

AD

**TECHNICAL REPORT
NATICK/TR-78/035**

FLUIDIZED BED BIODENITRIFICATION PROCESS

**Approved for public release;
distribution unlimited.**

August 1978

**UNITED STATES ARMY
NATICK RESEARCH and DEVELOPMENT COMMAND
NATICK, MASSACHUSETTS 01760**



Food Sciences Laboratory

Approved for public release; distribution unlimited.

Citation of trade names in this report does not constitute an official indorsement or approval of the use of such items.

Destroy this report when no longer needed. Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. (cont'd)

fluidized bed process can be operated continuously with stable, highly efficient nitrate removal efficiency over long time periods on simulated munitions manufacturing wastewater high in nitrate.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

PREFACE

Ability to remove high concentrations of nitrates from munition manufacturing and handling waste waters is an essential requirement for military pollution abatement systems. Information must be available concerning the capability of any specific process purporting to be suitable for such purposes. This report presents a laboratory scale evaluation of one such system.

TABLE OF CONTENTS

	<u>Page</u>
Preface	1
Table of Contents	3
List of Tables	4
Introduction	5
Materials and Methods	8
Fluidized Bed System	8
Deep Packed Column System	9
Mixed Vessel System	10
Nutrient Solution and Carbon Source	10
Nitrate Analysis	11
Results	12
Discussion and Conclusions	13
Fluidized Bed System	13
Mixed Vessel System	14
Deep Packed Column System	15
Bibliography	17

LIST OF FIGURES

	<u>Page</u>
Figure 1. Fluidized Bed System	18
Figure 2. Mixed Vessel System	19
Figure 3. Fluidized Bed Percent Reduction of Nitrate	20
Figure 4. Mixed Vessel Percent Reduction of Nitrate	21
Figure 5. Packed Bed Column Percent Reduction of Nitrate	22

FLUIDIZED BED BIODENITRIFICATION PROCESS

Introduction

Fluidized bed biodenitrification processes are similar in most technical characteristics to other biodenitrification processes such as the deep packed column or completely mixed vessel systems. All biodenitrification processes require a heterotrophic population of microorganisms capable of using nitrate as a terminal electron acceptor in the absence of molecular oxygen, a suitable nutrient to drive the metabolic processes which generate the demand for a terminal electron acceptor, and growth conditions within the range of conditions tolerated by the population of microorganisms. The way in which these requirements for biodenitrification are met by the various systems does vary. In the case of the completely mixed vessel systems the organisms are largely in suspension, held there in the form of relatively large floc particles by agitation of the liquid. A clarifier is required to retain solids in the system from which they would otherwise be lost in the overflow from the system. Other biodenitrification processes all minimize growth and activity of microorganisms in suspension by providing a supporting material upon which they can grow and carry out their nitrate reduction. The fluidized bed process has the advantages of a system containing a growth supporting medium without the disadvantages usually found in fixed matrix, columnar systems; the tendency to become plugged with growth producing high hydraulic head pressure, reduced flow, and channeling through the supporting medium. Fluidized bed columns main-

tain the growth supporting medium, usually finely divided charcoal or sand, in a state of agitation due to high upward liquid flow rate so that large particulate material can pass through the column and excess biomass is removed from the supporting material by abrasion.

Fluidized bed bionitrification processes have been known and used for several years, on at least pilot plant scale, in the treatment of nitrified domestic sewage.^{1, 2, 3} However, although both deep packed bed columns and mixed vessel systems have been evaluated on high nitrate munitions wastewater, no data were available at the inception of this study on the utility of fluidized bed columns in denitrifying very high nitrate content munitions manufacturing wastewater.^{4, 5, 6, 7, 8}

¹ Jeris, John S. 1971. High Rate Denitrification. Presentation to 44th Annual Conference of the Water Pollution Control Federation.

² Jeris, John S., and James A. Mueller. 1972. Biological Denitrification of Effluents in a Fluidized Granular Bed, Phase I. Final Report to New York State Department of Environmental Conservation.

³ Jeris, John S., and Roger W. Owens. 1975. Pilot-scale, High-rate Biological Denitrification. J. Water Poll. Control Fed. 47 (8): 2043-2057.

⁴ Gilkinson, T. H. 1971. Water Pollution Study Final Report. National Technical Information Service Report No. AD724,866.

⁵ Tucker, David O., Clifford W. Randell, and Paul H. King. 1974. Columnar Denitrification of a Munitions Manufacturing Wastewater. Presentation to 29th Annual Perdue Industrial Waste Treatment Conference, Lafayette, IN

⁶ Adams, Paul A., David S. Thorne, and John H. Whiting. 1975. Biological Denitrification of Nitrate Waste Effluents from Munitions Plants. Technical Report 4792. Picatinny Arsenal, Dover, New Jersey.

⁷ Wendt, Theodore M., and Arthur M. Kaplan. 1976. A Chemical-Biological Treatment Process for Cellulose Nitrate Disposal. J. Water Poll. Control Fed. 48 (4): 660-668.

⁸ Smith, L. L., and R. L. Dickinson. 1976. Propellant Plant Pollution Abatement Establishment of Methods for Removal of Nitrates from Munitions Plant Wastewater. Technical Report 4813. Picatinny Arsenal, Dover, New Jersey.

After this study was nearly completed, a patent was issued which demonstrated the applicability of a fluidized bed system, very much like the modified system described in this report, in denitrifying water very high in nitrate (i.e., in excess of 1000 mg/L nitrate) over short term periods.⁹

This study was conducted to determine whether a fluidized bed bio-denitrification process was suitable for long term treatment of high nitrate wastewater, simulating that found in munitions manufacturing facilities. In order to ensure that suitable conditions for denitrification were maintained for the fluidized bed process, more conventional, bench-scale mixed vessel and deep packed column systems were run under similar conditions as controls.

⁹Francis, Chester W., and Frank S. Brinkley. 1977. Biological Denitrification of High Concentrations Nitrate Waste. United States Patent No. 4,043,936 assigned to The United States of America as represented by the United States Energy Research and Development Administration, Washington, DC.

MATERIALS AND METHODS

The reaction vessel initially used in the fluidized bed system was a pyrex cylinder 62 centimeters in length and 3 centimeters in internal diameter. The column was sharply tapered at the lower, bottom end to a tubing connection 0.5 cm in internal diameter. The column was filled to approximately two-thirds its length with charcoal granules, 6 to 14 mesh size, which were retained in the column by a ceramic ball 1 cm in diameter in the bottom of the tapered section directly over the tubing connection. The ceramic ball acted as a classical ball valve, permitting upflow of liquid and suspended solids but blocking the downward flow of the column matrix upon cessation of liquid flow.

Approximately midway through the study the cylindrically shaped column was replaced by a conically shaped column with an internal diameter of 9 cm at its top, tapering gradually to a 0.5 cm internal diameter tubing connection at the bottom of its 55 cm height. As with the cylindrical column, the particulate, 6 to 14 mesh size charcoal granule contents of the conical column were retained by placing a 1 cm diameter ceramic ball just over the tubing connection. (Figure 1).

Upward liquid flow through the fluidized bed columns was obtained through the use of a Cole-Parmer Model 7545 variable speed drive with two Model 7015 tubing pump heads. A flow rate of approximately one liter/minute was required to fluidize the charcoal granules in the cylindrical column and fluidize the lower portion of the charcoal granule contents of the conical column. The large flow rate far exceeded the treatment capacities

of the fluidized bed columns, so the flow rate was maintained by recycling most of the liquid in the system with small additions of nutrient and nitrate solutions into the influent to the recycle pump by means of a second tubing pump (Cole-Parmer 10-channel Masterflex pump drive Model 7568 with Model 7015 tubing pump heads). The ten-channel tubing pump could not be operated without close supervision, so the system with this pump in place was operated continuously only eight hours a day, five days a week, and intermittently 10 to 15 minutes every two hours, overnight and on weekends. Late in the study (see Figure 3) the ten-channel pump was replaced by a Harvard apparatus pump Model 1201 which permitted continuous operation of all portions of the fluidized bed process except the recycle pump, which continued to be operated only 8 hours a day, 5 days a week.

A small square glass container 15 cm in height by 6.5 cm on each side was utilized to provide liquid for the recycle pump, to permit separation of liquid from the nitrogen gas product of denitrification, to trap any charcoal granules which may have been washed out of the column, and to permit overflow from the system to drain off (Figure 1). The tops of the fluidized bed columns were closed by rubber stoppers penetrated with glass tubing to convey column overflow via tubing to the recycle reservoir. Exposure of system contents to air was minimized to avoid suppression of bionitrification by molecular oxygen. Total volume of the fluidized bed system with the cylindrical column in place was 1700 mL and about 2100 mL with the conical column in place.

A deep packed column was run in parallel with the fluidized bed column using alternate channels of the nutrient-nitrate feed tubing pump (Figure 1).

The column was 62 cm in height and 3 cm internal diameter filled with 3 to 5 mm diameter glass beads. The column was operated in an upflow mode using the same sequences of operation as the fluidized bed column. No recycle was required for operation of the packed bed column.

The completely mixed suspended culture system was contained in an 1800 mL trypsinizing flask which was stirred by means of an air-driven magnetic stirrer (Figure 2). Overflow from the trypsinizing flask passed through a 500 mL conical-shaped sedimentation vessel from which solids were returned once daily on a five-day-a-week basis. This system of solids return was modified late in the study by addition of a 1-RPM bottom scraping device, and solids were pumped continuously by means of a Sage Instrument (Model 375 Orion Research, Inc.) tubing pump back to the trypsinizing flask at a rate slightly exceeding that required for solids recovery. Nearly all the settleable solids were recovered and returned to the reaction vessel using this modification. The completely mixed vessel system was operated using the same nutrients and simulated high nitrate wastes that were used in the fluidized bed system and the deep packed column system.

The nutrient solution used during the early phases of the study was composed of a 1.6% water solution of methanol, the carbon/energy source for denitrification most widely reported in the literature. Midway in the study the carbon/energy source material was changed to a 0.5% (volume-to-volume) solution of sweet dairy whey concentrate in water. Late in the study the carbon/energy source was changed to a 0.3% (volume-to-volume) water solution of sugar beet molasses, a sugar beet processing waste material composed of nearly 50% sucrose. The nitrate solution used in the study was

composed of 0.04-molar KNO_3 solution in water with 0.005 molar K_2HPO_4 added to provide sufficient phosphate for microbial activity.

Nitrate analyses were performed using a Corning Model 10 expanded scale pH meter with a Corning Nitrate Liquid Ion Electrode and an Orion Model 90-02 Double Junction Reference Electrode.

RESULTS

The results of nitrate analyses of influent and effluent samples from each process evaluated are presented in Figures 3, 4 and 5 as percent reduction in nitrate. In order to reduce the volume of data and day-to-day variability in readings, the data are presented as arithmetic means of percent reduction in nitrate in samples taken in consecutive seven-day periods. Each point represents the means of one to five analyses. Breaks in the lines connecting the points indicate omissions in data collection. Figure 3 presents the data collected from the fluidized bed process. Figures 4 and 5 present data collected from the completely mixed vessel system and the deep packed column system, respectively.

DISCUSSION AND CONCLUSIONS

The data for the fluidized bed column shown in Figure 3 in reality represent two different systems. The initial phases of the study were done using a tubular column with parallel sides. Initially, some success was experienced with this column operating eight hours of every twenty-four, 5 days a week with only intermittent feed of influent solution (approximately 20 minutes every four hours) at night and over weekends with no recycle except during daytime supervised operation. With increasing nitrate loading and increased flow rates after the first few weeks of operation, great instability in operation was experienced. Of particular concern was the tendency for bubbles of nitrogen to condense beneath a portion of the activated charcoal granule bed which was subsequently carried up the column into the overflow tubing which became plugged, resulting in excessive hydrostatic pressure and rupture of the tubing or failure of tubing connections. Modifications in mode of operation, feeding solutions and shape of the column midway through the study greatly minimized these problems and the fluidized bed column was successfully operated with high nitrate reducing efficiency over an extended period of time. The changes in equipment and mode of operation which made this efficient operation possible included a change to a cone-shaped column, feeding of influent solutions 24 hours a day, 7 days a week with recycle and fluidization being done continuously only during the 8-hour working day, 5 days a week, increased detention time, and change to sweet dairy whey as carbon/energy source.

After instituting the changes noted above, the performance of the fluidized bed column system was markedly improved and achieved several months of continuous operation with 99+% nitrate reduction efficiency. The only slight deviation from this high level of efficiency occurred during a one-week period during which the system was thoroughly cleaned and new tubing installed. Near the end of the study the carbon/energy source was changed from sweet dairy whey to sugar beet molasses. The nitrate reducing efficiency of the column was diminished during the period of time required by the biological system to become acclimatized to the changed nutrient composition and loading rate. Inefficient performance of the fluidized bed column was noted with every change in carbon/energy source, and a period of several days to several weeks was required to condition the system to the new nutritional regimen.

The mixed vessel system required several weeks to acclimatize to the initial conditions and nutrient levels and then showed very stable and efficient reduction of nitrate with only infrequent failures during the first half of the study. About midway in the study, the nutrient was changed from methanol to sweet dairy whey, which was very disruptive to the mixed vessel system largely due to the very slow pumping rate into that system. The slow pumping rate through very small inside diameter tubing caused problems due to the presence of solids in the sweet dairy whey and due to growth of organisms in the tubing. Both factors led to highly unstable performance and frequent loss of solids from the mixed vessel system which required several days to a week or more to overcome.

One of the deviations from efficient performance by the mixed vessel system during the first half of the study merits added comment and emphasis. The most noticeable failures of that system to perform efficiently are numbered one through five for the first half of the study. The deviations from highly efficient performance numbered 1, 2, 4, and 5 and can be readily explained by equipment failures, tubing failure or plugging, exhaustion of nitrate or nutrient leading to an imbalance and so forth. However, these causes of failure have been ruled out for the very sizeable deviation from efficient operation labeled number 3. The reduced efficiency during that period was apparently due to the addition of glycerol trinitrate to only the mixed vessel system at an influent concentration of 150 mg/L. Operation of the system during that period appeared to be normal with good growth and abundant solids being produced but with sharply reduced denitrification. After reduction of the glycerol trinitrate influent from 150 mg/L to less than 10 mg/L, nitrate reduction efficiency increased rapidly over a period of several days to the levels experienced before the glycerol trinitrate was added. Evidently, glycerol trinitrate interferes with denitrification at a concentration of 150 mg/L, which is approximately four times lower than the lowest concentration at which evidence of toxicity to microorganisms has been observed.

The deep packed column which was used was probably too small, with insufficient area on the glass bead packing to achieve efficient operation. Frequent cleaning of the column was required to avoid excessive hydraulic head pressures across the column, and the efficiency of the column was only good during operation immediately prior to cleaning.

After cleaning, efficiency was diminished until substantial growth had developed on the beads which permitted more efficient reduction of nitrate, but again generated a requirement for cleaning.

Based on this study the following conclusions can be drawn:

1. The fluidized bed bionitrification process can be operated efficiently over long periods of time on high nitrate, simulated munitions manufacturing wastewater.

2. The fluidized bed column bionitrification process has substantial advantages over other column systems which have been studied at pilot scale on munitions manufacturing wastewater. The fluidized bed process should be strongly considered for pilot scale study on high nitrate munitions manufacturing wastewater.

3. The mixed vessel system and the fluidized bed system recovered very rapidly and completely from two or three fold shock loading with nitrate or nutrient solutions.

4. The deep packed bed column used was not suitable for the concentrations of nitrate and the operating procedures used in this study, and therefore little useful information could be gained from the data gathered with that system.

Bibliography

- Adams, Paul A., David S. Thorne, and John H. Whiting. 1975. Biological Denitrification of Nitrate Waste Effluents from Munitions Plants. Technical Report 4792. Picatinny Arsenal, Dover, New Jersey.
- Francis, Chester W., and Frank S. Brinkley. 1977. Biological Denitrification of High Concentration Nitrate Waste. United States Patent No. 4,043,936 assigned to The United States of America as represented by United States Energy Research and Development Administration, Washington, DC.
- Gilkinson, T. H. 1971. Water Pollution Study Final Report. National Technical Information Service Report No. AD724,866.
- Jeris, John S. 1971. High Rate Denitrification. Presentation to 44th Annual Conference of the Water Pollution Control Federation.
- Jeris, John S., and James A. Mueller. 1972. Biological Denitrification of Effluents in a Fluidized Granular Bed, Phase I. Final Report to New York State Department of Environmental Conservation.
- Jeris, John S., and Roger W. Owens. 1975. Pilot-scale, High-rate Biological Denitrification. J. Water Pollution Control Federation. 47 (8): 2043-2057.
- Smith L. L., and R. L. Dickinson. 1976. Propellant Plant Pollution Abatement Establishment of Methods for Removal of Nitrates from Munitions Plant Wastewater. Technical Report 4913. Picatinny Arsenal, Dover, New Jersey.
- Tucker, David O., Clifford W. Randell, and Paul H. King. 1974. Columnar Denitrification of a Munitions Manufacturing Wastewater. Presentation to 29th Annual Perdue Industrial Waste Treatment Conference, Lafayette, Ind.
- Wendt, Theodore M., and Arthur M. Kaplan. 1976. A Chemical-Biological Treatment Process for Cellulose Nitrate Disposal. J. Water Pollution Control Federation. 48 (4): 660-668.

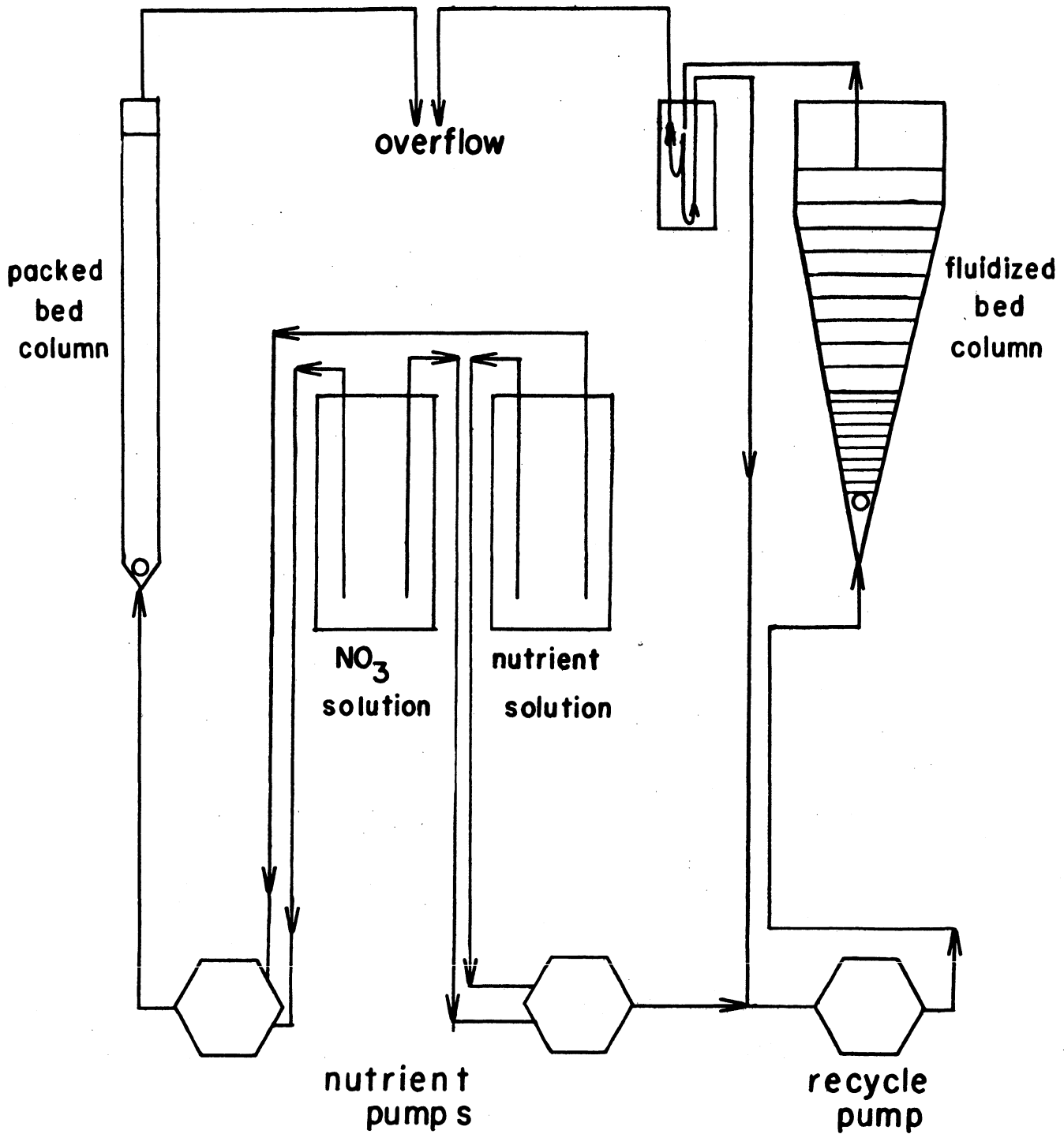


FIGURE I. FLUIDIZED BED SYSTEM

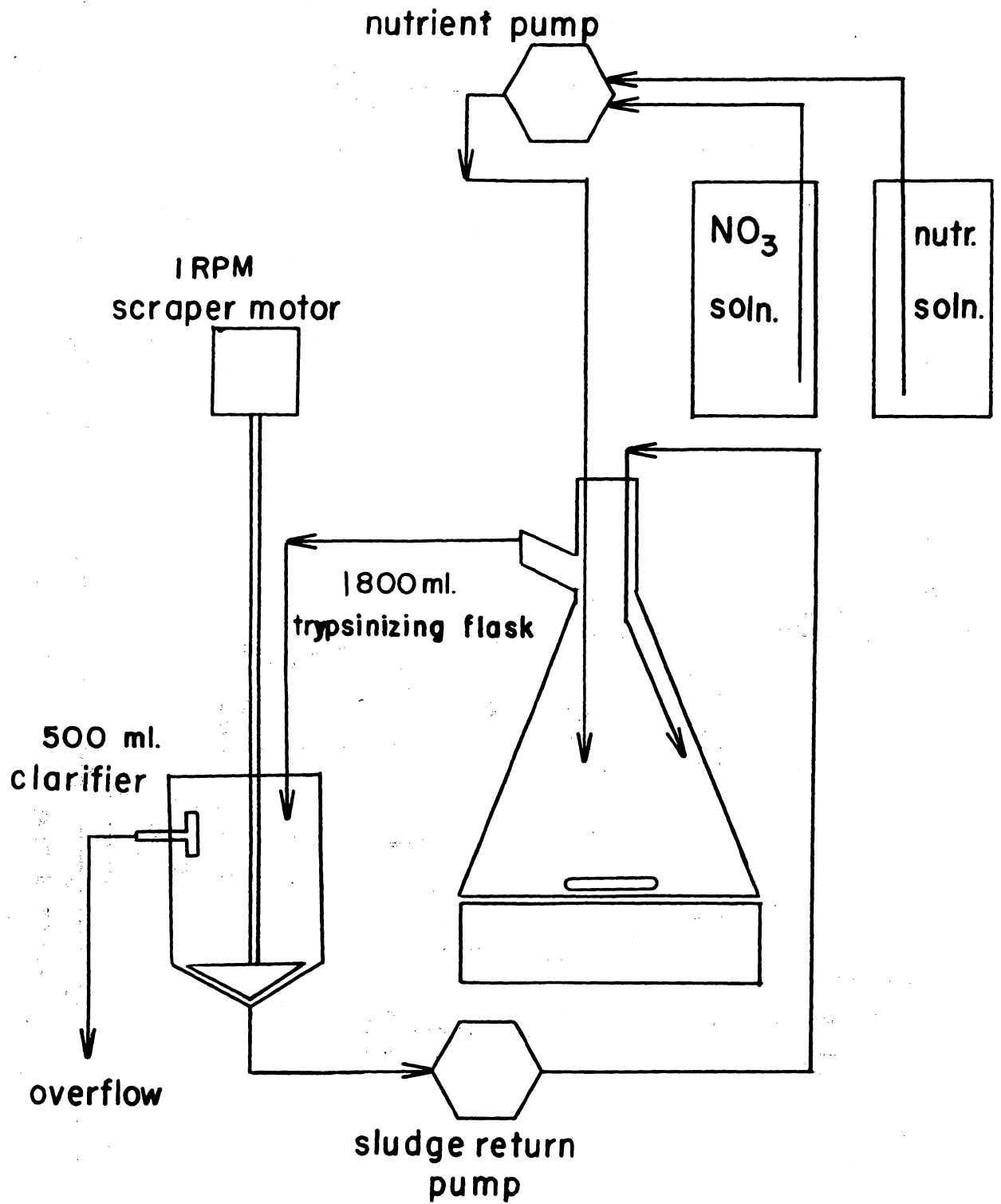


FIGURE 2. MIXED VESSEL SYSTEM

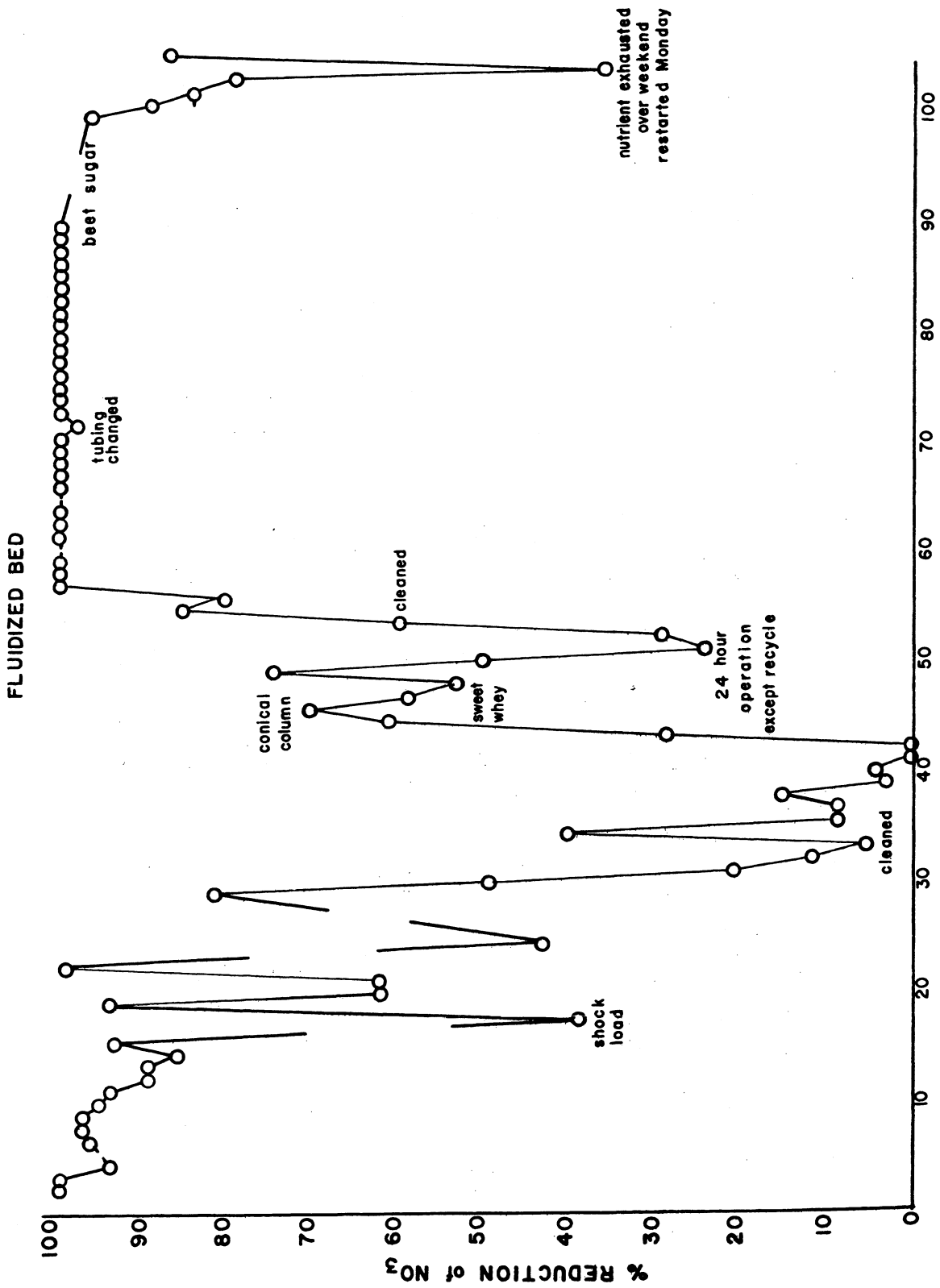


FIGURE 3 TIME IN CONSECUTIVE SEVEN DAY PERIODS

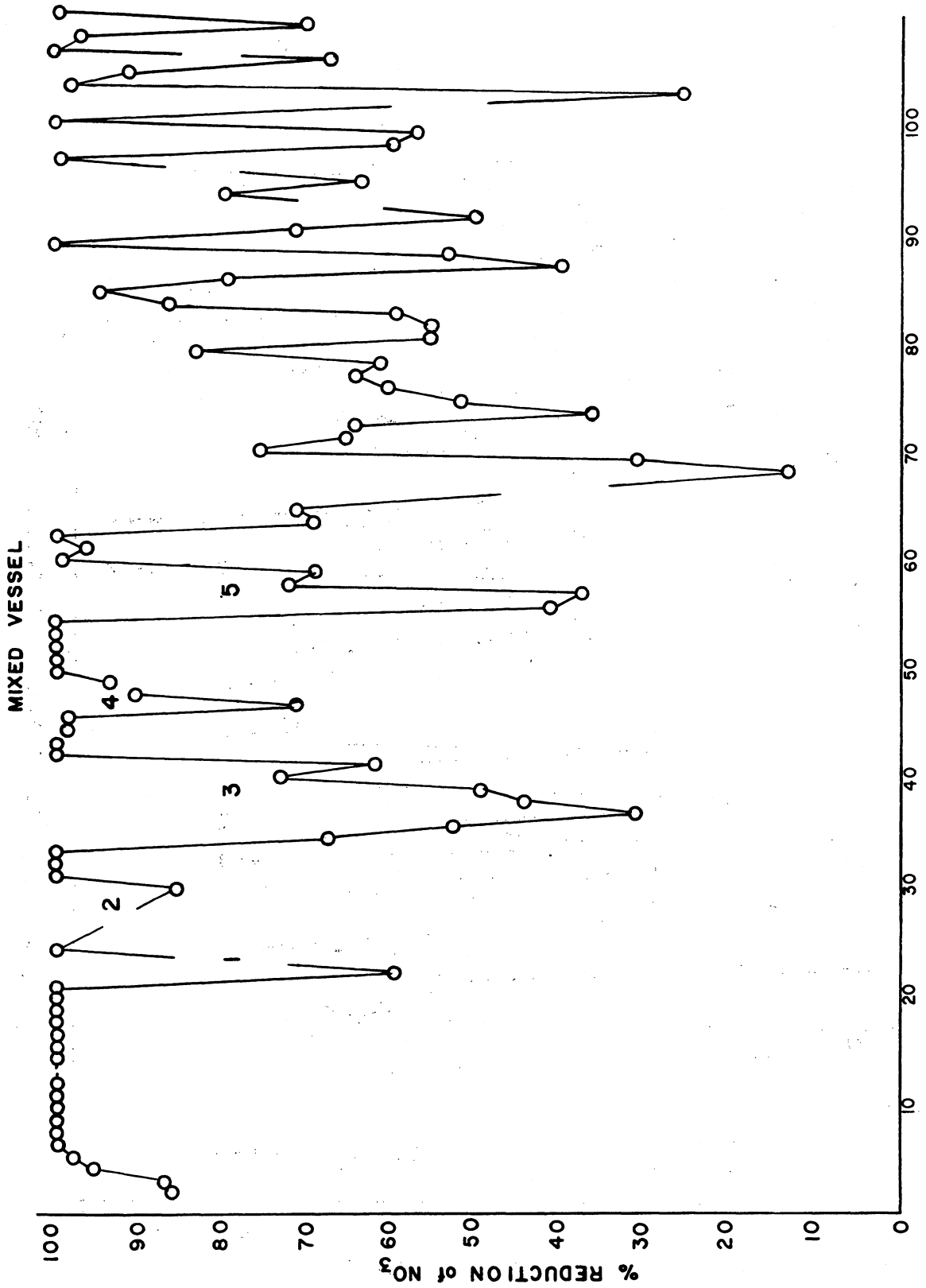


FIGURE 4 TIME IN CONSECUTIVE SEVEN DAY PERIODS

PACKED BED COLUMN

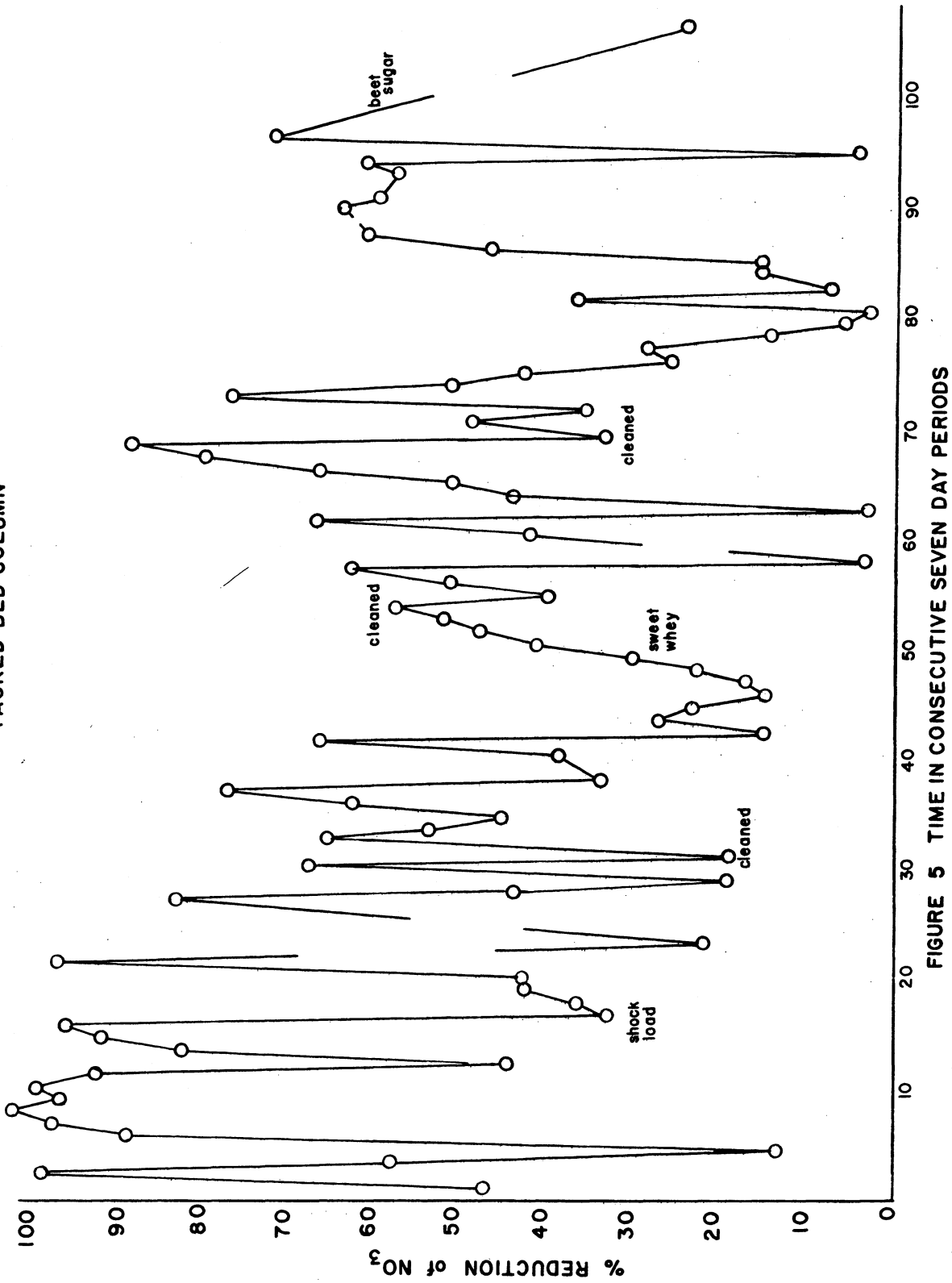


FIGURE 5 TIME IN CONSECUTIVE SEVEN DAY PERIODS

