitrification. In this type of unit, the mean cell residence time is a function of the amount of biomass present in the treatment unit and the biomass production per unit time. As in the case of an anaerobic pond, if the actual mean cell residence time drops below some minimum value, treatment will fail due to organism washout. Lawrence and McCarty define mean cell residence time for a complete mix activated sludge reactor with the following equation:

$$\theta^{-1} = YU - b$$

where:

θ = Mean cell residence time

U = Specific utilization of food to microorganism ratio = $\frac{dF/dk}{x}$

dF/dt = Rate of microbial substrate utilization per unit volume

X = Total weight of solids in the reactor

Y = Growth yield coefficient

b = Microorganism delay coefficient (11)

Carlson developed the following equation for required sludge concentration in a denitrification unit:

$$S = \frac{(D.O. + 2.86N)\ 10^{6}}{t\ (2.08)\ (1.0218)^{T-20}\ L(0.02T + 0.6\ \ L(0.02T + 0.6)-(D.O.+ 2.86N)}$$

Where:

S = Required sludge concentration (mg/l)

D.O. = Concentration of dissolved oxygen in influent to the denitrification unit (mg/l)

N = Concentration of nitrate-nitrogen in the influent (mg/l)

T = Temperature in the reactor (°C)

t = Detention time (hours)

L = Ultimate B.O.D. of the influent (mg/l) (27)

In small scale studies, Balakrishnam and Eckenfelder were able to obtain 80 - 90 percent nitrate reductions with a detention time of four hours and a mixed liquor suspended solids (MLSS) of 2800 mg/l. These studies were conducted using a nitrified domestic sewage effluent containing a total nitrogen content of 33 mg/l (28). Also, using domestic sewage with nitrate-nitrogen concentrations ranging from, 3 to 11 mg/l, investigators at Gulf South Research Institute obtained ninety percent denitrification at a detention time of 3½ hours. The same investigators found that using a methanol to nitrogen ratio of three and a MLSS concentration of 2000 mg/l, temperature had negligible effect on denitrification within the range of 5 to 30°C (29).

In treatment studies using a nitrate waste from Sunflower Army Ammunition Plant, Gickison was able to obtain the results outlined in Table XI (30). These results were obtained from a small scale activated sludge unit with an influent nitrate-nitrogen concentration ranging from 100 to 130 mg/l and a methanol to nitrate-nitrogen ratio of 2.5 (30).

TABLE XI

Results of an Activated Sludge Denitrification Unit (30)

Detention Time	Nitrate Removal	MLVSS	Load
3 days	77%	208 mg/l	0.04 mgN/mg MLVSS
5 days	88%	146 mg/l	0.37 mgN/mg MLVSS
10 days	97.6%	115 mg/l	0.22 mgN/mg MLVSS

A third anaerobic process design utilizes a reactor vessel filled with a biologically inert support medium. With this design the microorganisms are given a site on which to grow. This unit makes it possible for the mean cell residence time to be independent of both hydraulic detention time within the unit and the settleability of the microorganisms. Since the amount of solids in the reactor at any period of time cannot be measured, the mean cell residence time cannot be determined (11).

Column studies using a variety of media and varying detention times in anaerobic filters have been conducted by several investigators. St. Amant and McCarty experimented with several media including sand, coal, and commercially prepared trickling filter medium (31). They obtained the best results from one inch gravel which removed ninety percent of the nitrate from a 15 - 26 mg/l nitrate-nitrogen agricultural feed in one hour. In another study using $1\frac{1}{2}$ inch gravel, Seidel obtained ninety percent removal of nitrates from a nitrified sewage effluent in 1.5 hours (5). Pafford et al., working with irrigation underdrain effluent near Firebaugh, California, determined that a column filled with one inch diameter aggregate reduced nitrates from 20 mg/l to 2 mg/l in one hour (26). With extended operation the same authors experienced a rise in Kjeldahl nitrogen due to bacterial decay in the column. Short circuiting and high influent pressures were also experienced due to excessive growth in the column.

Parkhurst was able to obtain 15 mg/l total nitrogen reduction using a 25 mg/l nitrate-nitrogen feed and a column filled with 16 x 40 mesh activated carbon (34). These results were obtained while operating at a 36 minute detention time, but similar results were reported at detention times as low as five minutes.

Dravo Corporation has incorporated denitrification into its line of tertiary treatment package plants. This design incorporates denitrification into a deep bed filter used also for suspended solids removal. The company recommends a 45 minute detention time to assure a ninety-five percent nitrate removal. Short backwash "bumps" were used to prevent fouling of the filter by the nitrogen gas produced during denitrification (32). Jeris reported ninety percent nitrate removal of a 32 mg/l nitrate-nitrogen influent on an upflow fluidized bed column with 11 minutes detention time (33). Sixty-five percent nitrate removal was reported by the same author when a detention time of 7.5 minutes was used.

All of the above column studies used methanol as a carbon source.

MATERIALS AND METHODS

Small bench scale denitrification columns were constructed to investigate the feasibility of columnar denitrification of an industrial nitrate waste, to determine the amount of organic carbon needed for denitrification, and to define the detention time necessary for efficient operation of the columns. Two columns were constructed of clear plastic tubing with glass effluent weirs according to the description in Figure 4. The amount of water contained in the column when the water was at the top of the glass effluent weir was 260 mililiters. One column was filled with activated carbon while the other was filled with sand. Both the sand and the carbon were seived and the portion used in the columns during the studies passed the number 8 seive and was retained on the number 16 seive.

The columns were seeded by passing effluent through them from an activated sludge treatment plant serving a rest stop on Interstate 81 near Christiansburg, Va. The seed was enriched with potassium nitrate such that the final nitrate concentration in the seed was approximately 50 mg/l as N. After a period of three days the seed was discontinued and a synthetic feed of potassium nitrate and methanol was fed to the unit (100 mg/l nitrate and nitrogen and 150 mg/l organic carbon). The columns were maintained on this synthetic feed for approximately 3 1/2 months at which time an industrial feed obtained from the Radford Army Ammunition Plant (RAAP) located in Radford, Virginia was introduced. The industrial feed was a mixture of two wastewaters from different munitions manufacturing at RAAP.

The wastewater used as an organic carbon source in this study was

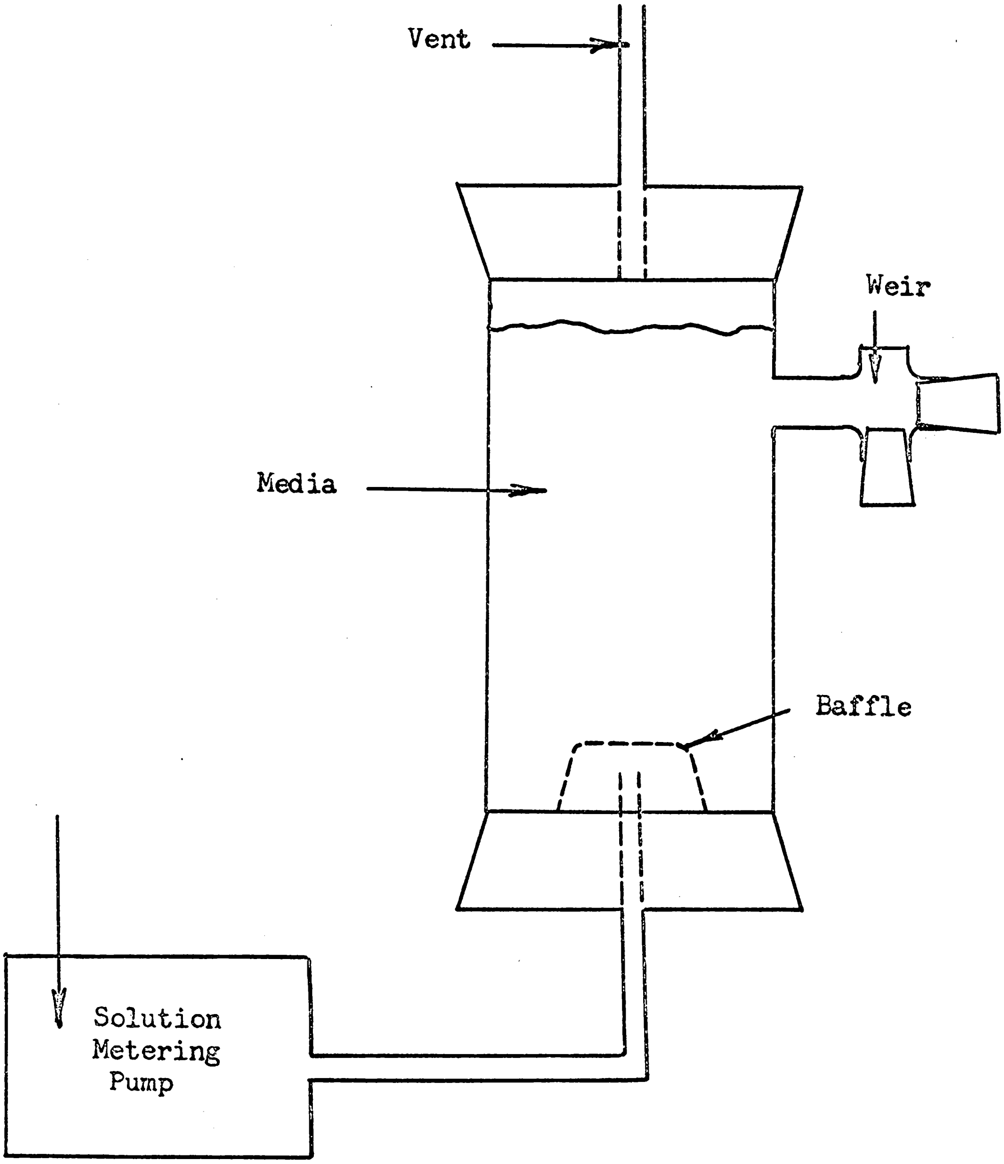


Figure 4: Up Flow Columns

the effluent from the water dry process referred to hereafter as the "Water Dry Process Waste" (WDPW). The WDPW was comprised primarily of ethyl alchol and diethyl ether with negligible amounts of nitrates. The organic carbon concentration of this waste was approximately 1000 mg/l. The nitrate rich wastewater was obtained from the nitroglycerine process. The organic carbon content of this waste was negligible while the nitrate concentration was approximately 167 mg/l nitrate as nitrogen and 3.5 mg/l nitrite as nitrogen. These two wastes were mixed to obtain a feed containing 150 mg/l organic carbon and 100 mg/l nitrate as nitrogen.

With the combined waste as a feed, the columns were operated for approximately one month for acclimation and then the effluents from both columns were analyzed to determine nitrate, nitrite and organic carbon concentrations. The operation of the column packed with activated carbon was discontinued after approximately one month of analysis because of the high influent pressures required to continue operation. The column packed with sand was operated for approximately 1 1/2 months after effluent analysis had commenced. All waste feeds used were treated with sodium sulfide to eliminate dissolved oxygen prior to introduction to the column.

Tracer studies to determine the actual detention time characteristics of the column packed with sand, both with and without biological growth, were performed during the course of the investigation. A 7.5% solution of anhydrous cupric sulfate was used as a tracer. Before introducing the cupric sulfate solutions into the columns, a 11.0% solution of anhydrous sodium chloride was pumped into the column for a period of time sufficiently long to assure that the sodium chloride solution had completely filled the voids. The sodium chloride solution was also continued after the introduction of the cupric sulfate solution. The use of the sodium chloride solution was necessary to minimize density currents that tend to occur when cupric sulfate is used as a tracer and tap water is used as feed. Data was taken on a Bausch and Lomb Spectronic 20 equipped with a flow-through cuvette. The flow through the column was maintained at approximately 4 ml/min.

Small bench scale batch denitrification units were constructed to investigate the denitrification of munitions waste on a batch basis. This phase of the study was initiated in an effort to determine the carbon requirements for denitrification of munitions waste. Operational problems associated with the batch process were also investigated. Batch units for further study were constructed as described in Figure 5. Five 1 liter aspirator bottles were used, each containing an initial nitrate concentration of 100 mg/l nitrate as nitrogen and varying organic carbon concentrations. The organic carbon concentrations were 96, 116, 126, 136, and 146 mg/l, respectively. The industrial wastes obtained from RAAP, previously described, were used in all batch studies. The system was purged of oxygen by displacement with nitrogen gas and the waste was treated with sodium sulfite to eliminate dissolved oxygen. Following start-up, samples were taken daily for approximately 18 days and then at greater intervals for an additional period of time. Analysis was performed on the samples taken from the batch studies to determine organic carbon nitrate and nitrite concentrations.

Organic carbon analysis was performed using the Beckman Model 215A Carbonacous Analyzer. Nitrate determinations were obtained using the Orion Nitrate Probe and Orion 404 meter. Nitrate determinations by the

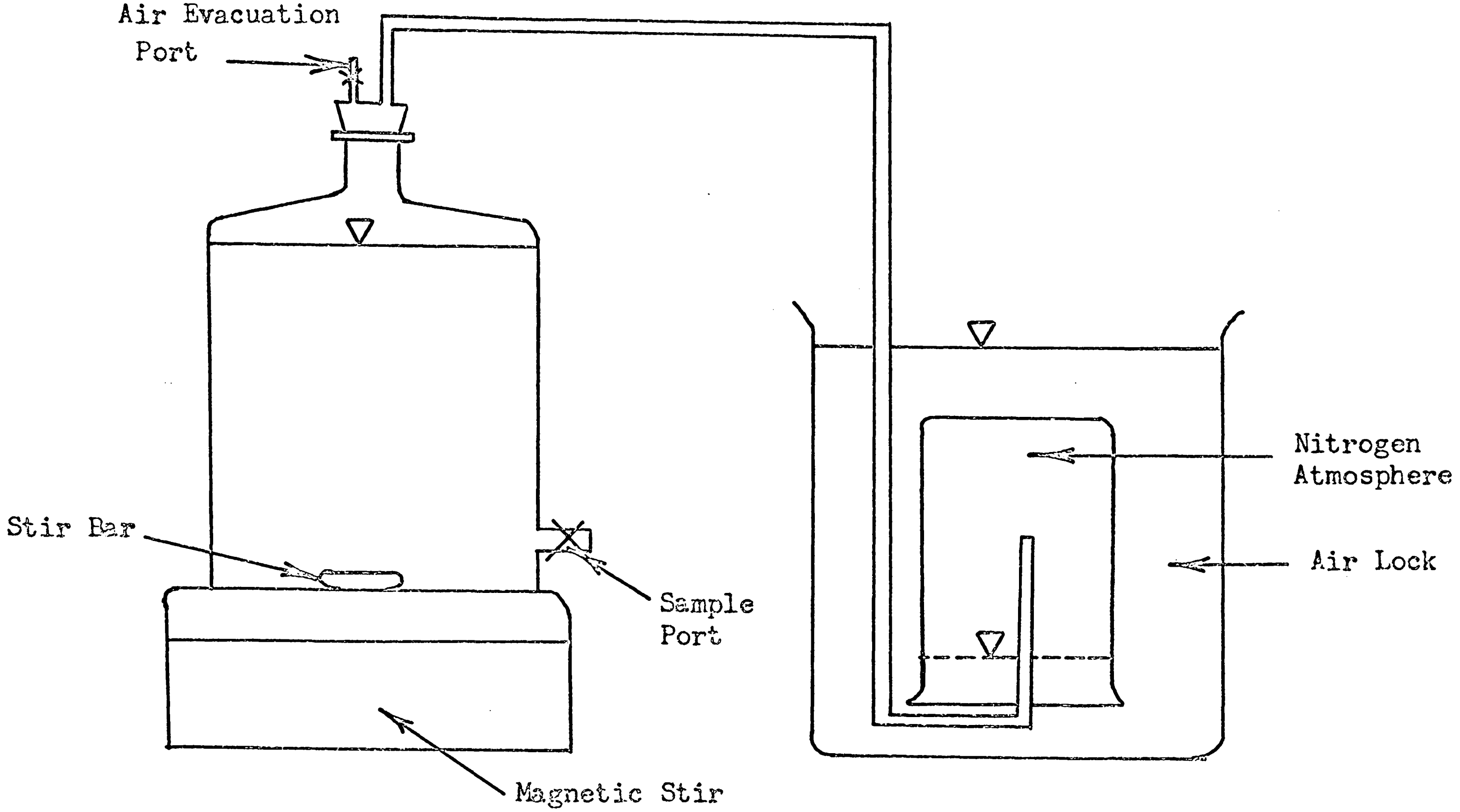


Figure 5: Batch Study Apparatus

probe were checked by the Cadmium Reduction Method as described by <u>Standard Methods</u> (35) and found to be acceptable. Nitrite determinations were partially performed on the Technicon Auto Analyser and partially by the method described in <u>Standard Methods</u> (35).

RESULTS

All data gathered during this entire study are presented in Appendices A, B, and C with exception of tracer studies performed on the sand column. Since the data from the tracer study are important only in a comparative sense, only the statistical interpretations of the tracer study are presented.

Basic data describing the operation of the columnar phase of this study are given in Appendix A and Appendix B. Data presented include daily analysis of organic carbon, nitrate nitrogen, nitrite nitrogen and total nitrogen removal efficiencies (nitrate plus nitrite), and empty column detention times.

Figures 6 and 7 outline the operation of the activated carbon column through the period data was taken on the column. The detention time (based on the volume of the empty column) maintained throughout the entire operation of the column was 9.1 hours. The average total nitrogen removal efficiency during the period was 98.95% while the average organic carbon removal was 62.1%.

During the operation of the activated carbon column several operational difficulties were encountered. Probably the most serious difficulty was the separation and rising of large clumps of activated carbon which were cemented together by active biomass. When this problem occurred, manual disruption of the clumps of activated carbon was employed. A problem associated with high influent pressures needed for column operation was also encountered. The required influent pressure increased to the point that it became impossible to continue the operation of the column. At

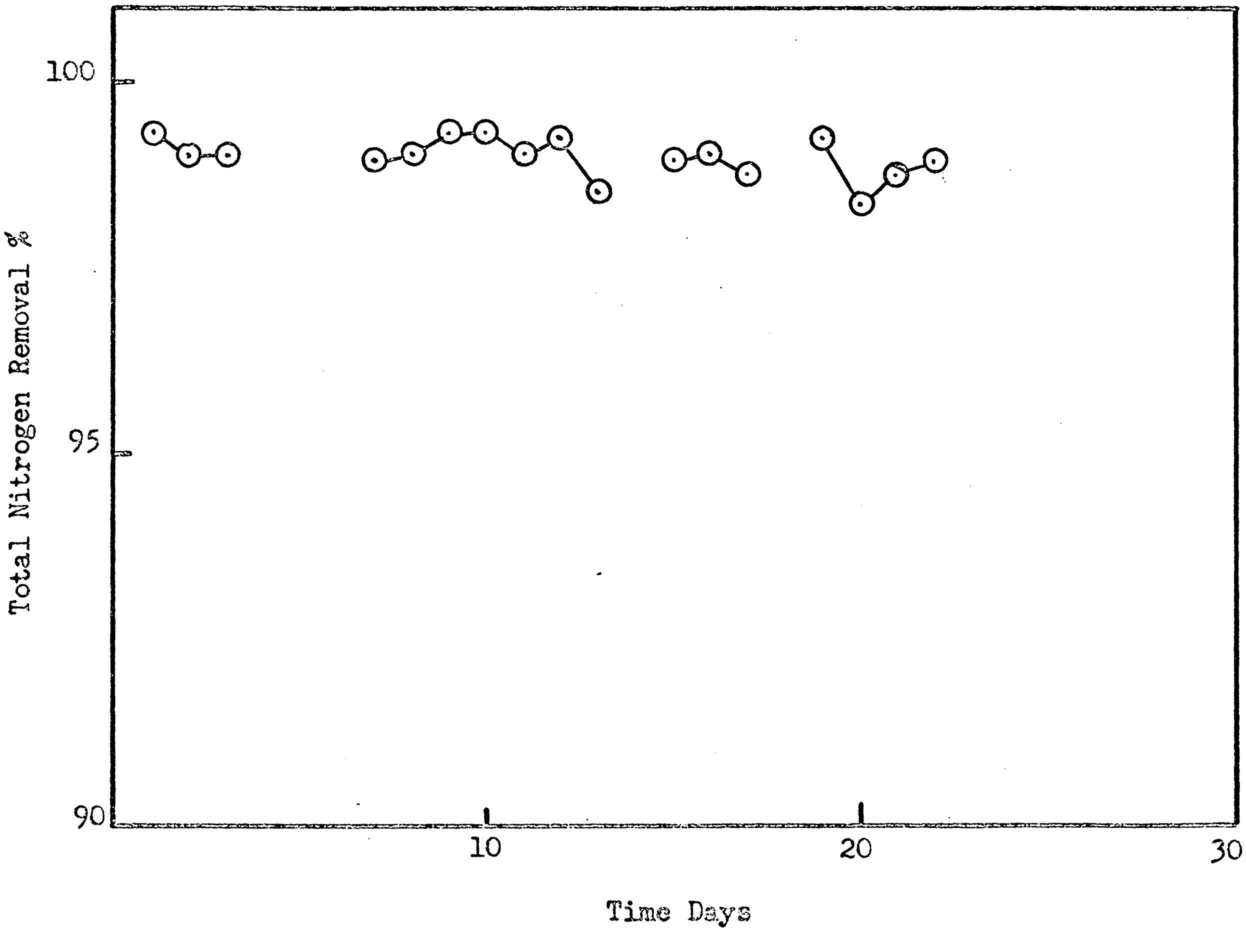


Figure 6: Total Nitrogen Removal in the Activated Carbon Column

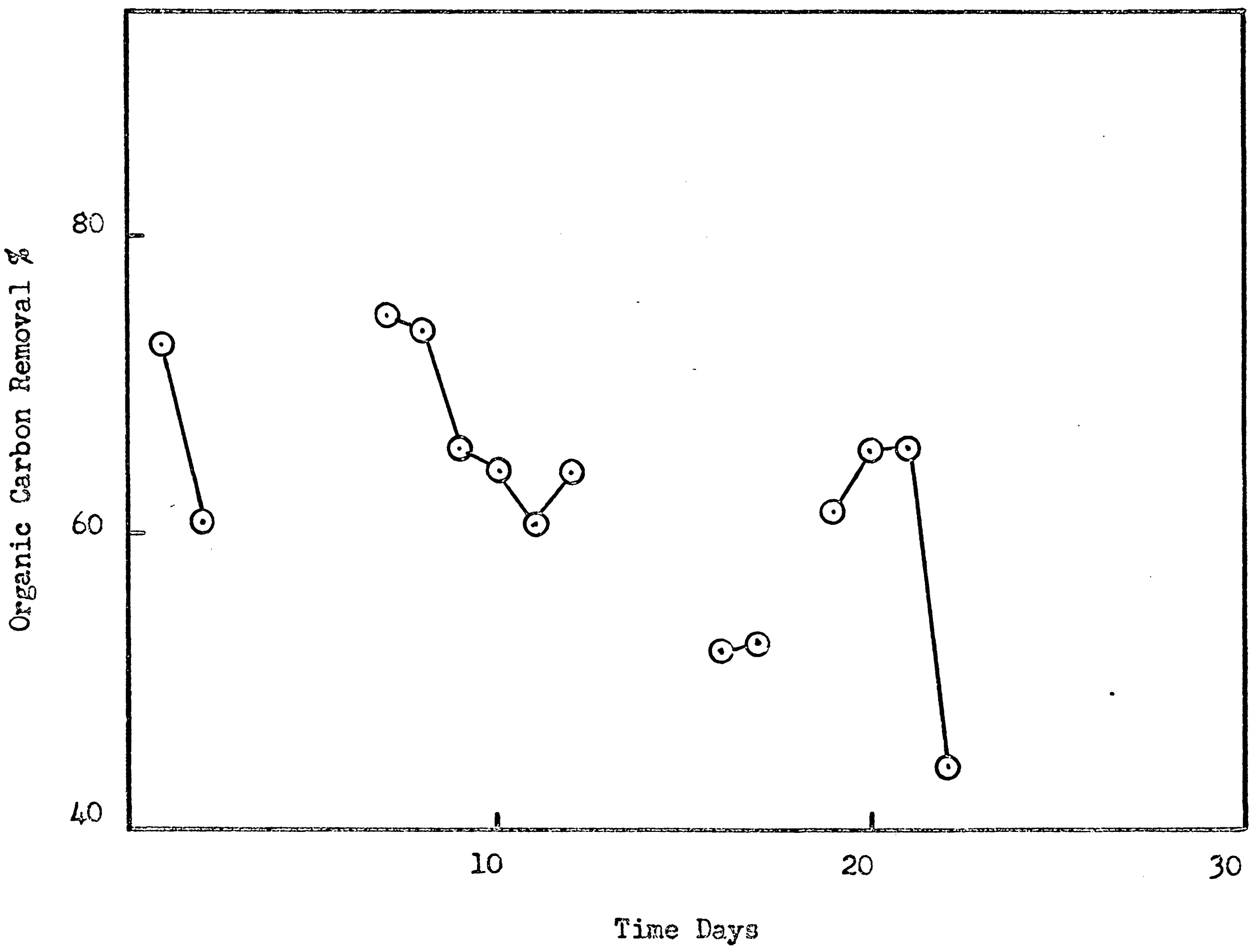


Figure 7: Organic Carbon Removal in the Activated Carbon Column

this point the activated carbon column was discontinued. The effluent from the activated carbon column throughout its operation exhibited hydrogen sulfide-type odors.

Figure 8 outlines the operation of the column packed with sand. Included in Figure 8 are total nitrogen removal efficiencies and detention times (based on the volume of the empty column) vs. time of operation. Table XII presents the various intervals at which the sand column was operated with specific detention times (based on empty column). Average organic carbon removal and total nitrogen removal efficiencies corresponding to the different detention times are also given in Table XII.

Figure 9 presents a plot of average total nitrogen removal efficiency vs. empty column detention time. Figure 10 presents average organic carbon removal efficiencies vs. empty column detention time.

It was felt that the operation of the sand column was sufficiently stable to provide a reliable estimate of the consumptive ratio (the ratio of actual organic carbon consumed to the amount theoretically needed for denitrification). Therefore a consumptive ratio was calculated for the first 17 days of operation. The consumptive ratio was determined to be 1.47 ± 0.11.

The results of the detention time investigations using copper sulfate as a tracer are presented in Figures 11 and 12. From these figures, values for the time of first detectable trace (Ti), time to the mode (Tm), time to the center of gravity of the area under the curve (Tg) and time to the half area ordinate (Ta) are calculated. The theoretical detention time with the column filled with sand (T) was calculated by draining the column with no biological growth after the detention time studies were completed

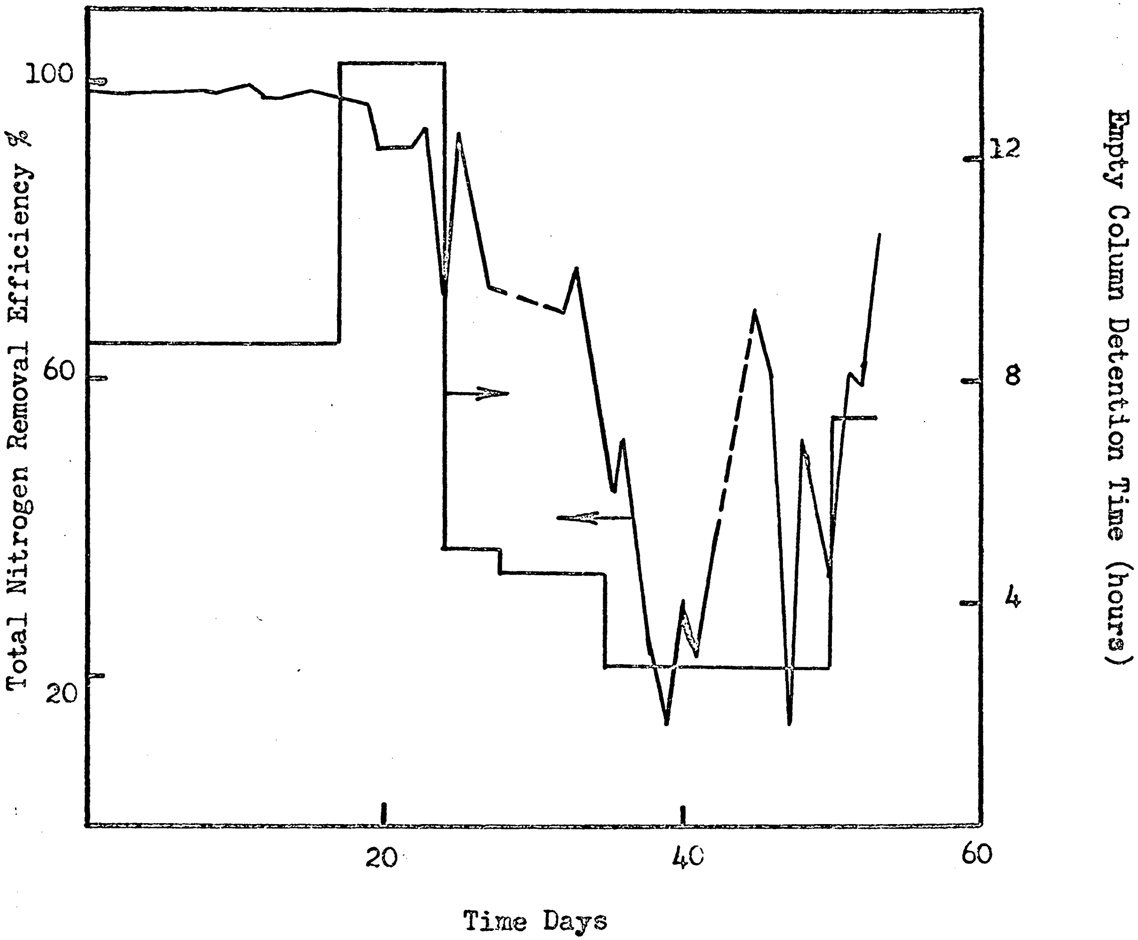


Figure 8: Sand Column Performance

TABLE XII

Sand Column Operation Data

Day	Detention Time Empty Column Hours	Average Total Nitrogen Removal Efficiency %	Average Organic Carbon Removal Efficiency %
1-17	8.76	98.92	64.7
17-24	13.67	94.00	76.0
24-28	5.00	78.90	-
28-35	4.6	67.80	55.5
35-50	2.87	37.90	15.6
50-53	7.35	67.10	-

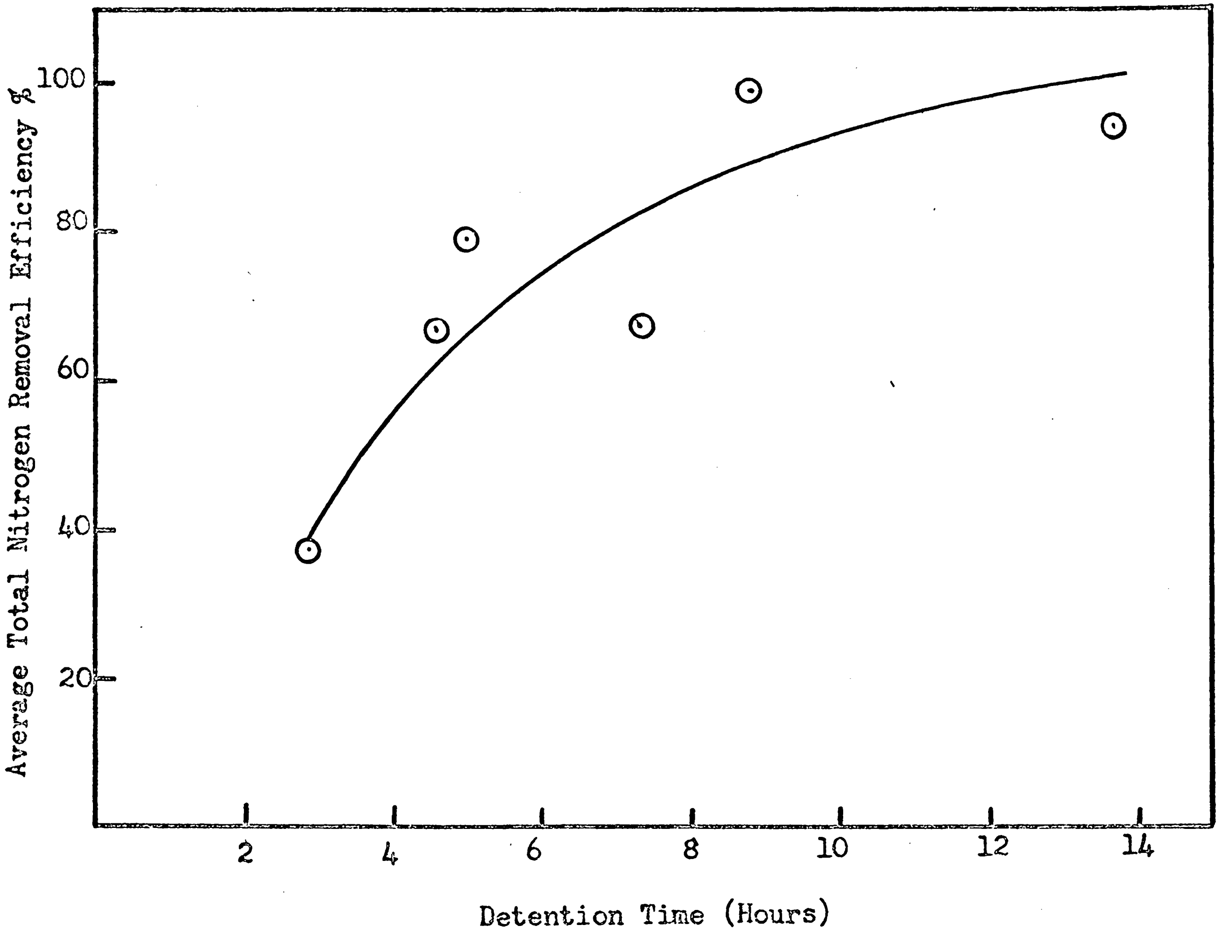


Figure 9: Total Nitrogen Removal Efficiency in the Sand Column

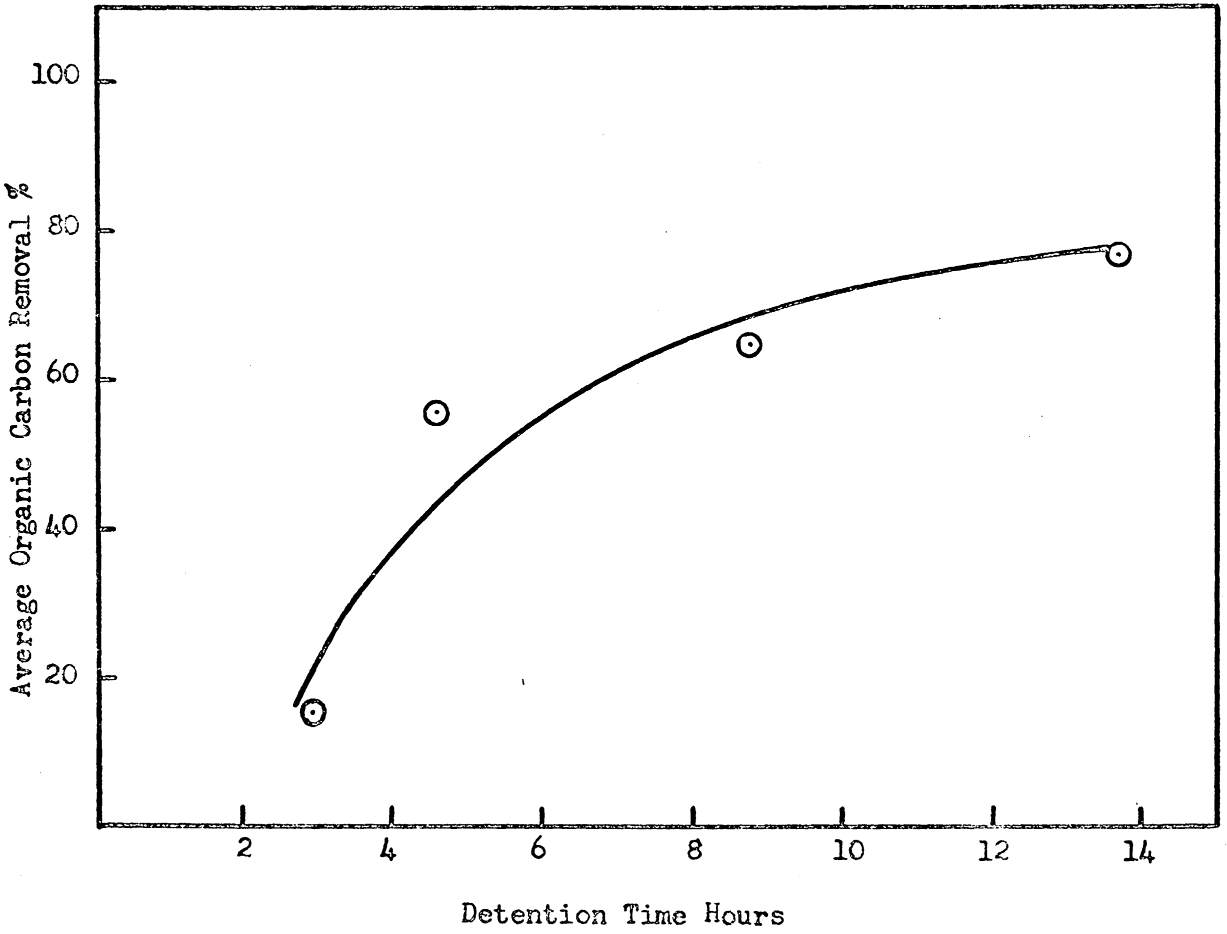


Figure 10: Organic Carbon Removal in the Sand Column

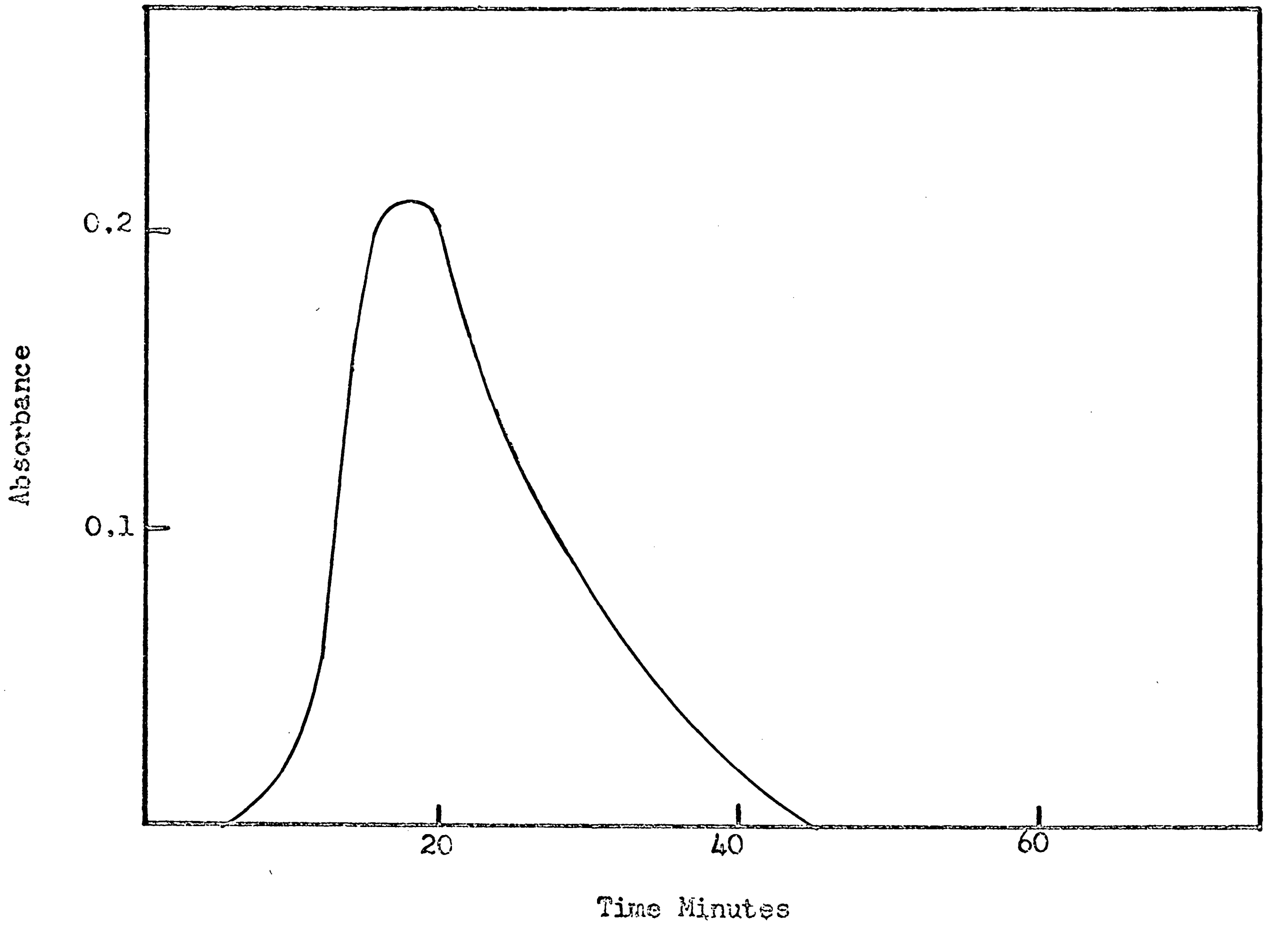


Figure 11: Trace Study Before Biological Growth

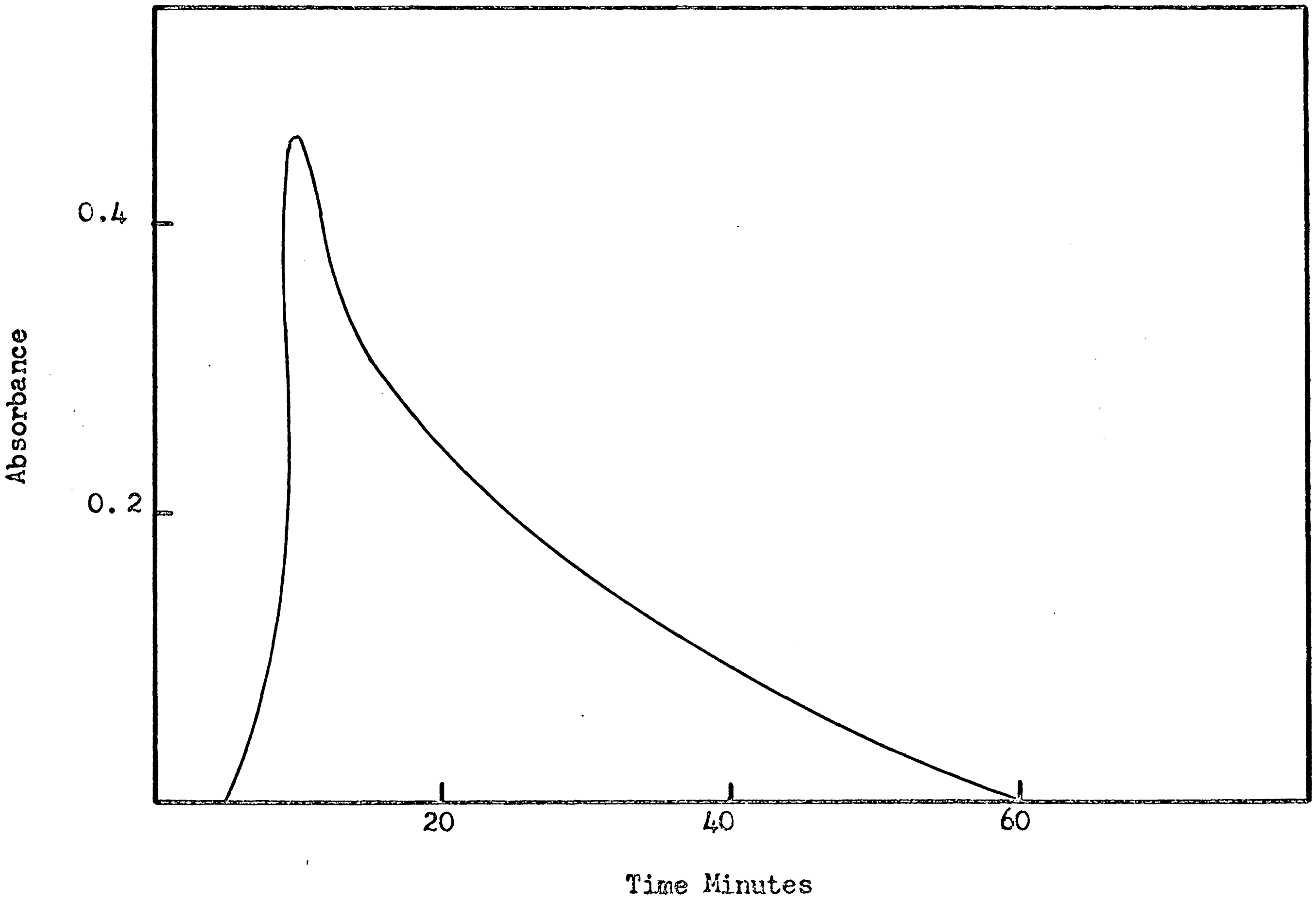


Figure 12: Tracer Study After Biological Growth

and measuring what was drained. The theoretical detention time when the column contained biological growth was estimated from the value of T obtained from the column with no biological growth. The statistical results of the tracer studies are presented in Table XIII.

Basic data describing the operation of the batch phase of this study are given in Appendix C. Data presented include values for organic carbon, nitrate nitrogen, and nitrite nitrogen. Figures 13 through 17 are plots of nitrate nitrogen, and nitrite nitrogen vs. time for each of the five different bottles used in this phase of the study. Figures 18 through 22 are plots of organic carbon vs. time for each of the five bottles. Because of the small volume of the daily samples taken during this phase biological solids concentration was not determined.

The data indicates a rise in nitrites accompanying the drop in nitrates. With the exception of Bottle I no significant drop in total nitrogen was observed. All bottles except Bottle IV show an increase in nitrite nitrogen to about 40 mg/l. In the case of Bottle IV, nitrite nitrogen leveled off at about 15 mg/l. Organic carbon drawdown in all cases was rapid during the initial phase of the study and either slowed drastically or stopped completely in the latter days of the study.

TABLE XIII

Detention Time Data

	Column with no biological growth	Column with biological growth
T(min.)	26.8	28.2
Tm(min.)	18.0	10.0
Tg(min.)	22.8	23.0
Ta(min.)	21.3	18.0
Ti(min.)	5.0	5.0
Tm/T	0.67	0.35
Tg/T	0.85	0.81
Ta/T	0.79	0.64
Tu/T	0.19	0.18

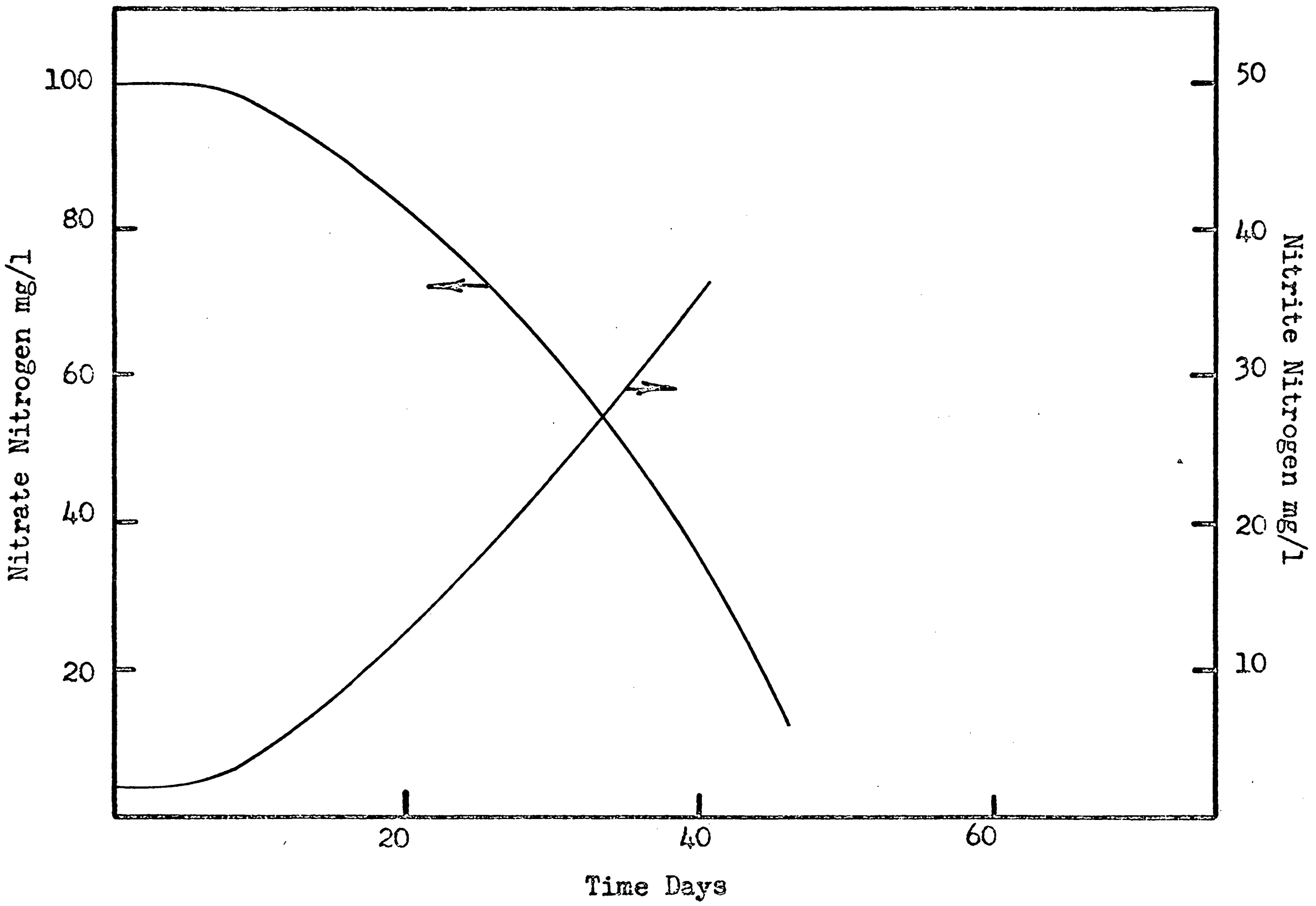


Figure 13: Denitrification Data Bottle I, Initial Organic Carbon Concentration 96 mg/l.

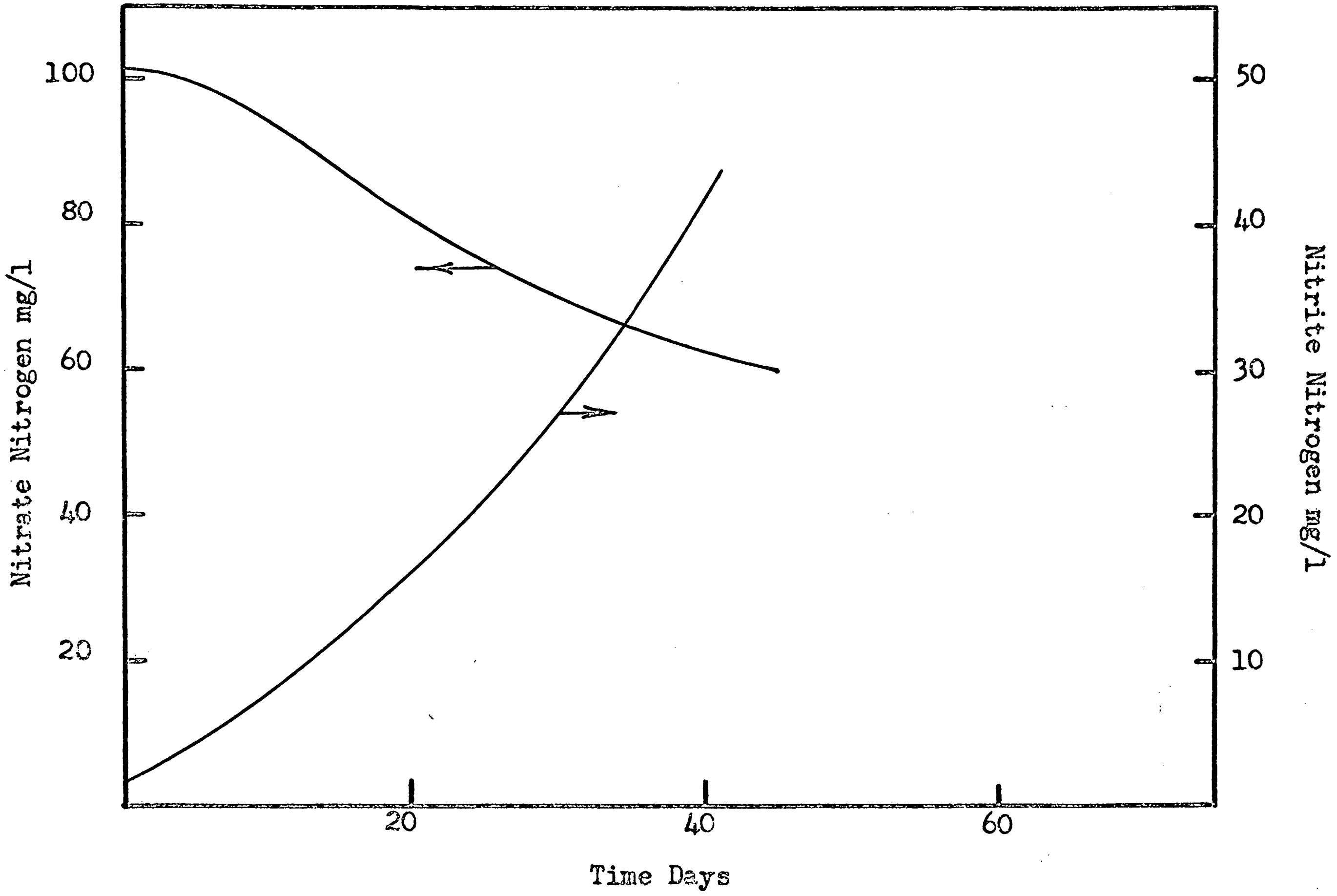


Figure 14: Denitrification Data Bottle II. Initial Organic Carbon Concentration 116 mg/l.

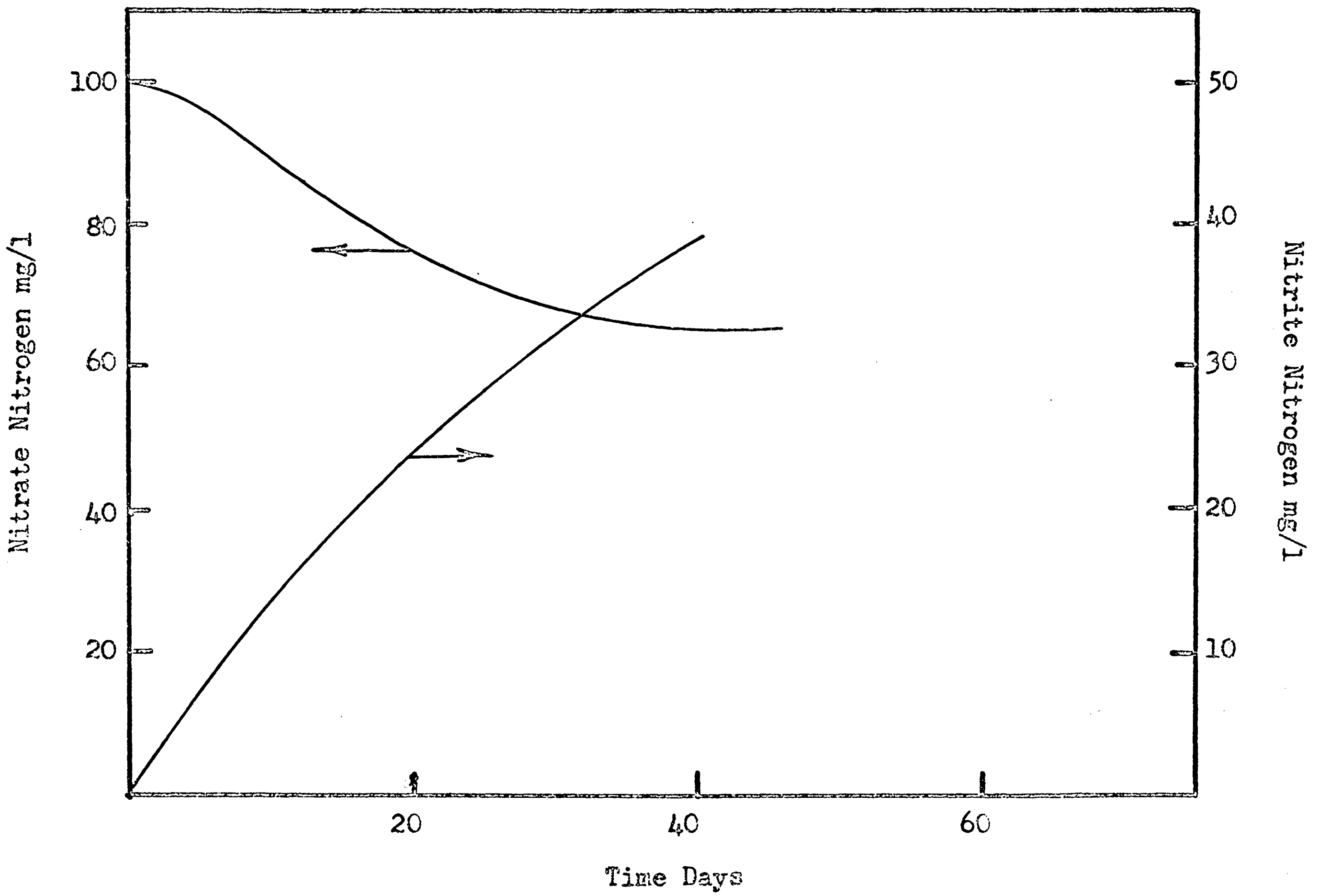


Figure 15: Denitrification Data Bottle III, Initial Organic Carbon Concentration 126 mg/l.

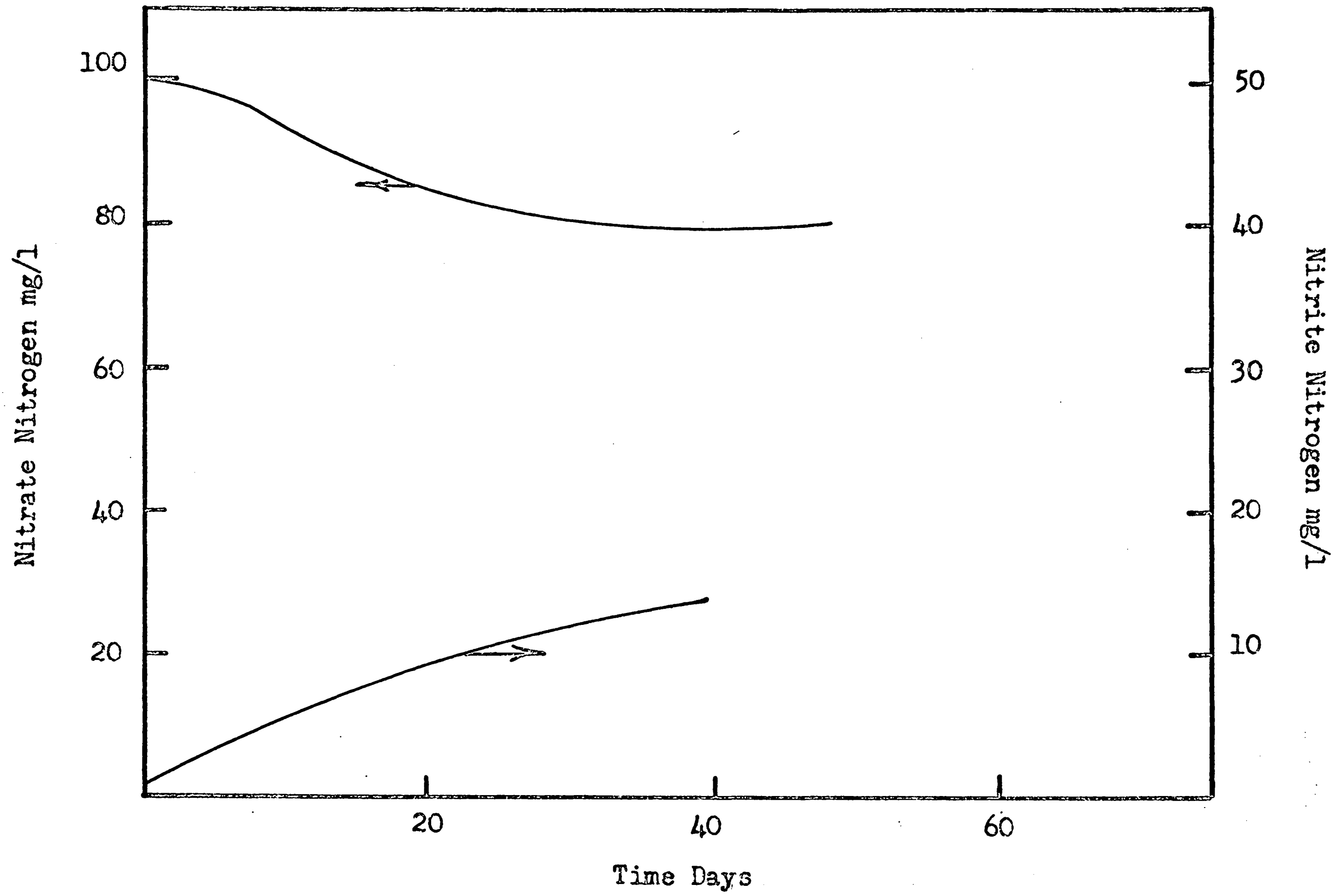


Figure 16: Denitrification Data Bottle IV. Initial Organic Carbon Concentration 136 mg/l.

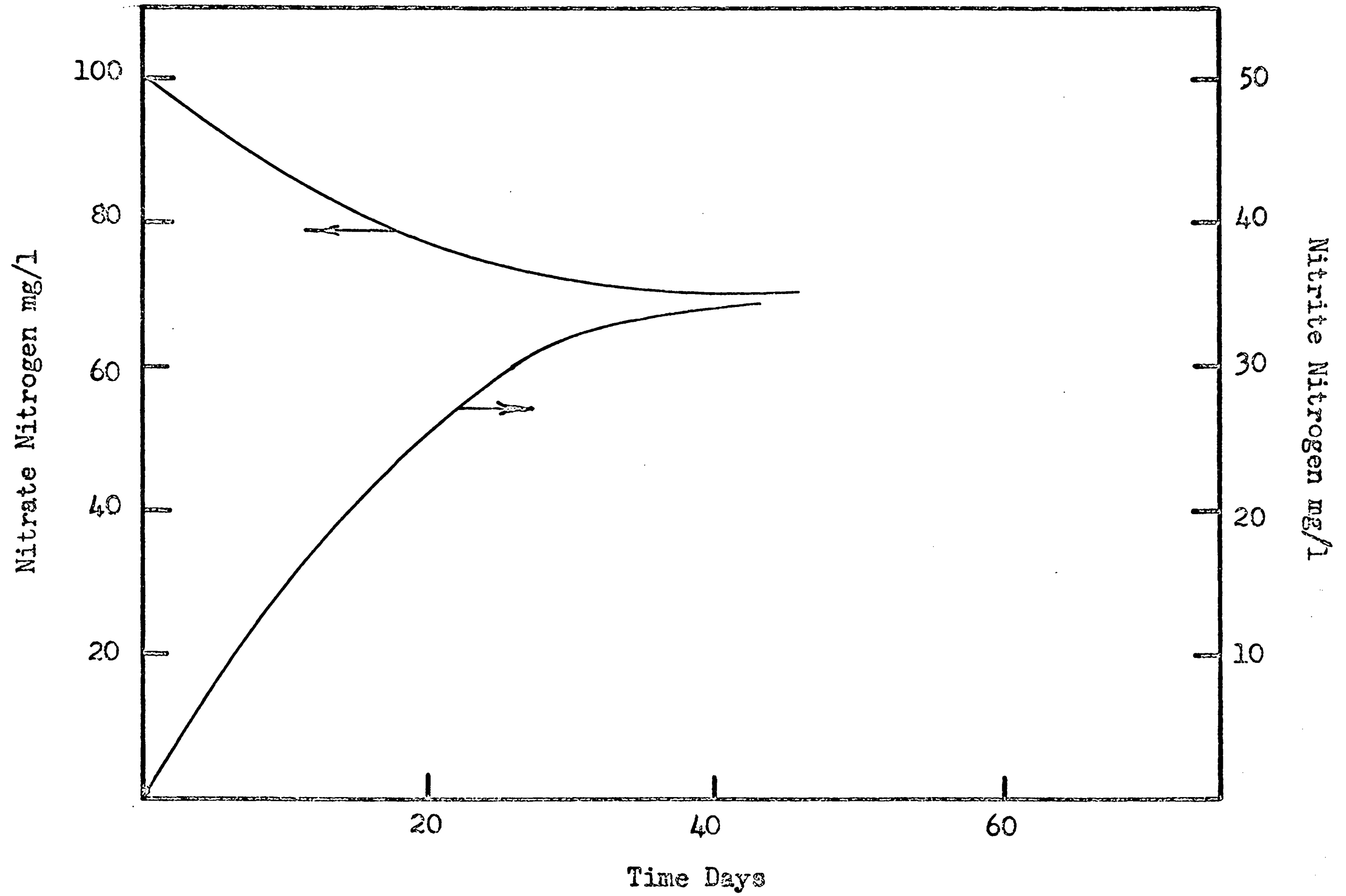


Figure 17: Denitrification Data Bottle V. Initial Organic Carbon Concentration 146 mg/l.

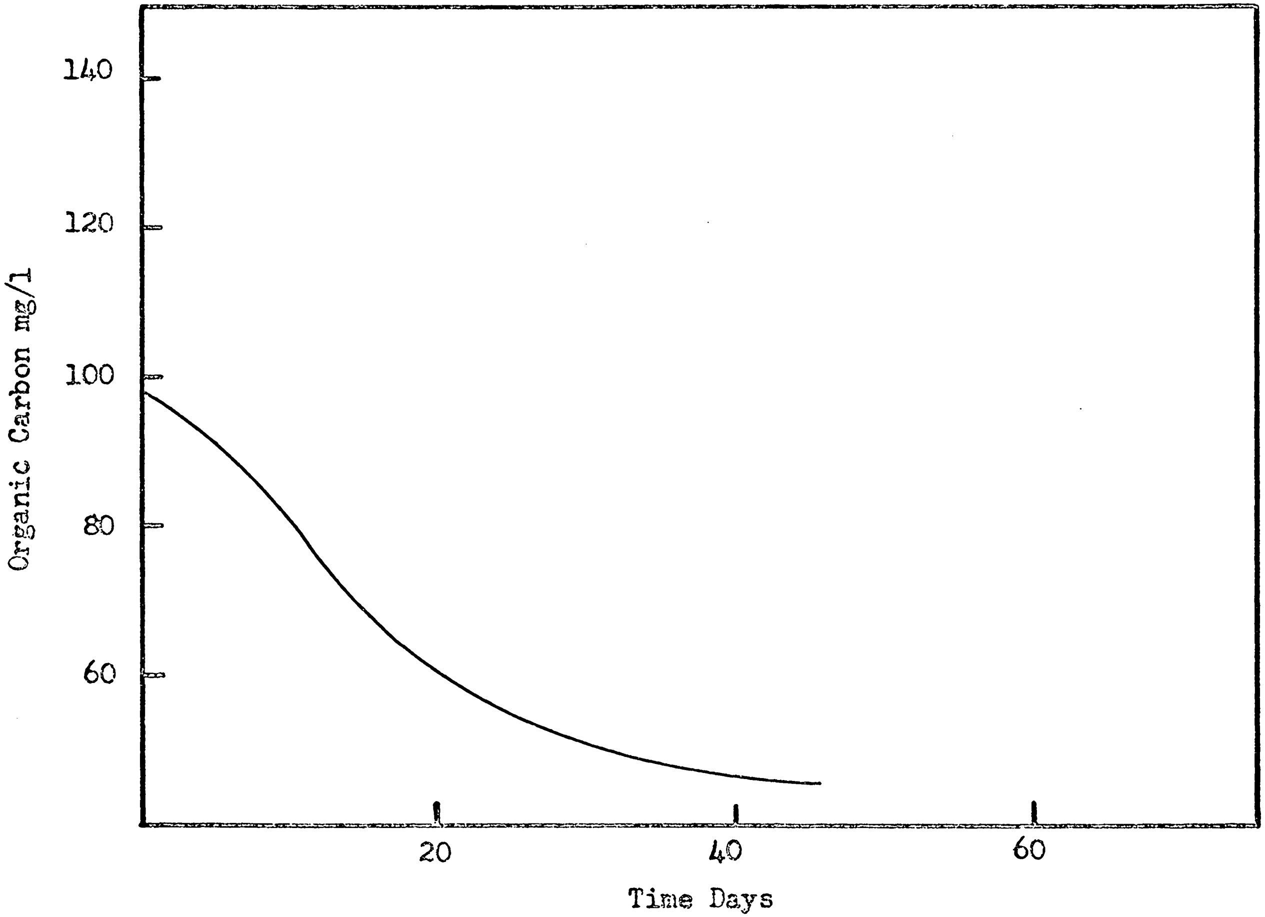


Figure 18: Organic Carbon Drawdown Bottle I

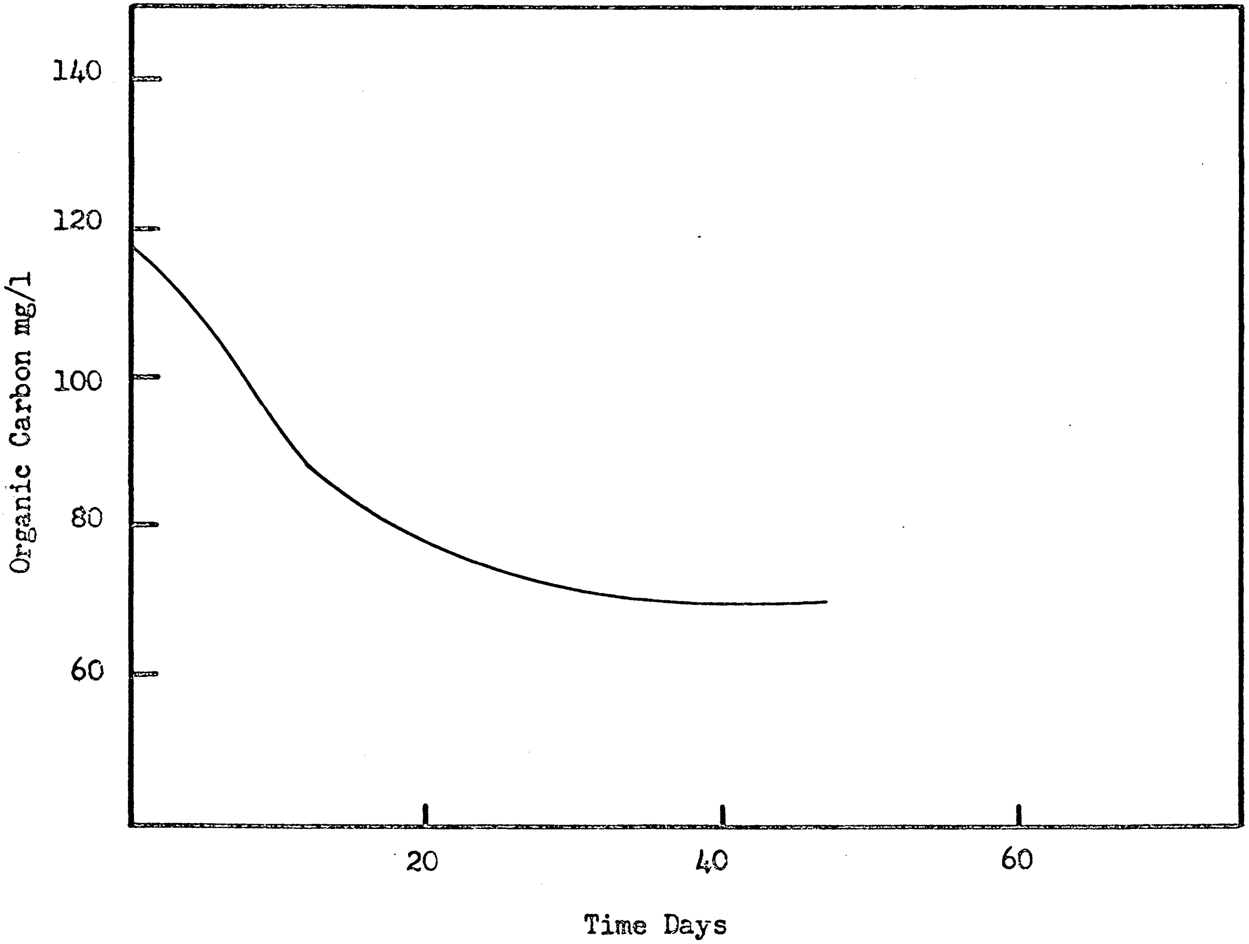


Figure 19: Organic Carbon Drawdown Bottle II

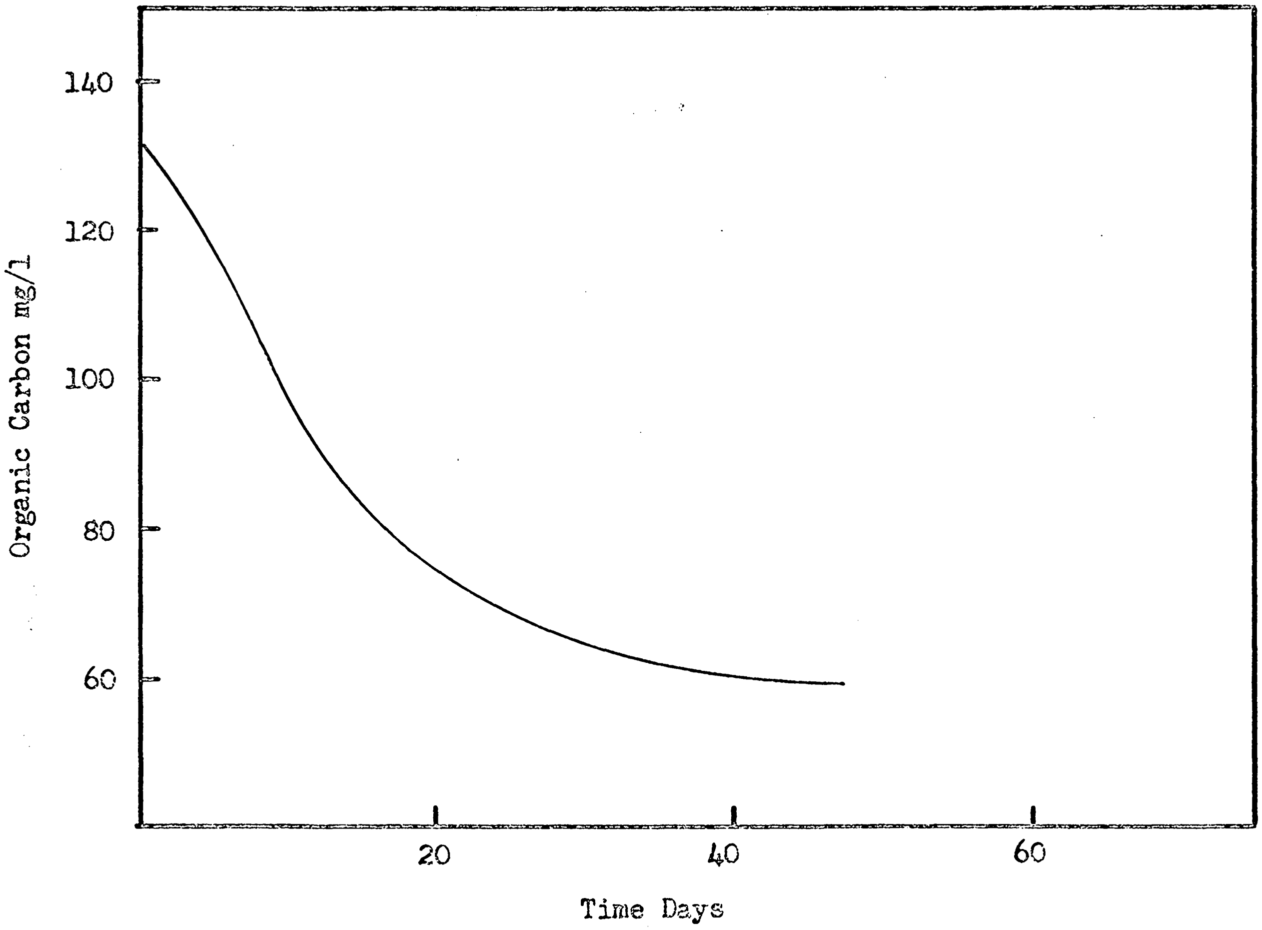


Figure 20: Organic Carbon Drawdown Bottle III

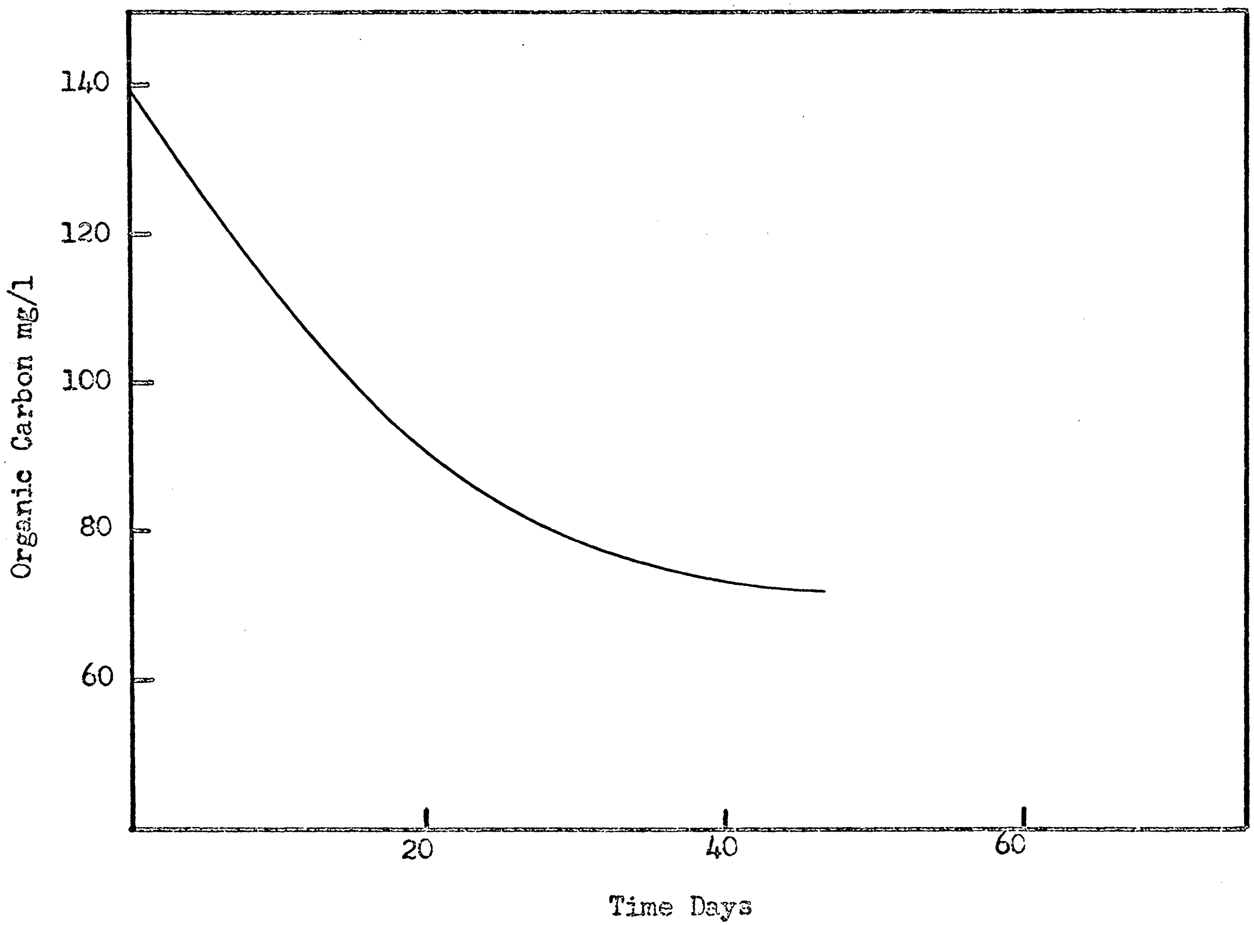


Figure 21: Organic Carbon Drawdown Bottle IV

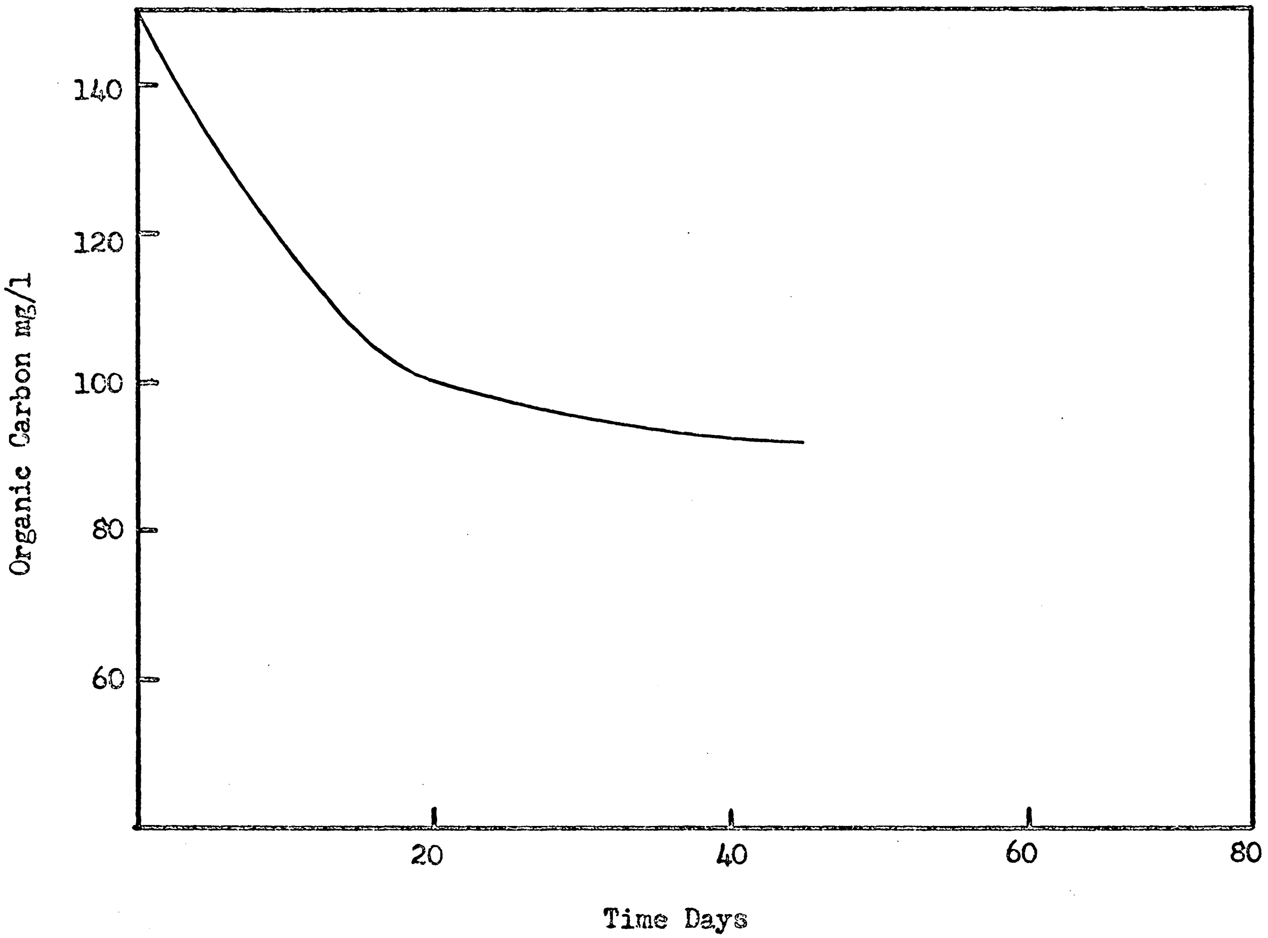


Figure 22: Organic Carbon Drawdown Bottle V

DISCUSSION

A discussion of the anaerobic denitrification work is presented below. Discussed first is the operation of the columns packed with activated carbon and sand, followed by a discussion of the batch denitrification work.

Throughout the entire period of operation of the activated carbon column very good denitrification results were achieved. Never in the course of the experiment did the total nitrogen removal fall below 98.3%. Removal efficiencies as high as 99.3% were observed with an average removal of 98.9%. These figures demonstrate the stability of operation and high removal efficiencies possible at an average empty column detention time of 9.1 hours.

The organic carbon removal efficiency fluctuated more than did the total nitrogen removal efficiencies. The highest removal efficiency noted was 74.6% while the lowest was 42.6% with an average of 61.2%. In terms of mg/l the organic carbon removal ranged from 111.9 to 63.9 averaging 91.8. One possible explanation for the greater fluctuation in organic carbon removal could be the intermittent "sloughing" of active biomass from the column into the effluent where it would be measured as organic carbon. Difficulty in metabolizing portions of the Water Dry Process Waste was not considered a contributory factor to the fluctuation of organic carbon removal. It should also be noted that the low value for average organic carbon removal could be misleading due to the fact that no attempt was made to reduce the organic carbon to a minimum consistant with high total nitrogen removals. The organic carbon in the feed was always in excess of the theoretical amount needed for denitrification.

Due primarily to the low specific gravity of activated carbon, large clumps of activated carbon and biomass separated and floated within the unit. It was felt that this problem was serious enough to make activated carbon unattractive as a material suitable for use in denitrification columns. High influent pressures which occurred within the activated carbon column were probably due to the design of an internal baffle in the column rather than media characteristics.

Odors were only associated with the effluent from the activated carbon column; the effluent from the sand column exhibited no foul odors. The presence of odors from the activated carbon column can be attributed to either a chemical reaction catalyzed by the activated carbon or to biological degradation of biomass or absorbed organic material within the column. Since the sand column exhibited no odors a reaction catalyzed by the activated carbon is a more plausible explanation.

During the initial period of operation of the sand column high total nitrogen removal and stable results were observed. Values as high as 99.9% removal was observed with the lowest removal being 98.0% for an average of 98.9%. During this period the empty column detention time was maintained at 8.76 hours. The organic carbon removal varied to a greater degree, varying from 54.6% to 88.0% and averaging 64.7%. In terms of mg/l, the organic carbon removal ranged from 81.9 to 132.0 with an average of 97.0. Again, it should be pointed out that throughout the operation of both the sand and activated carbon columns organic carbon was in excess of that needed for complete denitrification. As with the activated carbon column, the probable reason for widely fluctuating organic carbon removal stems from intermittent biomass release.

A sharp decrease in both total nitrogen removal and organic carbon removal was observed when either column was maintained at empty column detention times less than 8.76 hours. At no detention time less than 8.76 hours did the sand column achieve an 80% total nitrogen removal. Further, both the total nitrogen and organic carbon removal efficiencies exhibited considerable daily variation at detention times less than 8.76 hours.

No problem was experienced with rising sand-and-biomass clumps during the study. However, the sand bed did expand after denitrification commenced due to the gases generated during denitrification. High influent pressures also occurred during the operation of the sand column. During the period starting day 17 and ending day 24, particularly high influent pressures were observed, making it necessary to manually disrupt the sand bed and clear the biomass from the baffle in the column. During this period the column was operated at a high detention time because of the difficulty of pumping the influent through the column. The drop in total nitrogen removal which was observed during this period can be explained by the associated hydraulic problems, i.e., increased short circuiting. The increase in organic carbon removal during this period can not be explained. No odorous effluent was observed at any time from the sand column.

Based on the results of this study, it is apparent that the sorptive properties and surface texture of the media had no effect on the denitrification capabilities of the columns tested. The results strongly suggest that there is a definite advantage to using a dense material and one which is not capable of catalyzing undesirable chemical reactions within the unit.

The consumptive ratio (the ratio of the actual organic carbon consumed to the theoretical amount needed for denitrification) calculated over the first 17 days of operation of the sand column, was 1.47. Based on this value and a typical empirical formulation of $C_5H_7O_2N$ for bacterial cells (26) the following equation for overall nitrate reduction can be derived: $NO_3^- - N + 1.23$ Organic Carbon $0.078\ C_5H_7O_2N + 0.46\ N_2 + 0.84\ CO_2$. It can also be concluded that the denitrification of 100 mg/l of nitrate nitrogen consumes 105.94 mg/l of WDPW organic carbon to produce 62.9 mg/l of cells and 7.8 mg/l organic nitrogen. These values are identical to those established by McCarty for ethanol (23). It can easily be seen that while this process is predominately dissimilatory in nature, 7.8% of the influent nitrate nitrogen is assimilated into cell mass.

The biological solids produced during these studies settled poorly. While no specific analysis was performed no settling was observed when the effluent from the columns was allowed to stand in graduated cylinders overnight. This coupled with the fact that 62.9 mg/l biomass is produced per 100 mg/l nitrate nitrogen denitrified, demonstrates the necessity that effective solids removal be provided in any treatment design utilizing anaerobic columns. Because of the poor settling ability observed in this work, polymer addition and settlementation basins or mixed media filtration are probably the only sure methods of solids removal.

Based on tracer study data there was strong indication that the hydraulics of the sand column were altered by the biological growth within the column. The ratios of Ta/T and Ti/T are both indicators of the degree of short circuiting occurring within the column, while Tm/T and Tg/T are indicators of dead spaces. A drop in any of these ratios indicates hydraulic deterioration, i.e., more short circuiting or more dead spaces (36). While all 4 ratios were less for the column after biological growth had occurred, the most drastic reduction was in Tm/T. This indicates a sharp rise in dead spaces or a decline in active space within the column. The probable reason for the increase in dead spaces stems from the accumulation of gases within the column. These pockets of gas (mainly nitrogen and carbon dioxide) effectively reduce the active volume of the column. One can therefore conclude that provisions for effective gas removal from anaerobic columns would provide more effective operation. An automatic backwash surge or slowly rotating paddles within the column are possible ways to accomplish gas removal.

The batch phase of this study demonstrated how difficult it is to remove large amounts of nitrates on a batch basis. In all cases there was little if any drop in total nitrogen over a time span of 46 days. Toward the latter phase of the investigation the uptake of organic carbon tapered off. This can be taken as an indication of diminishing biological action. This drop-off occurred at a time when a biological population would have been established and operating under optimum conditions. This result, when large amounts of nitrate and nitrite were still available, indicates either inhibition or death of the biomass present in the bottles. The most likely reason for this occurrence was the high concentrations of nitrite resulting from partial denitrification. The indications are that the bacteriological population capable of reducing nitrate to nitrite developed too fast for the corresponding population needed to reduce nitrite to molecular nitrogen to develop. Thus, the nitrite concentration within the system increased to the point that it either killed or inhibited the biomass present. It should be remembered that partial denitrification (reduction of nitrates to nitrites) can be more detrimental to a receiving stream than no denitrification at all. Aside from the fact that nitrogen is still available for algal growth, nitrite will quickly be oxidized to nitrate creating an oxygen demand on the stream. Nitrite can also exhibit toxic effects on the biological community of the stream. Partial denitrification was exhibited to a much greater degree in the batch phase of this study than in either of the columns used in this study.

CONCLUSIONS

1. An industrial waste high in nitrates can be effectively denitrified by an anaerobic column of granular media. Removal efficiencies as great as 99.9% were obtained at theoretical column detention times of 8.76 hours.
2. A dense material such as sand is a more desirable media for denitrification columns than is a light material like activated carbon. The sorptive capacities or surface texture of the media has little if any effect on the denitrification capabilities of the columns.
3. Activated carbon when used as a denitrification column media produces a foul-smelling effluent. A foul-smelling odor does not occur when sand is used as the media.
4. Water Dry Process Waste produced during munitions manufacturing is a suitable carbon source for denitrification. Water Dry Process Waste exhibits a higher consumptive ratio (the ratio of the actual organic carbon consumed to the amount theoretically needed for denitrification) than does methanol.
5. Hydraulic considerations are fundamental in the design of denitrification columns. Design should assure effective gas release to keep the active volume of the column at a maximum.
6. Batch denitrification was not shown to be a feasible means of removing high concentrations of nitrates.

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APPENDIX A

Activated Carbon Column Data

Day	Effluent Organic Carbon mg/l	Organic Carbon Removal %	Effluent Nitrite Nitrogen mg/l	Effluent Nitrate Nitrogen	Total Nitrogen Removal %	Empty Column Detention Hrs.
1	41	72.5	.02	0.65	99.3	
2	59	60.6	.04	0.94	99.0	
3	86	42.6	.02	1.00	99.0	9.42
4	-	-	-	-	-	
5	-	-	-	-	-	
6	-	-	-	-	-	
7	38	74.6	.04	1.10	98.9	
8	40	73.2	.08	0.93	99.0	
9	52	65.4	.04	0.74	99.3	
10	54	64.0	.02	0.68	99.3	
11	59	60.6	.02	0.95	99.0	9.49
12	54	64.0	.04	0.80	99.2	
13	-	-	.08	1.50	98.5	
14	-	-	-	-	-	
15	-	-	.06	1.10	98.9	9.13
16	72	52.0	.03	1.00	99.0	
17	71	52.6	.04	1.30	98.7	12.40
18	-	-	-	-	-	
19	58	61.2	.02	0.75	99.2	
20	52	65.4	.45	1.30	98.3	
21	52	65.4	.04	1.30	98.7	
22	84	44.0	.08	1.05	98.9	

10.11 Hours Avg.

APPENDIX B

Sand Column Data

Day	Effluent Organic Carbon mg/l	Organic Carbon Removal %	Effluent Nitrite Nitrogen mg/l	Effluent Nitrate Nitrogen	Total Nitrogen Removal %	Empty Column Detention Hrs.
1	58.0	61.2	0.02	0.55	99.7	8.33
2	60.0	60.0	0.02	1.10	98.9	
3	54.0	64.0	0.18	1.17	98.2	8.67
4	-	-	-	-	-	
5	-	-	-	-	-	
6	-	-	-	-	-	
7	-	-	-	-	-	
8	62.0	58.7	0.04	0.70	99.4	
9	65.0	56.7	0.08	1.30	98.6	
10	60.0	60.0	0.04	0.80	99.2	
11	47.0	68.7	0.06	1.10	99.9	9.49
12	68.0	54.6	0.02	1.80	98.2	
13	18.0	88.0	0.08	2.00	98.0	
14	-	-	-	-	-	
15	46.0	62.6	0.04	1.00	99.0	8.35
16	39.5	73.7	0.03	0.64	99.3	
17	47.0	68.7	0.08	1.30	98.6	
18	-	-	-	-	-	12.35
19	24.0	84.0	0.08	2.50	97.5	
20	59.0	60.6	0.05	9.00	90.7	
21	10.0	93.4	0.04	8.50	91.7	
22	-	66.0	0.04	8.70	91.5	15.0
23	-	-	-	6.20	94.0	
24	-	-	0.72	27.00	73.0	
25	-	-	0.50	5.00	95.0	
26	-	-	0.40	17.00	83.0	4.95
27	-	-	0.72	27.00	73.0	
28	-	-	1.40	29.00	70.5	5.14
29	-	-	-	-	-	
30	-	-	-	-	-	-

APPENDIX B
(CONTINUED)

Sand Column Data

Day	Effluent Organic Carbon mg/l	Organic Carbon Removal %	Effluent Nitrite Nitrogen mg/l	Effluent Nitrate Nitrogen	Total Nitrogen Removal %	Empty Column Detention Hrs.
31	43.0	68.0	-	17.00	-	
32	50.5	66.4	2.03	30.00	68.0	
33	42.0	72.0	2.52	22.00	76.1	
34	90.0	40.0	2.38	40.00	58.7	
35	103.0	31.4	1.54	52.00	47.8	4.58
36	141.0	6.0	1.12	48.00	52.1	3.19
37	135.2	9.9	10.90	62.00	38.7	2.90
38	130.0	13.3	18.70	62.00	21.4	2.86
39	141.0	6.0	19.50	69.00	13.7	2.68
40	107.6	14.9	12.10	60.00	30.70	
41	-	-	14.00	65.00	23.00	
42	155.0	0	1.4	63.50	36.70	2.71
43	-	-	-	-	-	
44	-	-	-	-	-	
45	107.0	14.9	0.8	39.00	70.8	
46	104.0	30.7	1.1	40.00	59.9	
47	116.0	22.6	3.6	85.00	13.6	
48	117.0	22.0	2.0	47.00	52.2	3.34
49	-	-	-	-	-	
50	122.0	12.0	4.4	65.00	32.3	
51	-	-	3.0	36.50	61.5	7.35
52	-	-	4.4	36.50	60.1	
53	-	-	2.9	18.00	79.8	

APPENDIX C

Batch Study Data

	Bottle I			Bottle II			Bottle III		
Day	Organic Carbon mg/l	Nitrate Nitrogen mg/l	Nitrite Nitrogen mg/l	Organic Carbon mg/l	Nitrate Nitrogen mg/l	Nitrite Nitrogen mg/l	Organic Carbon mg/l	Nitrate Nitrogen mg/l	Nitrite Nitrogen mg/l
1	96			116			131.5		
2	93	100	2.6	114.5	102	2.7	126	99	2.8
3	93.5			117			122		
4	98			115			118		
5	91		2.0	108		4	112		5
6	84	100		103	96		106	94	
7	77			87			90		
8	72			91			94		
10	83	98	4.15	86	96	8.1	94	90	13.15
11	73			86			112		
12	87	92		114	92		105	84	
13	71			83			83		
14	70			86			87		
15	71			82			92		
16	65	88	9.3	86	82	13.0	93	83	15.7
17	73			95			81		
18	57.5	86		74.5	88		80	84	
20	64	94	8.55	82	85	15.7	79	102	30.5
22	59.5			72			76		
24	58.5	76		72	80		67	72	
27	46.5	70	12.3	81	73	25.6	67	68	29.4
31		56	33.5		64	49.0		66	51.1
38	48	47	30	85	68	40	72.7	69	36
40	78.5	32	37	76	60	43	69.4	68	40
42	62	21		94	62		71.2	64	
46	45.5	14		68.1	60		53.3	68	

APPENDIX C
(CONTINUED)

Batch Study Data

	Bottle IV			Bottle V		
Day	Organic Carbon mg/l	Nitrate Nitrogen mg/l	Nitrite Nitrogen mg/l	Organic Carbon mg/l	Nitrate Nitrogen mg/l	Nitrite Nitrogen mg/l
1	136			146.5		
2	135	98	2.5	147	98	2.9
3	137			147		
4	134			144		
5	120		4	126		5
6	112	96		134	92	
7	119			134		
8	104			122		
10	106	90	7.55	121	86	14.0
11	122			124		
12	117	86		133	84	
13	96			101		
14	92			102		
15	97			100		
16	100	84	5.9	105	78	18.2
17	100			111		
18	87	90		90	81	
20	93	88	9.8	92	75	25.6
22	82			97		
24	90	84		91.5	72	
27	76	82	8.1	84	70	31.4
31		76	15.7		65	53
38	90	84	5	107	80	32
40	84	86	6	97	77	34
42	107	78		109	76	
46	52	78		85	72	

COLUMNAR DENITRIFICATION OF A MUNITIONS WASTE

by

David Oscar Tucker

(ABSTRACT)

The removal of nitrate nitrogen from a munitions waste by means of bacterial reduction was investigated using packed anaerobic columns. The feasibility of using a munitions waste high in organic carbon (Water Dry Process Waste) as the organic carbon source was also investigated. Simultaneously the biological processing was accomplished in two manners, anaerobic packed columns and batch anaerobic vessels.

It was found that anaerobic columns were effective in reducing 100 mg/l nitrate nitrogen by as much as 99.9% operating at an empty column detention time of 8.76 hours. No difference in denitrification capacity was found between columns packed with activated carbon or sand, but the activated carbon was found to be an undesirable media because of its low specific gravity which permitted it to float after gasification began, and because of foul-smelling odors associated with the activated carbon effluent. The Water Dry Process Waste was found to be a suitable organic carbon source for denitrification and it had a consumptive ratio of 1.47. Batch vessels were found to be ineffective in significantly reducing total nitrogen over a period of 46 days. Buildup of high concentrations of nitrite within the vessels suggested inhibition of the biomass to an extent that further denitrification would not occur.