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2008

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W. J. Hunter  
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Published in *Nitrogen in the Environment: Sources, Problems, and Management, Second edition*, ed. J. L. Hatfield & R. F. Follett (Amsterdam, Boston, *et al.*: Academic Press/Elsevier, 2008).

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## Chapter 19. Remediation of Drinking Water for Rural Populations

W.J. Hunter

Soil-Plant Nutrient Research Unit, USDA-ARS, Fort Collins, CO, USA

Nitrate is the most common nitrogen contaminant in raw water supplies. In rural areas agricultural activities that involve the use of fertilizers and animal manures are major sources of nitrate contamination. Several processes are currently available that can effectively remove nitrate from raw water. Systems that are suitable for small rural communities include reverse osmosis, ion exchange, and electrodialysis. However, all of these systems move nitrate from raw water and concentrate it in a reject water or brine. Disposal of the reject water can be a major expense as well as an environmental issue. Several emerging systems are under development that convert nitrate to harmless nitrogen gas. These include biological denitrification systems and catalytic systems. The ability of these systems to convert the nitrate to nitrogen gas is a major advantage.

### 1. INTRODUCTION

Ammonia and nitrite can cause water quality problems but it is nitrate that is most often associated with the contamination of drinking water. Nitrate in rural drinking water supplies is a common and growing world-wide water quality problem. Natural sources of nitrate can contaminate groundwater sources (Edmunds and Gaye, 1997) but nitrate-N concentrations that exceed 2–3 mg/L usually indicate that the source is anthropogenic (Foster et al., 1982; Kross et al., 1993; Mueller et al., 1995). Contamination can result from a number of commercial activities (Table 1)

**Table 1.**

Releases of nitrate and nitrite to land and water in 1991 through 1993 by commercial activities.

Major industry	Metric Tons of Nitrate and Nitrite
N-fertilizers	22,766
Industrial inorganics	15,326
Metal ores	2,615
Industrial	2,309

USEPA, 1999.

but it is agricultural activity that has been the main source of nitrate contamination in groundwater (Hallberg and Keeney, 1993; Spalding and Exner, 1993; Wylie et al., 1995; Ator and Ferrari, 1997; Harter et al., 2002; Almasril and Kaluarachchi, 2004). In agricultural areas, runoff or seepage from animal holding pens, septic tanks, and dairy lagoons are key point sources of nitrate contamination. This contamination can damage drinking water supplies, especially when shallow aquifers are the source of the water (Keeney, 1986; Erickson, 1994; Almasril and Kaluarachchi, 2004). Fertilization of row crops is also an important source of groundwater contamination. Since 1950 the use of nitrogen fertilizers on row crops has increased sharply in most countries due to the expansion of intensive crop production, and contamination of groundwater supplies continues to increase as nitrates derived from animal wastes or fertilizers deposited years ago migrate slowly downward through the overlying soils to the aquifer (Gormly and Spalding, 1979; Hiscock et al., 1991; Spalding and Exner, 1993; Green and Shelef, 1994; Hamilton and Helsel, 1995; Schilling and Wolter, 2001), or migrates slowly within the aquifer (Hallberg, 1989). In Germany water samples containing 4.5–11.3 mg/L nitrate-N have shown a steady increase through most of the 20th century, rising from 2% of samples in 1915 to 21% of samples in 1975 and to 23 % of samples in 1989 (Piotrowski and Kraemer, 1998). In England the number of groundwater sites with nitrate levels that exceeded the European drinking water standard increased threefold between 1970 and 1990, and in sections of Denmark and the Netherlands, nitrate in groundwater samples has increased at an annual rate of 0.04–0.29  $\mu\text{g}$  nitrate-N/L (Green and Shelef, 1994).

In Europe the greatest problems occur in the northwest in Belgium, Denmark, Germany, and the Netherlands (Schrama, 1998). Models indicate that soil concentrations of nitrate are sufficiently high such that groundwaters in major parts of these countries are likely to exceed the European drinking water standard, while in France, Italy, and England problems are likely to be more localized (O'Tool, 1998). In rural areas of the United States, where groundwater is the main source of drinking water, it was estimated in 1993 that 2.4% of rural domestic wells exceed the US drinking water standard for nitrate (Benjamin and Belluck, 1994). The problem however is much greater than the national figure suggests because nitrate contamination problems tend to be localized. Drinking water problems, though clearly not limited to that portion of the country, are of greatest concern in the Great Plains (Spalding and Exner, 1993; Nolan et al., 1998). Hamilton and Helsel (1995) surveyed five regions in the United States and found that in central and western Connecticut, 12%; in south-central Kansas, 17%; in Long Island NY, 27%; in the Delmarva Peninsula of Delaware and Maryland, 33%; and in the high plains of Nebraska, 46% of well water samples collected were above the US standard for nitrate in drinking water. In Iowa 18%, and in Kansas 28% of private drinking water wells exceeded the drinking water standard (Kross et al., 1993). A northeastern Colorado survey found that 70% of sampled wells exceeded the US drinking water standard (Schuff, 1992; Wylie et al., 1994; Wylie et al., 1995). Nitrate contamination of drinking water supplies coupled with the difficulty of removing nitrate from water has forced a number of rural communities to abandon their wells and

seek cleaner sources of drinking water (Schuff, 1992; Spalding and Exner, 1993; Lasserre et al., 1999). Nitrate in water causes the abandonment of more drinking water sources than does contamination by toxic chemicals (O'Tool, 1998).

Ingestion of nitrate is a concern because of the effects that nitrite can have on human health (National Academy of Sciences, 1978; Train, 1979; Kross et al., 1993). Nitrate is not very toxic, but its presence in drinking water is a health concern because nitrate can be transformed into nitrite following ingestion. In unweaned infants this transformation of nitrate to nitrite occurs more readily than in older children or adults, and nitrate ingestion can cause methemoglobinemia or blue-baby syndrome, a condition where nitrite binds to hemoglobin. Its presence interferes with the binding of oxygen to hemoglobin and reduces the amount of oxygen that can be transported by the blood (Train, 1979). Methemoglobinemia is intensified by intestinal infections and most cases have occurred with rural water supplies of bad bacteriological quality where nitrate-N concentrations exceeded  $\sim 22$  mg/L. The condition is rare in properly disinfected water systems with nitrate-N concentrations below  $\sim 22$  mg/L (Croll, 1994). In adults, it has been suggested that nitrosamines may form following nitrate ingestion (National Academy of Sciences, 1978) and animal studies have shown that nitrosamines are potent carcinogens. Theoretically, nitrite might react with amines in the intestine to form nitrosamines, though intestinal conditions do not favor the reaction (Croll, 1994). A number of studies have investigated the relationship between nitrate in drinking water and cancer but results have been conflicting with some studies finding a correlation and others failing to find any correlation (Croll, 1994). Nitrate in water may indicate other water quality problems. If the nitrate is coming from human or animal wastes then microbial contamination may also be present.

In the United States the USEPA (1973) recommends that water used for human consumption contain no more than 10 mg/L nitrate-N and in Canada (Liem et al., 1996) the recommended guideline is 45 mg/L as nitrate ( $\sim 10$  mg/L nitrate-N). In Europe the maximum concentration allowed by the Drinking Water Directive (98/83/EC) is 50 mg/L as nitrate (11.3 mg/L nitrate-N). The World Health Organization recommends 50 mg/L nitrate as the maximum long-term exposure though, under its guidelines, short term exposure to amounts in excess of 50 mg/L as nitrate are acceptable (Croll, 1994). The National Academy of Sciences-National Research Council (Bruning-Fan and Kaneene, 1993) recommends that drinking water supplied to farm animals contain no more than 100 mg/L nitrate-N. While some feel that the current water quality standards are too conservative others disagree (Environmental Working Group, 1996; Avery 1999; L'hirondel and L'hirondel, 2002). Possible adverse health effects have been attributed to the consumption of waters that were within the current water quality standards for nitrate (DeRoos et al., 2003; Brender et al., 2004).

## 2. CURRENT PROCESSES

At the present time methods for removing nitrate from drinking water include reverse osmosis, electrodialysis, ion exchange, and distillation. Carbon adsorption

filters, mechanical filters of various types, and standard water softeners do not remove nitrate-N.

### 2.1. Reverse Osmosis

This process, as the name implies, is the reverse of osmosis. With reverse osmosis water pressure is used to force water through a thin-film composite or cellulose triacetate membrane (Harries et al., 1991; Kunz, 1997). In the process water moves from the more concentrated solute side of the membrane to the less concentrated solute side of the membrane. The pressure used to drive the process must be sufficient to overcome the osmotic pressure; thus, the higher the concentration of salts in the supply and reject waters, the higher the water pressure must be to operate the system. Under pressure, molecules of water dissolve into the membrane and pass through the membrane to the permeate side by the process of diffusion. Dissolved ions, such as salts, that are charged are likely to be rejected by the membrane. Contaminants such as nitrate, nitrite, ammonia, and other salts cannot dissolve into the membrane and remain on the concentrate side of the membrane. Uncharged molecules, such as organic contaminants are more likely to pass through the membrane. Thus reverse osmosis produces a permeate water with very low inorganic mineral content, and a brackish reject concentrate with high inorganic mineral content. Reverse osmosis works well with nitrate and nitrite. About 96–98% of monovalent and 98–99% of divalent ions are rejected by the system (Harries et al., 1991). With small home systems about 80–90% of nitrate is rejected (Kamrin et al., 1991; Olson et al., 1994). Better rejection of contaminants is achieved at higher pressures (Kamrin et al., 1991). Calcium can clog a reverse-osmosis membrane and systems should not be used with water that contains calcium at levels that exceed ~180 mg/L (Harries et al., 1991; Kunz, 1997). Pretreatment of the raw water with nanofiltration can reduce the amount of calcium present in the raw water (Bohdziewicz et al., 1999). Disposal of the reject water can be a problem with reverse osmosis systems. The reject water or brine from systems used to cleanse nitrate from drinking water would contain the rejected nitrate and other rejected salts. With community systems, the concentration and disposal of rejected salts can represent as much as 60% of the cost of operation of systems, such as reverse osmosis, that use physicochemical processes to separate nitrates from groundwater (Green and Shelef, 1994).

Reverse osmosis can be used for community or home water systems. In terms of water usage home systems are inefficient; 1–9 L of water will be rejected by the system for each liter of clean water produced (Kamrin et al., 1991; Kunz, 1997). With larger community systems about 0.33 L of water is rejected for each liter produced (Harries et al., 1991). Water pressure has an important impact on water use efficiency (Kamrin et al., 1991). Systems, like those that might be used by a small rural community, may require 1,400 kPa of water pressure when used with a supply water containing dissolved solids at a concentration of 1,000 mg/L and water pressures of up to 10,000 kPa are required for water with a dissolved solids concentration

of 35,000 mg/L (National Research Council, 1997). Residential systems that produce only 10–15 L of water a day for drinking and cooking may operate with as little as 280 kPa of water pressure (Kunz, 1997).

Reverse osmosis units used in homes may fit under a sink or may be installed on top of a counter. Such systems produce from 8 to 40 L of water per day that can be used for drinking or cooking (Kamrin et al., 1991; Kunz, 1997). The units usually consist of: (i) a sediment filter; (ii) a reverse-osmosis membrane; (iii) a small storage tank; and (iv) an activated carbon filter. The activated carbon filter used with home systems would remove organic contaminants that might have passed through the reverse osmosis membrane. The type of membrane used in the system, thin-film composite or cellulose triacetate, influences water use efficiency. Thin-film composite membranes are more efficient than cellulose triacetate membranes but are degraded by chlorine (Kamrin et al., 1991; Kunz, 1997). A prefilter can be used to protect the thin-film composite membrane from chlorine.

## 2.2. Electrodialysis

This is a water treatment process that produces demineralized water from water that has a high salt content. The process is suitable for small communities. For this process an electric current is used to force ions through a pair of semipermeable membranes, separating the ions from the contaminated supply water that does not pass through the membranes. The system employs two types of flat sheet membranes that are arranged in an alternating pattern; one membrane is permeable to cations and the other is permeable to anions. Contaminated water is cleansed of anions and cations as it flows between the two membranes (Figure 1). Feed waters supplied to electrodialysis units should have a turbidity that is less than 2.0 nephelometric turbidity units. In addition hydrogen sulfide and manganese levels should be less than 0.3 mg/L each and free chlorine levels should be less than 0.5 mg/L (Conlon, 1990). With electrodialysis systems about 70–85% of the water that is supplied to the system is available for use as low nitrate water (Harries et al., 1991). The other 15–30% of the water will contain high levels of nitrate and other ions. This concentrated reject water presents disposal problems similar to those noted for reverse osmosis. Since water cleansed by an electrodialysis system does not pass through a membrane, microorganisms and suspended particles are not removed during the electrodialysis step and another means of filtration must be provided to remove these water contaminants.

A similar process, electrodialysis reversal, periodically reverses the polarity of the electrodes reversing the movement of the ions. During the polarity reversal, an automatic valving arrangement reverses the water flow in order to prevent the mixing of cleansed and contaminated waters. The reversal reduces the buildup of deposits on the membranes and prolongs membrane life. Accumulations of deposits that can foul the membranes are a problem with electrodialysis systems (Osmonics, 1992; National Research Council, 1997).

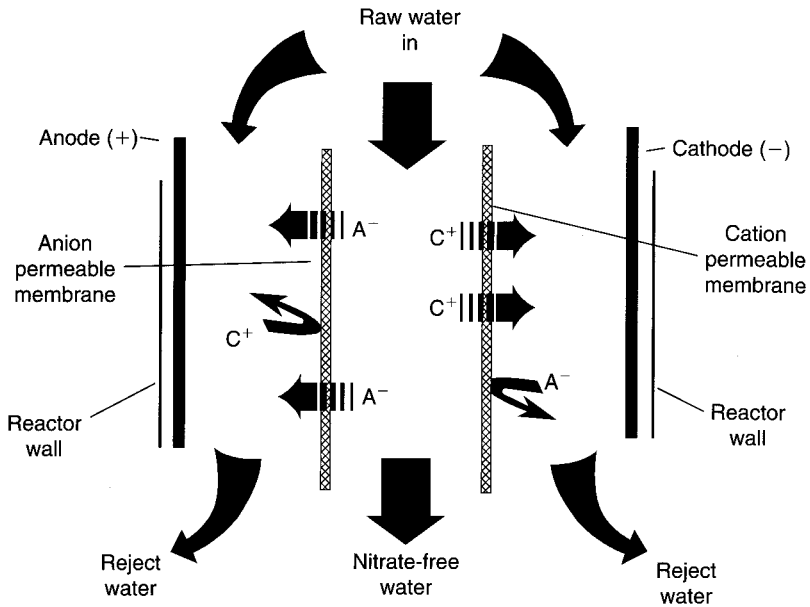


Figure 1. Electrodialysis membrane arrangement. As contaminated supply water flows through the center of the cell, between the two selective membranes, anions ( $A^-$ ) such as nitrate and nitrite move through the anion permeable membrane toward the anode while cations ( $C^+$ ) such as ammonia move through the cation permeable membrane toward the cathode. Water with greatly reduced ionic content exits from the center cell and contaminated reject water concentrates in the left and right cells.

### 2.3. Ion Exchange

Ion exchange can be used to supply nitrate-free water to households, animal operations, or communities. For this process charged beads are used to remove ionic contaminants from flowing water. There are two basic types of beads. Anion exchange beads are made from resins that have positive charges and cation exchange beads from resins that have a negative charge. Nitrate and nitrite, which have a negative ionic charge, will bind to the positively charged sites on the anion exchange beads. Thus water flowing through a bed composed of anion exchange beads would be cleansed of nitrate, nitrite, and other negatively charged ions. Ammonia, which carries a positive ionic charge, will not bind to an anion exchange bead but will bind to the negatively charged sites on a cationic exchange bead. Thus a cation exchange bed would be required to remove ammonia and other positively charged ions from water. Water that is nearly free of both anions and cations can be produced by flowing water sequentially through both types of exchange beds or by



flowing water through a mixed bed reactor that contains both anionic and cationic exchange beads.

Ion exchange reactors stop removing ions and must be regenerated when most of the charged sites on the beads become occupied. With anion exchange beads, hydroxide ions from a sodium hydroxide solution or chloride ions from a sodium chloride solution are used to displace the bound anions. With cation exchange beads, regeneration involves the use of protons from an acid solution or sodium or potassium ions. The waste solution produced during regeneration will contain used regenerate solution and high concentrations of the ions that were removed from the water. It is more difficult to dispose of ion exchange brine than to dispose of reverse osmosis or electrodialysis reject water because of the counter ions that are added during the ion exchange regeneration process (Cevaál et al., 1995). Disposal of the waste solution produced during regeneration can be a difficult and costly process (Croll, 1994; Green and Shelef, 1994; National Research Council, 1997).

During operation, water use efficiency with ion exchange reactors is almost 100%. Ion exchange units have no reject water; all of the water that enters an ion exchange reactor becomes treated water. The only losses that occur are during the regeneration process and the volume used here would represent 0.7–2% of the volume of treated water (Green and Shelef, 1994).

## **2.4. Distillation**

Distillation removes a wide range of contaminants from drinking water. The process cleanses raw water of contaminants by heating the water until it turns to steam. The steam is then condensed back to water in a condensation coil and purified water is collected in a separate vessel. Nonvolatile contaminants that were present in the raw water will remain in the boiler vessel and are periodically flushed into the septic or sewer system. The condensed water that collects in the second vessel is cleansed of nonvolatile contaminants. The process is an effective method for removing inorganic salts such as nitrate and nitrite from water, but this process may not remove some volatile organic and inorganic compounds.

Maintenance of a distillation system involves periodic cleaning of the boiler side of the unit to remove contaminants that build up over time. The amount of energy required by the unit and the small volume of water produced limits distillation to point-of-use applications such as home use or use in some commercial markets. Units may be mounted on the wall or placed on the countertop. Distillation removes beneficial minerals from the water and water produced by distillation may have a flat taste. The costs of operating a home distillation system may be higher than those with some other forms of home treatment systems (Kamrin et al., 1990).

## **2.5. Abandonment and Blending**

Abandonment of an existing contaminated drinking water supply is not a form of remediation but is an approach that is often used by rural households and communities to obtain drinking water that meets the EPA's guidelines for nitrate. With

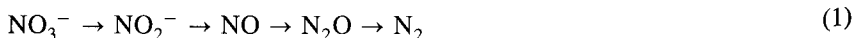
small water systems, such as those that are often used in rural areas, abandonment may be less expensive than attempting to remediate a contaminated water source (Nugent et al., 1993; National Research Council, 1997). Abandonment would include importing water from a distant source as well as the drilling of a new well or wells into a less contaminated aquifer. A new well may be drilled into a deeper or adjacent aquifer that is less contaminated, or the well may be placed in the same aquifer but distant from the source of contamination (i.e., a livestock pen or septic tank). Water from the less contaminated well may then be used directly or mixed with contaminated water to produce a blended-water that is acceptable for drinking. The use of bottled water purchased from a store or from a bottling company may also be considered a form of abandonment. This approach might be considered when the primary concern is for a short period of time such as water for infant food and drinking.

### 3. EMERGING TECHNOLOGIES

Several technologies are being investigated or proposed as methods for removing nitrate from drinking water. These emerging technologies include biological and abiotic denitrification, as well as several catalytic approaches.

#### 3.1. Biological Denitrification

Biological denitrification has been used to remove nitrate from wastewaters for many decades and in recent years the idea of using this process to remove nitrate from drinking water has gained ground, especially in Europe. Drinking water can be denitrified in above-ground bioreactors or *in situ* while it is still below ground. *In situ* treatment may be the most economical (Streile et al., 1991). Biological denitrification is a microbial respiratory process where facultative and anaerobic microorganisms use nitrate, rather than oxygen, as an electron acceptor for respiration. Many soil bacteria are able to carry out this process and are likely to do so in soils and waters where nitrate and a suitable electron donor (usually a carbon substrate) are present but oxygen is limiting. Naturally occurring microbial denitrifiers are ubiquitous in soil and water. Facultative microorganisms can use either nitrate or oxygen as an electron acceptor for respiration, and generally, if oxygen is available facultative microorganisms will use the oxygen first and then nitrate. It is advantageous to use the oxygen first because oxygen respiration yields about 20% more energy than nitrate respiration. Often, when oxygen is present respiratory denitrification for energy generation is inhibited (Carter et al., 1995). There are some microorganisms that carry out denitrification under aerobic conditions and utilize both oxygen and nitrate simultaneously (Robertson and Kuenen, 1984; Robertson et al., 1989; Robertson and Kuenen, 1990; and others). The steps involved in respiratory denitrification are:



Not all denitrifiers are able to reduce nitrate all the way to nitrogen gas, and nitrite, nitric oxide or nitrous oxide may accumulate when pure cultures of these microorganisms are incubated under denitrifying conditions (Hiscock et al., 1991). In nature a consortium of microorganisms would often be involved in the process and nitrogen gas would normally be the principal end product. However, environmental conditions such as nutrients, pH, or electron donor availability may influence the reduction process and may cause intermediates to accumulate. For example, nitrite may accumulate in large amounts when the amount of phosphate is inadequate (Kim et al., 2002; Hunter, 2003). While a number of factors affect the denitrification process it is usually the availability of an electron donor that limits the rate at which denitrification proceeds, and the addition of a carbon source or other electron donor to contaminated water often will stimulate denitrification (Myrold and Tiedje, 1985; and others).

### 3.2. *Ex Situ* Biological Reactors

Above-ground bioreactors using biological denitrification may be suitable for community water systems in rural areas. A system (Figure 2) would consist of one or more large tanks partially filled with a physical support for the denitrifying biomass. These tanks are where the denitrification process takes place and they are fed the raw water, substrate, and nutrients needed to drive the process. The effluent water from the tank(s) would contain much less nitrate than the influent water but would contain high numbers of bacteria, suspended solids, organic matter content, and turbidity. These waters also would be low in dissolved oxygen (Dahab and Sirigina, 1994; Hunter and Follett, 1997). These are water quality problems

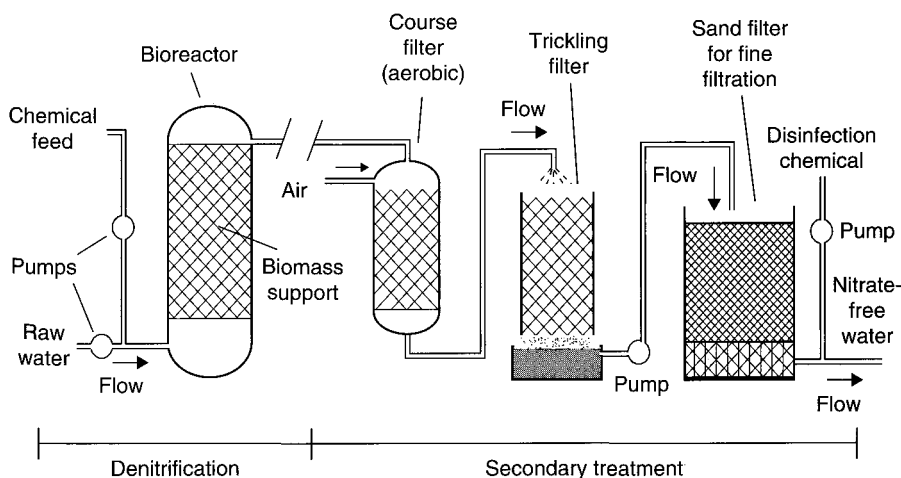


Figure 2. Flow diagram of a hypothetical biological denitrification reactor showing the major system components. Systems may have more than one bioreactor and components of the secondary treatment process may be combined into a single unit.

that must be corrected before the water can be consumed. Secondary treatment to improve the quality of the denitrified water would involve filtration, aeration, and disinfection to achieve the desired water quality (Roennefahrt, 1986; Dahab and Sirigina, 1994; Green and Shelef, 1994; Hunter and Follett, 1997; Silverstein and Carlson, 1999).

In the US a commercial-sized above-ground heterotrophic denitrification reactor was constructed in the town of Wiggins in rural eastern Colorado, USA. The system consisted of two upflow bioreactors, a single roughing filter that served to both filter and aerate the denitrified water, and a slow sand filter. Influent water was pumped into the first bioreactor at a rate of 38 L/min and contained ~20 mg/L nitrate-N mixed with a high-fructose corn syrup (52% fructose and 48% glucose) and phosphate. The bioreactors were 2.7 m high, 0.9 m in diameter and contained a buoyant (specific gravity = 0.96) and highly porous (94%) cylindrical polypropylene support material. Periodic air scour was used to remove excess microbial biomass. Effluent from the denitrification bioreactors flowed to a roughing filter that was 2.1 m high, 0.8 m in diameter and contained the same polypropylene support as the bioreactors but was operated as a downward-flow aerobic reactor. A slow sand filter followed the roughing filter. The system was operated for about 7 months as a demonstration project and yielded an oxygenated (3.8 mg/L) product water with acceptable turbidity (0.4 NTU), dissolved organic carbon (3.1 mg/L), and nitrate-N (4.3 mg/L) content (Silverstein and Carlson, 1999).

In Europe a number of pilot and demonstration systems have been constructed. The first above-ground denitrification reactor was installed in France in 1983 with later installations in Germany and Italy (Green and Shelef, 1994). Systems have been both fixed bed and fluidized bed reactors and have employed a number of different biomass supports. A partial listing of systems is presented in Table 2. Ethanol, methanol, acetate, cotton, hydrogen, sulfur, and natural gas all have been used or proposed as substrates for microbial denitrification processes (Green and Shelef, 1994; Houbroun et al., 1999; Rajapakse and Scutt, 1999; Soares et al., 2000; Rocca et al., 2005) with phosphate normally added as a nutritional supplement. Problems with the systems include the formation of a product water that is low in dissolved oxygen and high in bacteria and bacterial products. Also, if the system is operated with too much carbon substrate then residual substrate may be present in the finished water, but if too little substrate is supplied then nitrite may be present. Secondary treatment and disinfection can oxygenate and remove bacteria from the finished water. Careful monitoring of the amount of nitrate entering the system and metering of the amount of carbon substrate added is required to prevent the presence of carbon substrate and nitrite in the finished water.

Mansell and Schroeder (1999) conducted a series of studies with a membrane reactor that produced effluent water that was cleaner than that produced by other primary denitrification reactors. In their bench scale reactor a polytetrafluoroethylene membrane with a pore size of 0.02  $\mu\text{m}$  and porosity of 50% was used to separate the reactor into two sections or flow channels (Figure 3). A suspended culture of

**Table 2.**

Examples of configurations and electron donors used in denitrification reactors.

Biomass Support	Electron Donor	Nitrate Removed (kg N/m <sup>3</sup> /day)	Scale	Reference
Buoyant polypropylene	Corn syrup	0.3	2.28 m <sup>3</sup> /h	Silverstein and Carlson, 1999
Rotating bed	Acetic acid	1.8–9.8	Pilot	Mohseni-Bandpi et al., 1999
Sand fluidized bed	Ethanol/acetic acid	4.6	Pilot	Green and Shelef, 1994
Biolite fixed bed	Ethanol	1	50 m <sup>3</sup> /h	Green and Shelef, 1994
Clay fixed bed	Ethanol	1.2	400 m <sup>3</sup> /h	Rogalla et al., 1990
Polystyrene fixed bed	Methanol/acetic acid/Ethanol	1.4	800 m <sup>3</sup> /h	Roennefahrt, 1986
Sand fluidized bed	Methanol	5.4	Pilot	Green and Shelef, 1994
Sand moving bed	Methanol	2.7	11 m <sup>3</sup> /h	Green and Shelef, 1994
Sand fluidized bed	Methanol	3.5	250 m <sup>3</sup> /h	MacDonald, 1990
Fixed bed	Sulfur	0.2–0.4	Laboratory	Flere and Zhang, 1999
Fixed bed	Thiosulfate	1.5	Pilot	Trouve and Chazal, 1999
Fixed bed	Hydrogen	0.25	100 m <sup>3</sup> /h	Green and Shelef, 1994

denitrifying bacteria, from a culture vessel, was pumped by one side of the membrane, and the raw water to be denitrified was pumped by the other side of the membrane. The pore size of the membrane did not allow the bacteria to enter the raw water but nitrate in the raw water was able to flow through the membrane and was converted to nitrogen gas by the bacterial suspension. Methanol, the carbon source, and phosphate were supplied to the culture vessel. The raw water supplied to the reactor contained 20 or 30 mg/L nitrate-N and the reactor was able to reduce the nitrate in the water by

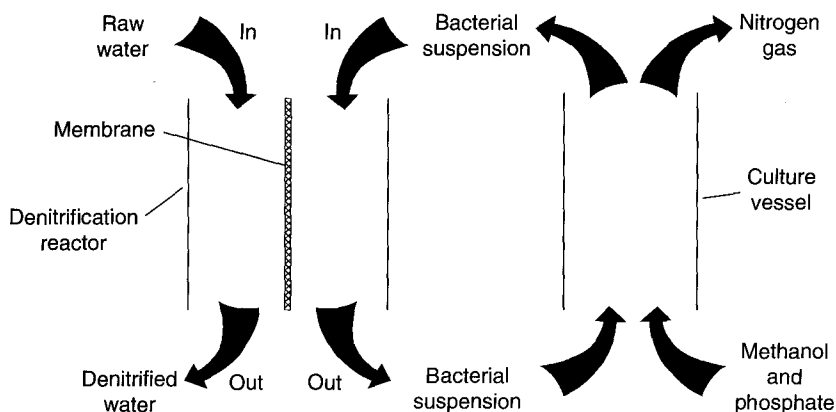
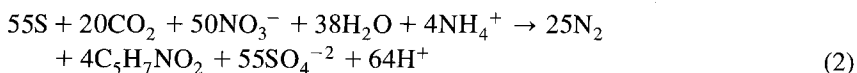


Figure 3. Schematic of a membrane denitrification reactor. Raw water is cleansed of nitrate as the water flows by one side of a porous membrane and a suspended culture of denitrifying bacteria flows by the other side of the membrane (Mansell and Schroeder, 1999).

41–72%. The system should produce water with fewer bacteria than other primary biological denitrification reactors.

Laboratory and pilot scale studies show that autotrophic denitrification using sulfur, rather than an organic carbon substrate, as an electron donor also can be used to remove nitrate from pumped ground or surface water. The reaction proceeds according to the following equation (Batchelor and Lawrence, 1978):



The water would be treated in denitrification reactors (Schippers et al., 1987; Kruithof et al., 1988; Lampe and Zhang, 1997; Flere and Zhang, 1999; Kimuraa et al., 2002) but contaminated surface water ponds might be treated by adding sulfur and limestone directly to the pond (Lampe and Zhang, 1997). The limestone serves as a buffer. One reported advantage of this system is the low amount of biomass produced (Lampe and Zhang, 1997; Flere and Zhang, 1999). The accumulation of microbial biomass can block the flow channels in a denitrification reactor decreasing its ability to remove nitrate.

Electrodes also can be used to serve as an electron donor for biological denitrification and this process is used in biofilm-electrode reactors (Dries et al., 1988). In these reactors autotrophic denitrifying microorganisms are immobilized on the surface of a cathode. Hydrogen is produced by the electrolysis of water and may serve as the electron donor, but the amounts of hydrogen produced are too small

to account for the amount of nitrate reduced suggesting that the electrode itself is the main electron donor (Gregory et al., 2004; Park et al., 2005). The process also may be useful for the remediation of groundwaters contaminated with chlorinated organic compounds or metals.

Above-ground denitrification reactors, because of their high installation costs and complexity of operation, are not suitable for home use though such units might be used by small rural communities with trained operators. Costs, however, might still be an issue. Green and Shelef (1994) compared biological denitrification with ion exchange and concluded that the two had similar costs of operation but that the biological denitrification unit was 2 to 3 times more expensive to install and more complex to operate. Tannehill et al. (1997) estimated the potential cost of removing nitrate from groundwater in six small communities in rural Nebraska and concluded that ion exchange would be the most cost-effective method for all six communities. Above-ground denitrification was estimated to be slightly more expensive than ion exchange at the present time though it was suggested that either of these two processes could become the best treatment method in the near future. Reverse osmosis, largely because of the cost of disposal of the waste brine produced, was predicted to be the most expensive option for all six communities.

### 3.3. *In Situ* Biological Denitrification

Several research and demonstration projects have looked at different approaches and schemes to remove nitrate from contaminated groundwater before it is pumped to the surface. It is envisioned that some approaches will offer an inexpensive method for removing nitrate from contaminated groundwater (Streile et al., 1991; Green and Shelef, 1994). Costs are reduced because less equipment and less oversight are needed for these processes. *In situ* treatment of groundwater, which uses part of the aquifer as a denitrification reactor to remove nitrate, can also provide a portion of the secondary treatment. Secondary treatment processes, which include the removal of organic residues, particulate filtration, oxygenation, and disinfection, would be required (Dahab and Sirigina, 1994; Hunter and Follett, 1997). Much of the secondary treatment can take place in the aquifer provided that distances and retention times are adequate (Green and Shelef, 1994).

Denitrification is a natural process that takes place in soils, surface waters, and groundwaters. Microorganisms capable of removing nitrate from water by denitrification are naturally present in soil and water. However, in soils that are below the root zone, the activity of denitrifying microorganisms is often severely restricted because of the absence of an appropriate electron donor. Most *in situ* treatment processes involve injecting an electron donor, usually a soluble carbon source, into the contaminated aquifer.

One approach simply involves the use of a single recharge well for the injection of a carbon substrate and a single pumping well to extract the denitrified water. This approach was used to remove nitrate from a gravel aquifer in the Netherlands. Groundwater, containing 18.1 mg/L nitrate-N, was pumped from the ground at a

rate of  $33\text{ m}^3/\text{h}$ , mixed with methanol ( $49\text{ mg/L}$ ) and injected back into the aquifer at a rate of  $20\text{ m}^3/\text{h}$  for 22 days. During this time the nitrate-N content of the water was reduced by 30%, although both an accumulation of nitrite and a decrease in the hydraulic conductivity between the two wells was observed (Hiscock et al., 1991). Another approach involves the use of small diameter injection wells arranged in a circle or daisy-pattern around a large diameter uptake well. The carbon source, often ethanol, is diluted with water from the uptake well and the mixture injected into the aquifer to provide an underground denitrification zone within the aquifer. A major portion of the water flowing to the uptake well would flow through this area and nitrate in the water would be removed by microbial activity as the water passes through this zone. In a study in France about 70% (Hamon and Fustec, 1991) and in a study in the United States about 16% of the nitrate was removed (McMahon et al., 1998) by this process, although aquifer plugging was a major problem in both studies. In contrast, Janda et al. (1988) had no problems with aquifer plugging in a full-scale study in a sand and gravel aquifer. Denatured ethanol was used as the carbon source to remove  $\sim 40\%$  of the nitrate from water containing  $22.6\text{ mg/L}$  nitrate-N during this 141 day study. A modification of the daisy-pattern, the "Nitredox" method developed by Braester and Martinell (1988), uses a second set of wells arranged in a concentric circle within the outer ring of injection wells. The outer wells are used for the injection of the carbon substrate to establish a denitrification zone and the wells in the inner circle are used to inject aerated water to establish a zone for secondary water treatment and to oxygenate the water. A "Nitredox" system consisting of a pumping well, eight oxidation wells at a radius of 10m, and 16 injection wells at a radius of 18m was used to reduce groundwater nitrate-N in a gravel aquifer in Austria from  $22.6$  to  $5.7\text{ mg/L}$  using methanol as the substrate. No problems with aquifer plugging were reported.

A simple approach for *in situ* denitrification involves the use of insoluble substrates to form denitrification walls or barriers. The barriers are placed between the source of nitrate contamination and the point of uptake (Figure 4). The barriers are constructed by digging a trench and backfilling it with a mixture of substrate and fine gravel. Thus the substrate is added when the barrier is constructed and the need for much of the equipment associated with above-ground denitrification reactors is eliminated. Nitrate is removed via denitrification when contaminated water flows through the barrier. Sawdust is an inexpensive substrate that has been shown to work well in denitrification barriers (Robertson and Cherry, 1995; Schipper and Vojvodic-Vukovic, 1998, 2001; Robertson and Anderson, 1999). Denitrification barriers should have a functional life of many years. Robertson and Cherry (1995) used a sawdust denitrification wall that contained 2% carbon to remove nitrate from a sewage leach field and estimated that it would last the 20 year design life of the leach field under the *in situ* conditions at the site. Blowes et al. (1994) estimated that a reactor that contained 5% carbon (as cellulose) might not require additional substrate for several decades. A number of organic and inorganic substrates could be used in denitrification barriers and the best choice might depend on what is



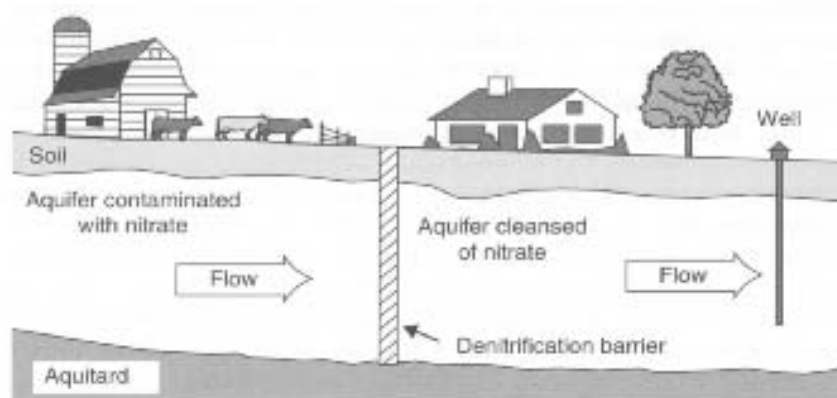


Figure 4. Hypothetical use of a denitrification barrier to remove nitrate from groundwater contaminated by farm animals.

locally available. Crop residue, mulch, compost, newspaper, cotton, sulfur, glycerol polylactate, and innocuous oils all have been shown to support denitrification and might be used in denitrification or in other types of remediation barriers (Blowes et al., 1994; Volokita et al., 1996a, b; Hunter et al., 1997; Lampe and Zhang, 1997; Flere and Zhang, 1999; Robertson et al., 2000).

A major limitation and expense associated with denitrification barriers is the digging and backfilling of the trench. The technology exists to dig deep trenches, but the problem is the cost associated with the trenches. Shallow trenches can be dug quickly and at relatively low cost but deeper trenches are much more difficult to dig and are considerably more costly (Gavaskar et al., 1998). The need for a trench can be eliminated by the use of an injectable substrate, and if the substrate is immiscible in water then the barrier that is created can be a stationary one. Glycerol polylactate is one example of a compound that can be injected into the aquifer as a slow release carbon substrate for the remediation of a number of groundwater contaminants. Glycerol polylactate is a proprietary commercial product sold as "Hydrogen Release Compound" (Regenesis, 2004). In addition to glycerol polylactate, vegetable oils and other edible oils and fats can be injected into an aquifer as a slow release carbon substrate for remediation. Vegetable oils are plentiful, inexpensive, nontoxic (Hunter and Follett, 1997), have high energy content, and are readily degraded by soil microorganisms (Hunter and Follett, 1994; Hunter et al., 1997) making them an excellent slow release substrate for use in remediation barriers. Soybean oil has been used to form stationary remediation barriers that are effective at removing nitrate, chlorate, perchlorate, selenite, and chlorinated organic compounds from groundwater (Hunter and Follett, 1994; Hunter et al., 1997; Hunter, 1999; Lee et al., 2000; Zenker et al., 2000; Lee et al., 2001; Hunter,

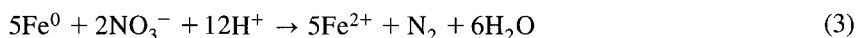
2002; Hunter and Kuykendall, 2005). Unmodified oil or emulsified oil may be used for remediation. When unmodified soybean oil is used multiple injections are used to create multiple pools of oil within the aquifer that slowly release carbon into the groundwater (Boulcault et al., 2000; Wiedemeier et al., 2001). Alternatively, multiple injections of emulsified oil may be used to create a permeable barrier (Lee et al., 2001). Both procedures have been successful but the trend appears to favor the use of emulsified oil. The oil emulsion may be created on site using commercial emulsifiers to blend the vegetable oil with water, detergents, and other nutrients or the emulsions may be purchased from a supplier. Several formulations based on soybean oil are available as commercial products. The size of the emulsion droplet is an important factor that influences the stability and movement of the emulsion within the aquifer matrix. If the droplets that make up the emulsion are too large the movement of the oil will be restricted (Coulibaly and Borden, 2004). Some movement is desired in order to create a functioning barrier (Hunter, 2005). *In situ* systems utilizing vegetable oil emulsions are proving to be a useful technology for the treatment of contaminated groundwater.

### 3.4. Abiotic *In Situ* Denitrification

Abiotic processes can be used *in situ* to remove nitrate from groundwater. *In situ* iron walls, composed of zero-valent iron mixed with sand or gravel, have been used to remove trichloroethene and other chlorinated organic compounds from groundwater. Zero-valent iron is a strong reducing agent that can displace the chloride from chlorinated organic compounds via a mechanism that is not completely understood. For example, when groundwater contaminated with trichloroethene flows through an iron wall, the iron becomes oxidized and the trichloroethene becomes dechlorinated to yield ethene and chloride as the primary products (Gavaskar et al., 1998). Zero-valent iron can serve as an electron donor to reduce nitrate (Szabo and Bartha, 1952; Young et al., 1964; Huang et al., 1998; and others). The mechanism may be due to the direct reduction of nitrate by  $\text{Fe}^0$ , or due to its indirect reduction by hydrogen, derived from a proton (Huang et al., 1998; Chew and Zhang, 1999). For the reaction to proceed at a significant rate, the pH must be low (Huang et al., 1998; Chen et al., 2005) or hydrogen must be supplied (Siantar et al., 1996). Huang et al. (1998) reported that pH is a critical factor in the reduction of nitrate by zero-valent iron and that significant reduction does not occur at pHs higher than  $\sim 5$ . In addition ammonia is a primary end product of the reaction (Cheng et al., 1997; Huang et al., 1998; Liao et al., 2003; Chen et al., 2005). In contrast, Choe et al. (2000) was successful at converting nitrate to nitrogen gas. The production of ammonia and requirement for a low pH would be major drawbacks in the use of the iron wall technology for drinking water remediation.

A modification of the iron wall process involves the coupling of the zero-valent iron reaction with electrokinetics. Electrokinetics is an electrical process where two electrodes are placed in the ground and a low-intensity direct current applied. The applied current causes the migration of ionic species in the soil (USEPA, 1995) and

the generation of  $H^+$  ions at the anode. Chew and Zhang (1999) conducted laboratory scale studies coupling electrokinetics with an iron wall located next to the anode. The system removed 93–96% of the nitrate from an artificial groundwater contained in a soil/sand column. Nitrogen gases (46–50%) and ammonia (~45%) were the principal end products. They suggest that the reaction to nitrogen gas may proceed according to the following equation:



Considerable refinement of this process would be needed before it could be used to remediate drinking water.

### 3.5. Catalytic Systems

A bimetallic catalyst with hydrogen gas as the reducing agent and one that uses immobilized enzymes with reducing power supplied by an electric current represents two of the more developed catalytic approaches. A 5% rhodium on carbon catalyst (Reddy and Lin, 2000) has been evaluated as a means of removing nitrate from water as have photocatalysts (Mori et al., 1999). These systems might be well suited for small point-of-use units such as home systems, as well as large scale operations. Advantages that these systems offer are the ability to produce water that is free of nitrate but that is not devoid of other beneficial minerals, and the ability to remove nitrate from the environment by converting the nitrate to nitrogen gas. Catalytic systems resemble denitrification systems in that they would not produce a nitrate-laden wastewater. This is a major advantage that these systems have over water treatment processes such as reverse osmosis, electrodialysis, and ion exchange that simply separate nitrate from the water stream and produces a waste that can be difficult to discard in an economically and environmentally acceptable manner. Also, catalytic systems, once fully developed, may be easier to operate and maintain than biological denitrification systems that depend on a living consortium of microorganisms to reduce the nitrate.

Bimetallic catalysts use supported palladium catalysts with copper or tin serving as the catalytic promoter and hydrogen as the source of electrons to reduce nitrate to nitrogen gas. The reduction of nitrate ( $NO_3^-$ ) to nitrogen gas ( $N_2$ ) involves its stepwise reduction with nitrite ( $NO_2^-$ ), nitric oxide (NO), and nitrous oxide ( $N_2O$ ) forming as intermediate products (Wärnå et al., 1994). Control problems exist with systems based on bimetallic catalysts in that they may take the reduction reaction too far and produce ammonium, or may fail to completely reduce the nitrate to nitrogen gas and produce nitrite instead (Hörold et al., 1993). Both of these products are more toxic than nitrate. The rhodium catalyst resembles the bimetallic catalysts in that it also requires hydrogen, an electric current, and follows the same reaction path. In studies with this catalyst only nitrate and nitrite were

monitored. Nitrate was observed to disappear with time and nitrite was not detected as a reduction product (Reddy and Lin, 2000).

UV light, with or without a catalyst, can be used to reduce nitrate. Silver or platinum in combination with titanium oxide (Kudo et al., 1987; Ohtani et al., 1988), zinc sulfate (Ranjit et al., 1994), and hollandite (Mori et al., 1999) have been used as photocatalysts to convert nitrate to ammonia in the presence of methanol or propanol. Gonzalez and Braun (1996) observed that a mixture of nitrate and methanol would react under UV light to yield nitrate, ammonia, and carbon dioxide. Unfortunately, the final nitrogen product of these systems is ammonia and not nitrogen gas.

Biological catalysts use enzymes immobilized on a matrix that can be packed into small reactors or columns to catalyze the reduction of nitrate to nitrogen gas (Holton, 1996). The steps and intermediates involved are the same as those given above for respiratory denitrification. Three enzymes are involved in the reduction of nitrate to nitrogen gas. These are nitrate reductase, nitrite reductase, and nitrous oxide reductase. Nitrate reductase reduces nitrate to nitrite, nitrite reductase reduces nitrite to nitrous oxide, and nitrous oxide reductase reduces nitrous oxide to nitrogen gas. The enzymes are bound to a support matrix and are placed into a reactor. The first reactor contains a support matrix with bound nitrate reductase and the second part of the reactor contains support matrix with bound nitrite reductase and nitrous oxide reductase (Figure 5). The two reactors are connected in sequence and as contaminated water flows through these reactors nitrate in the water is reduced to nitrite by the first reactor and then to nitrogen gas by the second reactor. An electric current provides reducing energy for the process (Mellor et al., 1992; Holton, 1996). The system, currently in the development stage, is being promoted as a system for home and farm use (Campbell and Campbell, 2000). Problems that must be overcome before the system can be marketed include improving the stability of the enzymes and reducing the cost of production (Holton, 1996).

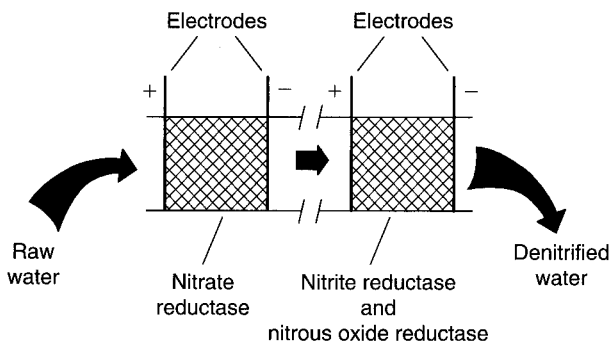


Figure 5. Schematic of a denitrification reactor that utilized enzymes to reduce nitrate to nitrogen gas (Campbell and Campbell, 2000).

#### 4. CONCLUSIONS

Reverse osmosis, ion exchange, and distillation can be used in home systems to remove nitrate from raw water. Reverse osmosis and distillation are small point-of-use systems that provide water for cooking and drinking. With these systems the small volume of reject water generated would be flushed to the septic system and would not normally present a disposal problem. A more important concern might be the volume of water used by some of the systems. Some emerging systems might prove suitable for home or farm use in the future. Biobarriers might be used to protect a well from a contaminated aquifer or to protect an aquifer used for drinking water from a source of nitrate pollution. Above-ground denitrification reactors might be used to provide nitrate-free water to rural communities in the not too distant future.

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