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The Feed Materials Production Center (FMPC), a U.S. Department of Energy facility at Fernald, Ohio, is constructing a fluidized-bed biodenitrification plant based on pilot work conducted at the Oak Ridge National Laboratory (ORNL) in the late 1970s and early 1980s (1,2). This plant is designed to treat approximately 600 to 800 L/min of wastewater having a nitrate concentration as high as 10 g/L. The effluent is to contain less than 0.1 g/L of nitrate.

Since this new facility is an extrapolation of the ORNL work to significantly larger scale equipment and to actual rather than synthetic wastewater, design verification studies have been performed to reduce uncertainties in the scaleup (3). The results of these studies are summarized in this report.

BIOLOGICAL DENITRIFICATION IN FLUIDIZED-BED BIOREACTORS

Certain bacterial species are able to remove nitrate from wastewaters by converting the nitrate to gaseous nitrogen under anaerobic conditions. The nitrate serves as the terminal electron acceptor in the absence of molecular oxygen. A carbon source, such as methanol or acetate, must be present to act as the electron donor during microbial respiration.

The general equation for biological denitrification is:

$$NO_3^- + \begin{matrix}\text{carbon}\\ \text{source}\end{matrix} \longrightarrow N_2 + CO_2 + H_2O + OH^- + \text{cells}. \quad (1)$$

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The production of hydroxyl ions causes the pH to rise. The denitrification rate is a function of pH; the optimum pH is in the range of 6.5 to 8.0. Outside of this range there is a sharp decrease in the biodentirification rate (4-7). The reaction is also exothermic, and hence the temperature may rise in the case of high concentrations of nitrate (and thus high extents of reaction).

In the fluidized-bed bioreactor process, bacterial films attach and grow on the surfaces of 30- to 60-mesh anthracite coal particles to form "bioparticles." The wastewater to be treated is pumped upward through a bed of bioparticles at a velocity sufficient to fluidize the bed. The carbon dioxide and nitrogen off-gases are vented to the atmosphere.

BIODENITRIFICATION AT THE FMPC

The nitrate wastewater at the FMPC arises from neutralization of nitric acid. These wastewaters, from several sources at the plant, will be collected in a 30-million-liter lagoon for flow equalization. Water from the lagoon will be pumped to the biodenitrification plant, which will utilize four fluidized-bed bioreactors in series, each 1.3-m diameter and 12-m tall. The design flow rate is 600 to 800 L/min, with nitrate reduction from 10 g/L in the influent to 0.1 g/L in the effluent to the sewage treatment plant.

DESIGN VERIFICATION STUDIES AT ORNL

The 12-m-tall bioreactors at the FMPC were simulated using two different bioreactor systems at ORNL. One bioreactor system contained two 10-cm-diameter, 6-m-tall, glass bioreactors operated in series. The other system was a single 10-cm-diameter, 12-m-tall, bioreactor constructed from PVC pipe. Both systems had sample ports located every 1 to 1.3 m along the length of the bioreactor for axial sampling studies. Off-gas was vented through wet-test meters. Both systems could be operated with varying recycle rates or once-through treatement of the wastewater. Effluent wastewater and entrained bioparticles were passed through a vibrating screen system to shear off excess biofilm and to recover the bioparticles for recycle to the column. A schematic of the two-column system is shown in Figure 1.

Various combinations of synthetic wastewater and actual wastewater shipped to ORNL from the FMPC were treated over a 9-month period. Details of these studies may be found elsewhere (3). The major findings during these studies are summarized below:

- Wastewater from the FMPC is biotreatable at sufficient rates to achieve the design performance of the biodenitrification plant. This design rate is 30 kg of N per m^3 of bed volume per day. The off-gas rate from the bioreactors is a reliable indicator of the real-time performance of the system, and correlates well with the nitrate destruction rate based on nitrate assays. Both methanol and ethanol worked well as carbon sources. (Theoretically, the reaction stoichiometry will be different for methanol than for ethanol, which should alter the quantity of hydroxyl produced. However, this effect was not carefully examined in our studies.)

- Metered addition of acid within the bioreactor at selected locations appears to be an effective means of mitigating the pH rise and thus maintaining high reaction rates. Sulfuric, acetic, and phosphoric acids were used in these studies at ORNL with equal performance. The amount of acid required (and perhaps the need for acid addition at all) depends on the natural buffering capacity of the wastewater, and on the particular carbon source, as noted above.

- Calcium in the wastewater leads to precipitation of calcium carbonate on the bioparticles and elsewhere in the bioreactor system. If this precipitation is excessive, it shuts down the biological action by covering over the bioparticles. We experienced this problem severely with FMPC wastewater containing 300 to 400 mg/L of calcium; biological destruction ceased within one week of exposure to this wastewater and the system had to be restarted. However, we were able to treat softened wastewater successfully on a long-term basis. Our evidence suggests that a calcium level of approximately 50 mg/L will probably be acceptable; concentrations significantly higher than 50 mg/L may lead to problems.

- Removal and replacement of approximately 2 to 5 % of the bed volume with fresh coal was shown to be an effective (and perhaps necessary) action to maintain high reaction rates. This action supplements the role of the vibrating screens in maintaining thin biofilms on the coal. Without removal and replenishment, the biofilms tend to overgrow and create large bioparticles that are ineffective catalysts, analogous to internal diffusional limitations in classical porous catalysts. Addition of fresh coal also serves to ensure that bioparticles are carried over into the vibrating screens for stripping of the excess biofilm.

- The temperature rise created by the exothermic reaction is of the order of 0.5 °C per meter of bioreactor height at the design reaction rate of the FMPC plant. Experimental results and theoretical predictions are shown in Table 1 for several periods in which the experimental biodenitrification rates were stable over several days. The free energy of reaction has been reported to be -138.6 kcal per mol of methanol (7), which is the basis for the theoretical calculations. For the total bioreactor height of 48 m at the FMPC, the total temperature rise (under adiabatic conditions) would be about 20°C. Temperature control of some sort may be needed to maintain an acceptable temperature for the biological activity. However, the temperature dependence of the biodenitrification rate is not well characterized.

Table 1. Comparison of the theoretical and measured temperature rise in the 12-m pilot bioreactor at various denitrification rates

Denitrification rate ($kg\ N/d \cdot m^3$)	Theoretical temperature rise (°C)	Experimental temperature rise ± standard deviation (°C)
8	1.5	0.93 ± 0.50
20	3.7	3.59 ± 0.52
30	5.5	4.46 ± 1.11

CONCLUSIONS AND CURRENT STATUS

Biodenitrification is expected to be an effective technology for treatment of the nitrate-containing wastewaters at the FMPC. Further testing with the full-scale bioreactors at the FMPC will be used to determine the particular operating conditions to achieve and maintain the desired biodenitrification rate. The only significant accomodation for biotreatment of the wastewater appears to be restriction of the calcium concentration to approximately 50 mg/L. Several strategies are being considered to meet this requirement. The biodenitrification plant is scheduled for startup during the spring or summer of 1987.

ACKNOWLEDGEMENT

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REFERENCES

1. C. W. Hancher, P. A. Taylor, and J. M. Napier, "Operation of a Fluidized-bed Bioreactor for Denitrification," Biotechnol. Bioeng. Symp. 8, 361–78 (1978).

2. J. F. Walker, Jr., C. W. Hancher, R. K. Genung, B. D. Patton, and M. Kowalchuk, "Biological Treatment of Nitrate Wastewater Using Fluidized-Bed Bioreactors," Biotechnol. Bioeng. Symp. 11, 415–27 (1981).

3. J. F. Walker, Jr., M. V. Helfrich, and T. L. Donaldson, "The Biodenitrification Development Program," ORNL/TM-10239,February 1987.

4. C. P. Leslie Grady, Jr. and Henry C. Lim, Biological Wastewater Treatment Theory and Application, Marcel Dekker, Inc., New York, 1980.

5. C. W. Francis and M. W. Callahan, "Biological Denitrification and Its Application in Treatment of High-Nitrate Waste Water," J. Environ. Qual. 4 (2) (1975).

6. C. C. Delwiche, Denitrification, Nitrification, and Atmospheric Nitrous Oxide, J. Wiley and Sons, New York, 1981.

7. Roger Knowles, "Denitrification," Microbiol. Rev., 43–70 (Mar 1982).

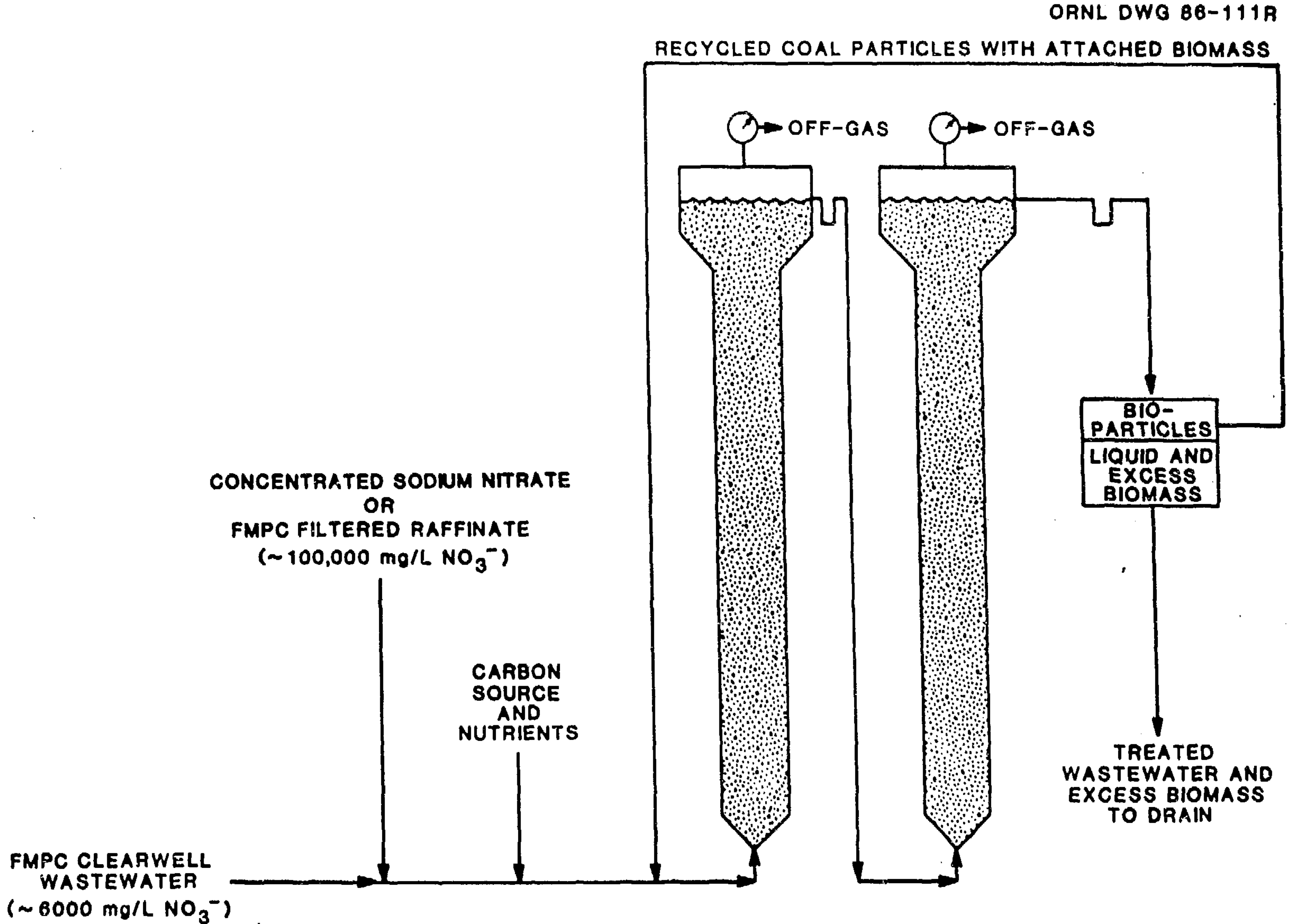

Fig. 1. Schematic diagram of the two-bioreactors-in-series pilot facility.