

Removal of Nitrate from Drinking Water- A Review

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Abstract

The concentration of nitrates in ground water is observed to be increasing in the world in general and Asian countries in particular. Ground water is still a main source of drinking water especially in rural areas of Asian countries. Nitrates are known to cause methaemoglobinemia in babies and intestinal cancer due to formation of nitrosamines in general population. Several treatment processes for the removal of nitrates from drinking water have been studied. These processes comprise; vegetative de-nitrification, reverse osmosis, electrodialysis, catalytic reduction, chemical reduction, ion exchange and biological denitrification. Combinations of two methods like combined ion exchange-biological denitrification have also been studied. Every method has merits and demerits, however, the methods based on ion exchange for the removal of nitrates from drinking water and regeneration of resin by biological denitrification appear to have edge over other methods. This communication presents a review on existing denitrification processes and spells out needs for future research.

Keywords: Nitrate, Denitrification, Drinking water, Pollution

Introduction

Nitrogen exists in the environment in several oxidation states, with ammonia, nitrate and diatomic nitrogen gas being the main forms. Nitrates constitute the final stage in the oxidation of nitrogen compounds and are; therefore a measure of the original quantity of organic matter with which water is associated. The nitrate contained in pure well waters derived from extensive catchments is largely the result of biological activity in the surface layers of soil enhanced by cultivation and the application of manures. The nitrate of stream of rivers may, however receive substantial increment from well-nitrified sewage effluents. Excessive use of nitrogenous fertilizers in agriculture has been one of the primary sources of high nitrates in ground water (De Roo 1980, Scheper et al., 1984). The increase in levels of nitrates nitrogen can also arise in intensively cultivated area under horticultural lots and under animal feed lots (Wilson *et al.* 1999). Presence of high level of nitrates has been reported in several countries (Pande and Hasan 1979 and Fried 1991, Spalding and Exner 1991, 1993 and Nixon 1992).

Sources of Nitrate

The primary source of all nitrates is atmospheric nitrogen gas, which is converted to organic nitrogen by some plant species by a process called nitrogen fixation. On the death of the plants, the organic compounds are decomposed by microorganisms to inorganic ammonium salts (ammonia fixation), which in turn are converted to nitrates by a process called nitrification. The intermediate product nitrite is generally short lived and seldom accumulates in significant quantities in any natural environment in environment that are depleted in oxygen, some microorganisms can use nitrate in place of gaseous oxygen to carry out their metabolic processes. The products of this reaction are nitrogen gas and/or nitrous oxide. This process is called denitrification (Hounslow

1995). Nitrate occurs in almost all natural waters and its concentration can go up to hundreds of mg/L except when contamination is present, they seldom exceed 20 mg/L. However 10 mg/L as $\text{NO}_3^- \text{N}$ or greater may be regarded as probable indication of contamination from fertilizers, municipal wastewater, feedlots, septic systems and sometimes the cultivation of grasslands.

Nitrogen chemistry in natural water is complex because nitrogen exists in different oxidation states such as NO_3^- (+5), NO_2^- (+3) and ammonium NH_4^+ (-3). The NO_3^- (+5) form is expected under oxidized conditions and NO_2^- is found under moderately reduced conditions. In addition, nitric oxide NO (g), nitrous oxide N_2O (g), and nitrogen (N_2) (g) are also expected in moderately reducing conditions (Stumm and Morgan 1996). Among several N species, NO_3^- is the most stable and is commonly found in groundwater associated with intensive agriculture. Nitrate itself is nontoxic. Doses up to 9 gm/day have been used to treat phosphatic kidney stones in humans without any adverse effect. Contamination of drinking water with nitrate presents a health hazard because NO_3^- can be reduced to NO_2^- in the gastrointestinal tract and causes 'Methaemoglobinaemia' alternatively called as 'Blue Baby Syndrome', a some times fatal disease to which infants are particularly susceptible and also affects adults deficient in glucose phosphate dehydrogenase. In addition nitrate and nitrite have a potential to form carcinogenic N-nitroso compounds, which is a postulated cause of stomach cancer. (Majumdar and Gupta 2000). Thus it is important to maintain low levels of nitrate in drinking water. WHO and U.S.E.P.A. have suggested the guideline value of 10 mg/L as $\text{NO}_3^- \text{N}$ (Lunkad 1994).

Nitrate contamination of our ground and surface water resources is becoming an ever increasing problem. In central Himalayan snow and ice, NO_3^- content is about 0.5 mg/L (Lunkad 1994) while world average river water contains 1.0 mg/L NO_3^- and the ultimate sink of terrestrial waters, the oceans, on average, have 0.67 mg/L NO_3^- (Mason and Moore 1985). In some parts of Europe, nitrate concentrations in ground water reached serious levels 20 years ago and have continued to increase (Barrenstein *et al.* 1986). In 1970 nitrate levels in 60 public supply groundwater sources in England and water intermittently exceeded guideline value, in 1980 this number increased to about 90; and in 1987 about 142 (House of Lords 1989). Surveys conducted in India have shown excessive level of nitrates in ground water (Pande *et al.* 1979, Gopal *et al.* 1977, Gupta 1981 and Handa *et al.* 1982).

Methods of Nitrate Removal

Nitrate is highly soluble in water and there are very few known insoluble compounds of nitrate. The removal of nitrate is therefore difficult using conventional flocculation and sedimentation methods. In view of this, technologies based on physico-chemical principles and biological denitrification has been used for the removal of nitrate from drinking water. Some of the prominent methods used for denitrification of drinking water are described below.

Reverse Osmosis

Reverse Osmosis (RO) is a pressure driven process, which is accomplished by passage of water through a membrane against the natural osmotic pressure to accomplish separation of water and ions. Membranes commonly used are made up of cellulose acetate (0.10 to 0.15 mm thick), while membranes made up of polyamides and composite membranes are also available.

In the reverse osmosis process, a thin membrane separates two salt solutions. Water from the side of lower salt concentration flows through the membrane to the solution of high concentration attempting to equalize the salt content, while the membrane allowing water flow blocks passage of salt ions. If pressure is applied to side of higher salt content, flow of water can be prevented. If pressure is increased the water flow is reversed and passes from salt water to the fresh water; in this manner the salt are separated from the solution. Reverse osmosis operating pressures vary between 350 and 1500 psi with a typical range of 600 to 800 psi. Because of high

rejection of salt ions, the necessary reduction of the nitrate concentration of well water may be achieved by treating only part of the total amount of water and bypassing the rest. Reverse osmosis, however, cannot separate nitrate selectively. Reverse osmosis generally results in a reduction of mineral content in water.

Rautenbach *et al.* 1986 commented that the economics of RO process requires high nitrate rejection of the membranes, high water flux at low driving forces and a high recovery rate. They informed that in most of the cases of high nitrate in ground water in Germany, the dissolved solids are below 600 mg/L and therefore, low pressure modules can be used for nitrate removal. Based on a pilot plant studies they reported that (1) all reverse osmosis membrane are not suitable for nitrate separation (2) feed treatment and recovery rate have to be adjusted individually to the feed water quality and composition, specially the levels of Ca, Sr, Ba, Si, HCO_3 and SO_4 and (3) permeate must be conditioned by process like CO_2 stripping, lime treatment to overcome CO_2 and consequently avoid passing of CO_2 through the membranes. They finally commented that the removal of nitrates by RO system is economically viable. Well water having nitrate concentration of 94 mg/L was reduced to 18 mg/L by RO process.

The concentrate resulting from the reverse osmosis system had a pH value of approximately 7.0 so that the wastewater could be directly discharged into the sewers without any further treatment.

Electro dialysis

In the electro dialysis (ED) process, ions are separated from the water by attracting them through selective ion-permeable membranes using an electrical potential. The unit consists of membranes interposed in the path of a direct current generated by end electrodes. Electro dialysis employs two different kinds of membranes- anion and cation selective membranes-, which are stacked alternatively from the diluate and retentate compartments. The feed is concentrated in the retentate compartment and depleted in the diluate compartment as a consequence of the selectivity of the membranes (Hammer 1991). An electro dialysis system requires a supply of pressurized water (50-75 psi), a membrane stack and a direct current power source. Nitrate removal efficiency in ED is about equal to that of reverse osmosis and the process requires lesser acid dosages than RO and higher water recovery rates.

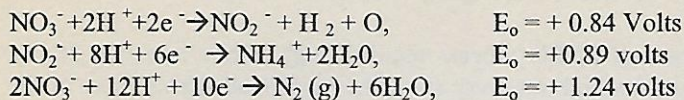
Inorganic and organic both types of membranes are used for electro dialysis process. White *et al.* 1991 used inorganic membranes for the electro dialysis (barium silicate, phosphate composite membrane). Adhikari *et al.* used electro dialysis for desalination of brackish water and 86.7-97.8 percent reduction in nitrate concentration resulted in water containing nitrate in the range of 26.0-144.0 mg/L and feed water TDS in the range of 6000-36000 mg/L. A selective nitrate removal process was developed by Miquel and Oldani 1991, which was effective in removing nitrate concentration from 50 mg NO_3/L to 25 mg NO_3/L without the addition of any chemical.

Nitrate has been removed by electro dialysis method using a nitrate specific anion exchange membrane (Indusekhar *et al.* 1991). Amine groups were incorporated in the membrane prepared from chloromethylated poly sulphone. The membrane exhibited a larger nitrate flux in comparison to chloride flux.

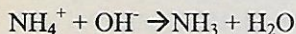
A pilot electro dialysis unit 'Micro Acilyzer. G5' with monovalent permselective membrane was used by Saddi 1998 for the removal of nitrate and chloride from groundwater. It was found that ED reduced both the nitrate and chloride level below the WHO guidelines at 77% recovery without any acid dose. The energy consumption per Kwh/g salt/m^3 product water was 0.48. The membrane selectivity depended strongly on the individual ion concentrations of the feed water. Linear flow velocity increase needed a longer process path length (membrane length) in order to reach the same product water quality.

Segall and Clifford 1992 presented theoretical fluid transport and chemical reaction equations for one and two dimensional fluid flow induced by an electric field. Laboratory columns and two dimensional model studies

examine electroosmosis (EO) as a method of contaminant removal. Nitrates dissolved in EO column influent water more through a column and are reduced at the cathode as follows:



At high pH, little N_2 is expected, but ammonia gas does evolve from the collected column effluent.



Catalytic Reduction

The catalytic reduction of nitrate represents an effective, selective and almost residue free process for the selective removal of nitrate from water. Nitrate and its intermediates like nitrite are selectively reduced to nitrogen on Pd-based bimetallic supported catalysts.

Horold *et al.* 1993 tested bimetallic catalysts to remove nitrate from drinking water. A catalyst with lead (5%) copper (1.25%) impregnated on Al_2O_3 was observed to completely remove nitrate from water having initial nitrate concentration of 100 mg NO_3^- / L. The reaction was completed in 50 minutes. The nitrate removal activity of the catalyst was 3.13 mg NO_3^- / min/g of catalyst, which was 30 times greater than that of microbial denitrification. The process operated effectively in the pH range of 6-8.

Reddy *et al.* 2000 designed and developed an apparatus for testing the catalytic reduction process under different redox potentials and evaluated the effectiveness of different catalysts in removal of nitrate from groundwater. Three catalysts Palladium (Pd), Platinum (Pt) and Rhodium (Rh) on 5-10% carbon were tested in this study. One litre of groundwater was amended with 0.5g catalysts and reacted at different redox potentials (340 to -400 mv) and reaction times (1-6 h). During the catalytic reduction process the pH was maintained around 6.5 by bubbling 5% carbon dioxide (CO_2). Initial nitrate concentrations ranged between 32 and 41 mg/L. Among the three catalysts, Rh was observed to be most effective in removing NO_3^- in groundwater samples. Results with Pt catalyst showed very slow reduction e.g. at -400 mv and 6 & 14 hours reaction times nitrate level decreased only by 25% and 44% respectively. Results suggest that Rh catalyst at -400mv and 6 hours reaction time can decrease NO_3^- concentration from 40 to 11.9 mg/L (68%) Nitrate was not detected during the nitrate reduction process. The re-oxidation of formerly reduced sample to 390 mv resulted in no increase in the concentration of NO_3^- and its reduction rate significantly increased on application of a small flow of current. Application of 4.6-6.1v to -250 mv and 6 hours reaction time resulted in 80% (40 to 7.9 mg/L) decrease in NO_3^- concentration. These results suggested that the Rh catalyst was effective in lowering NO_3^- concentrations in groundwater (Horold *et al.* 1993). The reaction is as under.

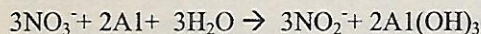


The proposed process has a potential for field application because Rh catalyst can be coated onto a fiberglass mesh and the desired redox potential can be acquired with a photo voltaic cell. This process could become potentially inexpensive method as the sunlight could be used as the energy source to activate the catalyst.

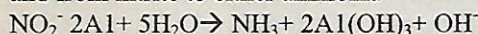
Chemical Reduction

Nitrate can be removed by its chemical reduction, to nitrogen. Murphy 1991 described a chemical denitrification process by use of powdered Al, which is a powerful reductant, can decompose water, NO_3^- and SO_4 and has an

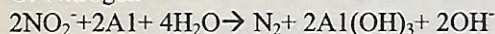
optimum pH 10.25 for nitrate reduction. Al powder reduces nitrate to ammonia, nitrogen and nitrite. The removal of nitrate ion by al may first occur by adsorption onto the particles. The reactions probably proceed to nitrite as under.



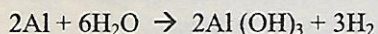
and from nitrite to either ammonia



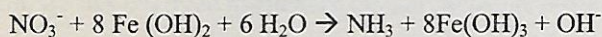
Or Nitrogen



This process can be effectively used in water treatment plants using lime for water softening. The pH is usually raised to or above 9.1 using lime, thus very little additional cost for pH change will be required. Al also reacts with water according to the following reaction.



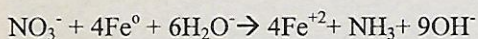
The loss of reductant decomposition of water can be minimized to less than 2% between pH 9.1 & 9.3 and 1.16 gm of Al is required to reduce 1 gm of nitrate. Nitrate reduction also occurs with iron under basic pH conditions. This reaction requires Fe: NO_3^- ratio of about 15:1 in presence of Cu catalyst and the process proceeds according to the following reaction (Sova 1986).



Iron is used by many workers for the successful removal of nitrate from water. Chemical reduction of nitrate by iron in hot sulphuric acid is quantitative but ammonia is not the principal product (Pepin-Lahlur 1930). Szabo *et al.* 1951 described NO_3^- reduction quantitatively by boiling ferrous hydroxide suspension in the presence of catalysts such as colloidal silver or copper hydroxide.

Young 1964 described reduction of nitrate with Ferrous Hydroxide at room temperature at pH 7.0-10.3. The initial nitrate concentration was 100 mg/L (as N) and colloidal copper hydroxide employed as a catalyst was proved to be optimum as 25mg/L (as Cu) and was used at that level in subsequent experiment. The best result obtained was 90% reduction of NO_3^- in four hours at pH 10.3. The reduction was slower and less complete at lower pH.

Young 1964 used powdered and coarse iron for the reduction of NO_3^- in water. Powdered iron (2g/L) was added in water at various pH levels, which results in 94, & 93% reduction of nitrate in five hours at pH 3.0 and 2.5 respectively. Coarse iron at 2g/L yielded 57% reduction in NO_3^- . Ammonia was the principal end product in each case. The balanced equation for this mechanism is,



The rate of reaction for the reduction of nitrate decreased when coarse iron was used. This is because of decreased surface area with increased particle size.

Cheng *et al.* 1997 described a method for the reduction of 12.5 mM nitrate solution to less than 0.1 mM by zero valent iron under aerobic conditions at room temperature and normal pressure. At pH 5.0 with a 0.05M sodium acetate/acetic acid buffer, nitrate was rapidly reduced to ammonia is a pseudo first order reaction.

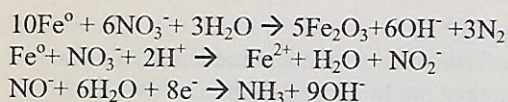
Ottley *et al.* 1997 described the significance of trace metal catalysed reduction of nitrate in deep ground water where organic carbon concentration were Very low, laboratory experiments were conducted in which nitrate was

reduced chemically by Fe (II) to ammonium at pH 8 and at 20°C in the presence of copper (II). Solid phase Cu rather than dissolved copper was directly involved in the nitrate reduction reactions catalysed by goethite.

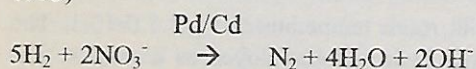
Zawaideh *et al.* 1998 demonstrated the effects of pH and addition of an organic buffer (HEPES) (4-(2-hydroxyethyl)-1-piperazine ethane sulfonic acid) on nitrate transformation in zero valent iron systems. Nitrate-nitrogen was removed by 94% when 0.01 M of HEPES was added to a non shaking batch reactor containing 20 mg/L nitrate-nitrogen and 41% (W/V) of Fe⁰. Shaking was proved to be effective in removal of nitrate. Using the response surface technology, it was found that nitrate removal was closely related to pH. At low pH (e.g. pH<2), the nitrate removal was fast and efficient (95% to 100%) this was because of formation of Fe²⁺ at low pH. At high pH (e.g.>11), the transformation of nitrate was fast and efficient only for low concentrations nitrate in Fe⁰ - H₂O system. At high pH (e.g. of 11), some solid compounds such as Fe(OH)₂, Fe(OH)₃ or FeCO₃ are formed which would eventually form a surface layer on Fe⁰ surface that would inhibit further decomposition of Fe⁰ (Stumm *et al.* 1996). Therefore the nitrate removal will not increase with initial nitrate concentration. At normal pH range (pH=6 to 8), nitrate removal was usually lower than 50% without buffer treatment. Mass transport of substrate to the iron surface proved to be important in achieving high removal efficiency.

Siantar *et al.* 1996 used zero valent iron on hydrogen/palladium catalyst (H₂/Pd- Alumina) for the treatment of nitrate-contaminated water.

Flis 1991 reported that iron may reduce nitrate to nitrogen, nitrite or ammonia depending on the reaction conditions.

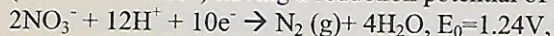


Nitrate can also be reduced to nitrogen using H₂ and Pd on copper under water treatment conditions (Sell *et al.* 1993)

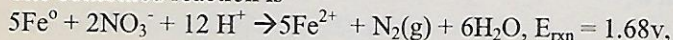


Chew and Zhang 1998 indicated that electrokinetics / iron wall process can be used to remediate nitrate-contaminated ground water. In the iron wall oxidative dissolution of Fe⁰ takes place resulting in the formation of Fe²⁺ ions.

(Fe⁰ → Fe²⁺ + 2e⁻) having a reduction potential of 0.44v (Sawyer *et al.* 1994)



The combined reaction is



Nitrates are anions, which will move to the anode in the electrokinetics. When only electrokinetics was used at various constant voltages, 25 to 37% of nitrate nitrogen was transformed. Amount of nitrate-nitrogen transformed improved when a Fe⁰ wall (20 g or about 8-10% by weight) was placed near the anode. For test runs at various constant voltages, the amount of nitrate-nitrogen ranged from 54 to 87%. By switching to constant currents, the amount of nitrate-nitrogen transformed was about 84 to 88%. The major transformation products were ammonia nitrogen and nitrogen gas. Nitrite nitrogen was less than 1% in all-experimental runs. Two localized pH conditions exist in the system, a low pH region near the anode and a high pH region near the cathode. Placing of an iron wall near the anode increase the pH in that area as time increases. Movement of the acid front did not flush across the cathode. High nitrate transformation efficiencies can be achieved with pH in the range of 4 to 10.

Ion Exchange

Ion exchange is a unit process in which ions of a given species are displaced from an insoluble exchange material by ions of different species from solution. In practice an ion exchange material is placed in a bed and the contaminant to be treated is passed through it. When ion exchange capacity of the bed is depleted, the feed is stopped and a regenerating solution (concentrated solution of NaCl or NaHCO_3) is passed through bed. Ion exchange materials both natural and synthetic are adsorbents which carry charged ionic groups. To maintain electroneutrality, each ionic site must have associated with it an ion of opposite charge (counter ion). The success of ion exchange depends on the ability of the counter ion to be replaced or exchanged for another ion of the same charge. When all counter ions have been replaced, the ion exchange material is exhausted. Acid or cationic resins will exchange cations such as Ca^{2+} or Mg^{2+} and base or anionic resin will exchange OH^- or Cl^- anions (Reeves 1972).

Guter 1981 tested a pilot-scale ion-exchange study conducted at McFarland, California for the removal of nitrate from groundwater containing nitrate-nitrogen in the range of 16-23 mg/L. He was able to remove nitrate almost completely.

Lin 1997 used Dowex-Sar as a strong base, anionic ion exchange resin of the Cl type. Regeneration was attained with a salt solution containing 10 % w/w salt in about 10 hours. The pH and temperature effect on the equilibrium exchange capacities for nitrate removal was seen to be rather small. A higher initial concentration of nitrate was observed to enhance the ion exchange process.

Basic bismuth nitrate has low solubility in water. Utilizing this property several bismuth compounds were examined by Fritsche 1993 for their ability to remove nitrate from water. Yellow Bismuth hydroxide, prepared by the reaction of bismuth salt solution with excessive sodium hydroxide proved to be an effective material for anion exchange. Besides nitrate, it also removes phosphates, sulfates and chlorides. The selectivity of the method, which is based on ion exchange with hydroxyl ion (OH^-) as counter ion depends on the pH value. Regeneration can be achieved by sodium hydroxide.

Hoek *et al.* 1988 used a strong base, macro porous anion exchange resin Amberlite IRA 996 for nitrate removal from ground water. Amberlite appeared to be more nitrate selective than sulfate selective in treating high nitrate concentrations in potable water. High nitrate concentration of 18 mg NO_3^- -N/L was reduced to 5-6 mg NO_3^- -N/L after the treatment with this resin at a flow rate of 35 Bed Volume (BV)/ hour.

Liang *et al.* 1999 studied the removal of nitrate from contaminated groundwater using three types of strong base anion resin. In type I resin three methyl groups make up the functional group, in type II an ethanol group replaces one of the methyl group of resin I and third type of resins were nitrate/sulfate selective (NSS) resins and similar to type I resin containing tri methyl amine functionality but ethyl, propyl or butyl groups substitutes. They observed that type I resin provided longer run before regeneration than the type II or NSS resins. The removal of nitrate was almost 100 percent up to 400 bed volumes in type I resin, up to 300 bed volumes in type II resin and up to 250 bed volumes in NSS resin. It was also observed that in type I resin bicarbonate interferes less with nitrate removal than it did in type II resin. Less regenerant salt was also required for regeneration producing less waste in type I resin than in type II or NSS resin.

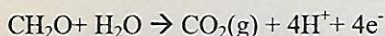
Hoell and Feuerstein 1985 developed a process called CARIX process to provide simultaneous removal of nitrate, sulfate and hardness. The CARIX process is based on the combined use of a weakly acidic cation exchanger in the hydrogen ion form and a strongly basic anion-exchanger in the bicarbonate (HCO_3^-) form. Both resins are regenerated simultaneously with carbon dioxide in a non-polluting fashion.

The nitrate ion exchange process involves multicomponent ion exchange with sulfate as the major competitor with nitrate for ion exchange sites. Conventional strong base anion exchange resins prefer divalent hydrophilic

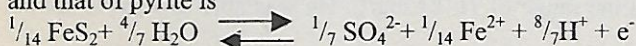
sulfate over monovalent hydrophobic nitrate. This sulfate preference needs to early nitrate breakthrough and causes nitrate peaking when nitrate breakthrough is exceeded. For high sulfate water greater than 140 mg/L, the nitrate selective TEA and PBA (Tri Ethyl Amine & Tri Butyl Amine) resins generally perform better than the conventional TMA (Tri Methyl Amine) resins for nitrate removal.

Biological Denitrification

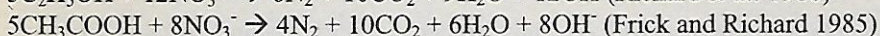
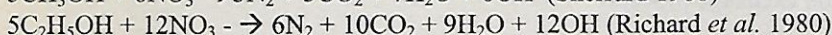
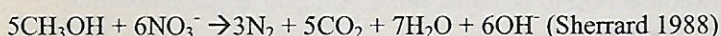
The process refers to the dissimilatory reduction by essentially aerobic bacteria of one or both of the ionic nitrogen oxides (NO_3^- and NO_2^-) to the gaseous (NO and N_2O) which may themselves be further reduced to dinitrogen (N_2). Denitrification is catalysed by either heterotrophic or autotrophic bacteria that derive their energy requirements by the oxidation of organic and inorganic material, respectively (Hiscock *et al.* 1991). The oxidation half reaction of carbohydrate is



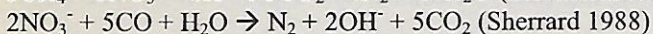
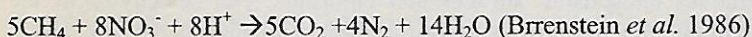
and that of pyrite is



Heterotrophic denitrifying microorganisms can use a variety of organic carbon sources; however most of the work regarding denitrification of water involves the use of methanol or acetic acid.

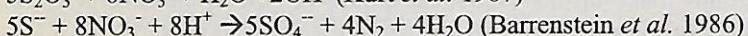
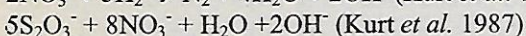
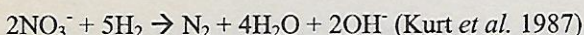


Methane and Carbon mono oxide can also be used as substrate for denitrification.



Denitrification can also be accomplished by autotrophic bacteria, which can use hydrogen or various reduced - sulfur compounds as energy sources.

The following stoichiometric relationship for hydrogen and sulfur has been reported.



Biological denitrification is commonly used in municipal and industrial wastewater treatment. However, it may be used to treat drinking water if bacterial contamination of the treated water can be avoided. Denitrification takes place under anionic conditions. Nitrate reduction to nitrogen gas occurs through a series of steps as follows (Knowles 1982).



Autotrophic denitrification

Flere and Zhang 1999 evaluated sulfur and limestone autotrophic denitrification (SLAD) processes with four laboratory scale fixed bed reactors. A maximum denitrification rate of 384g NO_3^- -N/ (m^3 day) was achieved at a loading rate between 600 and 700g NO_3^- -N/ (m^3 day). The effluent nitrite concentration started to rise gradually once the loading rate was above 600g NO_3^- -N/ (m^3 day). A loading rate between 175 and 225g of NO_3^- -

N/(m³day) achieved the maximum nitrate- N removal efficiency (approximately 95%). A SLAD column requires backwashing after 6 months of operation when the influent is synthetic ground water but will foul and requires backwashing within 1-2 months when the influent is real ground water.

Schippers *et al.* 1987 described denitrification using sulfur limestone filtration. Limestone granules were added to sulfur to maintain the pH because pH was reduced by the hydrogen ions, which was released in this process. Filtration was carried out at 0.5 m/h, similar to the rate used in slow sand filtration. The influent was degassed to remove nitrogen and oxygen and 0.3 mg PO₄⁻³/L phosphate was added. The pilot plant consisted of a vacuum degasser, a slow sulfur /limestone filtration unit, a cascade tray and an infiltration pond. The concentration of NO₃⁻ N was reduced from 20 to 3-5 mg/L at a filtration rate of 0.25 m/h.

Denitrification with sulfur/limestone was also achieved by Blecon *et al.* 1983 and Hoek *et al.* 1992. Some authors have evaluated reduced sulfur compounds such as sulfide and thiosulfate for the denitrification of water and domestic and industrial wastewater (Claus 1985, La Motta Diaz 1985 Martin 1982 and Batchelor 1978). Sulfate was the byproduct of denitrification using sulfur compounds.

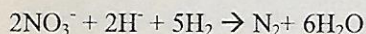
Lewandowski *et al.* 1987 evaluated autotrophic denitrification using calcium alginate beads containing elemental sulfur, calcium carbonate and *Thiobacillus denitrificans* suspended in a bench scale completely mixed batch reactor. Nitrate concentration was reduced from 27 mg/L to 6 mg/L in seven hours.

Nitrate has been removed in fixed film reactors using various support media composition, hydrogen generation, degassing technique and post-treatment methods. Various methods have been used to remove microorganisms and dissolved organic carbon from denitrified water (Gros and Ginocchio 1982 and Ginocchio 1984).

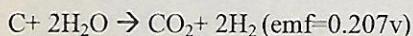
Kurt *et al.* 1987-used hydrogen for autotrophic denitrification in a bench scale fluidized bed reactor. Nitrate and hydrogen were assumed to be limiting substrates in the first denitrification step, and nitrite and hydrogen were assumed limiting in the second step. The nitrification rate was shown to be more strongly depended on the nitrate concentration than on hydrogen. A residence time of 4.5 hours was required from completed denitrification of water containing 25 mg/L NO₃⁻ N at the optimum pH of 7.5.

Gros *et al.* 1986 and Gros and Treutler 1986 reported on the performance of a commercial scale biological denitrification plant utilizing hydrogen, in Minchegladbach, West Germany and the process was given the trade name 'Denitropur'. The plant design incorporates indirect hydrogen saturation, phosphate addition, four-packed bed reactor in series, post aeration, flocculent addition, filtration and UV disinfection. Carbon dioxide was added as an inorganic carbon source and to buffer against an alkaline pH shift. The sludge production was less (approximately 0.2 kg/ per kg N removed). Residence time of one to two hours was required to remove 50 mg/L nitrate.

In electrode biofilm reactor, denitrifying organisms are immobilized on the cathode utilizing H₂ produced by the electrolysis of water and subsequently reduce nitrate to nitrogen gas.



carbon electrode was used as the anode, so that the CO₂ formation seems to occur instead of O₂ formation (Kinoshita 1988).



Sakakibara *et al.* 1994 used Electrochemical and biological reactor for denitrification. Denitrifying microorganisms were immobilized with a sodium alginate gel on a cathode electrode as the anode. Biological reductions of nitrate through the use of H₂ at the cathode and formations of inorganic carbons at the anode were

observed. Concentrations of nitrite and ammonium in effluent were less than 1mg-N/L. effluent nitrate concentration decreased with time and components of produced gas were H_2 , N_2 and CO_2 .

Heterotrophic Denitrification

Heterotrophic biological denitrification is a well-established process for wastewater treatment. This process has not been used in full scale in U.S. however there are several full scale plants being operated in Europe (Dahabet *et al.* 1991 and Gayle *et al.* 1989).

In heterotrophic biological denitrification, facultative microorganisms are contacted with the water supply containing nitrates and an added carbon source in an anoxic environment. Under the conditions the bacteria utilize nitrates as a terminal electron acceptor in lieu of molecular oxygen. In the process nitrate is reduced to nitrogen gas, which is harmless. Carbon source is necessary since it supplies the energy required by the microorganisms for respiration and synthesis (Dahab and Woodbury 1998).

The removal of nitrate nitrogen from groundwater by using two rotating biological contactors (RBC) in series was investigated by Bandpi and Elliott 1996. The first RBC reactor was operated under anoxic condition to remove nitrate-nitrogen. A fraction of effluent of the anoxic RBC was fed to a bench scale aerobic RBC to study the degradation of residual organic carbon and oxidation of nitrite nitrogen. Ethanol was used as a carbon source. The first reactor achieved 90% nitrate removal efficiency at a loading rate of 76mg/m²h. The optimum ethanol to nitrate-nitrogen ratio was found to be 2.35. Effluent removal of residual carbon and re-oxidation of nitrite was also achieved by aerobic biological process. Thus high nitrate removal with negligible residual carbon could be achieved by employing an anoxic denitrification followed by an aerobic process.

Bandpi and Elliott 1998 investigated a pilot scale rotating biological contactor (RBC) for the removal of nitrate-nitrogen from groundwater using three different carbon sources: methanol, ethanol and acetic acid. Optimum carbon sources to influent nitrate nitrogen ratio were established by varying the influent concentration of carbon sources. The optimum ratio of methanol, ethanol and acetic acid to nitrate-nitrogen ratios were found to be 2.9, 2.35 and 4.3 respectively. The nitrate-N removal efficiency averaged 93, 91 and 98 for methanol, ethanol and acetic acid at a loading rate of 76 mg/m²h. The results of this study showed that the acetic acid was the most efficient carbon source for removal of nitrate-nitrogen.

Hamzah 1996 used an anoxic static bed column to investigate the influence of type of carbon source and nitrate loading on the nitrate contaminated drinking water. Results showed that the system operated at 0.45kg NO_3 -N/m³. day loading of nitrate to treat waters having a nitrate concentration of 500 mg/L. On a stoichiometric basis, ethanol as a substrate for bioremediation gave better results as compared with methanol and acetic acid.

A study was carried out by Christensson 1994 in two anoxic chemostates to see the performance of ethanol and methanol as carbon source for denitrification. An efficient denitrification with ethanol was established in a short time, while denitrification with methanol required a substantial adoption time and never showed the same ability as denitrification with ethanol.

Akunna *et al.* 1993 used batch tests to determine the potentials of digested sludge to reduce nitrate and nitrite in the presence of five different carbon sources; Glucose, Glycerol, Acetic acid, Lactic acid and Methanol. Ammonium accumulation was found in glucose and glycerol media. Dissimilatory reduction to ammonium accounted for up to 50% of reduced nitrate and nitrite. Ammonification was higher than denitrification when glucose and glycerol were present in the media. Nitrate/ Nitrite reduction in acetic and lactic acid media was essentially a denitrification study. Up to 100% reduced nitrate and nitrite in the culture media with these acids were denitrified at average rates between 27 and 23 mg NO_3 -N/g MLVSS. Soares *et al.* 1988 conducted denitrification studies on groundwater containing 22.6 mg/L NO_3 -N using a down flow sand column with sucrose as the carbon source. Complete nitrate removal was achieved at C:N ratio of 2. Soares *et al.* 1991 studied microbiological denitrification in a sandy matrix by means of laboratory sand columns operated at

continuous and pulse feed regimes. Formate was used as the carbon source. The results suggest that pulse application of carbon source is preferable to a continuous supply regime because continuous supply of carbon source leads to almost complete clogging of the column.

Liessens *et al.* 1993 studied heterotrophic denitrification in a fluidized bed reactor for surface water at low temperature. Methanol was used as the reductant with a nitrate removal efficiency of 9.0 Kg NO_3^-/m^3 reactor day at 3.5 °C, the system, has shown superior performance compared with conventional fixed bed/biofilm reactors. With an influent concentration of 75 mg/L NO_3^- complete nitrate removal was achieved at an empty bed contact time of 15 minutes. Residual methanol was easily removed by the existing downstream drinking water treatment processes.

Various processes have been adapted and used for the denitrification of drinking water. Drinking water denitrification was studied on a membrane bioreactor pilot plant by Delanghe *et al.* 1994. The nitrate removal yields remained constant at 99%. The specific denitrification activities averaged 0.16 kg N- NO_3^- Kg⁻¹ MLSSd⁻¹ (Mixed Liquor Suspended Solid) at 20 °C. and pH 8. The permeation flux was about 0.5 m³ . m⁻² . d⁻¹ throughout the study and did not vary with an increase in the suspended solid concentration. The specific denitrification activity decreased by a factor 1.9 with a temperature decrease of 10 °C. The optimal pH was found to be 8.0-8.5. The ethanol was used as the carbon source and its consumption was 1.4 gC.g⁻¹N- NO_3^- . The pilot plant study showed that the shear stress on the ultra filtration membrane surfaces did not affect the specific denitrification activity of suspended cultures.

Dahab and Kalagiri 1996 studied a cyclically operated fixed film bio denitrification process to remove nitrates from drinking water. They also investigated the ability of two-stage system to remove nitrate and residual organics from treated water as compared to single stage units. The removal of nitrate was observed to be 98 and 95 percent in single stage and two stage denitrification reactors respectively at hydraulic retention time (HRT) of 1.0 and 0.5 hrs. They also observed that the two stage cyclic operation was more effective in maintaining low nitrite concentration than the single stage reactor.

Combined Ion Exchange Biological Denitrification

Ion exchange is a physical-chemical process where by means of an anion exchange resin nitrate is exchanged for chloride or bicarbonate. The process has a problem of regeneration of the resin, which requires a large excess of salt producing a voluminous brine with high nitrate, sulphate and chloride concentrations (Gauntlett 1975, Deguin 1982 Richard and Leprince 1982 and Hoek *et al.* 1988). Brine disposal is very difficult and requires careful consideration and adds to the operating cost. Biological denitrification is a process by which nitrate is converted to nitrogen gas denitrifying bacteria. A direct contact is created between ground water, which is generally free of microorganism and bacteria. In the case of heterotrophic denitrification, a carbon source has to be added to the ground water. Both cause a serious risk of the bacteriological contamination of the ground water, and extensive post treatment is necessary for the removal of microorganisms and organic substrate (Sorg 1979, Barlog 1980, Richard and Leprince 1982 and Sontheimer *et al.* 1982). Also the production of nitrite, an intermediate product of denitrification is a serious risk.

Therefore by combining ion exchange and biological denitrification process into one process, most problems connected with the separate techniques can be avoided (Hoek 1985, Hoek and Klapwijk 1985,1986). The basic concept of this process is to use sludge blanket reactor (SBR) to biologically denitrify the spent regenerant brine, which is then filtered, compensated with NaCl and reused. Bench scale test suggested that the salt consumption could be reduced by 50 percent and the salt discharge by 90% (Liu and Clifford 1996).

Hoek and Klapwijk 1987 described a combined ion- exchange (IX) and biological denitrification process in which nitrate is removed from ground water by ion exchange and for the regeneration of nitrate loaded resin a denitrification reactor is used. In contrast with traditional denitrification process there is no direct contact

between ground water and denitrifying bacteria. Also brine production and regeneration salt requirements are minimal as compared with conventional regeneration of ion exchange resins. Ion exchange resin Duolite A 165 was used for the removal of nitrate and an up flow sludge blanket reactor (USBR) was used for theregenerant denitrification which was able to denitrify highly saline solution containing 25-30 g/L NaHCO_3 and 10-15g NaCl/L . The process is suitable for treating water with high sulphate concentrations. The waste brine produced was 13- 20% of the amount produced in ion exchange columns. A sand filter was recommended between the USB denitrification reactor and the ion exchange column to remove the suspended solids from theregenerant before they reached the resin along with resin disinfection with per acetic added during disinfection.

Hoek *et al.* 1988 evaluated the combined process using ground water with sulphate -selective and nitrate selective resins. Regeneration with NaHCO_3 was possible but the regeneration efficiency was very low. Regeneration salt requirement and brine production was minimized by using closed circuit regenerator using biological denitrification reactor to remove nitrate from the regenerant. The combined process resulted in about 95% reduction of waste brine in comparison to the conventional ion exchange.

A bench scale ion exchange process with batch biological denitrification of the spent regenerant brine in a sequencing batch reactor (SBR) was developed by Clifford and Liu 1993. It consisted of chloride ion exchange and 0.5N (3%) NaCl regeneration followed by batch denitrification and reuse of the spent brine. Complete (>99%) denitrification of spent 0.5 NaCl brine was achieved in 20 hours using a non optimum methanol to nitrate- nitrogen ratio® of 2.2. At the optimum R value of 2.7, the time for greater than 95 percent denitrification was 8 hours. The research indicated that the combination procedure resulted in 50 percent reduction of regenerant consumption and 90 percent reduction in the mass of waste salt discharged. Compared with USBR, the SBR ad several advantages that were pertinent to small systems: simplicity, flexibility of operation, stability of effluent quality and built in equalization. Although the higher rate USBR requires less reactor volume, when equalization and brine were taken into account, the space occupied by the process was not much different.

Fonseca *et al.* 2000 developed a novel ion exchange membrane bioreactor able to prevent secondary pollution of biologically treated drinking water and specifically tested for water denitrification. This system combines ion selective membrane dialysis and biological conversion. The ion selective membrane facilitate the extraction of pollutant from the water to the biological compartment, hinders the transfer of organic and inorganic nutrients and confines the microbial culture involved in the conversion process within the bioreactor. In the study hereby a system was used to investigate the removal of nitrate from a synthetic groundwater containing 50 mg/L of nitrate-N. The treated water obtained was free of inorganic nutrients and ethanol, the carbon source was selected for the biological process, and the surface denitrification rate achieved was $7\text{g-N m}^{-2}\text{day}^{-1}$. This system proved to be effective in producing a treated water effluent that does not require the extensive post treatment associated with conventional biological treatment.

Vegetative Denitrification

Vegetation can prevent herbicides, pesticides and fertilizers from contaminating surface and ground water. Tree buffers can protect ground water from different contaminants at the contaminant site. At an agricultural test site on a Iowa farm, a 3-year-old popular crop planted by university of Iowa research team reduced $\text{NO}_3\text{-N}$ levels in leachate from fertilized fields. The trees were planted between the corn field and the stream along the stream bank. The average nitrate content of ground water leaving the corn field was 150 mg/L, which is more than 300 percent greater than EPA's permissible limit of 45 mg/L for nitrate in drinking water. Level was 8mg/L in the ground water between the field and the stream. Poplar trees were chosen because the trees take up soluble inorganic nitrogen through their roots, converting them into protein and nitrogen gas.

The occurrence of saturated and non-saturated soils in Riparian buffer strips provides ideal condition for denitrification. The rate of denitrification depends on the amount of organic carbon, the degree of soil saturation, the activity of denitrificant bacteria, the temperature and pH of the system (Engler and Patrick 1974, Reddy *et al.*

1978 and Schippers *et al.* 1993). Todd *et al.* 1983 observed that a forested buffer removed 82% of water borne nitrogen from agricultural runoff. Fennessy and Cronk 1997 reported that the denitrification is the predominant process for the nitrate removal in riparian zones. Vegetation in Riparian buffers serves as a source of carbon for microbial denitrification. They also reported that sedimentation; soil adsorption and microbial transformation are mechanisms by which nitrogen, phosphorous and solids are removed from agricultural runoff. Nitrate removal is favoured in forested areas with subsurface flow and is less in grassed areas with surface flow.

Brown 1971, studied removal of nitrate from subsurface agricultural drainage using algal system consisting of algae, harvesting and disposal as a possible means of removing nitrate. The findings showed that about 15-90% of the nitrate was assimilated by shallow algal culture.

Summary and Conclusions

Studies on the development of processes for the removal of nitrates from drinking water are either based on physico-chemical or biological denitrification system. Merits and demerits of a process are to be considered for finding its potential for full-scale application. In ion exchange process the water is passed through beds of ion-exchange resin beads, which absorbs nitrate in exchange for another anion. Counter flow regeneration is normally used for nitrate removal by ion exchange process. In this process the spent regenerant is disposed to agricultural field. Nitrate selective ion exchange resins are now available. The high nitrate capacities of these membranes prevent the displacement of nitrate by sulphate and also lower cost for regenerant chemical and waste disposal.

Reverse osmosis results in the production of treated water stream and waste disposal concentrated waste stream. The waste volumes in this case are larger as compared with ion exchange and operating costs are also higher.

Electrodialysis treats the water by selective removal of nitrate ions through a semi permeable membrane. The removal efficiency for nitrate is almost equal to that of reverse osmosis. Nitrate selective membranes are now available which makes the process more effective. In this process however pre treatment of water is required. The wastes are also very concentrated and create disposal problems.

Biological denitrification process occurs naturally in the presence of sufficient carbon source and anoxic conditions. The method may be used for treating drinking water by avoiding bacterial contamination of the treated water. Both autotrophic and heterotrophic processes have been used for denitrification. However heterotrophic process is faster than autotrophic. Autotrophic denitrification increases the sulfate concentration in water and operated at low carbon level results in nitrite production. These reasons impair the efficiency of the process. With fluidized sand bed excess biomass is removed without shutting down the process. The waste volumes are small and due to low level of dissolved solids the waste can be disposed to agricultural land. The process of denitrification using ion exchange for nitrate removal from drinking water and treatment of regenerant by biological denitrification shows that the process may find more adaptation in future. The method of converting nitrate into insoluble salt of some metal ion also has potential for future research. Some preliminary studies have been conducted on denitrification using zero valent iron. This process also appears to be a potential process for future research. Nature provides self-purification of water. The roots of plants are capable of absorbing nitrate through bacterial reaction and thereby reducing nitrate from water. Several studies have been conducted on the removal of nitrate by allowing the water to flow through the subsurface under plantation. This process has high potential for large-scale treatment of drinking water.

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