ADVANCED BIOLOGICAL TREATMENT OF AQUEOUS EFFLUENT FROM THE NUCLEAR FUEL CYCLE*

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INTRODUCTION

Many of the processing steps in the nuclear fuel cycle generate aqueous effluent streams bearing contaminants that can, because of their chemical or radiological properties, pose an environmental hazard. Concentration of such contaminants must be reduced to acceptable levels before the streams can be discharged to the environment. Two classes of contaminants, nitrates and heavy metals, are addressed in this study. Specific techniques aimed at the removal of nitrates and radioactive heavy metals by biological processes are being developed, tested, and demonstrated. Although cost comparisons between biological processes and current treatment methods will be presented, these comparisons may be misleading because biological processes yield environmentally better end results which are difficult to price.

Sources of Nitrates and Heavy Metals

It has been estimated that up to 2.5 million tons of dissolved nitrogen-bearing substances reach the surface waters of the U.S. each year.[1] The nitrogen waste discharged directly from industrial installations is estimated to be about 20% of the total.[2] Much of this nitrogen pollution is in the form of dissolved nitrates at high concentrations. These high concentrations can contribute to eutrophication[3] and can also constitute a health hazard.[4] Consequently, rigorous standards are being estalished for nitrates released in industrial effluents (e.g., the Department of Energy's Y-12 Plant at Oak Ridge, Tennessee is restricted to 45 g/m^3 as N), and there are indications that these restrictions will become even more stringent, perhaps as low as 10 to 15 g/m^3 as N in most states. Although the majority of industrial nitrate pollution is attributed to fertilizer and paper manufacturers, liquid effluents from the nuclear fuel cycle contribute significantly to the total problem. Process steps in the uranium fuel cycle that generate nitrate wastes including milling, refining and conversion, enrichment, fuel fabrication, and fuel reprocessing operations. Disposition of the nitrate (recovery, conversion, or discharge) will be governed by the economics of the process technologies which may be applied. In situations where nitrate recovery is not feasible, conversion of all nitrogen oxides, including NO_x to molecular nitrogen (chemically or biochemically), appears to be the only acceptable long-range solution.

Many operations in Department of Energy (DOE) and commercial nuclear processing facilities also generate aqueous waste streams which contain trace quantities of dissolved heavy metals, including radionuclides. There are a number of physical and/or chemical methods for isolating heavy metals from aqueous streams such as chemical precipitation, chemical oxidation or reduction, ion exchange, filtration or ultrafiltration, electrochemical treatment, and evaporative recovery.

However, when the initial heavy-metal concentration is in the range of 10 to 100 g/m^3 and a reduction to less than 1 g/m^3 must be achieved, these methods may be ineffective or uneconomic. In such situations, the adsorption of dissolved metal species by microorganisms often offers a safe and economical means of achieving a reduction in dissolved metal concentration to less than 1 g/m^3.

Regulations

Industrial liquid waste discharges are controlled by the U.S. Environmental Protection Agency (EPA), state water quality boards, and, occasionally, local regulations. The EPA issues effluent discharge permits under the National Pollutant Discharge Elimination System (NPDES). The NPDES permit authorizes a plant to discharge into a specified waterway from a set number of outfalls. Usually, the permit also sets limits on specific effluent parameters [e.g., flow rate, maximum biological oxygen demand (BOD), minimum dissolved oxygen, temperature ranges]. Sampling and analysis frequency are usually specified, and wastewater components such as BOD may be limited in concentration, in total mass discharged per day, or both. The NPDES permit is usually issued for a period of 5 years.

At present, no nationwide standards exist for limiting nitrate in wastewater. There are indirect limits on excessive nitrate discharges, such as one regulation which states "Other pollutants shall not be added to the water in quantities that may be detrimental to public health or impair the usefulness of the water as a source of domestic water supply."[5] The state of New York considers 10 mg/ℓ of nitrate to be the upper limit for potable water.[6] There are, however, few limits on the amount or concentration of nitrates actually leaving plant outfalls. It is expected that some limits will be uniformly imposed by 1983, but the anticipated levels are not known at this time.

At present, the discharges of heavy metals are more tightly controlled than those of nitrates. Several nuclear facilities have metals limits in their NPDES or state permits, but the exact limits vary from state to state. In fact, limits will vary between plants within a state, and even between different outfalls of the same plant, depending on location, receiving water, other pollutants discharged, etc. Occasionally, a state will require reporting of certain metal concentration levels even though it has no actual limit set in the permit. Some common elements mentioned in permits include iron, chromium, nickel, copper, zinc, mercury, cadmium, aluminum, and radionuclides such as uranium, plutonium, and radium. It is likely that limits on heavy metals in general will become more stringent by 1983.

Current Treatment Processes for Nitrate Disposal

Methods of nitrate disposal currently in use at NFC plants include storage in lagoons and discharge after dilution. Other methods include calcination and catalytic decomposition of NO_x to N_2, recycle, ion exchange, production of fertilizer, and biological denitrification.

Current Treatment Processes for Heavy Metals

Presently, the most common methods for treating wastewater to remove radio-nuclides and nonradioactive heavy metals involve some combination of settling,

storing in lagoons and outright dumping. In some cases, ion exchange or evaporation is used.

One accepted method for treating dissolved metals in wastewater consists of precipitati and settling. Generally, lime is added to increase the pH of the liquid and precipitate the metals. Settling, sometimes with flocculation, clarifies the liquid and produces a sludge containing most of the metal. The pH of the supernate is then lowered again to a permissible level by adding an acid, such as sulfuric acid. Disadvantages of this method are that a bulky sludge is produced (requiring further handling and disposal), other chemicals are added to the water, and the metal concentrations are not reduced to the low levels that are required (<1 g/m^3).

In many cases, where an effluent is considered to be too difficult or too radioactive to treat, it is simply stored in lagoons or ponds for indefinite periods. This is especially true of uranium mill tailings and tailing leach effluents, and of wastes from conversion plants that use nitric acid solvent extraction processes. Disadvantages of lagoons are the continuing need for more lagoon construction, storage rather than elimination of the waste, and possibilities of seepage from the lagoon.

Ion exchange is sometimes used to remove metals from wastewater. The disadvantages of ion exchange are regeneration (or disposal of resin if regeneration is not done) and the addition of another ion, usually chloride, to the water. Evaporation is used to concentrate waste liquids in certain cases, but evaporators are expensive and use a large amount of heat energy.

Another processing method that may be considered is the sorption or complexation or dissolved metal species by microorganisms:

$$M_{dissolved} + cells \rightarrow (M \cdot cells)_{insoluble\ complex}.$$
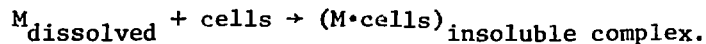
ADVANCED BIOLOGICAL TREATMENT

High-rate, biological denitrification has been experimentally demonstrated using engineering-scale fluidized-bed systems treating authentic nitrate wastes from the nuclear fuel cycle. Biological removal and concentration of heavy metals have been verified in bench-scale equipment, both batchwise and in continuous contactors.

Denitrification

Biological denitrification, as referred to in this paper, is the biological reduction of nitrate or nitrite to gaseous molecular nitrogen.[8] It commonly takes place in soil under anaerobic conditions by the various strains of facultative anaerobic bacteria which are responsible for recycling nitrogen compounds back to the atmospheric molecular nitrogen pool.[9] The reaction requires a carbon source, which has been successfully supplied in the form of various alcohols and acetates. The rate of denitrification is dependent on the type of carbon substrate supplied as well as on other operating parameters such as the pH and temperature of the system. With ethanol as the carbon source, the reaction may be written in unbalanced form as:

$$3NO_3^- + 2C_2H_5OH \rightarrow CO_2 + N_2 + H_2O + OH^- + X\ C_5H_7O_2N.$$
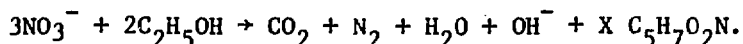
The chemical equation coefficients on nitrate and ethanol reflect the observation that the molar ratio of carbon consumed to nitrogen (as nitrate) reacted is about 1.3 to 1.5. The composition of the biomass may be given approximately as $C_5H_7O_2N$. The biomass yield is roughly 0.1 g per gram of nitrate consumed.

At the Oak Ridge National Laboratory, high-rate denitrification processes are being developed which utilize denitrifying bacteria adhering to particles of anthracite coal or sand. The particles, with adhering bacteria, are fluidized by flow of the aqueous stream being treated as it passes upward through a columnar bioreactor.[10] Two column geometries have been studied: tapered (inverted, truncated cone) and cylindrical (with a tapered top section). The tapered geometry permits operation over a wider range of flow rates than with a cylindrical geometry.

One of the fluidized-bed bioreactors tested is shown in Fig. 1. The reactor consists of a 51-mm-diam by 3.7-m-long cylindrical section beneath a tapered 51-mm to 76-mm-diam by 0.6-m-long solids disengaging zone. Sampling ports were located at 0.6-m intervals. With a sufficient population of denitrifying bacteria established, a fluidized-bed performance was evaluated using both ammonium nitrate and raffinate waste as feed and ethanol as the carbon source. The feed carbon/nitrate-nitrogen ratio (C/N) was maintained between 1.8 and 2.0. Typically, the carbon utilized was 1.2 times the nitrogen converted. A typical set of concentration profiles for nitrate, nitrite, and carbon (as ethanol) is shown in Fig. 2.

The reactor volumes (empty) of fluidized-bed systems studied ranged from 2 to 240 liters. Feed nitrate concentrations ranging from 100 to 7500 g/m^3 were treated, Achieving denitrification rates as high as 75 kg/day-m^3. Effluent concentrations of less than 1 g/m^3 were demonstrated. These results are summarized by the curve in Fig. 3.

Heavy-Metal Removal

Since the literature is replete with examples of metal uptake from aqueous solution by microorganisms, six microbial strains were surveyed to determine whether significant differences existed between species with regard to uranium isolation. The survey showed that species differences were quite pronounced (Table 1), and three cultures were selected for more detailed study. Pure strains of *Saccharomyces cerevisiae* (a yeast), *Pseudomonas aeruginosa* (a bacterium), and the mixed culture of denitrifying bacteria were tested to determine the effects of initial uranium concentration, hydrogen ion concentration, and temperature on the rate of uranium accumulation by cells in a single, well-mixed contacting stage. All three parameters affected the rate of uranium accumulation but had little effect on the equilibrium distribution coefficient in the range of parameter values studied. For a given set of conditions, the rate was strongly influenced by species differences (Fig. 4). For all three cultures, uranium accumulation by washed, resuspended cells was rapid and a high degree of uranium removal from solution was achieved. As an example, a cell concentration of 1900 g/m^3 (dry basis) succeeded in reducing the soluble uranium concentration from 10 g/m^3 to 0.5 g/m^3 in a 60-min contact, yielding distribution coefficients of approximately 17,000.
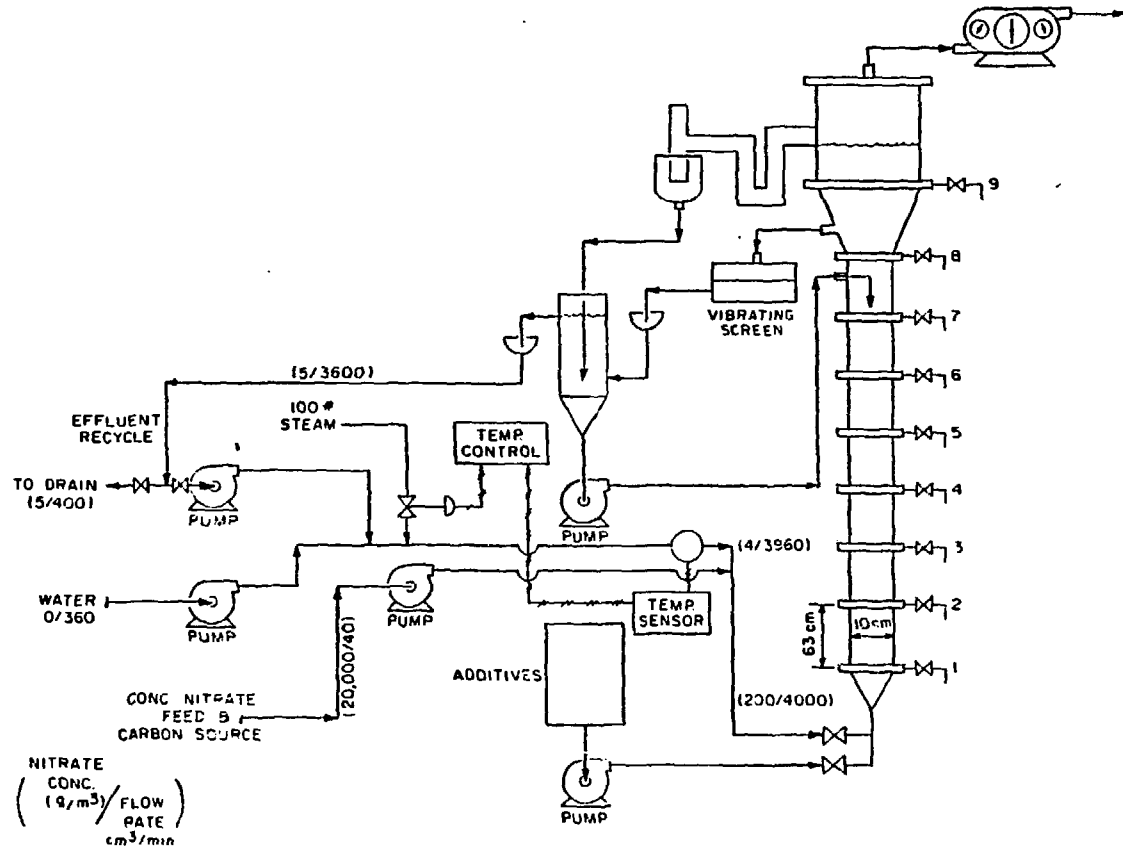
Fig. 3. Fluidized-bed bioreactor.
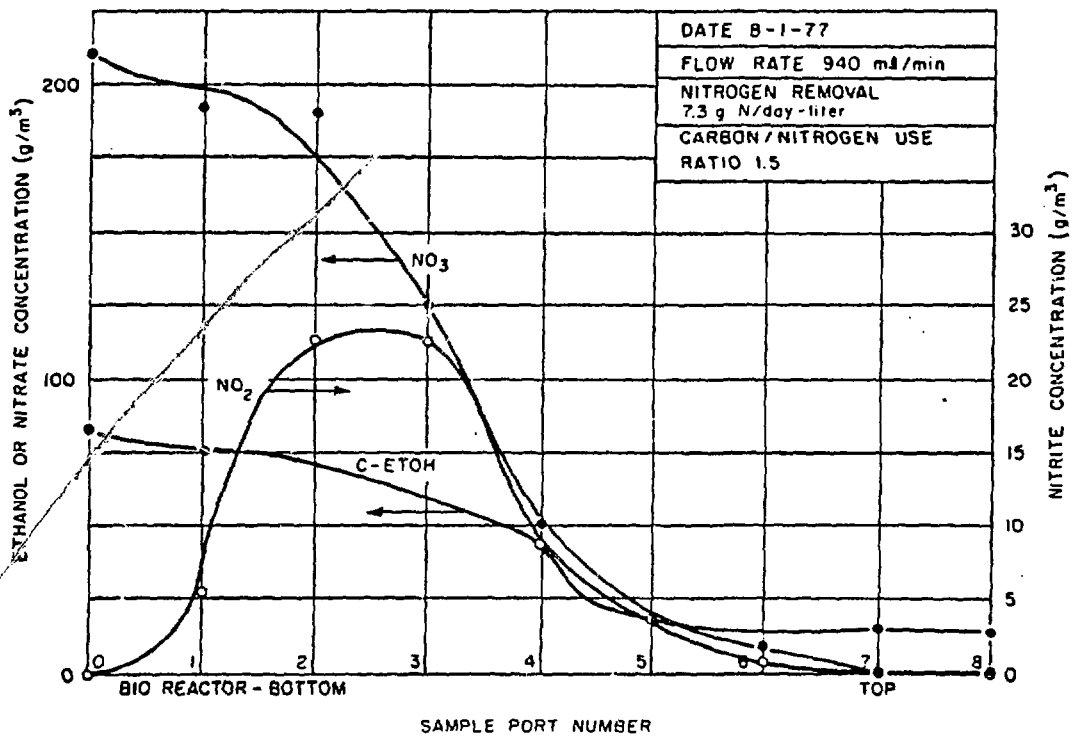
ORNL-DWG 77-1890R2

Fig. 4. Concentration profiles of nitrate, nitrite, and carbon (as ethanol).
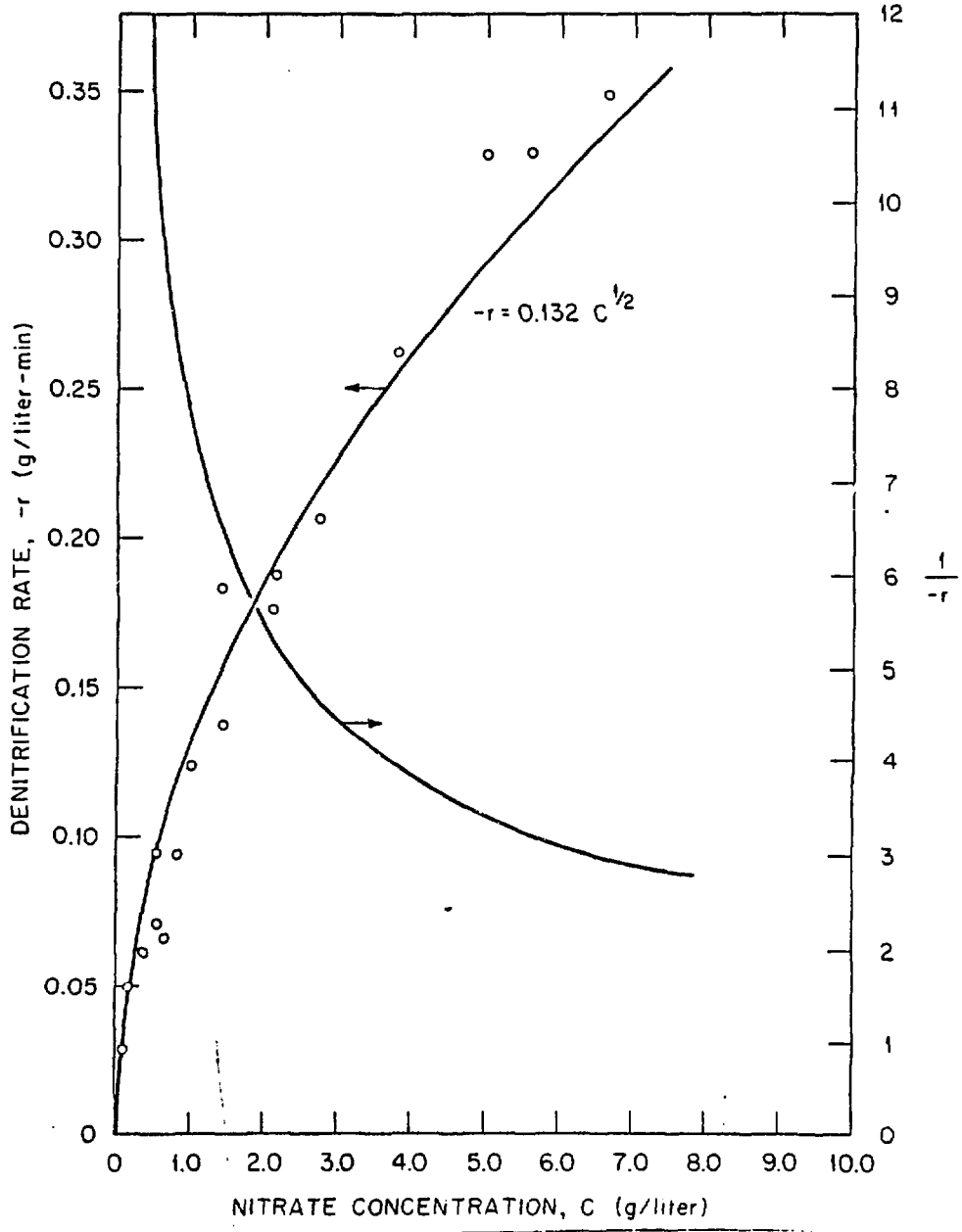
Fig. 3. Denitrification rate as a function of nitrate concentration.

Table 1. Isolation of uranium from solution by microorganisms
during resuspended contact. Initial uranium concentration
was 20 mg/liter. Temperature was 25°C.

Microorganism	Removal (%)	Cell concentration (dry basis) (g/liter)	Metal distribution[a] coefficient
Pseudomonas aeruginosa (Bacterium)	92	1.2	9,600
Zoogloea remigera (Bacterium)	72	1.0	2,730
Paecilomyces marquandii (Fungus)	94	1.2	13,100
Penicillium chrysogenum (Fungus)	97	3.1	10,300
Ashbya gossypii (Yeast)	73	7.0	390
Saccharomyces cerevisiae (Yeast)	95	1.3	15,000

[a]Metal distribution coefficient = $\dfrac{\text{g metal/g cells (dry)}}{\text{g metal/g solvent}}$.
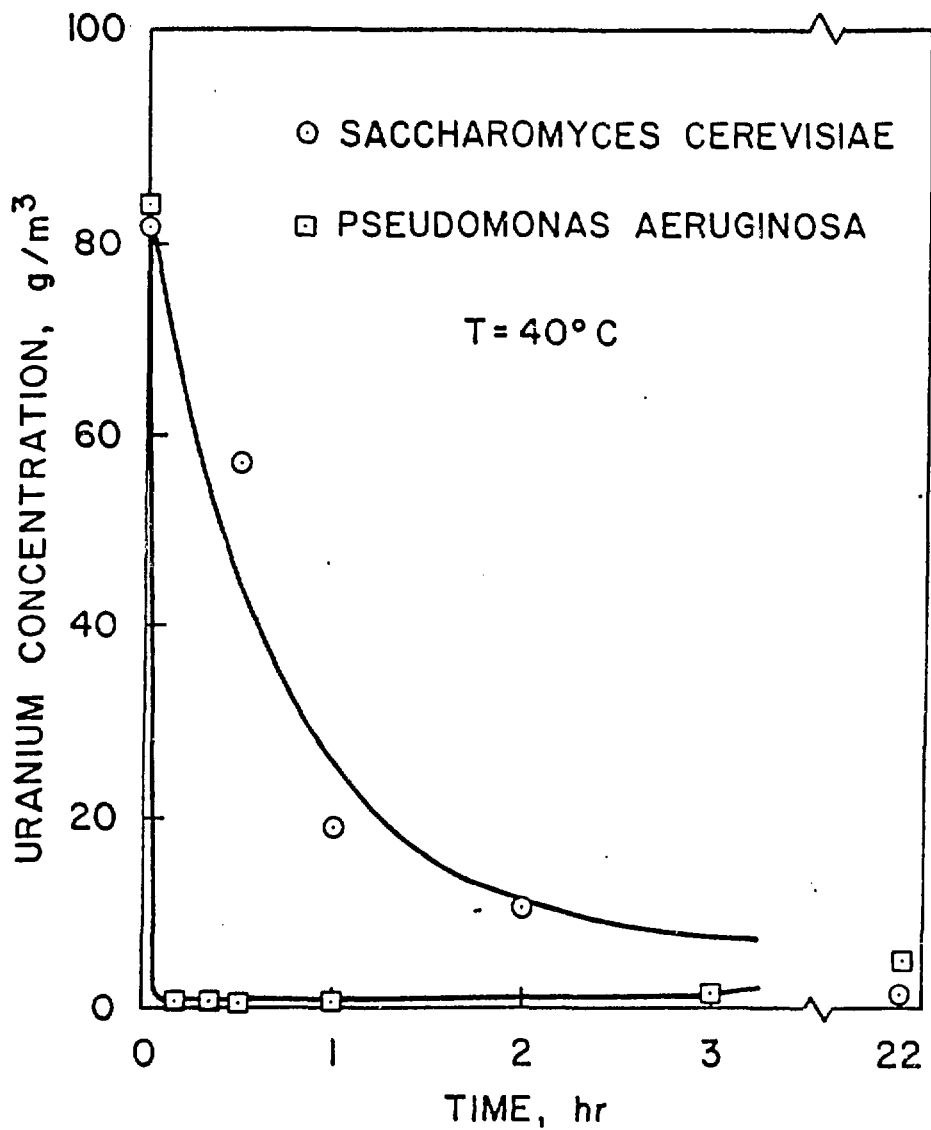
ORNL DWG 78-578

Fig. 4. Removal of uranium from aqueous solution by washed resus-
pended cells of Saccharomyces cerevisiae and Pseudomonas aeruginosa.

The denitrifying bacteria were then tested for effectiveness in removing uranium from a solvent extraction raffinate waste solution obtained from the Goodyear Atomic Gaseous Diffusion Plant in Portsmouth, Ohio. Adjustment of the solution pH to 4 followed by cell contact and centrifugation lowered the uranium concentration from 4 g/m^3 to < 0.02 g/m^3. Adjustment of pH to 8 resulted in reduction of other metals of interest (aluminum, iron, copper, chromium) to low solution concentrations (e.g., iron from 7340 g/m^3 to 2 g/m^3). Similar results were obtained with the raffinate waste supplemented with uranium for an initial soluble concentration of 100 g/m^3. On the basis of this information, a preliminary processing strategy was developed for aqueous waste streams which contain both nitrate and dissolved heavy metals (e.g., uranium). The conceptual process design consists of two primary unit operations--a bioreactor (which generates a "biosorbent" as a by-product of the nitrate conversion reaction), and a contactor (for removal of dissolved heavy metals by the "biosorbent"). The "biosorbent," excess cells from the denitrification bioreactor, is cycled to the contactor located upstream of the bioreactor in the flowsheet. Thus, the presence of possible growth-inhibiting heavy-metal constituents in the waste stream would not interfere with bioreactor performance, and the ability to use different process conditions for the two unit operations yields a more favorable overall process performance.

Several contactor designs for continuous heavy-metal removal have been tested, and a countercurrent contacting column has proved to be quite effective. By continuously feeding denitrifying bacteria grown on coal particles in the fluidized-bed denitrification bioreactor to the top and pumping a solution containing 25 g/m^3 uranium up through the column, an effluent uranium concentration of ∿0.5 g/m^3 was obtained with a liquid residence time of only ∿8 min (Fig. 5).

Pilot-Plant Tests

The DOE Gaseous Diffusion Plant at Portsmouth, Ohio (PGDP) and ORNL are engaged in a joint R&D effort to develop fluidized-bed denitrification bioreactor design data in support of a full-scale waste effluent design and installation program for PGDP. The nitrate load for the Portsmouth Plant in the mid-1980s is estimated at 40 MT of nitrate per year, at an average concentration of 30,000 $g(NO_3^-)/m^3$. Many of these wastes consist of solvent extraction raffinates and nitric acid cleaning solutions.

The pilot-plant tests being carried out at ORNL use both actual and synthetic raffinate waste. The solvent extraction raffinate is neutralized to pH 7.0 with NaOH, using critically safe in-line mixers, a slant tube clarifier, and a horizontal vacuum belt filter. The filtered effluent is stored in tanks. Any uranium present in the raffinate is precipitated at pH 7.0 along with the other constituents.

The neutralized and clarified raffinate is mixed with ethanol, as a carbon source, and the other trace nutrients needed for good biomass growth. The resulting feed mixture is fed (16 liters/min) to the biodenitrification pilot plant, which consists of two bioreactors, each about 7.5 m high, fabricated from 8-in.-diam sched 10 pipe and arranged in series (Fig. 6). Vibrating screens, 60 cm in diameter, are used for biomass removal.
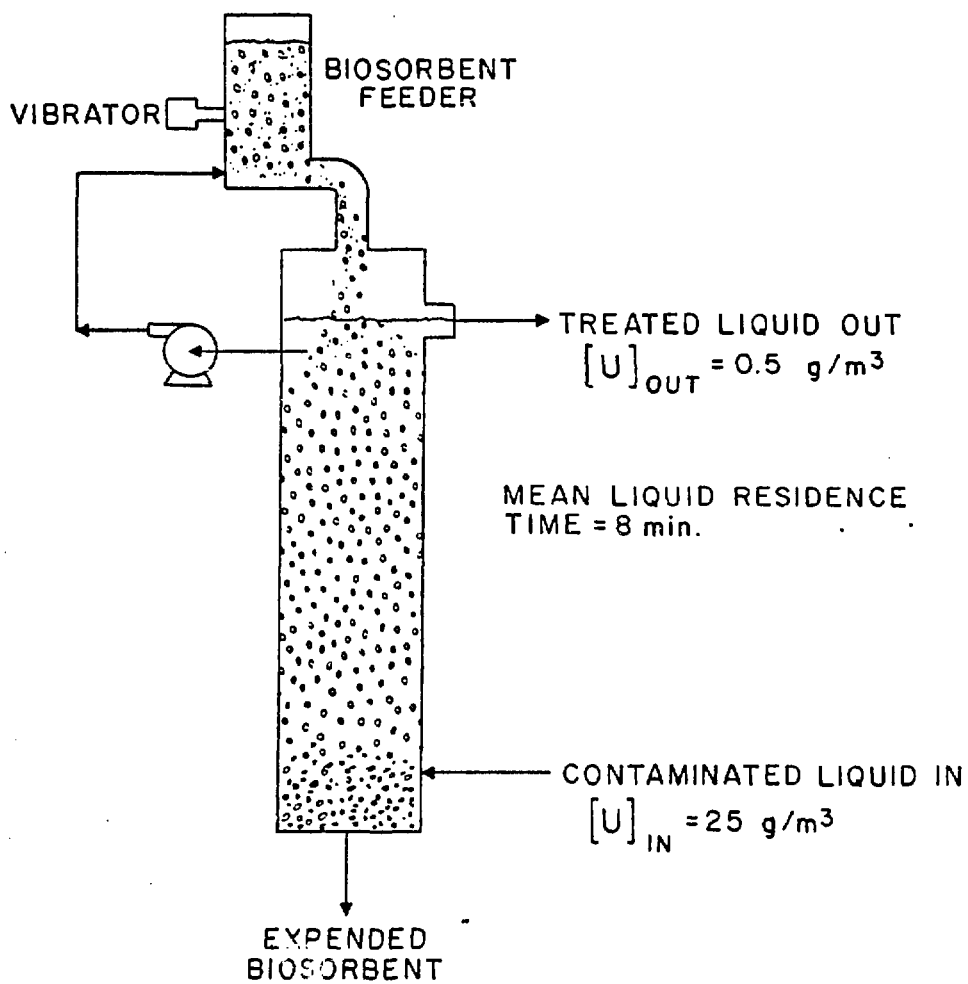
ORNL DWG 78-17599R

Fig. 8. Continuous countercurrent contactor for removal of heavy metals.

Fig. 6

ORNL Dwg. 79-363

Conclusions

The fluidized-bed biological denitrification process is an environmentally acceptable and economically sound method for the disposal of nonreusable sources of nitrate effluents. A very high denitrification rate can be obtained in a FBR as the result of a high concentration of denitrification bacteria in the bioreactor and the stagewise operation resulting from plug flow in the reactor.

The overall denitrification rate in an FBR ranges from 20- to 100-fold greater than that observed for an STR bioreactor. It has been shown that the system can be operated using Ca^{2+}, Na^+, or NH_4^+ cations at nitrate concentrations up to 1 g/liter without inhibition. Biological sorption of uranium and other radionuclides (particularly the actinides) from dilute aqueous waste streams shows considerable promise as a means of recovering these valuable resources and reducing the environmental impact, however, further development efforts are required.

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Fig. 1.   Fluidized-bed bioreactor.

Fig. 2.   Concentration profiles of nitrate, nitrite, and carbon (as ethanol).

Fig. 3.   Denitrification rate as a function of nitrate concentration.

Fig. 4.   Removal of uranium from aqueous solution by washed resuspended cells of *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa*.

Fig. 5.   Continuous countercurrent contactor for removal of heavy metals.

Fig. 6.   Pilot plant design.