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METHANOL REQUIREMENT AND TEMPERATURE EFFECTS IN WASTEWATER DENITRIFICATION

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METHANOL REQUIREMENT AND TEMPERATURE EFFECTS IN WASTEWATER DENITRIFICATION

by

Gulf South Research Institute
New Iberia, Louisiana 70560

for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

Biological denitrification was studied in two types of continuous-flow reactors as a function of the concentration of an organic additive (methanol), at 3 temperature regimes, and 3 dissolved oxygen (D.O.) levels. One of the reactors was packed with small diameter, about 3 mm, glass beads and is called the packed column reactor; the other reactor was a container having a concentration of suspended solids of about 2000 mg/l and is called the suspended growth reactor. The temperatures used were 30°C, 20°C, 5°C and dissolved oxygen levels were level I, less than or equal to 0.5 ppm, level II, 1.3 to 2.5 ppm, and level III, greater than or equal to 4.0 ppm.

The most efficient methanol:NO_3-N ratio for both reactors is between 2:1 and 3:1. The optimum ratio varies to a slight extent with temperature. For example, at 30°C, greater than or equal to 90% denitrification in both reactors was achieved with a methanol:NO_3-N ratio of 2:1. At 20°C, greater than 90% denitrification was achieved in the packed column reactor with a ratio of 2:1 but the suspended growth reactor required a ratio of 3:1 to achieve equivalent denitrification. At 5°C, the packed column reactor was functional at a methanol:NO_3-N ratio of 2:1 but the most efficient ratio was 3:1; the data from the suspended growth reactor indicate a ratio slightly greater than 3:1 was required at this temperature.

Dissolved oxygen was not a major factor governing the efficiency of either of the two denitrifying units. The most apparent effect was at D.O. levels I and III and this was usually, but not consistently, most apparent at methanol:NO_3-N ratios of less than or equal to 1:1. Both reactors were slightly more efficient at D.O. level I than at D.O. level III. The most effective methanol:NO_3-N ratio was between 2:1 and 3:1 for all D.O. levels, in both reactors.

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SECTION I

CONCLUSIONS

1. The optimum methanol:NO_3-N ratio for biological denitrification is between 2:1 and 3:1 at 20°C and 30°C, and slightly greater than 3:1 at 5°C.

2. Temperature affects biological denitrification only slightly, particularly at methanol:NO_3-N ratios less than optimum; at lower temperatures methanol:NO_3-N ratios have to be increased slightly to achieve the same amount of denitrification.

3. Dissolved oxygen does not appreciably affect biological denitrification; however, at lower dissolved oxygen levels the efficiency of the process is slightly enhanced.

4. The packed column reactor, described in the body of this report, is a more efficient denitrifying unit than the suspended growth reactor because it requires a shorter detention time.

5. An acclimation period is necessary if large temperature changes are experienced during biological denitrification.

SECTION II

RECOMMENDATIONS

This research was done with a pilot plant on a small scale as described elsewhere in this report. It is recommended that future work be done on a larger scale and that the design incorporate provisions for making several test runs per day or operational period, in order that a sufficient amount of data could be collected for suitable statistical analysis. This type of analysis would provide a more rigorous indication of optimum methanol:NO_3-N ratios between 2:1 and 3:1 for various temperatures.

The design of methanol storage facilities in an actual wastewater operation should be based on a maximum methanol:NO_3-N ratio of about 4:1 since varying environmental conditions, i.e., temperature, will necessitate a ratio between 2:1 and 3:1 and on occasion slightly more than 3:1. In order to avoid adverse temperature effects the methanol:NO_3-N ratio should always be greater than or equal to 2:1 and in lieu of specific information for lower temperatures (about 5°C) the ratio should be set at 3:1.

Additional design improvements could be made to the suspended growth reactor, particularly the manner in which the wastewater flows through it. An upward flow pattern would prevent clogging and insure a constant volume.

Some provision in plant design may be necessary for acclimation time, particularly at lower temperatures, i.e., 5°C, and at methanol:NO_3-N ratios well below the optimum.

Finally, a positive technique, such as gas chromatography, is needed to measure the utilization of methanol.

SECTION III

INTRODUCTION

The removal of eutrophying nutrients from wastewater effluent is of first rank priority in pollution control. One of the major problems is the removal of low concentrations of nitrogen from large volumes of water at an acceptable cost.

Biological denitrification seems to offer a practical solution to this problem since a satisfactory degree of nitrogen removal is possible and has been achieved by a number of workers using different process designs (1, 2, 3, 4, 5, 6, 7).

A variety of organic additives have been used to satisfy the metabolic hydrogen donor requirements of the denitrifying organisms. Of these, methanol appears to be one of the most satisfactory and economical (6, 7, 8, 9, 10, 11). In studies using methanol a high percentage removal of nitrogen was achieved but reports vary on the amount of methanol required in relation to nitrate-nitrogen (NO_3-N) removed. This variation ranges between 2 and 4 parts of methanol per part of nitrate-nitrogen on a weight basis. Some of these discrepancies may have been due to differences in experimental conditions, particularly temperature and the presence of dissolved oxygen in the nitrified effluent. Temperature, of course, affects sludge production and the endogenous metabolism of wastewater microbes, while dissolved oxygen is believed to be the preferred hydrogen acceptor when present with nitrate (12, 13) and thus will exert a "methanol demand," requiring approximately one part of methanol per part oxygen on a weight basis (9, 10, 11).

In a biological denitrification system involving large volumes of wastewater, it is obviously necessary to ensure that the methanol added is just sufficient to remove the nitrate present; addition of too little will leave residual nitrate and too much will cause an unnecessary increase in cost of treatment as well as an undesirable increase in the oxygen demand of the effluent. It is necessary, therefore, to determine how changes in operating temperatures affect denitrifying efficiency and methanol requirements, since systems of this type are required to operate over a wide range of seasonal temperature changes.

A recent study (7) of a continuous-flow suspended growth denitrifying reactor using methanol suggests that a contact time of about 180 minutes is required for a unit of this type. In contrast, studies with denitrifying flora developed on packed columns of sand or granular carbon, also using methanol, indicated that very rapid denitrification can occur; a concentration of 28 mg/l NO_3-N was reduced by 86 percent after a contact

time in the column of 5.5 minutes; after 22 minutes contact, the reduction was 93 percent (9). A coke-packed unit (3) using raw wastewater as the hydrogen donor also achieved rapid removal of nitrogen, 72 percent in 20 minutes. These reports suggest that packed columns may offer advantages over suspended growth reactors but there is a need for further data on their comparative operational performance.

This report describes the results of an experimental program in which biological denitrification was studied in the two types of continuous-flow reactors, packed column and suspended growth, as a function of methanol concentration at 3 temperature regimes and 3 dissolved oxygen levels.

Outline of Denitrification

Biological denitrification is the microbial conversion of nitrate and nitrite to nitrogen and nitrous oxide but molecular nitrogen is the usual and major end product. This reaction requires an organic energy source and, in the absence of oxygen, can be considered a two-step process when methanol is the energy source.

$$(1)\quad NO_3^- + 1/3\ CH_3OH \longrightarrow NO_2^- + 1/3\ CO_2 + 2/3\ H_2O$$

$$(2)\quad NO_2^- + 1/2\ CH_3OH \longrightarrow 1/2\ N_2 + 1/2\ CO_2 + 1/2\ H_2O + OH^-$$

If there is not enough methanol present or in the presence of excessive dissolved oxygen, the reaction will not go to completion, resulting in water high in nitrites.

SECTION IV

MATERIALS AND METHODS

A diagramatic layout of the denitrification pilot plant is given in Fig. 1 and appropriate explanatory legends are included. The system included two holding tanks (A and B), one for mixed liquor and one for the nitrified effluent. These were connected to a temperature-controlled reservoir (C) fitted with a recirculation system. The nitrified effluent flowed from the temperature-controlled reservoir into both the suspended growth reactor (J) and the packed column reactor (L). Continuous-flow through the reactors was maintained by means of pumps (H and M) and the appropriate methanol dose was maintained by means of infusion pumps (F and G) with a constant rate of infusion. Flowmeters (I and N) monitored the flow-rate into the two reactors. The methanol was stored in reservoirs (D and E).

Wastewater Collection and Nitrification

Sewage was collected once a week from the local sewage plant in New Iberia, Louisiana by means of a portable pump and three 190-liter polyethylene tanks carried in the back of a pickup truck. Mixed liquor was pumped from the point in the secondary treatment tank where aerated liquor flows into the final settling tank and just prior to the final chlorination. The mixed liquor was then trucked to the test facility, approximately 3 miles, and pumped into the first holding tank (A in Fig. 1), where it was aerated (S of A in Fig. 1) for 24 hours to insure maximum nitrification. After 24 hours, aeration was discontinued and the effluent transferred by means of gravity flow to the second holding tank (B in Fig. 1) but only after the sludge had settled. A screen was provided on the outflow of tank A to prevent large particles from entering tank B. The nitrified effluent in tank B was held no longer than 6 to 7 days after which a fresh supply was collected and prepared.

Deoxygenation Techniques

Initially, the nitrified effluent was deoxygenated by means of nitrogen gas. This was done by flushing the effluent with nitrogen (gas) in a column approximately 3 meters long and 7.5 cm in diameter. This technique was not satisfactory as the dissolved oxygen could not be lowered below 2.0 ppm, and it took a considerable time to deoxygenate a small amount (1 hr. for 5 liters) of nitrified effluent to this D.O. level. The 3-meter column was located where item C is (Fig. 1) and was

later replaced by item C - the temperature-controlled reservoir. In order to achieve D.O. levels of less than 2.0 ppm, it was necessary to discontinue aeration of the mixed liquor in tank A and hold it under these conditions for 1 to 2 hours; the holding time depended on the desired D.O. level and the temperature of the nitrified effluent. When the specified D.O. level was reached, the nitrified effluent was transferred to tank B, where the D.O. level was continuously monitored; it remained constant for at least 6 days for the particular test period. For each D.O. level, a fresh batch of nitrified effluent was brought in. No significant denitrification occurred in tank B under these procedures, and so nitrogen flushing in the 3-meter column was discontinued.

Dosing Systems

The nitrified effluent was pumped from the temperature-controlled reservoir (C) into the two reactors by means of two Cole-Palmer Masterflex infusion pumps (H and M in Fig. 1). The flow rates of these pumps could be adjusted separately to constant values.

The amount of methanol injected from reservoirs D and E (Fig. 1) into each reactor was controlled by means of separate infusion pumps (brand EMCEMO; F and G in Fig. 1). These pumps work at a constant flow setting. The dosing system devised for introducing the methanol proved to be reliable and particular confidence is placed in it. Briefly, it worked as follows: The particular methanol dosing ratio was calculated on a weight basis (methanol:NO_3-N ratio) and controlled by means of the infusion pumps and flowmeters. For example, if a 3:1 (methanol: NO_3-N) ratio was to be used for denitrifying an effluent containing 20 mg/l of NO_3-N then this requires 60 mg/l of methanol. If the rate of flow through the reactor is 15 ml/min then 0.9 mg/min of methanol is the necessary dose rate. Since the infusion pump had a set rate of 0.2 ml/min, each 0.2 ml it pumped must contain 0.9 mg of methanol. Thus, the concentration of methanol used in the reservoir was 4.5 g/l.

Denitrifying Units

A detailed diagram of the packed column reactor is given in Fig. 2 and appropriate explanatory legends are attached to it. This reactor (F in Fig. 2) had a capacity of approximately 2 liters and was packed with small-diameter, about 3 mm, glass beads to provide a large surface area for the denitrifying flora. It was also provided with a water jacket (E, through I and out D in Fig. 2) for temperature control and 4 outlets (J, K. L, and M in Fig. 2) for sampling. The 4 separate sampling points did not prove to be feasible from a plant management point of view and were not used. The flow of the nitrified effluent and the

methanol dose was upward; that is, the effluent entered through A, and was pumped by means of the pump (N) through the flowmeter (P), mixed with methanol and then forced upward into the column (F) and out C into a stainless steel collecting tank (Q).

A detailed diagram of the suspended growth reactor is given in Fig. 3 and appropriate explanatory legends are attached to it. This reactor consisted of a tube within a tube with a total capacity of approximately 4.5 liters. It was provided with a water jacket (E; cooling and/or heating water enters through item I and out item D; in Fig. 3) for temperature control. The inner cylinder (G in Fig. 3) was water permeable and made of polyethylene commercially known by the trademark VYON. It retained most of the suspended solids of the mixed liquor while allowing the effluent to pass through. Some loss of solids probably did occur, however. A magnetic stirrer (J in Fig. 3) insured proper mixing of the effluent and methanol (both entered the reactor through A in Fig. 3). The effluent passed through C (Fig. 3) into the annular space labeled F and eventually out through K into a stainless steel collecting tank. Temperature was monitored with a mercury thermometer.

The usual enrichment technique of continuous-flow inoculum of denitrifying organisms in both reactors over several weeks were used to develop an adequate growth of microbes. Periodic cleaning of both reactors was required in order to insure a continuous-flow operation; this usually resulted in a loss of denitrification efficiency for several days until the biomass of the microbes built up again to a maximum level.

In the beginning, detention time for the suspended growth reactor was arbitrarily set at 100 minutes. No denitrification was achieved at this holding time so the time was increased to 180 minutes and 78% denitrification was achieved at a methanol:NO_3-N ratio of 5. The detention time was then increased to 210 minutes and efficient denitrification was obtained. Since the suspended growth reactor had a volume of approximately 4.5 liters, a flow rate of 20 ml/min was used for the 210-minute detention time.

The empty-bed detention time of 15 minutes used for the packed column reactor was also arbitrarily decided on. Previous reports from work done elsewhere guided this initial time estimate. The packed column reactor had a volume of approximately 250 ml and a flow rate of 15 ml/min was used.

Daily Test Procedures

Experiments were carried out simultaneously with both the packed column and suspended growth reactors. Studies at 20°C and 30°C were initiated

first and then the temperature was stepped down in 5°C decrements over 11 days to the 5°C level. No operating problems resulted during the temperature changes.

Generally the plant was run continuously, on a 24 hour basis, with the exception of occasional breakdowns. Day to day continuous operational work consisted of (1) mechanical maintenance of the plant, (2) spot checking on various aspects of the nitrified effluent including temperature, dissolved oxygen, and methanol concentrations as required for each test run and (3) the tests for denitrification efficiency on both reactors.

For each methanol concentration tested, both reactors were allowed to equilibrate for 24 hours. This was done by changing methanol concentration, after the denitrification tests, for the experiment to be run on the following day. Denitrification tests were run in the afternoon hours. Methanol concentration for the next run was calculated on the basis of initial nitrate level in the effluent and this was determined by standard nitrate analysis. Methanol:NO_3-N ratios are expressed hereafter by a single integer or fraction and this always means X parts of methanol to 1 part of NO_3-N.

Temperature and dissolved oxygen were checked and recorded for each experimental setup on a daily basis. Temperature was maintained within the reactor at at plus or minus 0.5°C, and the dissolved oxygen level was not affected, provided the ambient temperature in the area of the holding tanks were maintained below or within 20°C to 25°C.

The size and design of the pilot plant caused operational problems. Breakdown of the small pumps on both the reactors and on the heating and cooling system was frequent until a suitable quality of pump could be obtained. Clogging of the discharge outlet (item K) was frequent in the suspended growth reactor. A larger-sized suspended growth reactor with minor modifications in design would be desirable. Such a reactor should be provided with an inlet at the bottom of the reactor rather than the top in order to provide an upward flow through the reactor which would prevent clogging and would insure an accurate means to maintain a constant volume.

Chemical Analyses

The laboratory analyses were carried out by procedures recommended by Standard Methods (14). The physical and chemical parameters that were monitored, usually on a daily basis, included temperature, pH, dissolved oxygen, NO_3-N, NO_2-N, and total suspended solids.

Temperature was measured by the usual mercury-type probe and/or a thermistor-type probe (Yellow Springs brand). The pH of the effluent was measured with a Beckman II Zeromatic pH meter.

Dissolved oxygen was measured by means of a D.O. meter (Yellow Springs brand) calibrated by the Standard Winkler chemical test.

Nitrate-nitrogen (NO_3-N) was determined by the phenoldisulfonic acid method. No prior treatment of the sample was required since the nitrified and denitrified effluents were relatively free of turbidity and color. Generally, 100 to 150 ml samples were collected. Sulfonic acid and potassium permanganate were used to convert all nitrite into nitrate form, followed by treatment with silver sulfate to remove chloride present in the sample. Chloride was removed by precipitation and filteration. The filtrate was neutralized with NaOH to about pH 7. A suitable aliquot was taken and heated; residues were digested with phenoldisulfonic acid. Color was developed with ammonium hydroxide. Samples were then diluted to 100 ml and read at 410 mμ in a Beckman DU Spectorphotometer.

Nitrite determinations were run by taking a suitable aliquot and diluting it to 50 ml. Sulfanilic acid was added and after a 3 to 5 minute period the color was developed by adding napthalamine hydrochloride. The solution was buffered with sodium acetate. Color was measured at 520 mμ in a Beckman DU Spectrophotometer.

Total suspended solids were measured by taking well-mixed samples in a volumetric flask. The sample (100 ml) was filtered through a weighed membrane filter using suction. The filter then was washed with 10 ml distilled water to remove soluble salts and dried with the solids at 103°C for 1 hour approximately in a mechanical convection oven until constant weights were achieved. It then was allowed to cool to room temperature in a dessicator before weighing. Results were expressed in terms of mg/l total suspended solids.

Units for Data Expression

Tables I through IV give the major results of this study. They have been expressed in a variety of ways. For example, the initial concentrations and residual concentrations of NO_3-N and NO_2-N are given in terms of mg/l and also in terms of percent change; that is, the percentage the residual concentration differs from the initial concentration. In some cases for NO_2-N, the residual was greater than the initial concentration. In short, there was an increase and, therefore, the percent change is greater than 100%. These percentage values have been marked with a plus sign. In addition, the overall percent of oxidized nitrogen removal is given. These values were derived by adding

both initial concentrations for NO_3-N and NO_2-N and dividing by the sum of the residual concentrations of NO_3-N and NO_2-N and subtracting from 100.

SECTION V.

OBJECTIVES

The objectives of this work were as follows:

1. To determine the most efficient methanol:NO_3-N ratio required to denitrify wastewater effluent at 30°C, 20°C, and 5°C in both packed column and suspended growth reactors.

2. To determine the effect of various concentrations of dissolved oxygen on the methanol required to achieve maximum denitrification.

3. To compare the packed column reactor with the suspended growth reactor, particularly with reference to their efficiency, consistency of operation, and feasibility of management.

SECTION VI.

RESULTS AND DISCUSSION

Methanol:NO_3-N Ratio and Temperature

The primary objective of this work was to determine the most efficient methanol:NO_3-N ratio (weight basis) in both the packed column and suspended growth reactors. This ratio is defined as that which produces maximum denitrification with a minimum of methanol under the specified conditions. In general, our data indicate that the most efficient methanol:NO_3-N ratio for both reactors lies between 2 and 3. At these ratios, denitrification was little affected by temperature and/or dissolved oxygen (D.O.); the latter aspect (D.O.) will be discussed in the next section.

Select data obtained at temperatures of 30°C, 20°C, 5°C and at various methanol:NO_3-N ratios are presented in Tables I and II as derived from the packed column and suspended growth reactors, respectively. These data are, however, summarized by Figs. 4 and 5, in the form of graphs, plotting percent denitrification on the basis of NO_3-N removal as a function of various methanol:NO_3-N ratios. The differences among the percentages of denitrification on the basis of NO_3-N removal (Figs. 4 and 5) and on the basis of total oxidized nitrogen removal (Tables I through IV) are slight (cf., ibid).

The packed column reactor achieved maximum denitrification on the basis of both NO_3-N and NO_2-N removal, at a ratio of 3, where 97%, 97%, and 96% denitrification were obtained at 30°C, 20°C and 5°C, respectively (Table I; see also Fig. 4). These values are means of at least two experimental runs. The highest denitrification values of any of the individual runs were 97% and 96%, at a ratio of 3, for 30°C and 5°C, respectively. At no time did we achieve a higher percentage of denitrification even though methanol was dosed at ratios of 4, 5, 6, 8, 12, 16, 24, 28, 32 and 40. (Some of these data are not included in this report.) At these higher ratios, the percent of denitrification was not appreciably increased and was usually in the low 90's or high 80's. Fig. 4, based on NO_3-N removal, indicates a leveling off between methanol:NO3-N ratios of 2 and 3 and if the former data were plotted on it, then a plateau would be readily apparent. Close examination of this figure will show that the curves indicate trends only and at ratios greater than 2 there are no significant differences due to temperature. Indeed, the curves actually intersect at these higher ratios. At ratios less than 2 a temperature effect is apparent and the spread (23%) is greatest at a ratio of 1/2, between 20°C and 30°C (see also Table I). The critical point therefore, in regard to an efficient methanol:NO_3-N ratio, is evident at a ratio of 2 for the packed column reactor.

The suspended growth reactor also achieved maximum denitrification, on the basis of both NO_3-N and NO_2-N removal, at a ratio of 3, where 96%, 91% and 91% denitrification were obtained at 30°C, 20°C and 5°C, respectively (Table II; see also Fig. 5). Higher values for percent denitrification were not obtained from this reactor at methanol:NO_3-N ratios greater than 3. Fig. 5 also indicates a leveling off between methanol:NO_3-N ratios of 2 and 3. Furthermore, denitrification in this reactor for ratios greater than 3 never exceeded 96%. Nonetheless, the test differences are greater for this reactor, though the spread is probably not significant at a ratio of 3; and hence it is concluded that there is little difference between the two reactors in efficiency due to temperature at optimum methanol ratios. Even at a ratio of 2, denitrification at 30°C is not much greater than at 20°C (90% vs. 86%) but at 5°C it drops off sharply to 67% which probably is significant. The spread in the data at ratios less than or equal to 2 is quite pronounced for the suspended growth reactor when compared to the packed column reactor (Figs. 4 and 5).

The results of temperature acclimation in both reactors to 5°C are presented in Figs. 6 and 7 in terms of NO_3-N removal. No apparent acclimation differences were found between the two reactors at 30°C and 20°C and the suspended growth reactor showed no adverse effects while operating at 5°C (Fig. 7). Only the packed column reactor (Fig. 6) exhibited a significant acclimation effect and this was present only at ratios less than or equal to 2 but it was apparently readily overcome within 4 to 6 days. It is difficult to account for this effect in the packed column reactor.

Additional data given in Table I on the packed column reactor supports the initial conclusion that the most efficient methanol:NO_3-N ratios lie between 2 and 3. For example, at 30°C, it is probable that this ratio is closer to 2 since the final NO_2-N value was zero indicating that methanol-nitrate reaction went to completion, as compared to ratios of less than or equal to 1, where the NO_2-N was either partly reduced or significantly increased. The latter values occur at ratios of 1/2 and 1/4 when values of plus 157% and plus 146%, respectively, were obtained for final NO_2-N levels. At 20°C, the most efficient ratio is also probably closer to 2 than 3, as the final nitrite values exhibit the same patterns as those of the 30°C test level. At 5°C, some temperature effect on the methanol:NO_3-N ratio is suggested since denitrification is markedly less at a ratio of 1 and the final NO_2-N value (44% reduction) at a ratio of 2 indicates an incomplete reaction and insufficient methanol dose. It is likely that the effective ratio lies closer to 3 than 2.

Additional data on the suspended growth reactor are presented in Table II. There is a more pronounced temperature effect on the methanol:NO_3-N

ratio for the suspended growth reactor than for the packed column (see also Fig. 5). For example, at 30°C, the most efficient methanol: NO_3-N ratio is closer to 2 than 3 as indicated by a 100% reduction of the initial NO_2-N value at a ratio of 2. At 20°C, the ratio lies closer to 3 since it was the only ratio at which complete removal of NO_2-N occurred. At 5°C, the ratio is very likely greater than 3 since some NO_2-N was present at the end of the test. Methanol:NO_3-N ratios greater than 3 at 5°C were not tested.

Comparing the results of the two reactors (see Tables I and II) at 30°C, the percent change in both NO_3-N and NO_2-N was virtually identical. The greatest difference in percentage denitrification was found at ratios of 1/2 and 1 and both were only of the order of 2%; the suspended growth reactor being slightly more efficient. This difference is probably not significant since a greater than or equal to 4% difference was often obtained between individual replicated runs in both reactors. For example, the packed column reactor once yielded 83% denitrification on the basis of NO_3-N removal at a ratio of 1 which is equivalent to the value of the suspended growth reactor given in Table II for the same ratio. It is concluded that there is little or no difference between the two reactors at 30°C in regard to denitrification except for detention time. At 20°C, data from the packed column indicate that it is slightly more efficient than the suspended growth reactor; denitrification in this reactor is greater at all ratios except 1, and the final NO_2-N values are considerably less than the suspended growth data in all cases. Because of the few data points, a statistical analysis could not be done on the results. However, significant differences probably do not exist between the two reactors at 20°C except in terms of detention time. At 5°C, data from the packed column suggest that it is more efficient than the suspended growth reactor. For example, 41%, 89%, and 96% denitrification was achieved at ratios of 1, 2 and 3, respectively, compared to corresponding results for the suspended growth reactor of 34%, 62% and 91%. For both reactors, our 5°C data suggest an optimum methanol:NO_3-N ratio of greater than or equal to 3.

It is concluded that the packed column reactor is a more efficient denitrifying plant than the suspended growth reactor mainly on the basis of detention time. Some of the results indicate that both reactors were more efficient at higher temperatures but only at methanol:NO_3-N ratios of less than 2. No marked temperature differences were observed at ratios of 2 and 3, in either reactor, at any of the 3 temperatures. Initially, at 5°C, the packed column reactor showed (see Fig. 6--on the basis of NO_3-N removal) a drop in denitrification efficiency but additional experiments indicated that it gradually became conditioned to this test temperature and its efficiency was then comparable to its performance at 20°C and 30°C.

Methanol:NO_3-N Ratio and Dissolved Oxygen

Experimental results on the effect of various concentrations of dissolved oxygen on methanol:NO_3-N ratio are listed in Tables III and IV for the packed column and suspended growth reactors, respectively. These experiments were carried out at 20°C, at 3 dissolved oxygen (D.O.) levels. The three D.O. levels were: Level I, less than or equal to 0.5 ppm; Level II, 1.3 to 2.5 ppm; and Level III, greater than or equal to 4.0 ppm.

In general, dissolved oxygen did not inhibit denitrification in either reactor to a major extent; this was particularly true for methanol: NO_3-N ratios greater than or equal to 2. For example, denitrification on the basis of both NO_3-N and NO_2-N removal, in the packed column reactor, for methanol:NO_3-N ratios greater than or equal to 2, averaged 97% at D.O. level I, 92% at D.O. level II and 92% at D.O. level III. These data indicate only a slight improvement in denitrification at D.O. I level (the lowest level). In order to demonstrate whether this difference is significant, more data would be required. Similarly, denitrification, on the basis of both NO_3-N and NO_2-N removal in the suspended growth reactor, for methanol:NO_3-N ratios greater than or equal to 2, averaged 93% at D.O. level I, 92% at D.O. level II and 88% at D.O. level III. Again these data indicate that the suspended growth reactor was slightly more efficient at the lowest D.O. (I) level. It is emphasized that these differences are within the range of variation that was found between individual and replicated experimental runs. For example, both reactors achieved maximum denitrification of 98% at the lowest D.O. level and at methanol:NO_3-N ratios of 6 and 28, (data for the latter ratio are not given) respectively. However, Tables III and IV clearly show that almost (1% to 7% difference) identical denitrification is possible at ratios between 2 and 3.

Considering the data on the packed column reactor in detail (Table III), maximum denitrification, on the basis of both NO_3-N and NO_2-N removal, of 98% was found at D.O. level I and a methanol:NO_3-N ratio of 6 but 96% denitrification was also achieved at a ratio of 2. The final values of NO_2-N were all zero for ratios greater than or equal to 2, indicating that the most efficient ratio is probably less than or equal to 2. At D.O. level II, maximum denitrification was 95% and 96% at methanol:NO_3-N ratios of 2 and 3. At a ratio of 4, denitrification was 85% and the NO_2-N was not completely removed. This may suggest some effect due to dissolved oxygen. However, when the results of D.O. level I and D.O. level II are compared, the packed column is definitely more efficient at the lower D.O. levels but only for methanol:NO_3-N ratios of less than or equal to 1. At D.O. level III, maximum denitrification was 94% at a ratio of 3, with complete removal of NO_2-N. At a methanol:NO_3-N ratio of 4, denitrification remained the same. For all 3 D.O. levels, the breaking point indicating the most efficient methanol:NO_3-N ratio, lies between 2 and 3.

Detailed data for the suspended growth reactor are presented in Table IV. No measurements of total suspended solids was obtained during these experiments but it is assumed that they were approximately 2000 mg/l. At D.O. level I the suspended growth reactor had a greater denitrifying capacity at methanol:NO_3-N ratios of less than or equal to 1 than at the other D.O. levels (this is similar to the packed column). At ratios of greater than or equal to 1 for D.O. level I, maximum denitrification (93%) was achieved and the final NO_2-N value was zero but only D.O. level III showed some loss of denitrification at methanol:NO_3-N ratios greater than or equal to 2. The maximum percentage differences of NO_3-N change, at ratios greater than or equal to 2, between D.O. level I and level II is 5%, between D.O. level I and level III is 9% and between D.O. level II and level III is 9%. These differences are probably not significant. In general, the NO_2-N data for this reactor at D.O. levels II and III are less consistent than for the packed column in that the final NO_2-N values are never zero and show no trend toward their complete removal at the higher methanol:NO_3-N ratios. This may have been an effect of low concentration of suspended solids.

Comparing the results from all three D.O. levels there are no consistent differences at methanol:NO_3-N ratios less than or equal to 1 in regard to denitrifying efficiency. For ratios greater than or equal to 2, the results at D.O. level I and level II are almost identical except the NO_2-N values are more consistent at D.O. level I. Some loss of denitrification efficiency is suggested at D.O. III, particularly at methanol:NO_3-N ratio of greater than or equal to 3.

Growth and Development of Suspended Solids

The initial buildup of denitrifying organisms in the packed column reactor was done at 20°C and it required 41 days in order to establish a flora that produced approximately 90% denitrification at methanol:NO_3-N ratios between 6 and 7. Almost 50% of the column was covered by a heavy microbial growth during the first 6 weeks and thereafter it became completely covered. The bottom of the column appeared to have the heaviest growth. Every two to three months the column required cleaning. This was done by flushing it with effluent but precautions were taken to avoid excess loss of the growth. The reactor was not used for experimental runs during the first 2 to 3 days after flushing.

At the end of the experiments, the packed column reactor was disconnected from the rest of the pilot plant and three separate sections with their enclosed glass beads were taken from it. These sections were from the top, middle and bottom of the column; each being 5 cm high by 5 cm in diameter. The beads in each section were carefully removed and washed several times until they were completely free of growth. The washings were collected and total suspended solids determinations were made on them.

Each section contained approximately 4000 beads with an average diameter of 3.28 mm. The total surface area of the beads was computed and the number of grams of solids was expressed in terms of this area and volume. The results are given in Table V. In the top section 0.49 gm of suspended solids were found while corresponding values for the middle and bottom sections were 0.66 gm and 2.99 gm, respectively. The bottom contained 4x to 6x more suspended solids than the middle or top sections. This would be expected based on its construction and the upward direction of flow. Also given in Table V are the amounts of volatile suspended solids for each of the sections of the packed column.

In the suspended growth reactor, flora adequate for denitrification was obtained within 6 days. The reactor was considered ready for operation when trial runs produced approximately 90% denitrification at methanol:NO_3-N ratios greater than or equal to 3. Some loss of suspended solids occurred during its operation and later on this problem was probably corrected to some extent by periodic dosing of the reactor with mixed liquor and determination of suspended solids.

The most efficient methanol:NO_3-N ratios in these studies for both the packed column and suspended growth reactors have been found by these studies to be between 2 and 3. For a particular operating temperature it can only be stated that the most efficient ratio is either close to 2 or close to 3. For example, in the packed column at 5°C the data indicated that the most efficient methanol:NO_3-N ratio is closer to 3 than 2, at 20°C and 30°C it is closer to 2 than 3. For the suspended growth reactor, the most efficient methanol:NO_3-N ratio at 5°C is probably greater than 3, at 20°C it is closer to 3 than 2, and at 30°C it is closer to 2 than 3.

Methanol:NO_3-N ratios between 2 and 3 were not tested because of the variability in the data produced at each of these ratios; that is, the percent denitrification achieved for methanol:NO_3-N ratios of 2 and 3 were often within plus or minus 2% and very often overlapped one another. Examples of these data are presented in Table VI. For the packed column reactor at 30°C, there was only plus 1.7% difference between the highest and lowest experimental runs using methanol:NO_3-N ratios of 2 and 3, respectively. At 20°C the difference in percent denitrification, using the same ratios, actually overlapped, and at 5°C the difference was plus 2.1%.

The same situation prevailed for the suspended growth reactor at 30°C and 20°C in that only plus 0.3% and plus 2.9% differences separated percent denitrification results for methanol:NO_3-N ratios of 2 and 3. At 5°C, however, the percent denitrification at methanol:NO_3-N ratios of 2 and 3 were well separated (plus 18.7% between corresponding high and low values).

On the basis of these data and the experimental schedule, methanol ratios between 2 and 3 were not investigated. Furthermore, the set-up of the pilot plant did not allow for more than one run per day. If a sufficient number of runs at various ratios between 2 and 3 could have been obtained then a statistical determination of the most efficient ratio would have likely been possible.

The difference between a methanol:NO_3-N ratio of 2 and 3 could be economically significant since chemical cost is directly related to dose. On the basis of our data, specifications for the design of a methanol storage should be sized for a maximum methanol:NO_3-N ratio of about 4 as actual operating dosage under environmental conditions will vary between 2 and slightly more than 3.

Future work should be done on a larger scale, particularly with the packed column reactor using smaller-sized packing material but this would probably require flushing being done more frequently. Also a positive method is needed to measure the utilization of methanol. Gas chromatographing might be the ideal method for this.

SECTION VII

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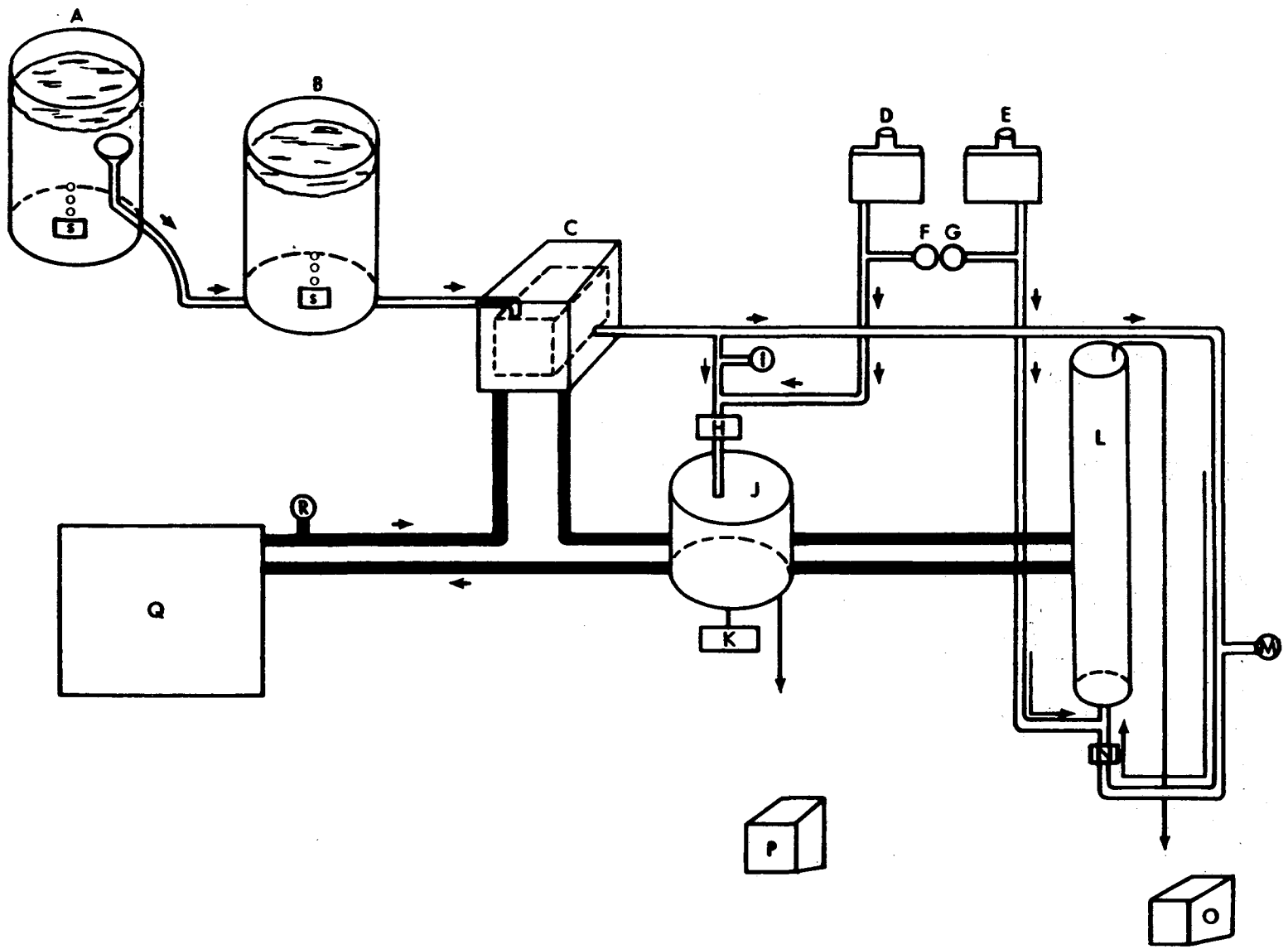

Fig. 1. DIAGRAMMATIC LAY-OUT OF DENITRIFICATION PILOT PLANT.

Explanatory Legend for Fig. 1

Diagrammatic Layout of Denitrification Plant

A. The holding tank for mixed liquor. It was made of polyethylene, had a capacity of about 570 liters, and was fitted with an air sparger and a funnel for gravitational transfer of nitrified effluent to the second holding tank.

B. The holding tank for nitrified effluent was made of polyethylene, had a capacity of about 570 liters, and was fitted with an air sparger at the bottom.

C. This is a steel tank 76 cm long by 38 cm high by 38 cm wide. It provided heating and cooling to the inside (dotted lines) stainless steel tank containing the effluent. The inside tank was 46 cm long by 15 cm high and 20 cm wide, with a capacity of about 5 liters.

D-E. Methanol reservoirs for the suspended growth and packed column reactors respectively. Each had a capacity of 2.5 liters.

F-G. Methanol dosing pumps (EMDECO) for the suspended growth and packed column reactors respectively.

H. Infusion pump (Cole-Palmer Masterflex) for maintaining the flow of nitrified effluent into the suspended growth reactor.

I. Laboratory flow meter with stainless steel float.

J. Suspended-growth reactor having a capacity of approximately 5 liters.

K. Magnetic stirrer.

L. Packed column reactor with a capacity of approximately 2 liters.

M. Infusion pump (Cole-Palmer Masterflex) for maintaining the flow of nitrified effluent into the packed column reactor.

N. Laboratory flowmeter with stainless steel float.

O-P. Stainless steel tanks used to collect the denitrified effluent from the packed column and the suspended growth reactors respectively.

Q. Heating and cooling system capable of maintaining temperature within the range of 4°C to 35°C at ± 0.5°C.

R. A 1/3 H.P. pump for recirculating the heated or cooled water for the reservoir and the two reactors.

S. Air sparger.

Explanatory Legend for Fig. 2

Detailed Diagram of Packed Column Reactor

A. Plexiglass tube for conducting nitrified effluent to the packed column reactor having an inside diameter of about 0.48 cm.

B. Entrance point for unstopping column.

C. Over-flow for denitrified effluent.

D. Outlet for recirculating water to the heating and cooling system.

E. Water jacket for temperature control of reactor, having dimensions of 8 cm in diameter by 91 cm high.

F. Plexiglass column, filled with 3 mm (approx.) glass beads. The column had a capacity of approximately 2 liters and was 5 cm in diameter and 100 cm high.

G. Methanol feeding line from the reservoir. It had an inside diameter of approximately 0.16 cm.

H. Infusion pump (double head) for dosing specific amounts of methanol (rate=0.2 ml/min.).

I. Inlet for recirculating water from the heating and cooling system.

J-K-L-M. Sampling points for denitrified effluent.

N. Infusion pump (Cole-Palmer Masterflex) maintaining flow of nitrified effluent into the packed column reactor.

O. Junction point where methanol and nitrified effluent were mixed prior to entrance into column.

P. Laboratory flowmeter with stainless steel float.

Q. Stainless steel collecting tank.

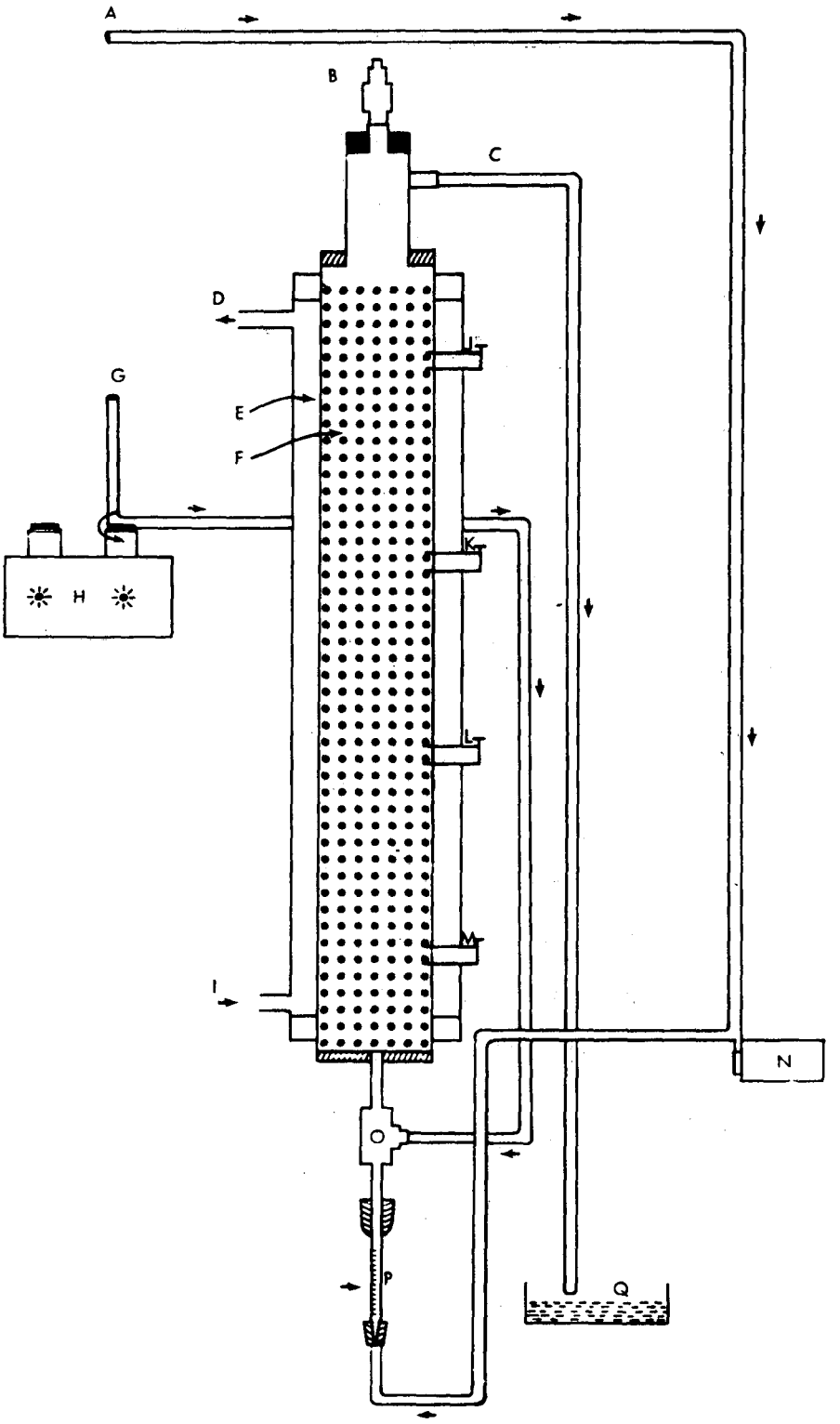

Fig. 2. DETAILED DIAGRAM OF PACKED COLUMN REACTOR.

Explanatory Legend for Fig. 3

Detailed Diagram of Suspended Growth Reactor

A. Plexiglass tube for input of nitrified effluent having an inside diameter of about 0.48 cm.

B. Mercury thermometer for measuring the inside temperature of the suspended growth reactor.

C. Nitrogen gas vent.

D. Outlet for recirculation of water to and from heating or cooling system.

E. Water jacket for temperature control.

F. Annular space between the water permeable (VYON) screen and the outer plexiglass cylinder. Total capacity is approximately 1 liter.

G. Water permeable polyethylene cylinder (I.D. 10 cm) to hold the suspended material (trade name VYON, 0.16 cm thickness).

H. Interior of the water permeable polyethylene cylinder. Total capacity is approximately 4.5 liters.

I. Inlet of water circulation jacket.

J. Magnetic stirrer for mixing and keeping the solids in suspension.

K. Outlet for denitrified effluent.

L. Magnetic stirrer.

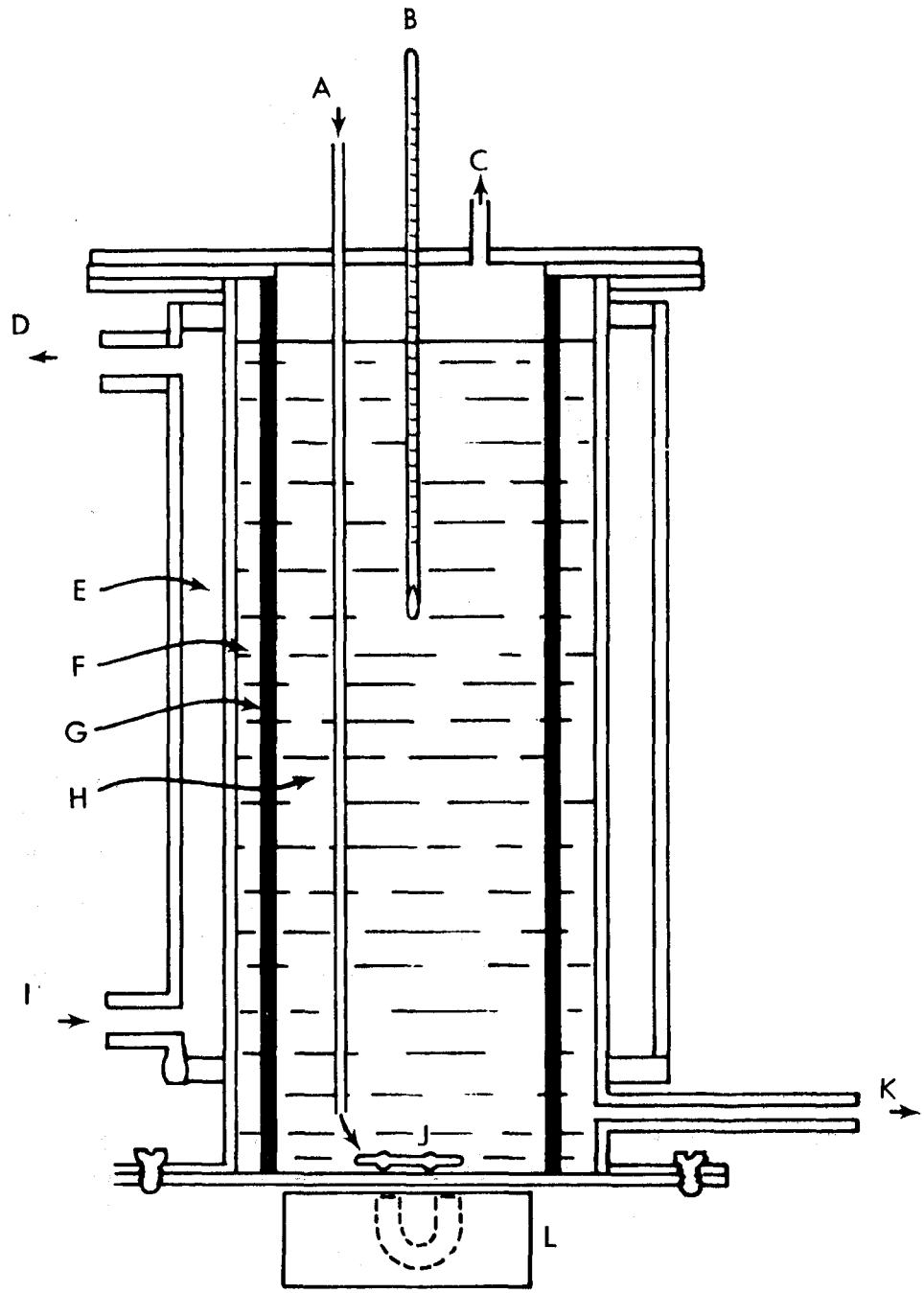

Fig. 3. DETAILED DIAGRAM OF SUSPENDED GROWTH REACTOR.

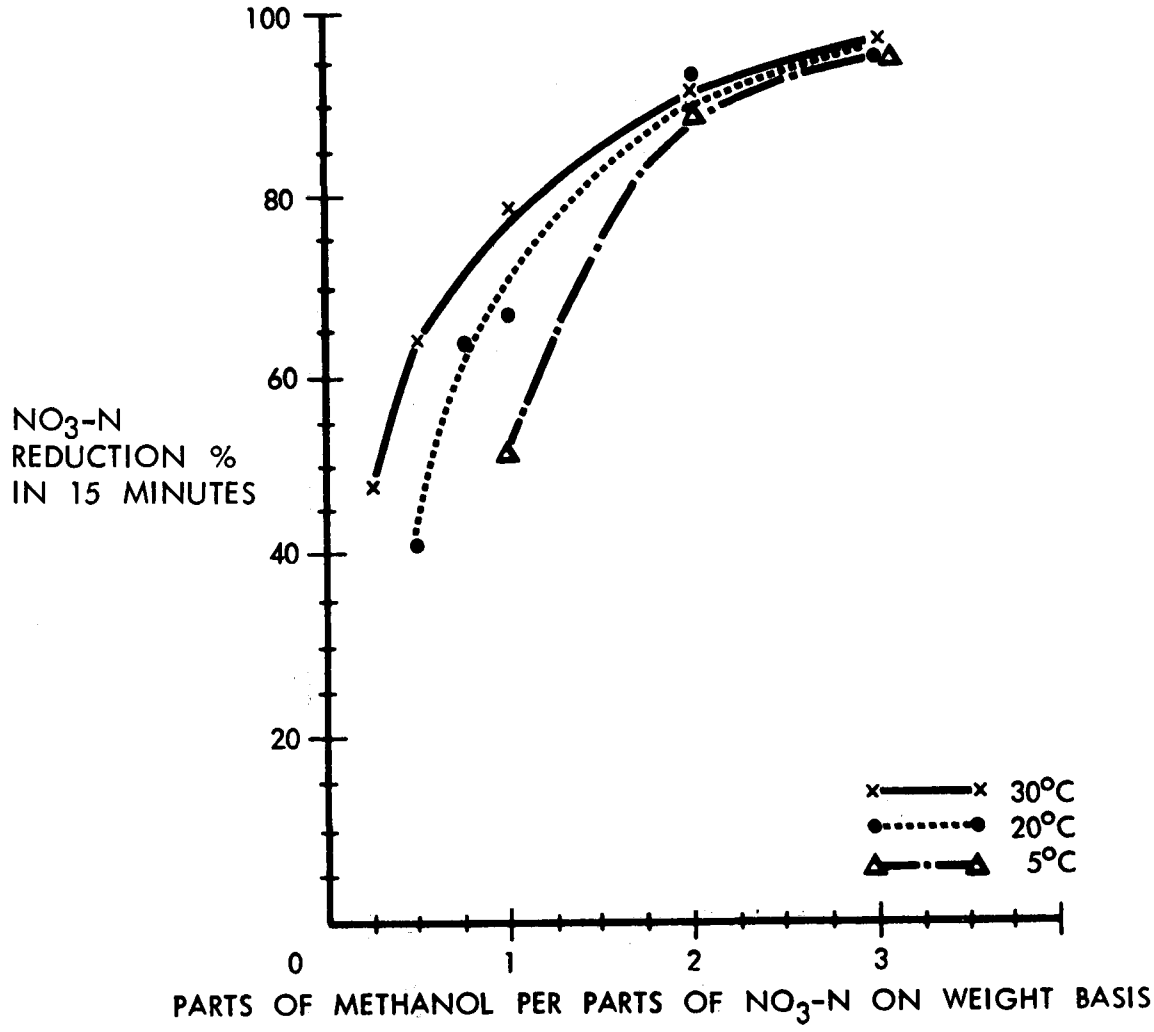

Fig. 4. DENITRIFICATION, BASED ON NO_3-N REMOVAL, IN PACKED COLUMN REACTOR AS A FUNCTION OF METHANOL CONCENTRATION AT THREE DIFFERENT TEMPERATURES. DISSOLVED OXYGEN LEVELS BETWEEN 2.3 AND 2.5 ppm.

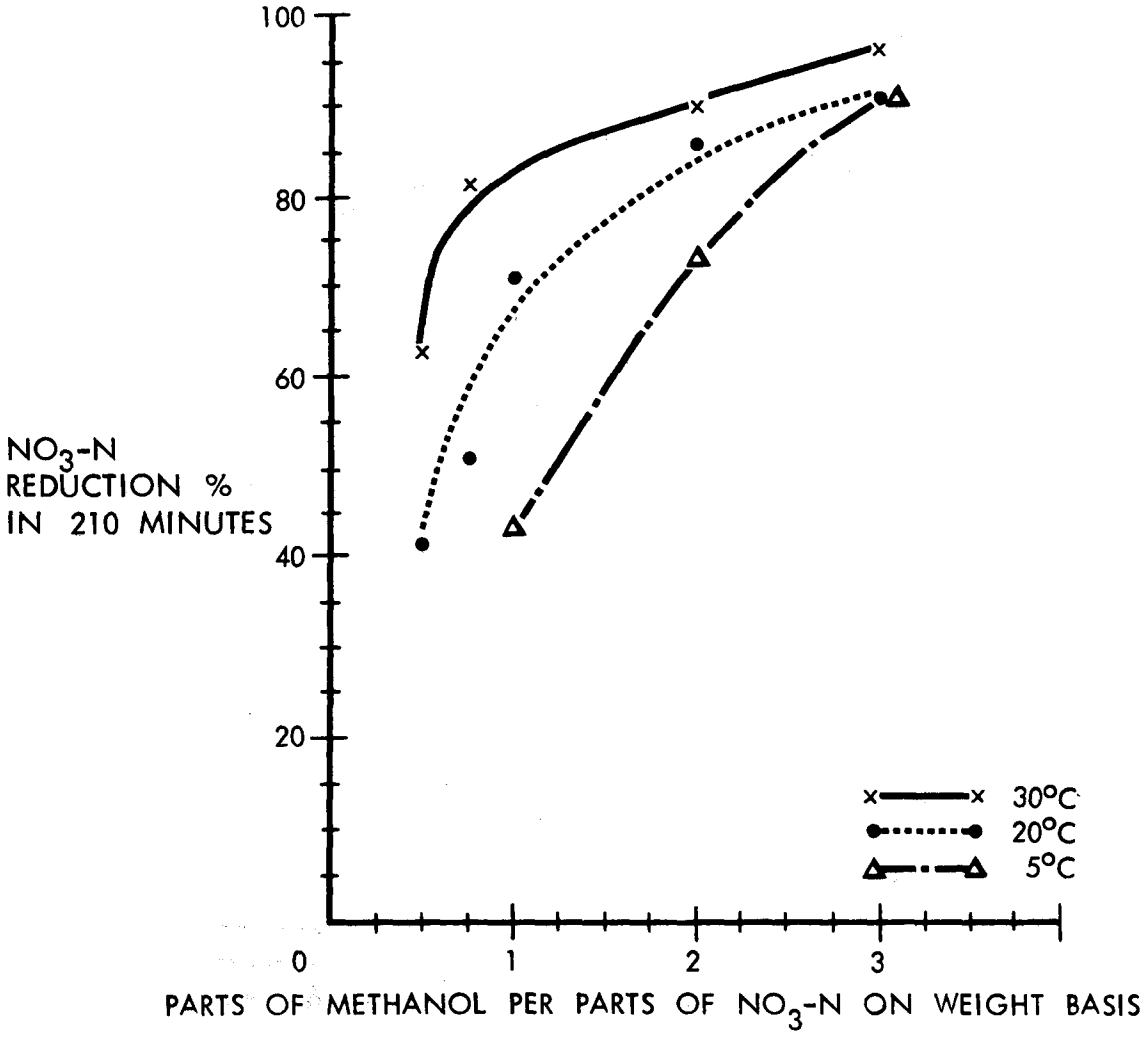

Fig. 5. DENITRIFICATION, BASED ON NO_3-N REMOVAL, IN SUSPENDED GROWTH REACTOR AS A FUNCTION OF METHANOL CONCENTRATION AT THREE DIFFERENT TEMPERATURES. DISSOLVED OXYGEN LEVELS BETWEEN 2.3 AND 2.6 ppm.

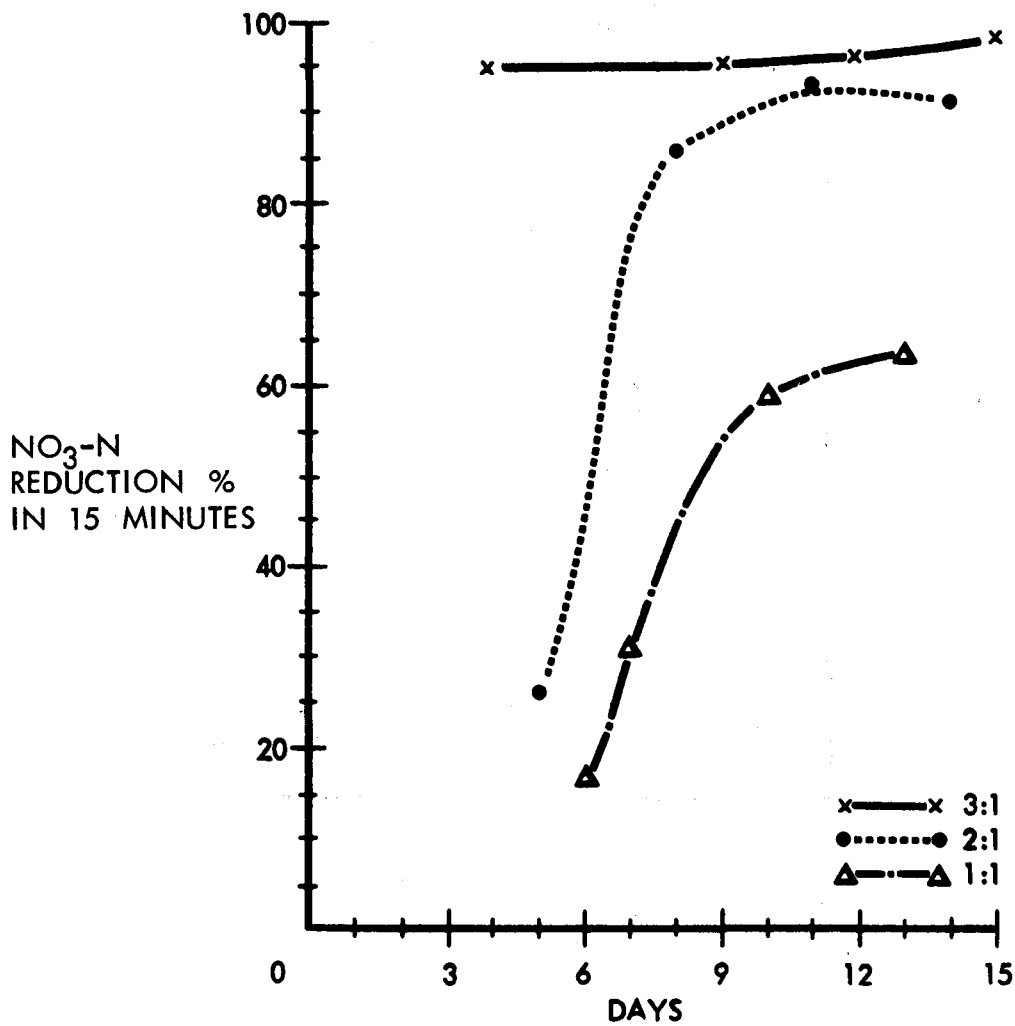

Fig. 6. DENITRIFICATION, BASED ON NO_3-N REMOVAL, IN PACKED COLUMN REACTOR AS A FUNCTION OF TIME DURING ACCLIMATION TO 5°C AT VARIOUS METHANOL: NO_3-N RATIOS (WEIGHT BASIS).

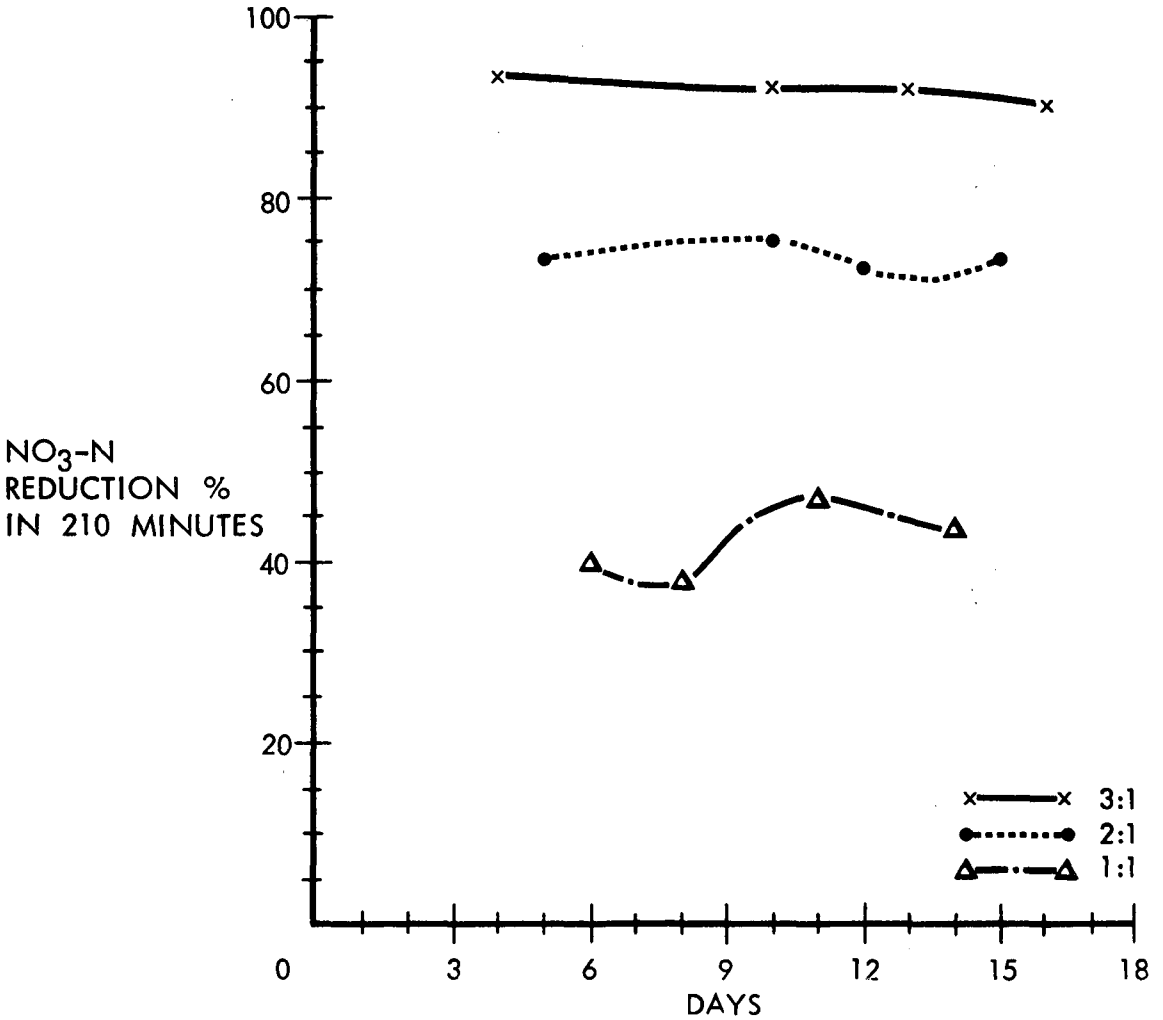

Fig. 7. DENITRIFICATION, BASED ON NO_3-N REMOVAL, IN SUSPENDED GROWTH REACTOR AS A FUNCTION OF TIME DURING ACCLIMATION TO 5°C AT VARIOUS METHANOL: NO_3-N RATIOS (WEIGHT BASIS).

Table I. Typical results from single pass experiments (15 mins.) with the packed column reactor. Those data marked with an asterisk represent percent reduction except those marked with a plus sign, under NO_2-N column, which represents an increase of the initial value.

Test #	Methanol: NO_3-N Weight Ratio	D.O. ppm	Initial Conc. (mg/l) NO_3-N	Initial Conc. (mg/l) NO_2-N	Residual Conc. (mg/l) NO_3-N	Residual Conc. (mg/l) NO_2-N	Percent Change* NO_3-N	Percent Change* NO_2-N	Overall Percent of Oxidized Nitrogen Removal
30°C									
1	1/4	2.5	11.5	0.29	6.0	0.42	48	+146	45
2	1/2	2.5	8.3	0.45	3.0	0.70	64	+157	58
3	1	2.4	8.5	0.19	1.9	0.11	78	43	77
4	2	2.4	6.0	0.02	0.6	0.00	91	100	91
5	3	2.5	8.9	0.11	0.3	0.00	97	100	97
20°C									
1	1/2	2.5	11.3	0.15	6.7	0.04	41	73	41
2	3/4	2.4	9.7	0.16	3.5	0.05	64	69	64
3	1	2.4	9.0	0.15	3.0	0.04	67	73	67
4	2	2.3	8.9	0.20	0.6	Trace	93	100	93
5	3	2.3	7.0	0.16	0.3	0.00	96	100	97
5°C									
1	1	2.5	9.9	0.27	4.9	1.06	50	+388	41
2	2	2.5	9.0	0.27	0.9	0.15	90	44	89
3	3	2.4	8.3	0.39	0.3	0.00	96	100	96

Table II. Typical data from single pass experiments (210 mins.) with the suspended growth reactor. Those data marked with an asterisk represent percent reduction except those marked with a plus sign, under NO_2-N column, which represents an increase of the initial value.

Test #	Methanol: NO_3-N Weight Ratio	D.O. ppm	Initial Conc. (mg/l) NO_3-N	Initial Conc. (mg/l) NO_2-N	Residual Conc. (mg/l) NO_3-N	Residual Conc. (mg/l) NO_2-N	Percent Change* NO_3-N	Percent Change* NO_2-N	Overall Percent of Oxidized Nitrogen Removal	Total Suspended Solids (mg/l)
30°C										
1	1/2	2.5	3.8	0.08	1.4	0.14	63	+175	60	1985
2	1	2.4	3.8	0.16	0.7	0.12	82	25	79	2016
3	2	2.6	3.0	Trace	0.3	Trace	90	100	90	1724
4	3	2.5	4.8	0.27	0.2	0.00	96	100	96	2035
20°C										
1	1/2	2.5	11.3	0.15	6.7	0.70	41	+467	36	227
2	3/4	2.4	9.7	0.16	4.7	0.26	52	+163	50	610
3	1	2.4	9.0	0.15	2.7	0.26	71	+173	68	2103
4	2	2.3	8.9	0.20	1.3	0.06	86	70	86	1997
5	3	2.3	7.0	0.16	0.6	0.00	91	100	91	2009
5°C										
1	1	2.5	9.7	0.29	5.5	1.08	43	+372	34	2050
2	2	2.4	8.3	0.39	2.3	0.61	73	+154	67	2115
3	3	2.5	8.5	0.25	0.7	0.08	91	68	91	2064

Table III. Typical data from dissolved oxygen experiments with the packed column reactor at 3 different D.O. levels (15 mins. - single pass). Those data marked with a single asterisk represent percent reduction except those marked with a plus sign, under NO_2-N column, which represents an increase of the initial value. The points marked with a double asterisk represent no change.

Test #	Methanol: NO_3-N Weight Ratio	D.O. ppm	Initial Conc. (mg/l) NO_3-N	Initial Conc. (mg/l) NO_2-N	Residual Conc. (mg/l) NO_3-N	Residual Conc. (mg/l) NO_2-N	Percent Change * NO_3-N	Percent Change * NO_2-N	Overall Percent of Oxidized Nitrogen Removal
D.O. I									
1	1/2	0.3	20.0	0.34	7.5	0.24	63	29	62
2	3/4	0.5	8.7	0.10	1.0	Trace	89	100	89
3	1	0.2	13.5	0.35	2.4	0.70	82	+200	78
4	2	0.2	15.6	0.05	0.5	0.00	97	100	97
5	3	0.5	8.6	0.16	0.3	0.00	97	100	97
6	4	0.2	18.0	0.05	0.7	0.00	96	100	96
7	6	0.4	20.0	0.05	0.3	0.00	98	100	98
D.O. II									
1	1/2	2.5	11.3	0.15	6.7	0.04	41	73	41
2	3/4	2.4	9.7	0.16	3.5	0.05	64	69	64
3	1	2.4	9.0	0.15	3.0	0.04	67	73	67
4	2	2.0	8.0	0.11	0.3	Trace	96	100	96
5	3	2.2	8.0	0.05	0.3	0.05	96	**	95
6	4	2.0	9.0	1.70	0.8	0.80	91	53	85
D.O. III									
1	1/2	5.0	15.0	0.25	7.0	0.70	53	+280	50
2	3/4	4.2	3.3	0.10	1.0	0.15	70	+150	66
3	1	4.0	17.0	0.18	5.0	0.75	71	+417	67
4	2	4.2	8.5	0.12	1.0	Trace	88	100	88
5	3	4.0	17.0	0.08	1.0	0.00	94	100	94
6	4	5.0	8.0	0.15	0.5	0.00	94	100	94

Table IV. Typical data from dissolved oxygen experiments with the suspended growth reactor at 3 different D.O. levels (210 mins. - single pass). Those data marked with a single asterisk represent percent reduction except those marked with a plus sign, under NO_2-N column, which represents an increase of the initial value. The points marked with a double asterisk represent no change.

Test #	Methanol: NO_3-N Weight Ratio	D.O. ppm	Initial Conc. (mg/l) NO_3-N	Initial Conc. (mg/l) NO_2-N	Residual Conc. (mg/l) NO_3-N	Residual Conc. (mg/l) NO_2-N	Percent Change* NO_3-N	Percent Change* NO_2-N	Overall Percent of Oxidized Nitrogen Removal
D.O. I									
1	1/2	0.3	20.0	0.34	10.4	0.46	48	+135	47
2	3/4	0.5	8.7	0.10	1.0	0.65	89	+650	81
3	1	0.2	13.5	0.28	1.0	Trace	93	100	93
4	2	0.2	13.5	0.35	1.0	0.00	93	100	93
5	3	0.5	8.6	0.16	0.6	0.08	93	50	92
D.O. II									
1	1/2	2.0	9.0	0.05	3.0	0.16	67	+320	65
2	3/4	2.0	6.7	0.14	1.7	0.09	75	36	74
3	1	1.3	10.0	0.15	2.4	0.15	76	**	75
4	2	2.0	8.0	0.11	0.7	0.28	92	+255	88
5	3	2.2	8.0	0.05	0.3	0.04	96	20	95
D.O. III									
1	1/2	5.0	15.0	0.25	8.0	0.30	47	+120	46
2	3/4	4.2	3.3	0.10	1.7	0.05	50	50	50
3	1	4.0	17.0	0.18	1.5	0.75	91	+417	87
4	2	4.3	12.0	0.65	1.0	0.05	92	92	92
5	3	4.0	17.0	0.08	2.5	0.25	85	+313	84
6	4	5.0	8.0	0.15	1.0	0.10	88	33	87

Table V. Total solids in the packed column reactor per 1668.9 cm^2 of surface area.

	A	B	
Location	Total Solids # gms per cm^2	Volatile Solids # gms per cm^2	Percent Column B is of Column A
Top	0.49	0.26	53.4
Middle	0.66	0.34	52.0
Bottom	2.99	2.18	72.8

Table VI. Typical results of individual experimental runs for dentrification in terms of total oxidized nitrogen removed with the packed column reactor (A) and the suspended growth reactor (B) at various temperatures and methanol:NO_3-N ratios. Dissolved oxygen levels were within the range indicated in Tables I and II.

Temperature	Methanol:NO_3-N Ratio	Individual Runs in % Denitrification (TONR)		
	A. Packed column reactor			
30°C	2	89.0	89.6	92.4
	3	94.1	96.2	98.8
20°C	2	93.2	95.9	
	3	95.3	96.5	
5°C	2	81.6	90.0	92.6
	3	94.7	96.6	97.5
	B. Suspended growth reactor			
30°C	2	89.7	90.0	92.1
	3	92.4	96.1	95.1
20°C	2	85.6	88.4	
	3	91.3	95.9	
5°C	2	67.6	66.2	67.2
	3	85.9	91.8	92.2

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
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Gulf South Research Institute, New Iberia, Louisiana

6 Title

METHANOL REQUIREMENT AND TEMPERATURE EFFECTS IN WASTEWATER DENITRIFICATION

10 Author(s)

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21 Note

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23 Descriptors (Starred First)

*Biological denitrification, *Wastewater treatment, *Methanol requirement, *Temperature effects, Dissolved oxygen effects, Packed column reactor, Suspended growth reactor.

25 Identifiers (Starred First)

*Water renovation, nutrient removal.

27 Abstract

A pilot-scale, denitrifying plant was built using two types of continuous-flow reactors, a packed column and a suspended growth chamber. Denitrification at three temperature regimes and three dissolved oxygen levels was studied as a function of the methanol:NO_3-N ratio. The most efficient ratio was usually found to be between 2:1 and 3:1. Effective denitrification at lower temperatures and high dissolved oxygen content required ratios equal to or slightly greater than 3:1.

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