

Methods of Removing Nitrates from Water

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A cooperative project consisting of the California Department of Water Resources, U.S. Bureau of Reclamation, and the Federal Water Pollution Control Administration was established in 1967 to develop an economical method of removing nitrate-nitrogen from the agricultural waste waters of the San Joaquin Valley of California. Estimated quantity of waste water in the year 2000 requiring treatment prior to disposal into the San Francisco Bay System is 700,000,000 gal per day. In order that the construction of the facilities necessary to transport the waste water to the San Francisco Bay system

can continue on schedule, an economical system for removing the nitrate had to be developed by January 1970. Pilot plant studies are presently under evaluation at the Interagency Agricultural Waste Water Treatment Center near Firebaugh, Calif. Methods of nitrate removal being studied are algae growth and harvesting and bacterial denitrification involving pond denitrification and filter denitrification. Desalination for possible reclamation of the waste waters by reverse osmosis and electrodialysis is also being evaluated.

The nearly 8 million acres of irrigable land in the California San Joaquin Valley comprises one of the richest agricultural areas in the world. Annual rainfall in the Valley varies from 4 to 12 in., while evaporation may exceed 70 in. per year. Therefore, irrigated agriculture is necessary for crop production. Sufficient imported water for irrigation will be provided by the California Water Project which is presently under construction; however, the imported irrigation water creates a disposal problem in the Valley. In a portion of the Valley, it is necessary to install under-field tile systems to remove the saline water from the crop root zone. After completion of the California Water Project, it is estimated that 1.5 million acres of the Valley will require such under-field tile systems [California Department of Water Resources Bulletin No. 127 (1965)].

Due to salt accumulation in the water collected by the tile systems, it is necessary to dispose ultimately of this water. The predicted quality of this wastewater is shown in Table I. It is estimated that by the year 2000 an annual flow of 500,000 acre-ft of tile drainage will require disposal. Peak summer flows are estimated at 700 million gal per day.

The U.S. Bureau of Reclamation has begun construction of the San Luis Drain to transport a portion of this tile drainage to the San Francisco Bay System for disposal (Price, 1968). The State of California is continuing studies with the aim of constructing a drain at a later date to provide drainage for the rest of the problem areas.

A 1967 Federal Water Pollution Control Administration report indicated that serious pollution problems would result if the tile drainage wastewaters were discharged without treatment into the San Francisco Bay System (U.S. Department of the Interior, 1967). Excessive uncontrolled algal growth is the problem anticipated. The report indicates that nitrogen, primarily in the nitrate form, is the most serious potential pollutant. One of the recommendations of the report is that no wastewater be emptied into the Bay System until a suitable method of nitrate removal has been developed.

As a result of this recommendation, three agencies (Federal Water Pollution Control Administration, U.S. Bureau of Reclamation, and the California Department of Water Re-

sources) formed an Interagency Nitrogen Removal Group to develop methods of removing nitrates from the tile drainage and to study problems associated with disposal of the tile drainage into the Bay System. At this time, an experimental field station to develop nitrate removal methods was established. This station is known as the Interagency Agricultural Waste Water Treatment Center and is located near Firebaugh, Calif., which is approximately 45 mi west of Fresno. The Center is guided by a committee consisting of a project director from the California Department of Water Resources and from the Federal Water Pollution Control Administration, and a representative of the U.S. Bureau of Reclamation. This committee is assisted by a Board of Consultants comprised of William Oswald and Clarence Golueke, University of California, Berkeley, and Perry McCarty, Stanford University.

The studies being conducted at the Agricultural Waste Water Treatment Center are the subject of this paper. Two basic methods of nitrogen removal are being evaluated at the Treatment Center. These methods are termed bacterial denitrification and algae stripping. Two methods of bacterial denitrification are being evaluated: pond denitrification and filter denitrification. Desalination of the tile drainage is also being evaluated.

DESALINATION

The Federal Water Pollution Control Administration, through an agreement with the Office of Saline Water (OSW), is evaluating two methods of desalting tile drainage water—reverse osmosis and electrodialysis.

The reverse osmosis unit being evaluated is equipped with a cellulose acetate membrane and operated at a pressure up to 750 psi. Using 6000 mg per l. of tile drainage water, up to 93% ion removal is being experienced with this unit.

With the electrodialysis unit being evaluated, about 30% of the ions are removed each time the tile drainage water is passed through the membrane stack.

Neither of the two units tested has significantly removed the boron. The reverse osmosis unit removes only about 20% of the nitrate, while the electrodialysis unit removes about 30%.

ALGAE STRIPPING

The basic theory of removing nitrogen by algae stripping is quite simple; that is, grow a dense crop of algae which ties up the nitrogen in their cell structure and then remove the algae

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Table I. Estimated Constituent Concentrations in San Joaquin Valley Agricultural Wastewaters

Chemical Constituents	Concentrations in mg/l	
	Initial	After 50 yr of Operation
Minerals		
Calcium	220	160
Magnesium	160	90
Sodium	1900	540
Potassium	20	10
Carbonate	0	0
Bicarbonate	220	200
Sulfate	3500	740
Chloride	1000	670
Nitrate	90	90
Boron	11	3
Total Dissolved Solids	6800	2500
	Non-Time Varying Constituents	
Nutrients		
Total Nitrogen	21	
Total + Organic Phosphate	0.35	
Pesticides	<0.001	
Others		
Dissolved Oxygen	5-10	
5-Day BOD	1-3	
COD	10-20	
Surfactant (ABS)	0.0	
Phenolic Material	0.001	
Grease and Oil	0.5	

from the water. It is, however, not as simple as it sounds. While algae will grow quite easily in this water, the concentration of algae that is required to remove 90% of the nitrate-nitrogen is another problem. Initial studies at Firebaugh indicated that agricultural wastewaters lack phosphate, iron, and carbon in the amounts required to grow this dense crop of algae. With the addition of approximately 2 mg per l. of phosphorus in the phosphate form, about 10 mg per l. of nitrate-nitrogen were removed. At this point it was obvious that other nutrients were limiting. With further study, it was determined that iron additions at approximately 2 mg per l. would tie up 15 to 17 mg per l. of nitrogen. It was then determined that carbon was limiting. Carbon dioxide additions, to maintain a pH of 8.0 to 8.5, were successful in that over 20 mg per l. of nitrate-nitrogen were converted to cell material by the algae. A very dense crop of algae, some 300 to 400 mg per l., was produced in our growth ponds. However, something in the addition of carbon dioxide created problems in the growth pond, and approximately 2 weeks after the first addition of carbon dioxide the algae died. We are now in the process of adding carbon dioxide at different rates and with different air mixtures to determine the proper method for adding carbon dioxide to the system. Certainly, phosphorus, iron, and carbon must be added as nutrients to remove the high concentration of nitrate-nitrogen.

The studies to determine the most efficient and economical depth have indicated that, while 8 in. of depth is more efficient than anything deeper, the algae that developed in the shallow depth are of a different species. They are diatoms, and a diatom may not have as great a value as a by-product as green algae. Also, the efficiency at this shallow depth was slightly greater than at either 12 or 16 in. of depth. A study is now being conducted to determine the effect of carbon dioxide additions at these deeper depths. If the growth ponds can be operated at 16 or 18 in. of depth, rather than 12 as now pre-

dicted, this would be a significant savings in pond area and treatment costs.

Studies were conducted to determine the amount and time of mixing required to enhance the algae growth. Four-hour mixing was better than mixing during all daylight hours or intermittent mixing during daylight hours of 15 min per hr. The time of mixing during the daylight hours did not have any significant effect; that is, 4 hr in the morning, 4 hr at midday, or 4 hr in the afternoon all gave the same amount of nitrogen removal.

The detention time-nitrogen removal relationship is linear and temperature-dependent. It appears from our studies to this point that the detention time requirement in the growth ponds is approximately 4 to 5 days during the warmer summer months, and about 15 days during the cooler winter period. This creates no problem, since the winter flows are approximately 20% of the peak summer flows. Therefore, a treatment facility can be designed for summer detention times and use about the same area of growth ponds for winter detention times.

The removal of algae from the water is an even more difficult problem than growing the algae. Methods are now being investigated on a pilot scale to determine the most economical and efficient method of separating the algae and then dewatering it before disposal. Results from other projects and from our jar tests indicate that flocculation and sedimentation may be the most economical method of algae separation. Centrifugation, microscreens, and sand filtration will also be investigated as methods of separation. After the algae is concentrated into a slurry, it must be dewatered. Centrifuges, a vacuum filter, and sand drying beds will be investigated as a method of dewatering the algae.

The disposal of the algae may support part of the cost of treatment. Several industries have expressed interest in the use of algae for such things as animal feed, soil conditioner, or for production of adhesives. In livestock feed, algae would replace the fish meal or protein supplement and have a value of approximately \$150 a ton. Poultry raisers are also interested in using algae for feed. Besides the protein, algae contains xanthophyll, which adds color to the flesh of the bird and to the egg yolk and increases the market value. The company interested in using algae as a soil conditioner predicts that algae may be used by the home gardener similar to the use of Milorganite (condition the soil as well as having some fertilizer value). Algae would have a value of about \$100 a ton as a soil conditioner. A value of about \$120 a ton could be realized by utilizing algae in the production of adhesives. If none of these methods of disposal are practiced, it may be necessary to dispose of algae by digestion. The methane gas produced would be used to provide power required for the treatment process. Laboratory experiments indicate that the methane produced by digestion would produce more power than required in the treatment process (Oswald and Golueke, 1960).

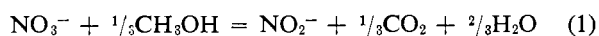
BACTERIAL DENITRIFICATION

During bacterial denitrification, microorganisms reduce nitrates and nitrites to nitrogen gas. A wide variety of common facultative bacteria have the ability to bring about denitrification; however, denitrification can only be carried out if the organisms were supplied with an organic energy source and only if oxygen were not available. Under such anaerobic conditions, the microorganisms can use nitrates or nitrites as terminal electron acceptors to bring about the oxidation of the energy source. This is the same way oxygen

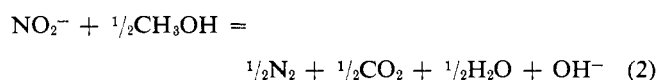
is used under aerobic conditions. Since the tile drainage waters are very low in organic materials, it is necessary that some be added. At the Center, we are using methanol (McCarty *et al.*, 1969; Tamblyn and Sword, 1969).

The denitrifying ability of microorganisms differs (Alexander, 1961). Some can reduce nitrates to nitrites only, some can reduce nitrites only to molecular nitrogen, while some can reduce both nitrates and nitrites to molecular nitrogen; however, it is normally considered that denitrification is a two-step process in which nitrates are reduced to nitrites and then from nitrites to nitrogen gas. Hence, the denitrification reaction with methanol would be:

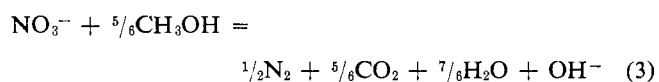
First Step:



Second Step:



Overall:



Thus, 1 mol of nitrates requires at least $\frac{5}{6}$ mol of methanol for complete denitrification, or 1.90 mg per l. of methanol is required for each mg per l. of nitrate nitrogen.

Any dissolved oxygen must be removed before denitrification can occur. This can be done biologically by the addition of more methanol.



Each mg per l. of dissolved oxygen requires at least 0.67 mg per l. of methanol to remove it.

Additional methanol is also required for bacterial growth. This amount can be evaluated from the consumptive ratio which is defined as the ratio of the total quantity of chemical required for denitrification to the stoichiometric requirement for denitrification and deoxygenation alone. The consumptive ratio for methanol has been evaluated to be 1:30 (McCarty *et al.*, 1969). Therefore, an additional amount of methanol must be added over the amounts shown in Equations 2, 3, and 4 in order to satisfy bacterial growth requirements. From this, we can develop a formula to represent the total concentration of methanol required for complete denitrification.

$$C_m = 2.47 N_0 + 1.48 N_1 + 0.87 D_0 \quad (5)$$

where:

- C_m = required methanol concentration, mg/l.
- N_0 = initial nitrate-nitrogen concentration, mg/l.
- N_1 = initial nitrite-nitrogen concentration, mg/l.
- D_0 = initial dissolved oxygen concentration, mg/l.

As mentioned, we are evaluating two methods of denitrification at the Center: pond denitrification and filter denitrification. In both methods, the organic carbon (methanol) requirements for denitrification of the tile drainage water have been close to the estimated quantity. To achieve more than 90% reduction of the 20 mg per l. of influent nitrate-nitrogen and 10 mg per l. of dissolved oxygen, approximately 60 mg per l. of methanol is required.

POND DENITRIFICATION

In this process, relatively deep ponds are used to develop the required anaerobic conditions. The tile drainage water, after methanol addition, enters near the bottom of the pond, and the effluent discharges near the top of the pond. The denitrifying organisms are free floating in the pond, with the more dense concentration near the bottom.

Initial pond denitrification studies at the Center were conducted in 3-ft diameter vertical concrete pipes, 6 to 11 ft deep, to simulate deep ponds. One-half of the simulated ponds were covered, while the other half remained uncovered. Denitrification was achieved in both covered and uncovered simulated ponds; however, higher nitrogen removal was achieved in the covered simulated pond.

Based on these results, two deep ponds were constructed at the Center. One pond is 60 ft wide by 200 ft long; the other 50 ft square. Both ponds are approximately 14 ft deep. The larger pond is covered with a floating styrofoam material to reduce algal growth and surface reaeration.

Pilot-scale studies in these ponds began in August 1968. A 90% nitrate-nitrogen removal has been achieved in the covered pond at a 10-day detention time. Removal efficiencies at a 5-day detention are presently being investigated. Experience during the winter of 1968 showed that a longer detention time (approximately 20 days) was required to obtain high nitrogen removal efficiencies when cooler water temperatures prevailed.

Removal efficiencies in the uncovered pond have never reached the 90% range. Presently, this pond is operating at a detention time of 15 days, with a nitrogen removal efficiency of 60%.

FILTER DENITRIFICATION

This method of denitrification is very similar to the deep pond process, except an aggregate bed is used. One advantage of this method over the pond system is that the surface area to which the bacteria can attach themselves is greatly increased, thus producing a greater concentration of bacteria. Also, since the bacteria are attached, the wastewater can be passed through the filter at a higher velocity without washing out the bacteria, as would happen in a deep pond where the microorganisms are "free floating." Because of these advantages, the nitrate-nitrogen is reduced to nitrogen gas more quickly than in deep ponds.

All filter denitrification studies at the Center are being performed in columns with a 6-ft media depth. An organic material (methanol) is added to the tile drainage wastewater just before it enters the bottom of the filter and flows upward.

Initial filter studies were accomplished using 4-in. diameter columns. These studies showed that the process was technically feasible under field conditions. Larger diameter (18-in. and 36-in.) filters were then constructed to investigate the effects of scaling up the units.

The major variables investigated were filter media and detention time. Some of the various media investigated include sand, activated carbon, coal, volcanic cinders, gravel, and a commercially produced plastic trickling filter media. Media size investigated ranges from sand to 3-in. diameter gravels. Detention times studied varied from $\frac{1}{2}$ hr to 2 hr. These represented flow rates from approximately 0.6 to 0.15 gal per min per sq ft. At all detention times studied, greater than 90% removal of the 20 mg per l. of nitrate-nitrogen was achieved.

The efficiency of this biological process is affected by the

temperature of the tile drainage water. The greatest drop in efficiency occurred when the temperature of the influent water was below approximately 10° C. A filter is presently being operated within a controlled environment so the effect of influent water temperature can be carefully monitored and studied.

The most satisfactory media evaluated was the 1-in. diameter gravel. A filter containing this media has been in operation for nearly a year at a detention time of 1 hr. The average total nitrogen removal for this period has been approximately 90% of the 20 mg per l. of influent nitrate-nitrogen. The temperature of the influent water reached a low of 12° C during this period. During this total period of operation, it has not been necessary to clean the filter.

A larger filter, 10 ft sq, has been in operation at the Center for the past few months. This filter, filled with 1-in. diameter gravel, has a false bottom as used for rapid sand filter construction for water treatment. The tile drainage water enters through this bottom and rises through the gravel media; the water is then collected at the top with a system of weirs. This filter will be used to evaluate hydraulic characteristics of large upflow filters.

COMPARISON OF BIOLOGICAL NITROGEN REMOVAL SYSTEMS

Land requirements for these three systems will vary greatly. Based on present knowledge, the algae stripping method will

require about 9000 acres of land, pond denitrification about 1100 acres, and filter denitrification about 150 acres.

Initial cost estimates for nitrogen removal by these three biological systems are nearly the same—around \$25 to \$30 per million gal based on an average influent nitrate-nitrogen concentration of 20 mg per l.

The schedule at the Center is set to complete our initial studies by this fall. This will allow the development of accurate costs for these nitrogen removal methods by fall 1970.

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