Treatment Technologies for Today and Tomorrow

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Nitrate in drinking waters poses human health risks, and nitrate contamination of groundwater has become widespread in the United States. In a study of more than 40 states, nitrate was the most frequently reported groundwater contaminant of concern (Fetter, 1993; USEPA, 1990). For example, in the Phoenix area (see map below), more than 40 percent of the 245 wells sampled in an 835-square-mile area had nitrate concentrations exceeding the U.S. Environmental Protection Agency's maximum contaminant level (MCL) for drinking water of 10 milligrams per liter (mg/l) nitrogen. Most of the wells with elevated nitrate levels are in areas that are or were used for agriculture.

Nitrate is a stable, highly soluble ion that is difficult to remove by traditional coagulation or adsorption processes. It belongs to a class of inorganic chemicals termed oxo-anions, which includes arsenate, bromate, chlorate, perchlorate, selenate, tungstate, and phosphate, and more generally to a group of oxidized polar pollutants that includes TCE and MTBE.

Risks from many oxidized pollutants can be mitigated through chemical or biological reduction to innocuous forms, such as the reduction of nitrate to nitrogen gas through denitrification. However, the drinking water treatment industry has not developed many reductive technologies to date.

Current options for treating nitrate-contaminated groundwater include blending and ion exchange, the most common approaches, as well as membrane separation and biological denitrification. Chemical denitrification technologies are still in development.

Blending

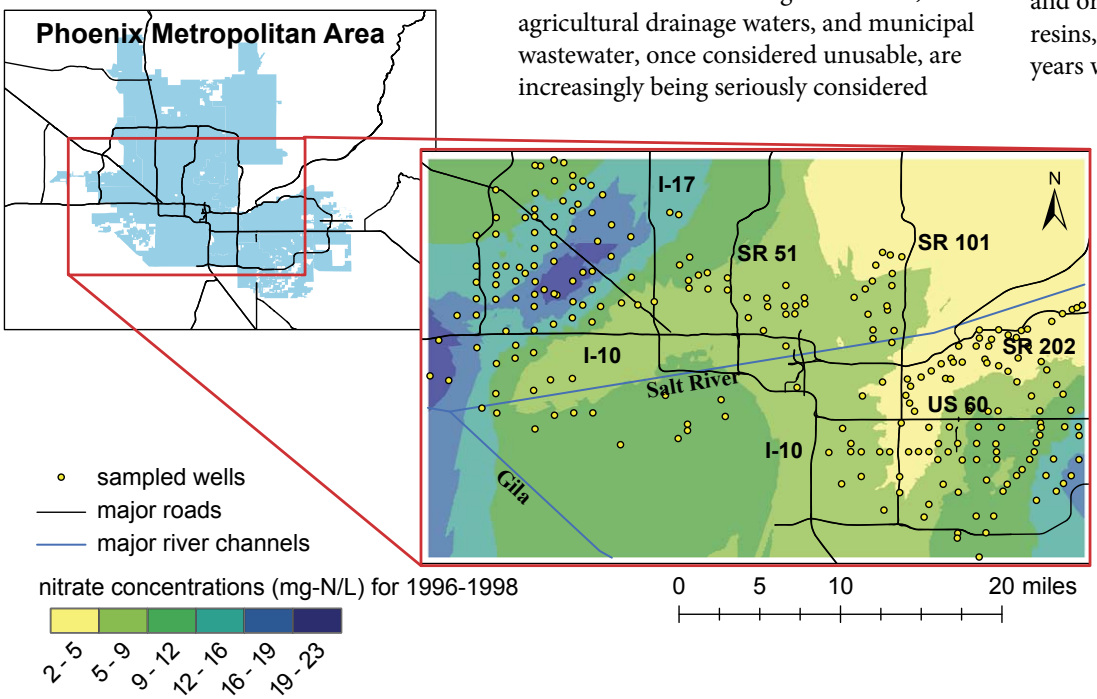
High-nitrate groundwater is largely managed by blending the groundwater with surface water that has lower nitrate concentrations. This approach is common for drinking water treatment in larger municipalities and obviously requires a second, low-nitrate water source. For example, in central Arizona, high-nitrate groundwater is pumped into canals conveying surface water to blend the nitrate level to well below the MCL. But contaminated groundwater, agricultural drainage waters, and municipal wastewater, once considered unusable, are increasingly being seriously considered as sources of municipal water in order to meet current and future drinking-water demands. Thus removing nitrate and other contaminants will become more critical.

Ion Exchange

Ion exchange (IX) is the most widely employed nitrate treatment technology, used at wellsites or other points of entry into potable water distribution systems. Such systems commonly treat less than one million gallons of water per day (MGD) to as much as 10 MGD. Although nitrate-selective IX resins have been developed, most are more selective toward sulfate than nitrate, therefore the impact of sulfate on nitrate exchange capacity must be considered.

IX technologies are simple to design, operate and monitor. They are cost-effective for smaller applications such as direct treatment of groundwater at well sites, usually feature fully automated regeneration sensors and equipment, and are regenerated using sodium chloride. IX is most suitable for waters with total dissolved solids (TDS) concentrations of less than 500 mg/l. Salts and organics in water eventually foul IX resins, but many systems operate for 5 to 10 years without requiring resin replacement.

The primary disadvantage of these systems is the production and costly disposal of concentrated brines, which can contain high concentrations of sodium chloride, nitrate, sulfate, and arsenate. Brines can be disposed of in sewers where adequate dilution is available, but long-term salinity control in some areas may limit this option in the future. Research is now underway to biologically treat IX regeneration brines to remove nitrate and prolong their use prior to disposal. Another major challenge facing the use of IX for nitrate removal is the release of nitrosamines or their precursors, which appear to be byproducts or impurities in the resins that are used. Nitrosamines



Nitrate concentrations (milligrams per liter as nitrogen) in groundwater in the Phoenix metropolitan area, 1996-1998.

are receiving increased regulatory visibility as potential carcinogens in drinking water at low part-per-trillion levels.

Membrane Separation

Reverse osmosis (RO) and electrodialysis (ED) are expensive options to remove nitrate, and are primarily used to treat waters high in TDS rather than solely nitrate pollution. These methods are currently used for nitrate removal in smaller communities and military bases. ED-based systems utilize electric current to pass positive ions (cations) or negative ions (anions) through a semipermeable membrane. The current can be adjusted to pass only cations and reject anions, such as nitrate. However, these membrane-based technologies require significant external energy inputs, which lead to high operating costs.

Both RO and ED produce concentrated brine streams that require disposal; pretreatment is usually necessary to prevent membrane fouling. Membrane treatment processes such as these can be a viable treatment option for municipalities with existing membrane technologies.

Biological Denitrification

Microbe-induced nitrate reduction ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$) can be accomplished using organic carbon electron donors such as methanol or acetic acid, or inorganic electron donors such as hydrogen or reduced sulfur. However, the dissolved oxygen content of the water must be lowered to about 0.1 mg/l for reduction to occur.

Various biological reactor designs that are commercially available use plastic media, buoyant polystyrene beads, sand media, or hollow-fiber membranes. These systems are being used across the Midwest and can treat up to a few MGD of flow. Recent advances in hollow-fiber membranes allow autotrophic bacteria to grow on the outside of the membrane in nitrate-laden water while hydrogen gas is slowly supplied from within the membranes. Nitrate and oxygen permeate into the biofilms growing on the membranes and are reduced in the anoxic environment within the biofilm; this approach shows significant promise for nitrate reduction.

Biological denitrification systems do not produce concentrated brine streams, but biofilm growth must be managed. The most significant drawbacks of biological systems are that they require start-up time after prolonged periods of closure (such as in response to seasonal water demand), require more operator support than nonbiological systems, and are less mature in the marketplace than IX systems.

Ion exchange is the most widely employed nitrate treatment technology, used at wellsites or other points of entry into the potable water distribution systems.

Chemical Denitrification

Metals such as platinum, palladium, tin, and copper can chemically reduce nitrate to other forms, but they usually require a low pH, often need the addition of hydrogen

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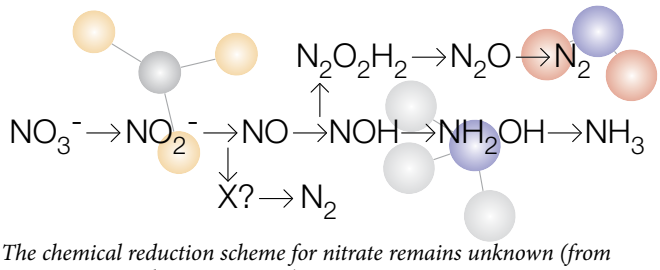
gas or another strong reductant, and perform best with added heat. As a result, full-scale treatment systems based on these catalysts are not yet used for drinking-water applications.

Zero-valent iron (Fe^0) has gained the most attention as a nitrate-reductant system. Both in-situ groundwater and above-ground treatment systems have been demonstrated at several sites and commercial vendors have recently entered the marketplace.

Oxidation of the iron ($Fe^0 \rightarrow Fe^{2+} \rightarrow Fe^{3+}$) frees electrons, which are then available for nitrate reduction. Like biological denitrification, these systems require low dissolved-oxygen levels to proceed favorably. The precise reactions for zero-valent iron and other chemical reduction processes are not well known for groundwater matrices (see reaction, above), but in most cases nitrate reduction in groundwater does not proceed to innocuous gases as it does in distilled water or in biological denitrification systems. Instead, the majority of the nitrogen transforms into ammonia, which poses other water-quality challenges that may necessitate further treatment.



The chemical reduction scheme for nitrate remains unknown (from Katsounaros and Kyiacou, 2008).

Once researchers discover how to force the reaction to nitrogen gas, widescale applications of these technologies may be developed for above-ground treatment systems. In the meantime, most reported applications (for example at Oak Ridge, Tennessee) are for in-situ barriers to prevent the migration of nitrate plumes.

Conclusions

Most nitrate treatment systems are geared toward treating groundwater, and often are operated only periodically to meet site-specific, often seasonal water demands. Reverse osmosis, electodialysis, and ion exchange require an input of electrical power or regeneration chemicals and also produce waste streams with high levels of nitrate and other salts. Biological denitrification treatment systems need the addition of an electron-donor source, and the effluent from these systems contains biomass and potentially residual organics. Furthermore, most biological systems require time for biological acclimation and so cannot be turned on or off as needed.

Despite the development of these technologies, a need remains for a low-cost, low-maintenance, efficient method to treat nitrate-contaminated groundwater. ■

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References

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