Octa Journal of Environmental Research
International Peer-Reviewed Journal
Oct. Jour. Env. Res. Vol. 1(3): 217-230 ***July - Sept, 2013***
Available online http://www.sciencebeingjournal.com ISSN 2321-3655
Research Article

Octa Journal of Environmental Research
(Oct. Jour. Env. Res.) ISSN: 2321-3655
Journal Homepage: http://www.sciencebeingjournal.com
Scientific Planet Society

NITRATE TOXICITY IN GROUNDWATER: ITS CLINICAL MANIFESTATIONS, PREVENTIVE MEASURES AND MITIGATION STRATEGIES

Raaz K. Maheshwari[a], A.K. Chauhan[b], Bhanwar Lal,[c] and A.K . Sharma[d]
a. Department of Chemistry, SBRM Govt PG College, Nagaur, Rajasthan
b. Department of Chemistry, SK Govt PG College, Sikar, Rajasthan
c. Department of Chemistry, Singhania University, Jhunjhunu, Rajasthan
d. Department of Environmental Sciences, SS Jain Subodh Girls' College, Sanganer, Jaipur, Rajasthan
*Corresponding author's Email: drraazecoethics151260@gmail.com

Received: 29 August 2013 Revised: 11 Sept. 2013 Accepted: 24th Sept 2013

Abstract: Groundwater pollution has become a drastic problem principally because of nature and wide spread use of modern chemicals viz. pesticides and fertilizers. Excessive application of fertilizers as well as organic wastes and sewage has been implicated in the nitrogen pollution of groundwater. Therefore, the issue of rising nitrate concentration in groundwater has become a subject of extensive research in India and Rajasthan in particular. In natural water, nitrate ((NO_3^-) N is usually <5mg/l. In fact, additional amount of excess nitrate in groundwater arise due to the biological oxidation of organic nitrogenous substances of sewage, industrial and agricultural origin. Water containing excess nitrate, when is ingested, enters GIT, where by the microbial action in non-oxidizing conditions, get reduced to nitrite (NO_2^-). In accordance with the UPSH drinking water standards, a limit of 10mg/l for NO_3^- and 0.1mg/l for NO_2^- must be regularly monitored in water supplies as they are deemed to be potentially hazardous to infants <5months old (methamoglobinemia: BBS).The long-term hazard in adults relates to the reaction in the digestive system between NO_3^- (>100ppm) and in organic matters (amine and /or amides) resulting in the production of nitrosamines (carcinogens). Number of cases (human and livestock), suffering from gastric cancer have been observed. Reverse osmosis (RO) process has great potential in the mitigation of nitrate ion containing waters. Generally, the presence of particular substances may affect the removal of specific ions. The presence of di-hydrogen phosphate ions (DHP-ions) in the feed solution enhances the nitrate removal efficiency of the polyamide RO membrane. In this present research work, a Flmtec TW30, polyamide thin-film composite, RO membrane was used for nitrate removal through RO set up. The rejection of individual nitrate was found to be around 76%. After addition of KH_2PO_4 to the feed containing nitrate ions the rejection was improved up to 84. This high level of increment in rejection of nitrate ion indicates the possible usage of KH_2PO_4 in RO for nitrate removal. This fact of removal is due to the K^+ ions binding to the electronic lone-pairs of polyamide membrane holding di-hydrogen phosphate ions. This establishes a negative layer on the surface of the membrane. The diffusion of nitrate through the membrane is diminished by the formed layer. Present manuscript delineates clinical manifestations of nitrate toxicity and mitigation of nitrate ion by means of state-of-the-art reverse osmosis technology.

Keywords*:* Reverse osmosis; Nitrate; KH_2PO_4; Polyamide membrane; Rejection; Methaemoglobin; Donnan effect; Electrostatic force; Electro-neutrality

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Postal address: 1/521, Hari Niwas, Housing Board Colony, Nagaur, Rajasthan 341 001

INTRODUCTION

It is well known that 70-80% of all illness in India is related to water contamination with women and children particularly susceptible. Much of the natural supply of potable water that is accessible faces stress from a growing world population, which increases basic demand for this natural resource, while reducing supply further through biological and industrial contamination. It is really shocking that India has only 4% of global water resources, whereas constitutes 16% of total world population. Major population centers in developing nations without established waste treatment or water treatment infrastructures often suffer from epidemic of water borne diseases. In these areas, raw sewage often directly contaminates the rivers and streams used for drinking, washing and cooking. In another cases, unchecked industrialization leads to water contamination through improper disposal of chemical and nuclear wastes. One third of the world's population is facing problem due to water shortage and poor drinking water quality. Effects includes massive out-breaks of diseases, malnourishment and crop failure. About 200 millions Indians are thirsting for clean and safe drinking water. With 4% water resources and 16% of world population, which is rising and likely to touch almost 25% in 2050, the situation will worsen in time to come. The report "Safe Drinking Water", brought out by Third World Academy of Sciences, reveals that people in most part of Asia and Africa do not have access to safe drinking water and even in relatively advanced countries such as India, safe drinking water is not readily available, particularly in rural areas. The formation of nitrates is an integral part of the nitrogen cycle in our environment. In moderate amounts, nitrate is a harmless constituent of food and water. Plants use nitrates from the soil to satisfy nutrient requirements and may accumulate nitrate in their leaves and stems. Due to its high mobility, nitrate also can leach into groundwater. If people or animals drink water high in nitrate, it may cause methemoglobinemia, an illness found especially in infants. Nitrates form when microorganisms break down fertilizers, decaying plants, manures or other organic residues. Usually plants take up these nitrates, but sometimes rain or irrigation water can leach them into groundwater. Although nitrate occurs naturally in some groundwater, in most cases higher levels are thought to result from human activities. Common sources of nitrate include:

- Fertilizers and manure,
- Animal feedlots,
- Municipal wastewater and sludge,
- Septic systems,
- N-fixation from atmosphere by legumes, bacteria and lightning.

Nitrate levels in groundwater have been increased beyond its maximum contaminant level due to increased and excessive usage of nitrogenous fertilizers in agricultural sector, changes in land-use patterns from pasture to arable, and increased recycling of domestic wastewater in low-land Rivers (Bohdziewicz et al., 1998).. The World Health Organization (WHO) guideline value for maximum contaminant level (MCL) of nitrate in drinking water is 50 mg NO_3^-/L (WHO 1998).. The Bureau of Indian Standards (IS-10500:2009) prescribed value for nitrate in drinking water is 45 mg NO_3^-/l (BIS 2009). The US Environmental Protection Agency (EPA) established a maximum contaminant level (MCL) of 10mg N-NO_3^-/dm^3 (Pontious 1993). The ingestion of high nitrate through drinking water, may cause the change of hemoglobin into methemoglobin, this happens when the nitrate is reduced to nitrite in the gastrointestinal tract and when it reaches into blood stream, oxidizes the iron atoms in hemoglobin from ferrous (Fe^{2+}) to ferric (Fe^{3+}) ion form, which become unable to carry oxygen in the bloodstream and produces methaemoglobin with consequent impairment of oxygen transportation. The illness is called methemoglobinemia or "Blue Baby Syndrome" (Maheshwari 2007). For breastfed infants, there is no evidence of an increased risk of methemoglobinemia from maternal ingestion of water with nitrate nitrogen concentrations as high as 100ppm, because these mothers do not produce milk with high nitrate concentrations. Furthermore, the predominant organism in the gastrointestinal tract (*Lactobacillus* species) of the breastfed infant does not reduce nitrate to nitrite (Dusdieker et al.,1996). [35]Greater concentration can be fatal to infants under 6 month of age (Kim-Shapiro et al., 2005). Other harmful effects are spontaneous abortions, the possibility of malformations in children, increased incidence of hyperthyroidism (goitre), and bladder cancer. Nitrate converts into nitrite and then nitrosamine which is generally considered to be cancerous (Weyer 2001).

Occurrence of Nitrates and Nitrites in Food and Water

Water plays a decisive and crucial role in location and growth of human settlements. Demand of water has been rising in the urban centers not only due to population explosion but also due to growth in commercial activities along with social needs and comforts. Consequently, the existing system of water supply and sanitation are crumbling. The issue of rising nitrate concentration in groundwater has become a subject of extensive research in India and abroad. Concern has been expressed recently about the increasing levels of nitrate ion (NO_3^-) in drinking water, particularly in well water in rural locations; the main source of this NO_3^- is runoff from agricultural lands into rivers and streams. Initially, oxidized animal wastes (manure) and unabsorbed ammonium nitrate (NH_4NO_3) and other nitrogen fertilizers were thought to be the main culprits. It now appears that intensive cultivation of land, even without the application of fertilizer, facilitates the oxidation of reduced nitrogen to nitrate in decomposed matter in the soil by providing aeration and moisture. There are entire ecosystems ranging from forests to coastal waters that are now being overwhelmed by nitrogen compounds (Figure 1). Excess nitrate ion in wastewater flowing into seawater, for example, the Baltic Sea, has resulted has resulted in algae blooms that pollute the water after they die.

Nitrate is essential for the growth of many plant species, including most of those we consume. Yet it becomes a formidable hazard if it gets into water in excess. It's perceived mainly due to excessive use of chemical fertilizers but much of nitrate found in soil is produced by the microbial decomposition of plant residues (Write et al., 1999). Nitrate ions normally don't cause this effect in bodies of freshwater, where P rather than N is usually the nutrient; increasing the NO_3^- concentration there without an increase in P levels doesn't lead to an increased amount of plant growth. There are, however, instances where N rather than P temporarily becomes the limiting nutrient even in fresh waters. Modernization of agriculture has led to excessive use of nitrogenous fertilizers. About ¼th of applied fertilizer is not used by the crop plants and is leached down. These chemicals, usually nitrates, find their way into groundwater aquifers, increasing the concentration of nitrates in drinking water. Excessive addition of nitrates in modern agricultural field has become serious health hazard in rural areas. In cities, improper disposal of sewage material and inadequate sanitation services lead to this problem. The nitrates being soluble in water percolate through layers of soil into deeper layers of earth and ultimately find their way to underground stores of water (Maheshwari 2004).

Figure 1. Contaminated water drainage

ESTIMATION OF NITRATE ION

a) UV SPECTROPHOTOMETRIC PROCEDURE

Measurement of the UV- absorption at 220nm enables rapid determination of nitrate. The nitrate calibration curves follow Beer's law up to 11mg/l NO_3^- N. Because dissolved organic matter may also get absorbed at 220nm and NO_3^- doesn't get absorbed at 275nm, a second measurement can be made at 275nm to correct the NO_3^- value. The extent of empirical corrections is related to the nature and concentration of the organic matter and may vary from one water sample to another. Filtration of the sample is intended to remove possible interference from suspended particles. Readings of the absorbance or transmittance are taken against redistilled water set at zero absorbance or 100% transmittance. At 220nm, the NO_3^- readings are taken and at wavelength of 275nm readings are also observed due to dissolved organic matter. In order to obtain the absorbance due to NO_3^- , the reading at 275nm from the reading at 220nm was subtracted 2x. From the graph of standard values and absorbance data, equivalent values of NO_3^- were obtained.

b) ISE PROCEDURE

Nitrate ISE contains a sensing module having a liquid internal filling solution in contact with gelled, organophillic membrane containing a nitrate ion –selective ion-exchanger. Nitrate ISE develops a potential across a thin porous inert membrane that holds in place a water-immiscible liquid ion-exchanger. The electrode responds only to ionized NO_3^- activity between ~ 10^{-1} and 10^{-5}M (0.2 to 1400mg/l NO_3^-) the lower limit of detection is determined by the small but finite solubility of the liquid ion-exchanger. TISAB 2M KCl finds is use in removing interference. The potential difference is measured with nitrate ISE and SCE forming a cell.

Even since early 1990s, the agriculturally advanced states of Punjab and Haryana, where fertilizers have been intensively used, have wells with nitrate well above the safe limits prescribed by the WHO. Ozha and Jain (1992) studied nitrate in groundwater of some districts of Rajasthan. They noted greatest frequencies of waters having nitrate above 100mg/l in Churu district (77.99%) followed by Nagaur (53.07%), Barmer (53.66%) and Jalaur (40.39%) districts. Lowest frequency (3.04%) of such waters was recorded in Bikaner district. In another study by Ozha, et. al., (1993) in Churu district maximum nitrate level was recorded as 2400 mg/l and 32% samples contained nitrate up to 50 mg/l. Rai et al.(1997) reported a range of 15-590 mg/l in water of 60 wells in the desert city of Jodhpur. They also attributed to 57 cases of gastric cancer over three years study of high nitrate level in drinking water. Kalsotra, et al. (1996) noted objectionable nitrate concentration in the sources of water in Jammu district.

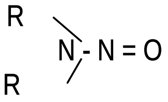
Chemobiokinetics and Pathophysiological Impact of Nitrate Ion

Nitrate, the most highly oxidized form of the N compounds is commonly present in natural waters, because it's the end product of the aerobic decomposition of organic nitrogenous matter. Excess NO_3^- ion in drinking water is a potential health hazard since it can result in *methemoglobinemia* in newborn infants, as well as in adults with a particular enzyme deficiency. Breastfed infants are not at risk of nitrate poisoning from mothers who ingest water with high nitrate content (up to 100ppm nitrate nitrogen), because nitrate concentration does not increase significantly in the milk (Dusdieker et al., 1996). Methemoglobinemia generally manifests with few clinical signs other than cyanosis. Methemoglobin represents only 1% of the total hemoglobin of the healthy adult, although it can be slightly higher in preterm and term newborn infants. Obvious cyanosis can occur with methemoglobin concentrations as low as 3% in infants with low hemoglobin concentrations. Symptoms are usually minimal until methemoglobin concentrations exceed 20%. The mucous membranes of infants with methemoglobinemia tend to have brown (rather than blue) discoloration. This discoloration increases with the concentration of methemoglobin, as do the manifestations of irritability, tachypnea, and altered mental status. In the absence of respiratory symptoms, history of cardiovascular disease, abnormal pulse, or abnormal pulse oximetry, a diagnosis of methemoglobinemia should be considered in a child who becomes acutely cyanotic and fails to respond to oxygen administration. When significant concentrations of methemoglobin (>30%) are present, a pulse oximeter is very misleading and will detect only mild to moderate oxygen desaturations in the 82% to 86% range (Wright et al., 1999).

The pathological process, in brief, runs as follows:
Bacteria, for example in unsterilized milk-feeding bottles or in the baby's stomach, reduce some of NO_3^- to NO_2^-. Nitrate in drinking water is a serious concern as nitrite is formed by the reduction of nitrate in the intestinal tract leading to BBS in infants fed with preprocessed baby foods. The nitrite combines with and oxidizes the hemoglobin in blood, and thereby prevents the proper absorption and transfer to the cells of oxygen. The baby turns blue and suffers respiratory failure. (In almost all adults, the oxidized hemoglobin is readily oxidized back to its oxygen-carrying form, and the nitrite is readily oxidized to nitrate; as well, nitrate is mainly absorbed in the digestive tract of adults before reduction to nitrite can occur.) Recently, an increase in the risk of acquiring *non-Hodgkin's lymphoma* has been found for persons consuming drinking water having the higher levels (long-term average of 4ppm N as nitrate) of nitrate in drinking water of some communities in Nebraska. Excess nitrate is also of concern because of its potential link with stomach cancer.

The long –term hazard relates to the reaction in the digestive system of the body, between nitrates (>100ppm) and organic matters (amines and/or amides) resulting in the production of *nitrosamines*, some of which are believed to be carcinogenic (Hawksworth et al., 1975). By the series of the reaction it is proposed that the nitrates in water may be converted into N-Nitroso-compounds that directly act as carcinogens.. Several cases of nitrate poisoning related to human beings and livestock have been reported in various areas of Rajasthan. It has been investigated that pregnant women consuming nitrate rich water, transfer this content to developing embryo through placenta. Nitrate content has been detected in human milk and lactating mothers pass this content to infants through breast-feeding. The water-borne ailments, due to consumption of nitrate rich water, are spreading at an alarming rate and becoming rampant as deadly cocktail of potentially lethal hazards. The problem is that the nitrites could subsequently react with amines to produce N-nitrosamines, compounds which are known to be carcinogenic in animals. N-nitrosamines are amines in which 2 organic groups and an –N=O unit are bonded to the central N:

R_2NNO or

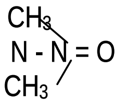


$$R_2N-N=O$$

N – nitrosamines

of concern not only with respect to its production in the stomach and its occurrence in foods and beverages (e.g. cheeses, fried bacon, smoked and/ or cured meat and fish, and beer), but also as an environmental pollutant in drinking water, is the compound in which the methyl group, CH_3: it's called N-nitrosadimethylamine, a.k.a. NDMA for short:

R_2NNO or



$$(CH_3)_2N-N=O$$

NDMA

Nitrate (NO_3^-) $\longrightarrow$ Nitrite (NO_2^-) $\longrightarrow$ N-Nitroso-compounds

This organic liquid is somewhat soluble in water (~4g/l) and somewhat soluble in organic liquids. It's a probable human carcinogen and a potent one if extrapolation from animal studies is a reliable guide. It can transfer a methyl group to N or O of a DNA base, and thereby alters the instructional code for protein synthesis in the cell. In the early 1980s, it was found that NDMA was present in beer to the extent of ~3000ppt. since that time commercial brewers have modified the drying of malt so that the current levels of NDMA in American and Canadian beer are only ~70ppt. large quantities of nitrate are employed to "cure" pork products such as bacon and hot dogs. In these foods, some of the nitrate ion is biochemically reduced to nitrite ion, which prevents the growth of the organism responsible for botulism. Nitrite ion also gives these meats their characteristic taste and color by combining with hemoproteins in blood. Nitrosamines are produced from excess nitrite during frying (e.g. of bacon) and in the stomach, as discussed earlier. Government agencies have instituted programs to decrease the residual nitrite levels in cured meats. Some manufactures of these foods now add vitamin C or E to the meat in order to block the formation of nitrosamines. Based upon the average levels of NDMA in various foods and the average daily intake for each of them, most of us now ingest more NDMA from consumption of cheese (which is often treated with nitrates) than from any other source. Even though the commercial production of NDMA has been phased out, it can be formed as a byproduct due to the use of amines in industrial processes such as rubber tire manufacturing, leather tanning and pesticide production.

Nitrate represents the highest oxidized form of nitrogen. Nitrate compounds are widely distributed in soil, plants and most waters. In natural water, nitrate nitrogen is usually less than 5mg/l. Additional amounts of nitrate and nitrite arise from the use of fertilizers and from discharge of sewage effluents (Tebutt 1928). In fact, the most important source of nitrate is biological oxidation of organic nitrogenous substances of sewage, industrial and agricultural origin. Many groundwater resources have significant quantities of nitrate due to leaching with the percolating water. Sewage and other waste rich in nitrates also contaminate groundwater. In Rajasthan, people bore deep hole in the ground into which is injected sewage and other domestic waste. High amount of nitrates are generally indicative of pollution. Thus water can be a significant source of nitrate and nitrate in the diet. Beside nitrate, ammonia (NH_3) also contaminates surface and groundwater. Nitrites are intermediate products of both in the oxidation of ammonia and in the reduction of nitrate, which occurs in wastewater treatment plants, water distribution system and natural water. Seepage of excessive nitrates into groundwater followed by its consumption can produce the fatal illness, methaemoglobinaemia (Blue-baby Syndrome) in young babies (Bosch et al., 1950). In many villages and townships where groundwater is the only source of drinking water, methaemoglobinaemia is prominent in bottle-fed infants in particular, because they are very sensitive to this pollutant, as they don’t have developed immune system. What happens is that when water-containing nitrate is ingested, it goes to intestine where, by the bacterial action in non-oxidizing conditions, nitrate is normally reduced to nitrites (a strong oxidizing agent). Due to more toxic in nature, nitrite can arise problems in young babies and there is a possibility of a long-term chronic hazard in adults too. Nitrite ion converts Fe (II) of hemoglobin to Fe (III) thereby forming methaemoglobin, which reduces the oxygen carrying capacity of the blood leading to suffocation and injury to respiratory and cardio-vascular system.

Nitrates are reduced to nitrites through microbial action in the upper gastrointestinal tract of the body. The nitrites cause an increased formation of methemoglobin (oxidised hemoglobin - Hb^{+2}), which is devoid of oxygen carrying capacity, in the blood. The health risk from exposure to nitrates is therefore related not only to their concentration in drinking water and food, but also to conditions conducive to their reduction to nitrites and to the protective auto reduction capacity of red blood corpuscles (RBCs) through cytochrome b_5 reductase, an intracellular enzyme of RBCs. The cytochrome b_5 reductase is required for regeneration of reduced cytochrome b_5 from oxidised cytochrome b_5 using NADH as an electron donor. The reduced cytochrome b_5 in the RBCs is necessary for the reduction of oxidised hemoglobin to reduced hemoglobin, which is necessary for oxygen carrying capacity of blood. Ingested inorganic or organic nitrates get converted to nitrite by microflora in oral cavity and in gastrointestinal tract by intestinal microflora . This will result in increased oxidation of hemoglobin to methemoglobin and increased production of nitric oxide. The conversion of nitrite to nitric oxide is non-enzymatic. The oxidation of hemoglobin to methemoglobin results in the formation of the superoxide radical, by the transfer of single electron. The enzyme superoxide dismutase, present in the erythrocytes, catalyses the conversion of superoxide radical ($O_{\cdot}$) to H_2O_2 and O_2. The $H_2O_{2,}$ gets decomposed, by glutathion peroxidase or catalase, both also present in erythrocytes. Once the rate of oxidation of hemoglobin increases sufficiently in erythrocytes and overwhelms the protective and reductive capacities (e.g. cytochrome b_5 reductase system, etc.) of the cells, there is increased production of reactive free radicals of nitric oxide ($NO_{\cdot}$) and oxygen ($O_{\cdot}$). Hemoglobin scavenges nitric oxide through the high affinity ferrous sites on heme to form S-nitrosothiol (with an affinity to nitric oxide 8000x than their affinity for oxygen) by binding at b 93 cysteine residues on the globin chain. As hemoglobin binds oxygen in the lungs its binding affinity to S-nitrosothiol is increased. As hemoglobin releases oxygen at the periphery its affinity for S-nitrosothiol is reduced and nitric oxide is released in the tissues. The thiol group of S-Nitrosothiol essentially protects nitric oxide from being scavenged by the binding site on heme. Thus in addition to carrying oxygen, haemoglobin acts as a carrier of nitric oxide. The enhanced release of nitric oxide from nitrosohaemoglobin in hypoxic tissue in turn reduces regional vascular resistance (Hawksworth et al., 1975).

The production of excessive quantities of methemoglobin is due to the presence of nitrate reducing bacteria in the infant's upper gastro-intestinal tract. These bacteria are capable of converting the ingested nitrate into nitrite, which on absorption oxidizes hemoglobin to methemoglobin. It's due to the less acidic pH in infant's stomach which accelerate the growth of nitrate-reducing bacteria. The nitrate ion itself isn't harmful as it's absorbed in the GIT and excreted rapidly via kidney. In an affected child, the nitrates are converted into nitrites prior to absorption. Infants have a relatively higher fluid intake and increases considerably in hot climate, which in turn increases the quantity of nitrate ingested.

$$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O$$

$$\underset{\text{(Hemoglobin)}}{Fe^{2+}} \xrightarrow{\text{Nitrite ion}} \underset{\text{(Methemoglobin)}}{Fe^{3+}}$$

Although there is no enforceable drinking water standard for livestock, do not allow animals to drink water with more than 100 mg/l NO_3-N. This is especially true of young animals. They are affected by nitrates the same way as human babies. Older animals may tolerate higher levels. Ruminant animals (cattle, sheep) are susceptible to nitrate poisoning because bacteria present in the rumen convert nitrate to nitrite. Nonruminant animals (swine, chickens) rapidly eliminate nitrate in their urine. Horses are monogastric, but their large cecum acts much like a rumen. This makes them more susceptible to nitrate poisoning than other monogastric animals. It is difficult to determine the toxicity of nitrate in animals because it depends on the rate at which the substance is consumed. A few hundred milligrams of nitrate may cause poisoning if consumed in a few hours. But spread over a whole day, 1,000 mg nitrate may cause no signs of toxicity. Common symptoms include abdominal pain, diarrhea, muscular weakness or poor coordination. Affected animals will have blood that is a chocolate-brown color. If the problem is diagnosed in time, they can fully recover with a treatment of methylene blue. Pregnant animals may abort within a few days. Nitrate also exists in animal feeds and fodder. Drought-stressed forage plants commonly have high nitrate levels. These feeds can have an additive effect when consumed with high nitrate drinking water.

Nitrate Standards

In accordance to the UPSH drinking water standards, a limit of 10 mg/l of nitrate and 0.1mg/l for nitrite must be regularly monitored in water supplies as they are deemed to be potentially hazardous to infants less than five months old. In Rajasthan, vast number of malnourished people, especially in rural areas face, acute gastric disorders. The BIS permits up to 100ppm nitrate in safe drinking water. However the more stringent norms of USA, say that presence of nitrate beyond 45ppm can be fatal for infants. The expenditure of public money on nitrate level reductions in drinking water has become a controversial subject. In Great Britain, in particular, hundreds of millions of dollars have been spent on achieving the 50ppm maximum levels of nitrate ion set by the EEC. The US, EPA regulatory limit is 10ppm of nitrate N. The level of NDMA in drinking water drawn from groundwater is of concern in some localities that industrial point sources of the compound. For example, following the discovery that the water supply of one town had been contaminated by up to 100ppt NDMA from a tire factory, the province of Ontario, Canada adopted a guideline maximum of 6ppt of NDMA in drinking water, which corresponds to a lifetime cancer risk of 1 in 100,000. By contrast, the guideline for water in the US is set at 0.68ppt, which corresponds to a cancer risk of 1 in a million, but which actually lies considerably below the detection limit (~5ppt) for the compound.

Nitrate Mitigation Strategies

Desalination is the natural continuous process, which is essential for the water cycle. Precipitation, such as rain, snowfall on ground, which finally flows either in the sea or goes back to the atmosphere through evaporation or percolates in the sub soil is a process of a natural desalination. During the travel of the surface water towards sea it dissolves minerals and other materials and becomes salty. Once it arrives to the oceans, natural evaporation removes part of the water in to the atmosphere as cloud while remaining water available n the ocean becomes very salty. The evaporated water from the ocean is given back to the earth in the form of rain or snow, which again travels back to ocean and the cycle continues. Desalination technologies besides producing desalted water for human consumption and industrial requirement they also found to be advantageous in the recovery of water from waste streams. As such, all desalination processes remove nitrate ions indiscriminately from water as it removes all other ions. However, there are many groundwater sources, which despite having TDS contents well within the recommended by various health regulatory bodies, containing nitrate ions in concentrations exceeding the recommended limits. In such cases, the various desalination processes (Figure. 2) prove to be too uneconomical and the demand for a process suitable to remove the excessive nitrate ions selectively becomes mandatory.

Figure 2. Desalination Process

A nitrate ion-selective anion exchanger based on divinylbenzine copolymer resin beads has been developed by Defense Research Laboratory (Jodhpur). The resin is capable to remove nitrate ions selectively from water in the presence of sulphate (SO_4^{--}) ions. The extent of nitrate removal depends upon the flow rate as well as the ratio of the NO_3^- ions to SO_4^{--} ions in water. While the conventional anion exchange resin removes more of the SO_4^{--} ions in comparison to NO_3^- ions, the selective resin removes more of NO_3^- ions, exhibiting good selectivity for NO_3^- ions. So far, a commercial nitrate removal plant hasn't come into existence in India. However, since 1990, the largest nitrate removal plant has become operational in Britain. The capacity of the plant is 4.5Ml/day and is based on ion-exchange technology.

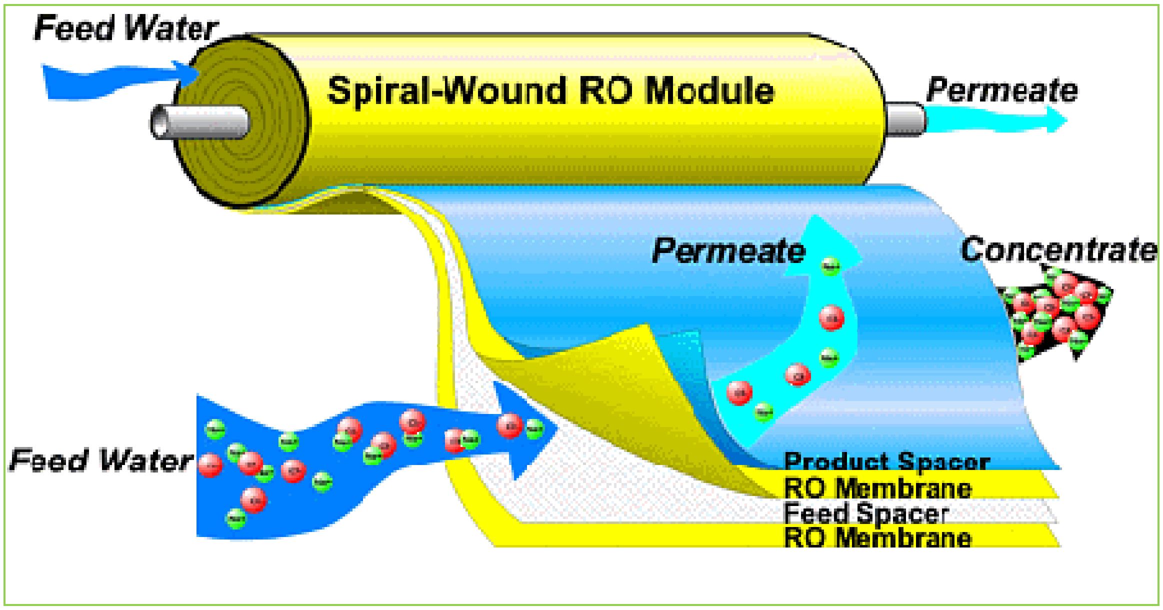


Figure 3. RO Membrane

The dissolved nitrate gets rectified but passing the water through nitrate-selective anion-exchange resin contained in three steel pressure vessels 1.5m diameter and 4m high.

This paper delineates an attempt at removal of nitrate ions from drinking water and influence of di-hydrogen phosphate on removal efficiency of polyamide RO membrane (Figure. 3) because the technology is well known and very effectively applied for the removal of salts. Ratanatamskul et al. reported 70 nitrate removal using ultra low pressure nanofiltration membrane (Ratanatamskul, et al., 1998). Bohdziewicz et al. obtained nitrate removal of 76 using cellulose acetate RO membrane for the removal of nitrate from groundwater Bohdziewicz et al.,1999).. Qin et al. reported 85 rejection for nitrate using RO polyamide membrane (Qin et al., 2004). Balannec et al. studied phosphate rejections of three RO membrane; Desal 3SF (Polyamide/Polysulfone), TFC-HR (Composite polyamide), and BW30 (Composite polyamide). Phosphate removals of 99.6, 100, and 99.8% were obtained, respectively (Balannec et al., 2005). Molinari et al. (2010) studied the interactions between polyamide RO membrane and nitrate ions.They observed that copper nitrate was absorbed on reverse osmosis polyamide membrane during treatment a solution containing copper nitrate. The process was described principally to copper ion binding to the electronic lone-pair of membrane amino-groups by means of Lewis acid–base interaction which holds NO_3^- ions. Madaeni and Koocheki (2010) observed that the feed solution containing potassium di-hydrogen phosphate ions provides binding with carbonyl group of polyamide membrane (Figure. 4).

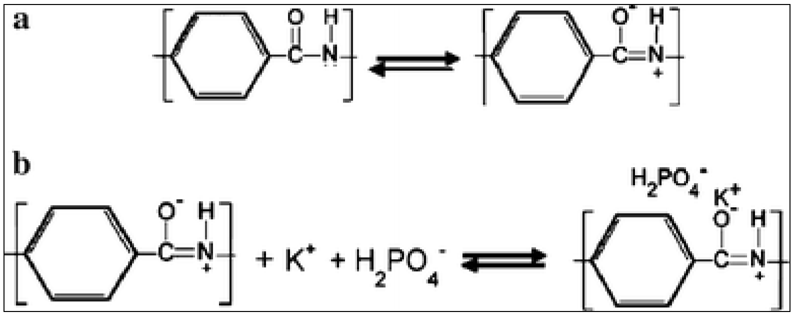


Figure 4. Binding mechanism of potassium DHP on polyamide membrane

MATERIALS AND METHODS

The RO system (Figure 8) was equipped with module having polyamide thin-film composite membrane (DOW FILMTEC™ TW30-1812-100), a pressure pump, pressure gauge, pressure controller and feed tank. Feed solutions were prepared using deionized water at the pH 6. The experiments were performed at the pressure of 5 and 7 bars. For nitrate determination, the ultraviolet spectrophotometric screening method was applied at the wavelength of 220 nm while DHP was determined by vanadomolybdophosphoric acid colorimetric method at wavelength of 400-490 nm. The observed % rejection (R) derives from the following relation:

$$\% R = (1 - C_p/C_f) \times 100$$

Where C_p and C_f are the concentrations of the nitrate in permeate and feed solution, respectively. The rejections were tested for two samples, one of which contained only potassium nitrate of conc. 50mg $N\text{-}NO_3^-$/L and other sample contained nitrate of conc. 50mg $N\text{-}NO_3^-$ /L with potassium DHP of conc. 100mg $H_2PO_4^-$/L. The rejection results are presented in 5 and 7 bar transmembrane pressures.

RESULTS AND DISCUSSION

DHP ion exhibited the highest rejection and rejection sequence was independent of the transmembrane pressure (Figure. 5 and 6). The experimental data (which is shown in Figure. 5, 6 and 7) indicate that the rejection of nitrate ions before and after addition of KH_2PO_4 is around 76 and 84 respectively. This means the improvement in rejection of NO_3^- ions is due to the presence of $H_2PO_4^-$ ions. In other words when nitrate ions were mixed with DHP at an appropriate concentration, the rejection was improved to 84. This is an important fact as the removal of nitrate ions from drinking water as well as wastewater take place more efficiently under the presence of KH_2PO_4. In summary, the nitrate ion with a larger molar volume corresponding to a larger surface area would have a lower surface charge density around the molecule compared to smaller molar volume of the ion. Thus the donnan effect between nitrate and membrane (which is negatively charged) is weaker and because of electro-neutrality condition its rejection is lower than other ions like Cl^- . (Wang et al., 2005; Maheshwari and Rani 2007; Maheshwari and Rani 2011; Rani et al., 2006; Maheshwari 2007. Solute permeability depends on the properties of ions and membrane. The interaction between membrane and ions may affect the membrane performance.

Polyamide has electronic lone-pair in amino group that is able to make a resonance structure with carbonyl group. The feed solution containing potassium and DHP ions provide binding with membrane. This provides a negative layer on the surface of the membrane. Diffusion of anions through the membrane is reduced due to the electrostatic force of repulsion by formed negative layer. This layer prevents the passage of anions through the membrane leading to an improvement in ion rejection. From figure 3, it was also found that rejection of nitrate increases with increased initial feed pressure on feed side of membrane. It was also seen from figure 4 and 5, that the %age rejection was more for phosphate compared to nitrate at same pressure of 5 and 7 bar respectively.

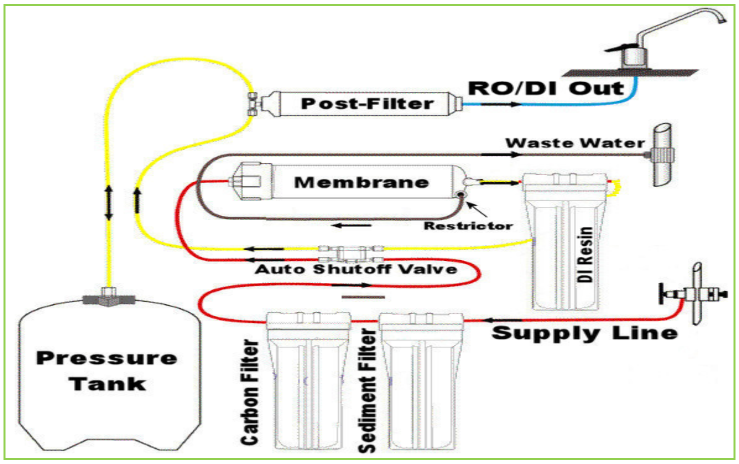


Figure 5. RO System

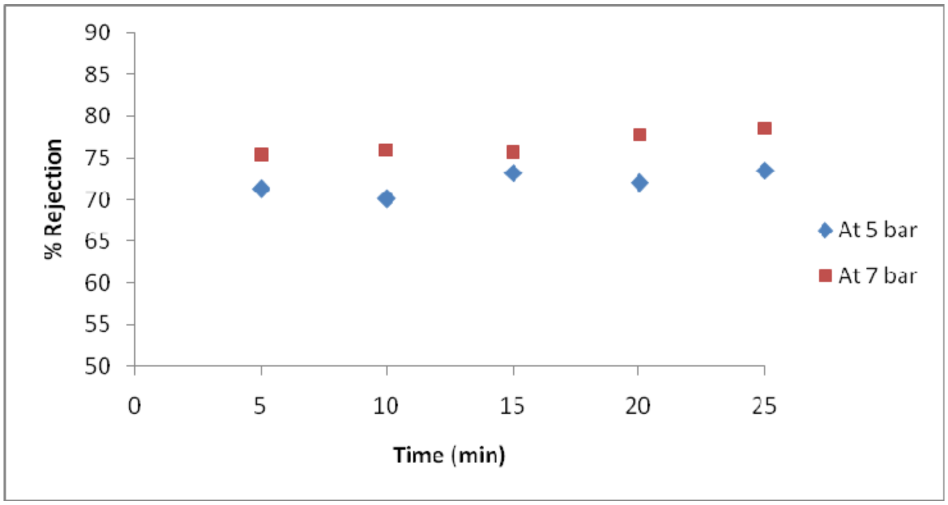


Figure 6. Individual nitrate rejection DHP

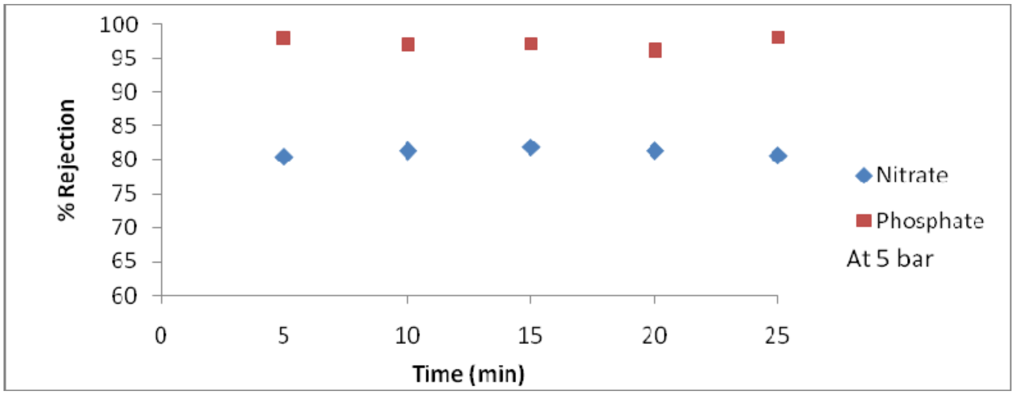


Figure 7. Rjection of nitrate with DHP at 5 bar pressure

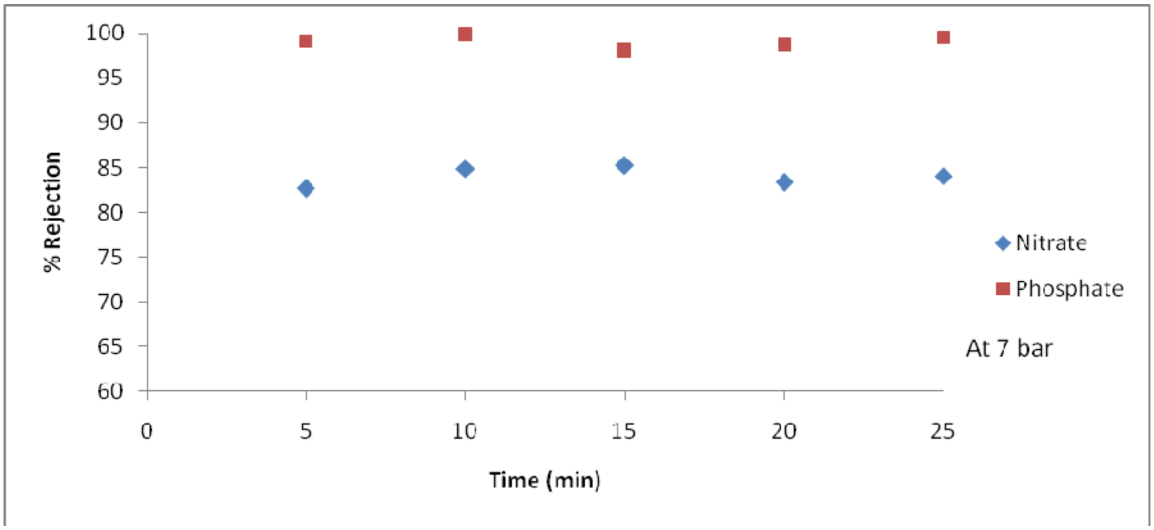


Figure 8. Rejection of nitrate with DHP at 7 bar pressure

CONCLUSION

Excessive application of nitrogenous fertilizer as well as organic waste and sewage (landfills and pasture urine), has been implicated in the nitrate pollution of groundwater. Nitrate pollution has become one of the key environmental issues because of its implications on human and animal health as well. With the increasing use of nitrogenous fertilizers and huge amount of organic wastes generated by massive population, nitrate contamination in many regions of our country has assumed alarming proportions and may become serious problem in the forth coming years. Urbanization has introduced plethora of dilemmas including overexploitation as well as quality deterioration of groundwater resources. Genesis of high nitrate contents in groundwater resources include leakage from old sewage systems and soak pits, lack of solid waste disposal system, seepage from unlined drains (carrying effluents and sewerages), cattle excreta from cattle dairies and use of excessive nitrate fertilizers for gardening etc. porous and permeable alluvial geo-formations along with shallower depth of groundwater levels have facilitated rapid pollution. RO experiment was conducted and it was found that the removal of individual nitrate ions was around 76 and it enhances up to 84 in the presence of $H_2PO_4^-$ ions. It was also observed that the removal efficiency of the membrane for DHP was around more than 99 as this would be helpful for removal of nitrate to a great extent since phosphate itself remove nearly completely from the feed solution without creating extra burden of its removal. The rejections of nitrate and phosphate ions were found to be increased with increase in feed pressure. The K^+ ion in the feed solution provides binding with polyamide membrane which holds DHP ions. This establishes a negative layer which diminishes the diffusion of negatively charged nitrate ions through the membrane. It was advisable to run the setup at an appropriate feed pressure so that the rejection in retentate should be large.

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CONFLICT OF INTEREST: Nothing