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FOR

INVESTIGATION OF BIOCHEMICAL STABILIZATION OF AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS BY UNSATURATED FLOW THROUGH POROUS MEDIA

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INVESTIGATION OF BIOCHEMICAL STABILIZATION OF AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS BY UNSATURATED FLOW THROUGH POROUS MEDIA

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Authorization

This investigation was originally authorized by the Director, Office of Grants and Research Contracts, Office of Space Science and Applications, NASA on 28 April 1965 for a period of one year. The grant was supplemented and the authorization extended through a second year in a letter from the Acting Director, OGRC, OSSA, NASA on 10 March 1966. In the original application and subsequent reapplication for this project grant, it was anticipated that the planned investigation would require about three years; but further extension beyond April 1968 may be desirable.

Background and Rationale

In manned space flights of long duration it will be necessary to purify and reutilize urine and other wastewaters. Many purification processes involving physical, chemical, and electrolytic phenomena have been investigated by various contractors and several such processes show promise. In view of the fact that 65 to 70 percent of the solids in human urine are organic (primarily urea) it would appear logical to utilize an aerobic biological process to stabilize organic waste waters prior to demineralization by a physical or chemical technique.

One aerobic biological treatment system that has not been investigated for space vehicles is intermittent two-phase filtration through fine porous media. This process offers certain inherent advantages in a zero-gravity environment. Although intermittent filtration through sand is known to be an effective treatment for municipal waste waters, its ability to produce a stabilized effluent from urine and other liquid wastes in space vehicles remains to be evaluated.

Objectives

It is the broad intent of this project to study and evaluate many of the parameters associated with the intermittent aerobic filtration of aqueous solutions of organic compounds, especially the major constituents of urine, in flow through unsaturated porous media. These parameters include hydraulic and organic loading rates, the extent of biodegradation, analyses of breakdown products in the effluent, characteristics of the porous media, oxygen or air requirements, and the production of carbon dioxide.

Brief Summaries of Prevous Status Reports

The first report, covering the period from 15 May 1965 to 15 November 1965, described the design and construction of 20 sand columns, dosing devices, air-flow circulation and measurement, and effluent collection apparatus. It also presented results on some preliminary analyses of urine and estimates of total oxygen reuqirements.

The second status report for the period from 15 November 1965 to 15 April 1966 consisted primarily of a paper presented by Dr. H. G. Schwartz, Jr. at a conference at the Ames Research Center on 14 and 15 April 1966. Dr. Schwartz described the progress during the entire first year and presented a rational approach to further investigation. Most of the period covered by the second status report was devoted to ripening the columns with settled municipal sewage in an attempt to develop stable growths of nitrifying organisms in the porous media. It was demonstrated that well-ripened columns could convert almost all of the Kjeldahl nitrogen in sewage to stabilized nitrates in the effluent. This period was also used to resolve several difficulties arising with the uniform flow of air through the columns.

Personnel

This project is being conducted under the direction of Dr. J. E. McKee, Professor of Environmental Health Engineering. He was assisted initially by Mr. Albert B. Pincince, a Ph.D. candidate, and later by Dr. H. G. Schwartz, Jr., a post-doctoral Research Fellow, both of whom received support from a USPHS Training Grant. Mr. Pincince's involvement with the main project has diminished in the past year as he has concentrated on a specialized facet of intermittent sand filtration, viz oxygen transfer mechanisms and rates. His doctoral research, however, continues to have a direct bearing on the main project and close rapport is maintained with his work.

Dr. Schwartz devoted almost full time to this project between 1 November 1965 and 9 September 1966 when he left to accept a position with the firm of Sverdrup and Parcel in St. Louis. Dr. Maria Puerta was employed on 13 September 1966 to replace Dr. Schwartz. She came to Caltech with very fine credentials including a B.S. degree in chemical engineering from the Antioquia University of Medellin, Columbia (1951) and a doctorate in soil science from the Technological University of Berlin (1965) where she had conducted research on the percolation of municipal

sewage in the irrigated fields of Berlin. Unfortunately it became necessary to terminate her services on 7 October 1966 because of language difficulties, lack of familiarity with modern instrumentation, and emotional instability.

Shortly thereafter, Mr. Jack R. Livingston was employed as project engineer. A chemical engineering graduate of Brigham Young University, Mr. Livingston has had about six years of research experience with Rocketdyne Corporation on processes for demineralization by freezing. He has rapidly grasped the objectives, procedures, and spirit of this project and will undoubtedly make many fine contributions to its successful continuation.

As indicated in the last status report, Mr. Don Markewich replaced Mr. Jesse Watt as analytical technician on the project in March 1966. Mr. Markewich has a B.S. degree in soil science from California Polytechnic College and several years of experience with agricultural agencies in relation to the chemistry and biology of soils.

Progress During Past Half Year

As indicated in the second status report, 14 columns of 0.56-mm sand were being ripened with settled municipal sewage in order to develop cultures of bacteria capable of stabilizing ammonia to nitrates. Two additional columns containing 0.12-mm sand were also being ripened; but experience has shown that such fine sand is not suitable for intermittent application of settled sewage or urine. Ripening action and modifications in the air flow through the columns continued through most of July 1966.

On 28 July 1966, columns 1-6 incl., 8, 9, 14, and 15 were placed on a urine feed, with concentrations as follows:--

Columns 1 & 2	-------	full-strength urine			
Columns 3 & 4	-------	50% urine,	50%	distilled	water
Columns 5 & 6	-------	20% "	80%	"	"
Columns 8 & 9	-------	10% "	90%	"	"
Columns 14 & 15	-----	5% "	95%	"	"

Natural urine from up to nine donors is collected regularly, frozen, thawed and blended when 4 to 5 gallons have been collected, then placed in liter plastic bottles and refrozen. One liter is thawed and used each day for dosing all ten columns. Each column receives 100-150 ml per day (or 34-52 cm per day) of the stated dilution. The hydraulic dosing system consists of a constant-head supply bottle feeding through a solenoid hydraulic valve controlled by a time switch, which is engaged 12 times each day for a period of about two seconds. During this brief interval about 12.5 ml of feed water are dosed to a column. All percolate is collected and measured. All air passing through each column is also collected and measured. A schematic diagram of this apparatus was presented in the second status report.

The raw urine and the percolate from all 10 columns are being assayed for chemical oxygen demand (COD), Kjeldahl nitrogen, nitrates, nitrites, urea, creatinine, chlorides, and pH. Some difficulty has been experienced in getting reliable results for some of these tests, owing to

various interferences in concentrated solutions. The results to date do not appear to demonstrate proper nitrogen balances. Indeed, losses of ammonia to the atmosphere may be significant. The accuracies of these tests are currently being subjected to close scrutiny by Mr. Livingston.

It had been anticipated that the sewage-ripened columns would be capable of converting most of the organic nitrogenous compounds in urine to stabilized nitrates, after a reasonable period of acclimatization to the urine feed. Such has not been the case to date, however. The columns at all dilutions have been almost 100 percent effective in destroying both urine and creatinine, but the end product has been ammonia rather than nitrates.

As the first step in its biodegradation, urea is hydrolyzed to carbon dioxide and ammonia, thus

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$$

also

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$$

and

$$2NH_3 + 2H_2O \rightarrow 2NH_4^+ + 2OH^-$$

These processes do not require atmospheric or dissolved oxygen. Furthermore, they raise the pH value (producing two hydroxyl ions for every hydrogen ion) and they provide a large buffering capacity related to the dissociation constants for bicarbonates and ammonium hydroxide.

In results to date, the pH value of the urine feed has varied from 5.9 to 6.3; whereas the pH value of the percolate has ranged from 8.5 to 9.3, with most values about 8.8. Since urea is seldom present in the percolate and the pH value has risen, it is evident that conversion of urea to ammonium and bicarbonate ions is essentially completed in the columns.

With an abundance of nitrifying organisms in the ripened columns, it had been anticipated that most of the ammonium ions would be converted to nitrates, as shown below, at least for the more-diluted feed waters:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

This process requires dissolved oxygen from atmospheric sources and it causes a drop in the pH value. Every mole of minus-three nitrogen (e.g. ammonia) requires two moles of oxygen; and 14 mg/l of nitrogen utilizes 64 mg/l of oxygen for this stabilization. In the total conversion of one mole of urea to bicarbonates and nitrates, approximately five hydrogen ions and only three hydroxyl ions are produced (depending on the final pH value) and

hence one might expect a well-nitrified percolate to have a pH value even lower than that of the feed water. In the results to date, however, there has been no evidence of pH drop or nitrification, even with the most-diluted feed water.

The Kjeldahl nitrogen for the undiluted urine used in the project averages about 10,000 mg/l as N. If 150 ml are applied daily to a column, the total nitrogen dose is 1,500 mg and the total oxygen requirement for complete nitrification is $\frac{64}{14} \times 1500 = 6850$ mg. This weight is equivalent to $6850 \times \frac{22.4}{32.0} = 4,800$ ml of pure oxygen at STP. If air is used as the source of oxygen, approximately 24,000 ml of air would be required. For a 10-percent urine dilution, approximately 2,400 ml of air will be needed.

In the experiments to date, however, only about 4,000 ml of air per day have been passed through each column. Based on the availability of oxygen alone, this volume of air should suffice for complete nitrification in the 5-percent and 10-percent urine columns. Furthermore, it should provide for 83.3 percent stabilization in the 20-percent urine column, 33.3 percent stabilization at the 1:1 dilution, and 16.7 percent stabilization for the undiluted urine. Yet, there has been no evidence of oxidation of Kjeldahl nitrogen to nitrates or nitrites even in the most-diluted columns. It is evident, therefore, that insufficient oxygen is not the sole reason for ineffective nitrification. It is possible that the proper cultures are not present but that they might develop in sufficient time. For that reason, the present dosing routine will be continued, at least for a few more months.

Future Developments

If it becomes evident that nitrification will not occur, even for the most-diluted feedwaters, we propose to modify the air flow through all columns to provide a great excess of available oxygen. Prior experiments with pure oxygen (see second status report) indicated that nitrifying bacteria did not perform well in pure oxygen tensions, but it may even be advisable to repeat this experiment.

In view of the difficulties being experienced in stabilization of a substance as complex as natural urine, and in light of complications of interfering substances in analyses, consideration is being given to work with a synthetic urine comprising known concentrations of the principal mineral salts plus pure urea and a carbon source such as glucose. Synthetic urine will simplify the analytical procedures and perhaps lead to better nitrogen balances through the system. Consideration is also being given to seeding the columns artificially with cultures of known nitrifying bacteria.