

TREATMENT ALTERNATIVES FOR NITRATE CONTAMINATED GROUNDWATER SUPPLIES

MOHAMED F. DAHAB, Ph.D., P.E.

*Department of Civil Engineering
University of Nebraska-Lincoln*

ABSTRACT

Nitrate concentrations in groundwater supplies throughout many areas in the United States, particularly in the Midwest, have steadily increased well past the Maximum Contaminant Limit established by the Safe Drinking Water Act of 1974 and its amendments of 1986. The concern over nitrate contamination stems from the fact that these salts have been linked to infant methemoglobinemia (blue-baby syndrome). Nitrates also have been linked to the formation of nitrosoamines and nitrosoamides, which are potent carcinogens. There are several methods of removing nitrates from groundwater supplies with varying degrees of efficiency, cost, and relative ease. These methods include anion exchange, biological denitrification, reverse osmosis, electro dialysis, and potentially chemical precipitation. The technical feasibility and economics of these processes indicate that only the first three can be considered viable at the present. This article is intended to discuss the relative technical feasibility of removing nitrates from groundwater supplies when using the above mentioned methods. Results from bench-scale experiments as well as data from the literature are used to develop a basis of comparison. The results of this effort indicate that ion-exchange is most advantageous when dealing with moderate nitrate contamination situations. However, in extreme contamination cases, biological denitrification followed by other water purification processes seems to be the most effective method of treatment.

The methods by which nitrates can be removed from groundwater supplies are basically limited to three processes that show some potential for full-scale application [1]. These processes are ion exchange, biological denitrification, and reverse osmosis. There are other methods that can be used to partially reduce nitrate concentrations. These methods include electro dialysis, distillation, and to a very limited degree, chemical precipitation. Available data

indicate that both electro dialysis and distillation are not likely to be cost effective when applied on a large-scale basis because of the excessive energy required to operate these systems [2]. These systems might be useful for very limited scale applications where the cost of energy may be considered of secondary importance. Electro dialysis may become more attractive if nitrate specific membranes are developed. Currently, available electro dialysis membranes tend to favor divalent ions such as calcium, magnesium, and sulfates over monovalent ions such as nitrates [2]. Chemical precipitation, as discussed later, is associated with excessive sludge production as well as the need for a copper catalyst to drive the reaction forward. These two disadvantages seem to make this process of very limited utility at the present time [1, 3].

In general, three categories of nitrate pollution control strategies can be identified:

- a. reduce or eliminate nitrate at the source by reducing or ending the use of substances which produce nitrates and by managing the industrial, urban, and agricultural systems which generate nitrates as efficiently as possible this can be done by minimizing leaching and nitrogen losses so that natural purification systems can have a maximum impact or by providing treatment at the sources themselves to reduce nitrate discharges;
- b. seek alternative water supplies either for direct consumption or for mixing with contaminated water; the use of bottled water is an extreme example of this approach; and
- c. reduce the nitrate content or eliminate nitrates altogether by treatment of contaminated water.

Category (a) is deemed impractical since it can be safely assumed that it is economically and politically infeasible to enforce stringent enough fertilizer control actions that would reduce or eliminate nitrate contamination. In addition, it would also require a very long period of time to detect measurable results. Category (b) is a reasonable approach to the contamination problem provided that there are water supplies available to permit practical economic use. In many situations, category (c) is probably the most reasonable approach to providing adequate and safe water supplies.

SOURCES AND EFFECTS OF NITRATE CONTAMINATION

Nitrate concentrations in groundwater supplies have been steadily increasing over the years due to the combined effects of several factors including extensive use of chemical fertilizers, uncontrolled animal feeding operations, as well as urban and industrial pollution. Concerns over these increases are very legitimate due to the potential ill effects of nitrates on the health and well-being of what seems to be a very wide range of water users particularly those with very young children.

The principal problem caused by nitrate contamination is the link between high nitrate concentrations in water and the incidence of methemoglobinemia (blue-baby syndrome) in young children. This link is very well established for water supplies with nitrate concentrations exceeding the nominal limit of 10 mg/L (as nitrogen) [2, 4-6]. In addition, high nitrate levels have been linked to the formation of nitrosoamines and nitrosoamides which in turn have been identified as extremely potent cancer causing agents [5]. Although the link between nitrates and the formation of nitroso compounds is not very well understood at the present time, the normal sequence of nitrate reduction in the intestinal tract of the human body (i.e., the conversion of nitrates into nitrites) suggests that this link is very logical since nitrites are the normal precursors to the formation of nitroso compounds. It appears that it is only a matter of time before this link is fully established [5, 6].

Ingestion of nitrates at high concentrations may also lead to other ill-effects on the human health. Shuval and Gruner indicated that prolonged nitrate exposure led to changes in the heart blood vessels as well as behavioral effects in laboratory animals [6]. Other physiological effects may become apparent as more data are gathered on the possible dangers of nitrate contamination.

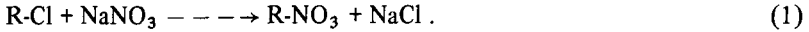
METHODS OF NITRATE REDUCTION IN WATER SUPPLIES

Conventional water treatment methods such as lime and soda-ash softening, filtration, and cation-exchange softening have no measurable effects on reducing nitrate concentrations in water supplies. The molecular stability and high solubility are the primary reasons behind the resiliency of these salts. There are, however, several methods that can be used to reduce nitrate concentrations in potable water supplies with varying degrees of efficiency and ease. As pointed out earlier, the methods that offer the most economic potential are ion exchange, biological denitrification, and reverse osmosis. Distillation and electrodialysis may be advantageous under some circumstances where the cost of energy is not a primary consideration. Chemical precipitation using iron salts has also been investigated as a potential method of nitrate reduction [3]. It appears, however, that this method is not very efficient in addition to being quite costly since post iron precipitation treatment will be required.

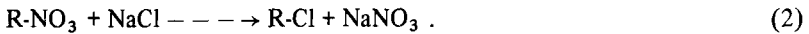
Nitrate Removal Using Ion Exchange

Removal of nitrates from drinking water supplies using ion exchange offers a great potential for application at small and medium sized treatment plants [1, 2]. Application would be very similar to domestic (or commercial) ion exchange softeners currently available in the market place. In ion exchange treatment, the contaminated water supply is passed through an exchange resin

bed. During contact, nitrate ions in the water are exchanged for similarly-charged ions (e.g., chloride). This process will continue until the bed exchange capacity is exhausted. The exchange reaction can be depicted by the following reaction:



In the above reaction, “R” represents the resin immobile (i.e., solid) phase. When the resin’s exchange capacity is used up, the resin bed must be taken out of service and regenerated. Regeneration restores the bed’s exchange capacity to its original state by reversing the reaction and thus forcing the nitrates out of the resin under the action of a concentrated (brine) solution. The regeneration reaction can be depicted as follows:



After regeneration is completed, the bed is rinsed and normal operation is restored.

Ion exchange water softening systems can be manufactured in various sizes ranging from small individual systems (i.e., single household units) to sizes large enough for community-sized application. Whether nitrate removal ion exchange systems can be similarly adapted remains to be seen.

To date, nitrate removal by ion exchange is limited by two basic problems that must be fully addressed before widespread application could be realized [2, 7, 8]. The first problem deals with providing a resin of high selectivity for nitrates over other ions that are commonly present in most groundwater supplies; often at higher concentrations than nitrates. As an example, sulfates are normally present in most groundwater supplies at concentrations that are normally several times those of nitrates. Anion exchange resins are more selective for sulfates than they are for nitrates [2, 9]. Guter [7] and Lauch and Guter [8] reported that a series of nitrate selective resins were developed and tested at McFarland, California. However, currently it is not clear how stable these resins are under prolonged use and how economical these resins are to produce. The experiments at the California site indicated that a treatment cost (for nitrate removal only) of at least \$0.242 per one thousand gallons of product water is to be expected when treating well waters with a nitrate-nitrogen concentration of 16 mg/L to a final concentration of about 7.0 mg/L [8]. This amounts to a nitrate removal efficiency of about 56 percent. The treatment costs reported by Lauch and Guter exclude costs of spent brine (regenerant) disposal [8].

The second problem associated with ion exchange removal of nitrates involves providing an adequate resin regenerant such that regenerant disposal does not become a problem in itself. Currently, regenerant disposal may account for a major fraction of the overall cost of the process [2, 10]. Alternatives available for regenerant disposal include discharge to the local municipal waste treatment

works, application to land, and transport to other treatment works, among others. It is estimated that proper regenerant disposal will easily double the costs of treatment reported by Lauch and Guter [8].

Nitrate Reduction Using Reverse Osmosis

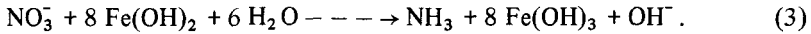
Reverse osmosis is a process whereby ionic species (e.g., nitrates) present in the water supply are removed by forcing the water to be transported across a semipermeable membrane and effectively leaving the nitrates behind. This process is accomplished by subjecting the water supply in the reverse osmosis cell to pressures exceeding its corresponding osmotic pressure. Such pressures can easily reach 300 to 400 psig when treating brackish water and up to 1000 psig when treating (i.e., desalinating) seawater [2, 4, 9].

Membranes used in the manufacture of reverse osmosis units are often made of cellulose acetates. Other materials such as polyamides and thin film composite membranes have been used [2]. These membranes must be constructed in such a manner as to withstand high pressures. Reverse osmosis membranes generally do not exhibit high selectivity (or preference) for any given ion although the degree of salt rejection seems to be directly related to the valency of ions present in the water supply [2, 9]. As a consequence, the reverse osmosis process generally results in better removals of multivalent ions than monovalent ions. Accordingly, it has been suggested that reverse osmosis could be used to remove sulfates from the water supply before ion exchange treatment for nitrate removal [2]. Because reverse osmosis results in the removal of many ionic species that are present in the water supply such as sodium chloride, calcium chloride as well as other minerals, including nitrate salts, a significant reduction in the mineral content of the water is accomplished [2].

Despite the high energy input required to produce the pressures required to drive reverse osmosis units, this process can be fairly comparable to other processes under some situations and therefore merits a close investigation when considering potential processes for nitrate and other dissolved solids removal. There are some full-scale reverse osmosis plants across the United States most of which were built for total dissolved solids (TDS) reduction [11]. It should be noted that it might be possible to economically justify reverse osmosis as a very viable nitrate removal or reduction process by allocating a significant portion of the process capital and operating costs to the reduction of other dissolved solids that may be present in the groundwater supply. This type of cost allocation system is plausible particularly if the water supply requires treatment for hardness reduction (i.e., softening) or reduction of other chemical constituents such as sulfates and chlorides. Reverse osmosis costs are reported to be about \$1.00 per thousand gallons of product water [8]. This cost does not include the costs of disposal of the product brine.

Nitrate Removal Using Chemical Denitrification

Nitrates can be reduced chemically to ammonia using iron salts under basic pH conditions according to the following reaction [3] :



Although the stoichiometric Fe:NO₃ is 7:1 according to equation (3), it was reported that this reaction required an actual Fe:NO₃ ratio of about 15:1 [3]. In addition, a copper catalyst was required to carry the reaction to completion.

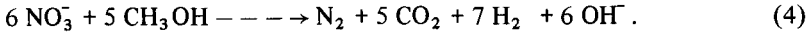
According to the above reaction, the basic problems with chemical denitrification are the resultant large quantities of iron sludge, the need for a copper catalyst, and the subsequent production of ammonia. The iron sludge must be handled, recycled, or properly disposed of. The effects of the copper catalyst are not exactly known since no data as to residual copper concentrations in the treated water are available. Any residual copper in the treated water must be below the established limit under the Safe Drinking Water Act [2]. In addition, any ammonia produced in this reaction must be removed using ion exchange or other treatment systems. Ammonia can interfere with subsequent disinfection by chlorination if it is above the desired limit necessary to prolonging the chlorine residual. According to Sova [3], the economy of using chemical denitrification is not attractive even under conditions where the influent nitrate concentration is marginally above the current established limit.

Nitrate Removal Using Biological Denitrification

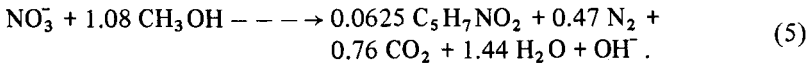
Biological denitrification is a well established process in the realm of wastewater treatment. However, this process has not been introduced to the field of water treatment on any significant scale. There are some experimental (full-scale) demonstration plants being operated in Europe [12]. In addition, there is one small demonstration plant currently being evaluated in the United States. The primary reason behind the slow transfer of technology from the wastewater treatment to potable water treatment is the obvious concern over potential bacterial contamination of the treated water supply. This is obviously a very legitimate concern and must be kept in mind when designing such treatment processes for water treatment.

Dahab [13] and Dahab and Grachek [1] reported on the potential for using biological denitrification for nitrate reduction in groundwater supplies in laboratory-scale experiments. The results indicated that this process can be expected to reduce the nitrate concentration in the influent water supply from as high as 100 mg/L (as N) to levels within the 1.0 mg/L (as N) range [1, 13]. These removals translate into an efficiency of nearly 100 percent which is not matched by any other process available for nitrate reduction. However, some residual soluble as well as insoluble organic matter should be expected in the denitrified water supply. Further treatment should reduce these solids to levels sufficient to meet drinking water standards [1].

In biological denitrification, facultative microorganisms are contacted with the water supply containing nitrates and an added carbon source under anoxic conditions (i.e., devoid of molecular oxygen). Under these conditions, the bacteria utilize nitrates as a terminal electron acceptor in lieu of molecular oxygen. In the process, nitrates are reduced to nitrogen gas which is harmless. The extraneous carbon source is necessary since it supplies the energy required by the microorganisms for respiration and synthesis. If methanol is used as a carbon source, the reaction could be written as follows [14]:



The above equation only describes the energy reaction. If bacterial synthesis is considered, the overall denitrification reaction can be written as follows [14]:



When a simple carbon source is chosen such as methanol or acetic acid, the biological solids produced during this process will be correspondingly low; a useful characteristic in that the overall sludge production is minimized [15].

In the work reported by Dahab and Grachek, acetic acid was used as the carbon source for laboratory scale denitrification reactors that were about five inches in diameter and four feet in height [1]. Both reactors were of the static-bed type. Two types of commercially-available packing materials were used as the bacterial support matrices. These reactors were compared to a third reactor of the expanded-bed-type in which uniform sand of a median size of about 0.8 mm was used as the bacterial support medium. All of these reactors were operated for a period of about one year using synthetically prepared water with influent nitrate concentrations ranging from 100 to 200 mg/L. These studies resulted in average nitrate removal efficiencies of 98 and 100 percent when the influent nitrate concentration was 100 mg/L using static-bed reactors [1]. The removal efficiency was not nearly as good in the expanded bed reactor. These results are illustrated graphically in Figure 1.

Although nitrates were nearly depleted in the denitrification reactors, the effluent from these columns contained residual suspended as well as dissolved organic solids. The suspended solids were made up of bacterial mass that was dislodged from the reactors by the hydrodynamic shear caused by the upwards movement of water and product gas in the reactors. The dissolved solids were presumed to be made up of residual carbon that was not entirely depleted during the reaction.

Residual organics remaining in, or imparted to the water by the denitrification system, must be removed from the water supply to avoid problems when disinfecting by chlorination. Such problems may develop when chlorine is added to water containing residual organics thus leading to the possible formation of halogenated organics [2]. Some halogenated organics are suspected

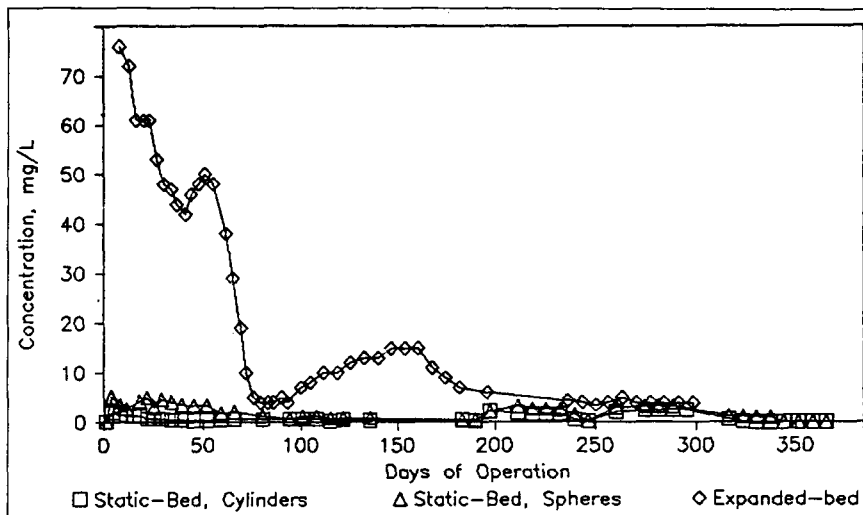


Figure 1. Nitrate data from biological test reactors.

carcinogens and therefore an alternative disinfection method such as ozonation may be required if residual organics are not completely removed.

Full-scale application of biological denitrification has been implemented at many locations in the United States for wastewater treatment using both suspended as well as attached growth septums [15]. Because the technology would be substantially similar if this process was to be applied to water treatment, it is anticipated that the experience gained in the treatment of wastewater will be valuable in the potable water treatment field. Full-scale application of biological denitrification can be envisioned under several scenarios which are designed to decrease the opportunity for bacterial contamination of the water supply and enhance subsequent treatment required to polish the denitrified effluent to meet drinking water standards. These scenarios may include:

1. biological denitrification followed by natural storage — Natural storage would provide an opportunity for the water supply to be aerated. The aeration would allow for residual organics to be oxidized by the same biological solids discharged as suspended solids from the denitrification process. Storage before further treatment also allows for the dampening of any small effluent nitrate peaks that might result from the process on occasion.
2. biological denitrification followed by mechanical aeration before treatment — Mechanical aeration will be necessary in large-scale applications where natural aeration will not be sufficient to accomplish the same results.

3. biological denitrification followed by chemical treatment to remove hardness as well as residual suspended solids — This alternative will be useful where the raw water conditions are such that softening using lime and soda-ash is required. This sequence is generally followed by filtration on granular media and disinfection.

The above scenarios were presented as examples under which biological denitrification could be introduced and managed as an integral unit(s) within the overall scheme of potable water purification. The choice of any particular scenario and the subsequent treatment that might be necessary must be carefully evaluated within a more encompassing picture that should also include alternative nitrate reduction methods as discussed earlier.

Accurate cost estimates of biological denitrification for water treatment are difficult to make because there are no actual full-scale treatment systems in operation. However, since the biological denitrification process is quite similar to systems employed in wastewater treatment, cost estimates can be made on that basis. Since post-denitrification treatment will be required to elevate the denitrified water to drinking water quality levels, the costs of this additional treatment must also be accounted for. Based on these assumptions, it is estimated that nitrate removal using biological denitrification will cost about \$0.65 per thousand gallons of water treated. This cost estimate was made on the assumption of a water supply with an influent nitrate-nitrogen concentration of 50 mg/L, a treatment efficiency of 90 percent, and a plant size of one million gallons daily. This cost estimate was based on EPA data [16] and updated to 1987 levels using the standard Engineering News Record Index. Additional water treatment was estimated to bring the total denitrification cost to about \$1.00 per thousand gallons.

PROCESS COST COMPARISON

At the estimated costs above, biological denitrification does not seem to be a cost-effective method of treatment; at least in comparison to ion exchange. However, the treatment cost estimates for ion exchange and reverse osmosis did not include the cost of brine disposal and therefore are not realistic. A more practical comparison can be made in terms of the actual cost per unit weight of nitrate-nitrogen removed. Using the cost data provided by Lauch and Guter, the cost of treatment per pound of nitrate-nitrogen removed is \$3.00 when using ion exchange and \$12.00 when using reverse osmosis (again, without accounting for brine disposal costs) [8]. The estimated cost per pound of nitrate-nitrogen removed is \$2.67 when using biological denitrification. This latter estimate is conservative since a treatment efficiency of only 90 percent was assumed when in fact a much higher efficiency can be expected as demonstrated earlier [1]. The lower cost associated with biological denitrification is the result of the higher efficiency of this process.

CONCLUSIONS

Based on the preceding discussion of nitrate removal alternatives, the following conclusions can be made:

1. Biological denitrification of water supplies appears to be a feasible alternative for nitrate removal. Based on laboratory-scale experiments, this process can reduce nitrate concentrations as high as 100 mg/L to levels well below the established maximum contaminant level.
2. Based on initial cost estimates, it is apparent that ion exchange might be more of an expedient alternative than biological denitrification or reverse osmosis in situations where groundwater contamination is moderate. The latter alternative seems to be the least feasible from an economics standpoint.
3. In situations where nitrate contamination is quite severe, biological denitrification probably is the best available alternative for nitrate reduction or removal. However, it must be realized that additional treatment will be required to remove suspended and dissolved organic solids imparted by this process. It must also be realized that water disinfection by chlorination might no longer be advisable to avoid the potential for halogenated methanes formation.

ACKNOWLEDGMENTS

The work reported above was supported by the Department of Civil Engineering and the Engineering Research Center at the University of Nebraska-Lincoln. Assistance provided by the University of Nebraska-Lincoln Water Resources Center is also acknowledged.

REFERENCES

1. M. F. Dahab and R. Grachek, Biological Denitrification of Water Supplies, submitted to *ASCE Journal of Environmental Engineering*, February 1987.
2. J. M. Montgomery, Consulting Engineers, Inc., *Water Treatment, Principles and Design*, John Wiley and Sons, New York, NY, 1985.
3. R. J. Sova, The Chemical Removal of Nitrate from Water Supplies Using Ferrous Sulfates and Pickle Liquor, Master of Science Thesis, University of Nebraska-Lincoln Libraries, Lincoln, NB, 1986.
4. D. R. Andersen, *Nitrates in Water Supplies: Basis for Concern and Status of Treatment Processes*, Department of Civil Engineering, University of Nebraska-Lincoln, Lincoln, NB, 1980.
5. S. S. Mirvish, N-nitroso Compounds, Nitrite and Nitrate: Possible Implications For the Causation of Human Cancer, *Progress in Water Technology*, 8:4/5, p. 195, 1977.

6. H. I. Shuval, et al., Infact Methemoglobinemia and Other Health Effects of Nitrates in Drinking Water, *Progress in Water Technology*, 12, p. 173, 1980.
7. G. A. Guter, *Removal of Nitrate From Contaminated Water Supplies For Public Use: Final Report*, U. S. EPA Report No. 600/S2-82-042, 1982.
8. R. P. Lauch and G. A. Guter, Ion Exchange for Removal of Nitrate From Well Water, *Journal of the American Water Works Association*, 78:5, pp. 83-88, 1986.
9. W. J. Weber, *Physicochemical Processes for Water Quality Control*, John Wiley and Sons, Inc., New York, NY, 1972.
10. D. Clifford and C-C. Lin, Ion Exchange and Membrane Processes for Nitrate Removal from Water, *Proc. National Conference on Environmental Engineering*, Boulder, CO, July 6-8, 1983.
11. M. Ashton, Reverse Osmosis Can Be Cost-Effective, *Public Works*, 117:8, p. 55, 1986.
12. Water Services, Developments in Denitrification, *Water Services*, 90:1084, p. 233, 1986.
13. M. F. Dahab, Potential For Nitrate Removal From Water Supplies Using Biological Denitrification, *Proc. National Conference on Environmental Engineering*, Boston, MA, July 1-3, 1985.
14. Metcalf and Eddy, Inc., *Wastewater Engineering: Collection, Treatment, Reuse*, Second Edition, McGraw-Hill, New York, NY, 1979.
15. U. S. Environmental Protection Agency, *Process Design Manual for Nitrogen Control*, *EPA Technology Transfer*, Washington, D.C., 1975.
16. _____, *Innovative and Alternative Technology Assessment Manual*, Office of Water Program Operation, EPA, Washington, D. C., 1980.

Direct reprint requests to:

Mohamed F. Dahab
Assistant Professor
Department of Civil Engineering
University of Nebraska-Lincoln
Lincoln, NE 68588