Assessing Innovative Technologies for Nitrate Removal from Drinking Water

by

Shoeleh Shams

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Several health problems may be caused by excess nitrate in drinking water, the most important of which being methemoglobinemia, a potentially fatal disorder, in infants under six months of age.

Many different parts of the world have been facing the problem of nitrate contaminated surface and groundwaters due in large part to excessive use of nitrate-based chemical fertilizers. In the Region of Waterloo, Ontario, Canada some groundwater sources have nitrate concentrations approaching the Health Canada and Ontario Ministry of the Environment maximum acceptable concentration (MAC) of 10 mg NO_3^--N/L.

Finding a practical and economical way to reduce nitrate concentrations in representative groundwater in the Region of Waterloo was the overall objective of this research. To achieve this goal, nitrate removal technologies including biological denitrification, ion exchange (IX), reverse osmosis (RO), electrodialysis (ED), and chemical denitrification were reviewed and compared. IX and RO were found to be the most promising technologies for nitrate removal. They have also been approved by the United States Environmental Protection Agency (USEPA) as Best Available Technologies (BAT).

To investigate the feasibility of IX and RO for nitrate removal from representative groundwater in the Region of Waterloo, bench-scale experiments were conducted and compared. These technologies could be considered for application at full- or point-of-use (POU)-scale. Decision support assistance for the selection of the appropriate technology for different technical and economical conditions is provided as an outcome of this work.

Two nitrate-selective ion exchange resins (Dowex™ NSR-1 and Purolite® A-520E), two non-selective resins (Purolite® A-300E and Amberlite® IRA400 Cl), and a commercially-available RO POU device (Culligan® Aqua-Cleer® model RO30), which included a particle filter and a carbon block, were tested with deionized water and real groundwater.[*]

IX results confirmed that production time before resin exhaustion was influenced by operating conditions, specifically bed depth as would be expected. It was also confirmed that the presence of competing anions (sulfate, chloride) and alkalinity adversely affected performance, with sulfate being the main competitor for nitrate removal. The extent of these effects was quantified for the conditions tested. At the end of the runs, the non-selective resins were prone to potential nitrate displacement and release into product water and are therefore not recommended. The nitrate-selective resins did not

release previously adsorbed nitrate as their capacity became exhausted. Purolite® A-520E was identified as the best alternative amongst the four resins for removing nitrate from the representative groundwater source.

The RO unit removed roughly 80% of the nitrate from groundwater. Background ions didn't appear to compete with each other for removal by RO units, so RO might be a more appropriate technology than IX for nitrate removal from waters with high concentrations of sulfate or TDS. Since RO removes other background ions as well as nitrate, the product water of RO is low in alkalinity and can potentially be corrosive, if water from a small full-scale system is pumped through a communal distribution system. Post-treatment including pH adjustment, addition of caustic soda, and/or corrosion inhibitors may be required.

While the carbon block did not play a substantial role with respect to removal of nitrate in the groundwater tested, a potential issue was identified when running RO systems without the carbon block. In deionized water (and presumably in very low alkalinity real waters) it was noted that RO nitrate removal efficiency dropped substantially as the alkalinity of the influent water approached zero.

With respect to the scale of application of IX and RO devices, IX can be applied at full-scale without requiring large amounts of space. However, if feed water contains high concentrations of sulfate or TDS, nitrate leakage happens sooner and regeneration would be needed at more frequent intervals. Also, chloride concentrations in IX product water might exceed aesthetic objectives (AO) and should be monitored in cases of high feed water TDS. POU IX devices are not recommended when feed water nitrate concentration is high due to potential nitrate leakage into the product water when the resin is nearing exhaustion which increases public health risk. Issues associated with RO application at full-scale are high energy demand, low recovery, high costs, need of pre-treatment (fouling control), and post-treatment (corrosion control). On the other hand, POU RO devices may be acceptable since low recovery is of less importance in a household system, and product water corrosivity is less relevant. POU RO devices are preferable to POU IX units due to their lower risk of nitrate leakage into treated water.

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[*] Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Chapter 1

Introduction

Nitrate, a naturally occurring ion, arises due to degradation of nitrogen-containing compounds. But, its high concentrations are caused by excessive application of chemical fertilizers (Rupert, 2008). Nitrate exposure can lead to several health problems such as spontaneous abortion, increased infant mortality, birth defects, abdominal pain, diarrhea, vomiting, diabetes, hypertension, respiratory tract infections, changes in the immune system, and methemoglobinemia (Kross et al., 1992; Lohumi et al., 2004; Fewtrell, 2004; Greer and Shannon, 2005; Ward et al., 2005; van Grinsven, 2006; Rachid et al., 2006)

To limit the risk to human health from nitrate in drinking water, the Maximum Acceptable Concentration (MAC) and Maximum Contaminant Level (MCL) are set to be 10 mg NO_3^-- N/L (45 mg NO_3^-/L) in Canada and the United States respectively, while the World Health Organization (WHO) and the European Community have set the MCL at 11.3 mg NO_3^-- N/L (50 mg NO_3^-/L) (European Community, 1998; Ontario Ministry of the Environment, 2006; USEPA, 2006; WHO, 2006; Health Canada, 2007).

To remove nitrate from drinking water there are several treatment technologies. The two most common are ion exchange (IX) and reverse osmosis (RO) both of which have been approved by EPA as Best Available Technologies (BAT) (USEPA, 2004). Ion exchange is a process in which the target ion replaces another less well adsorbed ion on a resin. This process is a promising technology for nitrate removal because of its simplicity, effectiveness, and relatively low cost (Symons et al., 2001; Bae et al., 2002; Boumediene and Achour, 2004). In the case of reverse osmosis (RO) water passes through a semipermeable membrane, and nitrate and other ions are rejected. The driving force in RO is pressure that exceeds the solution's typical osmotic pressure (Symons et al., 2001; Darbi et al., 2003). Another technology for nitrate removal is chemical denitrification in which iron or aluminum is used to reduce nitrate to ammonia or nitrogen gas. Biological denitrification is widely used for the treatment of municipal and industrial wastewater by degradation of microorganisms, but is less commonly used in drinking water applications (Soares, 2000). The remaining nitrate treatment technology is electrodialysis (ED) in which ions pass through a semipermeable membrane due to the driving force of an electric field (Symons et al., 2001).

1.1 Research Motivation

In the Region of Waterloo (Ontario, Canada) an investigation by Water and Earth Science Associates Ltd. (WESA) was conducted in 2004 to assess the nitrate concentrations in groundwater in the St. Agatha well field which is located in the central portion of the 315 km^2 Waterloo Moraine. This well field is operated by the Region and supplies the Strauss Court subdivision area of town with disinfected groundwater. In addition, there are two wells with associated private communal water distribution systems in the area. In the period from 2000 to 2003, nitrate levels in two of those wells varied between 5 to 8 NO_3^--N/L, and in the other two nitrate levels ranged from 8 to 9.5 NO_3^--N/L. It was reported that increasing the pumping rate increased the nitrate level. The report cautioned that if continuous use of these water sources was anticipated, then treatment to reduce nitrate concentrations may be necessary (WESA, 2004).

The overall goal of this research was to find a practical and economical way to reduce nitrate concentrations in representative groundwater in the Region of Waterloo such that wells with increasing nitrate concentrations can continue to be used and decommissioned wells can potentially be returned to service.

1.2 Approach

To achieve the goal of this research, ion exchange (IX) and point-of-use (POU) reverse osmosis (RO) technologies were investigated using deionized (DI) water spiked with nitrate and other competing anions, and also groundwater from the Region of Waterloo. This investigation was conducted at bench-scale in order to evaluate a wider spectrum of technologies and conditions for their potential for application in full-scale plant or in home POU units, in the Region of Waterloo.

To investigate and compare the feasibility of IX and RO technologies, two nitrate-selective ion exchange resins (Dowex™ NSR-1 and Purolite® A-520E), two non-selective resins (Purolite® A-300E and Amberlite® IRA400 Cl), and a commercially-available RO POU device (Culligan® Aqua-Cleer® model RO30), including a particle filter and a carbon block, were tested. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

1.3 Objectives

Specific objectives of this research were to:

1. Identify ion exchange resins best suited to treat several source waters representative of the Region’s groundwater, based on nitrate removal efficiency and run length (to resin regeneration).
2. Study the effect of operation conditions (hydraulic loading and bed depth) on ion exchange resin nitrate removal performance.
3. Investigate the influence of individual competing anions and mixtures of these on ion exchange resin nitrate removal performance.
4. Determine if competing anion issues can be dealt with through rigorous investigation of available resins using spiked and actual groundwaters leading to the selection of an appropriate resin, or if pretreatment will be required.
5. Compare the performance of nitrate-selective and non-selective resins under a variety of conditions and assess the performance of nitrate-selective resins.
6. Test a commercially-available NSF certified point-of-use reverse osmosis unit as a stand-alone device for nitrate removal from spiked and actual Region’s groundwater at different pressures.
7. Investigate the influence of individual background anions and mixtures of these on the RO unit’s nitrate removal performance.
8. Determine if pre-filters (particle filter and carbon block) play a role in the nitrate removal efficiency of the RO unit to investigate the potential ability of filtration and adsorption methods for nitrate removal.
9. Assess the application of IX and RO technologies as full-scale units and point-of-use (POU) devices, provide guidance on how to select the appropriate technology and compare them under different conditions.

1.4 Thesis Organization

This thesis consists of seven chapters as described below.

Following this introduction, Chapter 2 presents the sources, frequency, and chemistry of nitrate contaminated waters. Health issues associated with nitrate exposure and current drinking water regulations are also reviewed. Nitrate treatment technologies, their advantages and disadvantages, and applications are briefly described in this chapter, while IX and RO are discussed in more detail.

Details of the apparatus and operation of both the IX and RO systems are discussed in Chapter 3. Also, some information on commercially available IX resins and RO units are presented in this chapter. Experimental methods used to determine the concentration of target ions, as well as the materials are also discussed.

Experiments conducted using ion exchange are summarized in Chapter 4. Effects of operating conditions and competing anions on the performance of the resins for nitrate removal are discussed by presenting and evaluating the characteristics of product water for each experiment. A recommendation for the best suited ion exchange resin to treat the groundwater in the Region of Waterloo is made.

Results of experiments conducted using RO unit are documented in Chapter 5. These results include investigating the influence of background anions and presence of pre-filters on nitrate removal efficiency of the unit. The system is tested for nitrate removal from a real groundwater and the characteristics of product and reject water are discussed.

Chapter 6 is dedicated to summarizing the results of the two technologies and comparing their performances. The applications of both technologies in the water treatment industry as full-scale plants and POU devices are discussed.

Finally, conclusions of this research and recommendations are presented in Chapter 7.

Chapter 2

Literature Review

The prevalence, sources, and chemistry of nitrate as well as the potential health implications associated with exposure to nitrate are discussed. A brief overview of nitrate treatment technologies is presented while ion exchange (IX) and reverse osmosis (RO) are discussed in more detail.

2.1 Nitrate in Drinking Water

2.1.1 Nitrate Prevalence, Sources, and Chemistry

Many different parts of the world have been facing the problem of nitrate contaminated surface and groundwaters (Kapoor and Viraraghavan, 1997; Shrimali and Singh, 2001). To investigate the extent of this contamination in the United States, various surveys have been conducted by different agencies. It was reported that among 140 contaminants measured in 1500 public wells in the United States, nitrate most frequently exceeded the United States Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) of 10 mg NO_3^--N/L (Squillace et al., 2002). A USEPA survey in 1990 revealed that up to 1,130 public and approximately 250,000 private domestic water supply wells exceeded the MCL of 10 mg NO_3^--N/L for nitrate (EPA, 1990). Another study conducted by the USEPA in 1992 revealed that three million people, including 43,500 infants, consumed drinking water with nitrate concentrations over the MCL (Luk and Au-Yeung, 2002). The U.S. Geological Survey (USGS) has conducted several surveys to investigate nitrate prevalence in the United States in the current decade. According to their report in 2000 on data collected from 33 main aquifers during 1992-1995, more than 15% of samples from 4 of the aquifers were nitrate contaminated. It is also indicated that nitrate level is higher in shallow groundwater wells than in deep ground water sources (Nolan and Stoner, 2000). Furthermore, results from the samples collected during a National-Water Quality Assessment Program by the U.S. Geological Survey (USGS) showed that 11% of samples from 1255 domestic wells and 2% of samples from 242 public water supply wells exceeded the USEPA MCL (10 mg NO_3^--N/L) for nitrate (Squillace et al., 2002). The USGS did another survey on the national-scale comparing data from 495 wells during 1988-1995 and 2000-2004. The objective of the study was to investigate the trend of nitrate concentrations in the United States. It was found that nitrate concentration in 29% of the wells had increased considerably. And, nitrate concentration exceeded the USEPA MCL in 12.5% of the wells (Rupert, 2008). Also, according to a more recent USGS study on 2100 domestic wells across the United States, concentrations of nitrate were greater than the USEPA MCL in about 4% of the wells (DeSimone et al., 2009).

Significant sources of nitrate in water include nitrate-based chemical fertilizers, decaying vegetable and animal and human waste, domestic effluents (sewage sludge disposal and industrial discharge), atmospheric washout, septic systems, pesticides, and waste contamination through storm and urban runoff (Hell et al., 1998; Luk and Au-Yeung, 2002; Nataraj et al., 2006; Samatya et al., 2006). Of these, synthetic fertilizers are the major contributors to water contamination (Rupert, 2008). All these products can be converted to nitrate through a series of bacterial reactions collectively known as nitrification. In the nitrification process, bacteria degrade nitrogen-containing compounds and release ammonia. Some bacteria such as *Nitrosomonas* can oxidize the released ammonia to nitrite, and other bacteria such as *Nitrobactor* further oxidize the nitrite to nitrate (Shrimali and Singh, 2001).

2.1.2 Nitrate Health Issues and Drinking Water Regulations

Several health problems may be caused by excess nitrate in water sources. Normally, nitrate is eliminated through the kidneys before converting to nitrite (Greer and Shannon, 2005), but it is reported that high intake by pregnant women can cause spontaneous abortion and birth defects such as neural tube defect (Ward et al., 2005; van Grinsven, 2006). However, nitrate might not be the only contaminant that causes the adverse reproductive effects, and the relationship between consuming nitrate and reproductive issues is neither completely clear nor consistent, and needs to be studied in more details (Ward et al., 2005; Manassaram et al., 2006; van Grinsven, 2006). In adults with reduced stomach acidity or deficient in the methemoglobin reductase enzyme, high amounts of nitrate may cause abdominal pain, diarrhea, vomiting, diabetes, hypertension, respiratory tract infections, and changes in the immune system (Lohumi et al., 2004; Fewtrell, 2004).

Nitrate is converted to nitrite through microbial reduction. The reaction between nitrite and secondary or tertiary amine in acidic mediums such as the human stomach can result in the formation of N-nitroso compounds (NOC), which are known to be carcinogenic, teratogenic, and mutagenic (Pontius, 1993; Mikuska and Vecera, 2003; van Grinsven, 2006). NOC might cause cancers such as stomach and bladder cancer. However, studies that investigated relations between drinking water nitrate contamination and cancer risks have resulted in contradictory conclusions (Ward et al., 2005; van Grinsven, 2006; Chiu et al., 2007). The most important health concern associated with nitrate is that it causes methemoglobinemia, a potentially fatal disorder, in infants under six month of age. Methemoglobin (MetHb) is a form of hemoglobin (Hb) that cannot bind oxygen. Nitrite transforms Hb to MetHb by oxidizing the ferrous iron in hemoglobin to the ferric form (Kross et al., 1992; Greer and Shannon, 2005; Rachid et al., 2006). However, based on the limited data, it is not possible to specify an exact level as a safe nitrate intake level for all infants (Greer and Shannon, 2005). On the other hand, it is also reported that many cases of methemoglobinemia in infants might be caused by overproduction of nitric oxide due to gastrointestinal infection and inflammation and not by consuming drinking water nitrate. Therefore, some researchers have suggested increasing the current nitrate standard levels (Avery, 1999; van Grinsven, 2006)

Despite conflicting research findings, standards have been set for nitrate in drinking water. The USEPA maximum contaminant level (MCL) for nitrate is 10 mg NO_3^--N/L (USEPA, 2006), whereas the World Health Organization (WHO) and the European Community have set an MCL of 50 mg NO_3^-/L which is equal to 11.3 mg NO_3^--N/L (WHO, 2006; European Community, 1998). Health Canada has set the maximum acceptable concentrations (MAC) of nitrate in drinking water of 45 mg NO_3^-/L (10 mg NO_3^--N/L) (Health Canada, 2008). The MAC of nitrate as regulated by the Ontario Ministry of the Environment is also 10 mg NO_3^--N/L (Ontario Ministry of the Environment, 2006).

2.2 Nitrate Treatment Technologies

At high nitrate concentrations, water must be treated to meet regulated concentrations. But, it is almost impossible to remove nitrate by conventional drinking water treatment methods such as coagulation and filtration due to its high stability and solubility, as well as its low potential for coprecipitation or adsorption in water (Luk and Au-Yeung, 2002; USEPA, 2003). Therefore, other technologies including biological denitrification, ion exchange (IX), reverse osmosis (RO), electrodialysis (ED), and chemical denitrification have been studied or applied to remove nitrate from drinking water (Kapoor and Viraraghavan, 1997; Luk and Au-Yeung, 2002; Samatya et al., 2006). Among these methods, the first four have been applied at full-scale. WHO has suggested biological denitrification and IX as nitrate removal methods (WHO, 1992), while IX, RO, and ED are approved by EPA as Best Available Technologies (BAT) for removing nitrate (USEPA, 2004). Each of these technologies has its own strengths and drawbacks and their feasibility is weighted against factors such as cost, water quality improvement, residuals handling, and post-treatment requirements.

2.3 Ion Exchange (IX)

Ion exchange is a reversible chemical process in which ions from an insoluble permanent solid medium (the ion exchanger-usually a resin) are exchanged for ions in a solution or fluid mixture surrounding the insoluble medium (Symons et al., 2001; MWH, 2005). The direction of the exchange depends on the selective attraction of the ion exchange resin for the specific ions present and the concentration of the ions in the solution. Both cation and anion exchange are used to remove hardness or contaminants. Cation exchange is commonly used for water softening (Symons et al., 2001). The first full-scale IX treatment plant that used synthetic resins was built in 1946 for the purpose of water softening.

Ion exchange resin is a bead-like material that removes ions from water. Synthetic ion exchange resin is a manufactured ion exchange resin, commonly made with cross-linked polymers having exchangeable functional groups (Symons et al., 2001). Strong acid cation (SAC), and weak acid cation (WAC) are the two general types of resins that can exchange cations. Strong base anion (SBA) and weak base anion (WBA) are used for removing anions such as nitrate (MWH, 2005). Ion exchange resins exchange ions in a selective order based on the chemical and physical properties of both resin and ions. This characteristic is called selectivity and for regular SBA resins is found to be as follows:

$SO_4^{2-} > ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > OH^-$ (Helfferich, 1995; MWH, 2005)

SBA resins are available in two main forms. The functional group of Type 1 consists of three methyl groups, while an ethanol group replaces one of the methyl groups to form SBA Type 2. The chemical stability of SBA Type 1 is greater than Type 2. But, regeneration efficiency and capacity is higher for SBA Type 2 resins (Liang et al., 1999; MWH, 2005).

However, SBA resins with higher selectivity for nitrate than sulfate have been developed and used for nitrate removal (Kapoor and Viraraghavan, 1997; Liang et al., 1999). The functional group of these resins are ethyl, propyl, or butyl groups (Liang et al., 1999). Their characteristics and applications are explained in section 2.3.4.3.

SBA resins are typically manufactured in chloride, bicarbonate, or hydroxide forms. The most common form of SBA resins is the chloride form that exchanges anions for chloride (Kapoor and Viraraghavan, 1997; MWH, 2005).

2.3.1 Application of IX for Nitrate Removal from Drinking Water

IX has been introduced by WHO as a nitrate removal technology (WHO, 1992), and approved as a Best Available Technology (BAT) for nitrate removal by USEPA (USEPA, 2004). Numerous studies have investigated the feasibility of nitrate removal from drinking water by IX and full-scale IX plants have been built and operated to treat nitrate in groundwater.

A 695 GPM (44L/s) IX plant in the City of McFarland, California was built by McFarland Mutual Water Company in 1983. A nitrate-selective resin (A-101-D, Duolite, Rohm and Hass) was used and regenerated by NaCl through partial regeneration, and the waste was disposed at a waste water treatment plant. Nitrate was reduced from 16 to 2.6 mg NO_3^--N/L in this plant and a blend of 70% of treated water and 30% of untreated water was conveyed to the distribution system. Total annual costs (capital, operations, and maintenance) of the plant were reported to be 24.2 US cents/1000 gal (Lauch and Guter, 1986).

Basin Water Inc. (Rancho Cucamonga, CA) has built several fully-automated multiple-bed (partial regeneration) IX systems for wellhead treatment of nitrate contaminated wells in the United States. This patented system is constructed in a standard shipping size container and has been delivered to the client sites listed in Table 2-1 (Ruppenthal, 2004; Basin Water, 2005; Taylor, 2005; Ruppenthal, 2007). Resin types used for these projects, are proprietary and as such not identified.

Table 2-1: Full-scale IX nitrate removal installations by Basin Water Inc.

Costumer	**Site**	**Year installed**	**Flow**		**Reference**
			GPM	**L/s**	
City of Avondale	Avondale, Arizona	2003	600 + 1300	38 + 82	Ruppenthal, 2004, Ruppenthal, 2007
California Water Service Company	Salinas, California	2002	3×1000	3×63	Basin Water, 2005
East Valley Water District	East Valley, San Bernardino Highland, California	2003	1000	63	Basin Water, 2005
Hi-Desert Water District	Yucca Valley, California	2002	2500	157	Basin Water, 2005
City of Pomona	Pomona, southern California	Late 1990's	1000	63	Taylor, 2005
Southern California Water Company	not specified	-	2000	126	Basin Water, 2005

In all sites, nitrate concentrations exceeded the USEPA MCL (10 mg NO_3^--N/L), and are now being treated to acceptable levels, and a blend of treated and untreated water is being conveyed to consumers where possible. The waste produced by this system is in the range of 0.1-0.5% which is quite low (Ruppenthal, 2004; Basin Water, 2005; Taylor, 2005; Ruppenthal, 2007).

2.3.2 Factors Influencing Nitrate Removal by IX

Several factors influence practicality and efficiency of nitrate removal by IX. These factors can be categorized into four main groups including operating conditions, feed water characteristics, type of resin, and finally regeneration and waste disposal. Experimental details in published research on these factors are listed in Table 2-2.

Table 2-2: Experimental details of published IX nitrate removal research.

Resin	**Supplier**	**Resin Volume** (L)	**Column**		**Regenerant**	**Hydraulic loading or flow**	**Scale**	**Flow direction**		**Reference**
			d (cm)	**h** (cm)				**feed**	**regeneration**	
Amberlite® 400	Rohm and Hass	0.018	1	30 (resin)	NaCl (1N)	NS	bench	NS	NS	Korngold, 1972
Dowex™ 21k	Dowex	0.470, 0.325	3.8	122	NaCl (8%)	14-15 BV/h	bench	NS	down	Buelow et al., 1975
Amberlite® IRA 400	Rohm and Hass	4, 60	NS	NS	NaCl (4 eq/L)	NS	pilot	down	down	Dore et al., 1986
Duolite™ A-101-D	Rohm and Hass	2400	3 columns 180	300	NaCl (6%)	21.6 m/h	full	down	down	Lauch and Guter, 1986
Ionac® (ASB-1, A-554, SR-6)	Sybron Chemicals	0.150	2.5	60	NaCl	9.19 m/h	bench	down	NS	Liang et al., 1999
Ionac® A-554	Sybron Chemicals	28.32	25.4	137	NaCl	26.4-45.6 m^3/h	field study	NS	NS	Darbi et al., 2003
Purolite® A 520E	Purolite	0.05	8	180	NaCl (10%)	9.75 m/h	bench	down	down	Boumediene and Achour, 2004
Ionac® ASB-1	Sybron Chemicals	10	NS	NS	NaCl (3M)	2.65 mL/min	bench	NS	NS	Kim and Benjamin, 2004
Amberlite™ IRN-78	Rohm and Hass	0.1-1	NA (batch test)		NA	NA	bench	NA	NA	de Heredia et al., 2006
Purolite® A 520E	Purolite	0.0005	0.7	NS	NaCl (5%)	NS	bench	down	NS	Samatya et al., 2006

NA = not applicable

NS = not specified

2.3.2.1 Operating Conditions

Operating parameters such as flow rate, hydraulic loading (surface area loading rate), contact time, resin volume, bed depth, and headloss are factors that influence efficiencies of target contaminant removal and should be considered when designing an IX system. Contact time is directly related to the bed depth, and inversely related to flow rate and hydraulic loading. Therefore, decreasing the flow rate and increasing the bed depth can increase the removal capacity of the system (Helfferich, 1995; MWH, 2005). These statements are in agreement with experimental observations (Boumediene and Achour, 2004; Samatya et al., 2006). However, decreasing the flow rate increases the process time, and increasing the bed depth (resin volume) increases cost (Helfferich, 1995). Thus, these parameters should be optimized for each project.

2.3.2.2 Feed Water Characteristics

Feed water characteristics can influence the performance of IX resins. In general, higher total dissolved solids (TDS) loading lowers capacity (Korngold, 1972; Buelow et al., 1975; Helfferich, 1995; Darbi et al., 2003). Specifically, regarding the selectivity of resins, it can be assumed that competing ions might significantly affect nitrate removal capacity of the resins. In such cases, pre-treatment of the feed water to remove the competing ion or a more appropriate resin should be considered.

Investigating the effect of feed water nitrate concentration, it was observed, not unexpectedly that ionic leakage occurred earlier and nitrate removal capacity of resins decreased with increasing feed water nitrate concentration (Korngold, 1972; Boumediene and Achour, 2004). Results of a study by Samatya et al. (2006) using both groundwater and deionized water spiked with nitrate, showed that the breakthrough point of nitrate in the groundwater tested was about half that for the synthetic water due to the presence of other competitive background ions and much higher concentration of nitrate in groundwater (synthetic water: 100 mg NO_3^-/L, groundwater: 195 mg NO_3^-/L) (Samatya et al., 2006).

Dore et al. (1986) indicated that the capacity of Amberlite® IRA 400 resin for nitrate removal decreased in the presence of high sulfate concentrations (Dore et al. 1986).

Moreover, the results of an investigation by de Heredia et al. (2006) on the ability of Amberlite® IRN-78 ion-exchange resin for the removal of nitrate showed that capacity of the resin decreased as chloride ion concentration in the feed water increased (de Heredia et al., 2006).

The effect of the presence of silica and iron on nitrate removal was investigated by Buelow et al. (1975). It was observed that adding 20 mg/L of silica to the feed water sample could reduce the nitrate removal capacity of the resin, although silica was not totally removed by the resin. And, NaCl was not able to remove the adsorbed silica during the regeneration process. Therefore, it was concluded that although silica inhibited nitrate removal, it didn't replace nitrate. To clean the silica-contaminated resin, a 4% heated sodium hydroxide was used. It was also observed that 0.07 mg/L of iron reduced nitrate removal by precipitating on the resin causing fouling. Regenerating the resin with NaCl couldn't remove all the iron and return the resin to its base capacity. The fouling problem did not occur when the iron concentration in the feed water was 0.02 mg/L or less. Finally, lime softening was suggested as an effective pre-treatment method to reduce the amount of iron (Buelow et al., 1975).

Dore et al. (1986) examined the efficiency of an SBA (Amberlite® IRA 400) resin for removal of organic pollutants while removing nitrate, and concluded that the resin has a low adsorption capacity for organics and didn't alter the organic characteristics of the water. Evolution of N-dimethylnitrosamine during the denitrification cycles was also investigated in their study, and it was confirmed that these compounds were not formed when using Amberlite® IRA 400 resin (Dore et al., 1986). Liang et al. (1999) have also investigated the effects of volatile organic chemicals (VOCs), strong oxidants such as chlorine, and arsenic adsorption on IX resin performance. Results show that arsenic was also adsorbed to the resins, but didn't affect their nitrate removal capacity. Moreover, resins adsorbed some VOCs and showed some changes in IX capacity. And, the performance also declined to some extent due to exposure to chlorine. But, to investigate the long term effects of VOCs and oxidation on resins further tests were recommended (Liang et al., 1999).

2.3.2.3 Resin Selection

Choosing an appropriate resin is one of the key elements that should be considered when designing an IX system. Selecting several resins for preliminary assessment and investigating and comparing their performance is suggested (MWH, 2005). Several commercially available resins and their specifications are listed in Chapter 3.

Resins with smaller particle size have more capacity for exchanging ions. However, it can cause high flow resistance or headloss (Helfferich, 1995).

As previously discussed, nitrate removal capacity declines in the presence of sulfate due to preferential adsorption of sulfate. As a solution to this problem, resins with higher selectivity for nitrate rather than sulfate have been developed by changing the characteristics of matrix and functional groups of the resins. These resins are called nitrate-selective (Kapoor and Viraraghavan, 1997; Linag et al., 1999).

A study by Buelow et al. in 1975 concluded that sulfate reduced nitrate removal capacity of a nitrate-selective resin (See Table 2-2 for resins used in studies discussed in this paragraph). Also, the presence of alkalinity (as bicarbonate) in addition to sulfate further reduced the capacity. And, addition of chloride to those two anions reduced the nitrate removal capacity even further. While individually sulfate most adversely reduced nitrate adsorption capacity, alkalinity was least competitive (Buelow et al., 1975). Boumediene and Achour (2004) also used a nitrate-selective resin for their study on the effect of sulfate. The results showed that presence of sulfate could accelerate the time to nitrate leakage, and reduced the overall nitrate removal capacity of the nitrate-selective resin (Boumediene and Achour, 2004). Samatya et al. (2006) also investigated the influence of chloride and sulfate on the capacity of a nitrate-selective resin and showed that the breakthrough point of nitrate occurred earlier in the presence of chloride than in the presence of sulfate. The change was largest in the presence of both chloride and sulfate (Samatya et al., 2006). Based on the results of these studies, background anions can adversely affect the nitrate removal even for nitrate-selective resins. But, none of the above studies compared the capacity reduction of a non nitrate-selective resin under the same conditions. Nor was there discussion on the benefits of nitrate-selective resins in presence of competing background anions.

To develop design criteria for a 25 MGD nitrate removal IX plant, Liang et al. (1999) compared the performance of two non nitrate-selective (Type 1 and Type 2) resins and one nitrate-selective resin. The functional group of resin Type 1 was made of three methyl groups, while ethanol group replaced one of those methyl groups to form resin Type 2. It was shown that nitrate-selective resin performed better than the two other resins in the presence of sulfate since it preferentially adsorbed nitrate to sulfate and didn’t desorb nitrate to adsorb sulfate. Thus the breakthrough of sulfate occurred earlier than nitrate and nitrate was not dumped. Also nitrate-selective resin resisted oxidative reagents (chlorine) better than the non selective resins. Conversely, the nitrate-selective resin was most affected by the presence arsenic, and resin Type 1 had the best performance in that condition and when VOCs were present. Finally, resin Type 1 was selected as the best performing resin for nitrate removal from the San Gabriel Valley due to its longer runs before being exhausted and needing less regenerant for regeneration (Liang et al., 1999).

2.3.2.4 Regeneration

Regeneration is the periodic restoration of an ion exchange resin back to a usable form by employing a regenerant to displace ions removed during the treatment process. Ion exchange resins are regenerated by reversing the exchange reaction between the exchanging ions and ions that are removed during treatment and retained on the resin. The regenerant typically contains a high concentration of the exchanging ions to drive the exchange reaction in a reverse direction from the normal service cycle (Symons et al., 2001). For instance, the chloride form SBA resins (such as those used for nitrate removal) are regenerated with a concentrated solution of NaCl (Kapoor and Viraraghavan 1997; MWH, 2005; Samatya et al., 2006).

One of the main drawbacks to IX at full-scale is resin regeneration and the costs associated with preparing the brine and its disposal (Kapoor and Viraraghavan, 1997; Kim and Benjamin, 2004). Regeneration of an ion exchange resin can be done in either concurrent (the same flow direction as the influent) or countercurrent (the opposite flow direction of the influent) process. But, countercurrent regeneration cannot be used if there is a risk of fluidizing the resin (MWH, 2005). Partial regeneration processes have made it possible to have a continuous treatment as well as producing less brine waste than other conventional regeneration systems. In this process, the IX system consists of more than one column. When some freshly regenerated columns are in their service modes, others are in different steps of regeneration process. (Lauch and Guter, 1986; MWH, 2005).

Buelow et al. (1975) showed that amount of regenerant required is directly related to the feed water quality and TDS (Buelow et al., 1975). To reduce the regenerant required, Lauch and Guter (1986) developed the practice of partial regeneration at the McFarland IX Plant in California. The plant consisted of three IX columns operated in a loop of service and regeneration modes (Lauch and Guter, 1986).

It was reported that in general applying cocurrent regeneration is more advantageous in the process of nitrate removal by IX due to producing less leakage of nitrate in the effluent water (MWH, 2005). However, Boumediene and Achour (2004) recommended a counter-current regeneration process for nitrate removal to reduce the regeneration rate.

In 1972 Korngold found that sea water could be effectively used as regenerant, but the concentration of sulfate ion in the product water was to some extent higher than when of using NaCl as a regenerant (Korngold, 1972).

To investigate the approach of using regenerant brine more efficiently, Kim and Benjamin (2004) developed a method of regeneration in which sulfate was separated from other ions of the brine by precipitating as either $BaSO_4(s)$ or $CaSO_4(s)$. This modification allowed the brine to be used more than once and significantly decreased the amount of regenerant needed especially if the influent nitrate concentration was low. It was also indicated that precipitation of sulfate as $BaSO_4(s)$ was easier since it was five orders of magnitude less soluble than $CaSO_4(s)$. However, $CaSO_4(s)$ could increase the regenerant usage 30-40% more than $BaSO_4(s)$ (Kim and Benjamin, 2004). It should be noted that the Ontario Ministry of the Environment and Health Canada have set a MAC for Barium at 1 mg/L (Ontario Ministry of the Environment, 2006; Health Canada, 2008). Therefore, addition of barium to the regeneration brine should be done carefully to avoid potential risk of its being adsorbed to the resin and released into treated water.

2.3.2.5 Waste Disposal

Disposing the regeneration brine is one of the main shortcomings of IX. This critical factor should be considered when designing a full-scale IX plant (Kapoor and Viraraghavan, 1997; Kim and Benjamin, 2004; MWH, 2005).

Darbi et al. (2003) conducted a field study comparing biological denitrification, IX, and reverse osmosis (RO) technologies for nitrate removal from drinking water. It was reported that although IX is a promising technology for nitrate removal, the amount of regenerant should be selected carefully to diminish the problems of disposal (Darbi, 2003).

2.4 Reverse Osmosis

Reverse osmosis (RO) is a pressure-driven membrane separation process in which feed water passes through a semipermeable membrane due to a pressure difference at the opposite sides of the membrane (Symons et al., 2001; Darbi et al., 2003; MWH, 2005). For a pressure-driven membrane process, the concentrated solution containing substances that do not pass through the membrane is called the reject water or concentrate. (Symons et al., 2001). The main application of RO is desalination of seawater and brackish water, and the first commercial RO desalination plant was built in Goalinga, California in 1965 (MWH, 2005). However, RO membranes can be used for the removal of natural organic matter (NOM), microorganisms, inorganic contaminants such as arsenic, nitrate, nitrite, selenium, barium, and fluoride, and for softening (Symons et al., 2001; Bebee et al., 2006; MWH, 2005; Bergman, 2007).

2.4.1 Membranes

A reverse osmosis membrane is a synthetic membrane used for separation. The separation capability of the process is dependent on the physical and chemical properties of the membrane. (Symons et al., 2001; MWH, 2005). RO membranes should be made of a permeable but not porous material that can reject dissolved solutes while passing the water. Typical materials for RO membranes are cellulose acetate (CA) and polyamide (PA) (MWH, 2005; Bergman, 2007).

The first RO membranes were made from CA at the University of California in 1949 for desalination of seawater. CA membranes are more hydrophilic than PA membranes, and therefore less vulnerable to fouling. Also, CA membranes can tolerate up to 1 mg/L of chlorine, while PA membranes deteriorate at any concentration of free chlorine (MWH, 2005; Bergman, 2007).

However, CA membranes may hydrolyze to acetate and lose their rejection capacity over time. Also, PA membranes are more resistant to biodegradation and tolerate wider pH ranges, and have higher removal capacities (MWH, 2005; Bergman, 2007).

2.4.2 Mechanism of Removal

The fundamental rejection mechanisms of membranes include electrostatic repulsion and diffusion. Electrostatic repulsion causes the feed water anions to be rejected at the surface of the membrane due to the negative charges of functional groups in membrane materials, and cations might be rejected to sustain electroneutrality in the water. Therefore divalent ions such as sulfate are rejected better than monovalent ions such as nitrate. Feed water and its solutes also dissolve and diffuse through the membrane. Large molecules may be rejected better due to their lower diffusion potential. Solubility of the molecule is another factor in diffusion (MWH, 2005; Bergman, 2007). It is reported that typically nitrate cannot be rejected as well as other anions such as sulfate or chloride (Elyanow and Persechino, 2005). It was also observed that nitrate could not be rejected by RO membranes as well as ammonia and total organic carbon (TOC) (Bellona et al., 2008). Nanofilteration (NF) membranes have lower rejection of monovalent ions when compared to RO membranes specifically designed for nitrate (MWH, 2005; Bellona et al., 2008).

2.4.3 Recovery

In a membrane water treatment system, the fraction of the feed water that is converted to product is called recovery. In equation form,

$$\text{Recovery}\ (\%) = (Qp/Qf)\times 100$$

Where:

Qp = product flow rate or volume

Qf = feed water flow rate or volume (Symons et al., 2001).

Recovery of a seawater RO system is about 50%, while it is reported to vary between 40 to 90 percent in full-scale nitrate removal RO plants (Bilidt, 1985; Schoeman and Steyn, 2003; Elyanow and Persechino, 2005). The maximum recovery reported for commercially available point-of-use RO devices is 38% (Lancaster, 2007).

Osmotic pressure and solubility of solutes are the main factors that limit the recovery. Using a multi-stage RO system can recirculate the reject water into the system and increase recovery. In this way, reject water from one stage of RO is treated in another stage and the final reject water becomes more concentrated. Therefore, disposal regulations should be considered when designing multi-stage systems and recovery should be optimized regarding taking this into account (MWH, 2005).

Another strategy to increase the recovery of the system is blending feed and product water. However, regulations might limit this method (Bergman, 2007).

2.4.4 Application of RO for Nitrate Removal from Drinking Water

RO has been designated to be one of the best available technologies (BAT) for removing nitrate as well as some other inorganic contaminants by EPA (USEPA 2004). Since RO can remove several organic and inorganic contaminants, it can be a feasible alternative for removing nitrate in cases that the raw water contains high TDS, hardness, or organics, and nitrate is not the only contaminant to be removed (Cevaal et al., 1995; Darbi et al., 2003). Some studies have assessed nitrate removal from drinking water by RO, and several full-scale RO plants have been built and are in operation to treat nitrate in groundwater.

Full-scale RO plants are in use for nitrate removal from the groundwater in the cities of Riverside and Tusain in southern California. Also, Chino Basin Desalter Authority has several RO facilities for nitrate removal from groundwater (Bergman, 2007). Details of some other full-scale RO plants are listed in Table 2-3.

Table 2-3: Details of some full-scale RO nitrate removal projects.

Site	**RO membrane**	**Removal (%)**	**Rcovery (%)**	**Flow**		**Reference**
				GPM	**L/s**	
Yemen	DDS-HR95	80	75-90	31	2.0	Bilidt, 1985
France	DDS-HR95	52	75-90	22	1.4	Bilidt, 1985
Brighton, Colorado	Hydranautics 8040-LAY-CPA2	97	80	2772	174	Cevaal et al., 1995
Zava-Giyani, South Africa	Environmental Products USA 4040-LHA-CPA2	97	50	10	0.6	Schoeman and Steyn, 2003
Milan, Italy (13 sites)	GE	95-98	77-88	31-248	2-16	Elyanow and Persechino, 2005

An RO field study was conducted by Darbi et al. (2003) as well as biological denitrification and IX to compare the technologies for nitrate removal from groundwater of Winnipeg, Manitoba. A Filmtec WGR-600 was the membrane used and it was found that it could achieve 85% removal of nitrate from the water, while IX and biological denitrification could remove 90% and 96% of nitrate, respectively. RO and IX were ultimately found unacceptable for the project due to their waste disposal problems (Darbi et al., 2003).

2.4.5 Factors Influencing Nitrate Removal by RO

The main factors that should be considered in designing an RO system are membrane type, feed water characteristics, pre-treatment, post-treatment, blending, residual disposal, recovery, and energy recovery (MWH, 2005; Bergman, 2007). The feasibility of an RO system for removing nitrate from drinking water is also influenced by the parameters mentioned above.

2.4.5.1 Membrane Selection

Polyamide membranes are known to be more effective than cellulose acetate membranes for removing nitrate. The maximum percent of nitrate removal by polyamide membranes is reported to be 97 (Cevaal et al., 1995; Kapoor and Viraraghavan, 1997, Bergman, 2007). Another factor in selecting a membrane is its required pressure. Membranes with lower pressures are more cost effective. Stability of the membrane for removing nitrate or other target contaminants should also be evaluated (Cevaal et al., 1995). Considering all of these mentioned factors, Cevaal et al.(1995) picked Fluid System’s TFCL 4821 LP polyamide membrane over 3 other polyamide membranes for removing nitrate, hardness, TDS, and trihalomethane (THM) precursors from groundwater of Brighton, Colorado (Cevaal et al., 1995).

Nanofiltration (NF) membranes have lower nitrate removal efficiencies than RO membranes (Bergman, 2007). However, a recent study by Bellona et al. (2008) on comparing the efficiency of eleven membranes including six NF, four low-pressure reverse osmosis (LPRO), and one RO membranes showed that all LPRO and three of the NF membranes could remove considerable amounts of nitrate. The removal efficiency of LPRO membranes tested was around 95%. The NF membranes that could remove nitrate were Hydranautics ESNA1-LF, Koch Membrane Systems TFC-S, and Dow/Filmtec NF-90, and their achieved nitrate percent removals were 91.4, 77.6, and 79.3, respectively. The evaluation was performed at laboratory scale and its purpose was to select a commercially available membrane for water reuse applications in California. Toray Industries TMG10 (LPRO) and Dow/Filmtec NF-90 (NF) were also tested at pilot and full-scale at the California water facility (Bellona et al., 2008).

2.4.5.2 Pre-treatment

A reverse osmosis system might need a pre-treatment process for different reasons. Scaling or fouling is one of the main concerns of an RO membrane which can negatively impact the performance of the system. Organic matter, solutes, particulates, and biological contaminants are causes of fouling that should be controlled by an appropriate pre-treatment based on the properties of feed water characteristics (Kapoor and Viraraghavan, 1997; MWH, 2005; Bergman, 2007).

Pre-filtration can help removing particulates and control this type of fouling. This step might be limited to a cartridge filter in treating groundwater that contains low particle content or MF or UF in certain waters while coagulation, flocculation, sedimentation, and granular filtration might be essential for waters with high particulate matter. Antiscalant addition and pH adjustment are the suggested methods for preventing solute scaling such as calcium carbonate precipitation. (Darbi et al., 2003; MWH, 2005; Bergman, 2007). By adjusting pH to an acidic value, carbonate converts to carbon dioxide and passes through membrane (MWH, 2005). Sulfuric and hydrochloric acid are used typically for pH adjustment (Darbi et al., 2003). pH adjustment cannot control scaling of some salts such as calcium sulfate. Addition of antiscalant chemicals can control this type of scaling by preventing crystal formation and growth (Darbi et al., 2003; MWH, 2005). Biofouling can be prevented by disinfectant addition in the feed water prior to the RO process. Certain membranes are sensitive to oxidants which could lead to the degradation of the membrane. Therefore an appropriate disinfectant that matches the membrane type should be chosen (Darbi et al., 2003; MWH, 2005; Bergman, 2007).

Sulfuric acid was selected for pH adjustment and control scaling in Brighton, Colorado’s nitrate removal RO plant. The reason for choosing sulfuric acid over hydrochloric acid was its cheaper price. Also a polyacrylic acid was used as an anti-scalant. To reduce biofouling problems in that project, chlorination was selected as a reliable alternative. The location of chlorine feed tank and feed water pipeline valves were modified later to reduce the potential for chlorine to reach the membrane due to the membrane degradation problem that occurred (Cevaal et al., 1995)

A field study was conducted by Darbi et al. (2003) to remove nitrate from the groundwater of Winnipeg, Manitoba. To control potential fouling caused by the very high feed water hardness (1161 mg/L as $CaCO_3$), a USF Watergroup TMI DA0 softener was installed prior to a Filmtec WGR-600 RO membrane. (Darbi et al., 2003).

Several pre-treatment processes were designed in a nitrate removal RO plant in South Africa by Schoeman and Steyn (2003). The pre-treatment included passing feed water through sand filters, adding sulfuric acid and an anti-scalant continuously, and finally passing the water through a 5 micron cartridge filter (Schoeman and Steyn, 2003). However, it was not mentioned in this study whether the pre-treatment process included disinfection to control potential biofouling.

Bohdziewicz et al. (1999) investigated a different approach for pre-treatment. To reduce the scaling caused by calcium sulfate and calcium carbonate salts, an NF membrane (SX10) was installed as a pre-treatment step prior to RO membrane (SS10). NF could remove enough bivalent ions ($Ca2^{+}$, CO_3^{2-}, and SO_4^{2-}) to prevent such formations. The overall recovery of this combination (68.6%) was lower than the recovery of RO alone (80%) (Bohdziewicz et al., 1999). To evaluate the feasibility of using NF as an alternative to typical pre-treatment methods, it should be compared based on its efficiencies and long-term costs.

2.4.5.3 Post-treatment

All RO systems need a proper post-treatment method specifically to readjust water quality following treatment. Choosing the post-treatment method depends on the feed and product water characteristics, and chemicals added during pre-treatment. The most common RO post-treatment steps are pH and alkalinity adjustment, degasification, disinfection, and corrosion inhibitor addition or blending feed and product water (MWH, 2005; Bergman, 2007).

As discussed previously, pH is sometimes adjusted in pre-treatment processes to prevent scaling. Thus it should be readjusted in post-treatment process. pH is sometimes adjusted in pre-treatment processes to prevent scaling. This adjustment converts carbonate to carbon dioxide which should be removed from the product water by degasification method. Degasifiers can also remove hydrogen sulfide in case it exists in the source water. Also the alkalinity and hardness are very low in the product water which makes it corrosive. To adjust the alkalinity and prevent corrosion, alkaline chemicals or corrosion inhibitors can be injected to system. Caustic soda can be used to adjust both pH and alkalinity (MWH, 2005; Bergman, 2007). In South Africa's nitrate removal RO plant, caustic soda was added as a post-treatment to readjust pH (Schoeman and Steyn, 2003).

To control the lead and copper corrosion problem caused by low alkalinity in product water, zinc orthophosphate was added to the product water of Brighton, Colorado's RO plant. Post-treatment of this project also included adding caustic soda and stripping carbon dioxide (Cevaal et al., 1995).

2.4.5.4 Blending

Blending feed and product water is another strategy to stabilize the product water and adjust pH and alkalinity. In this way production and recovery of the system will also be increased (MWH, 2005; Bergman, 2007), and the overall costs will be reduced consequently.

Nitrate regulations limit the extent to which blending can be utilized though (MWH, 2005; Bergman, 2007). Blending proportions for Brighton, Colorado's RO plant varied from season to season. It was designed to blend a minimum of 20% feed water with 80% product water during winter months, while maximum 60% feed water is blended with 40% product water in summer (Cevaal et al., 1995).

Blending is not permitted by some regulations in cases of having highly concentrated feed waters. The California Department of Health Services (CDHS, 1997) classifies some water sources as 'extremely impaired sources', and requires the entire flow from those sources to pass through a treatment process. If the feed water exceeds 3 times an MCL based on acute health effects, it is classified as extremely impaired and cannot be blended with product waters in RO systems (CDHS, 1997; Bebee et al., 2006). Chino Basin groundwater in the southwestern region of the Inland Empire (Riverside and San Bernardino counties, California) was an extremely impaired source due to its nitrate concentration being about four to five times the MCL (10 mg NO_3^--N/L). Also the TDS of this source exceeded the secondary maximum contaminant level (SMCL) by about three times (Bebee et al., 2006). Utilizing an RO system for this water source wouldn't be economical due to its high pressure requirements and operational costs for treating the entire feed water. Another concern with using RO without blending could be the production of corrosive product water due to low TDS in product water. To solve this problem, Bebee et al. (2006) designed an innovative treatment process (RO in parallel with IX) to reduce nitrate and TDS. This process could treat the entire feed water flow while reducing the high costs of RO by passing a part of the feed water through IX. In addition, by blending product waters of RO and IX, TDS was maintained in product water and potential corrosion problem was controlled (Bebee et al., 2006).

2.4.5.5 Residual Disposal

One of the key factors in designing an RO treatment system is proposing an appropriate and economical way to dispose the residuals. Residuals are categorized in two main groups, one being reject water and the second being chemical cleaning (clean in place - CIP) residuals. Reject water contains particulates and solutes and is much more concentrated than the feed water, while CIP waste is generated by an acidic or basic solution used in pre-treatment, post-treatment, or membrane cleaning processes (AWWA Membrane Residuals Management Subcommittee, 2004; MWH, 2005; Bergman, 2007). CIP residuals can be disposed with the reject water, but sometimes it needs to be treated before disposal (MWH, 2005). The reject water from a nitrate removal RO system contains high concentrations of nitrate and should be discharged properly (Bilidt, 1985; Darbi et al., 2003).

The most common membrane residual disposal methods are surface water discharge, municipal sewer discharge, and deep well injection. Other alternatives such as landfills, evaporation ponds, and irrigation have also been used in some cases (Schoeman and Steyn, 2003, MWH, 2005; Bergman, 2007). Also, some beneficial uses of reject water such as stock watering and water supply for reconstructed brackish water wetlands have been suggested and evaluated (Schoeman and Steyn, 2003, MWH, 2005). Typically domestic wastewater treatment plants are good recipients from a nitrate removal RO plant (Bilidt, 1985; Darbi et al., 2003).

Schoeman and Steyn (2003) proposed using the reject water of South Africa nitrate removal RO plant for stock watering. But conditions for stock watering should be considered in terms of nitrate, TDS and other potential contaminants. Therefore, they had to keep the recovery of the RO system at 50% to meet the related regulations (Schoeman and Steyn, 2003). It is important to recall that agriculture is one of the key contributors to nitrate contamination of water. It may not be appropriate to dispose of it in agricultural settings.

To control the concentrations of the reject water for a safe disposal to the South Platte River, recovery was limited to 80% in Brighton, Colorado's RO plant. The accepted maximum level of barium sulfate in the reject water to be disposed is 40 times the saturation level. To maintain that concentration, recovery couldn't be increased higher than 80% (Cevaal et al., 1995).

2.4.5.6 Energy Recovery

RO is a pressure driven technology which demands high energy and costs regarding using electrical power to operate high pressure pumps. This drawback makes RO a less favorable technology and limits its applications (Kapoor and Viraraghavan, 1997; Luk and Au-Yeung 2002; MWH, 2005; Bergman, 2007). Recirculation of pressure into the system can minimize the energy costs. Energy recovery (ER) devices such as reverse-running turbopumps and pressure exchangers can be coupled to the feed water pumps and use the pressure at the reject water for pumping the feed water. Thus, the reject water energy won't be wasted and more than 90% could return to the system (MWH, 2005; Bergman, 2007). Pressure can also be recovered between the stages which can eliminate using booster pumps and reduce costs (MWH, 2005).

2.5 Biological Denitrification

Biological denitrification is one of the most effective technologies for nitrate removal since it only removes nitrate and doesn't change concentrations of other background ions. In this method nitrate is microbially reduced to nitrogen gas. Although this process is commonly applied in wastewater treatment, its application for drinking and groundwater treatment has been investigated in lab studies and only occasionally developed in full-scale plants (Roennefahrt, 1986; Bockle et al., 1986; Janda et al., 1988; Braester and Martinell, 1988; van der Hoek et al., 1992; Liessens et al., 1993; Mateju et al., 1992; Soares, 2000). However, potential contamination of the treated water with these microorganisms and their metabolic byproducts are the drawbacks of this technology (Shrimali and Singh, 2001; Samatya et al., 2006). These problems result in increased disinfectant demand or the need of post-treatment of the product water by filtration. In addition, low production rates and cold temperature restrictions can also be considered as a disadvantage of biological denitrification (Kapoor and Viraraghavan, 1997; Samatya et al., 2006).

2.5.1 General Principles of Biological Denitrification

Many anaerobic bacteria respire by using nitrate as opposed to oxygen as their electron acceptor. This process leads to formation of a number of nitrogen intermediates and ultimately the evolution of nitrogen gas, which is called biological denitrification. Its steps can be summarized as follows: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ (Hiscoock et al., 1991; Mateju et al., 1992; Kapoor and Viraraghavan, 1997; Soares, 2000; Shrimali and Singh, 2001)

Biological denitrification can occur naturally, and to use it as a treatment system, suitable organic or inorganic carbon and energy sources may be required (Soares, 2000). This includes adequate amounts of C, H, O, N, P, and S, minor amounts of minerals (K, Na, Mg, Ca, and Fe), and trace amounts of metals (Mn, Zn, Cu, Co, and Mo) that can be found sufficiently in most groundwaters (Hiscoock et al., 1991). Oxygen has an inhibitory effect on denitrification due to its competition with nitrate as an electron acceptor. However, in certain species, denitrification can arise in the presence of oxygen (Mateju et al., 1992; Shrimali and Singh, 2001). Another important controlling factor is temperature. Denitrification decreases at low temperatures as with biological processes (Kapoor and Viraraghavan, 1997).

2.5.2 Process Systems

Treatment can occur directly in the aquifer (in situ), or in above ground reactors. The process of in situ treatment usually consists of a central pumping well surround by injection wells through which the substrate is injected (Matejuet al., 1992). The stable temperature in the ground is an advantage of this method especially in cold climates. However, it has some problems such as slow rates in aquifers, high risks of clogging, and complicated control on substrate distribution due to the inhomogeneity and lack of isotropy of aquifers. Thus, this process is applicable only under certain geological conditions which are limited. Above ground denitrification can run with packed-bed or fluidized-bed reactors. Fluidized bed reactors are preferred because they afford higher denitrification rates per reactor volume, and clogging and channeling problems are not a concern, but more process control may be required to avoid breakthrough of biomass (Matejuet al., 1992; Kapoor and Viraraghavan, 1997; Soares, 2000).

Biological denitrification systems are driven by either heterotrophic or autotrophic bacteria. In heterotrophic denitrification, the source of carbon and energy is an organic compound, while in autotrophic denitrification the carbon source is inorganic, and the energy source is also an inorganic compound (Matejuet al., 1992; Soares, 2000; Shrimali and Singh, 2001). Most full-scale applications use heterotrophic processes, since autotrophic bacteria grow slowly and consequently the denitrification rate will be lower. On the other hand, in the case of heterotrophic processes, extensive post-treatment of denitrified water is required to remove bacteria and residual organic carbon (Matejuet al., 1992; Kapoor and Viraraghavan, 1997; Haugen et al., 2002). Table 2-4 lists examples of the full-scale application of biological denitrification in drinking water treatment projects.

Table 2-4: Full-scale biological denitrification projects in drinking water.

Process system	**Site**	**Reference**
heterotrophic/reactors	Langenfeld and Monheim, Germany	Roennefahrt, 1986
heterotrophic/reactors	Neuss, Germany	Bockle et al., 1986
hydrogenotrophic/reactors	Monchengladback, Germany	Gross and Treutter, 1986
heterotrophic/in situ	Vsetaty, Czech Republic	Janda et al., 1988
heterotrophic/in situ	Drosing, Austria	Braester and Martinell, 1988
Autotrophic (sulphur-limestone)/reactors	Montferland, The Netherlands	van der Hoek et al., 1992
heterotrophic/reactors	Blankaart, Belgium	Liessens et al., 1993

2.5.2.1 Heterotrophic Processes

The most applied and studied denitrification process is heterotrophic denitrification. Heterotrophic bacteria require an organic carbon source such as methanol, ethanol, glucose, acetate, and acetic acid that have been widely used in studies, and among them methanol is the least expensive. However, methanol is not permitted for use in drinking water treatment application in some countries (Matejuet al., 1992; Soares, 2000; Aslan and Turkman, 2003). Moreover, some researchers have used other alternative substances such as volatile fatty acids, shredded newspaper, wheat straw, unprocessed short fiber cotton, atrazine, natural gas methane, elemental sulphur, and sugar or glucose syrup as the organic carbon source (Aslan and Turkman, 2003).

2.5.2.2 Autotrophic Processes

Some bacteria are able to achieve autotrophic denitrification by using hydrogen gas and various reduced-sulphur compounds as microbial energy sources, and carbon dioxide or bicarbonate as the carbon sources. The main advantage of autotrophic processes is that the risk of biological regrowth and formation of biomass is much less because of slower growth of autotrophs. The low cost of inorganic substrates used in this method is another important advantage (Matejuet al., 1992; Soares, 2000; Mansell and Schroeder, 2002).

2.5.2.3 Hydrogenotrophic Processes

Hydrogenotrophic denitrification is an autotrophic process that uses hydrogen gas as the electron donor. This technology has been developed at lab-, pilot-, and full-scales. The advantages of this technology are: producing less microbial biomass, low cost of hydrogen, its non-toxicity, and its low solubility in water that allows it to be easily removed after treatment. On the other hand, the high flammability of hydrogen, and its explosive potential must be taken into consideration. However, hollow-fiber membrane dissolution systems have been developed to more safely dissolve hydrogen into water (Ergas and Reuss, 2001; Haugen et al., 2002; Mansell and Schroeder, 2002; Lee and Rittmann, 2002).

2.6 Chemical Denitrification

The electron-donating tendency of zero-valent metals can reduce several anions. So these metals have been investigated as developing water treatment technologies to remove contaminants such as nitrate. Iron and aluminum powder are considered as effective zero-valent metals for the chemical process of nitrate removal from drinking water, known as chemical denitrification (Shrimali and Singh 2001; Luk and Au-Yeung 2002).

2.6.1 Nitrate Reduction with Iron

Zero-valent iron has been widely used to reduce nitrate (NO_3^-). Iron is oxidized to ferrous ion (Fe^{2+}), and nitrate is reduced to ammonia or nitrogen gas (N_2). Oxidation of Fe^0 to Fe^{2+} is the anodic half-reaction, in the process, and H^+ or dissolved oxygen, as electron acceptors, are involved in the cathodic half-reaction in anaerobic and aerobic systems respectively. The final products of chemical reduction of nitrate by iron are N_2 or NH_3, depending on the experimental conditions (Cheng et al., 1997; Yang and Lee, 2005; Kumar and Chakraborty, 2006). Pathways for nitrate reduction by zero-valent iron proposed by various researchers are listed in Table 2-5.

The large demand of iron and its relative costs, long reaction time, pH constraints, and need of post-treatment to remove ammonia are the main drawbacks that limit the use of this technology (Luk and Au-Yeung, 2002; Kumar and Chakraborty, 2006).

Table 2-5: Proposed pathways for nitrate reduction by zero-valent iron.

Proposed pathway(s)	**Reference**
$6NO_3^- + 10Fe^0 + 3H_2O \rightarrow 5Fe_2O_3 + 3N_{2(g)} + 6OH^-$ $NO_3^- + Fe^0 + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O$	Siantar et al., 1995-1996
$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O$	Cheng et al., 1997
$NO_3^- + Fe^0 + 2H_3O^+ \rightarrow Fe^{2+} + NO_2^- + 3H_2O$ $NO_3^- + 4Fe^0 + 10H_3O^+ \rightarrow 4Fe^{2+} + NH_4^+ + 13H_2O$	Huang et al., 1998
$NO_3^- + Fe^0 + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O$ $2NO_3^- + 5Fe^0 + 6H_2O \rightarrow 5Fe^{2+} + N_{2(g)} + 12OH^-$	Choe et al., 2000
$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O$ $NO_2^- + 3Fe^0 + 8H^+ \rightarrow 3Fe^{2+} + NH_4^+ + 2H_2O$	Alowitz and Schere, 2002
$NO_3^- + 2.82Fe^0 + .75Fe^{2+} + 2.25H_2O \rightarrow NH_4^+ + 1.19Fe_3O_4 + .5OH^-$	Huang and Zhang, 2002
$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O$ $NO_3^- + 8Fe^0 + 10H^+ \rightarrow 8Fe^{3+} + NH_4^+ + 3H_2O$	Huang and Zhang, 2004
$NO_3^- + 4Fe^0 + 7H_2O^+ \rightarrow 4Fe^{2+} + NH_4^+ + 10OH^-$	Choe et al., 2004

2.6.2 Nitrate Reduction with Aluminium

Powdered zero-valent aluminium can also be used to reduce nitrate to nitrite, and eventually to ammonia or nitrogen gas. The nitrate to ammonia reduction process is described by the following chemical reactions (Murphy, 1991; Kapoor and Viraraghavan, 1997; Luk and Au-Yeung, 2002):

$$3NO_3^- + 2Al^0 + 3H_2O \rightarrow 3NO_2^- + 2Al(OH)_3 \downarrow$$

$$NO_2^- + 2Al^0 + 5H_2O \rightarrow NH_3(g) + 2Al(OH)_3 \downarrow + OH^-$$

Overall:

$$3NO_3^- + 8Al^0 + 18H_2O \rightarrow 3NH_3(g) + 8Al(OH)_3 \downarrow + 3OH^-$$

And the nitrate to nitrogen reduction process is described by the following chemical reactions:

$$3NO_3^- + 2Al^0 + 3H_2O \rightarrow 3NO_2^- + 2Al(OH)_3 \downarrow$$

$$2NO_2^- + 2Al^0 + 4H_2O \rightarrow N_2(g) + 2Al(OH)_3 \downarrow + 2OH^-$$

Overall:

$$6NO_3^- + 10Al^0 + 18H_2O \rightarrow 3N_2(g) + 10Al(OH)_3 \downarrow + 6OH^-$$

(Murphy, 1991; Kapoor and Viraraghavan, 1997; Luk and Au-Yeung, 2002; Kumar and Chakraborty, 2006)

Disadvantages of this method include its low efficiency especially for removing nitrate from waters with high original nitrate concentrations, pH constraints, and the need for post-treatment to remove ammonia (Kapoor and Viraraghavan, 1997; Luk and Au-Yeung, 2002; Kumar and Chakraborty, 2006).

2.7 Electrodialysis

Electrodialysis (ED) is a desalting process driven by an electrical potential difference between oppositely charged electrodes. Ions are transferred by electric current flow through cation and anion membranes, depending on ion charge, from a less concentrated solution to a more concentrated one, leaving a demineralized stream (Symons et al., 2001).

Similar to RO, water treatment by ED is also limited to soft waters due to membrane scaling problems. Therefore, this technology also needs pre-treatment. To minimize membrane scaling and reduce the need for pre-treatment, use of a modified ED method known as electrodialysis reversal (EDR) was investigated (Rautenbach et al., 1987; Kapoor and Viraraghavan, 1997). Electrodialysis Reversal (EDR) is an electrodialysis process in which the electrical polarity of the electrodes is reversed on a set time cycle, thereby reversing the direction flow of ions in the system providing fouling control (Symons et al., 2001). However, operating EDR is more complicated and needs close monitoring (Rautenbach et al., 1987; Kapoor and Viraraghavan, 1997). Around six EDR drinking water plants have been built in the US and are operating in the 4-10 MGD range (Bebee et al., 2006)

One of the main advantages of ED is its higher percent of recovery comparing to RO. But, both ED and RO methods generate highly concentrated wastes and need careful consideration with respect to disposal. In general, ED is a more complex system than RO and demands high energy and costs (Rautenbach et al., 1987; Kapoor and Viraraghavan, 1997; Hell et al., 1998). To reduce the energy and costs associated, increasing the efficiency of the system by maximizing the amount of nitrate removed per membrane area was investigated. To achieve this, an ED system was developed by modifying the membranes to anion exchange membranes that could selectively remove nitrate (Eyal and Kedem, 1988).

A full-scale ED plant using anion exchange membranes was designed and built by Austrian Energy in 1997. The plant removed 66% of the feed water nitrate, but after several months of operation the plant was shut down due to the problems associated with waste disposal in the local sewage treatment system (Hell et al., 1998).

2.8 Comparison and Research Needs

In order to narrow down the available efficient and cost effective remedial techniques that can be applicable for this research, all of these technologies were compared based on their different characteristics. The technologies discussed above and their attributes are summarized in Table 2-6.

Conventional drinking water treatment methods were reported to be incapable of removing nitrate, but this was not confirmed in the literature by experimental data.

Table 2-6: Comparison of Nitrate Removal Technologies.

Method	IX	RO	ED	Chemical	Biological	Hydrogenotrophic
Status	full scale	full scale	full scale	research phase	full scale	pilot plant research phase
Application	groundwater, wastewater	groundwater, industrial waste	specialized wastewater	ground and surface water	wastewater, surface Water	better for groundwater
Start-up period	minutes	minutes	minutes	hours	weeks	weeks
Waste Disposal	brine regenerant	high TDS disposal	high TDS disposal	none	biomass disposal	none
Pre-treatment	sulfate, organics, chloride	fouling control	fouling control	lime softening	dissolved oxygen	H_2 addition
Temperature	insignificant	insignificant	insignificant	25°C (Al)	2-6°C (lower limit)	20°C (optimum)
Optimum pH	insignificant	insignificant	insignificant	$\leq$ 4.5 (Fe) 9.1-9.3 (Al)	insignificant	7
Operation	stable	stable	complex	stable	close monitoring	monitoring
Max Reported Efficiency	90%	97%	65%	70%	100%	96%
Cost	moderate	high	high	high	moderate	moderate
Post-treatment	corrosive product	corrosive product	corrosive product	ammonia	microorganisms	microorganisms
Advantages	short time period, simple and effective, relatively low cost	short time period, hardness reduction,	simple separation, hardness reduction	high efficiency	very selective reduction	relatively cost effective, less microbial biomass
Disadvantages	disposal problems	high pressure, need for pre-treatment, and post-treatment, disposal problems	need for pre-treatment, close monitoring, expensive, disposal problems	post treatment for ammonia, expensive, pH constraints, lime softening	contamination post treatment, low reaction rate, temperature constraints	long time, pH constraint, explosion and safety concerns, temperature constraints
References	Korngold 1972, Buelow et al. 1975, Dore et al. 1986, Lauch and Guter 1986, Liang et al. 1999, Darbi et al. 2003, Boumediene and Achour 2004, Kim and Benjamin 2004, de Heredia et al. 2006, Samatya et al. 2006, Ruppenthal 2004, Taylor 2005, Basin Water 2005, Ruppenthal 2007	Bilidt 1985, Cevaal et al. 1995, Bohdziewicz et al. 1999, Darbi et al. 2003, Schoeman and Steyn 2003, Bebee et al. 2006, Bellona et al. 2008	Rautenbach et al. 1987, Eyal and Kedem 1988, Hell et al. 1998, Nataraj et al. 2006	Murphy 1991, Siantar et al. 1996, Cheng et al. 1997, Huang et al. 1997, Choe et al. 2000, Alowitz and Schere 2002, Huang and Zhang 2002, Luk and Au-yeung 2002, Huang and Zhang 2004, Yang and Lee 2005	Roennefahrt 1986, Bockle et al. 1986, Janda et al. 1988, Braester and Martinell 1988, Hiscock et al. 1991, Mateju et al. 1991, van der Hoek et al. 1992, Liessens et al. 1993, Volokita et al. 1996, Shrimali and Singh 2000, Soares 2000, Aslan and Turkman 2003,	Gross and Treutter 1986, Haugen et al. 2001, Mansell and Schroeder 2002, Smith et al. 2005

Chemical denitrification is still in the research phase, and its nitrate removal efficiency is not very high. ED is one of the most expensive technologies which needs close monitoring.

Nitrate removal using heterotrophic, autotrophic, and hydrogenotrophic bacteria, biological denitrification, are methods with potentially very high removal efficiencies. But these technologies were not considered for this project due to long start up times and potential of microorganisms leaking into the product water.

Ion exchange and reverse osmosis are efficient treatment technologies with short start-up time and minimal temperature and pH constraints. Since time and efficiency are important factors in removing nitrate from groundwater, IX and RO technologies are more appropriate to be investigated.

These technologies are being used for nitrate removal from groundwater in full-scale treatment plants. However, the number of RO projects for nitrate removal from groundwater is very limited and effect of background ions on nitrate removal by this technology, if investigated, has not been reported. Most research involving the performance of IX has been conducted with synthetic feed water, and the combination of spiked ions in the feed water has been based on constant ratios not resembling real groundwater. Also, there is very little comparative research on the performance, benefits, and concerns of nitrate-selective and non-selective IX resins under different feed water conditions.

In cases where the construction of full-scale plants is not economical or practical; IX and RO technologies can be used at point-of-use (POU) scale for drinking water treatment. RO point-of-use devices are commercially available, and using IX as a POU technology is not very complicated based on its similarity to POU water softeners (cation exchange) which are well-known and widely used by consumers. However, this aspect and its concerns were not discussed in the literature and need to be assessed for both IX and RO technologies. There is also a gap in the literature comparing these two technologies under different technical and economical conditions.

To investigate and compare the feasibility of IX and RO technologies for removing nitrate from groundwater sources in the Region of Waterloo in full-scale or POU devices, four IX resins (two nitrate-selective, and two non-selective) and a commercially-available RO POU device which included a particle filter and a carbon block were tested under different operating and feed water conditions. Results are presented in Chapters 4 and 5, and comparisons of IX and RO and different strategies for using them are discussed in Chapter 6.

Chapter 3

Materials and Methods

This research involved testing of two source waters; spiked deionized (DI) water and real groundwater collected in the Region of Waterloo. Chemical preparation and dose calculations as well as the equipment and experimental methods employed to measure parameters of concern are discussed in this chapter. Apparatus and operation of both the IX and RO systems are described in detail. Some commercially available IX resins and RO units are also introduced in this chapter.

3.1 Groundwater

In the Region of Waterloo, Ontario, groundwater is the main source of potable water which is provided by pumping wells in 50 well fields (WHI, 2009). Some of these wells are reported to have elevated nitrate concentrations (WESA, 2004). To deal with this, the Region of Waterloo has implemented well-specific initiative priorities for nitrate reduction as a part of a Water Resources Protection Strategy (WRPS). Based on the WRPS schedule, the nitrate reduction initiative started in 2007 and will continue until the end of 2010 (Region of Waterloo, 2008). This research was conducted using representative groundwater in the Region of Waterloo to find a practical and economical way to reduce nitrate concentrations in wells with elevated nitrate concentrations and decommissioned wells.

To perform the experiments of this research 2 different groundwater sites (GW1 and GW2) were selected based on their elevated nitrate concentrations, and presence of other competing background anions (sulfate, chloride) and alkalinity. IX experiments were conducted using GW1 and GW2 collected on March 26th and April 9th, 2009, respectively. Their characteristics are presented in Table 4-15. GW2 was selected as the groundwater source for conducting RO experiments and was sampled on July 20th, 2009. Characteristics of GW2 source measured on that date are presented in Table 5-6.

3.2 Spiked deionized (DI) Water

Several experiments were conducted using DI water spiked with nitrate and other background anions (sulfate, chloride, and alkalinity). Concentrations chosen for spiking DI water were generally higher than what has been observed in groundwater in the Region of Waterloo, and were chosen to simulate a groundwater with high concentrations of nitrate and other anions which would challenge the technologies investigated.

For IX experiments, concentrations of sulfate, chloride, and alkalinity (as $CaCO_3$) were 68, 76, and 246 mg/L, respectively, and 23 mg NO_3^--N/L was chosen as the nitrate concentration for the tests. For RO experiments, alkalinity varied between 0-246 mg/L as $CaCO_3$ in different experiments, and 5, 10, and 23 mg NO_3^--N/L were chosen as nitrate concentrations for different tests.

The stock solutions were prepared by adding sodium nitrate, sodium sulfate, sodium chloride, and sodium bicarbonate into DI water.

3.2.1 Dosage Calculation

A sample dosing calculation for the 23 mg NO_3^--N/L nitrate solution is shown below. Calculations for other anions were done in a similar way.

The goal was to prepare a 1 L stock solution of sodium nitrate such that adding that stock solution to the 50 L tank would result in 23 mg NO_3^--N/L which is equal to 100 mg/L of nitrate

$(\frac{62\text{ (g/mol) nitrate}}{14\text{ (g/mol) nitrogen}} \times 23\text{ mg/L})$.

For dilutions, $C_1V_1 = C_2V_2$

Where,

C_1 = Desired strength of stock solution (mg/L)

C_2 = Target nitrate concentration (100 mg/L)

V_1 = Volume of flask (1 L)

V_2 = Volume of tank (50 L)

Solving for C_1,

$C_1 = C_2V_2/V_1$ = 100 (mg/L) x (50L) / (1L) = 5000 mg/L nitrate (6855 mg/L as $NaNO_3$)

Therefore, stock solution contains 5000 mg/L nitrate which is equal to 6855 mg/L $NaNO_3$ $(\frac{85\text{(g/mol) sodium nitrate}}{62\text{(g/mol) nitrate}} \times 5000\text{ mg/L})$.

The mass of sodium nitrate needed to make the stock solution was calculated as below.

$C_1 = M_1/V_1$

Solving for M_1:

$M_1 = C_1V_1 = 6855$ (mg/L) x 1 (L) = 6855 (mg)

Thus, 6855 mg of sodium nitrate was weighed and dissolved in 1 L of DI water, and then diluted into 50L in the tank.

3.3 Experimental Methods

Parameters that were measured for IX experiments include nitrate, sulfate, chloride, and alkalinity. For RO experiments, all the above parameters were measured as well as pH, conductivity, temperature, and total dissolved solids (TDS).

Chemical parameters measured in this study and the methods of their measurement are summarized in Table 3-1 and discussed in the next sections.

Table 3-1: Summary of parameters measured and methods followed.

Parameter	**Instrument**	**Method**	**Standard methods** (APHA, AWWA, and WEF, 2005)
Nitrate	Dionex IC (IonPac® AS9-HC column)	Ion chromatography	4110 B
Sulfate	Dionex IC (IonPac® AS9-HC column)	Ion chromatography	4110 B
Chloride	Dionex IC (IonPac® AS9-HC column)	Ion chromatography	4110 B
Alkalinity	-	Titration method	2320 B
pH	Orion model 720A pH meter	Electrometric method	4500-H^+ B
Conductivity	Hach CO150 model 50150 Conductivity meter	Laboratory method	2510 B
Temperature	Hach CO150 model 50150 Conductivity meter	Laboratory method	2510 B
TDS	Hach CO150 model 50150 Conductivity meter	Laboratory method	2510 A

3.3.1 pH

An ORION model 720A pH meter was used to measure pH. The pH meter was calibrated prior to each use and at intervals of 1 h. Calibration was performed using three buffers (3 points) with pHs of 4, 7, and 10. This method is described as an electrometric method in section 4500-H^+ B in Standard Methods (APHA, AWWA, and WEF, 2005). All pH measurements were conducted in duplicate to ensure consistency.

3.3.2 Conductivity, Temperature, and TDS

Conductivity and temperature were measured using a Hach CO150 model 50150 conductivity meter. This method is described as a laboratory method in section 2510 B in Standard Methods (APHA, AWWA, and WEF, 2005). One point calibration was conducted prior to use of the device.

TDS was calculated based on the measured conductivity. To calculate TDS, conductivity can be multiplied by an empirical factor in the range of 0.5-0.9 (MWH, 2005) which is also explained in section 2510 A in Standard Methods (APHA, AWWA, WEF, 2005). Typically applied empirical factors are in the range of 0.65-0.7, and for this research it was chosen to be 0.67.

3.3.3 Alkalinity

To determine the alkalinity of samples, the titration method in Standard Methods 2320 B was employed (APHA, AWWA, WEF, 2005). Bromocresol green and sulfuric acid (0.02 N) were used as the indicator and titrant, respectively. Total alkalinity was measured using the equation below.

Alkalinity (mg $CaCO_3$/L) = (A x N x 50000) / volume of sample (mL)

Where,

A = volume of standard acid used (mL)

N = normality of standard acid

3.3.4 Nitrate, Sulfate, and Chloride

Nitrate, sulfate, and chloride concentrations were determined by ion chromatography (IC) which is explained in section 4110 B Standard Methods (APHA, AWWA, WEF, 2005). The IC used was a Dionex with IonPac® AS9-HC 4mm x 250 mm analytical and IonPac® AG9-HC 4 mm x 50 mm guard column. Sodium carbonate (9 mM) and sulfuric acid (50 mN) were used as eluent and regenerant, respectively (Dionex, 2008). The IC was calibrated in the range of 1-10 and 10-250 mg/L for all the three anions. In cases where the concentration of a sample was found to be higher than 250 mg/L, it was diluted and measured again which only occurred for some chloride samples. Dionex Peaknet Chromatography Workstation software was employed to process the data for calibration and determination.

3.4 Calculations

3.4.1 Percent Removal

Removal of all ions, alkalinity, and TDS were calculated based on the equation below (MWH, 2005).

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

Where,

C_f = concentration in feed water

C_p = concentration in product water

C_f and C_p should be of the same dimensions which was mg/L in this research.

3.4.2 Recovery

Recovery of the RO system was determined as below (MWH, 2005).

Recovery (%) = $100 \times (Qp / Qf)$

Where,

Q_f = feed water flow

Q_p = product water flow

Q_f and Q_p should be of the same dimensions which was mL/min in this research.

3.4.3 Statistical Calculations

The statistical calculations used in this research are briefly described below.

3.4.3.1 Average (mean)

All the samples were measured in triplicate or duplicate and the average was determined as below (Montgomery, 2007):

$$\overline{\mathrm{X}} = \frac{1}{\mathrm{n}} + \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{X}_{\mathrm{i}}$$

Where,

n = number of samples

3.4.3.2 Standard Deviation

Standard deviations were calculated for the triplicate samples. The standard deviation was estimated based on the equation below (Montgomery, 2007).

$$\mathrm{S}(\mathrm{X}) = \sqrt{\frac{\sum_{\mathrm{i}=1}^{\mathrm{n}} (\mathrm{X}_{\mathrm{i}} - \overline{\mathrm{X}})^{2}}{\mathrm{n}-1}}$$

Where,

$\overline{\mathrm{X}}$ = average of samples

n = number of samples

3.4.3.3 Confidence Interval

For triplicate samples taken in RO experiments confidence intervals were calculated based on a t-distribution method with a confidence level of 95%. Confidence intervals were calculated as below (Montgomery, 2007).

$$\mathrm{t}_{0.95,\mathrm{n}-1} \times \frac{\mathrm{S}}{\sqrt{\mathrm{n}}}$$

Where,

$t_{0.95,\, n-1}$ = t-distribution factor for 95% confidence level

S = standard deviation

n = number of samples

3.5 Ion Exchange

3.5.1 Resins

SBA (strong base anion) IX resins for nitrate removal from drinking water are commercially available. Some of these resins are listed in Table 3-2. Among them 'PWA' designated resins produced by Rohm and Hass and Dow Chemical Company Dowex™ NSR-1 resin are certified by NSF International under NSF/ANSI Standard 61 (2004) as drinking water system components, but PWA resins were not available. Ionac SR-7 by Sybron Chemicals is also certified, but it was not being produced at the time of this study.

It should be noted that NSF/ANSI Standard 61 Drinking Water System Components - Health Effects (2004) doesn't certify nitrate reduction. It establishes minimum health effects requirements for products that contact drinking water, including ion exchange resins. FDA Regulation 21 addresses safe use of ion exchange resins in the treatment of food (U.S. FDA, 2009).

Nitrate-selective resins Dowex™ NSR-1 (Sigma-Aldrich Co.), and Purolite® A-520 E (Purrolite Canada) were selected for this study. The nonselective resins Amberlite® IRA 400 Cl (Sigma-Aldrich Co.) and Purolite® A-300E (Purolite Canada) were also tested. Amberlite® IRA 400 Cl is a Type 1 resin, while Purolite® A-300E is a Type 2, and Purolite® A-520 E and Dowex™ NSR-1 (triethylamine) are nitrate selective. Product data sheets for these resins are presented in Appendix A.

Table 3-2: Potential nitrate removal resins.

Manufacturer	**Resin**	**Regenerant**	**Max. temp.** (°C)	**Typical service flow rate**		**Hydraulic loading** (m/h)	**Certification**
				(gpm/ft^3)	(BV/h = m$_s^3$/h/m$_r^3$)		
Purolite ®	A-200	NS	35 OH- 85 Cl-	NS	NS	NS	NC
	A-300E	NaOH (4%)	40.5 OH- 77 Cl-	1-5	8-40	NS	FDA Regulation 21
	A-400	NaOH (4-6%)	60 OH- 100 Cl	1-5	8-40	NS	NC
	A-520E *	NaCl (3-10%)	100	1-4	8-32	NS	NC
	A-600		60 OH- 100 Cl-	NS	NS	NS	NC
Rohm and Haas	Amberlite® IRA400 Cl	NaOH (2-4%)	60 OH- 77 Cl-	1-3	8-24	NS	NC
	Amberlite™ PWA5 *	NaCl (6-12%)	75	0.6-5	5-40	NS	ANSI/NSF 61
	Amberlite™ PWA6	NaCl (6-12%)	75	0.6-5	5-40	NS	ANSI/NSF 61
	Amberlite™ PWA12	NaCl (6-12%) CO2 (CARIX)	NS	0.5-5	5-40	NS	ANSI/NSF 61
	Amberlite™ PWA15	NaCl (6-12%)	60	0.6-5	5-40	NS	ANSI/NSF 61
Sybron Cehmicals	Ionac® A-554	NaCl/KCl (6-10%)	77	NS	NS	5-25	FDA Regulation 21
	Ionac® SR-6 *	NaCl/KCl (6-10%)	100	NS	NS	5-24	NC
	Ionac® SR-7 *	NaCl (6-10%)	100	NS	NS	5-24	ANSI/NSF 61
DOW Chemical Company	Dowex™ NSR-1 *	NaCl (3-10%)	50	NS	NS	5-60	ANSI/NSF 61
Thermax	Tulsion® A-2XMP	NaOH (1-5%) Na2CO3 (1-5%) NH4OH (1-5%)	80	5 (max)	40(max)	NS	NC
Indion Resins	INDION NSSR *	NaCl (5-10%)	100	1-4	8-30	NS	NC
Lewatit®	Mono Plus M600 *	NaOH	30	NS	NS	60(max)	NC

*= nitrate selective
NC= not certified
NS = not specified

3.5.2 Equipment

Figure 3-1 shows a schematic laboratory bench-scale set-up for nitrate removal by IX. Feed water (groundwater or spiked DI water prepared as explained in section 3.2.1) were stored in a 50 L low-density polyethylene, Nalgene (VWR) tank. A stainless steel 50 L tank was also used when two tests were run at the same time.

The stainless steel column containing the resin was 3.5 cm (d) × 40 cm (h) with a volume of 380 mL. MasterFlex® L/S™ pump model 7520-10 and EASY-LOAD head model 77202-50 (Cole-Parmer, Barrington, Illinois) were used to provide the required flow rate and pressure (Figure 3-1 and 3-2).

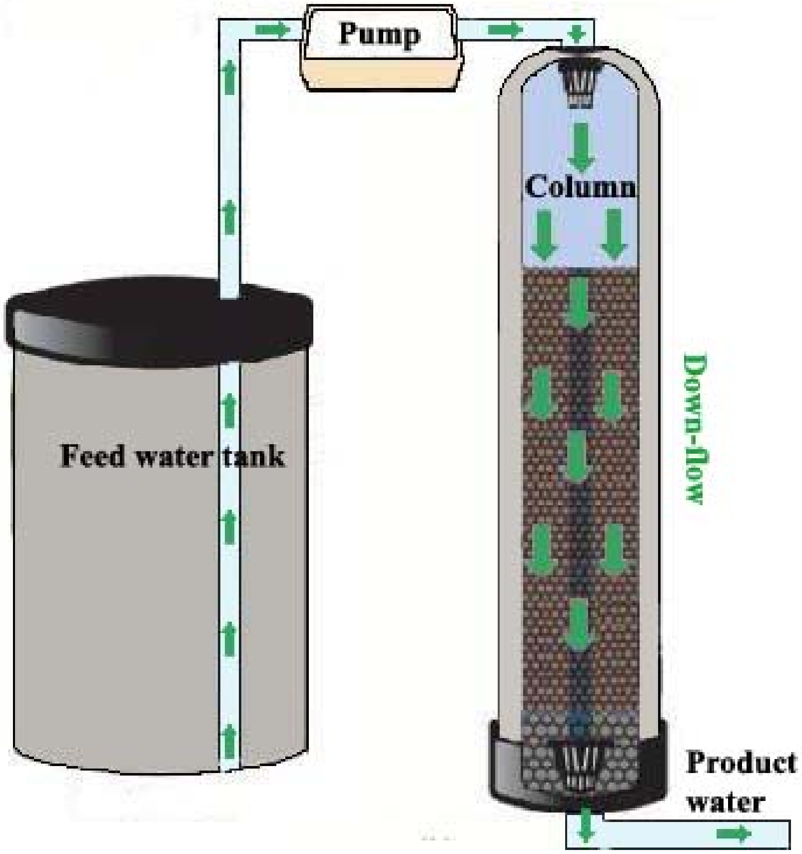

Figure 3-1: Schematic IX bench-scale nitrate removal set-up (modified from Kirby Water Conditioning: http://www.kirbywater.com/home/primer.html).

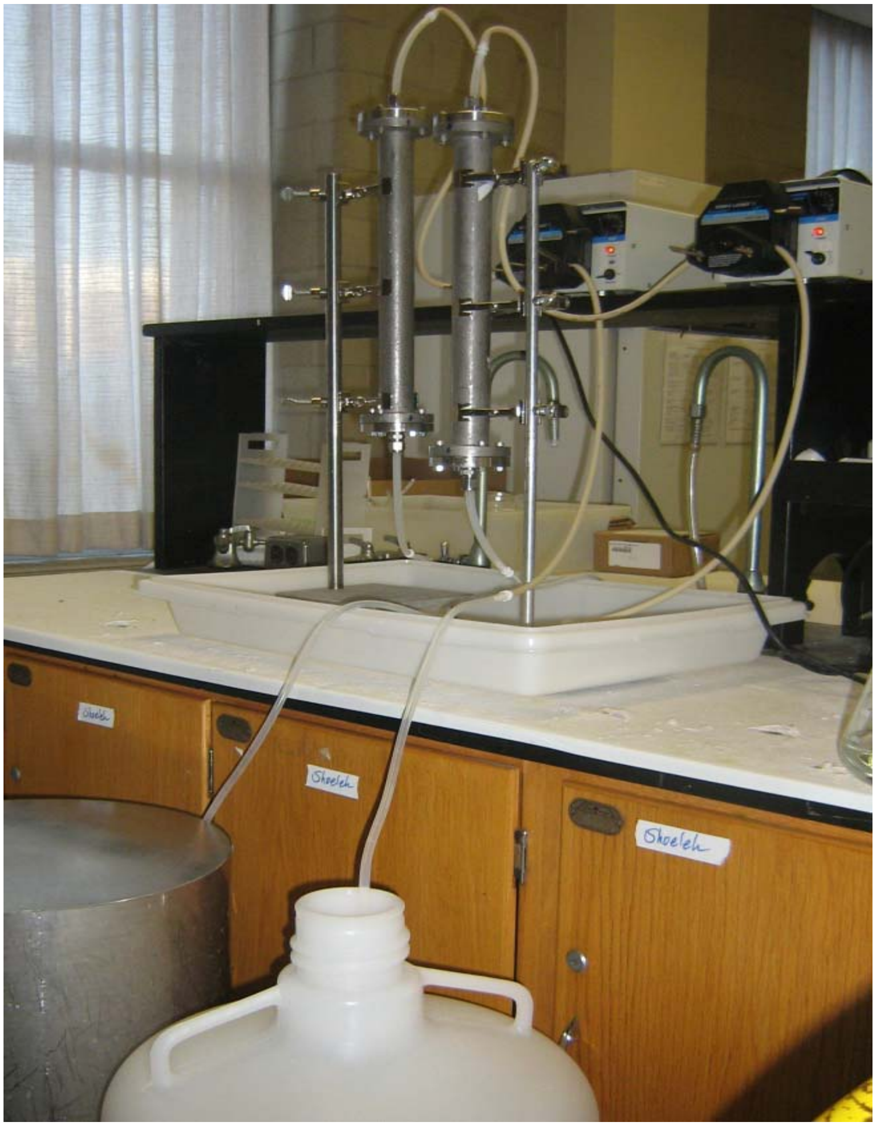

Figure 3-2: IX bench-scale nitrate removal set-up.

3.5.3 Operation

Resins should be hydrated prior to charging them to the column and rinsed before conducting experiments. A wetting procedure provided by Sigma-Aldrich Co. was conducted to hydrate the resins as follows:

1. Transfer the dry resin to a 500 mL beaker. Add sufficient distilled DI water to cover the resin bed by 1-2 in (2.5-5 cm)

2. Stir the resin gently to ensure complete mixing. Allow the material to stand for 15 minutes.
3. Carefully decant most of the water and replace it with fresh distilled, DI water. Stir the mixture, then allow it to stand for 5-10 minutes.

After charging the resin to the column it was rinsed with DI water for approximately 20 minutes at a flow rate of 83 mL/min to remove any residuals, manufacturing chemicals, or shipping preservatives. Rinsing and all the experiments were conducted on a down-flow direction. Flow was measured manually using a graduated cylinder and a chronometer.

To optimize the operating conditions, some experiments were conducted (Section 4.2.1) and based on their results the conditions summarized in Table 3-3 were selected to conduct all the tests.

Table 3-3: Operating conditions for IX experiments.

Bed depth (m)	**Hydraulic loading (m/h)**	**Resin volume (mL)**	**Flow rate**		**EBCT (min)**
			(BV/h)	**(mL/min)**	
0.1	5.2	100	50	83	1.2

The number of bed volumes (BV) is a unitless measure (volume of solution/volume of resin). For each run, 1000 bed volumes (BV) (100L) of the feed water was pumped through the resin which lasted 20 hours. Samples were collected from the product water at 50 BV (1 h) intervals.

Used resin was emptied from the column and washed thoroughly with Milli-Q water after each experiment. The resins were stored in plastic bottles in a wet condition (soaking Milli-Q water, suggested by supplier) after being used.

3.6 Reverse Osmosis

Several different suppliers claim their low-pressure RO units can remove nitrate from drinking water. Among these units some are certified for nitrate removal by NSF International under NSF/ANSI Standard 58 as reverse osmosis drinking water treatment systems. Table 3-4 summarizes the certified units offered by suppliers that have authorized dealers in Canada.

Table 3-4: NSF/ANSI Standard 58 certified RO units for nitrate removal.

Supplier	**Dealer**	**RO model**	**Product rate** (mL/min)	**Filter**	**Operating pressure** (kpa)	**Nitrate removal** (%)	**Feed water restrictions**		
							pH	**Max. hardness** (mg/L)	**Max. turbidity** (NTU)
Culligan International Company	Culligan®, Kitchener	Aqua Cleer®	83	Particle filter, carbon block	276-827 (40-120 psi)	80	5-10	171 (10 gpg)	10
Cuno, Incorporated	Elma Water Technologies, Richmond Hill	SQC4 Purificare	28.88	Sediment filter, carbon filter	345-551	79.2	NS	NS	10
Flowmatic Systems, Inc.	FLOWMATIC, Toronto/ London	FMR05-M	132	Sediment filter, carbon filter	207-689	NS	3-11	256	1
General Electric Company	Home Depot	GXRM10GXX	10	Carbon filter	276-862	80	4-10	171	NS
Kinetico Incorporated	DBA Crystal Clear water Centres, Waterloo/ Kitchener	K5 drinking Water Station	32	NS	241-862	77	NS	NS	NS
Rainsoft Division of Aquion Water Treatment Products, LLC	Rainsoft of London, London/ Superior Water Conditioners, Hamilton	Ultrefiner® PF22N-CB	22.3	Carbon filter	276-689	87	NS	NS	NS
		Ultrefiner® UF50N-CBVCD	40.5	Carbon filter	276-689	86	NS	NS	NS
The Leveredge	Allen Water Treatment, Kitchener	AvantaPure	37	Sediment filter, carbon filter	NS	NS	NS	NS	NS

NS = not specified

Most of these units are equipped with a particle (sediment) filter and/or carbon filter prior to the RO membrane. However, the carbon filter is sometimes used as a post filter after the RO membrane. Particle (sediment) filters are capable of removing sediment and particulate material such as sand, rust, and dirt from the feed water. Some carbon filters contain loose granular activated carbon (GAC) while others are in the form of a block. A carbon block is defined as a fused, water permeable porous structure containing, at a minimum, activated carbon and a binding material. These carbon filters are described as being able to reduce taste and odor of chlorine as well as other elements that may cause unpleasant taste and smell in water. Both filters help to control fouling and scaling of the RO membrane. Carbon filters also protect the RO membrane from being damaged by chlorine. Using softeners is also suggested to protect the RO membrane when feed water hardness is high.

3.6.1 Equipment

A Culligan® Aqua-Cleer® (model RO30) drinking water system was selected from among the certified RO units based on its production rate, required pressure, and availability (convenient purchase and maintenance). The unit's specification sheet is provided in Appendix B.

This unit includes a 5 micron particle filter, a 5 micron carbon block with acid washed activated carbon material, and a 30 GPD RO membrane that consists of a membrane envelope wound around a perforated tube (Figure 3-3 and 3-4). The components are intended for use in series, but individual components can be tested in isolation or in combination with only one other element. As an example, Figure 3-5 shows RO membrane preceded by only carbon block.

Figure 3-3: Culligan® Aqua-Cleer® (model RO30) drinking water system.

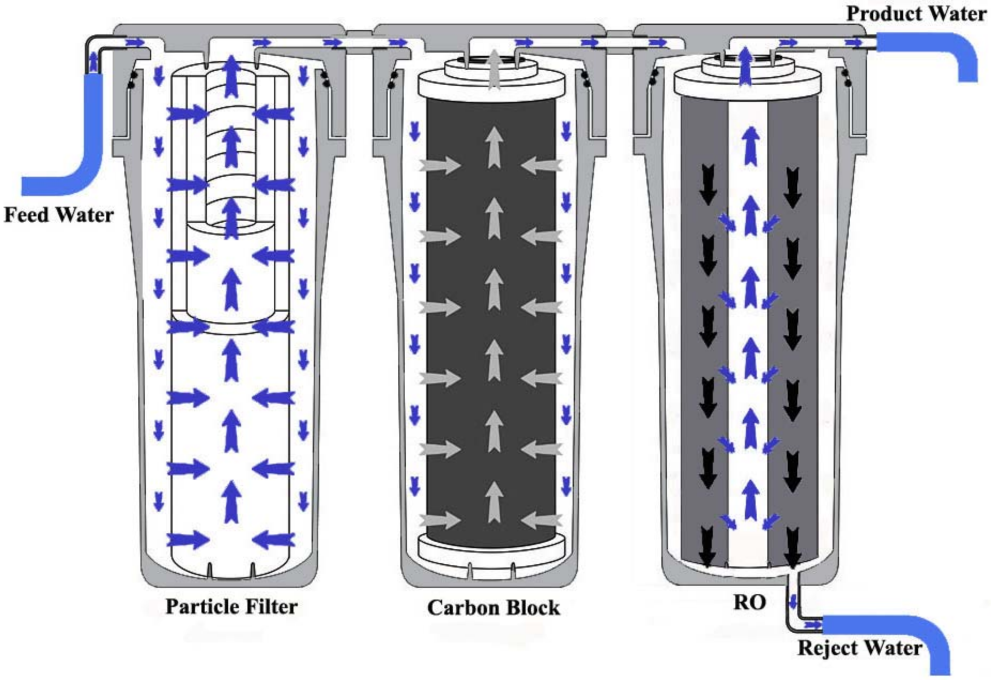

Figure 3-4: Details of the Culligan® Aqua-Cleer® (model RO30) drinking water system (modified from PurePro USA Corp., Illinois, USA).

Figure 3-5: RO membrane preceded by only carbon block.

Feed water (groundwater or spiked DI water prepared as explained in section 3.2.1) was stored in a 50 L Low-Density Polyethylene, NALGENE (VWR) tank.

Pressure was applied to the system by an Aquatec DPP 5800 demand/delivery high pressure pump supplied by Culligan. The pump can produce pressure up to 60 psi (414 Kpa) which is sufficient for the Culligan® Aqua-Cleer® (model RO30) drinking water system. To measure the pressure, an Ashcroft Duraliff stainless steel pressure gauge was installed on the feed water tubing right after the pump.

A GE727 (150 mm) Gilmont Instruments flowmeter (± 5%) was used to measure the feed water flow. Product and reject water flows were measured manually by using a graduated cylinder and a chronometer.

3.6.2 Operation

Prior to conducting experiments, the system was flushed with DI water for approximately one hour at 50 psi (300 mL/min) to remove any residual, manufacturing chemicals or shipping preservatives.

The tests were conducted at 50 psi according to NSF/ANSI Standard 58 (2007). However, pressures of 40 and 60 psi were also investigated since 40 psi is the minimum pressure recommended by the unit manufacturer and 60 psi is the maximum that could be pumped by Aquatec DPP 5800 pump.

To examine the effect of filters and the RO membrane, some tests were done using the RO membrane alone or preceded by the particle filter and/or the carbon block filter. Components can be easily removed from the system by twisting and capping. The cap was submerged in feed water prior to use.

NSF Standard 58 (NSF/ANSI, 2007) indicates that sampling should begin only after 15 minutes of application. Pressure should be maintained and product water should be discarded prior to that time. To find a reliable time to initiate sampling, some experiments were conducted and based on their results the system stabilized after 15 minutes. Therefore, sampling times were chosen to be 15, 20, and 25 minutes for all the tests.

Each run lasted approximately 30 minutes, and 86 tests were conducted. The average feed water flow was 300 mL/min. Therefore, total volume of water pumped through the RO unit was approximately 800 L based on the calculations below. The RO membrane was not changed or cleaned at any time during these experiments.

Volume for conducting tests = number of tests × run time × flow = 86 × 30 min × 300 = 774 L

Volume for flushing = flushing time × flow = 60 min × 300 mL/min = 18 L

Therefore,

Total volume = volume for conducting tests + volume for flushing = 774 L + 18 L = 792 L~800L

3.7 Quality Control

To control the quality of the results and ensure their accuracy and consistency, several measures were taken including the following:

- The same bottle or batch of each chemical was used throughout the project, and always weighed with the same scale (Sartorius scale ± 0.1 mg).
- To meet the sampling and handling requirements of Standard Methods 1060 B (APHA, AWWA, WEF, 2005), each sample was taken in 4 or 5 glass vials (each 40 mL) and refrigerated immediately after being taken. Conductivity was measured during the run, and pH was measured after sampling. Titration and IC were conducted to measure alkalinity and anions within 48 hours of taking the samples.
- IC measurements were conducted in duplicate or triplicate, with one calibration curve in the range of 1-10 mg/L, and another for 10-250 mg/L for all the three anions (standards: 1, 2, 5, 10, 20, 40, 60, 80, 100, 130, 160, 190, 220, and 250 mg/L). One Milli-Q water blank sample was used after measuring 5 samples and 3 standard samples were used in each run to ensure accuracy and consistency.
- Alkalinity was measured in triplicate or duplicate. pH and conductivity, measurements were conducted in duplicate for all the samples.
- Resins were hydrated and rinsed prior to conducting experiments according to Sigma-Aldrich Co. procedure. RO unit was also flushed prior to use. Rinsing or flushing is to remove any residuals, manufacturing chemicals, or shipping preservatives
- To meet NSF/ANSI Standard 58 requirements (pressure, sampling time, feed water concentration) for RO units, a certified RO unit was selected and operated at 50 psi. Samples were taken after 15 minutes of run (20, 25, and 30 min). Maximum nitrate concentration in the feed water tested (23 mg NO_3^--N/L) was a bit lower than the NSF of 30 (± 10%) mg NO_3^--N/L (NSF/ANSI Standard 58, 2007). The 23 mg NO_3^--N/L (100 mg NO_3^-/L) was chosen to simulate a groundwater with high concentrations of nitrate and is higher than what has been observed and recorded in the history of groundwater of the Region of Waterloo.

- All containers, vials, flasks, and beakers were cleaned using a washing machine (with deionized water and acid rinses) after each use, and rinsed with sample water prior to use.

Chapter 4

Evaluation of Ion Exchange Resins for Nitrate Removal

4.1 Introduction

Two nitrate-selective and two non-selective SBA (Strong Base Anion) ion exchange (IX) resins were chosen from various available resins based on their characteristics as discussed in Chapter 3. Nitrate-selective resins are formulated in such a way as to adsorb nitrate preferentially versus sulfate and are able to exchange nitrate for sulfate as well as other anions. Dowex™ NSR-1 and Purolite® A-520E are nitrate-selective, and Purolite® A-300E and Amberlite® IRA400 Cl are non-selective.

Several experiments were conducted to investigate the performance of the resins and compare them under different conditions for nitrate removal. These experiments were categorized in seven groups and are listed in Table 4-1. The first five groups were performed using deionized (DI) water spiked with nitrate and other competing anions and the last two used groundwater collected in the Region of Waterloo, Ontario as their feed waters. Target anions included nitrate, sulfate, chloride, and alkalinity (bicarbonate). Concentrations of sulfate, chloride, and alkalinity (as $CaCO_3$) were 68, 76, and 246 mg/L, respectively, and 23 mg NO_3^--N/L was chosen as the nitrate concentration for different tests. These concentrations are close to or slightly higher than what has been observed and recorded in the history of groundwater of the Region, and were chosen to simulate a groundwater with high concentrations of anions.

For each experiment, 1000 bed volumes (BV) of the test water was pumped through the resin and samples were collected from the product water at 50 BV intervals. The number of bed volumes is a unitless measure (volume of solution/volume of resin) that indicates the capacity of a system to remove contaminants (Symons et al., 2001). In this study bulk volumes of resins were used to determine BVs. Effective capacity of a resin is the amount of ions that it can exchange in a column operation. This parameter is site specific (MWH, 2005) and can be measured in meq/mL of resin, or BV (Lauch and Guter, 1986; MWH, 2005; Samatya et al., 2006).

Breakthrough curves for each experiment were generated based on the measured concentrations of anions in the product water, and selected representative examples are presented in this chapter or Appendix C. It should be noted that to provide a consistent visual comparison, the same vertical scales were chosen for all nitrate breakthrough curves and also for all product water breakthrough curves.

Table 4-1: Conditions for ion exchange experiments.

Experiment no.	**Investigation**		**Feed water**	**Bed depth (m)**	**Hydraulic loading (m/h)**
4-1	Effect of operating conditions (hydraulic loading, bed depth, contact time)		DI spiked with nitrate	0.05, 0.1	5.2, 10.4
4-2	Effect of competing anions	Effect of sulfate	DI spiked with nitrate in combination with sulfate	0.1	5.2
4-3		Effect of chloride	DI spiked with nitrate in combination with chloride	0.1	5.2
4-4		Effect of alkalinity (bicarbonate)	DI spiked with nitrate in combination with alkalinity (bicarbonate)	0.1	5.2
4-5		Effect of combination of all competing anions	DI spiked with nitrate in combination with all competing anions	0.1	5.2
4-6	Resin performance using real groundwater		GW1	0.1	5.2
4-7			GW2	0.1	5.2

DI = dionized water; GW1 = groundwater site 1; GW2 = groundwater site 2

4.2 Experiments using Spiked Deionized Water

4.2.1 Optimization of Operating Conditions

This set of experiments was conducted to optimize operating conditions: contact time, hydraulic loading, and bed depth. Since contact time is a function of bed depth and hydraulic loading only the effect of the last two factors was investigated. In all these experiments deionized water spiked with 23 mg NO_3^--N/L was used as a feed water. To investigate the effect of bed depth, resin volume was changed from 100 mL to 50 mL reducing the bed depth from 0.1 m to 0.05 m. And, flow rates were chosen to be 83 and 167 mL/min to study the effect of hydraulic loading at 5.2 and 10.4 m/h.

4.2.1.1 Experiments using Dowex™ NSR-1

Four experiments were conducted to quantify the effects of contact time, hydraulic loading, and bed depth on the performance of Dowex™ NSR-1 (Table 4-2).

Table 4-2: Conditions for optimization of operating condition experiments on Dowex™ NSR-1.

Experiment no.	**Bed depth (m)**	**Hydraulic loading (m/h)**	**Resin volume (mL)**	**Flow rate**		**EBCT (min)**
				(BV/h)	**(mL/min)**	
4-1-1	0.1	5.2	100	50	83	1.2
4-1-2	0.05	5.2	50	100	83	0.6
4-1-3	0.1	10.4	100	100	167	0.6
4-1-4	0.05	10.4	50	200	167	0.3

EBCT = empty bed contact time

The breakthrough curve generated for experiment 4-1-1 is presented in Figure 4-1. As shown in the figure, before reaching 500 BV the resin can entirely exchange nitrate for chloride, and the nitrate removal is 100%. At 500 BV the resin begins to become exhausted and can’t exchange all the nitrate. At 1000 BV the resin is totally exhausted; the feed water nitrate passes through the resin without any change to its initial concentrations and nitrate is not removed. Breakthrough curves for the rest of these experiments are presented in Figures C-1 – C3 (Appendix C).

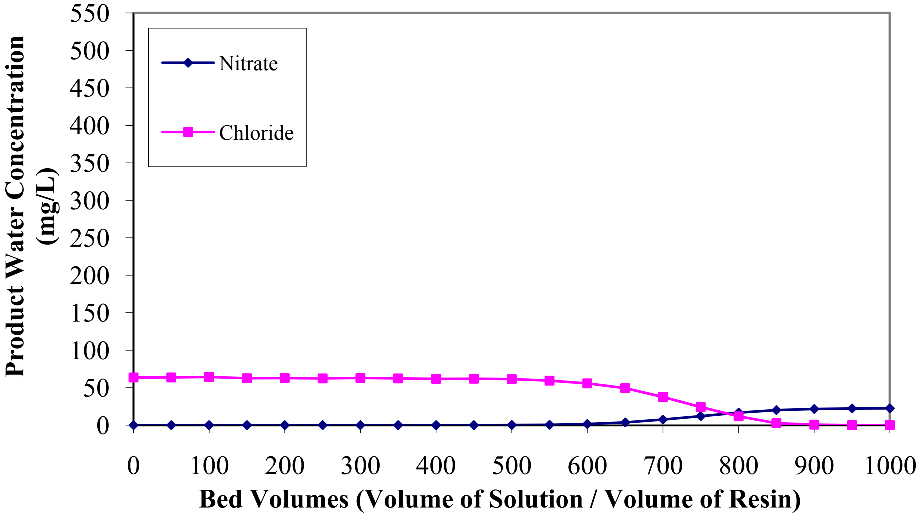

Figure 4-1: Breakthrough curve of 100 mL Dowex™ NSR-1 at a hydraulic loading of 5.2 m/h. Nitrate and chloride were measured as N and Cl-, respectively. Experiment 4-1-1. (Feed water nitrate = 23 mg NO_3^--N/L).

Figure 4-2 compares the breakthrough curves of all four optimization-of-operating-condition experiments on Dowex™ NSR-1, and Table 4-3 presents the capacity of the resin (BV) to decrease nitrate to less than the Ontario MAC (10 mg NO_3^--N/L). Results show that decreasing contact time by decreasing bed depth or increasing hydraulic loading decreases the capacity of the resin and shifts the breakthrough point backward. It also shows that, bed depth (resin volume) is the more important of the two factors, and hydraulic loading is not of a great importance at loadings tested.

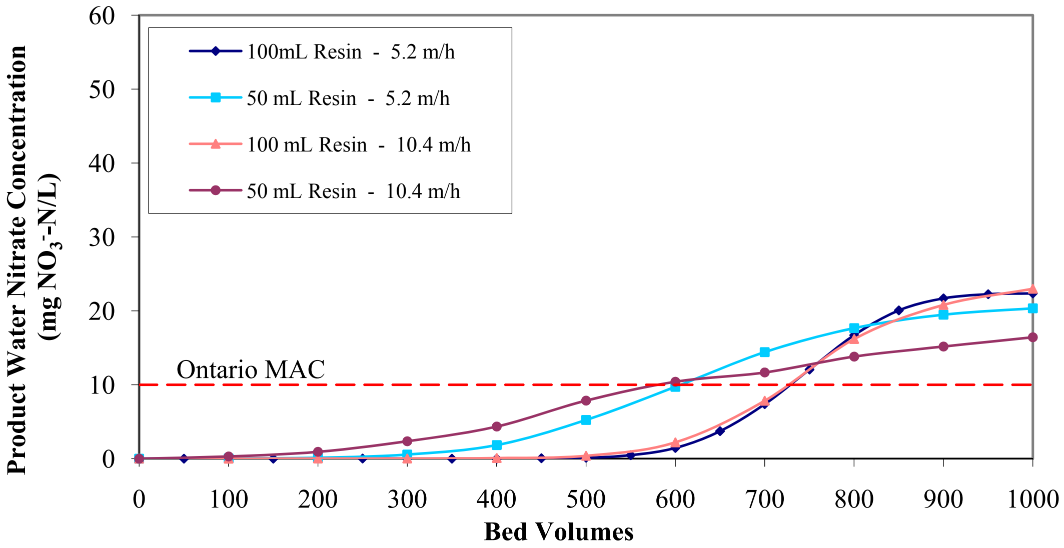

Figure 4-2: Comparison of nitrate breakthrough curves for optimization of operating condition experiments on Dowex™ NSR-1. (Feed water nitrate = 23 mg NO_3^--N/L).

Table 4-3: Capacity of Dowex™ NSR-1 for maintaining nitrate concentrations less than the Ontario MAC (10 mg NO_3^--N/L).

Experiment no.	**Resin volume (mL)**	**Hydraulic loading (m/h)**	**Bed depth (m)**	**EBCT (min)**	**Resin capacity (BV)**
4-1-1	100	5.2	0.1	1.2	730
4-1-2	50	5.2	0.05	0.6	605
4-1-3	100	10.4	0.1	0.6	730
4-1-4	50	10.4	0.05	0.3	580

Feed water nitrate concentration = 23 mg NO_3^- - N/L

4.2.1.2 Experiments using Purolite® A-520E, Purolite® A-300E, and Amberlite® IRA400 Cl

Results of previous experiments showed that changing hydraulic loading didn't have a significant effect on the breakthrough curve. Thus, hydraulic loading for the remaining experiments was set at 5.2 m/h (largely to conserve water), and two experiments were conducted to quantify the effects of contact time and bed depth on the performance of the remaining resins. Conditions for these experiments are listed in Table 4-4, and their breakthrough curves are presented in Figures C4 – C9 (Appendix C).

Table 4-4: Conditions for optimization of operating condition experiments on Purolite A-520E, Purolite® A-300E, and Amberlite® IRA400 Cl. Experiment 4-1.

Experiment no.	**Resin**	**Bed depth (m)**	**Hydraulic loading (m/h)**	**Resin volume (mL)**	**Flow rate**		**EBCT (min)**
					(BV/h)	**(mL/min)**	
4-1-5	Purolite® A-520E	0.1	5.2	100	50	83	1.2
4-1-6	Purolite® A-520E	0.05	5.2	50	100	83	0.6
4-1-7	Purolite® A-300E	0.1	5.2	100	50	83	1.2
4-1-8	Purolite® A-300E	0.05	5.2	50	100	83	0.6
4-1-9	Amberlite® IRA400 Cl	0.1	5.2	100	50	83	1.2
4-1-10	Amberlite® IRA400 Cl	0.05	5.2	50	100	83	0.6

Figures 4-3, 4-4, and 4-5 compare the breakthrough curves of the two optimization-of-operating-condition experiments using Purolite® A-520E, Purolite® A-300E, and Amberlite® IRA400 Cl, respectively. Table 4-5 presents the capacity of all the resins (BV) for decreasing nitrate to less than the MAC (10 mg NO_3^--N/L) at a hydraulic loading of 5.2 m/h and bed depths of 0.1 and 0.05 m. A comparison of breakthrough curves of all the experiments conducted under the condition of 5.2 m/h hydraulic loading, and bed depth of 0.1 is presented in Figure 4-6, and for bed depth of 0.05 m in Figure C10 (Appendix C). Decreasing the contact time by decreasing the resin volume (bed depth) adversely affected the performance of all the resins, especially the nitrate-selective resins. Therefore, the resin volume was chosen to be 100 mL (bed depth of 0.1 m) for the remaining deionized water experiments and testing the resins for nitrate removal from groundwater. It can also be concluded that performance of both nitrate-selective resins (Dowex™ NSR-1 and Purolite® A-520E) and their capacities before reaching MAC are quite similar (comparing Figures 4-2 and 4-3). In addition, it can be seen from the results that non-selective resins (Purolite® A-300E, and Amberlite® IRA400 Cl) have greater capacities than nitrate-selective resins, while Amberlite® IRA400 Cl could effectively remove nitrate in both operating conditions. As explained at the beginning of this section, feed water chosen for conducting these experiments contained only nitrate and no anions that could potentially compete with nitrate for adsorption on the non-selective resins. This may be the reason why the non-selective resins performed better in these experiments. This is discussed further in the next section.

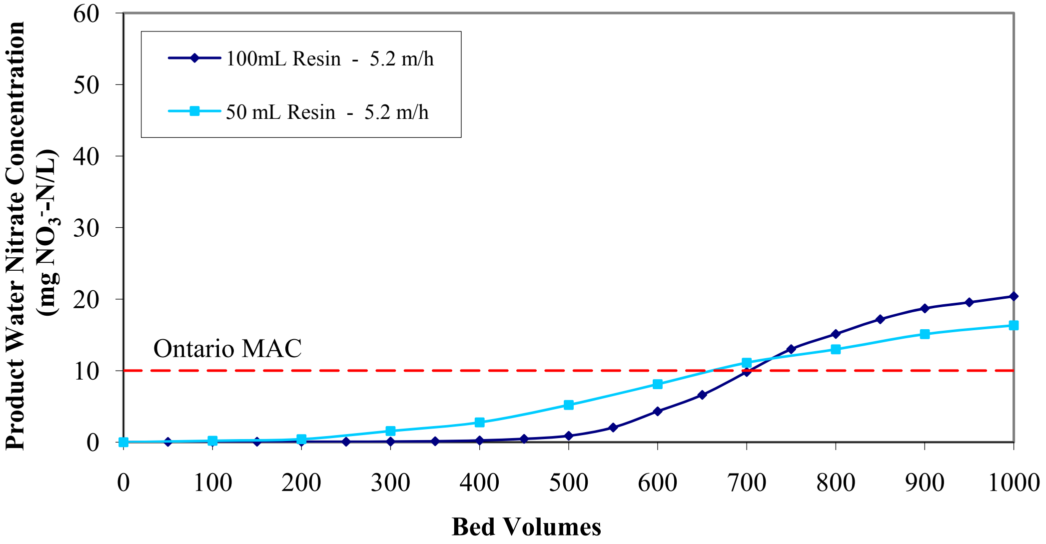

Figure 4-3: Comparison of nitrate breakthrough curves for optimization of operating condition experiments on Purolite® A-520E. (Feed water nitrate = 23 mg NO_3^--N/L).

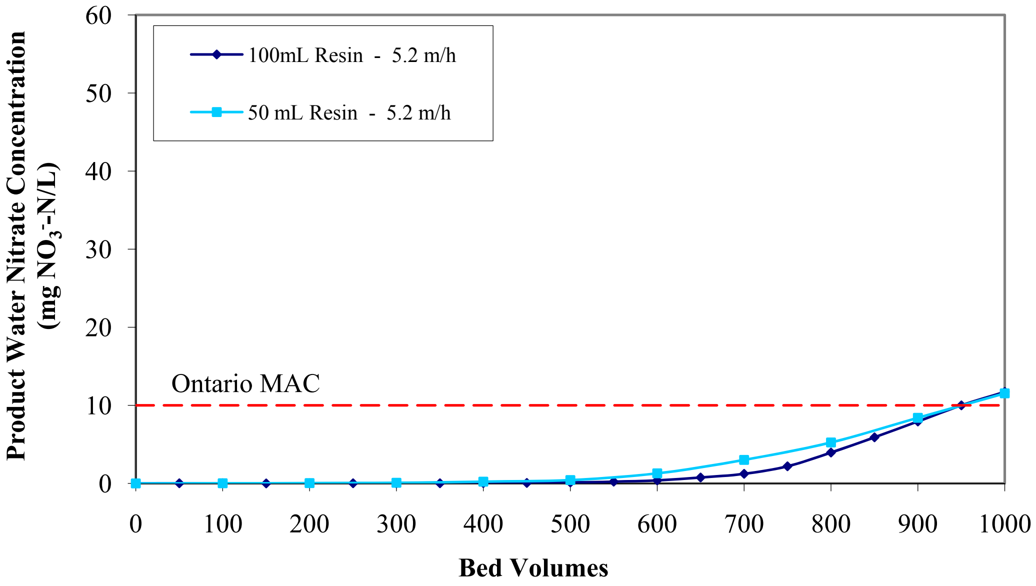

Figure 4-4: Comparison of nitrate breakthrough curves for optimization of operating condition experiments on Purolite® A-300E. (Feed water nitrate = 23 mg NO_3^--N/L).

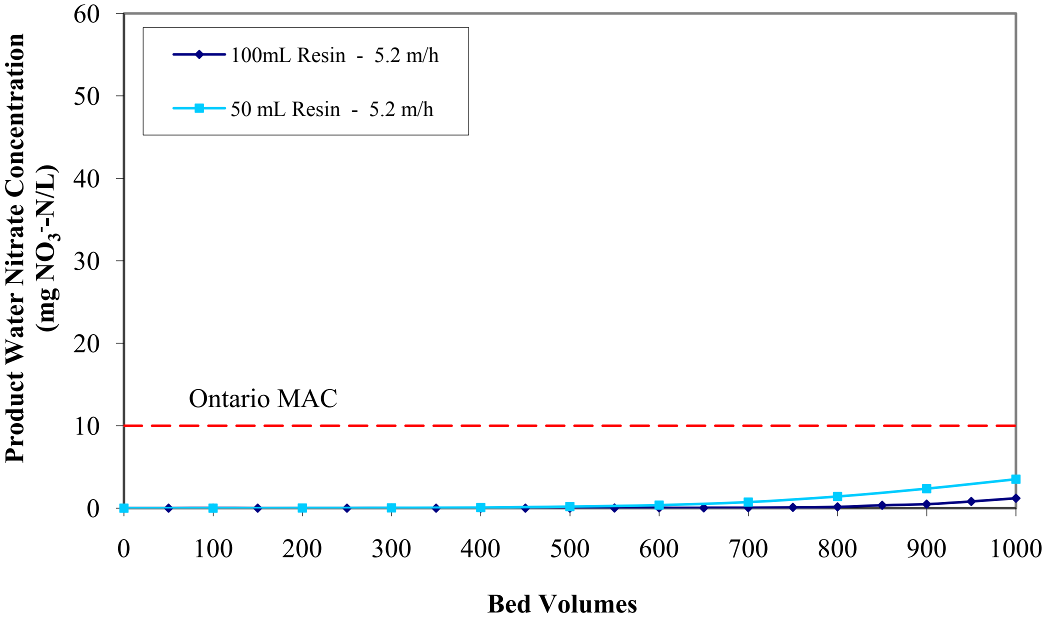

Figure 4-5: Comparison of nitrate breakthrough curves for optimization of operating condition experiments on Amberlite® IRA400 Cl. (Feed water nitrate = 23 mg NO_3^--N/L).

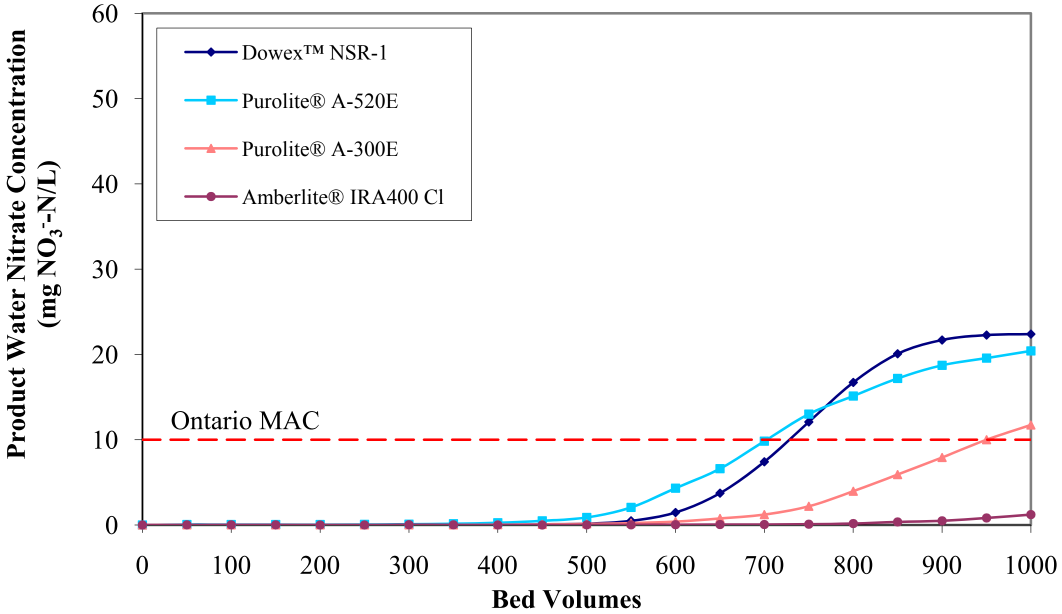

Figure 4-6: Comparison of different resins at a hydraulic loading of 5.2 m/h and bed depth of 0.1 m. (Feed water nitrate = 23 mg NO_3^--N/L).

Table 4-5: Capacity of the resins (BV) for maintaining nitrate concentrations less than the Ontario MAC (10 mg NO_3^--N/L)*.

Resin / **Operating condition**	**Dowex™ NSR-1**[**]	**Purolite A-520E**[**]	**Purolite A-300E**	**Amberlite® IRA400 Cl**
hydraulic loading 5.2 m/h, bed depth 0.1 m	730	700	950	>1000
hydraulic loading 5.2 m/h, bed depth 0.05 m	605	660	950	>1000

* = feed water nitrate concentration = 23 mg NO_3^--N/L

** = nitrate selective resins

4.2.2 Investigating the Effect of Background Anions

The resins used for this study exchanged nitrate for chloride, but when all of their chloride is desorbed and their exchange capacity for chloride is exhausted, they exchange anions in the influent for other adsorbed anions based on their adsorption affinity, with stronger adsorbing anions replacing weaker adsorbing ones. Since sulfate is preferentially adsorbed over nitrate, nitrate-selective anion exchange resins are designed and modified to overcome this problem. The goal of this section was to study the performance of all four resins for nitrate removal in the presence of other background anions. Sulfate, chloride, and alkalinity (bicarbonate) were chosen as competing anions, and their effects were investigated individually and in combination. The reason for investigating effect of anions individually was to better understand the adsorption characteristics of the resins tested. Mixing the anions in the feed water was done to investigate their combined effect on the selective resins. Concentrations of sulfate, chloride, and alkalinity (as $CaCO_3$) were 68, 76, and 246 mg/L, respectively, and 23 mg NO_3^--N/L was chosen as nitrate concentration. Operating conditions for all experiments in this section were set at a bed depth of 0.1 m, and a hydraulic loading of 5.2 m/h (contact time = 1.2 min).

4.2.2.1 Effect of Sulfate (experiment 4-2)

The effect of having sulfate in the presence of nitrate in the feed water was investigated on the performance of all the four resins. As mentioned previously, Dowex™ NSR-1 and Purolite® A-520E are described as being nitrate-selective by their producers.

Table 4-6: Conditions for experiment 4-2.

Nitrate concentration (mg NO_3^--N/L)	**Sulfate concentration (mg SO_4^{2-}/L)**
23	68

The breakthrough curve regenerated for experiment 4-2 on Purolite® A-520E is shown in Figure 4-7. As can be seen, both sulfate and nitrate were exchanged for chloride and completely removed in the first 150 BV. Leakage started at 150 and 300 BV for sulfate and nitrate, respectively. The amount of sulfate exceeded its original concentration after 350 BV which shows that the resin started replacing adsorbed sulfate with nitrate which is the main characteristic of a nitrate-selective resin. Finally, the resin became totally exhausted after 850 BV. Dowex™ NSR-1, which is also nitrate-selective, performed similarly under the same conditions, and its breakthrough curve can be seen in Figure C-11 (Appendix C).

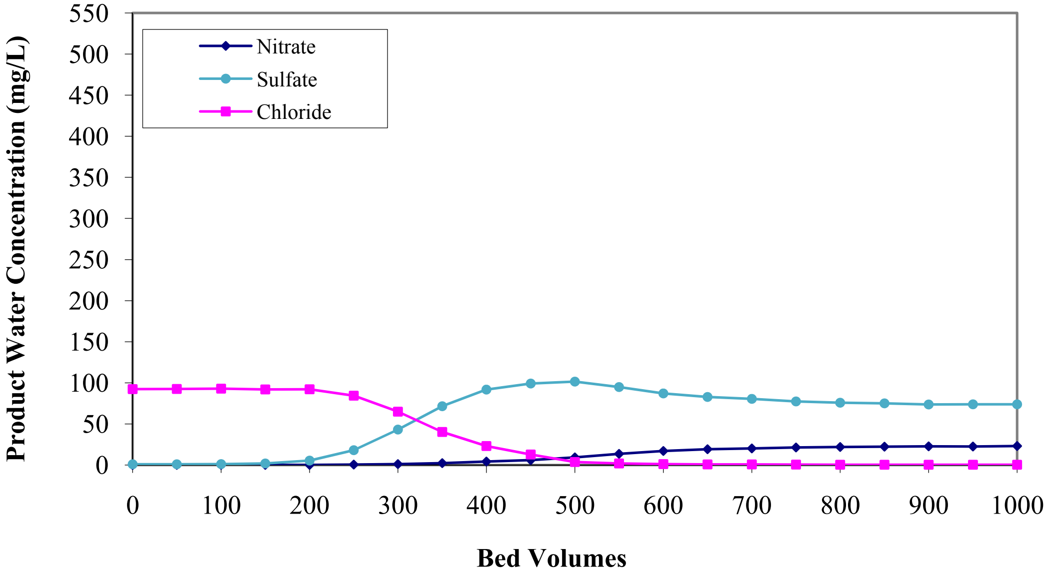

Figure 4-7: Breakthrough curve showing the effect of sulfate on Purolite® A-520E. (Nitrate, sulfate, and chloride were measured as N, SO42-, and Cl-, respectively). Experiment 4-2.

Results of experiment 4-2 which was designed to investigate the effect of sulfate on the non-selective resin Purolite® A-300E are presented in Figure 4-8.

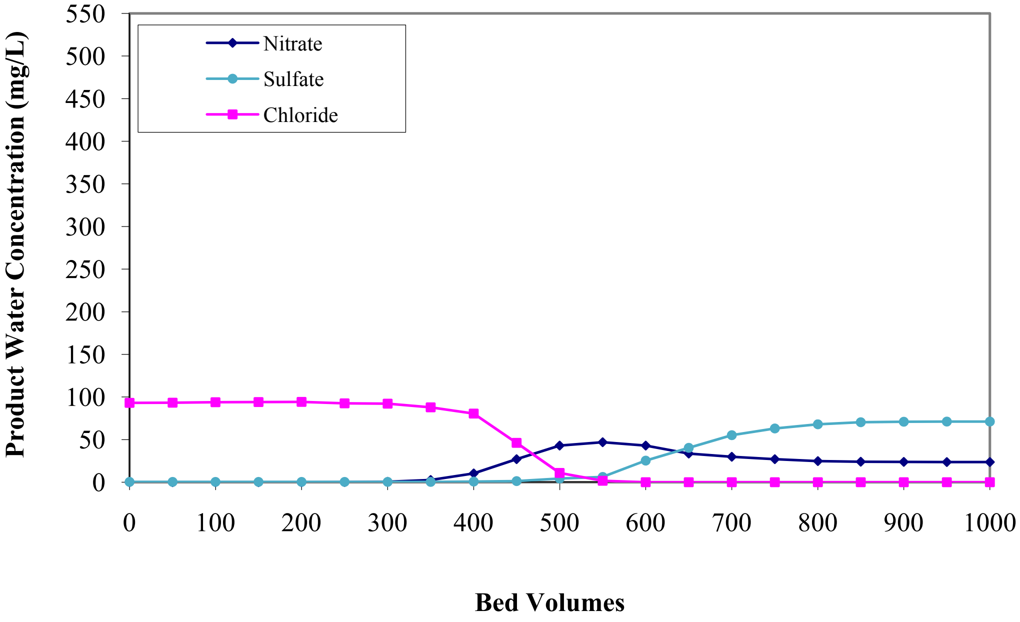

Figure 4-8: Breakthrough curve showing the effect of sulfate on Purolite® A-300E. (Nitrate, sulfate, and chloride were measured as N, SO42-, and Cl-, respectively). Experiment 4-2.

Purolite® A-300E is a non-selective resin, and its performance in the presence of sulfate is different from the performance of nitrate-selective resins. In this case, nitrate leakage occurred at 250 BV while it happened at 400 BV for sulfate. In addition, at 440 BV the concentration of nitrate exceeded its original concentration since resin replaced previously adsorbed nitrate for sulfate. The other non-selective resin (Amberlite® IRA400 Cl) performed similarly under the same conditions (Figure C-12, Appendix C).

Comparing nitrate breakthrough curves for all the resins in Figure 4-9 and their capacity for decreasing nitrate to less than MAC (10 mg NO_3^--N/L) in Table 4-7 show that non-selective resins had similar adsorption curves, while Amberlite® IRA400 Cl had the greatest capacity amongst all the four. However, using this resin for removing nitrate in the presence of sulfate needs a carefully designed and maintained regeneration process to avoid releasing adsorbed nitrate into the product water. Also, both nitrate-selective resins had similar breakthrough curves while the capacity of Purolite® A-520E was greater.

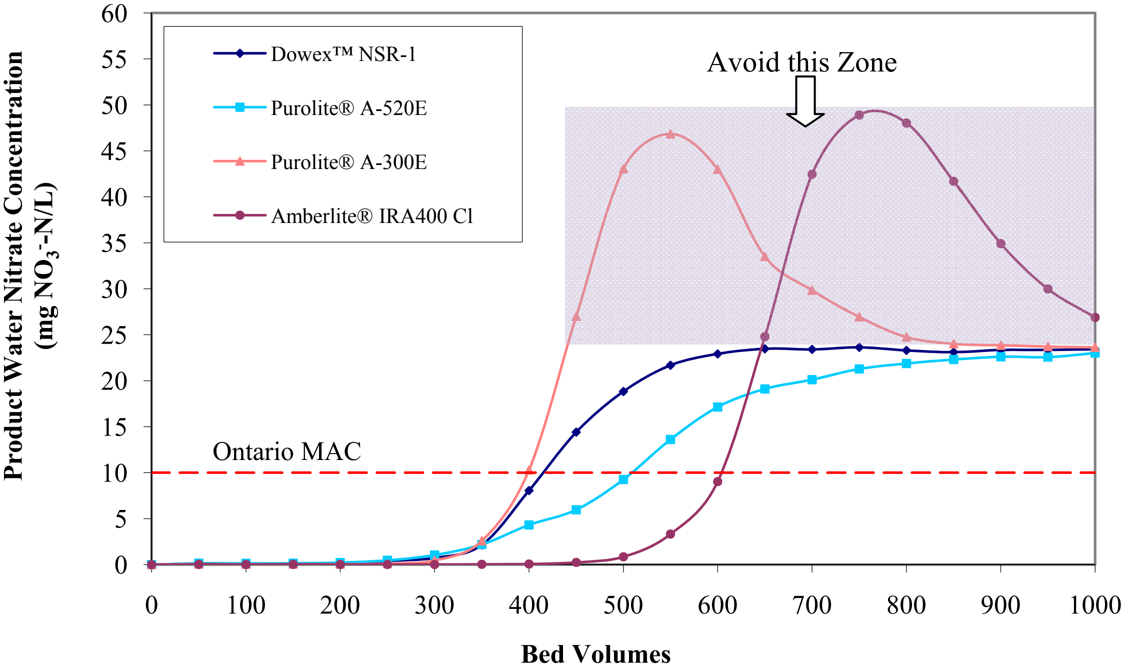

Figure 4-9: Comparison of different resins in the presence of sulfate. Experiment 4-2.

Table 4-7: Capacity of the resins for maintaining nitrate concentrations less than the Ontario MAC (10 mg NO_3^--N/L) in the presence of sulfate (in deionized water). Experiment 4-2.

Resin	**Resin capacity (BV)**
Dowex™ NSR-1*	415
Purolite® A-520E*	510
Purolite® A-300E	400
Amberlite® IRA400 Cl	605

* = nitrate selective resins

4.2.2.2 Effect of Chloride (experiment 4-3)

Chloride is less preferentially adsorbed than nitrate and SBA resins cannot exchange it for nitrate at typical drinking water concentrations. However, the presence of this anion in the feed water might affect the capacity of the resin for decreasing nitrate. The effect of having chloride along with nitrate in the feed water was investigated on the performance of all four resins. Table 4-8 lists the conditions for these experiments. They were all conducted at a bed depth of 0.1 m, and hydraulic loading of 5.2 m/h (contact time = 1.2 min).

Table 4-8: Conditions for experiment 4-3.

Nitrate concentration (mg NO_3^--N/L)	**Chloride concentration (mg Cl^-/L)**
23	76

Breakthrough curves for experiment 4-3 for Purolite® A-520E show that nitrate was simply exchanged for chloride and the resin became exhausted at the end of the run (Figure 4-10). Similar results for other resins are presented in Figures C-13 – C-15 (Appendix C).

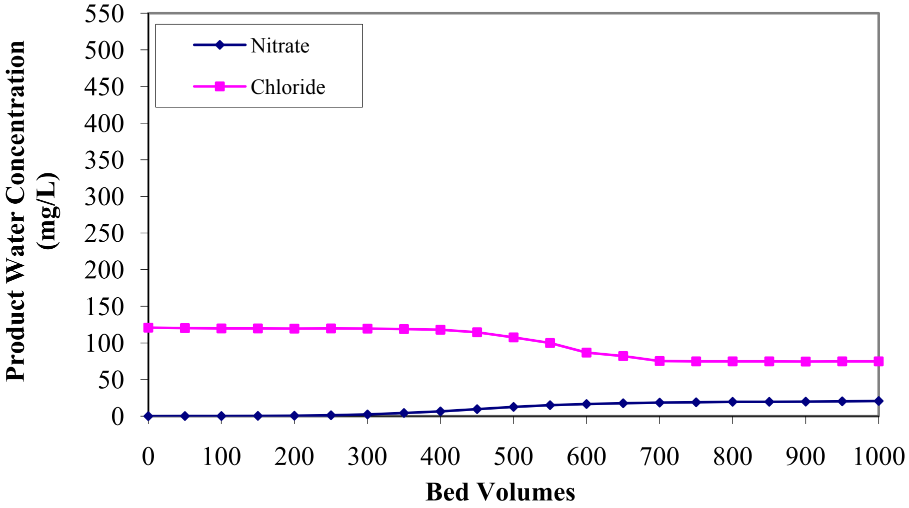

Figure 4-10: Breakthrough curve showing the effect of chloride on Purolite® A-520E. (Nitrate and chloride were measured as N and Cl-, respectively). Experiment 4-3.

Comparing the performance of the resins in the presence of chloride demonstrates that both non-selective resins treated more water before reaching the MAC than the two nitrate-selective resins, which is similar to the results of the tests where nitrate had no competitor and was the only constituent of the feed water. It was also observed that Amberlite® IRA400 Cl had a considerably higher capacity for decreasing nitrate to less than the Ontario MAC (Figure 4-11, Table 4-9).

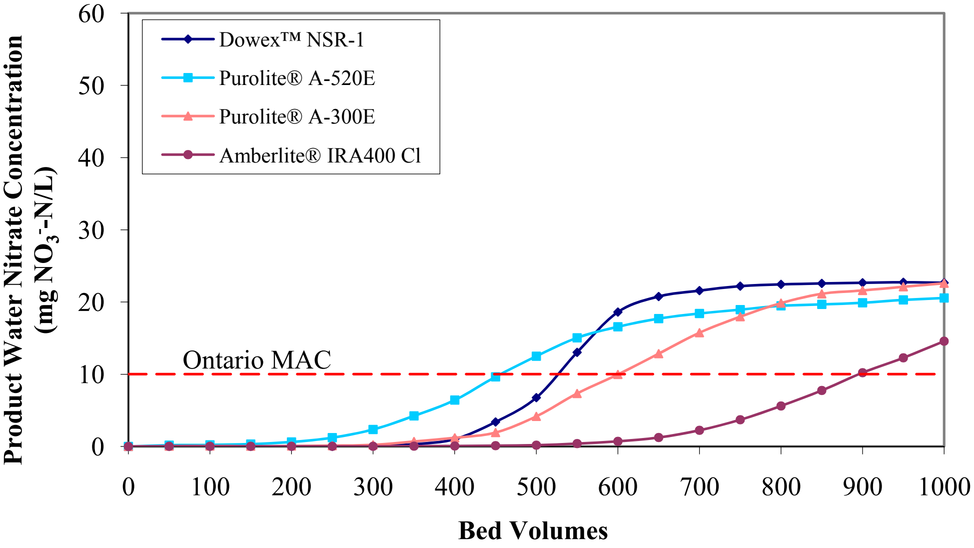

Figure 4-11: Comparison of different resins in the presence of chloride. Experiment 4-3.

Table 4-9: Capacity of the resins for maintaining nitrate concentrations less than the Ontario MAC (10 mg NO_3^--N/L) in the presence of chloride (in deionized water). Experiment 4-3.

Resin	**Resin capacity (BV)**
Dowex™ NSR-1*	525
Purolite® A-520E*	455
Purolite® A-300E	600
Amberlite® IRA400 Cl	895

* = nitrate selective resins

4.2.2.3 Effect of Alkalinity (experiment 4-4)

Regarding the affinity of SBA resins for adsorbing anions, bicarbonate (alkalinity) is the least well adsorbed amongst all the four anions investigated in this study. Therefore, it would be expected that nitrate removals shouldn't be adversely affected in the presence of alkalinity. To confirm this assumption, alkalinity (bicarbonate) was added to nitrate in the feed water and all the resins were studied under this condition. Operating conditions were the same as those of previous experiments and feed water conditions are listed in Table 4-4.

Table 4-10: Conditions for experiment 4-4.

Nitrate concentration **(mg NO_3^--N/L)**	**Alkalinity** **(mg/L as $CaCO_3$)**
23	246

Referring to Figure 4-12 for Purolite® A-520E, although alkalinity was adsorbed to the resin and exchanged for chloride at the beginning, its leakage started shortly afterwards. At 350 BV, alkalinity exceeded its original value for a short while showing the tendency of the resin to exchange nitrate for alkalinity. Performances of other resins at the presence of alkalinity are plotted in Figures C-16 – C-18 (Appendix C), and show that alkalinity affected all the resins similarly.

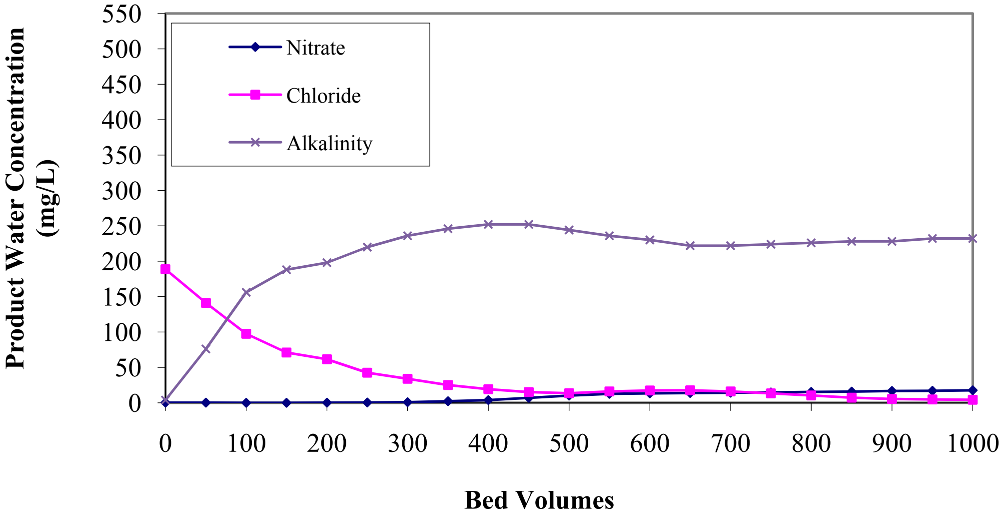

Figure 4-12: Breakthrough curve showing the effect of alkalinity on Purolite® A-520E. (Nitrate, chloride, and alkalinity were measured as N, Cl-, and CaCO3, respectively). Experiment 4-4.

A comparison of the results of all the resins in the presence of alkalinity is shown in Figure 4-13 and Table 4-11. Amberlite® IRA400 Cl removed nitrate for a longer period of time than the three other resins which is in concurrence with the results of experiments 4-1 and 4-3. Thus, it can be seen that the non-selective Amberlite® IRA400 Cl is the most appropriate choice for removing nitrate from deionized water that doesn't contain sulfate.

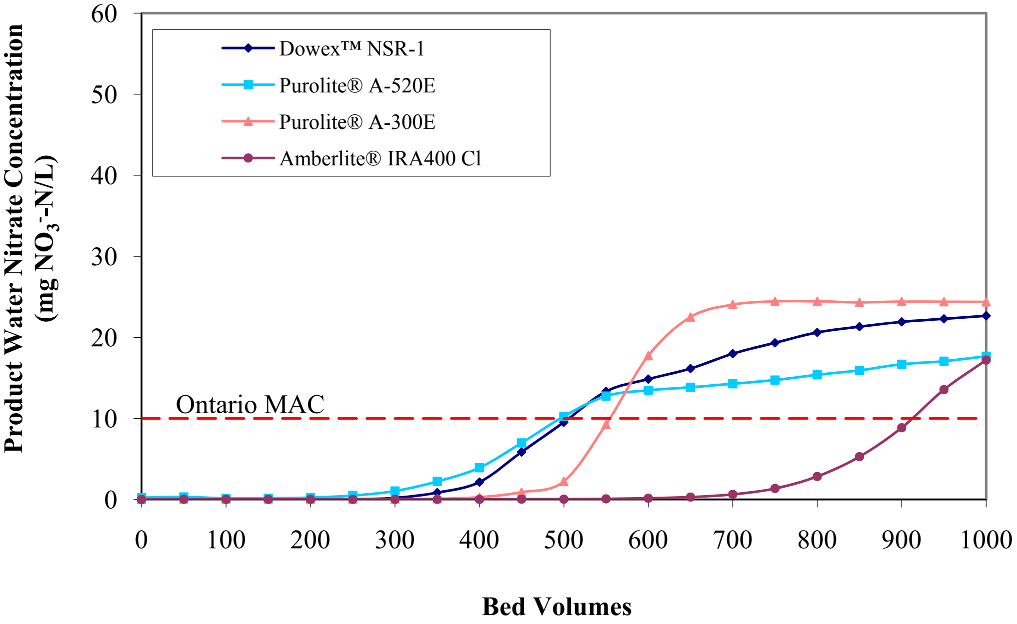

Figure 4-13: Comparison of different resins in the presence of alkalinity. Experiment 4-4.

Table 4-11: Capacity of the resins for maintaining nitrate concentrations less than the Ontario MAC (10 mg NO_3^--N/L) in the presence of alkalinity (in deionized water). Experiment 4-4.

Resin	**Resin capacity (BV)**
Dowex™ NSR-1*	505
Purolite® A-520E*	495
Purolite® A-300E	555
Amberlite® IRA400 Cl	915

* nitrate selective resins

4.2.2.4 Effect of Combination of Anions (experiment 4-5)

In the previous experiments the effect of each individual anion on the performance of the resins for nitrate removal was investigated. But in most real waters, all the anions occur in combination. To simulate the effect of multiple anions on performance of the resins, deionized water was spiked with all the anions as in Table 4-12.

Table 4-12: Conditions for experiment 4-5.

Nitrate concentration (mg NO_3^--N/L)	**Sulfate concentration (mg SO_4^{2-}/L)**	**Chloride concentration (mg Cl^-/L)**	**Alkalinity (mg $CaCO_3$/L)**
23	68	76	246

Breakthrough curves generated for experiment 4-5 on Purolite® A-520E are presented in Figure 4-14. As shown, both sulfate and nitrate were completely removed and alkalinity was partially removed at the start of the run. Sulfate started to breakthrough earlier than nitrate and its concentration exceeded its original feed concentration after 270 BV which shows that the resin started desorbing sulfate to adsorb nitrate. This was also concluded from the results of experiments 4-2 for Dowex™ NSR-1 and Purolite® A-520E where nitrate-selective resins encountered sulfate in the feed water. Similar results were seen in experiment 4-5 for Dowex™ NSR-1 in Figure C-19 (Appendix C).

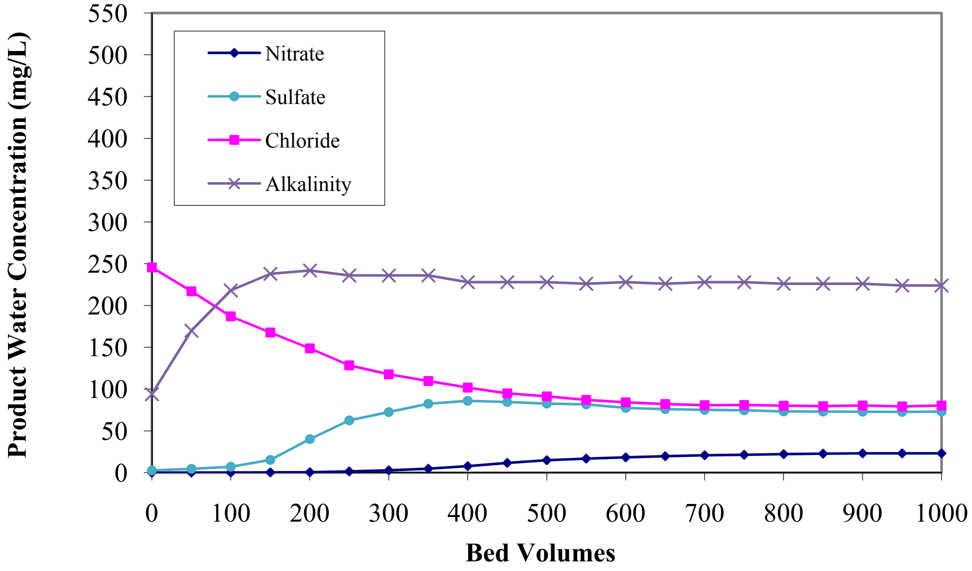

Figure 4-14: Breakthrough curve for effect of combination of the competing anions on Purolite® A-520E performance. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO42-, Cl-, and CaCO3, respectively). Experiment 4-5.

Figure 4-15 presents the results of experiment 4-5 for Purolite® A-300E. This resin is non-selective, and as discussed for experiment 4-2 for that resin, its performance in the presence of sulfate is opposite that of Dowex™ NSR-1 and Purolite® A-520E which are nitrate-selective.

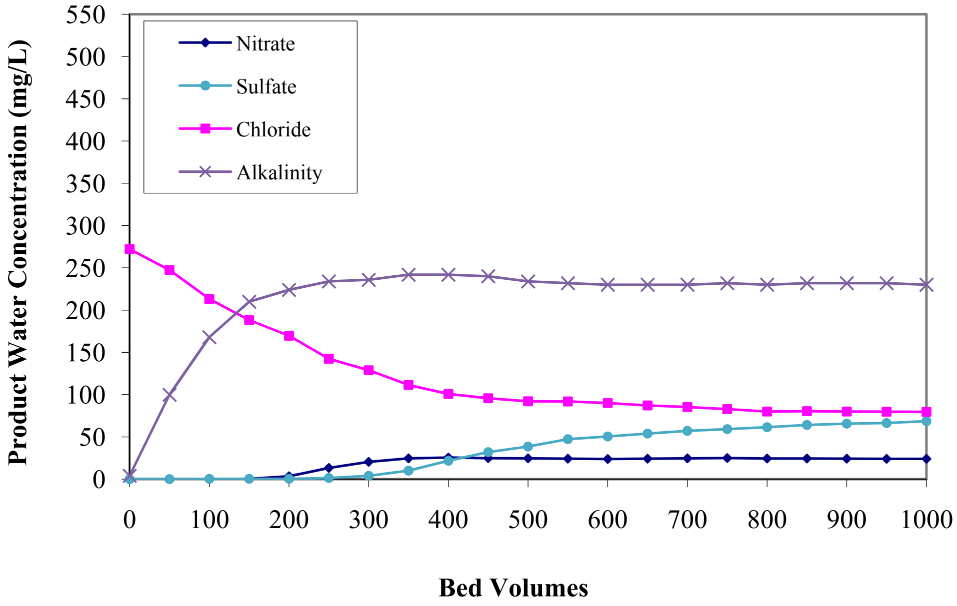

Figure 4-15: Breakthrough curve for effect of combination of the competing anions on Purolite® A-300E performance. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO42-, Cl-, and CaCO3, respectively. Experiment 4-5).

In this case, nitrate leakage occurred earlier than for sulfate. In addition, the concentration of nitrate exceeded its feed concentration since the resin started desorbing nitrate to adsorb more sulfate. Amberlite® IRA400 Cl had a similar performance under the same conditions based on its results in Figure C-20 (Appendix C).

Comparing nitrate breakthrough curves for all the resins in Figure 4-16 and their capacity for decreasing nitrate to less than the Ontario MAC (10 mg NO_3^--N/L) in Table 4-13 shows that in contrast to previous experiments, Amberlite® IRA400 Cl couldn't be designated as the resin with the highest capacity for nitrate removal. Moreover, Purolite® A-520E showed greater capacity than the other nitrate-selective resin (Dowex™ NSR-1) as it also did in experiment 4-2. So, it can be concluded that Purolite® A-520E performs better than Dowex™ NSR-1 in the presence of sulfate although the opposite is true for waters with no sulfate.

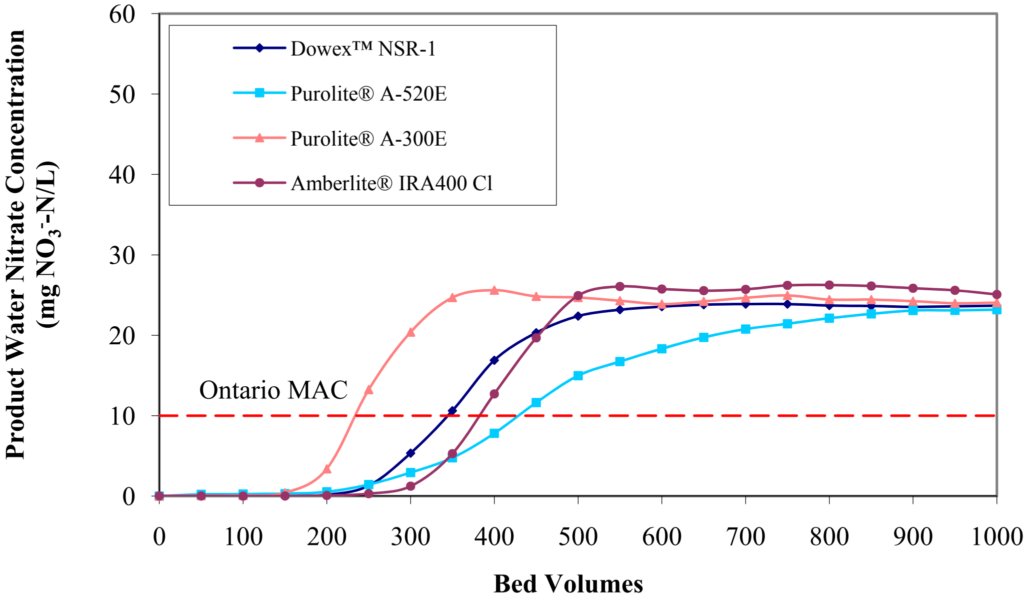

Figure 4-16: Comparison of different resins in the presence of all competing anions (in spiked DI water). Experiment 4-5.

Table 4-13: Capacity of the resins for maintaining nitrate concentrations less than the Ontario MAC (10 mg NO_3^--N/L) in the presence of all competing anions (in deionized water). Experiment 4-5.

Resin	**Resin capacity (BV)**
Dowex™ NSR-1*	345
Purolite® A-520E*	430
Purolite® A-300E	235
Amberlite® IRA400 Cl	380

* = nitrate selective resins

4.2.2.5 Comparison of performance of resins

To compare the performance of each resin at different feed water blends, breakthrough curves are plotted in Figures 4-17 to 4-20. Also, the capacities for decreasing nitrate to less than the Ontario MAC (10 mg NO_3^--N/L) are compared in Table 4-14. Regarding the results, each resin performed best when nitrate was not blended with other anions. So, all anions, even the weaker adsorbing ones, negatively impacted nitrate removal, while sulfate was the most important competitor, and the effect of chloride and alkalinity were almost identical. The poorest performance of each resin occurred when exposed to the feed water that contained all the competing anions. On the other hand, the capacity of nitrate-selective resins (Dowex™ NSR-1 and Purolite® A-520E) were not affected to the same extent as that of the non-selective ones. Especially, it can be seen that sulfate couldn't challenge Purolite® A-520E more than other anions did, and therefore this resin's performance was the best amongst the resins tested when faced with a blend of competing anions. It can also be concluded that although non-selective resins (Purolite® A-300E and Amberlite® IRA400 Cl), especially Amberlite® IRA400 Cl, performed extremely well in the absence of competing anions, they may not be reliable for removing nitrate from real waters that contain background anions. The reason is that they are highly affected by the presence of competing anions, and might start releasing previously adsorbed nitrate if a careful regeneration practice is not maintained. Overall, Purolite® A-520E appears to be the best alternative amongst the four resins for removing nitrate from highly concentrated waters (in deionized water). But, to validate this declaration for groundwater different tests were conducted and are presented in next sections.

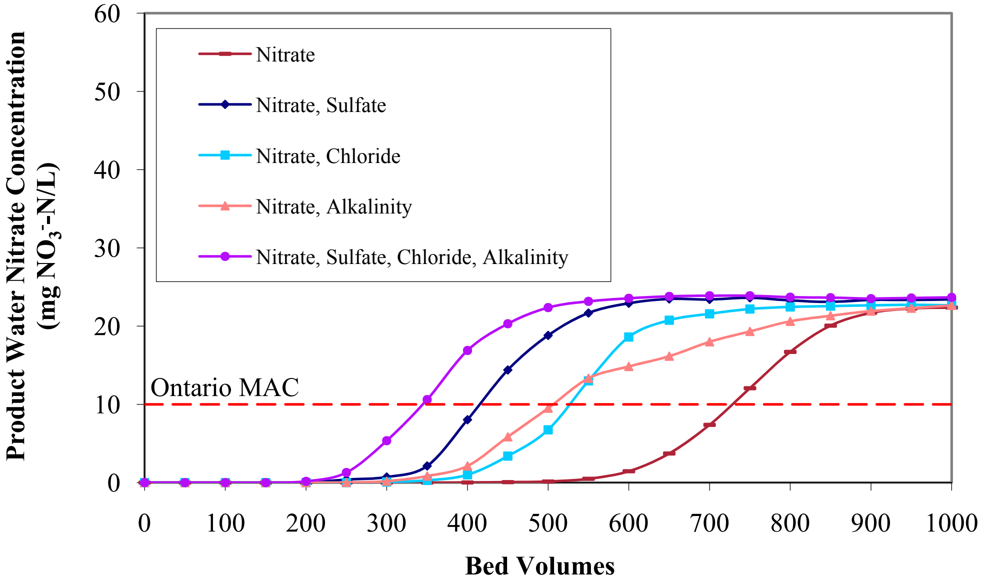

Figure 4-17: Comparison of the effect of competing anions on Dowex™ NSR-1 (nitrate-selective).

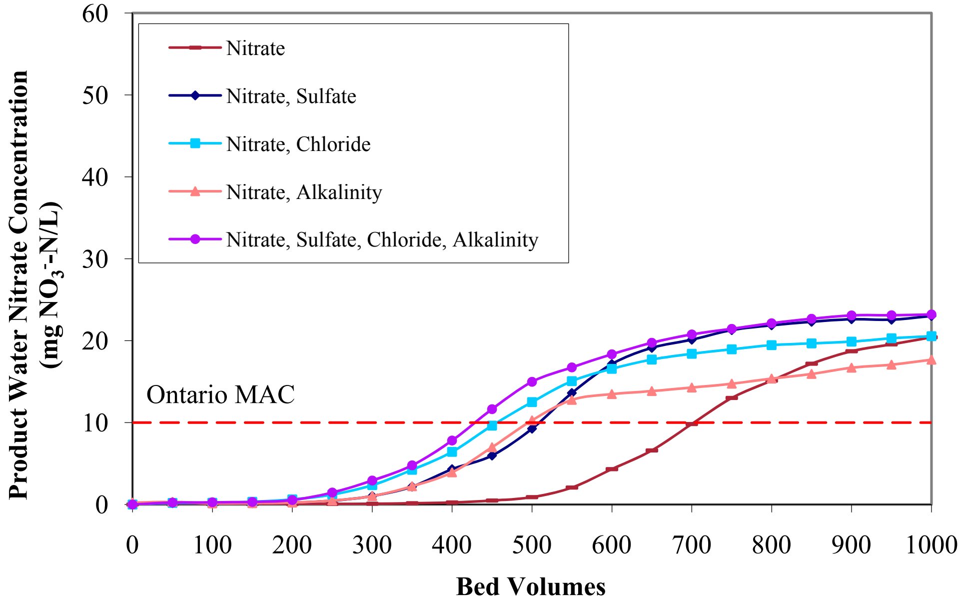

Figure 4-18:Comparison of the effect of competing anions on Purolite® A-520E (nitrate-selective).

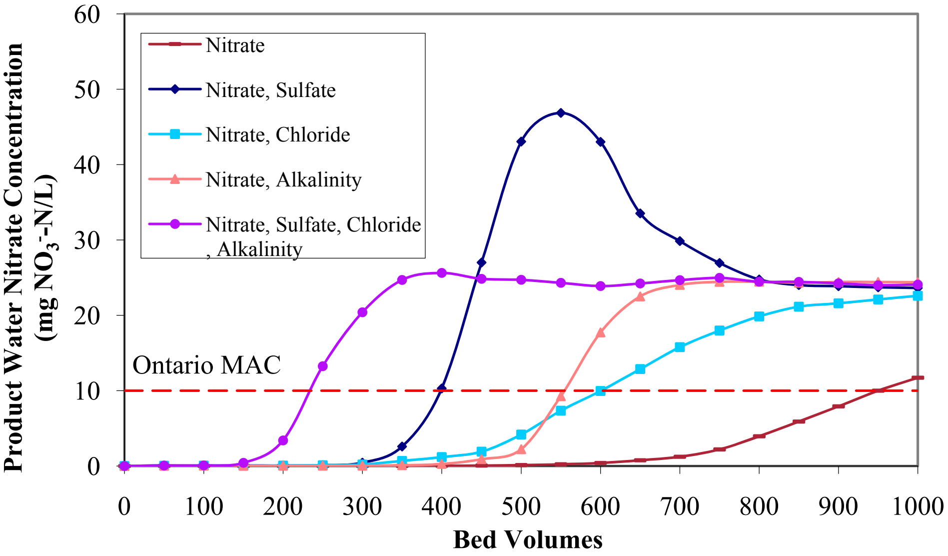

Figure 4-19: Comparison of the effect of competing anions on Purolite® A-300E (non-selective).

Figure 4-20 compares breakthrough curves of Amberlite® IRA400 Cl in the presence of different background anions.

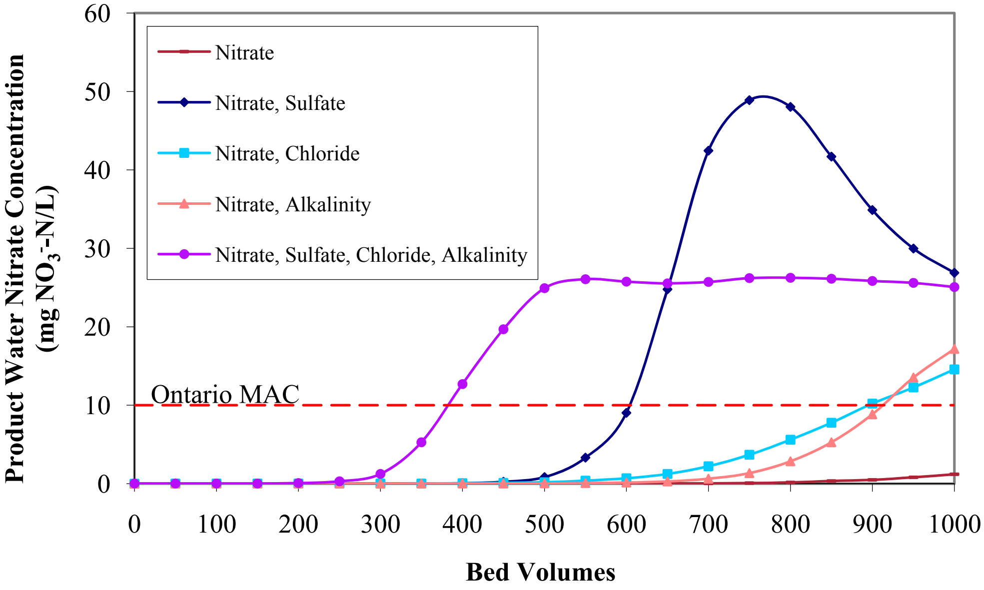

Figure 4-20: Comparison of the effect of competing anions on Amberlite® IRA400 Cl (non-selective).

Table 4-14: Capacity of the resins for maintaining nitrate concentrations less than the Ontario MAC (10 mg NO_3^--N/L) in the presence of different competing anions (in deionized water). (Feed water nitrate concentration = 23 mg NO_3^--N/L).

Resin / **Feed water**	**Dowex™ NSR-1**	**Purolite® A-520E**	**Purolite® A-300E**	**Amberlite® IRA400 Cl**
Nitrate	730	705	950	**>1000**
Nitrate + Sulfate	415	510	400	**605**
Nitrate + Chloride	525	455	600	**895**
Nitrate + Alkalinity	505	495	555	**915**
Nitrate + Sulfate + Chloride + Alkalinity	345	**430**	235	380

Note: best performing resin highlighted in bold

4.3 Experiments using Groundwater

This set of experiments was done to investigate the capacity of different resins and determine which is most suitable for nitrate removal from groundwater collected in the region. The characteristics of the two samples (GW1 and GW2) collected from different sources of groundwater are listed in table 4-15. All experiments were run with 100 mL of resin (bed depth of 0.1 m) at a hydraulic loading of 5.2 m/h (EBCT = 1.2 min).

Table 4-15: Groundwater characteristics.

Groundwater	**Experiment no.**	**Raw water (mg/L)***			
		Nitrate (as N)	**Sulfate (as SO_4^{2-})**	**Chloride (as Cl^-)**	**Alkalinity (as $CaCO_3$)**
GW1	4-6	6.58 ± 0.05	23 ± 1	60 ± 2	296 ± 2
GW2	4-7	6.70 ± 0.06	36 ± 1	73 ± 1	306 ± 2

* n=3

4.3.1 GW1 (experiment 4-6)

On March 26th, 2009 GW1 sample was collected from the Region of Waterloo, Ontario. This sample had nitrate concentrations in the 6.6 mg NO_3^--N/L range and elevated concentrations of competing anions (Table 4-15). The performance of Dowex™ NSR-1 and Purolite® A-520E for nitrate removal from this sample was investigated. Breakthrough curves are shown in Figures C-21 and C-22 (Appendix C).

From the previous experiments, it was concluded that Purolite® A-520E showed the best performance for removing nitrate from feed waters that contained a blend of other anions. Figure 4-21 compares nitrate removal from GW1 by Dowex™ NSR-1 and Purolite® A-520E and supports that conclusion. However, in this case the performance of the resins was less substantially different.

Since both resins were nitrate selective, adsorbed nitrate was not displaced by sulfate and remained at the influent level when the resin was exhausted. The initial nitrate concentration was 6.6 mg NO_3^--N/L which is below the MAC. Nitrate started breaking through at around 350 BV for both resins and Dowex™ NSR-1 became exhausted at 950 BV, while Purolite® A-520E wasn't exhausted within the time allotted for the test.

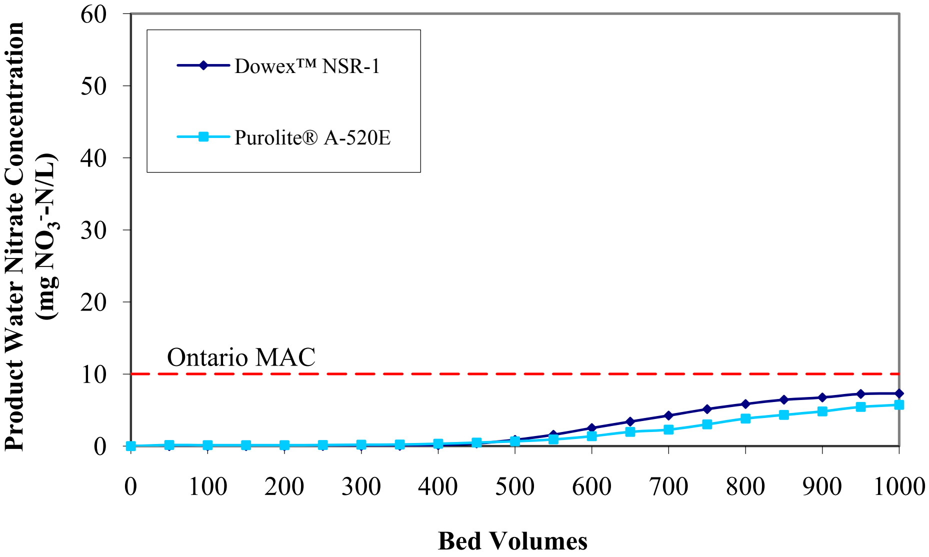

Figure 4-21: Nitrate removal from GW1 with nitrate selective resins.

4.3.2 GW2 (experiment 4-7)

Occasionally it was difficult to collect water from GW1. As a result, the GW2 source in the Region of Waterloo was chosen for the remaining IX experiments (Table 4-15). The nitrate concentrations in these two sources were quite similar and the concentrations of other anions in GW2 were also elevated. On April 9th, 2009 a 400L sample was collected. Performance of all four resins for nitrate removal from this groundwater were investigated in experiment 4-7.

Breakthrough curves of these experiments are shown in Figures C-23 – C26 (Appendix C), and Figure 4-22 compares them with each other. The nitrate-selective resins (Dowex™ NSR-1 and Purolite® A-520E) performed similarly to what was observed in experiment 4-6, and Purolite® A-520E had more capacity for nitrate removal. Purolite® A-300E appears to perform similarly to Purolite® A-520E in this range. But, since this resin is non-selective, at some point it is likely to break through the 10 mg NO_3^--N/L MAC level while the Purolite® A-520E cannot. The reason is that, when a nitrate selective resin becomes totally exhausted, the nitrate concentration in its product water reaches the nitrate concentration in the feed water (6.7 mg NO_3^--N/L in this experiment) but does not exceed it. On the other hand, non-selective resins desorb some previously adsorbed nitrate to adsorb other anions prior to their total exhaustion and therefore, nitrate concentration in product water might exceed its original value (6.7 mg NO_3^--N/L in this experiment) or increase to even higher levels. If the capacity of the Purolite® A-300E was noticeably greater than the capacity of Purolite® A-520E, and maintaining a robust regeneration process was achievable, it could be chosen as the best alternative resin. But, the capacities of these two resins were quite similar, and thus, among the four resins examined, Purolite® A-520E was the most promising for removing nitrate from the groundwater tested.

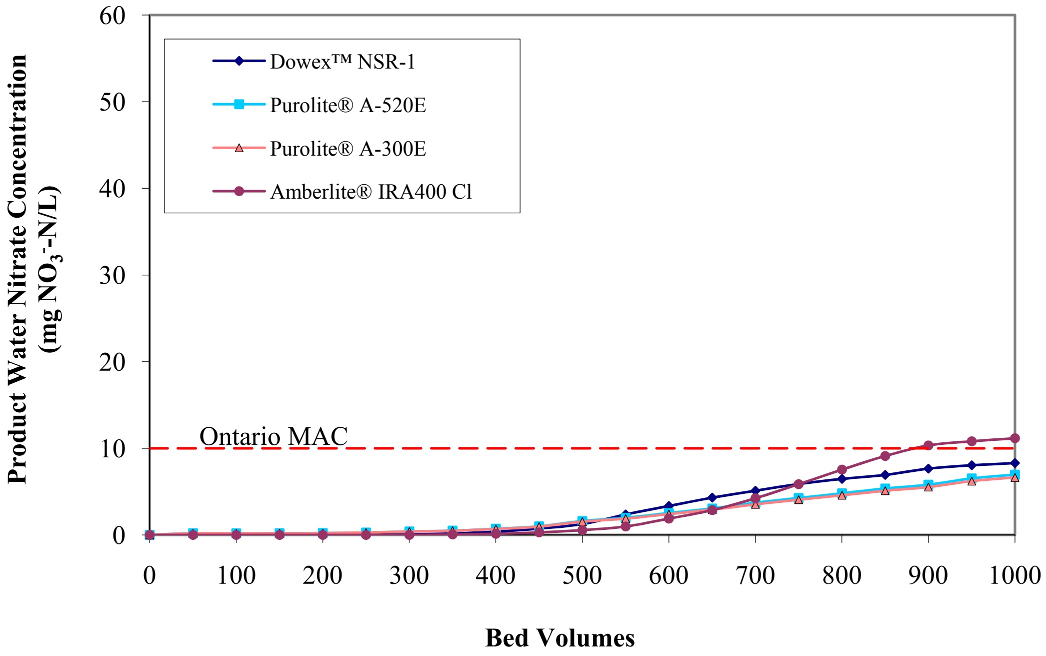

Figure 4-22: Comparison of different resins for the removal of nitrate from GW2.

Figure 4-23 presents the breakthrough curve in GW2 using Purolite® A-520E and the concentrations of all target anions and alkalinity in the product water. Trends of breakthrough curves for each ion are similar to what observed in experiment 4-5 for Purolite® A-520E (Figure 4-14). Sulfate exceeded its initial value at 500 BV and returned to it at 850 BV. Alkalinity increased through the first 250 BV and remained relatively stable after that, while nitrate and chloride met their initial concentrations at the end of the run. Regarding the Ontario Ministry of the Environment Guidelines (Ontario Ministry of the Environment, 2006), none of the concentrations exceeded the drinking water standards, aesthetic objectives (AO), or operational guidelines (OG) even when they exceeded their feed water value. The data supports the selection of Purolite-A520E as an appropriate and promising resin for removing nitrate from the groundwater tested.

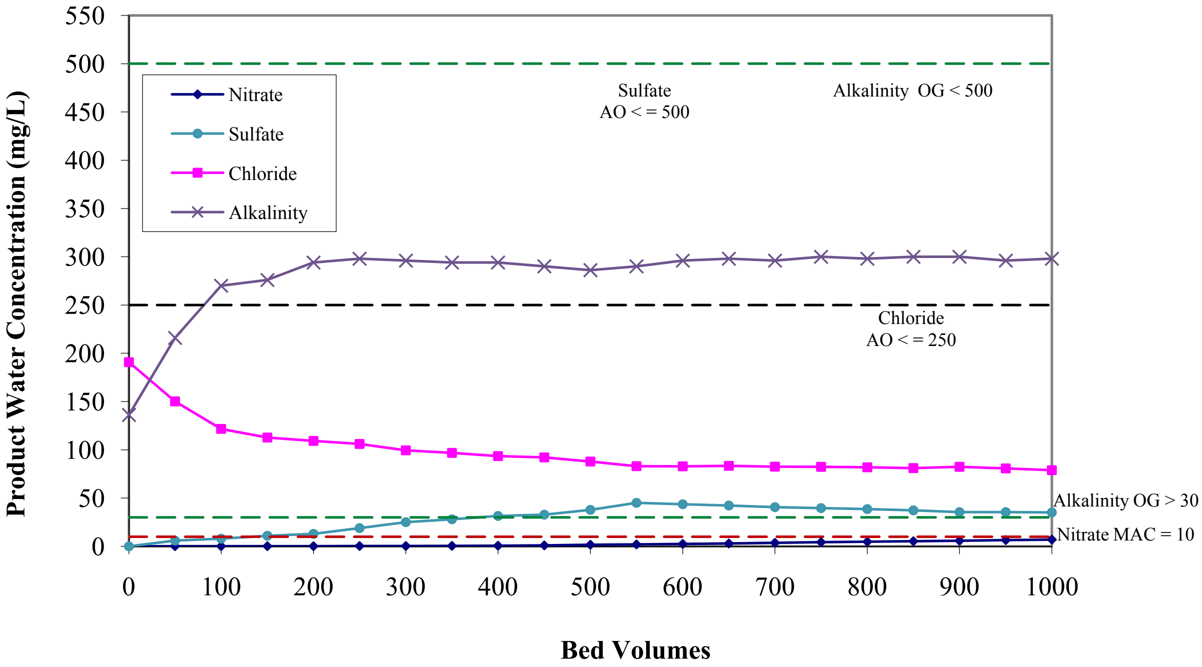

Figure 4-23: Breakthrough curve for GW2 using Purolite® A-520E. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO42-, Cl-, and CaCO3, respectively). Experiment 4-7.

4.4 Summary of Results

The performance of four ion exchange resins for nitrate removal was investigated and compared under different operating and feed water anion concentrations. To evaluate the efficiency of this technology for nitrate removal, several groups of tests were performed using deionized water spiked with nitrate and other competing anions as well as untreated groundwater from GW1 and GW2 in the Region of Waterloo. The concentrations of anions for spiking DI water were chosen to simulate the groundwater of the Region of Waterloo based on historical highest observed concentrations. Performance of nitrate-selective resins and their benefits were investigated and compared to non-selective resins to fill gaps in the literature. Chapter 6 of this thesis provides additional, more detailed interpretation of the results of the IX experiments and those of the RO experiments discussed in Chapter 5. The following conclusions were drawn from the results of the experiments:

- Each of the investigated resins can exchange nitrate for chloride prior to their exhaustion.
- Not unexpectedly, decreasing contact time by decreasing bed depth or increasing hydraulic loading decreases the capacity of the resin. Bed depth has a more important impact, while hydraulic loading is not of great importance at loadings tested (5.2 and 10.4 m/h).
- All anions, even the ones that are less well adsorbed than nitrate, can reduce the capacity of both non-selective and nitrate-selective resins for nitrate removal. Among the anions studied, sulfate had the most negative impact, while the effect of chloride and alkalinity were almost identical. Resin performance was most dramatically affected when exposed to feed waters containing all the competing anions.
- In the absence of competing anions, non-selective resins performed better than nitrate-selective resins for nitrate removal.
- A potential drawback to using non-selective resins in the presence of competing anions is that they start exchanging sulfate for nitrate as the resin becomes exhausted which then allows some adsorbed nitrate to desorb, increasing product water nitrate concentration. They therefore present a risk if good regeneration practice is not maintained.
- The behavior of nitrate-selective resins in the presence of competing anions is opposite to that of the non-selective resins. They desorb sulfate to adsorb more nitrate.
- Of the nitrate selective resins, Purolite® A-520E performs better than Dowex™ NSR-1 in the presence of sulfate, and is the best alternative amongst the four resins for removing nitrate from highly concentrated waters.
- For removing nitrate from the groundwater tested in the region of Waterloo, performance of both nitrate-selective resins were good, with Purolite® A-520E being more likely to maintain optimum nitrate removal capacity. Although Purolite® A-300E performance was promising, experiments with deionized water showed that

under conditions of high anion composition nitrate could be released in high concentrations.

Chapter 5

Conditions Affecting Performance of a Commercially- Available Reverse Osmosis Point-of-Use Device

5.1 Introduction

A Culligan® Aqua-Cleer® (model RO30) reverse osmosis (RO) drinking water system (certified to NSF Standard 58) was selected to compare with ion exchange for nitrate removal. The unit consisted of a particle filter, a carbon block filter, and a reverse osmosis membrane. The manufacturer describes the carbon block filter as being able to reduce taste and odor of chlorine as well as other elements that may cause unpleasant taste and smell in water. The particle filter is for removing sand, rust, and dirt from the feed water. The carbon block and particle filters help to control fouling and scaling of the RO membrane.

Several experiments were conducted to investigate the performance of the RO unit under different conditions for nitrate removal. These experiments can be categorized in eight main groups that are listed in Table 5-1. The first seven groups were performed using deionized (DI) water spiked with nitrate and other competing anions, and the final one used groundwater from the Region of Waterloo, Ontario. Target anions included nitrate, sulfate, chloride, and alkalinity. Concentrations of sulfate and chloride used in the experiments were 68 and 76 mg/L, respectively. Alkalinity varied between 0-246 mg/L as $CaCO_3$ in different experiments. Finally 5, 10, and 23 mg NO_3^--N/L were chosen as nitrate concentrations for different tests. These concentrations are generally higher than what has been observed in groundwater in the Region of Waterloo, and were chosen to simulate a groundwater with high concentrations of nitrate and other anions. For each experiment, one sample was collected from the RO feed water except in the case of groundwater where feed water was sampled three times. Three samples were collected from product (permeate) and reject (concentrate) water at elapsed times of 15, 20, and 25 minutes, but in some cases they were sampled only twice at 20 and 25 minutes. Product water is the treated water and reject water is the concentrated solution containing substances that do not pass through the membrane (Symons et al., 2001). Concentrations of the target ions of all samples were measured as well as conductivity, temperature, and flow. pH and total dissolved solids (TDS) were measured for some samples. Detailed conditions of each of the eight set of tests are summarized in Table 5-1 and Appendix D.

Table 5-1: Conditions for reverse osmosis experiments.

Experiment no.	**Investigation**	**Feed water**	**Pressure (psi)**	**Treatment**
5-1	Effect of operating conditions (pressure, pre-filters)	DI spiked with nitrate	40, 60	RO with and without carbon block and particle filter
5-2	Sampling time	DI spiked with nitrate	50	RO + carbon block + particle filter
5-3-1	Effect of feed water nitrate concentration with different pre-treatments	DI spiked with different concentrations of nitrate	40, 50	RO + particle filter with and without carbon block
5-3-2	Effect of background ions with different pre-treatments	DI spiked with nitrate alone and nitrate in combination with sulfate, chloride, alkalinity, or all	40, 50	RO + particle filter with and without carbon block
5-4-1	Effect of carbon block in presence and absence of alkalinity	DI spiked with nitrate alone and nitrate in combination with alkalinity	50	RO + particle filter with and without carbon block
5-4-2	Effect of carbon block at different alkalinities	DI spiked with nitrate and alkalinity in combination with sulfate or chloride.	50	RO + particle filter with and without carbon block
5-4-3	Effect of carbon block at different alkalinities	DI spiked with nitrate and alkalinity in combination with sulfate and chloride.	50	RO + particle filter without carbon block
5-5	Performance of the unit with different treatment combinations on groundwater	GW2	50	All possible combinations of RO, carbon block, and particle filter

Note: 40 psi = 276 kPa, 50 psi = 344 kPa, 60 psi = 413 kPa

5.2 Experiments using Spiked Deionized Water

5.2.1 Investigation of Operating Conditions (pressure and pre-filters)

This set of experiments was conducted to study the effect of pressure and pre-treatment methods. In all these experiments DI water spiked with 23 mg NO_3^--N/L was used as feed water.

Pressures of 40 and 60 psi were chosen for investigation as 40 psi is the minimum pressure recommended by the unit manufacturer and 60 psi is the maximum that could be pumped by the pump used. However, according to NSF International, RO system tests should be conducted at 50 psi (NSF/ANSI Standard 58, 2007), and this pressure was used for the remaining experiments.

As discussed in Chapter 3, the components of the RO drinking water system included a particle filter, a carbon block filter, and a reverse osmosis membrane all of which are intended for use in series but individual components can be tested in isolation. To examine the effect of filters and the RO membrane, experiment 5-1 was done using the RO membrane alone or preceded by a particle filter and/or a carbon block filter. Feed water used for these experiments was DI water spiked with 23 mg NO_3^--N/L.

Figure 5-1, Table 5-2, and Tables D-1 - D-2 (Appendix D) summarize data from experiment 5-1. Nitrate removals were calculated as explained in Chapter 3, and each of them is the average of the removal for three individual samples. The confidence intervals for all the data in this chapter were calculated based on a t-distribution method with a confidence level of 95%.

Changing the feed water pressure from 40 to 60 psi didn’t have a significant impact on the performance of the unit, but using a carbon block filter as a pre-treatment to RO unit increased the removal of nitrate. This finding was unexpected and was further investigated in detail with different feed water blends using RO with and without a carbon block. Results are discussed in upcoming sections.

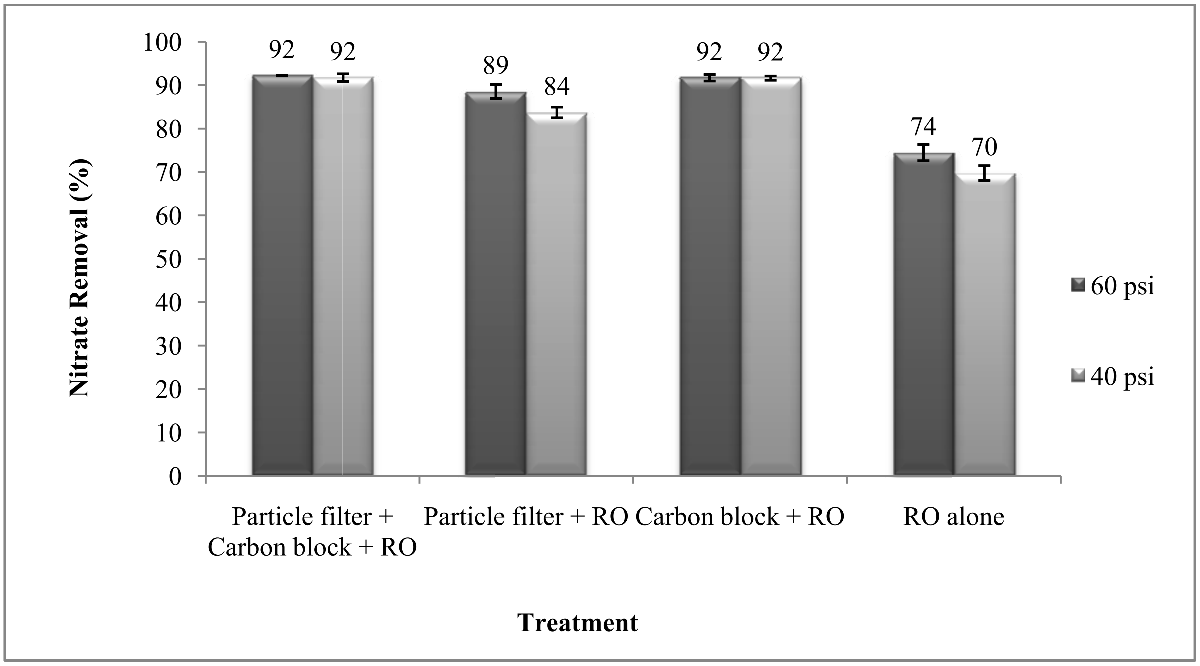

Figure 5-1: Nitrate removal using RO with and without a particle filter and carbon block at 40 and 60 psi. Feed water: DI water spiked with 23 mg NO_3^--N/L. Experiment 5-1.

Table 5-2: Nitrate removal summary for experiment 5-1.

Pressure (psi)	Treatment	Nitrate removal (%)	Confidence interval (%)	Nitrate removal range (%)
60	Particle filter + Carbon Block + RO	92	0.1	92-92
40	Particle filter + Carbon Block + RO	92	0.9	91-93
60	Particle filter + RO	89	1.6	87-91
40	Particle filter + RO	84	1.2	83-85
60	Carbon block + RO	92	0.7	91-93
40	Carbon block + RO	92	0.5	92-92
60	RO alone	74	1.9	72-76
40	RO alone	70	1.7	68-72

5.2.2 Recovery of the Drinking Water System

As explained in Chapter 2, recovery of an RO system is the fraction of the feed water that is converted to product water (Symons et al., 2001).

Table 5-3 represents the feed and product water flows and the calculated recovery for experiment 5-1. Based on the results, average recovery of the system for experiments conducted at 60 psi was 31.5%, while it was 28.5% at 40 psi. It can be concluded that, in the pressure range tested, recovery slightly increased by increasing the pressure. The overall average of the recovery was 30% which is the same as the average value observed in future experiments conducted at 50 psi (Table D-3, Appendix D).

Table 5-3: Recovery of the system for experiment 5-1.

Pressure (psi)	**Treatment**	**Feed water flow (mL/min)**	**Product water flow (mL/min)**	**Recovery (%)**
60	Particle filter + Carbon Block + RO	355	112	32
60	Carbon block + RO	350	110	31
60	Particle filter + RO	350	110	31
60	RO alone	355	114	32
40	Particle filter + Carbon Block + RO	270	75	28
40	Carbon block + RO	270	76	28
40	Particle filter + RO	270	77	29
40	RO alone	275	80	29

5.2.3 Optimization of Sampling Time

The RO manufacturer suggested maintaining the pressure and discarding the product water for approximately 10-15 minutes prior to taking samples. This is consistent with NSF Standard 58 (NSF/ANSI, 2007). To find a reliable time to initiate sampling, experiment 5-2 was conducted and samples from product and reject water were taken at different elapsed times. Feed water used for this experiment was DI water spiked with 23 mg NO_3^--N/L, and all tests were conducted at 50 psi. The particle filter and carbon block both preceded the RO in this set.

Based on the results shown in Figures 5-2 and 5-3, the system stabilized after 15 minutes. Therefore, sampling times were chosen to be 15, 20, and 25 minutes for all the tests. A similar test was conducted on GW2 and results (Figures D-1 and D-2, Appendix D) concurred with each other.

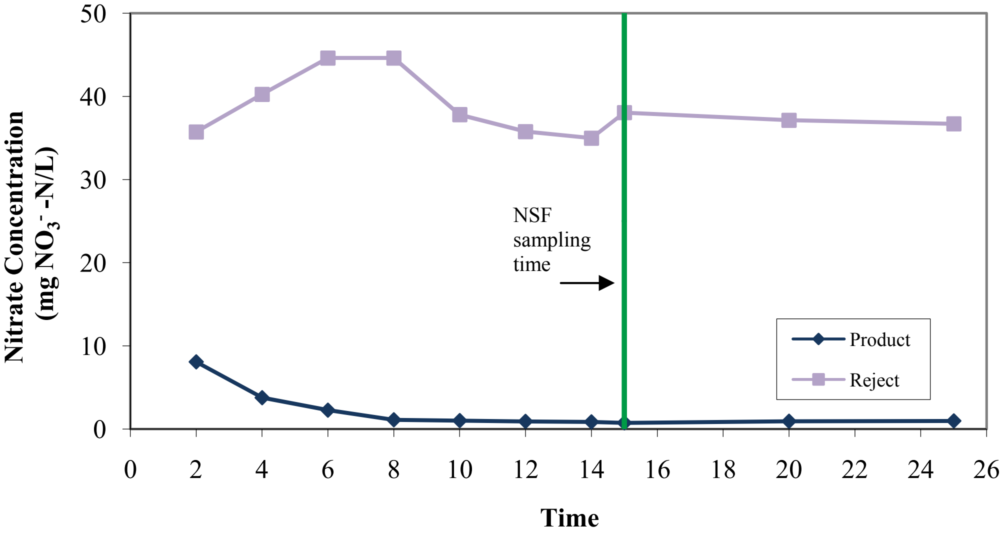

Figure 5-2: Nitrate concentration in product and reject water over time. Treatment: RO preceded by carbon block and particle filter at 50 psi. Feed water: DI water spiked with 23 mg NO_3^--N/L. Experiment 5-2.

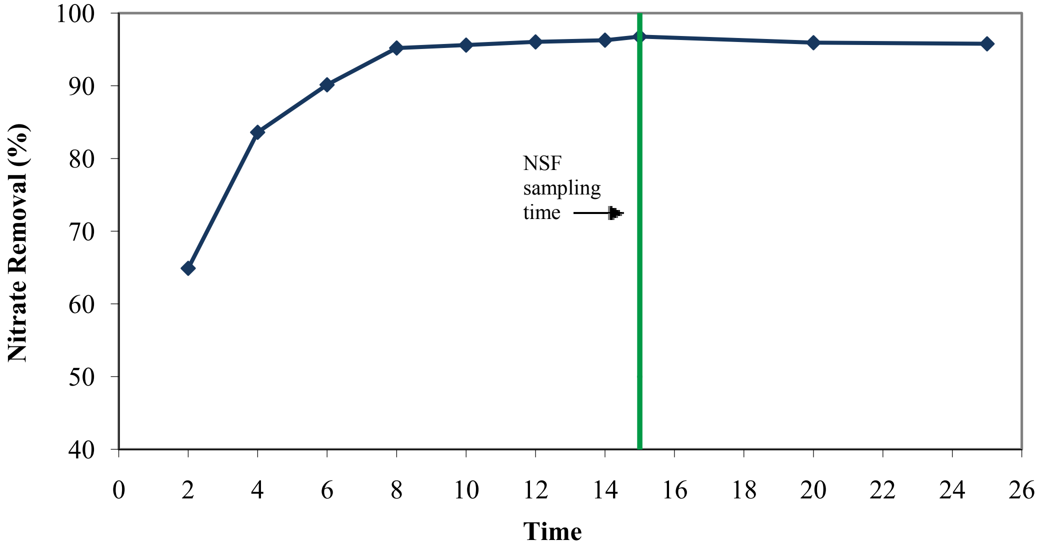

Figure 5-3: Nitrate removal over time. Treatment: RO preceded by carbon block and particle filter at 50 psi. Feed water: DI water spiked with 23 mg NO_3^--N/L. Experiment 5-2.

5.2.4 The Effect of Feed Water Blend under Different Operating Conditions

To investigate the effect of feed water blend on the performance of the RO unit for nitrate removal, two sets of experiments were conducted. The first set (5-3-1) examined the effect of different concentrations of nitrate while set 5-3-2 studied impact of having other background anions in the feed water.

5.2.4.1 Investigating the Effect of Feed Water Nitrate Concentration

Deionized water with nitrate concentrations of 5, 10, and 23 mg NO_3^--N/L were chosen for this set of experiments. To see the effect of the feed water under different operating conditions tests were conducted at 40 and 50 psi. At 40 psi both the particle filter and carbon block preceded the RO membrane as pre-filters. The test was also repeated at 50 psi without using the carbon block (Tables D-4 and D-5, Appendix D).

Figure 5-4 shows that removal efficiencies appear to be slightly higher at higher concentrations of feed water nitrate when the carbon block was used, but according to the confidence intervals in Table 5-4 the increase is not statistically significant. However, in the case where the carbon block was not used as a pre-filter, nitrate removal efficiency was significantly impaired. Also, in this case percent nitrate removal was positively correlated to increase in the nitrate concentration in feed water. In addition the results don’t show a significant change in removal by a 10 psi change in pressure which reinforces the results of experiment 5-1. It can also be concluded that the carbon block can considerably boost the unit performance for nitrate removal under the conditions investigated. This outcome was similar to that observed previously (Figure 5-1), and will be discussed further in the next sections.

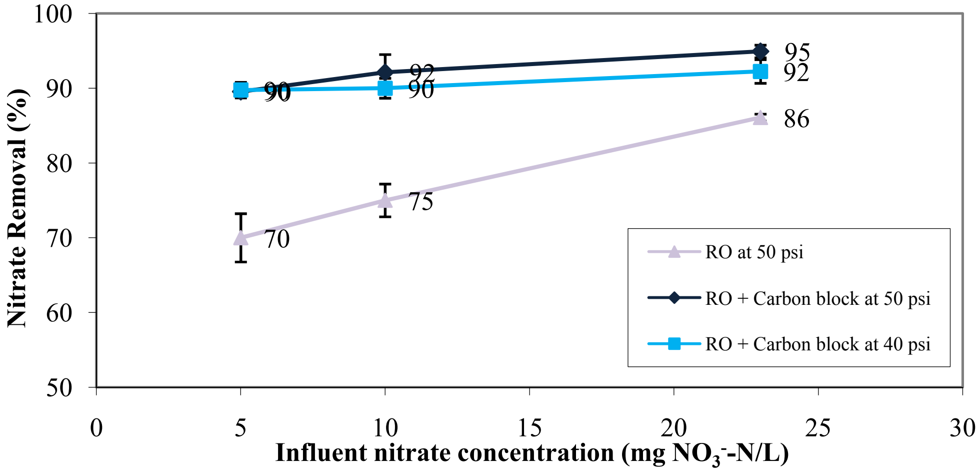

Figure 5-4: Nitrate removal from deionized water with different nitrate concentrations at 40 and 50 psi. Treatment: RO alone and RO preceded by carbon block. Experiment 5-3-1.

Table 5-4: Nitrate removal summary for experiment 5-3-1.*

Feed water nitrate concentration (mg NO_3^--N/L)	**Treatment**	**Nitrate removal (%)**	**Confidence interval (%)**	**Nitrate removal range (%)**
5	RO at 50 psi	70	3.2	67-73
10	RO at 50 psi	75	2.2	73-77
23	RO at 50 psi	86	0.5	86-86
5	RO + Carbon block at 50 psi	90	0.2	90-90
10	RO + Carbon block at 50 psi	92	2.4	90-94
23	RO + Carbon block at 50 psi	95	0.8	94-96
5	RO + Carbon block at 40 psi	90	1.0	89-91
10	RO + Carbon block at 40 psi	90	1.3	89-91
23	RO + Carbon block at 40 psi	92	1.6	90-94

* = All experiments conducted using nitrate-spiked deionized water.

5.2.4.2 Investigating the Effect of Competing Anions

Experiment 5-3-2 compares the effect of competing anions on the performance of the unit for removing nitrate. To study this effect under different operating conditions tests were conducted at 40 and 50 psi. At 40 psi both the particle filter and carbon block preceded the RO membrane, but tests were also done without using the carbon block at 50 psi. Feed waters for these tests were DI water spiked with nitrate (23 mg NO_3^--N/L) alone, and nitrate blended individually with sulfate (68 mg/L as SO_4^{2-}), chloride (76 mg/L as Cl^-), alkalinity (246 mg/L as $CaCO_3$), or a combination of all these anions (Tables D-6 – D-8, Appendix D).

Results (Figure 5-5 and Table 5-5) show that as expected, based on previous results, changing the pressure in this range doesn't affect the removal efficiency of the unit. Background ions don't appear to compete with each other for being removed by the unit.

It can also be observed that without using the carbon block, nitrate removal drops considerably in experiments without feed water alkalinity, while this effect is not observed for alkalinity blended feed waters. This drop is greater when nitrate is combined with sulfate or chloride in the feed water (Figure 5-5 and Table 5-5). Referring back to the results of experiment 5-1 and 5-3-1, it was shown that using the carbon block as a pre-treatment could increase the performance of the unit for nitrate removal. Feed water for those experiments was a blend of DI water and nitrate alone. These results are in agreement with each other and back up earlier observations that the carbon block can affect the system performance at no, or low alkalinity.

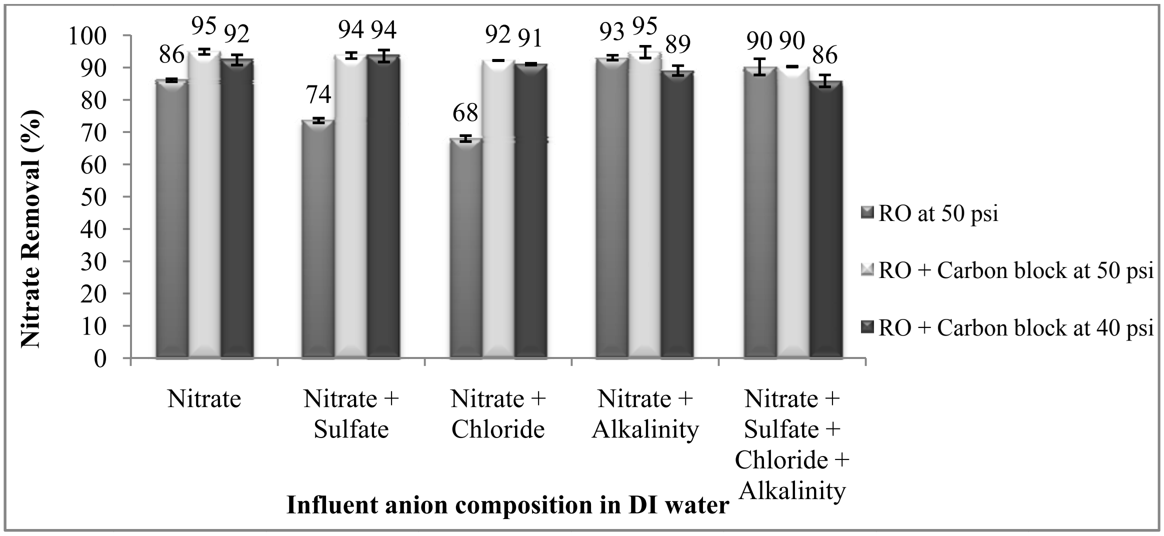

Figure 5-5: Nitrate removal from feed waters of different composition at 40 and 50 psi. Treatment: RO alone and RO preceded by carbon block. Concentration of nitrate, sulfate, chloride, and alkalinity: 23 (mg NO_3^--N/L), 68 (as SO_4^{2-}), 76 (as Cl^-), 246 (as $CaCO_3$) mg/L, respectively. Experiment 5-3-2.

Table 5-5: Nitrate removal for experiment 5-3-2 (in spiked deionized water).

Feed water anion composition in DI water	**Treatment**	**Nitrate removal (%)**	**Confidence interval (%)**	**Nitrate removal range (%)**
Nitrate	RO at 50 psi	86	0.46	86-86
Nitrate + Sulfate	RO at 50 psi	74	0.72	73-75
Nitrate + Chloride	RO at 50 psi	68	0.92	67-69
Nitrate + Alkalinity	RO at 50 psi	93	0.77	92-94
Nitrate + Sulfate + Chloride + Alkalinity	RO at 50 psi	90	2.52	88-92
Nitrate	RO + Carbon block at 50 psi	95	0.84	94-96
Nitrate + Sulfate	RO + Carbon block at 50 psi	94	0.95	93-95
Nitrate + Chloride	RO + Carbon block at 50 psi	92	0.01	92-92
Nitrate + Alkalinity	RO + Carbon block at 50 psi	95	1.81	93-97
Nitrate + Sulfate + Chloride + Alkalinity	RO + Carbon block at 50 psi	90	0.12	90-90
Nitrate	RO + Carbon block at 40 psi	92	1.58	90-94
Nitrate + Sulfate	RO + Carbon block at 40 psi	94	1.86	92-96
Nitrate + Chloride	RO + Carbon block at 40 psi	91	0.27	91-91
Nitrate + Alkalinity	RO + Carbon block at 40 psi	89	1.53	87-91
Nitrate + Sulfate + Chloride + Alkalinity	RO + Carbon block at 40 psi	86	1.85	84-88

5.2.5 Investigating the Effect of Using a Carbon Block in Combination with RO under Conditions of Varying Alkalinity

As mentioned previously, no alkalinity or low alkalinity decreased nitrate removal when the carbon block filter was not used. To investigate this observation, experiment 5-4-1 examined the change in nitrate removal by changing the alkalinity in feed water while using RO with and without the carbon block filter. A particle filter was used as a pre-filter in all these experiments and all were performed at 50 psi. Feed water used for these experiments was DI water spiked with 23 mg NO_3^--N/L at alkalinities in the range of 0-246 mg/L (as $CaCO_3$) (Tables D-9 and D-10, Appendix D).

Results shown in Figure 5-6 confirm that using RO without the carbon block can decrease nitrate removal of feed waters with low alkalinities.

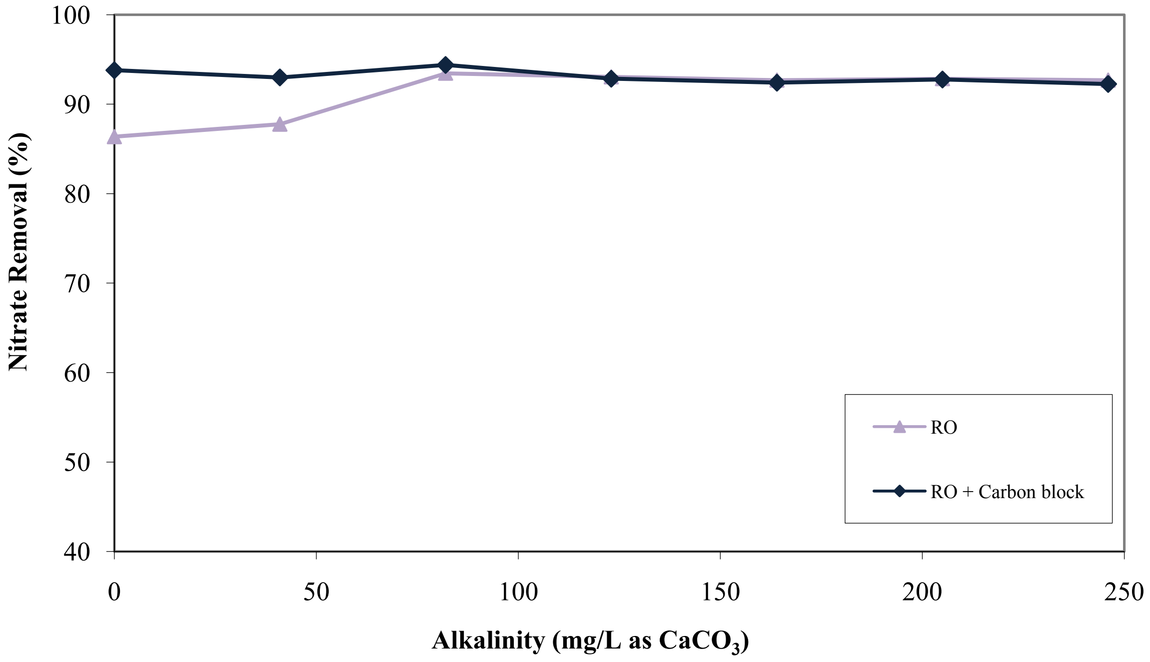

Figure 5-6: RO vs. carbon block + RO for nitrate removal at selected alkalinities. Feed water was DI water spiked with 23 mg NO_3^--N/L and different alkalinities. Experiment 5-4-1.

To determine if pH was somehow responsible for this phenomenon, product water pH was plotted versus feed water alkalinity concentration for both cases of using RO with and without carbon block as a pre-filter (Figure 5-7). As can be seen the carbon block can decrease the product water pH. The reason might be the active material in the filter which is described as being acid washed activated carbon by the producer. As explained in Chapter 2, reducing pH is a way to control scaling of the RO membrane. This graph was plotted for experiment 5-4-2 and the results concur (Figures D-3, Appendix D).

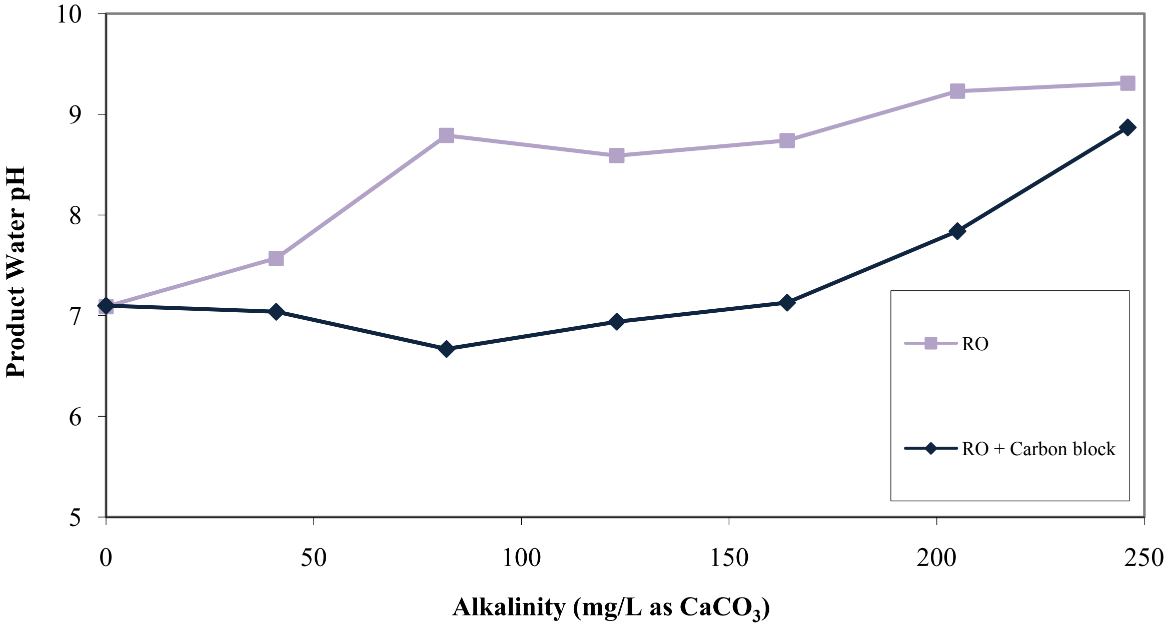

Figure 5-7: Comparison of product water pH using RO and RO + carbon block. Feed water was DI water spiked with 23 mg NO_3^--N/L and different alkalinities.

To more accurately determine the lower limit (critical) alkalinity concentration, experiment 5-4-2 was conducted with feed waters of DI water spiked with 23 mg NO_3^--N/L combined with sulfate (68 mg/L as SO_4^{2-}) or chloride (76 mg/L Cl^-) and alkalinity concentrations lower than 82 mg/L as $CaCO_3$. All tests were done at 50 psi (Tables D-11 - D-13, Appendix D).

As can be seen in Figure 5-8, nitrate removal is substantially impaired using RO without a carbon block when alkalinity is less than 41 mg/L (as $CaCO_3$), and this drop is more dramatic when the feed water is blended with sulfate or chloride. It should be noted that the horizontal scale of Figure 5-8 has been compressed from that in Figure 5-6 to assist with the interpretation of data in this Figure and Figure 5-9.

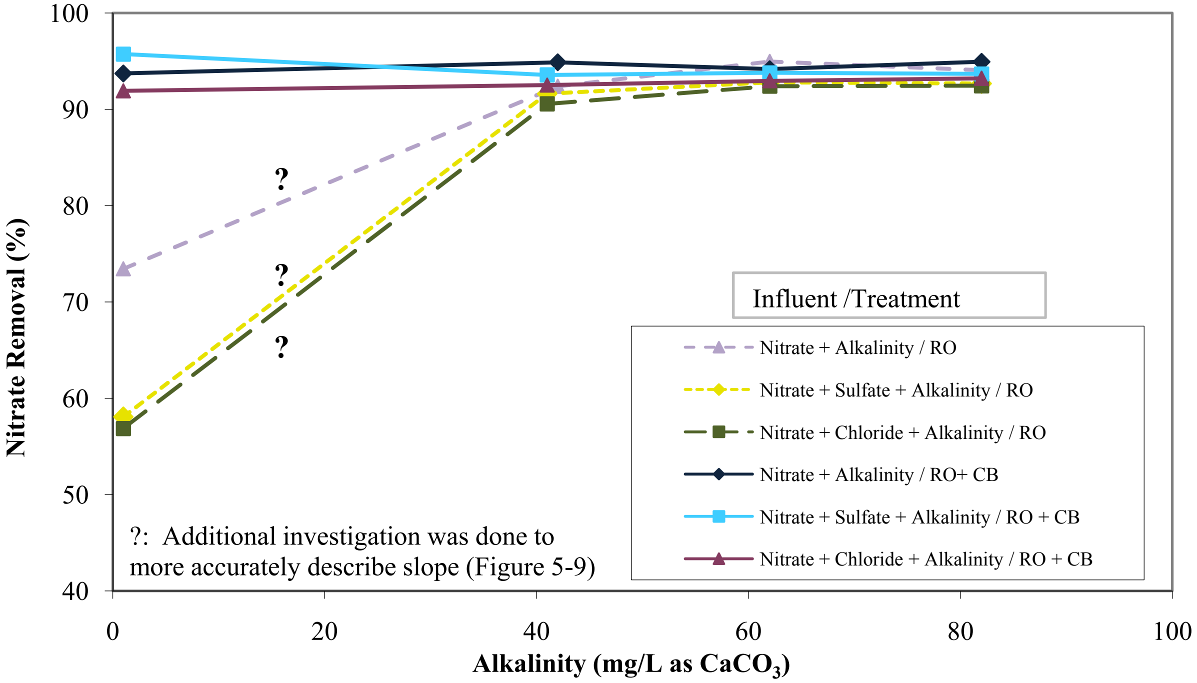

Figure 5-8: Comparison of nitrate removal from different feed waters using RO and RO preceded by carbon block (CB). Concentrations of nitrate (as N), sulfate (as SO42-), chloride (as Cl-): 23, 68, 76 mg/L, respectively. Experiment 5-4-2.

To further narrow down the critical alkalinity for nitrate removal by RO, experiment 5-4-3 was conducted without using the carbon block as a pre-filter to RO and feed waters with 23 mg NO_3^--N/L blended with less than 41 mg/L of alkalinity (as $CaCO_3$) with and without sulfate (68 mg/L as SO_4^{2-}) and chloride (76 mg/L as Cl^-). 50 psi was the applied pressure for these experiments. In this experiment the critical alkalinity was 8 mg/L as $CaCO_3$ (Tables D-14 – D-16, Appendix D).

A substantial drop in nitrate removal efficiencies by RO without using the carbon block only happens at very low levels of alkalinity which only infrequently occur in real water but can occur nonetheless (Figure 5-9). This finding has not been investigated in the RO literature, and the causes couldn't be determined due to the limited proprietary information on the carbon block and RO membrane composition. In addition, it was demonstrated that the

RO unit efficiencies are slightly impacted by elevated levels of competing anions which was also concluded from the results of experiment 5-3-2.

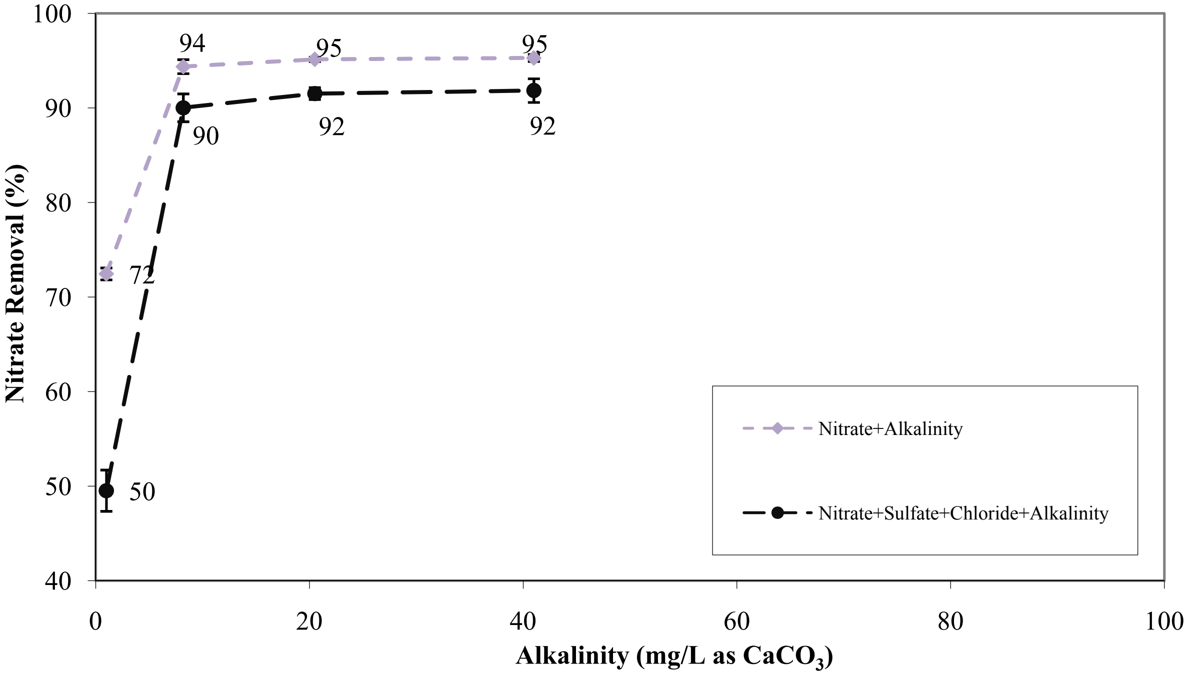

Figure 5-9: Product water nitrate removal vs. alkalinity in DI water spiked with 23 mg NO_3^--N/L and different alkalinities using RO without carbon block. Experiment 5-4-3.

5.3 Experiments using Groundwater

5.3.1 GW2

GW2, a groundwater source in the Region of Waterloo was chosen for experiment 5-5, and on July 20th, 2009 a sample was collected. This source was selected because nitrate is present, and the elevated concentration of other background anions make a good candidate for such tests. Performance of the RO membrane with and without a particle filter and carbon block for nitrate removal from this groundwater was investigated. Also experiments without the RO were conducted to test the role of pre-filters on nitrate removal and co-incidentally investigate the ability of filtration and adsorption (conventional methods) for removing target anions (Table D-17, Appendix D). All the experiments were performed at 50 psi, with feed water, product, and reject flows of 300, 83, and 217 mL/min, respectively. Feed water characteristics are listed in Table 5-6.

Table 5-6: GW2 characteristics.

Concentration (mg/L), n=3				pH	TDS (mg/L)
Nitrate (as N)	**Sulfate (as SO_4^{2-})**	**Chloride (as Cl^-)**	**Alkalinity (as CaCO3)**		
7.00 ± 0.03	38 ± 1	75 ± 1	288 ± 2	7.9	529

Results show that the RO unit is highly efficient at removing other ions and total dissolved solids (TDS), with nitrate removal being around 80%, which is consistent with the RO manufacturer claims (Figure 5-10).

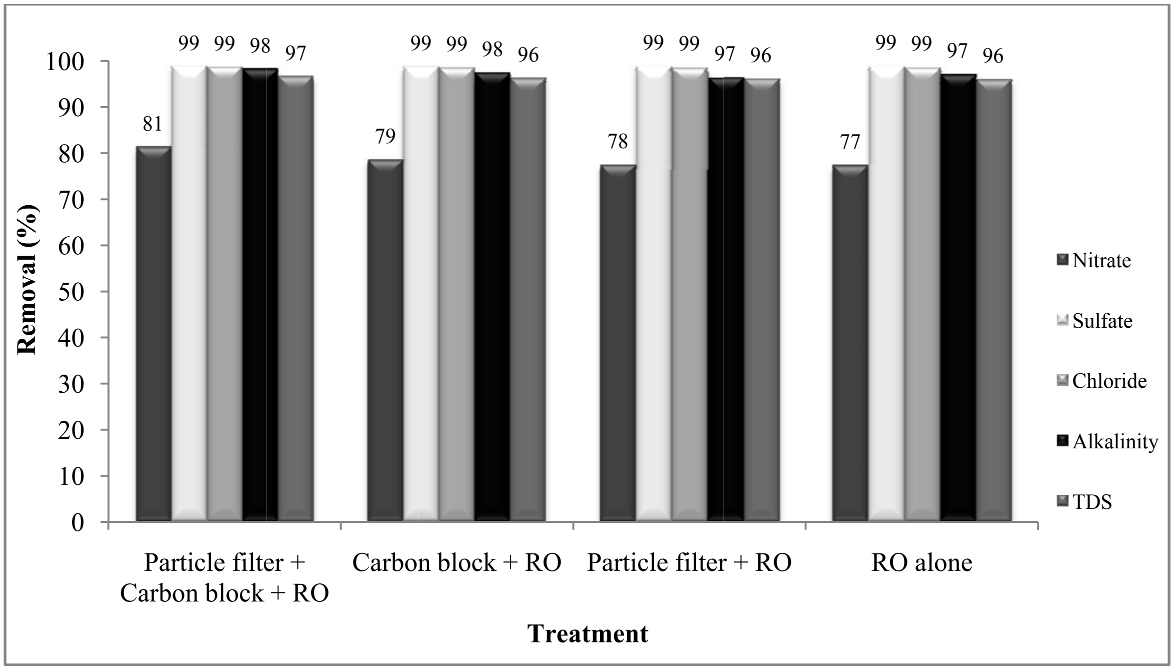

Figure 5-10: Removal of background ions from GW2 using RO with different pre-treatment at 50 psi. Experiment 5-5. n=3.

As shown in Figure 5-11, neither the particle filter nor the carbon block substantially reduced concentrations of the target ions. By extension this observation confirms that conventional methods (filtration and adsorption) are not capable of removing anions, which was noted in nitrate removal literature without any supporting experimental data. Since the feed water contains considerable alkalinity the results are in agreement with observations from the bicarbonate-spiked deionized water experiments. It should be noted that the vertical scale of Figure 5-11 was chosen to be consistent with Figure 5-10 to provide visual comparison of these two graphs. The difference between 0 and 3% removal is inconsequential.

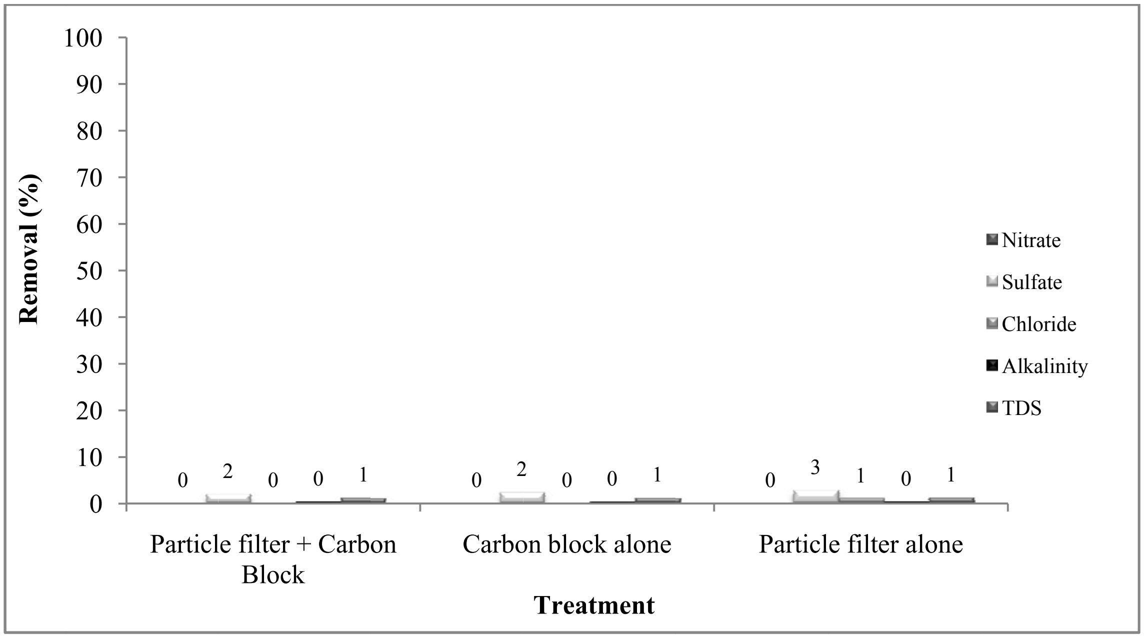

Figure 5-11: Removal of background ions from GW2 using a particle filter and/or carbon block at 50 psi. Experiment 5-5.

Concentrations of different ions and TDS in product water for experiment 5-5 are presented in Table 5-7 and Figure 5-12. Based on these results, product water contains very low concentrations of target ions and TDS. The only concern of the product water is that alkalinities are lower than the Ontario Ministry of the Environment Guidelines drinking water operational guidelines (OG > 30 mg/L as $CaCO_3$) (Ontario Ministry of the Environment, 2006). Therefore, product water could potentially be blended with untreated feed water to stabilize the chemistry of the treated water and reduce corrosion potential.

Table 5-7: Product water characteristics for Experiment 5-5.

Particle filter	**Carbon block**	**RO**	**Product water concentration (mg/L), n=3**				
			Nitrate (as N)	**Sulfate (as SO_4^{2-})**	**Chloride (as Cl^-)**	**Alkalinity (as $CaCO_3$)**	**TDS**
Yes	Yes	Yes	1.33 ± 0.07	0.48 ± 0.04	0.98 ± 0.06	5 ± 1	18
No	Yes	Yes	1.50 ± 0.12	0.49 ± 0.14	1.07 ± 0.04	7 ± 1	19
Yes	No	Yes	1.53 ± 0.04	0.44 ± 0.01	1.05 ± 0.01	10 ± 0	20
No	No	Yes	1.64 ± 0.11	0.44 ± 0.02	1.02 ± 0.03	8 ± 0	20

Note: Samples were taken after 25 minutes of running the system.

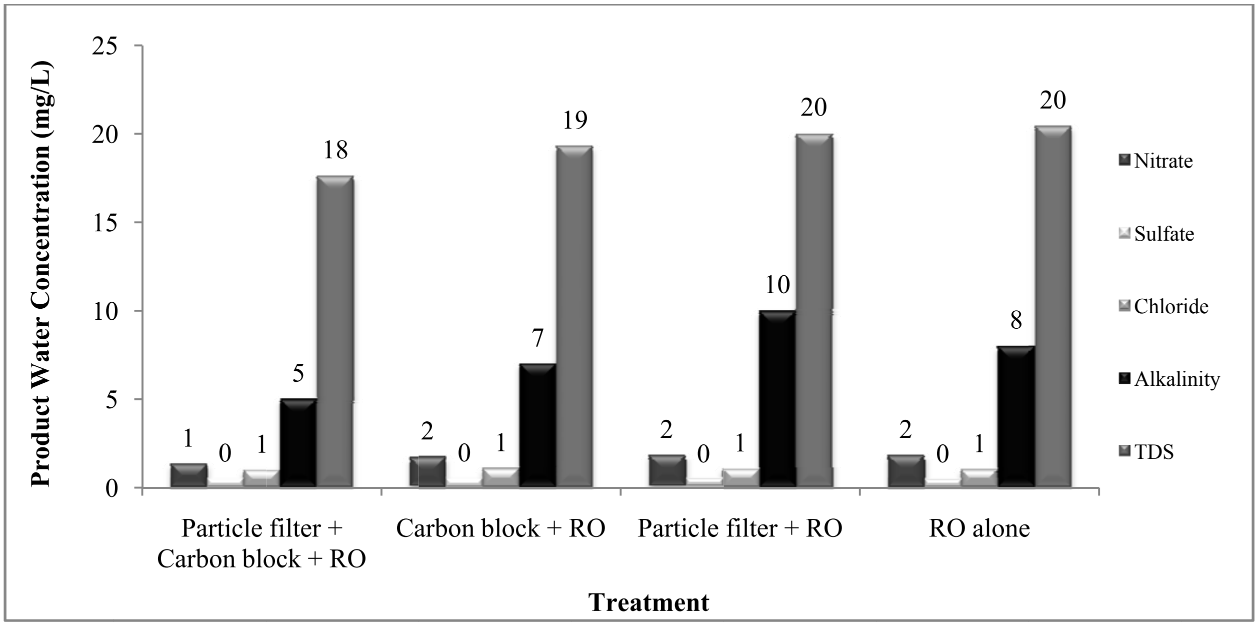

Figure 5-12: Anion concentration in RO product water with different pre-treatment at 50 psi. Feed water: GW2. Nitrate, sulfate, chloride, and alkalinity concentrations were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively. Experiment 5-5.

Table 5-8 and Figure 5-13 show concentrations of different ions and TDS in reject water for experiment 5-5. Encouragingly only TDS exceeds the Ontario Ministry of the

Environment Guidelines drinking water standards or aesthetic objectives (Ontario Ministry of the Environment, 2006). This will facilitate disposal of the reject water.

Table 5-8: Reject water characteristics for Experiment 5-5.

Prticle filter	**Carbon block**	**RO**	**Reject water concentration (mg/L), n=3**				
			Nitrate (as N)	**Sulfate (as SO_4^{2-})**	**Chloride (as Cl^-)**	**Alkalinity (as $CaCO_3$)**	**TDS**
Yes	Yes	Yes	7.2 ± 0.1	47.8 ± 0.2	89.5 ± 1.5	363 ± 4	639
No	Yes	Yes	8.2 ± 0.1	48.3 ± 0.3	90.1 ± 0.7	366 ± 0	643
Yes	No	Yes	8.7 ± 0.1	48.5 ± 0.5	90.4 ± 0.6	368 ± 0	649
No	No	Yes	8.7 ± 0.1	48.2 ± 0.1	89.9 ± 0.8	368 ± 0	650

Note: Samples were taken after 25 minutes of running the system.

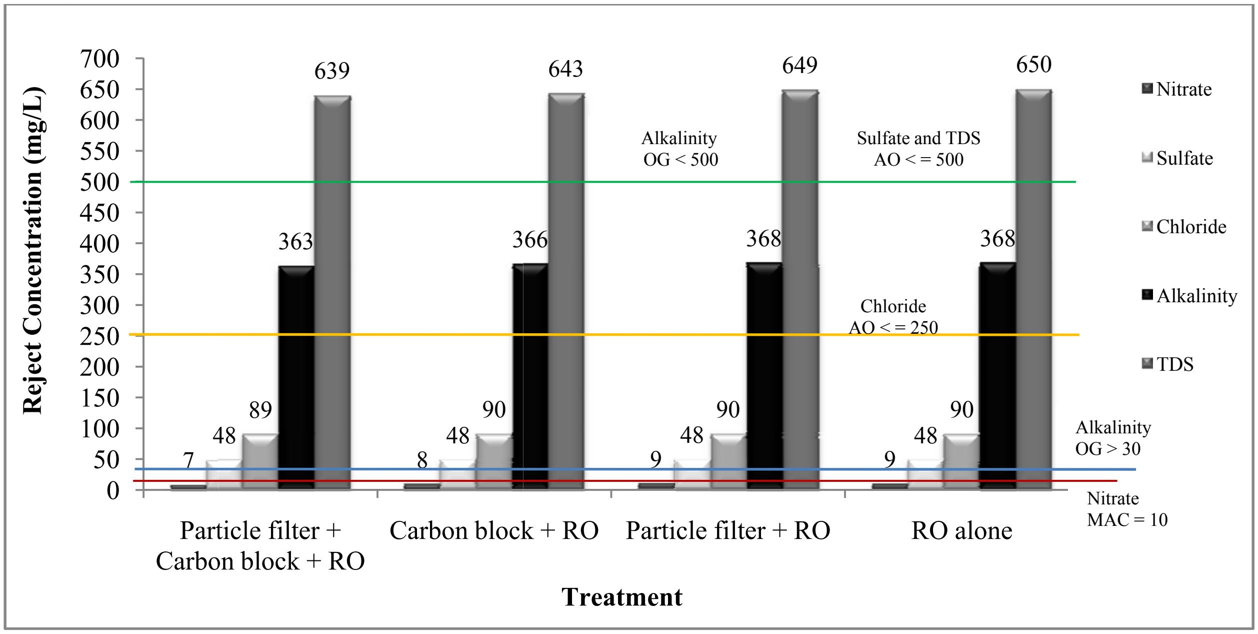

Figure 5-13: Anion concentration in RO reject with different pre-treatment at 50 psi. Feed water: GW2. Nitrate, sulfate, chloride, and alkalinity concentrations were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively. Experiment 5-5.

It can be concluded that the RO unit removed just enough nitrate to keep the reject concentration of nitrate and other ions at reasonable levels for disposal. But, this would be different for full-scale RO plants with higher recoveries and reject concentrations.

5.4 Summary of Results

The objective of using the RO unit in this study was to investigate the performance of this technology for nitrate removal under different operating and feed water blend conditions. For this purpose, several groups of tests were performed using DI water spiked with nitrate and competing anions. The concentrations of anions for spiking DI water were chosen to simulate the groundwater of the Region of Waterloo based on the highest observed concentrations of anions investigated in this study. The last group of experiments used groundwater from GW2 as its feed water to evaluate the efficiency of the unit for removing nitrate and other ions from groundwater. Application of POU RO devices and their different characteristics such as sampling time, recovery, effect of pre-filters, and operating conditions was not thoroughly reported in the literature. Also, no studies investigating how background ions might affect nitrate removal by POU RO units could be found. The following conclusions were drawn from the results of the experiments on spiked DI water:

- Product water quality from the RO system doesn’t stabilize immediately after pumping, and requires pressure to be maintained for 15 minutes prior to taking samples. In-home point of use (POU) systems have a storage tank which alleviates this through dilution.
- The product water recovery of the unit is approximately 30% based on the product and reject flows measured. This is of practical importance when it comes to cost and sustainability. However, nitrate is only of human health concern as it relates to ingestion. Therefore only water for drinking/cooking needs to be treated, which is less than 1% of all water in the public water system (Cotruvo and Cotruvo, 2003), making such units feasible for point-of-use application where required.
- There was no significant change in removal efficiency by changing the pressure in rather a small range (40-60 psi).

- Background ions don’t appear to compete with each other for removal by POU RO units.
- A substantial drop in nitrate removal efficiency by RO without using the carbon block only happens for feed waters at very low levels of alkalinity. This drop is more significant when the feed water is blended with sulfate or chloride.
- Using the carbon block can decrease the product water pH.

Findings from tests on real groundwater included the following:

- The RO unit can remove around 80% of nitrate from groundwater while the removal efficiency is much higher for other background ions and TDS. However, the recovery of the unit is around 30%.
- Neither the particle filter nor the carbon block plays a role in the removal of target ions from the real water tested.
- Product water contains very low concentrations of target ions and TDS, and can be potentially blended with untreated water.
- Reject water concentrations don’t exceed the Ontario Ministry of the Environment Guidelines limits except for the TDS (Ontario Ministry of the Environment, 2006), and can be easily disposed of (from a waste-handling perspective).

It should be mentioned that these were short term tests in which membrane fouling was not relevant. Longer term studies should be conducted to confirm the appropriateness of reverse osmosis under real world conditions.

Chapter 6

Summary and Relevance to the Drinking Water Industry

6.1 Summary of Results

This chapter provides a discussion of the overall findings of this research making connections and comparisons between all the nitrate removal technologies investigated. In addition, the application of IX and RO in industry in full-scale and point-of-use (POU) devices is discussed. Finally, this summary draws conclusions that accomplish the overall objective of this study, which was to find a practical and economical way to reduce nitrate concentrations in representative groundwater in the Region of Waterloo.

6.1.1 Summary of IX Results

The performance of two nitrate-selective ion exchange resins, Dowex™ NSR-1 and Purolite® A-520E, and two non-selective resins, Purolite® A-300E and Amberlite® IRA400 Cl was investigated and compared under different operating conditions and feed water anion concentrations, and finally for representative untreated groundwater collected in the Region of Waterloo.

Each of the investigated resins exchanged nitrate for chloride prior to their exhaustion. The optimum bed depth, hydraulic loading, and empty bed contact time were chosen to be 0.1 m, 5.2 m/h, and 1.2 min, respectively. In the absence of competing anions, non-selective resins performed better than nitrate-selective resins for nitrate removal. But, capacity of all the resins for nitrate removal was negatively affected in the presence of competing anions, especially sulfate. In non-selective resins not only the capacity was dramatically affected, but also some adsorbed nitrate was released into the product water. Therefore, using nitrate-selective resins for removing nitrate from a groundwater containing other background anions is suggested unless a very robust regeneration practice is achievable.

Of the nitrate selective resins, Purolite® A-520E showed greater capacity for nitrate removal from the groundwater in the Region of Waterloo than Dowex™ NSR-1. Performance of Purolite® A-300E non-selective resin was also promising and quite similar to Purolite® A-520E in removing nitrate from the groundwater. However, this resin is not suggested due to potential risk of releasing nitrate into the product water. Overall, Purolite® A-520E is the most promising resin tested for removing nitrate from the groundwater in the Region of Waterloo. Although nitrate is exchanged for chloride and chloride is released into the product water, its concentration in groundwater experiments didn't exceed the Ontario Ministry of the Environment aesthetic objectives. Neither did the concentrations of other background anions (Ontario Ministry of the Environment, 2006) prior to exhaustion of the resin. Therefore, the product water doesn't need any post-treatment except for disinfection, and the only other issues are designing an appropriate regeneration process and considering disposal of the brine.

6.1.2 Summary of RO Results

The performance of a Culligan® Aqua-Cleer® (model RO30) point-of-use RO unit was investigated under different operating conditions and feed water blend conditions, and also for representative untreated groundwater in the Region of Waterloo.

The product (treated) water recovery of the unit was approximately 30%, and the RO system didn't stabilize immediately upon start-up, and requires pressure to be maintained for 15 minutes. Background ions don't appear to compete with each other for removal by POU RO units. The only concern about background ions is that for feed waters at very low levels of alkalinity a substantial drop in nitrate removal efficiency occurs if the associated carbon block is bypassed. This drop is more significant when the feed water is blended with sulfate or chloride.

The RO unit was able to remove around 80% of nitrate from groundwater while the removal efficiency was much higher for other background ions and TDS. Neither the particle filter nor the carbon block played a role in the removal of target ions from the real water tested. Using the carbon block decreased the product water pH.

Product water contains very low concentrations of target ions and TDS, and can be potentially corrosive due to its low alkalinity. To control the corrosion as well as increasing the recovery of the system, product water can generally be blended with untreated water. In this case, reject water concentrations didn't exceed the drinking water Ontario Ministry of the

Environment Guidelines limits, except for TDS, and can be disposed of without restriction (Ontario Ministry of the Environment, 2006). The method of disposal is an important factor that should be considered when designing.

6.1.3 Comparison of IX and RO

An overall comparison of IX and RO follows.

IX removes nitrate with a decreasing efficiency prior to complete exhaustion of the resin. In groundwater tests, product water before exhaustion had nitrate concentrations less than the MAC and other background anions were less than limits indicated in the in the Ontario Ministry of the Environment aesthetic objectives and/or operational guidelines. On the other hand, RO removes nitrate as well as all other background ions at varying efficiencies. Thus, the product water of RO contains low alkalinity and is potentially corrosive and might need post-treatment.

Recovery of the RO system is relatively low at 30%, and product water may need to be blended with feed water to increase the recovery and control potential corrosion problems.

Background anions, especially sulfate, compete with nitrate for removal in IX applications, while this is not an issue in RO systems. Therefore in cases of having a high sulfate and TDS feed water, RO might be a more appropriate technology for nitrate removal.

Both IX and RO technologies have waste disposal issues. These are more critical for RO due to the larger amounts of its waste and higher concentrations. However, an appropriate regeneration process for IX should be designed to regenerate the resin at an optimum time prior to exhaustion and decrease the amount of brine.

6.2 Application

IX and RO can be applied at both full-scale and POU-scale. To select the most appropriate alternative, technical, economical, and social aspects of each procedure should be carefully considered.

6.2.1 Full-Scale

IX and RO have been approved by the USEPA as Best Available Technologies (BAT) for removing nitrate (USEPA, 2004) and have been applied at full-scale plants. On other hand, treating all the source water at a full-scale plant to reduce the concentration of a contaminant with a stringent MCL (such as nitrate) increases construction and maintenance costs (Cotruvo and Cotruvo, 2003). Economic and space restrictions are the main constraints at full-scale plants, while application of POU devices is restricted by technical, regulatory, and social issues. Therefore, in cases of having enough space and capital, conventional full-scale treatment might be a better alternative. However, both IX and RO technologies have waste disposal problems that should be considered when designing a full-scale plant.

6.2.1.1 IX

Based on the results of this research, IX product water before exhaustion has acceptable nitrate (less than the 10 mg NO_3^--N/L MAC) and other background anion concentrations (Ontario Ministry of the Environment, 2006). Therefore, this technology doesn't need any post-treatment process except for disinfection. IX is a simple and effective method and can be applied at full-scale. In addition, fully-automated nitrate removal IX systems that don't need large amounts of space are commercially available from Basin Water Inc. (Rancho Cucamonga, CA) to be used in cases of having space restrictions (Basin Water, 2005).

On the other hand, background anions, especially sulfate, compete with nitrate for removal when using IX technology. Therefore, if feed water contains high concentrations of sulfate or TDS, nitrate leakage happens sooner and regeneration would be needed in higher dosage and shorter intervals. In addition, since nitrate and other anions are exchanged for chloride, chloride concentrations in product water might exceed regulatory levels and should be measured in cases of high feed water TDS.

6.2.1.2 RO

RO is generally a more expensive technology than IX due to its high energy demand and low recovery (Luk and Au-Yeung 2002; MWH, 2005; Bergman, 2007).

But, as discussed before, RO might be a more appropriate technology for nitrate removal if concentrations of sulfate or TDS are high in feed water. It should also be mentioned that, since RO removes other background ions as well as nitrate, the product water of RO contains low alkalinity and can potentially be corrosive and might need post-treatment.

Blending product with feed water is an alternative to control corrosion problems as well as increasing the recovery and consequently decreasing the costs (MWH, 2005; Bergman, 2007). However, nitrate regulations may limit the extent to which blending can be utilized (MWH, 2005; Bergman, 2007). In addition, blending is not permitted in cases of having ‘extremely impaired sources’ of water (CDHS, 1997). Application of RO in parallel with IX is recommended in these cases. This process can treat the entire feed water, while reducing the high costs of RO by passing a part of the feed water through IX and controlling any potential corrosion problems by blending the product waters of RO and IX (Bebee et al., 2006).

6.2.2 Point-of-Use-Scale

In some situations using POU or point-of-entry (POE) devices are suggested as treatment alternatives to reduce the costs of modifying or building public water systems (PWS) (Cotruvo and Cotruvo, 2003).

POU devices are designed to treat the water that is consumed only for drinking and cooking, and are connected to a single tap in the household (USEPA, 2002; USEPA, 2006; Hamouda et al., 2008). These devices are good treatment alternatives for remote and small communities that use groundwater.

However, it is recommended that only POU devices that are certified by NSF/ANSI and have mechanical warnings such as alarms or auto-shutoff (Cotruvo and Cotruvo, 2003; Hamouda et al., 2008) be utilized. Another crucial concern associated with POU devices is educating customers with regard to their responsibilities. Inappropriate operation or maintenance of POU units can increase health risks to users (USEPA, 2002; Anderson and Sakaji, 2007; Hamouda et al., 2008).

6.2.2.1 IX

POU ion exchange devices are commercially available, with the majority of them being cation exchange cartridges used as water softeners. However, some manufacturers provide cartridges with anion exchange resins (none are currently certified to NSF/ANSI). Social, regulatory, and technical aspects are important considerations in designing and applying POU IX units for nitrate removal. These units must be certified and have auto-shutoff systems due to health risks that might be caused by improper maintenance.

Based on findings of this research, the concentration of nitrate in the product water reaches its feed water concentration after the total exhaustion of the resin, or even exceeds that initial value in cases of using non-selective resins. Thus, training the customers to regenerate the resin at the designed time, and having auto-shutoff systems are very crucial. To avoid public health risks, the use of POU IX devices is not recommended when feed water nitrate concentration is high. Also, as discussed before, IX may not be an appropriate treatment alternative for feed waters with high concentrations of TDS or sulfate.

6.2.2.2 RO

Various point-of-use RO devices are commercially available, some of which are certified to NSF/ANSI standards. These units usually have essential pre-treatment filters that reduce membrane fouling. Rather than having to deal with social issues (such as educating customers) and technical issues that might arise, POU RO devices may be preferable to full-scale RO plants.

For a POU RO unit low recovery is offset by the fact that only water for drinking/cooking needs to be treated, which is less than 1% of all water used in a home (Cotruvo and Cotruvo, 2003). In addition, since the water is consumed at the point of treatment, its corrosion potential is not important. Therefore, there is no need for a post-treatment process to increase alkalinity.

6.3 Summary

Figure 6-1 provides decision support assistance for the selection of the appropriate nitrate removal technology for a variety of conditions.

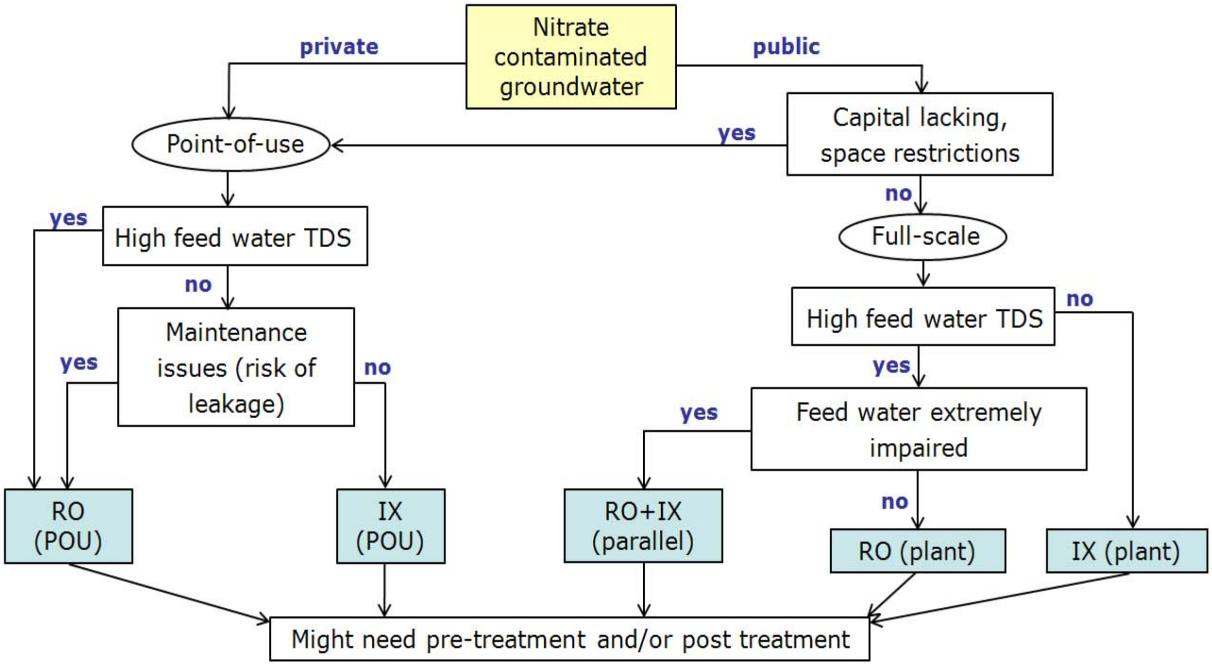

Figure 6-1: Options for nitrate removal using IX and/or RO under varying conditions.

Chapter 7

Conclusions and Recommendations

The nitrate removal capability of two nitrate-selective ion exchange (IX) resins (Dowex™ NSR-1 and Purolite® A-520E), two non-selective resins (Purolite® A-300E and Amberlite® IRA400 Cl), and a commercially-available reverse osmosis (RO) point-of-use (POU) device (Culligan® Aqua-Cleer® model RO30), including a particle filter and a carbon block were tested using spiked deionized water and representative groundwater collected in the Region of Waterloo, Ontario, Canada. Tests were conducted at bench-scale in order to evaluate a wider spectrum technologies and conditions for their potential for application in full-scale plants or in home POU units, in the Region of Waterloo. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

7.1 Conclusions

The following conclusions were made from the results of this research:

7.1.1 IX

1. Purolite® A-520E, anitrate-selective resin was the most promising of the four resins tested for removing nitrate from the groundwater in the Region of Waterloo.

2. The capacity of all tested resins for nitrate removal was negatively impacted in the presence of competing anions, especially sulfate. Therefore, if feed water contains elevated concentrations of sulfate or total dissolved solids (TDS), resins become exhausted sooner and regeneration would be needed at more frequent intervals.

3. To avoid exposure to nitrate at concentrations higher than regulated values caused by inadequate regeneration intervals or poor maintenance of POU devices, the use of such devices should be carefully considered when concentrations of nitrate, sulfate, or TDS are substantially elevated in the feed water.

4. In the presence of competing anions the capacity of non-selective resins was dramatically affected. In addition, some adsorbed nitrate was released into the

product water. Thus, using non nitrate-selective resins for removing nitrate from a groundwater containing other background anions is not suggested at full-scale unless a very robust regeneration practice is achievable. Non nitrate selective resins are not recommended for use in IX POU devices under any conditions.

5. In IX, nitrate and other anions are exchanged for chloride. Consequently, chloride concentrations in product water might exceed aesthetic objectives and should be monitored in cases of high feed water TDS.

6. The product (treated) water from the IX experiments conducted on groundwater didn’t need any post-treatment since concentrations of other regulated parameters didn’t exceed Ontario Ministry of the Environment standards. While most full-scale systems will require some form of disinfection following IX, special consideration should be given to the design of an appropriate regeneration process and brine disposal issues.

7.1.2 RO

1. The RO unit was able to remove around 80% of nitrate from groundwater while the removal efficiency was much higher for other background ions and TDS (> 98%).

2. The product water recovery of the unit was approximately 30% which is low. However, the effect of this is minimized for a POU RO unit as only water for drinking/cooking needs to be treated.

3. Individually, neither the particle filter nor the carbon block played a role in the removal of target ions from the real water tested.

4. Background ions don’t appear to compete with each other for removal by POU RO units.

5. For feed waters with very low levels of alkalinity a substantial drop in nitrate removal efficiency occurs if the associated carbon block is bypassed. This drop is more substantial when the feed water contains sulfate or chloride.

6. Using the carbon block decreased the product water pH.

7. Product water contains very low concentrations of target ions and TDS, and can potentially be corrosive due to its low alkalinity and might need post-treatment (if being delivered through a communal distribution system or in-home plumbing).

8. In the RO experiments conducted on the representative groundwater in the Region of Waterloo, reject water concentrations didn't exceed the drinking water Ontario Ministry of the Environment regulatory limits, except for TDS (which is an aesthetic objective), and can be disposed of without restriction.

7.2 Recommendations

Recommendations for further investigation regarding this research are provided below.

7.2.1 IX

1. Optimization of operating conditions experiments for IX resins were limited due to long run times and associated time restrictions. A wider range of bed depths and hydraulic loading could be examined to find the optimum operating condition for each resin.

2. Fresh resins were employed to do all the IX experiments. Resins might not return to their original capacity after several exhaustion and regeneration cycles. Long term use and effect of regeneration on capacity of resins for nitrate removal should be studied.

7.2.2 RO

1. The RO experiments were conducted over very short periods early in the life of the RO membrane. The long term operational stability of the RO unit was not

ascertained. Fouling and scaling may influence the properties of the membrane, which could impact nitrate removal performance. The lifetime of the RO membrane and pre-filters should be estimated prior to making decisions which impact real water treatment system design choices.

2. The use of a carbon block increased nitrate removal for feed waters at very low levels of alkalinity, but the reason was not established. Further investigations to answer why bypassing the carbon block caused a substantial drop in nitrate removal efficiency for feed waters at very low levels of alkalinity is recommended.
3. The effect of pressure on the recovery of the RO system should be assessed under site-specific circumstances.

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Appendices

Appendix A

Product Data Sheets for Ion Exchange Resins (Dowex™ NSR-1, Purolite® A-520 E, Purolite® A-300 E, and Amberlite® IRA 400 Cl)

DOWEX™ NSR-1

A Strong Base, Nitrate Selective, Anion Exchange Resin

Product	Type	Matrix	Functional group
DOWEX™ NSR-1	Triethylamine strong base anion	Styrene-DVB, macroporous	Quaternary amine

Guaranteed Sales Specifications		
Total exchange capacity, min.		0.9 min
Water content	%	53 - 63
Bead size distribution Particle size (mesh)	Mesh, thru 14	100 max
	On 16 mesh	3 max
	Thru 40 mesh	5 max

Typical Physical and Chemical Properties		
Ionic form as delivered		Cl^-
Total shrink ($Cl \Rightarrow NO_3$), approx.	%	5
Whole uncracked beads, min.	%	90
Particle density, approx.	g/mL	0.68
Shipping weight, approx.	lbs/ft^3	42

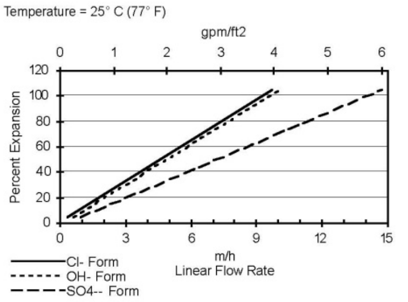
Recommended Operating Conditions

• Maximum operating temperature:	
Cl^- form	100°C (212°F)
• pH range	0 - 14
• pH range operational	4.5 - 8.5
• Bed depth, min.	800 mm (2.6 ft)
• Flow rates:	
Service/fast rinse	5 - 60 m/h (2 - 24 gpm/ft^2)
Backwash	See Figure 1
Co-current regeneration/displacement rinse	1 - 10 m/h (0.4 - 4 gpm/ft^2)
Counter-current regeneration/displacement rinse	5 - 20 m/h (2 - 8 gpm/ft^2)
• Total rinse requirement	3 - 6 bed volumes (0.3 - 0.6 gpm/ft^2)
• Regenerant:	
Type	NaCl (3 - 10%)
Temperature	Ambient or up to 50°C (122°F)
• Organic loading, max.	3 g $KMnO_4$/L resin

Typical Properties and Applications

DOWEX™ NSR-1 is a macroporous strong base anion resin supplied in the Cl^- form, based upon a triethylamine chemistry. The NSR-1 is designed to have better selectivity for nitrate in the presence of moderate to high concentrations of sulfate ions, as compared to standard type I or type II strong base anion resins. The DOWEX NSR-1 resin is certified under ANSI STD 61, making DOWEX NSR-1 the resin of choice for nitrate retention and removal from water streams that also contain sulfate.

Figure 1. Backwash Expansion Data

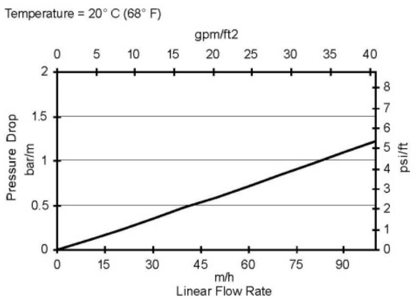


For other temperatures use:

$F_T = F_{77°F}\ [1 + 0.008\ (T_{°F} - 77)]$, where $F \equiv gpm/ft^2$

$F_T = F_{25°C}\ [1 + 0.008\ (1.8T_{°C} - 45)]$, where $F \equiv m/h$

Figure 2. Pressure Drop Data



For other temperatures use:

$P_T = P_{20°C}\ /\ (0.026\ T_{°C} + 0.48)$, where $P \equiv bar/m$

$P_T = P_{68°F}\ /\ (0.014\ T_{°F} + 0.05)$, where $P \equiv psi/ft$

Note: These resins may be subject to drinking water application restrictions in some countries: please check the application status before use and sale.

DOWEX™ Ion Exchange Resins
For more information about DOWEX resins, call the Dow Water Solutions business:

North America:	1-800-447-4369
Latin America:	(+55) 11-5188-9222
Europe:	(+32) 3-450-2240
Pacific:	+60 3 7958 3392
Japan:	+813 5460 2100
China:	+86 21 2301 9000

http://www.dowex.com

Warning: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

PUROLITE®
ION EXCHANGE RESINS

ISO 9002
REGISTERED FIRM
FM 40552

A-520E

Macroporous Strong Base Anion Exchange Resin

(For the selective removal of nitrate)

Technical Data

PRODUCT DESCRIPTION

Purolite A-520E is a macroporous strong base anion resin which is specially designed for the removal of nitrates from water for potable processes. The macroporous matrix and special ion exchange group functionality imparts ideal nitrate selectivity to **Purolite A-520E** making this resin particularly suitable for nitrate removal even when moderate to high concentrations of sulphate are present. Hence this resin gives superior performance in nitrate removal applications when compared with standard exchange resins.

A requirement of the nitrate removal process is to produce potable water meeting the quality standard defined by the European Economic Community in the Directive No. 80/778 of July 1980. This directive limits the nitrates to a maximum admissable concentration (M.A.C.) of 50 mg NO_3/l. The U.S.A. drinking water regulations limit nitrates to 45 mg NO_3/l.

Typical Physical & Chemical Characteristics	
Polymer Matrix Structure	Macroporous Styrene-Divinylbenzene
Physical Form and Appearance	Opaque Cream Spherical Beads
Whole Bead Count	95% min.
Functional Groups	Quaternary Ammonium
Ionic Form, as shipped	Cl^-
Shipping Weight (approx.)	680 g/l (42.5 lb/ft^3)
Screen Size Range:	
- U.S. Standard Screen	16 - 50 mesh, wet
Particle Size Range	+1200 mm <5%, -300 mm <1%
Moisture Retention, Cl^- form	50 - 56%
Reversible Swelling $Cl^- \rightarrow SO_4/NO_3$	negligible
Total Exchange Capacity, Cl^- form,	
wet, volumetric	0.9 meq/ml min.
dry, weight	2.8 meq/g min.
Operating Temperature, Cl^- Form	100°C (212°F) max.
pH Range, Stability	0 - 14
pH Range, operating	4.5 - 8.5

Standard Operating Conditions
Nitrate Removal

Operation	Rate	Solution	Minutes	Amount
Service	8 - 32 BV/h 1 - 4 gpm/ft^3	Influent water to be treated	per design	per design
Backwash	Refer to Fig. 2	Influent water 10 - 20°C (50 - 68°F)	5 - 20	1.5 - 4 BV 10 - 25 gal/ft^3
Regeneration	2 - 5 BV/h 0.25 - 0.6 gpm/ft^3	3 - 10% NaCl	20 - 60	90 - 250 g/l 7.8 - 15.6 lb/ft^3
Rinse, (slow)	2 - 5 BV/h 0.25 - 0.6 gpm/ft^3	Influent water	20 - 60	2 - 5 BV 15 - 40 gal/ft^3
Rinse, (fast)	8 - 32 BV/h 1 - 4 gpm/ft^3	Influent water	-	-

Backwash Expansion 50% to 75%
Design Rising Space 100%
"Gallons" refer to U.S. Gallon = 3.785 litres

REGENERATION

Sodium chloride is generally preferred for regeneration for reasons of cost and efficiency. When available sea water can be used quite effectively. The use of softened water for make up of regenerant and rinse is often recommended to avoid the precipitation of calcium carbonate in and around the **Purolite A-520E** (or any other resin used in this application). Although the precipitation is not particularly detrimental in the short term, the long term effects may include increased resin attrition and leakage of nitrates.

PRECONDITIONING PROCEDURE

Purolite A-520E is processed to insure that it meets the requirements for use in the treatment of potable water.

On installation it is recommended that the resin be regenerated with two bed volumes of 6% NaCl followed by a rinse of four bed volumes of potable water, prior to use.

HYDRAULIC CHARACTERISTICS

The pressure drop or headloss across a properly classified bed of ion exchange resin depends on the particle size distribution, bed depth, and void volume of the exchange material as well as on the viscosity (and hence on the temperature) of the influent solution. Factors affecting any of these parameters, for example the presence of particulate matter filtered out by the bed, abnormal compressability of the resin, or the incomplete classification of the bed will have an adverse effect and result in an increased headloss.

Depending on the quality of the influent water, the application and the design of the plant, service flow rates may vary from 10 - 40 bed volumes/hour (1 - 5 gpm/ft^3). Typical pressure drop data is given in Fig. 1.

Fig. 1 PRESSURE DROP CHARACTERISTICS

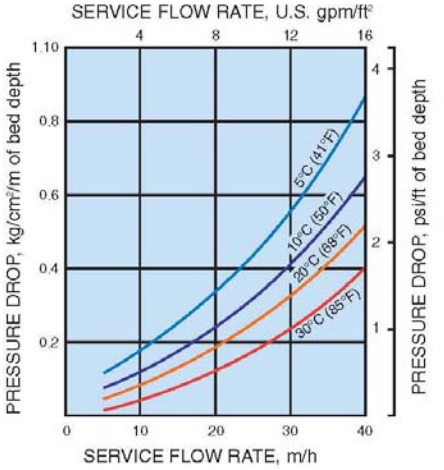
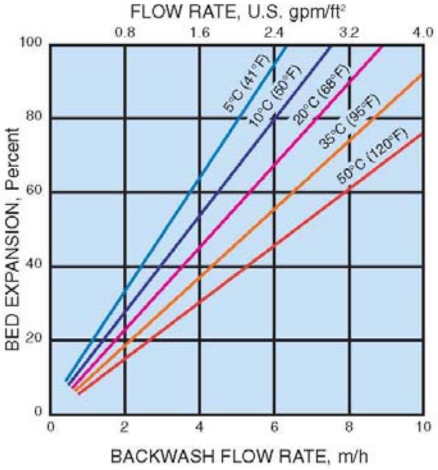


Fig. 2 BACKWASH EXPANSION



During upflow backwash, the resin bed should be expanded in volume by between 50 and 70%. This operation will free it from any particulate matter, clear the bed of bubbles and voids, and reclassify the resin particles, ensuring minimum resistance to flow. Bed expansion increases with flow rate and decreases with temperature, as shown in Fig. 2. Care should be taken to avoid over expansion of the bed.

Conversion of Units	
1 m/h (cubic meters per square meter per hour)	= 0.341 gpm/ft² = 0.409 U.S. gpm/ft²
1 kg/cm²/m (kilograms per square cm per meter of bed)	= 4.33 psi/ft = 1.03 atmos/m = 10 ft H_2O/ft

OPERATING PERFORMANCE

The high selectivity of **Purolite A-520E** for nitrate over sulphate ensures that any necessary reduction in nitrate levels can be achieved even in the presence of high influent sulphate concentration. Hence it so offers the advantage over standard strong base resins that its exchange capacity for nitrates is less affected by a high influent concentration of sulphate. For this reason, although **Purolite A-520E** has a lower total exchange capacity than standard strong base anion resin, its use can produce advantageously higher throughputs for the following reasons.

Both standard gel type or macroporous strong base resins are quite capable of effective nitrate removal where sulphate to total anion ratios are low. However, on account of the high selectivity for sulphate in dilute solutions which follows the order,

$$HCO_3^- < Cl^- < NO_3^- < SO_4^=$$

selective displacement of nitrate by sulphate results in the effective nitrate removal capacity being reduced by sulphate loading. Apart from the obvious disadvantage of the reduction of treated water obtained on cycling, the exchange of both nitrate and sulphate by chloride will result in a less palatable and sometimes less acceptable water than the influent supply, in that the treated water may be more corrosive and the limits for chloride concentration may be exceeded.

PUROLITE A-520E, CO-FLOW REGENERATION

Fig. 3 OPERATING CAPACITY

VS. $\frac{NO_3^-}{NO_3^- + SO_4^=}$ RATIO

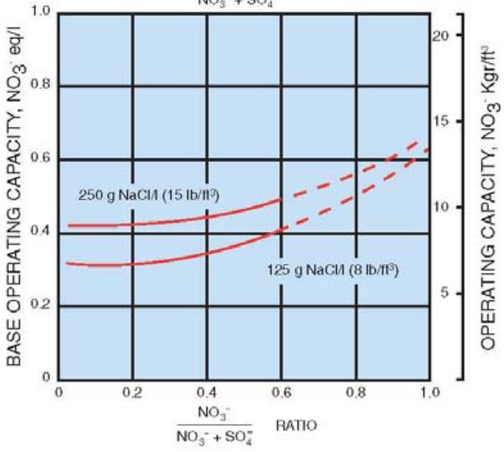


Fig. 4 NITRATE LEAKAGE

VS. $\frac{NO_3^-}{NO_3^- + SO_4^=}$ RATIO

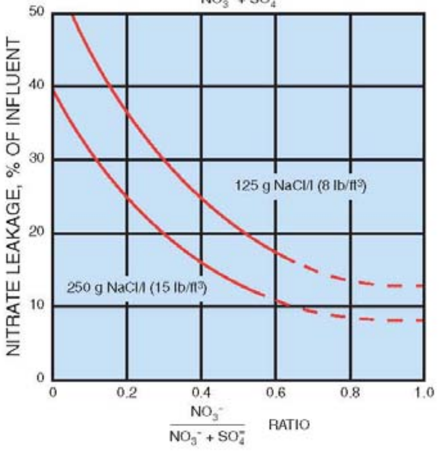


Fig. 3 and Fig. 4 give the operating capacity and nitrate leakage respectively which may be obtained using co-current regeneration at the given regeneration levels. Values obtained from Fig. 3 are expressed in terms of nitrate throughput, corrected for nitrate leakage, and hence may not be used directly to determine the throughput of water. All ion concentration values are either on a ppm or a meq/l basis for ratio determination.

Calculation for throughtput of treated water	
cyclic output (liters) = $\frac{V \times OC}{L - l_n} \times 10^3$	where V = resin volume (liters) OC = operating capacity (eq/l) L = nitrate load (meq/l) l_n = nitrate leakage (meq/l)
or cyclic output (U.S. gal) = $\frac{V_f \times OC_k \times 10^3}{0.058 (L_p - l_{np})}$	where V_f = resin volume (ft^3) OC_k = operating capacity (kgr/ft^3) L_p = nitrate load (ppm as $CaCO_3$) $_{np}$ = nitrate leakage (ppm as $CaCO_3$)

Similarly Fig. 5 and Fig. 6 give the values for counter-current regeneration. It should be noted that in this case the nitrate leakage is lower for a given regeneration level. Hence the possibility to blend treated with untreated water on a 50% basis is a useful option which can make counter-current regeneration attractive. On the other hand the choice of co-current regeneration can result in the production of higher volumes of treated water of satisfactory quality for direct use. The higher leakage (l_n, l_{np}, in the equations above) so reduces the load on the ion exchange bed that for a given operating capacity greater throughputs per cycle are obtained. This latter effect can influence the throughput more than differences in basic operating capacity. It therefore follows that both capacity and leakage for alternative modes of regeneration should be evaluated before recommending specific design conditions.

PUROLITE A-520E, COUNTER-FLOW REGENERATION

Fig. 5 OPERATING CAPACITY

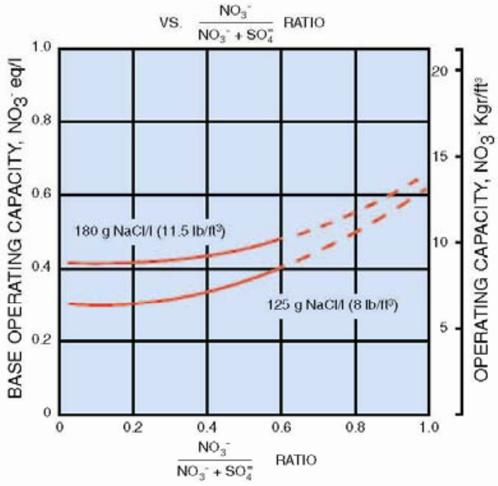
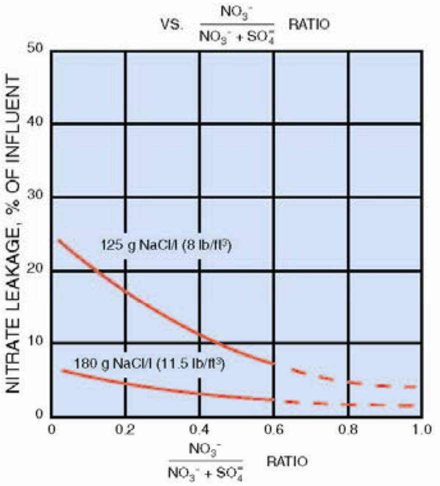


Fig. 6 NITRATE LEAKAGE



Presupposing that the objective of the nitrate removal treatment is to obtain potable water of a quality which meets the World Health Organization (WHO) limit, where the nitrate/(nitrate + sulphate) ratio is higher than 0.6, a nitrate selective resin is not necessary. A standard strong base resin can give higher throughputs as a result of its higher total capacity. It will be seen that up to the ratio of 0.6 the curves in Figs. 3 - 6 are continuous to show where **Purolite A-520E** is the recommended resin. The discontinuous curves are given so that comparisons may be made with alternative resins. Where lower leakages than the WHO limit are required, for example in the processing of certain foods, **Purolite A-520E** will often give a superior performance to the standard resins even where nitrate/(nitrate + sulphate) ratios are higher than 0.6. One particular advantage here is that there is no slug of highly concentrated nitrate at breakthrough as is found with standard resins, hence the possibility to excessively contaminate the food product by overrunning the bed is avoided.

EXAMPLE OF CALCULATION

How to use Figs. 3 through 6.

It is assumed that it is required to treat a well water of the following analysis to produce a nitrate concentration of less than 50 mg/l.

WATER ANALYSIS

Anions	ppm	meq/l	ppm as $CaCO_3$	Cations	ppm	meq/l
Nitrate	93	1.5(L)	$76(L_p)$	Calcium	90	4.5
Sulphate	98	2.0	100	Magnesium	18	1.5
Chloride	71	2.0	100	Sodium	30	1.3
[HCO_3*	122	2.0	100]	Potassium	8	0.2
Total Anions		7.5		Total Cations		7.5
Equivalent Mineral Acidity (EMA)		5.5				

$$\frac{\text{Nitrate}}{\text{Nitrate + Sulphate}} = \frac{NO_3^-}{NO_3^- + SO_4^=} = \frac{76}{76 + 100} = 0.43$$

*Note: Unless concentration of bicarbonates is well above average it does not affect the performance to a significant extent.

A regeneration level of 125 g NaCl/l has first been chosen, using co-current regeneration.
To calculate the cyclic throughput from the equations given above;

From Fig. 3, Base Capacity at 0.43 for $\frac{NO_3^-}{NO_3^- + SO_4^=} = 0.36$ eq/l

From Fig. 4, Leakage at $\frac{0.43\ NO_3^-}{NO_3^- + SO_4^=} = 23\%$

Hence for each litre of resin, throughput $= (0.36/1.15) \times 10^3$ liters
$= 313$ liters

And for each cubic foot of resin, $= [7.9/(0.058 \times 57.7)] \times 10^3$
$= 2360$ U.S. gal.

Depending upon the throughput requirement the resin volume is chosen so as to operate within the flow rate stipulations given in the standard operating conditions above. A design factor of 0.9 is also recommended as is customary. Hence throughput/liter of resin for design purposes will be 313 x 0.9 = 281.7 liters (2124 U.S. gal/ft^3).

In this example the leakage is 17.3 ppm as $CaCO_3$ (21.4 ppm as NO_3), hence the useful option to blend treated water with raw water on a 50% basis could be applied. It would be of no advantage to move to counter-current regeneration in this case. Reference to Fig. 5 will show that the basic capacity curve is very similar. However the throughput will be lower, because the reduced leakage increases the ion exchange load for a given throughput. When on the other hand nitrate concentrations or ratios are higher, it may be advantageous to operate counter-current rather than increase the regeneration level while operating co-current. In this way a suitable blend may be obtained with lower regenerant costs (and costs of disposal).

NOTES

PUROLITE®
ION EXCHANGE RESINS

WORLDWIDE OFFICES

USA: www.puroliteUSA.com
International: www.purolite.com

U.S.A.
The Purolite Company
150 Monument Road
Bala Cynwyd, PA 19004
Phone: (1) 610-668-9090
Toll Free: 800-343-1500
Telefax: (1) 610-668-8139
Email: sales@puroliteUSA.com

TEXAS
The Purolite Company
1700 West Loop South
Suite 740
Houston, TX 77027
Toll Free: 800-562-6488
Telefax: (1) 713-627-7890

CANADA
The Purolite Company
625 Wabanaki Drive
Unit #2
Kitchener, Ontario N2C 2G3
Toll Free: 800-461 -1500
or (1) 519-896-6674
Telefax: (1) 519-896-6679

UNITED KINGDOM
Purolite International Limited
Kershaw House
Great West Road
Junction with Lampton Road
Hounslow, TW5 OBU
Sales Phone: (44) 181 -570-4454
Telefax: (44) 181-572-7726

European Marketing
Phone: (44) 181-577-1222
Telefax (44) 181-577-1136

GERMANY
Purolite Deutschland GmbH
Harkort Strasse 25
40880 Ratingen
Phone: (49) 2102-46033
Telefax: (49) 2102-443663

FRANCE
Purolite International SARL
34 Avenue Matignon
75008 Paris
Phone: (33) 1-4256-4563
Telex: 648856
Telefax: (33) 1-4563-3826

SPAIN
Purolite Iberica S.A.
Parc Tecnologic del Valles
Centre Empreses Noves Tecnologies
08290 Cerdanyola del Valles (Barcelona)
Phone: (34) 3-582-0266
Telefax: (34) 3-582-0268

EGYPT
Purolite International Middle East
Cairo Liaison Office
12 Obour Gardens
Fifth Floor, App. No. 55
Salah Salem Street
Nasr City, Cairo
Phone: (20) 2-4021477
Telefax: (20) 2-4021478

ITALY
Purolite International S.r.l.
Viale Coni Zugna 29
20144 Milan
Phone: (39) 02-481-8145
Telefax: (39) 02-4801-2359

ROMANIA
Purolite Romania
International Business Center Modern
B-dul Carol I No. 34-36
5th Floor
Bucharest, Sector 2
Phone: (40) 1-250-5053/5028
Telefax: (40) 1-250-5999

POLAND
Head Office
Radus Spolka z o.o.
ul Przebendowskich 33
81-543 Gdynia
Phone/Fax (48) 58-6248118

GLIWICE
Radus Spolka z o.o.
ul Górnych Walów 25
44-100 Gliwice
Phone: (48) 32-315-931
Telefax: (48) 32-315-931

SLASK
Radus Spolka z o.o.
ul 3 Maja 3/33
32-600 Oswiecim
Phone: (48) 33-425-603
Telefax: (48) 33-425-603

CZECH & SLOVAK REPUBLICS
Purolite International
Nad Mazankou 17
182 00 Prague 8
Phone: (420) 2-688-1086
Telefax: (420) 2-688-1086

RUSSIA
Head Office
Purolite International
10th Floor
36 Lyusinovskaya Street
Moscow
Phone: (7) 095-564-8120
Telefax: (7) 095-564-8121

ST. PETERSBURG
Purolite International Limited
12 Building A Tambovskaya St.
St. Petersburg
192007 Russian Federation
Phone: (7) 812-327-8530
Telefax: (7) 812-327-9079

KAZAKHSTAN
Purolite RH Limited
Office 205
240 Dostyk AV.
Almaty 480051
Phone: (7) 3272-641-234
Telefax: (7) 3272-641-234

SINGAPORE
Purolite International (Singapore)
PTE Limited
32-04 The Concourse
300 Beach Road, 199555
Phone: (65) 297-0889
297-1453
Telefax: (65) 297-1986

CHINA
Head office
Purolite (China) Company, Ltd.
Chengguan Town
Deqing County
Zhejiang Province 313200
Phone: (86) 572-842-2908
Telefax: (86) 572-842-3954

TAIWAN
Purolite International
16F-2, No. 191
Fu-hsing N. Road,Taipei
Phone: (886) 2-546-7078
Telefax: (886) 2-546-7069

MEXICO
Purolite International, S.A. De C.V.
World Trade Center
Montecito 38, Piso 33,Oficina-19
Mexico D.F. 03810
Phone: (52) 5-488-0904
Telefax: (52) 5-488-0906

UKRAINE
Purolite International Limited
2 Korolenko Street.
Dnepropetrovsk 320070
Phone: (38) 0562-320-065
0562-320-066
Telefax: (38) 0562-320-067

KOREA
Purolite International (Korea) LLC
Dae Yeon Bldg., Suite 403
943-30 Daechi-dong
Kangnam-gu, Seoul
Phone: (82) 2-3453-7062/7063
Telefax: (82) 2-3453-7064

PUROLITE®
ION EXCHANGE RESINS

ISO 9002
FM 40352

A-300, A-300E

Strong Base Type II Anion Exchange Resin

Technical Data

PRODUCT DESCRIPTION

Purolite A-300 is a Type II, strongly basic gel anion exchange resin with outstanding operating capacity and excellent regeneration efficiency. **A-300** removes all ions including silica and CO_2, however, it operates best on waters having a high percentage of strong acids (FMA). **A-300** can be used in all types of demineralization equipment where regeneration efficiency and high operating capacities are needed. **Purolite A-300** has excellent physical stability which allows for long life and better efficiency within the operating bed. Whole bead counts are a minimum of 92% clear beads with mechanical strengths ranging over 300 grams. **Purolite A-300** can be regenerated with sodium chloride to remove alkalinity from different water supplies. This dealkalization by ion exchange prevents the formation of insoluble carbonate precipitates and stops corrosion due to the formation of carbonic acid. **A-300** can also remove nitrates when regenerated with salt. In some dealkalization cases, small amounts of caustic is used in combination with salt during the regeneration in order to enhance the resin operation. This addition gives higher operating capacity and lower silica leakage. **Purolite A-300E** is a Type II strong base anion devoid of taste and odor. **A-300E** meets the requirements of paragraph 173.25 of the FDA Code of Federal Regulations no. 21.

Capacities and Leakages of **A-300** or **A-300E** are based on the regenerant reaching the bed at either 70°C or 95°F. With some water supplies, it will be necessary to preheat the bed prior to the introduction of the regenerant. In water supplies where the alkalinity is in excess of 50%, keep in mind that you may be unable to achieve these leakages and capacities. This is because CO_2 passing from the cation reacts with anionic sites forming HCO_3. During the regeneration process of the anion, HCO_3 is displaced by NaOH. Additional NaOH then reacts with the HCO_3 forming Na_2CO_3. Since the above leakages and capacities are based on having excess NaOH above theory, it may be necessary to compensate for this problem.

Typical Physical & Chemical Characteristics

Polymer Matrix Structure	Polystyrene Crosslinked divinylbenzene
Physical Form and Appearance	Clear Spherical Beads
Whole Bead Count	92% min.
Functional Groups	$R(CH_3)_2(C_2H_4OH)N^+$
Ionic Form, as shipped	Cl^-
Shipping Weight (approx.)	705 g/l (44 lb/ft^3)
Screen Size Range: - U.S. Standard Screen	16 - 50 mesh, wet
Particle Size Range	+1.2 mm <5%, -0.3 mm <1%
Chemical Resitance	Unaffected by dilute acids, alkalies and most solvents
Moisture Retention, Cl^- form	40 - 45%
Swelling Salt → OH	10% max.
Uniformity Coefficient	1.7 max.
Total Exchange Capacity, Cl^- form,	
wet, volumetric	1.45 - 1.6 eq/l min.
dry, weight	3.5 - 3.7 eq/kg min.
Operating Temperature, OH^- Form	105°F max. [Recommended 95°F]
Cl^- Form	170°F max.
pH Range, Stability	No Limitations

Standard Operating Conditions
(Two-Stage Demineralizer)

Operation	Rate	Solution	Minutes	Amount
Service	1.0 - 5.0 gpm/ft^3	Effluent from Cation exchanger	per design	per design
Backwash	Refer to fig. 1	Influent water	5 - 20	10 - 25 gal/ft^3
Regeneration	0.2 - 0.8 gpm/ft^3	4% NaOH	60	4 - 10 lb/ft^3
Rinse, (slow)	0.2 - 0.8 gpm/ft^3	Decationized water	60	15 - 30 gal/ft^3
Rinse, (fast)	1.0 - 5.0 gpm/ft^3	Decationized water	-	25 - 45 gal/ft^3

Backwash Expansion 50% to 75%

Design Rising Space 100%

"Gallons" refer to U.S. Gallon = 3.785 litres

HYDRAULICS

Pressure drop of a fluid passing through an ion exchange column is related to the flow rate, viscosity and temperature of the fluid. Typical values of pressure drop are found in Figure 2. Backwash removes all particulate matter filtered out by the exchanger and regrades the bed eliminating any channels which may have formed. Normally a backwash rate that expands the bed 50- 75% for 5 to 10 minutes or till the effluent is clear is recommended. Flow rate for the backwash should be achieved gradually to prevent resin loss. See Figure 1.

REGENERATION

Purolite A-300 is supplied in the chloride form and must be regenerated with a good grade of sodium hydroxide. Both the slow and fast rinse remove the excess regenerant from the exchanger bed. The slow rinse displaces the regenerant while the fast rinse rinses out all excess regenerant.

Influent Limitation

Maximum Free Chlorine	0.05 ppm
Maximum Turbidity	5 A.P.H.A. Units
Maximum Iron and Heavy Metals	0.1 ppm

Fig. 1 BED EXPANSION VS. BACKWASH FLOW RATE

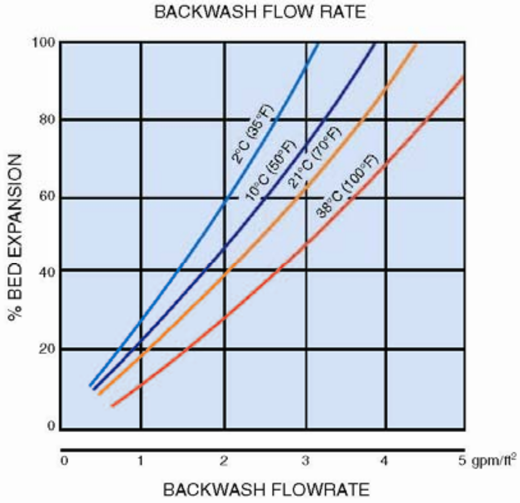
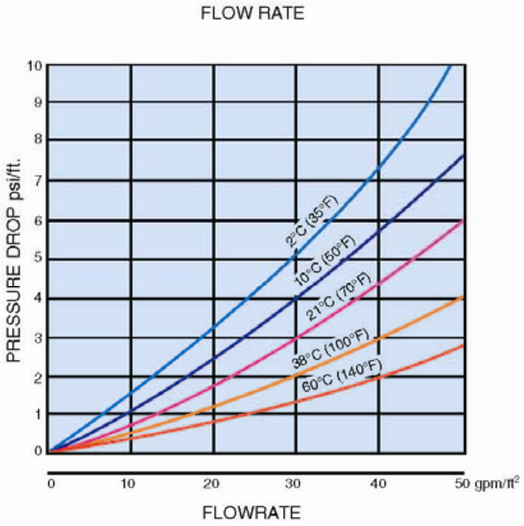
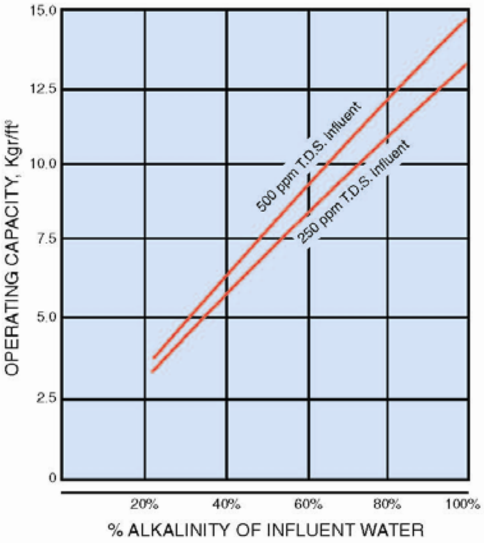


Fig. 2 PRESSURE DROP VS. FLOW RATE



DEALKALIZATION CAPACITY

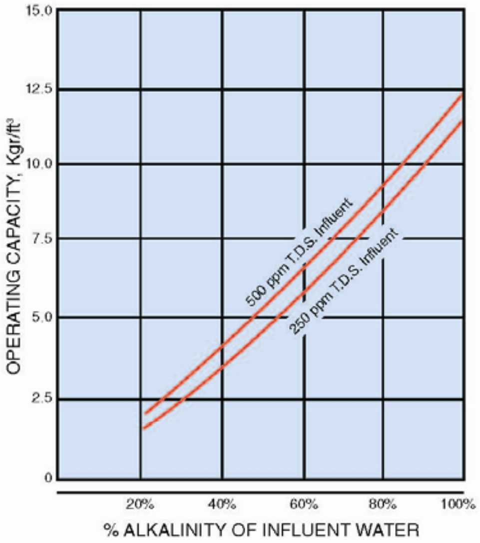
Fig. 3 CAPACITY FOR DEALKALIZATION



Capacity for Dealkalization
5 lbs. NaCl/ft³
0.25 lbs. NaOH/ft³

Down Flow Regeneration
30 inch Bed Depth
Flowrate of 2 gpm/ft³
To 10% Alkalinity End Point

Fig. 4 CAPACITY FOR DEALKALIZATION

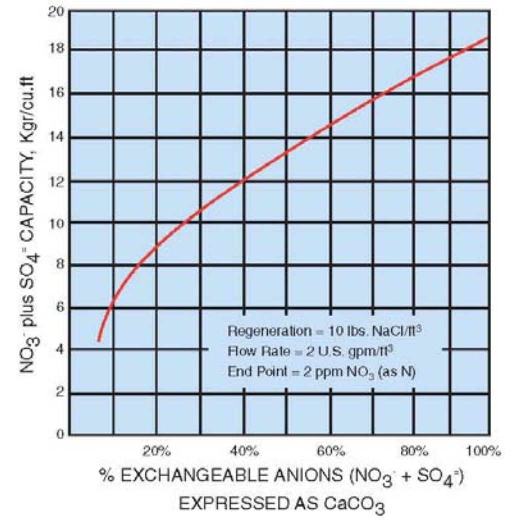


Capacity for Dealkalization
5 lbs. NaCl/ft³

Down Flow Regeneration
30 inch Bed Depth
Flowrate of 2 gpm/ft³
To 10% Alkalinity End Point

NITRATE REMOVAL

CAPACITY FOR NITRATE (NO_3)
PLUS SULFATE (SO_4) REMOVAL



CAPACITY IN KILOGRAINS/ft³

lbs. NaOH/ft³ @ 21°C (70°F) 100% Concentration	% Silica of Total Anion Analysis			
	10%	20%	30%	40%
4	20.0	19.0	17.9	17.3
5	22.7	21.0	19.9	19.0
6	24.0	22.6	21.8	20.4
7	25.2	23.7	23.1	21.8
8	25.8	24.6	24.0	22.9
9	26.3	25.2	24.7	23.7
10	26.6	25.5	25.0	24.3

BASE OPERATING CAPACITY Kgr

lbs. NaOH/ft³ @ 35°C (95°F) 100% Concentration	% Silica of Total Anion Analysis			
	10%	20%	30%	40%
4	22.9	22.0	21.0	20.1
5	24.1	23.1	22.2	21.3
6	25.0	24.0	23.0	22.2
7	26.0	24.9	23.8	23.1
8	26.7	25.4	24.5	23.8
9	26.9	26.0	25.2	24.4
10	27.0	26.2	25.4	24.6

BASE OPERATING CAPACITY Kgr

CHLORIDE CORRECTION

Percent chlorides have a direct effect on the capacity of **A-300**, The chloride correction factor must be multiplied by the capacity to determine your true capacity.

% Chlorides	0	10	20	30	40	50	60	70	80	90	100
Correctional Factor	1.00	.93	.91	.88	.87	.86	.84	.83	.82	.81	.80

Example: Base operating Capacity x Chloride Correction = Operating Capacity

SILICA LEAKAGE as ppm $CaCO_3$

lbs. NaOH/ft³ @ 21°C (70°F) 100% Concentration	% Silica of Total Anion Analysis			
	10%	20%	30%	40%
4	0.22	0.49	0.83	1.24
5	0.13	0.30	0.41	0.58
6	0.08	0.15	0.26	0.39
7	0.06	0.10	0.18	0.27
8	0.05	0.08	0.14	0.21
9	0.04	0.07	0.13	0.18
10	0.02	0.05	0.11	0.15

BASE SILICA LEAKAGE ppm $CaCO_3$

lbs. NaOH/ft³ @ 35°C (95°F) 100% Concentration	% Silica of Total Anion Analysis			
	10%	20%	30%	40%
4	0.10	0.20	0.33	0.50
5	0.05	0.11	0.18	0.25
6	0.04	0.06	0.10	0.16
7	0.03	0.05	0.08	0.11
8	0.02	0.04	0.06	0.09
9	0.01	0.03	0.05	0.08
10	0.01	0.03	0.05	0.07

BASE SILICA LEAKAGE ppm $CaCO_3$

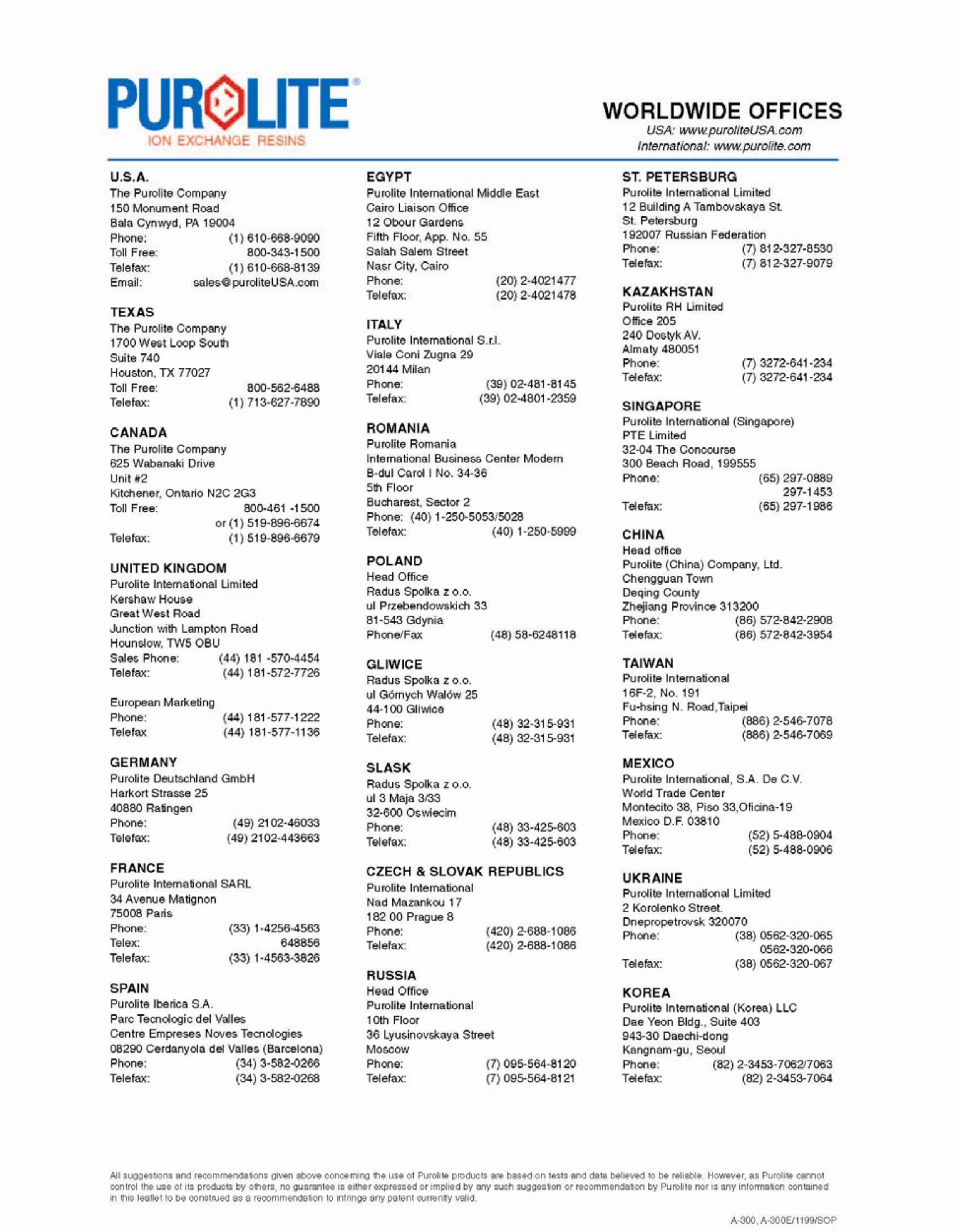
SILICA CORRECTION FACTOR

Sodium leaking through the cation will pass through the anion linking with the hydroxide group to form NaOH. As NaOH migrates down the anion bed, silica is pushed off as in the regeneration process. The higher the sodium, the higher the silica leakage.

EFFECT OF SODIUM LEAKAGE ON SILICA LEAKAGE

Regenerant Leakage	lbs. NaOH			
	4	6	8	10
1 ppm Na	1.15	1.1	1.05	1.02
3 ppm Na	1.38	1.25	1.15	1.11
5 ppm Na	1.6	1.4	1.27	1.18
7 ppm Na	1.9	1.6	1.35	1.2

Example: Base Silica Leakage x Correction Factor for Silica Leakage = Silica Leakage



PUROLITE®
ION EXCHANGE RESINS

WORLDWIDE OFFICES

USA: www.puroliteUSA.com
International: www.purolite.com

U.S.A.
The Purolite Company
150 Monument Road
Bala Cynwyd, PA 19004
Phone: (1) 610-668-9090
Toll Free: 800-343-1500
Telefax: (1) 610-668-8139
Email: sales@puroliteUSA.com

TEXAS
The Purolite Company
1700 West Loop South
Suite 740
Houston, TX 77027
Toll Free: 800-562-6488
Telefax: (1) 713-627-7890

CANADA
The Purolite Company
625 Wabanaki Drive
Unit #2
Kitchener, Ontario N2C 2G3
Toll Free: 800-461 -1500
or (1) 519-896-6674
Telefax: (1) 519-896-6679

UNITED KINGDOM
Purolite International Limited
Kershaw House
Great West Road
Junction with Lampton Road
Hounslow, TW5 OBU
Sales Phone: (44) 181 -570-4454
Telefax: (44) 181-572-7726

European Marketing
Phone: (44) 181-577-1222
Telefax (44) 181-577-1136

GERMANY
Purolite Deutschland GmbH
Harkort Strasse 25
40880 Ratingen
Phone: (49) 2102-46033
Telefax: (49) 2102-443663

FRANCE
Purolite International SARL
34 Avenue Matignon
75008 Paris
Phone: (33) 1-4256-4563
Telex: 648856
Telefax: (33) 1-4563-3826

SPAIN
Purolite Iberica S.A.
Parc Tecnologic del Valles
Centre Empreses Noves Tecnologies
08290 Cerdanyola del Valles (Barcelona)
Phone: (34) 3-582-0266
Telefax: (34) 3-582-0268

EGYPT
Purolite International Middle East
Cairo Liaison Office
12 Obour Gardens
Fifth Floor, App. No. 55
Salah Salem Street
Nasr City, Cairo
Phone: (20) 2-4021477
Telefax: (20) 2-4021478

ITALY
Purolite International S.r.l.
Viale Coni Zugna 29
20144 Milan
Phone: (39) 02-481-8145
Telefax: (39) 02-4801-2359

ROMANIA
Purolite Romania
International Business Center Modern
B-dul Carol I No. 34-36
5th Floor
Bucharest, Sector 2
Phone: (40) 1-250-5053/5028
Telefax: (40) 1-250-5999

POLAND
Head Office
Radus Spolka z o.o.
ul Przebendowskich 33
81-543 Gdynia
Phone/Fax (48) 58-6248118

GLIWICE
Radus Spolka z o.o.
ul Górnych Walów 25
44-100 Gliwice
Phone: (48) 32-315-931
Telefax: (48) 32-315-931

SLASK
Radus Spolka z o.o.
ul 3 Maja 3/33
32-600 Oswiecim
Phone: (48) 33-425-603
Telefax: (48) 33-425-603

CZECH & SLOVAK REPUBLICS
Purolite International
Nad Mazankou 17
182 00 Prague 8
Phone: (420) 2-688-1086
Telefax: (420) 2-688-1086

RUSSIA
Head Office
Purolite International
10th Floor
36 Lyusinovskaya Street
Moscow
Phone: (7) 095-564-8120
Telefax: (7) 095-564-8121

ST. PETERSBURG
Purolite International Limited
12 Building A Tambovskaya St.
St. Petersburg
192007 Russian Federation
Phone: (7) 812-327-8530
Telefax: (7) 812-327-9079

KAZAKHSTAN
Purolite RH Limited
Office 205
240 Dostyk AV.
Almaty 480051
Phone: (7) 3272-641-234
Telefax: (7) 3272-641-234

SINGAPORE
Purolite International (Singapore)
PTE Limited
32-04 The Concourse
300 Beach Road, 199555
Phone: (65) 297-0889
297-1453
Telefax: (65) 297-1986

CHINA
Head office
Purolite (China) Company, Ltd.
Chengguan Town
Deqing County
Zhejiang Province 313200
Phone: (86) 572-842-2908
Telefax: (86) 572-842-3954

TAIWAN
Purolite International
16F-2, No. 191
Fu-hsing N. Road, Taipei
Phone: (886) 2-546-7078
Telefax: (886) 2-546-7069

MEXICO
Purolite International, S.A. De C.V.
World Trade Center
Montecito 38, Piso 33, Oficina-19
Mexico D.F. 03810
Phone: (52) 5-488-0904
Telefax: (52) 5-488-0906

UKRAINE
Purolite International Limited
2 Korolenko Street.
Dnepropetrovsk 320070
Phone: (38) 0562-320-065
0562-320-066
Telefax: (38) 0562-320-067

KOREA
Purolite International (Korea) LLC
Dae Yeon Bldg., Suite 403
943-30 Daechi-dong
Kangnam-gu, Seoul
Phone: (82) 2-3453-7062/7063
Telefax: (82) 2-3453-7064

AMBERLITE® IRA400 Cl

Strong Base Anion Exchanger

Remove banner

PRODUCT DATA SHEET

AMBERLITE IRA400 Cl is a type 1, gelular, premium grade, strongly basic, anion exchange resin. It is based on crosslinked polystyrene and has high regeneration efficiency and excellent rinse performance. It is used in co-flow regeneration and conventional counterflow systems with downflow loading and upflow regeneration with air or water hold-down. Combined with a strong acid cation exchanger, AMBERLITE IRA400 Cl resin reduces both strong and weak acid concentrations to extremely low levels. Its main use is water demineralization. Other fields of application include the treatment of electroplating waste and the isolation of anionic metals.

PROPERTIES

Matrix	Polystyrene divinylbenzene copolymer
Functional Groups	Quaternary Ammonium
Physical Form	Pale yellow translucent beads
Ionic Form as shipped	Chloride
Total Exchange Capacity	≥ 1.40 meq/ml (Cl^- form)
Moisture Holding Capacity	40 to 47 % (Cl^- form)
Shipping Weight	45 lbs/ft^3
Harmonic Mean Size	0.60 to 0.75 mm
Uniformity Coefficient	≤ 1.6
Screen Grading (wet)	16 to 50 mesh (US Standard Screens)
Screen Analysis	5 % maximum on 16 mesh (US Standard Screens) 3 % maxium thru 50 mesh
Maximum reversible swelling	$Cl^- \rightarrow OH^-$: approximately 30 %

SUGGESTED OPERATING CONDITIONS

pH range	0 to 14
Maximum operating temperature	140 °F (OH^- form) / 170 °F (Cl^- form)
Minimum bed depth	24 inches
Service flow rate	1 to 3 gpm/ft^3
Regenerants (100% basis)	NaOH
Flow rate	0.25 to 0.5 gpm/ft^3
Concentration	2 to 4 %
Level	2 to 12 lbs/ft^3
Minimum contact time	30 minutes
Rinse flow rate	0.25 to 0.5 gpm/ ft^3 initially to displace regenerant, then 1.5 gpm/ft^3
Rinse water requirements	75 gal/ft^3 (approximate)

LIMITS OF USE

AMBERLITE IRA400 Cl is suitable for industrial uses. For all other specific applications such as pharmaceutical, food processing or potable water applications, it is recommended that all potential users seek advice from Rohm and Haas Company in order to determine the best resin choice and optimum operating conditions.

HYDRAULIC CHARACTERISTICS

Figure 1 shows the expected pressure drop per foot of bed depth of AMBERLITE IRA400 Cl in normal downflow operation with water at various temperatures as a function of flow rate.
Figure 2 shows the bed expansion of AMBERLITE IRA400 Cl as a function of backwash flow rate and water temperature. AMBERLITE IRA400 Cl should be backwashed for 10 minutes after each operating cycle to reclassify the resin beads and purge the bed of suspended insoluble material which may collect on top of the resin.

Fig. 1 : Pressure Drop

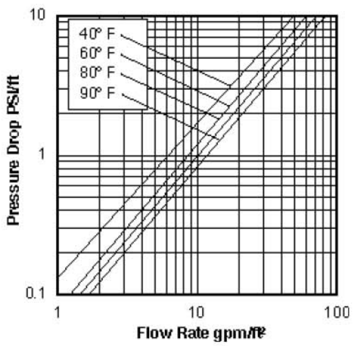
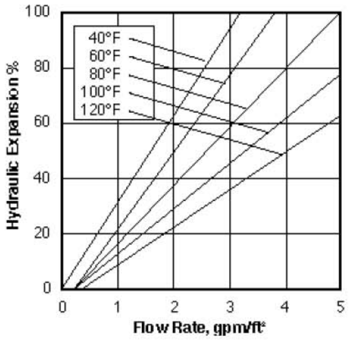


Fig. 2 : Bed Expansion



Rohm and Haas/Ion Exchange Resins - Philadelphia, PA - Tel. (800) RH AMBER - Fax: (215)) 409-4534
Rohm and Haas/Ion Exchange Resins - 75579 Paris Cedex 12 - Tel. (33) 1 40 02 50 00 - Fax : 1 43 45 28 19

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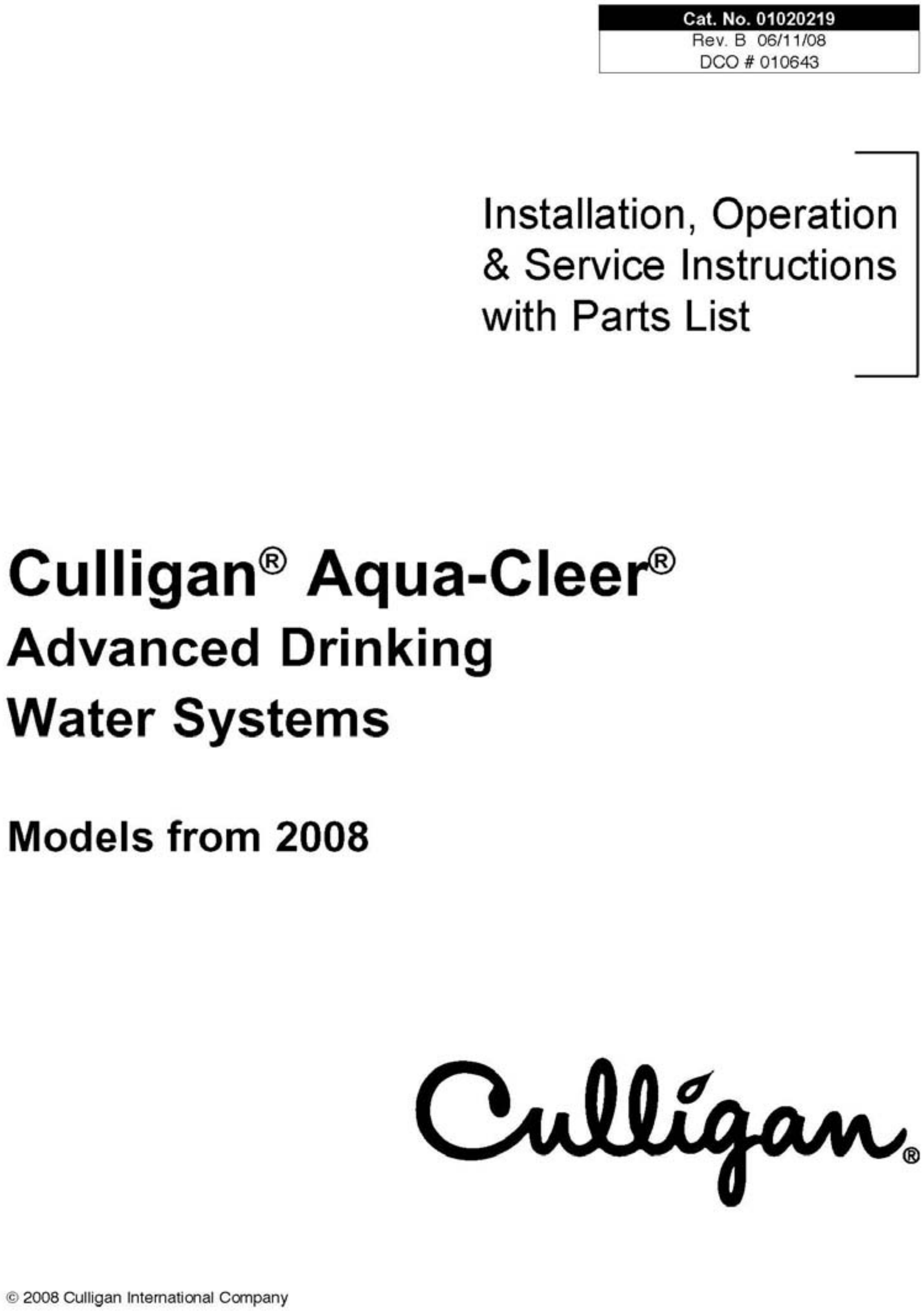
Appendix B

System Specifications for Culligan® Aqua-Cleer® Reverse Osmosis unit



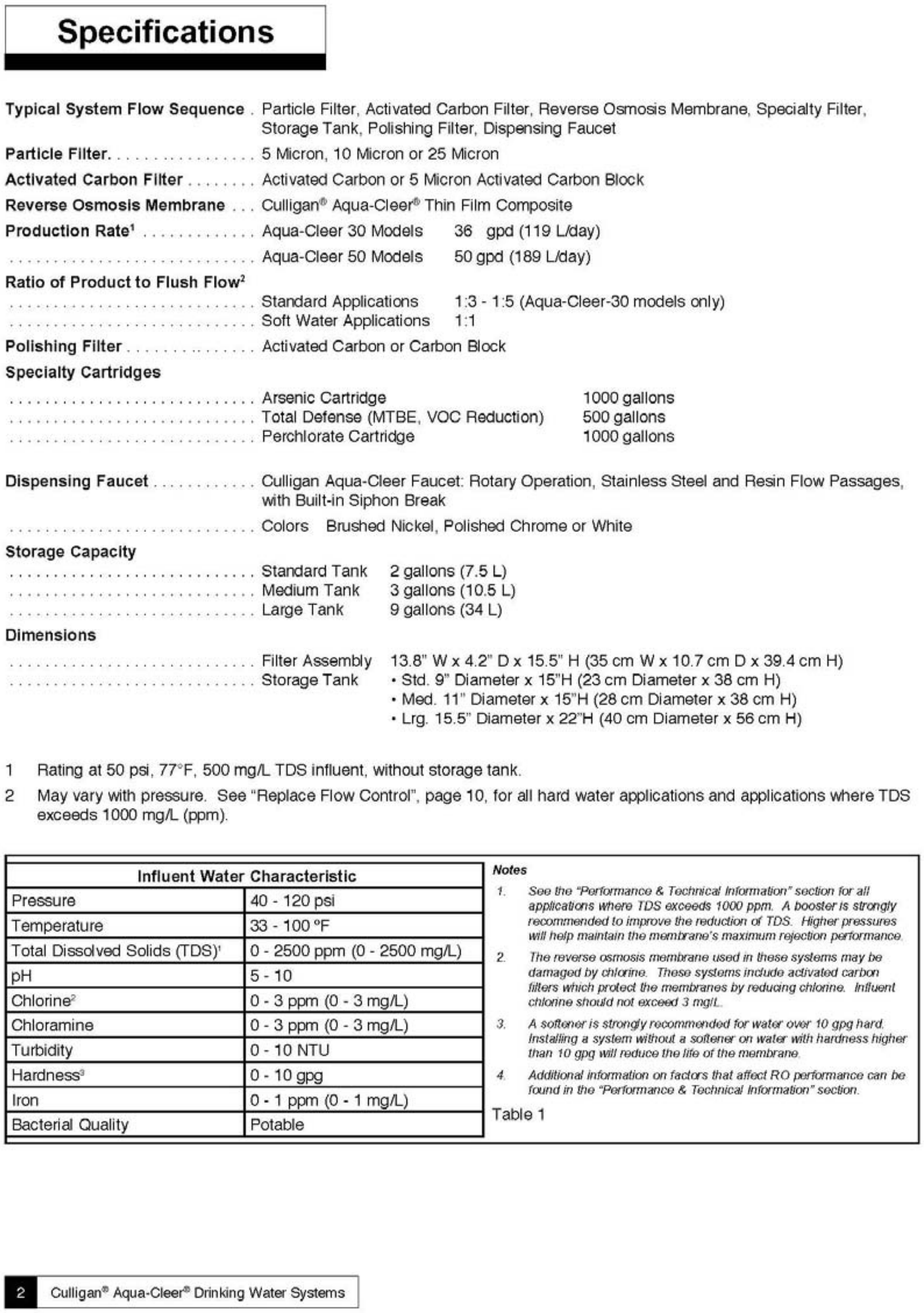
Cat. No. 01020219
Rev. B 06/11/08
DCO # 010643

Installation, Operation
& Service Instructions
with Parts List

Culligan® Aqua-Cleer®
Advanced Drinking Water Systems

Models from 2008

Culligan®



Specifications

Typical System Flow Sequence	Particle Filter, Activated Carbon Filter, Reverse Osmosis Membrane, Specialty Filter, Storage Tank, Polishing Filter, Dispensing Faucet	
Particle Filter	5 Micron, 10 Micron or 25 Micron	
Activated Carbon Filter	Activated Carbon or 5 Micron Activated Carbon Block	
Reverse Osmosis Membrane	Culligan® Aqua-Cleer® Thin Film Composite	
Production Rate[1]	Aqua-Cleer 30 Models	36 gpd (119 L/day)
	Aqua-Cleer 50 Models	50 gpd (189 L/day)
Ratio of Product to Flush Flow[2]		
	Standard Applications	1:3 - 1:5 (Aqua-Cleer-30 models only)
	Soft Water Applications	1:1
Polishing Filter	Activated Carbon or Carbon Block	
Specialty Cartridges		
	Arsenic Cartridge	1000 gallons
	Total Defense (MTBE, VOC Reduction)	500 gallons
	Perchlorate Cartridge	1000 gallons
Dispensing Faucet	Culligan Aqua-Cleer Faucet: Rotary Operation, Stainless Steel and Resin Flow Passages, with Built-in Siphon Break	
	Colors	Brushed Nickel, Polished Chrome or White
Storage Capacity		
	Standard Tank	2 gallons (7.5 L)
	Medium Tank	3 gallons (10.5 L)
	Large Tank	9 gallons (34 L)
Dimensions		
	Filter Assembly	13.8" W x 4.2" D x 15.5" H (35 cm W x 10.7 cm D x 39.4 cm H)
	Storage Tank	• Std. 9" Diameter x 15"H (23 cm Diameter x 38 cm H) • Med. 11" Diameter x 15"H (28 cm Diameter x 38 cm H) • Lrg. 15.5" Diameter x 22"H (40 cm Diameter x 56 cm H)

1 Rating at 50 psi, 77°F, 500 mg/L TDS influent, without storage tank.

2 May vary with pressure. See "Replace Flow Control", page 10, for all hard water applications and applications where TDS exceeds 1000 mg/L (ppm).

Influent Water Characteristic	
Pressure	40 - 120 psi
Temperature	33 - 100 °F
Total Dissolved Solids (TDS)[1]	0 - 2500 ppm (0 - 2500 mg/L)
pH	5 - 10
Chlorine[2]	0 - 3 ppm (0 - 3 mg/L)
Chloramine	0 - 3 ppm (0 - 3 mg/L)
Turbidity	0 - 10 NTU
Hardness[3]	0 - 10 gpg
Iron	0 - 1 ppm (0 - 1 mg/L)
Bacterial Quality	Potable

Notes

1. *See the "Performance & Technical Information" section for all applications where TDS exceeds 1000 ppm. A booster is strongly recommended to improve the reduction of TDS. Higher pressures will help maintain the membrane's maximum rejection performance.*
2. *The reverse osmosis membrane used in these systems may be damaged by chlorine. These systems include activated carbon filters which protect the membranes by reducing chlorine. Influent chlorine should not exceed 3 mg/L.*
3. *A softener is strongly recommended for water over 10 gpg hard. Installing a system without a softener on water with hardness higher than 10 gpg will reduce the life of the membrane.*
4. *Additional information on factors that affect RO performance can be found in the "Performance & Technical Information" section.*

Table 1

Component Description

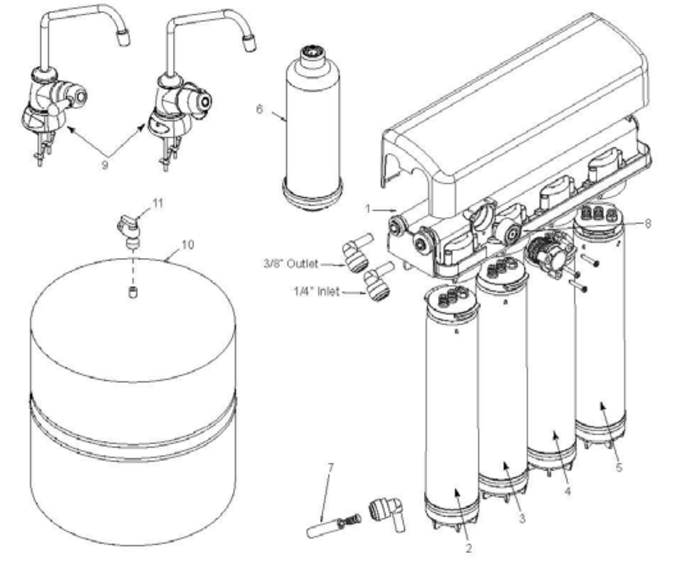


Figure 2

Item	Description
1	Manifold Assembly
2	5 Micron Sediment Filter
	10 Micron Sediment Filter
	25 Micron Sediment Filter
3	Carbon Block Filter
	Granular Activated Carbon Filter
4	30 GPD Reverse Osmosis Membrane
	50 GPD Reverse Osmosis Membrane
	Nanofiltration Reverse Osmosis Membrane
5	Arsenic Filter
	Perchlorate Filter
	Carbon Block Filter (MTBE, VOC)
	Purifier Cartridge
	Healthy Cartridge (Add Calcium & Magnesium back into water for better taste)
6	Post Carbon Filter
7	Flow Control
8	Automatic Shut-off Valve
9	Faucet
10	2 Gallon Storage Tank
	3 Gallon Storage Tank
	9 Gallon Storage Tank
11	Ball Valve
*	Monitor (Not Shown)

Performance & Technical Information

The performance of the Aqua-Cleer® system can be characterized and judged by the quality and quantity of the water produced by the system. By measuring the contaminant removal performance and flow rates of the system, its operating status can be easily evaluated.

Factors Which Affect Performance

Performance of the reverse osmosis membrane is affected by several factors which must be considered when judging the condition of the system. The main factors which affect system performance are pressure, temperature, total dissolved solids level, recovery and pH.

Pressure

Water pressure affects both the quantity and quality of the water produced by the RO membrane. Generally, the more water pressure, the better the performance of the system. Be careful not to go below 40 psi or exceed 120 psi, the minimum and maximum operating pressure of the Aqua-Cleer system.

Temperature

The reverse osmosis process slows with decreasing temperature. To compensate, a temperature correction factor is used to adjust the actual performance of the RO membrane filter to the standard temperature of 77°F (25°C). This allows the performance of the unit to be accurately gauged against Culligan's published standards. Temperature does not affect the concentrate flow rate.

Total Dissolved Solids

The minimum driving force which is necessary to stop or reverse the natural osmosis process is termed osmotic pressure. As the total dissolved solids level of the feed water increases, the amount of osmotic pressure increases and acts as back pressure against the reverse osmosis process. Osmotic pressure becomes significant at TDS levels above 500 mg/L (ppm).

Hardness

Hardness is the most common membrane foulant. If ignored, this relatively harmless component of feed water will scale a membrane over time. Use of a softener will reduce the fouling effect on a membrane. One way to detect too much hardness in the feed water is the weight of a membrane installed for a period of time. A fouled membrane (dried) will weigh significantly more than a new membrane. The increase in weight is a result of precipitated hardness inside the membrane.

Iron

Iron is another common membrane foulant. There are a variety of types of iron, some of which cannot be removed by an iron filter. Clear water iron can be removed more effectively by a softener. Particulate iron can be removed more effectively by a 1 micron filter. Organic-bound iron can be removed only by activated carbon or macroporous anion resin. If there is enough iron to exceed the EPA secondary drinking water standard and softening the water is not an option and the iron is soluble, then an iron filter is appropriate. If none of these are an option then regular replacement of membranes will have to be accepted.

Note: Increased weight of the RO cartridge may be a foulant other than hardness.

Product Water Recovery

Product water recovery plays an important role in determining membrane and system performance. Recovery refers to the amount of water produced in relation to the amount of water sent to drain. The standard calculation is:

% Recovery = Product Water ÷ (Product Water + Waste Water) x 100

The Aqua-Cleer 30 uses a flow control assembly to restrict the flow of waste water to the drain. This restriction helps maintain pressure against the membrane. The sizing of the flow control assembly determines the recovery rating of the system. The Aqua-Cleer -30 is manufactured with a recovery rating designed to be around 25%. Depending on temperature, pressure and tolerances the actual recovery value may be slightly different for each system.

For maximum efficiency on most soft water installations the standard flow control assembly can be replaced with a 40% flow control assembly.

Adjusting the recovery rating requires replacing the flow control assembly. Refer to the page 10 for a detailed description of steps involved in this modification.

Performance Measurements

Note: *Changing the flow control voids the NSF listing. Remove the NSF data label from the system if you adjust the flow control.*

When collecting water samples from the manifold, insert a short 2”-3” length of tubing into the fitting on the manifold to catch the water sample.

Measuring TDS Levels

This procedure requires the use of a Total Dissolved Solids (TDS) meter (figure 17) (P/N D0-4705-04). On a triple-range meter, always set the instrument on its highest scale and work down until the proper scale is reached. The meter can be damaged if the needle is allowed to run off the scale.

To accurately check RO membrane performance, water samples should be taken directly from the product water outlet on the manifold assembly. Avoid taking samples from the faucet.

Measure and record the TDS level of the feed water and product water as follows:

- Rinse the cell cup twice with water to be tested, then fill to the top.
- Press the button on the front of the meter and read the dial for the dissolved solids content of the product water in parts per million (ppm).

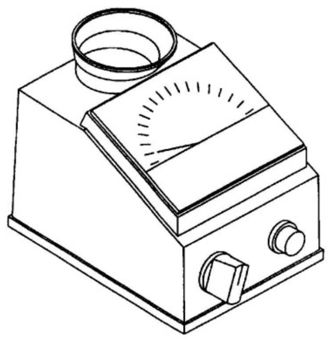


Figure 17

Measuring Flow Rates

To measure flow rates, it is necessary to use a graduated cylinder (100 ml suggested), and a watch or stopwatch with a second hand. Measure and record the product and concentrate flow rates as follows:

- Collect the water sample directly from the manifold for exactly one minute or exactly two minutes.
- Convert the measured flow rate to gallons per day (gpd) as follows:

one minute sample: ml collected x 0.40 conversion = gpd
two minute sample: ml collected x 0.20 conversion = gpd

Measuring Temperature

Use a thermometer to measure the temperature of the product water. It is most convenient to take this reading when the product water flow rate is checked.

Checking System Performance

Procedure

The following procedure is summarized on the Performance Worksheet printed on the last page of this manual. It details the measurement and evaluation of the key aspects of Aqua-Cleer system performance:

- Quality of water produced
- Quantity of water produced and stored
- Efficiency of operation

This procedure should be used to evaluate and record the performance of a new system and to check the performance of an operational system. The results of the new system performance evaluation should be retained as a benchmark of system performance in the years to come.

Checking Quality

Measure and record the TDS level of both the product water and the feed water. Calculate the percent removal of TDS as follows:

$$\text{Removal} = \frac{(\text{Feed Water TDS} - \text{Product Water TDS}) \times 100\%}{(\text{Feed Water TDS})}$$

As an example, consider a system which is producing 50 mg/L product water from a 1000 mg/L source:

$$[(1000 - 50) \div 1000] \times 100\% = 95\% \text{ Removal}$$

Checking Quantity Produced

Measure and record both the flow rate and temperature of the product water. Record the temperature correction factor from table 3, page 26, which corresponds to the measured flow rate to the 77°F (25°C) standard as follows:

Adjusted Flow Rate = Measured Flow Rate ÷ Temperature Correction Factor

As an example, if the above system is producing 24.15 gpd at 60°F, the Temperature Correction Factor from Table 3 is 0.69.

24.15 gpd ÷ 0.69 = 35 gpd @ 77°F

The TDS levels of the product and feed water were measured in the previous section. To accurately predict the performance of the RO module, the feed water pressure must be adjusted to account for osmotic pressure. Calculate osmotic pressure as follows:

Osmotic Pressure = 1 psi for every 100 mg/L TDS

From the previous example system: 1000 ÷ 100 = 10 psi Osmotic Pressure

Since osmotic pressure acts as back pressure against the RO process, it is subtracted from the measured feed water pressure to determine the effective module pressure. Measure the feed water pressure and calculate the effective module pressure as follows:

Effective Module Pressure = Measured Pressure - Osmotic Pressure

If the pressure measured from our example system is 60 psi: 60 - 10 = 50 psi Effective Module Pressure

Using the effective module pressure, read the standard product flow rate from flow graphs 2, 3 and 4. For our example system, we find the standard product flow is 35 gpd at 50 psi. Comparing this to the adjusted flow rate, we find the example system operating within the limits of the published standard.

Checking Quantity Stored

Following the guidelines below will allow you to predict the volume of water which will be stored by the tank as well as reduce the risk of damage to the storage tank.

The storage tank uses a rubber bladder attached to the tank wall with air pressure on one side to push product water out of the tank. This bladder is stretched when the tank is filled with water. Too much stretching can damage the bladder or pull it away from the tank's wall causing failure. We've prepared a easy method to determine the proper air pressure based on the application's requirements.

The 70% rule

We recommend that the tank never hold more than 70% of its internal volume as water. Table 2, page 25, lists the water volumes versus tank size based on air pressure and product pressure. Values are listed for 5, 10 & 15 psi air pressure settings. Note: Before using the table adjust the influent water pressure to product pressure.

Influent Water Pressure x 0.67 = Product Pressure

Table 2

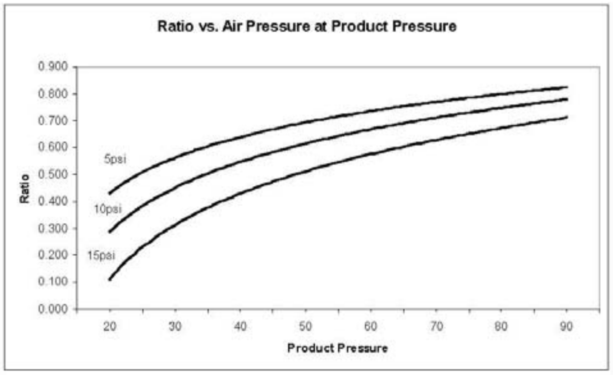
@ 5 PSI Precharge	**Product Water Pressure**						
Culligan Model	**Total**	20	30	40	50	60	70
	Gallons	43.2%	56.0%	64.0%	69.6%	73.6%	76.7%
01005095 (2 Gallon)	3.2	1.4	1.8	2.0	2.2	2.4	2.5
01004776 (3 Gallon)	4.4	1.9	2.5	2.8	3.1	3.2	3.4
01004765 (9 Gallon)	14	6.0	7.8	9.0	9.7	10.3	10.7

@ 10 PSI Precharge	**Product Water Pressure**						
Culligan Model	**Total**	20	30	40	50	60	70
	Gallons	28.8%	44.7%	54.8%	61.8%	66.9%	70.8%
01005095 (2 Gallon)	3.2	0.9	1.4	1.8	2.0	2.1	2.3
01004776 (3 Gallon)	4.4	1.3	2.0	2.4	2.7	2.9	3.1
01004765 (9 Gallon)	14	4.0	6.3	7.7	8.7	9.4	9.9

@ 15 PSI Precharge	**Product Water Pressure**						
Culligan Model	**Total**	20	30	40	50	60	70
	Gallons	11.7%	30.9%	43.0%	50.1%	57.4%	63.8%
01005095 (2 Gallon)	3.2	0.3	0.9	1.3	1.5	1.8	2.0
01004776 (3 Gallon)	4.4	0.5	1.4	2.0	2.2	2.6	2.9
01004765 (9 Gallon)	14	2.0	4.6	6.0	7.5	8.2	8.8

How to use the tables above

1. Determine the product water pressure by attaching a pressure gauge to the feed line.
2. Select your tank size and see what ratio you get at 5 psi air pressure using your calculated product pressure. (Ex. 50 psi product pressure at 5 psi for 2 gallon tank has a ratio of 69.6%)
3. If ratio is above 70% then the air pressure should be increased. Look at graph 1 to determine relative air pressure to maintain a 70% or lower ratio.
4. Once air pressure and ratio is identified take the total tank volume and multiply it by the ratio value to get the water storage capacity of the tank. (Ex. @10 psi air pressure (pre-charge) and 50 psi product water pressure ratio is 61.8%. Capacity for 3 gallon tank is 4.4 x .618 = 2.7 gallons)



Graph 1

Checking Efficiency

Measure and record the product water flow and the concentrate water flow. Calculate the percent recovery as follows:

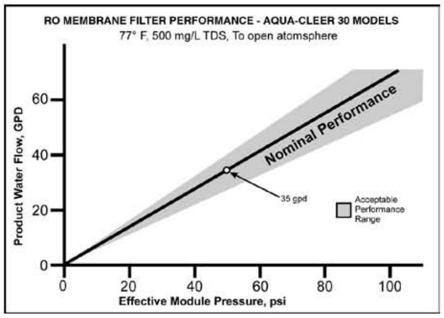
$$\% \text{ Recovery} = \frac{\text{Product Water Flow}}{(\text{Product Water Flow} + \text{Conc. Water Flow})} \times 100\%$$

If the concentrate flow rate for the example system is measured at 66 gpd:

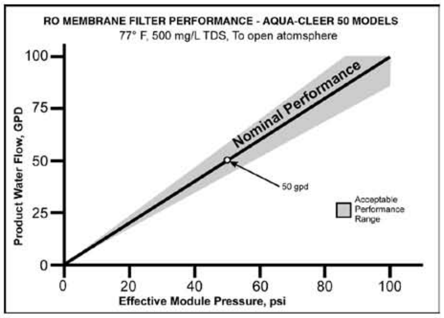
$$22 \text{ gpd} \div (22 \text{ gpd} + 66 \text{ gpd}) \times 100\% = 25\% \text{ Recovery}$$

Table 3 - Temperature Correction Factors (77° F [25° C] rating multiplied by correction factor equals capacity)

Feed Water Temperature		**Correction Factor**	**Feed Water Temperature**		**Correction Factor**	**Feed Water Temperature**		**Correction Factor**
°F	**°C**		**°F**	**°C**		**°F**	**°C**	
36	2	0.33	52	11	0.56	68	20	0.83
38	3	0.34	54	12	0.59	70	21	0.87
40	4	0.37	56	13	0.63	72	22	0.90
42	6	0.40	58	14	0.65	74	23	0.94
44	7	0.43	60	16	0.69	76	24	0.96
46	8	0.46	62	17	0.72	77	25	1.00
48	9	0.50	64	18	0.76	78	26	1.03
50	10.0	0.52	66	19	0.79	80	27	1.06



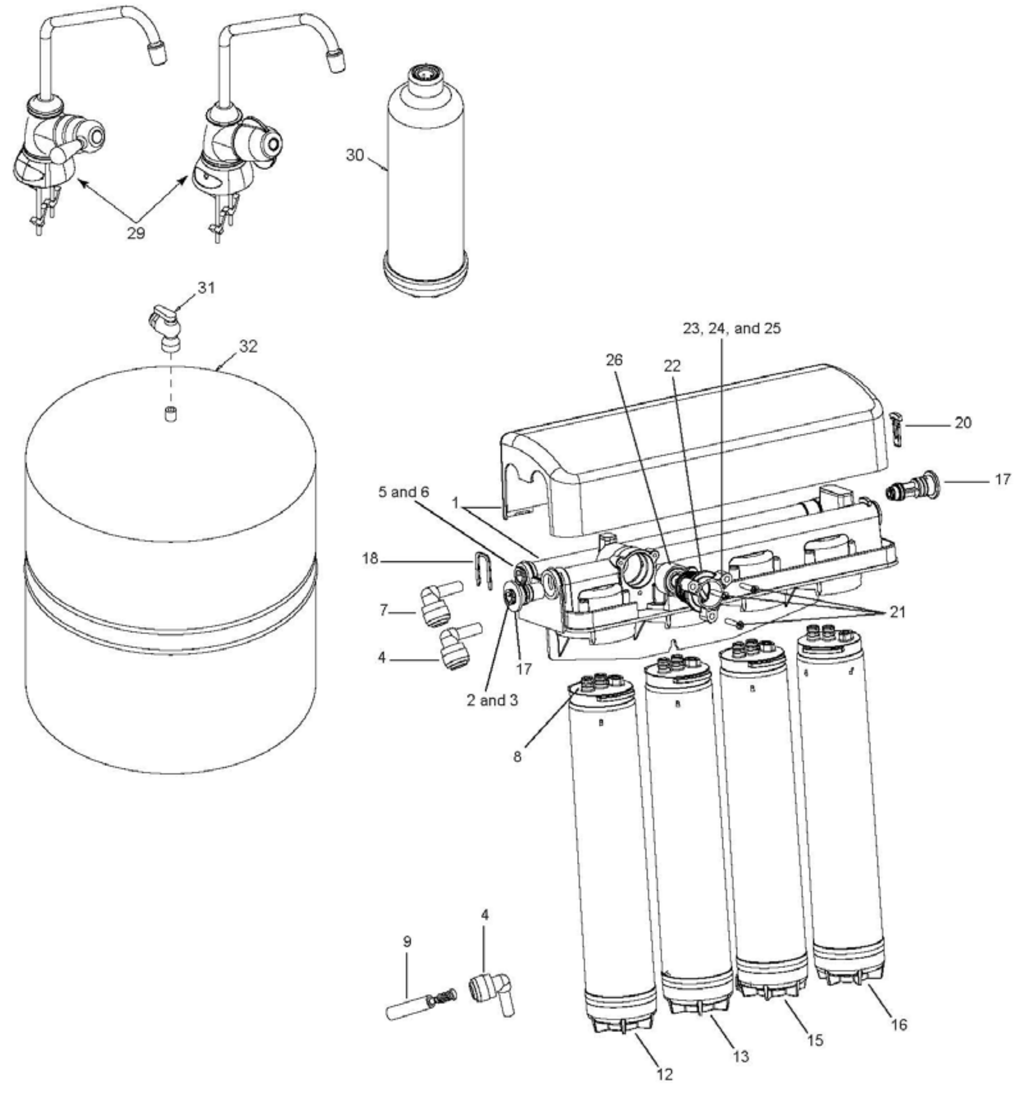
Graph 2



Graph 3

Parts List

Aqua-Cleer Drinking Water System



Item	Part No.	Description	Qty.
1	P1-0202-57	Manifold Assm., 6 PK	1
2	P1-00094-13	O-Ring 1/4", 25 PK	1
3	P1-0044-33	Collar, 1/4", 25 PK	1
4	P1-0047-13	Push-in Elbow 1/4", 10 PK	1
5	P1-0094-14	O-Ring 3/8", 25 PK	1
6	P1-0043-26	Collar, 3/8", 25 PK	1
7	P1-0047-14	Push-in Elbow 3/8", 10 PK	1
8	P1-0205-19	O-Ring, 50 PK	4ea/ Cartridge
9	P1-0205-21	Flow Control Assembly, 30 GPD, 10 PK (Red)	1
	P1-0205-22	Flow Control Assembly, 50 GPD, 10 PK (Black)	1
	P1-0205-23	Flow Control Assembly (50% Recovery), 30 GPD, 10 PK (Green)	1
	P1-0205-24	Flow Control Assembly (50% Recovery), 30 GPD, 10 PK (Yellow)	1
	P1020772	Flow Control Assembly (25% Recovery), 30 GPD, 10 PK (Orange)	1
	P1020773	Flow Control Assembly (25% Recovery), NanoFilter and 50 GPD, 10 PK (White)	1
12	P1-0202-58	Particle Filter Element, 5 Micron, 12 PK	1
	P1-0202-60	Particle Filter Element, 10 Micron, 12 PK	
	P1-0202-62	Particle Filter Element, 25 Micron, 12 PK	
13	P1-0202-64	Granular Carbon Prefilter, 12 PK	1
	P1-0202-66	Carbon Block Prefilter, 12 PK	
15	P1-0202-68	RO Module, 30 GPD, 12 PK	1
	P1-0202-70	RO Module, 50 GPD, 12 PK	
	P1-0202-71	RO Module, Nanofilter, 12 PK	
	P1-0202-74	Total Defense Cartridge (VOC Reduction), 12 PK	1
17	P1-0205-25	Check Valve Assembly, 10 PK	1
18	P1-0205-26	Front Clip, 10 PK	1
20	P1-0205-28	Rear Clip, 10 PK	1

21	P0-4021-96	Screw #10.9 X 1.00" Phil. Pan Head, 50 PK	3
23	P1-0043-22	O-Ring Large ASV, 10 PK	1
24	P1-0043-21	O-Ring Medium ASV, 10 PK	1
25	P1-0043-20	O-Ring Small ASV, 10 PK	1
Item	Part No.	Description	Qty.
27	01-0205-30	Shutoff Cap Assm. (Includes Items 22, 23, 24, 25, 26), 10 PK	1
29	01-0184-01	Faucet, Chrome, Non-Electric	1
	01-0084-02	Faucet, White, Non-Electric	
	01-0186-07	Faucet, Brushed Nickel, Non-Electric	
	01-0184-68	Faucet, Chrome, Electric	
	01-0084-69	Faucet, White, Electric	
	01-0186-04	Faucet, Brushed Nickel, Electric	
30	P1-0042-91	GAC Carbon Post Filter 10 Pk	1
	01-0047-68	GAC Carbon Post Filter 50 Pk	
	01-0146-12	Carbon Block Post Filter 10 Pk	
	01-0146-13	Carbon Block Post Filter 50Pk	
*	01-0107-48	Mounting Clip, Polishing Filter	
31	01-0045-50	Plastic Ball Valve, .25 NPTFemale X .375 J. G.	1
32	01-0050-95	Storage Tank (2 Gallon)	1
	01-0047-76	Storage Tank (3 Gallon)	
	01-0047-65	Storage Tank (9 Gallon)	
	01-0100-64	Storage Tank Stand, Plastic	
*	00-4021-84	Tubing, - 1/4" O.D.	
	01-0002-87	Tubing -3/8" O.D.	
*	01-0196-19	Aqua-Cleer Sentry™ Monitor	
*	P1-0047-15	Tee 3/8 x 3/8 x 3/8	1
*	P1-0060-26	Storage Tank Bracket, Steel Gallon Tank, 3 PK	
*	P1-0040-61	Storage Tank Bracket, Steel Gallon Tank, 3 PK	
*	P1-0047-28	Icemaker Tee, 3/8"x3/8"x1/4"	
*	P1-0202-77	Sanitation Cartridge, 6 PK	1
*	P1-0203-92	Single Head Assembly, 6 PK	1
*	P1-0202-79	Bypass Cartridge, 12 PK	1

Appendix C

Ion Exchange Results

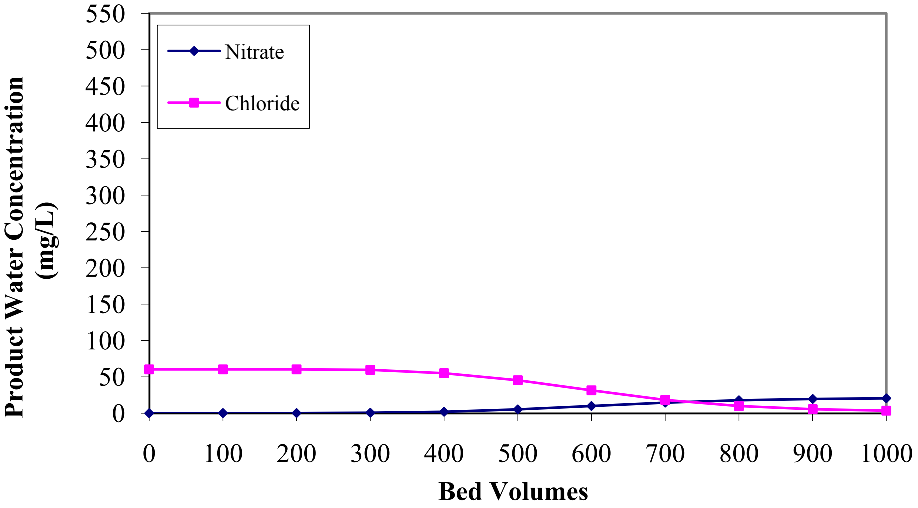


Figure C-1: Breakthrough curve of 50 mL Dowex™ NSR-1 at a hydraulic loading of 5.2 m/h. Nitrate and chloride were measured as N and Cl^-, respectively. Experiment 4-1-2. (Feed water nitrate = 23 mg NO_3^--N/L)

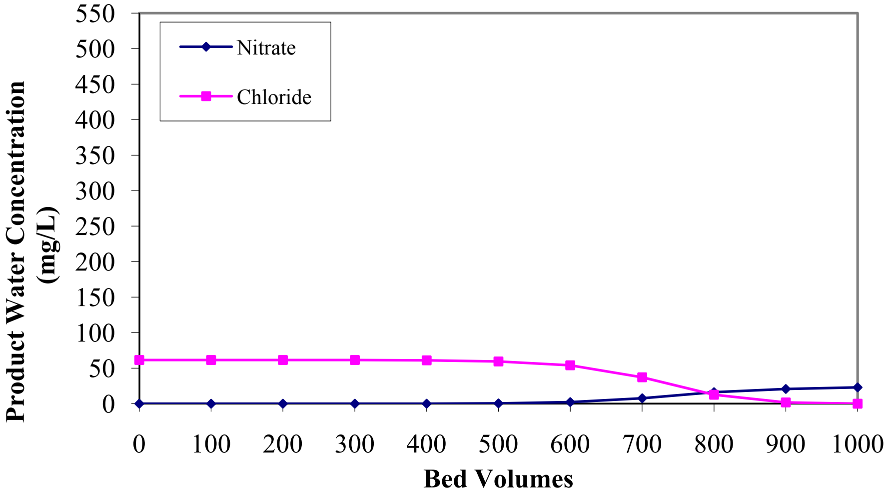


Figure C-2: Breakthrough curve of 100 mL Dowex™ NSR-1 at a hydraulic loading of 10.4 m/h. Nitrate and chloride were measured as N and Cl^-, respectively. Experiment 4-1-3. (Feed water nitrate = 23 mg NO_3^--N/L)

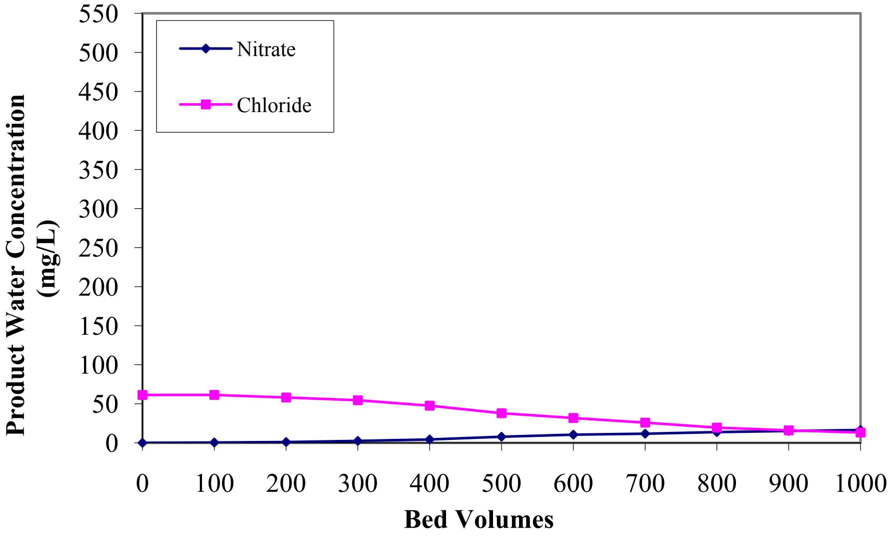


Figure C-3: Breakthrough curve of 50 mL Dowex™ NSR-1 at a hydraulic loading of 10.4 m/h. Nitrate and chloride were measured as N and Cl^-, respectively. Experiment 4-1-4. (Feed water nitrate = 23 mg NO_3^--N/L)

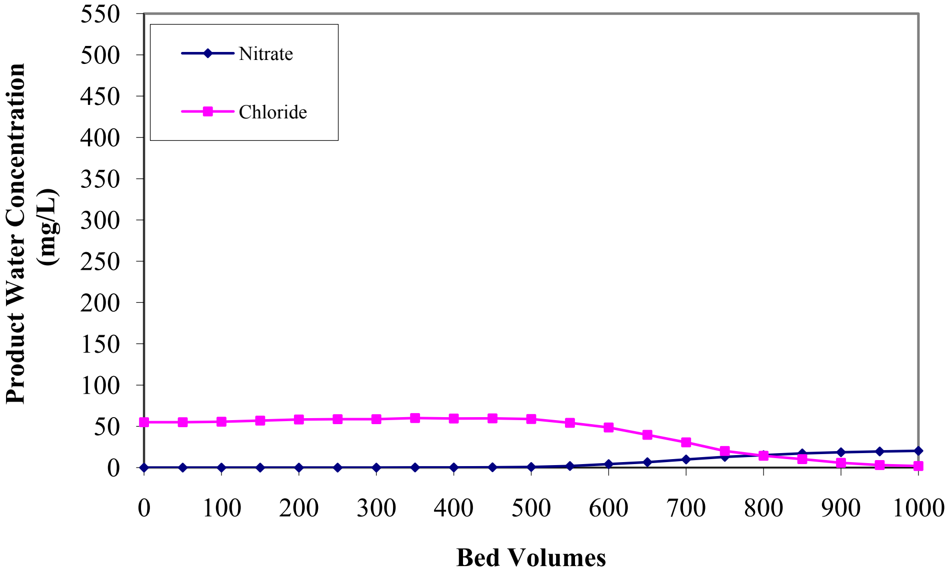


Figure C-4: Breakthrough curve of 100 mL Purolite® A-520E at a hydraulic loading of 5.2 m/h. Nitrate and chloride were measured as N and Cl^-, respectively. Experiment 4-1-5. (Feed water nitrate = 23 mg NO_3^--N/L)

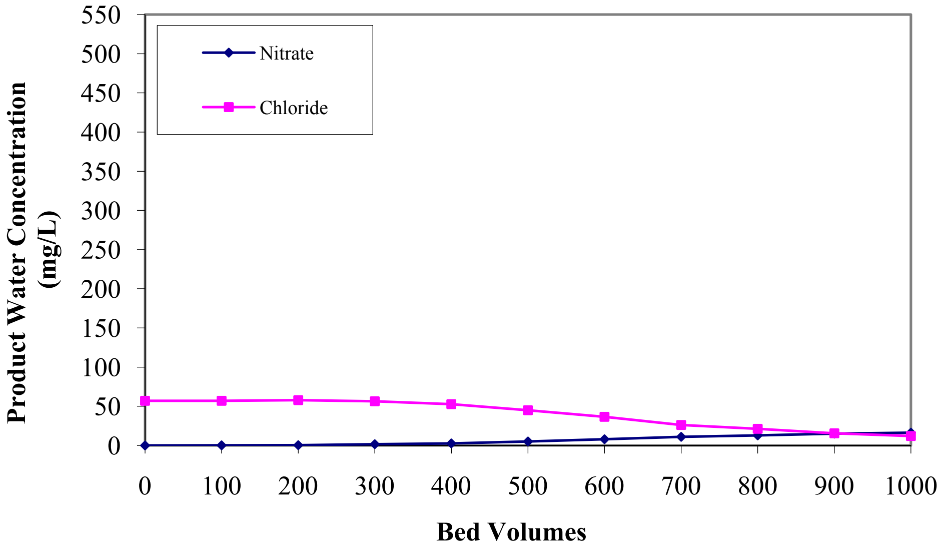


Figure C-5: Breakthrough curve of 50 mL Purolite® A-520E at a hydraulic loading of 5.2 m/h. Nitrate and chloride were measured as N and Cl^-, respectively. Experiment 4-1-6. (Feed water nitrate = 23 mg NO_3^--N/L)

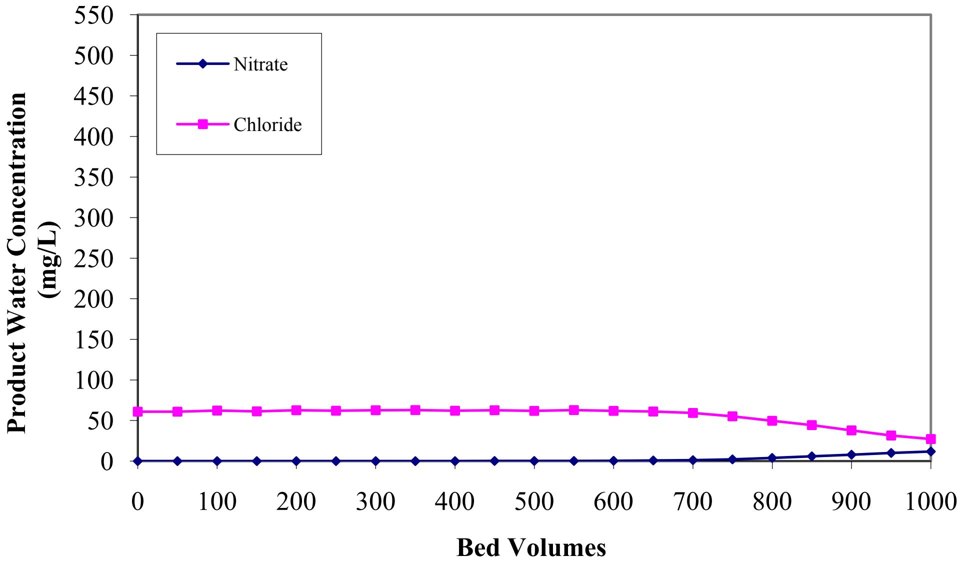


Figure C-6: Breakthrough curve of 100 mL Purolite® A-300E at a hydraulic loading of 5.2 m/h. Nitrate and chloride were measured as N and Cl^-, respectively. Experiment 4-1-7. (Feed water nitrate = 23 mg NO_3^--N/L)

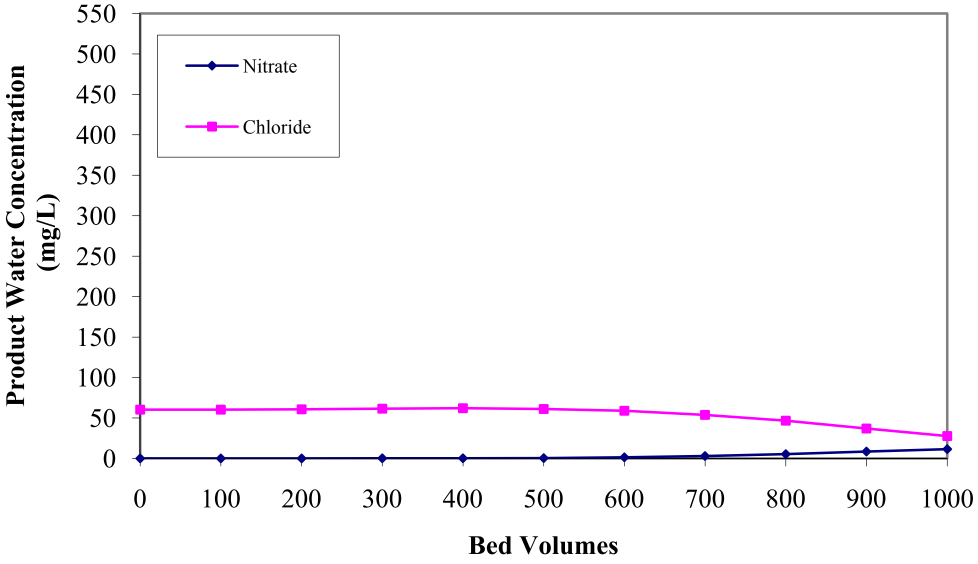


Figure C-7: Breakthrough curve of 50 mL Purolite® A-300E at a hydraulic loading of 5.2 m/h. Nitrate and chloride were measured as N and Cl^-, respectively. Experiment 4-1-8. (Feed water nitrate = 23 mg NO_3^--N/L)

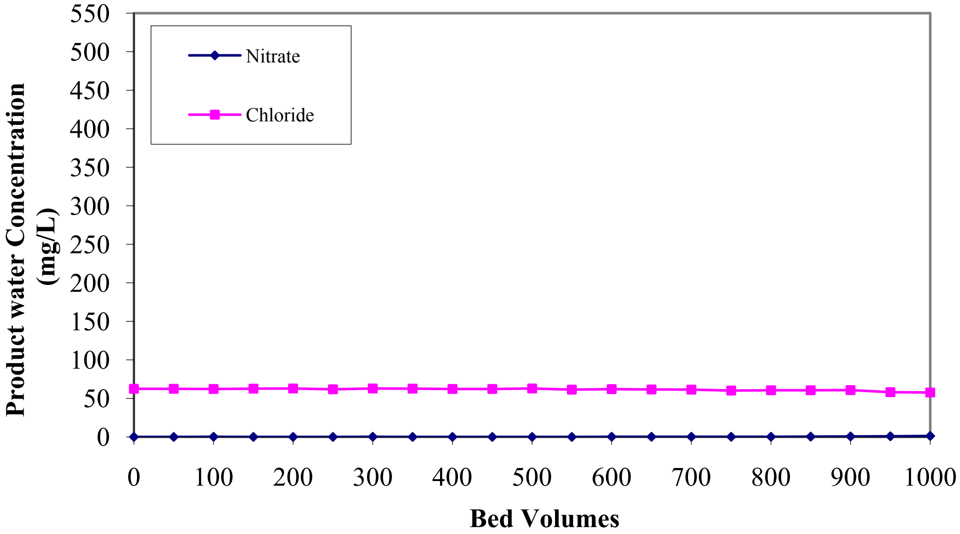


Figure C-8: Breakthrough curve of 100 mL Amberlite® IRA400 Cl at a hydraulic loading of 5.2 m/h. Nitrate and chloride were measured as N and Cl^-, respectively. Experiment 4-1-9. (Feed water nitrate = 23 mg NO_3^--N/L)

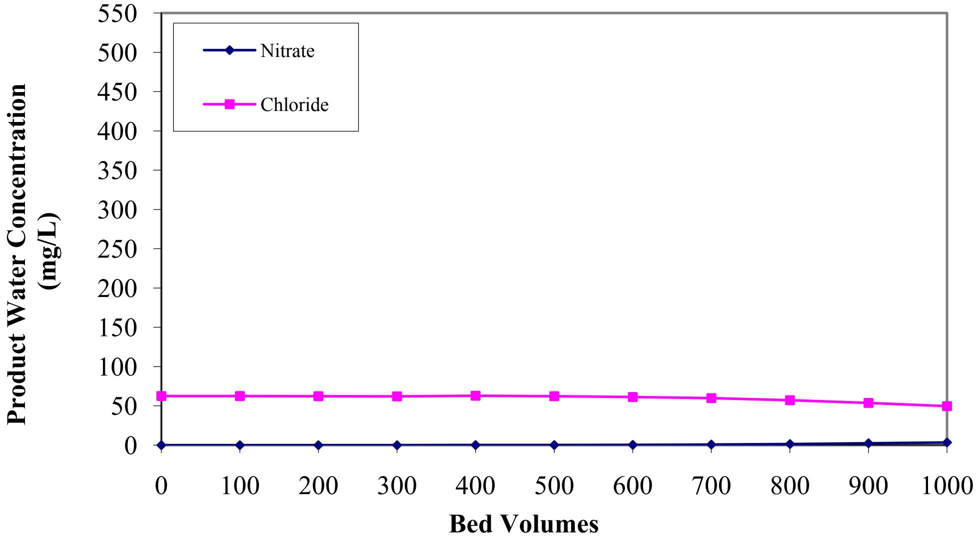


Figure C-9: Breakthrough curve of 50 mL Amberlite® IRA400 Cl at a hydraulic loading of 5.2 m/h. Nitrate and chloride were measured as N and Cl^-, respectively. Experiment 4-1-10. (Feed water nitrate = 23 mg NO_3^--N/L)

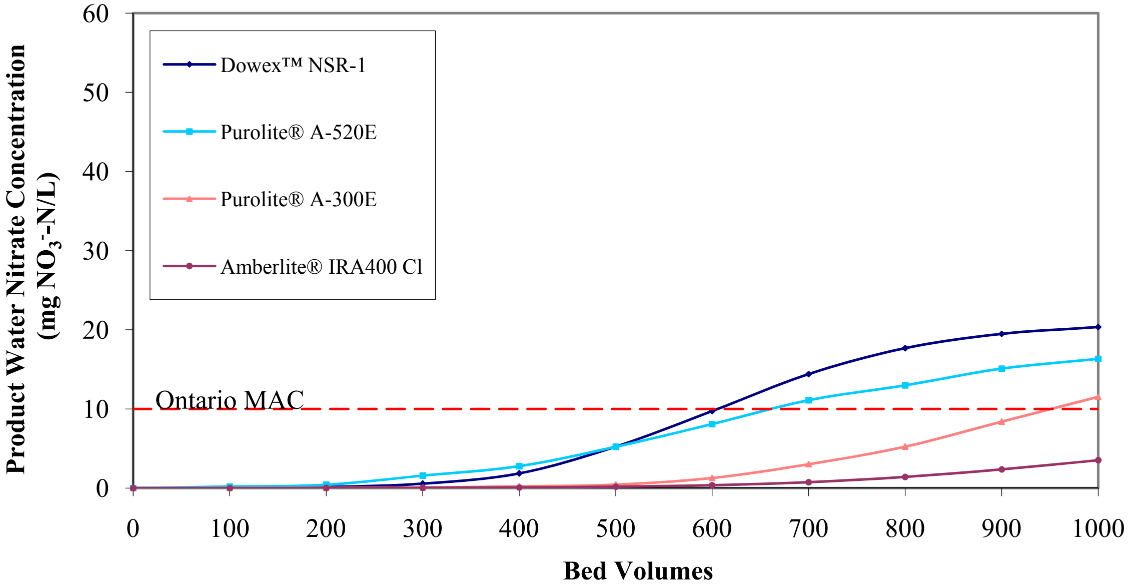


Figure C-10: Comparison of different resins at a hydraulic loading of 5.2 m/h and bed depth of 0.05 m. (Feed water nitrate = 23 mg NO_3^--N/L)

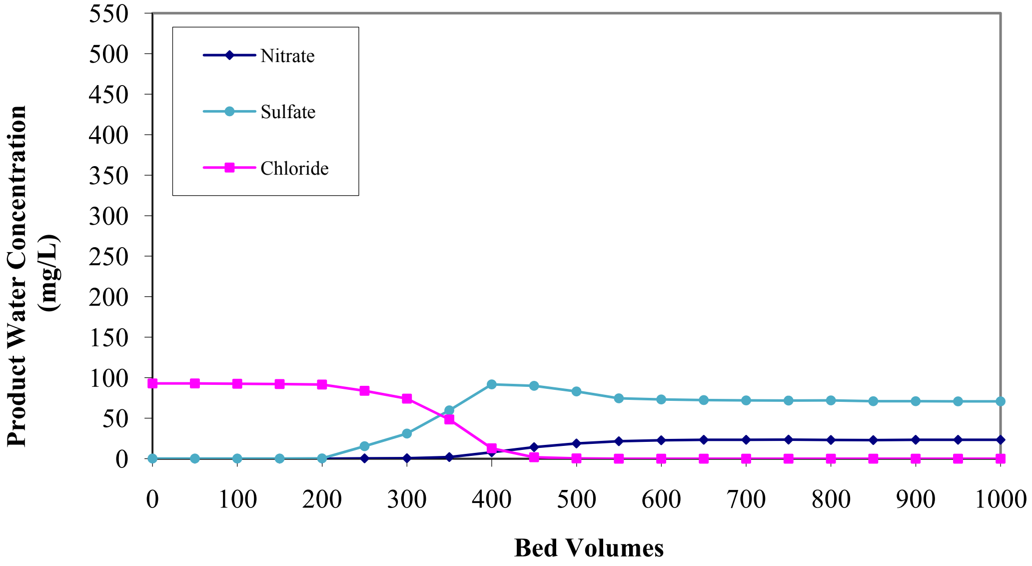


Figure C-11: Breakthrough curve showing the effect of sulfate on Dowex™ NSR-1. (Nitrate, sulfate, and chloride were measured as N, SO_4^{2-}, and Cl^-, respectively). Experiment 4-2.

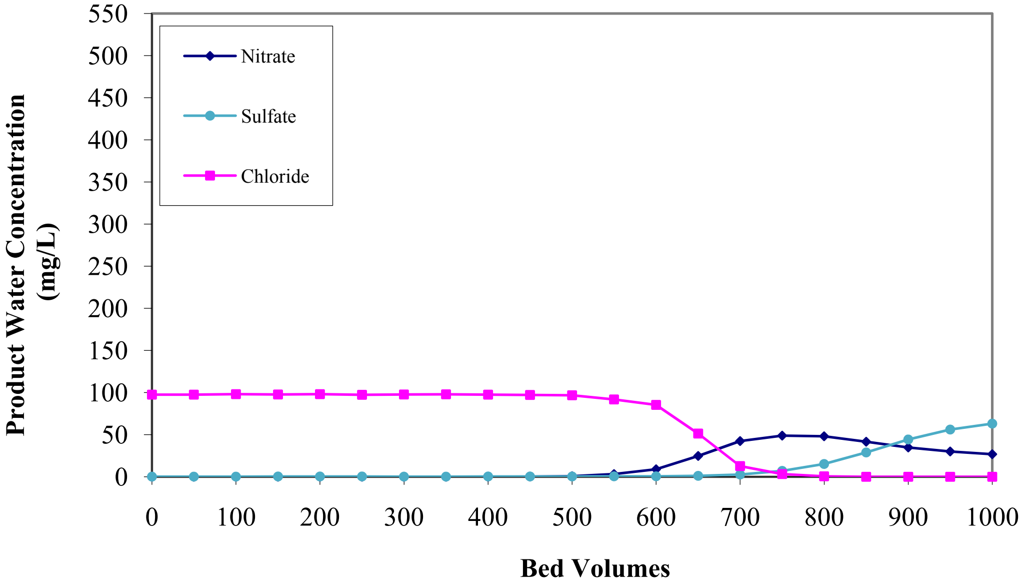


Figure C-12: Breakthrough curve showing the effect of sulfate on Amberlite® IRA400 Cl. (Nitrate, sulfate, and chloride were measured as N, SO_4^{2-}, and Cl^-, respectively). Experiment 4-2.

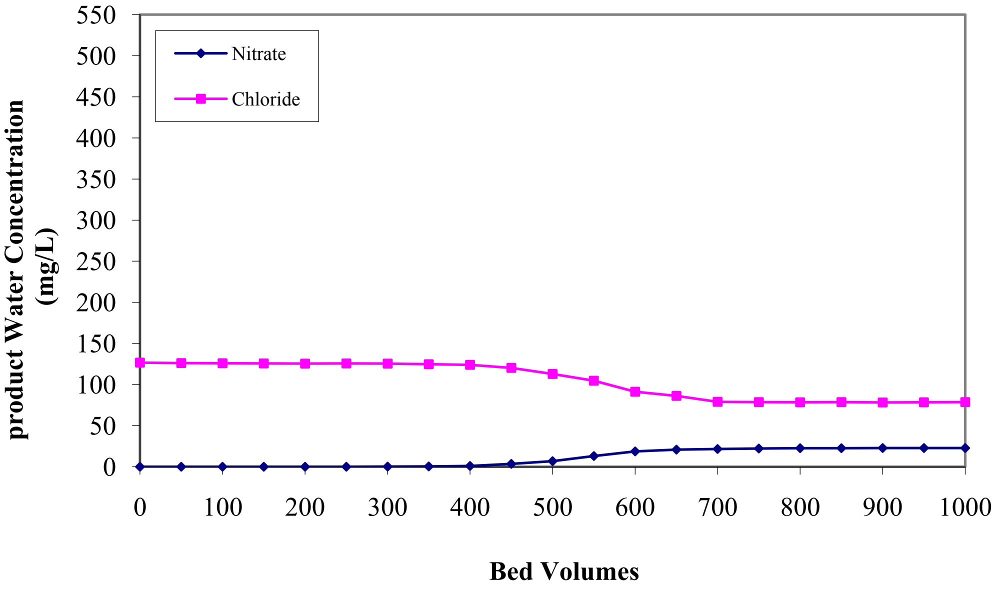


Figure C-13: Breakthrough curve showing the effect of chloride on Dowex™ NSR-1. (Nitrate and chloride were measured as N and Cl^-, respectively). Experiment 4-3.

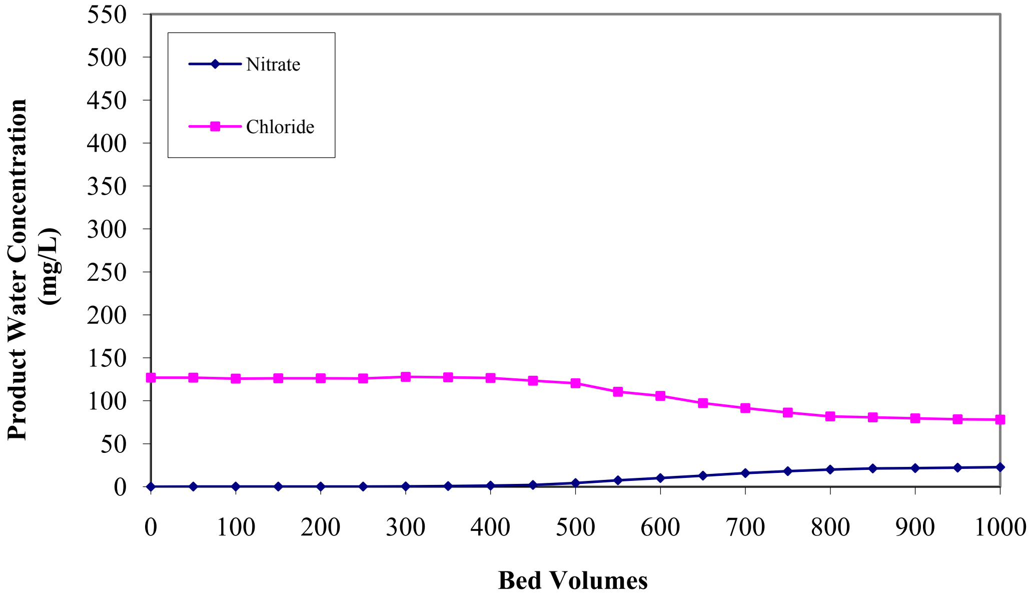


Figure C-14: Breakthrough curve showing the effect of chloride on Purolite® A-300E. (Nitrate and chloride were measured as N and Cl^-, respectively). Experiment 4-3.

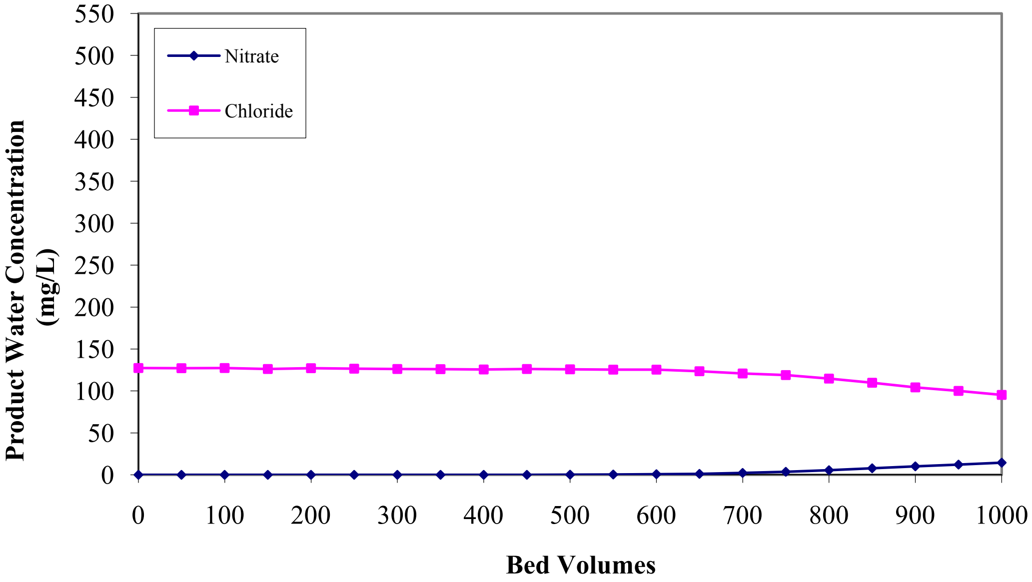


Figure C-15: Breakthrough curve showing the effect of chloride on Amberlite® IRA400 Cl. (Nitrate and chloride were measured as N and Cl^-, respectively). Experiment 4-3.

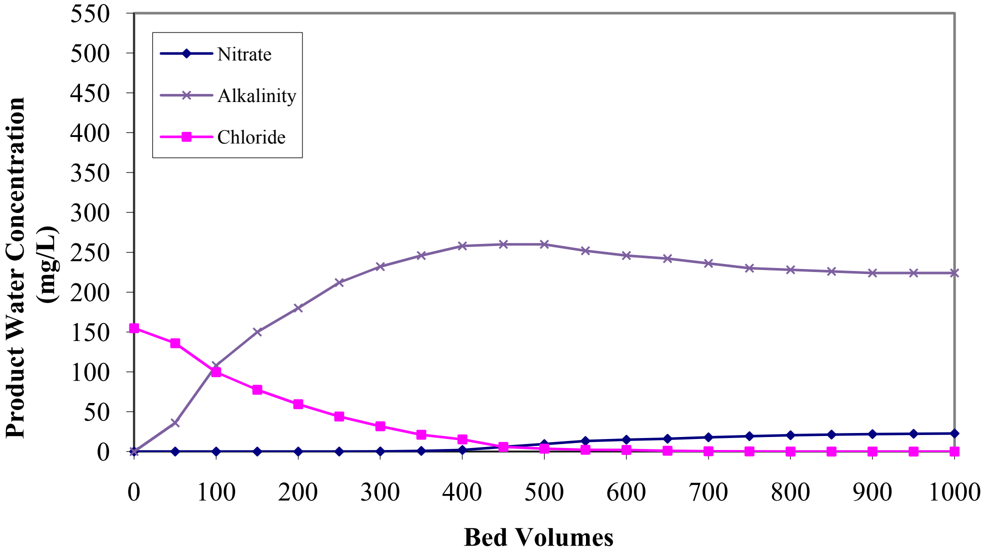


Figure C-16: Breakthrough curve showing the effect of alkalinity on Dowex™ NSR-1. (Nitrate, chloride, and alkalinity were measured as N, Cl^-, and $CaCO_3$, respectively). Experiment 4-4.

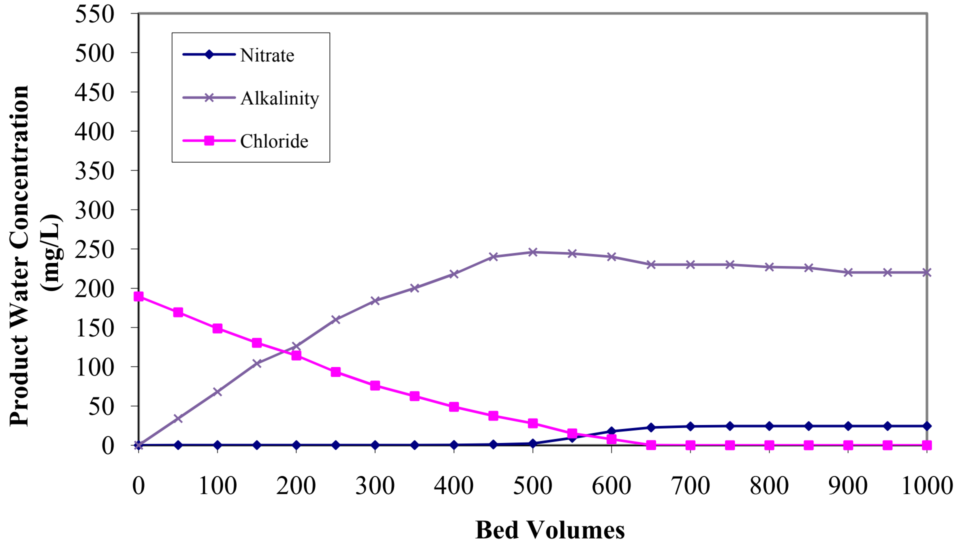


Figure C-17: Breakthrough curve showing the effect of alkalinity on Purolite® A-300E. (Nitrate, chloride, and alkalinity were measured as N, Cl^-, and $CaCO_3$, respectively). Experiment 4-4.

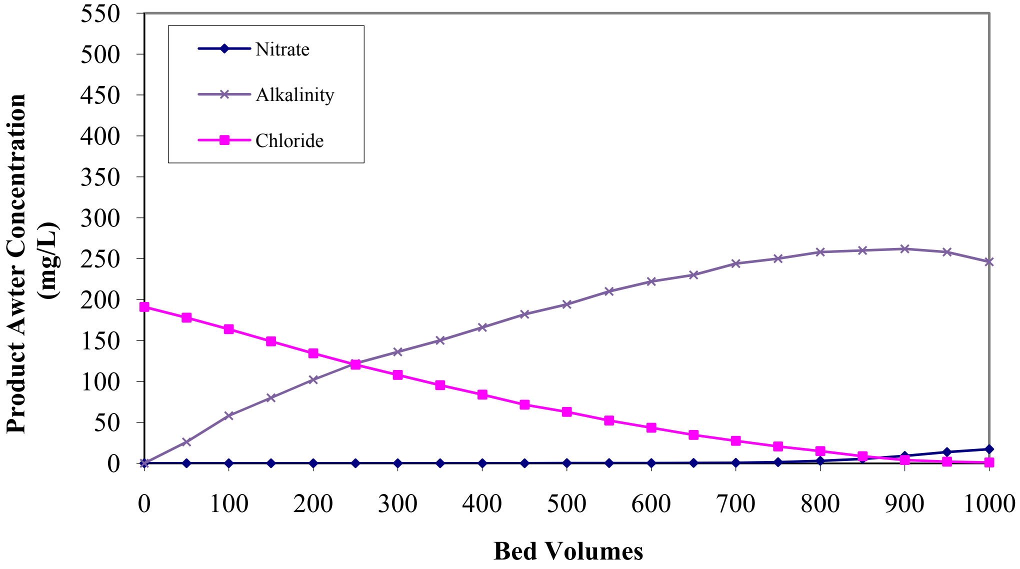


Figure C-18: Breakthrough curve showing the effect of alkalinity on Amberlite® IRA400 Cl. (Nitrate, chloride, and alkalinity were measured as N, Cl^-, and $CaCO_3$, respectively). Experiment 4-4.

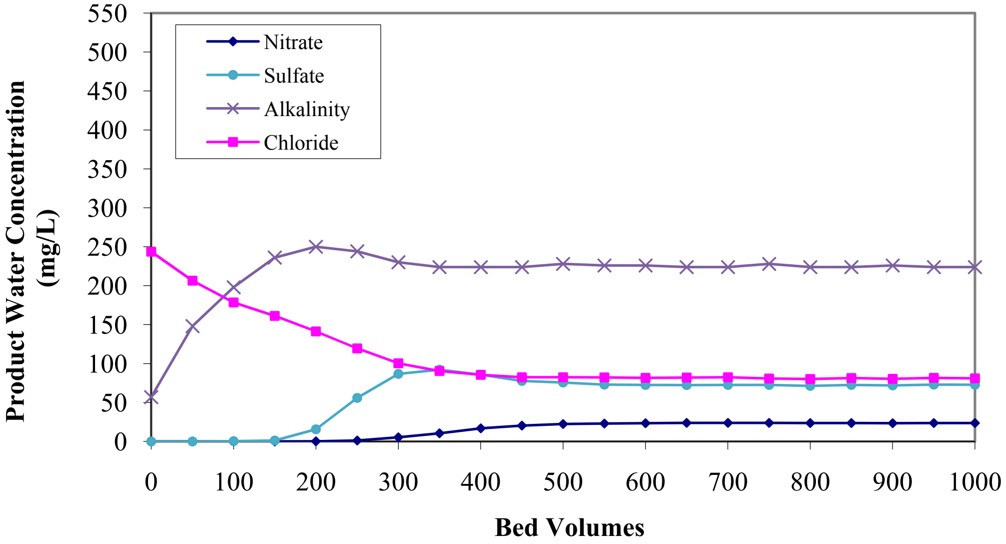


Figure C-19: Breakthrough curve for effect of combination of the competing anions on Dowex™ NSR-1 performance. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively). Experiment 4-5.

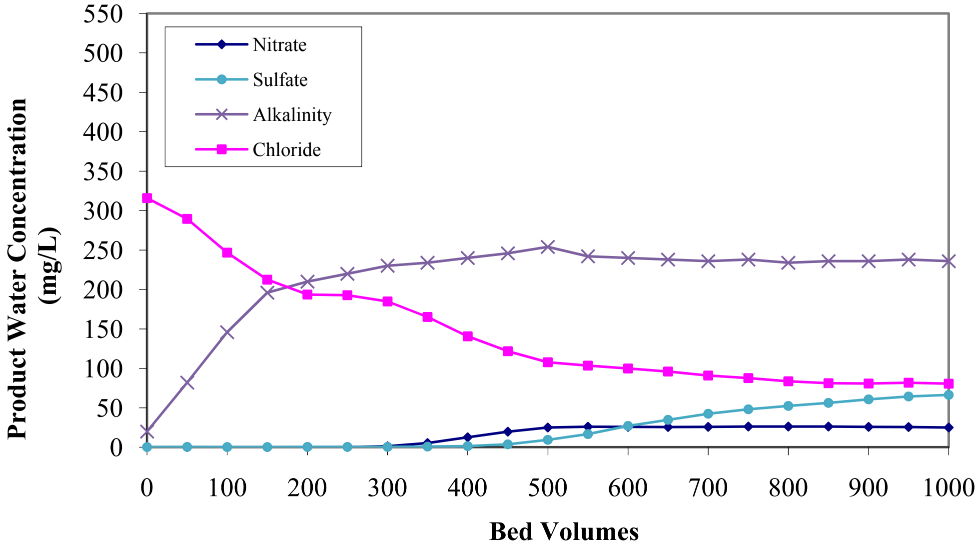


Figure C-20: Breakthrough curve for effect of combination of the competing anions on Amberlite® IRA400 Cl performance. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively). Experiment 4-5.

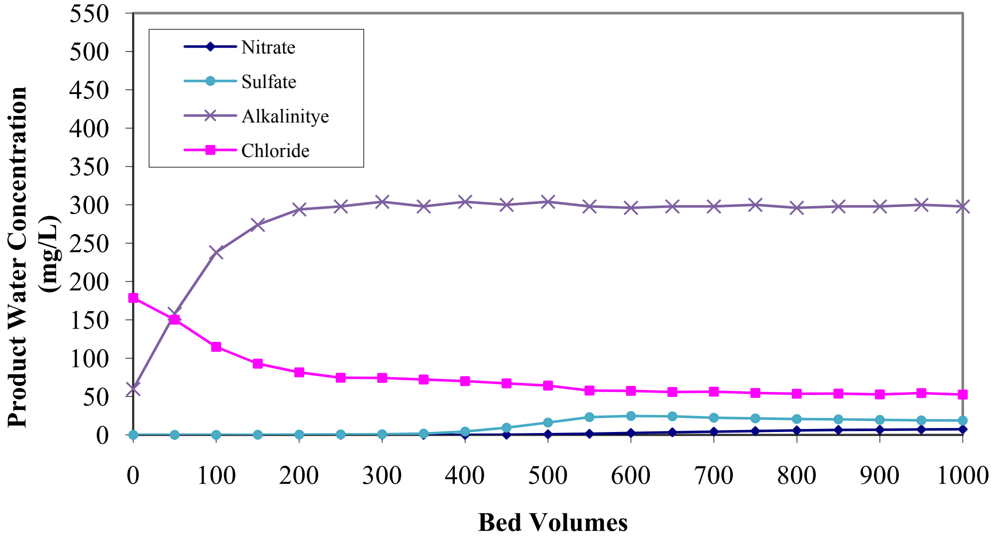


Figure C-21: Breakthrough curve for GW1 using Dowex™ NSR-1. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively). Experiment 4-6.

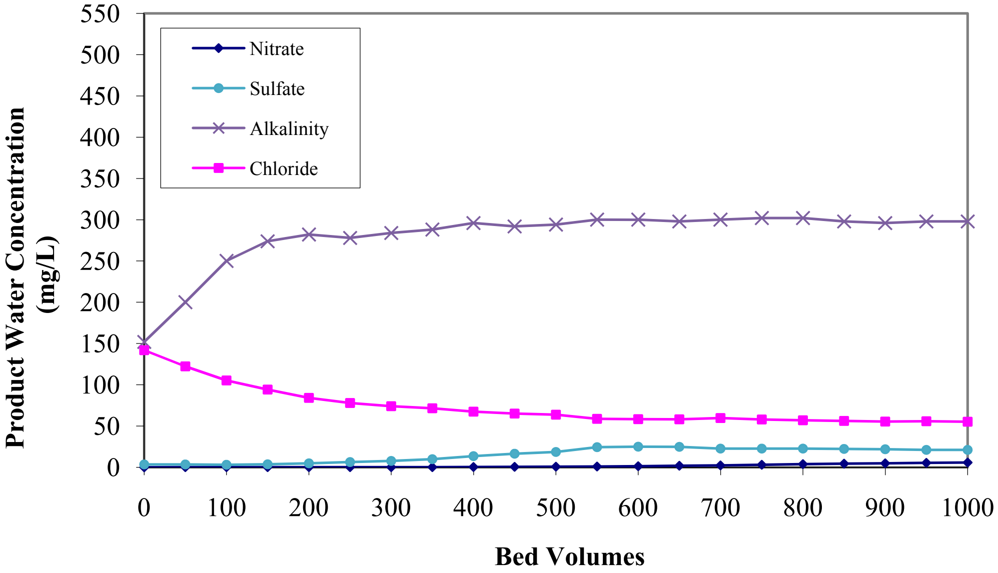


Figure C-22: Breakthrough curve for GW1 using Purolite® A-520E. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively). Experiment 4-6.

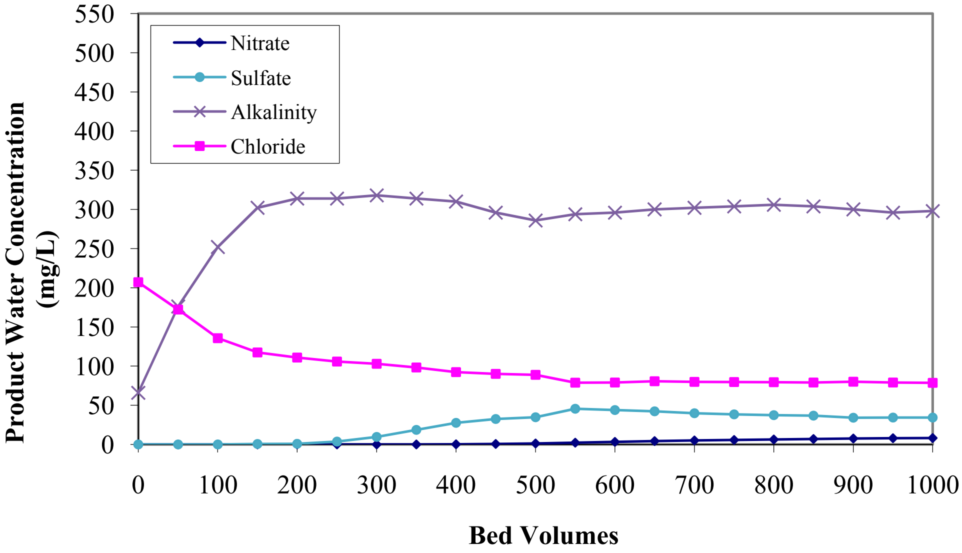


Figure C-23: Breakthrough curve for GW2 using Dowex™ NSR-1. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively). Experiment 4-7.

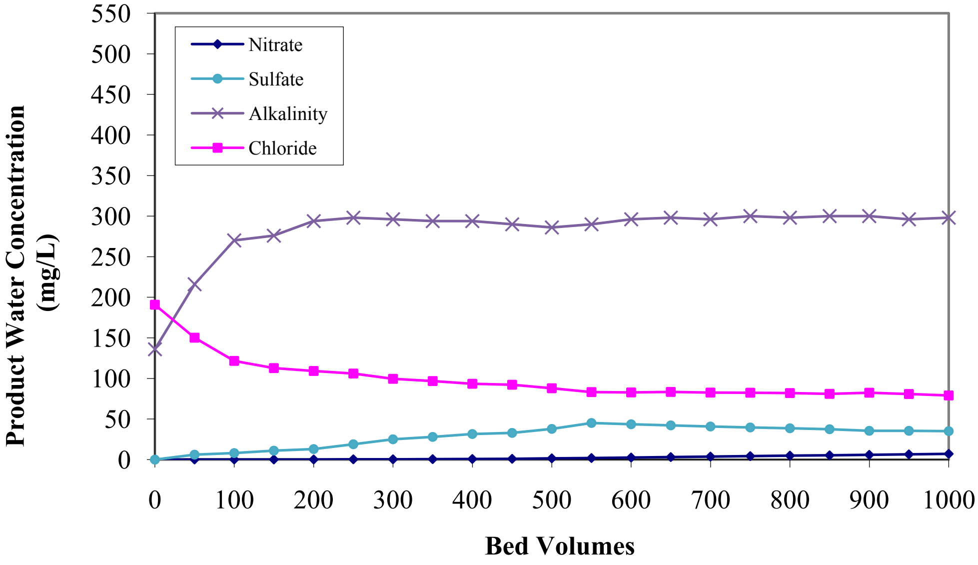


Figure C-24: Breakthrough curve for GW2 using Purolite® A-520E. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively). Experiment 4-7.

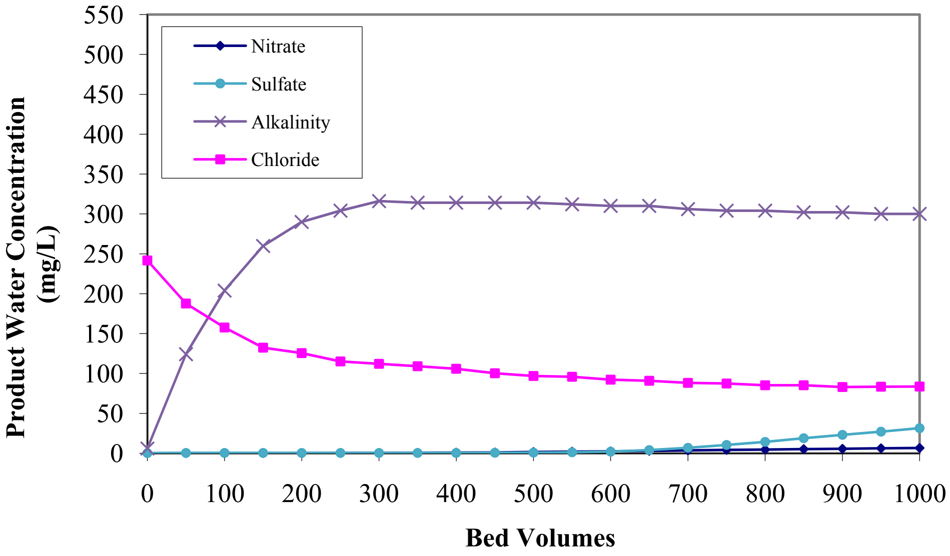


Figure C-25: Breakthrough curve for GW2 using Purolite® A-300E. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively). Experiment 4-7.

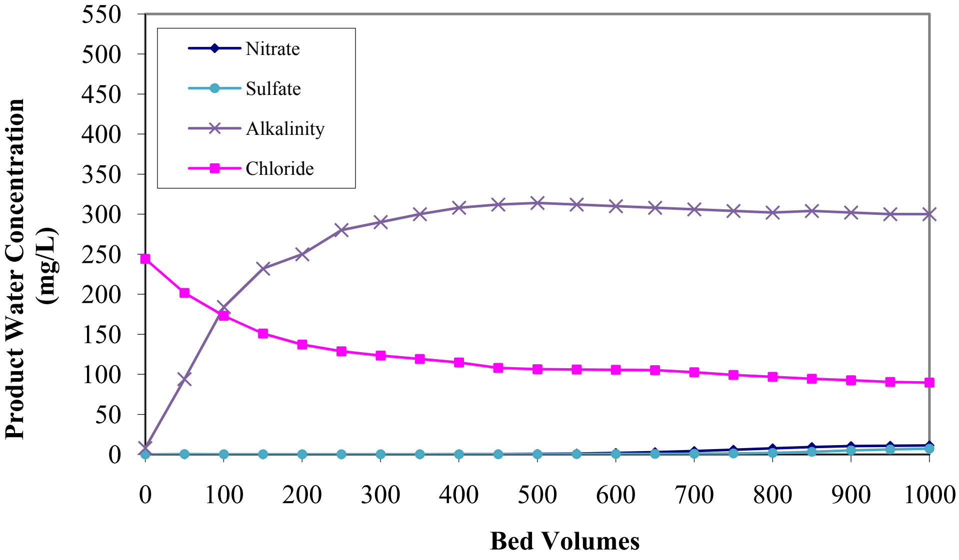


Figure C-26: Breakthrough curve for GW2 using Amberlite® IRA400 Cl. (Nitrate, sulfate, chloride, and alkalinity were measured as N, SO_4^{2-}, Cl^-, and $CaCO_3$, respectively). Experiment 4-7.

Appendix D

Reverse Osmosis Results

Table D-1: Conductivity and temperature summary for experiment 5-1.

Pressure (psi)	Treatment	Conductivity (µS/cm)			Temperature (°C)		
		Feed water	Product water	Reject water	Feed water	Product water	Reject water
60	Particle filter + Carbon Block + RO	140	10	195	22.4	23.3	23.4
40	Particle filter + Carbon Block + RO	140	13	190	22.4	23.4	23.4
60	Particle filter + RO	145	15	202	22.2	23.1	23.0
40	Particle filter + RO	139	20	184	22.4	23.4	23.3
60	Carbon block + RO	145	12	201	22.2	23.1	23.1
40	Carbon block + RO	140	12	191	22.2	23.5	23.5
60	RO alone	145	34	189	22.2	23.3	23.2
40	RO alone	140	37	181	22.2	23.5	23.4

Table D-2: Nitrate concentration summary for experiment 5-1 (in spiked deionized water).

Pressure (psi)	**Treatment**	**Nitrate concentration (mg NO_3^--N/L)**		
		Feed water	**Product water**	**Reject water**
60	Particle filter + Carbon Block + RO	23	2	34
40	Particle filter + Carbon Block + RO	23	2	33
60	Particle filter + RO	23	3	34
40	Particle filter + RO	23	4	32
60	Carbon block + RO	23	2	34
40	Carbon block + RO	23	2	34
60	RO alone	23	6	33
40	RO alone	23	7	31

Table D-3: Overall recovery of the system.

Experiment	**Pressure (psi)**	**Flow (mL/min)**			**Recovery (%)**
		Feed water	**Product water**	**Reject water**	
5-1	40	271	77	197	28
5-1	60	353	112	243	32
5-2	50	310	93	220	30
5-3-1	40	273	89	191	33
5-3-1	50	313	96	223	31
5-3-2	40	277	80	191	29
5-3-2	50	308	88	227	29
5-4-1	50	283	84	193	30
5-4-2	50	303	83	221	28
5-4-3	50	305	85	220	28
5-5	50	293	84	206	29

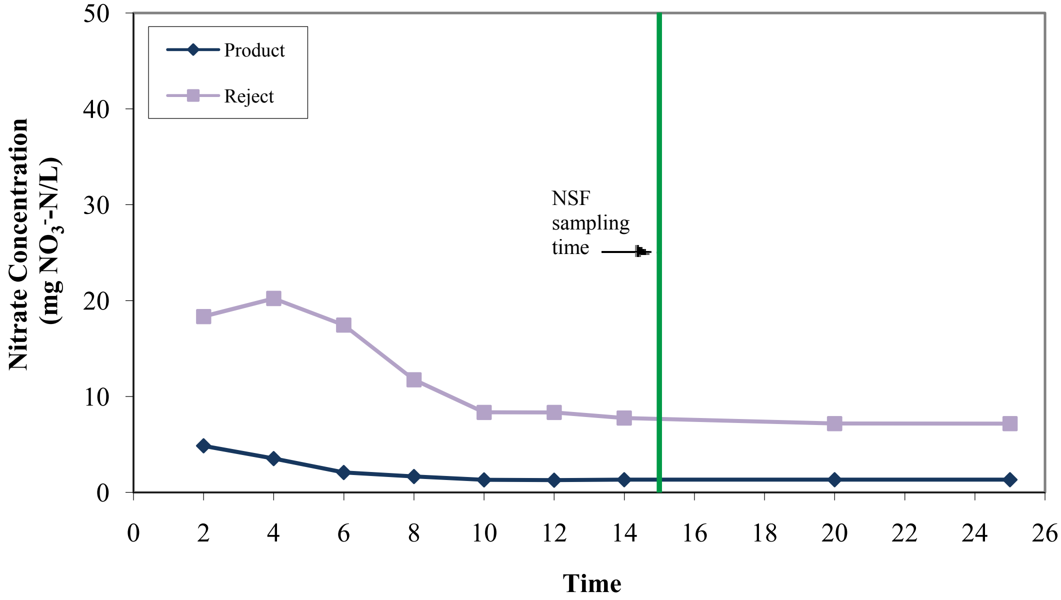


Figure D-1: Nitrate concentration in product and reject water over time. Treatment: RO preceded by carbon block and particle filter at 50 psi. Feed water: GW2. Experiment 5-5.

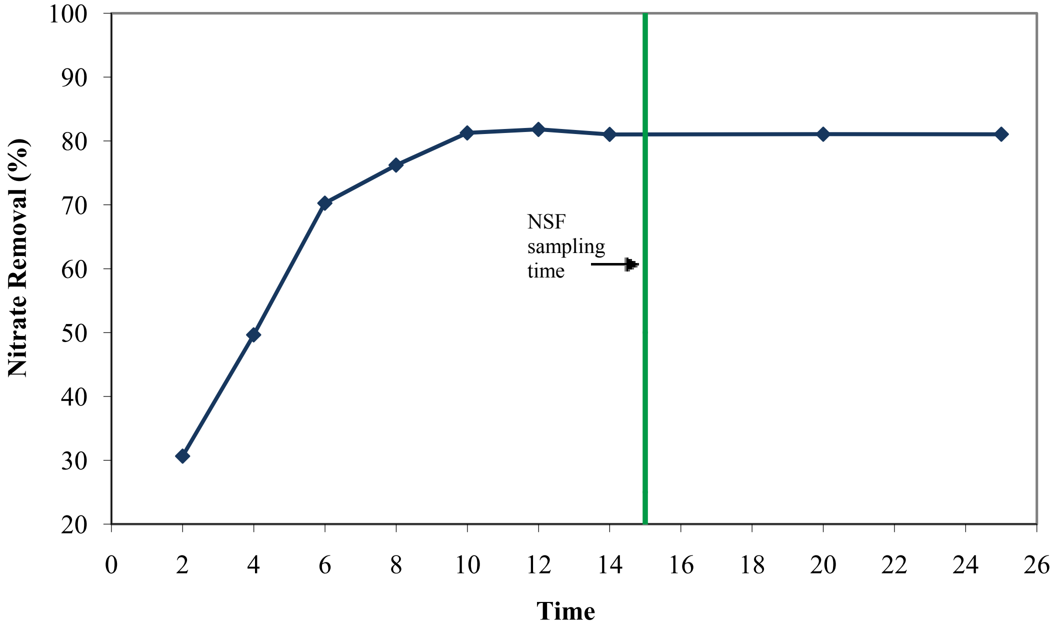


Figure D-2: Nitrate removal over time. Treatment: RO preceded by carbon block and particle filter at 50 psi. Feed water: GW2. Experiment 5-5.

Table D-4: Conductivity and temperature summary for experiment 5-3-1.

Feed water nitrate concentration (mg NO_3^--N/L)	**Treatment**	**Conductivity (µS/cm)**			**Temperature (°C)**		
		Feed water	**Product water**	**Reject water**	**Feed water**	**Product water**	**Reject water**
5	RO at 50 psi	34	11	45	23.5	24.3	24.1
10	RO at 50 psi	63	19	83	23.4	24.2	24.2
23	RO at 50 psi	136	17	189	22.8	23.7	23.7
5	RO + Carbon block at 50 psi	34	3	49	23.5	24.4	24.2
10	RO + Carbon block at 50 psi	63	5	89	23.4	23.8	24.1
23	RO + Carbon block at 50 psi	136	9	185	22.8	23.7	238.0
5	RO + Carbon block at 40 psi	34	3	54	23.8	24.7	24.7
10	RO + Carbon block at 40 psi	62	6	94	23.2	24.1	24.2
23	RO + Carbon block at 40 psi	132	13	193	22.3	23.4	23.4

Table D-5: Nitrate concentration summary for experiment 5-3-1 (in spiked deionized water).

Treatment	**Nitrate concentration (mg NO_3^--N/L)**		
	Feed water	**Product water**	**Reject water**
RO at 50 psi	5	2	8
RO at 50 psi	10	3	14
RO at 50 psi	23	3	36
RO + Carbon block at 50 psi	5	1	8
RO + Carbon block at 50 psi	10	1	15
RO + Carbon block at 50 psi	23	1	37
RO + Carbon block at 40 psi	5	1	8
RO + Carbon block at 40 psi	10	1	15
RO + Carbon block at 40 psi	23	2	34

Table D-6: Conductivity and temperature summary for experiment 5-3-2. Feed water concentration of nitrate, sulfate, chloride, and alkalinity: 23 (mg NO_3^--N/L), 68(as SO_4^{2-}), 76 (as Cl^-), 246 (as $CaCO_3$) mg/L, respectively (in deionized water).

Feed water anion composition in DI water	Treatment	Conductivity (µS/cm)			Temperature (°C)		
		Feed water	Product water	Reject water	Product water	Feed water	Reject water
Nitrate	RO at 50 psi	136	17	189	22.8	23.7	23.7
Nitrate + Sulfate	RO at 50 psi	326	40	427	22.8	23.8	23.5
Nitrate + Chloride	RO at 50 psi	400	60	525	22.4	23.5	23.4
Nitrate + Alkalinity	RO at 50 psi	465	19	607	21.0	22.4	22.7
Nitrate + Sulfate + Chloride + Alkalinity	RO at 50 psi	837	27	1114	21.5	22.7	22.7
Nitrate	RO + Carbon block at 50 psi	91	6	124	22.8	23.7	238.0
Nitrate + Sulfate	RO + Carbon block at 50 psi	326	12	424	22.8	23.7	23.8
Nitrate + Chloride	RO + Carbon block at 50 psi	400	16	529	22.4	23.2	23.4
Nitrate + Alkalinity	RO + Carbon block at 50 psi	465	18	600	21.0	22.3	22.4
Nitrate + Sulfate + Chloride + Alkalinity	RO + Carbon block at 50 psi	837	29	1100	21.5	22.6	22.5
Nitrate	RO + Carbon block at 40 psi	324	14	420	22.3	23.5	23.5
Nitrate + Sulfate	RO + Carbon block at 40 psi	404	19	519	22.1	23.4	23.3
Nitrate + Chloride	RO + Carbon block at 40 psi	460	19	605	22.3	23.5	23.5
Nitrate + Alkalinity	RO + Carbon block at 40 psi	841	28	1108	22.2	23.4	23.4
Nitrate + Sulfate + Chloride + Alkalinity	RO + Carbon block at 40 psi	324	14	420	22.3	23.5	23.5

Table D-7: Product water characteristics for experiment 5-3-2. Feed water concentration of nitrate, sulfate, chloride, and alkalinity: 23 (mg NO_3^--N/L), 68(as SO_4^{2-}), 76 (as Cl^-), 246 (as $CaCO_3$) mg/L, respectively (in deionized water).

Feed water anion composition in DI water	**Treatment**	**Product water pH**	**Product water concentration (mg/L)**			
			Nitrate	**Sulfate**	**Chloride**	**Alkalinity**
Nitrate	RO at 50 psi	6.6	3	0	0	0
Nitrate + Sulfate	RO at 50 psi	6.9	6	0	0	0
Nitrate + Chloride	RO at 50 psi	6.6	7	0	3	0
Nitrate + Alkalinity	RO at 50 psi	9.2	2	0	0	11
Nitrate + Sulfate + Chloride + Alkalinity	RO at 50 psi	9.0	2	0	0	12
Nitrate	RO + Carbon block at 50 psi	7.2	1	0	0	0
Nitrate + Sulfate	RO + Carbon block at 50 psi	8.5	1	0	0	0
Nitrate + Chloride	RO + Carbon block at 50 psi	9.2	2	0	0	0
Nitrate + Alkalinity	RO + Carbon block at 50 psi	9.7	1	0	0	12
Nitrate + Sulfate + Chloride + Alkalinity	RO + Carbon block at 50 psi	9.1	2	0	0	10
Nitrate	RO + Carbon block at 40 psi	Not measured	1	0	0	0
Nitrate + Sulfate	RO + Carbon block at 40 psi	Not measured	2	0	1	0
Nitrate + Chloride	RO + Carbon block at 40 psi	Not measured	3	0	0	6
Nitrate + Alkalinity	RO + Carbon block at 40 psi	Not measured	3	0	1	9
Nitrate + Sulfate + Chloride + Alkalinity	RO + Carbon block at 40 psi	Not measured	1	0	0	0

Table D-8: Reject water characteristics for experiment 5-3-2. Feed water concentration of nitrate, sulfate, chloride, and alkalinity: 23 (mg NO_3^--N/L), 68(as SO_4^{2-}), 76 (as Cl^-), 246 (as $CaCO_3$) mg/L, respectively (in deionized water).

Feed water anion composition in DI water	**Treatment**	**Reject water pH**	**Reject water concentration (mg/L)**			
			Nitrate	**Sulfate**	**Chloride**	**Alkalinity**
Nitrate	RO at 50 psi	6.9	36	0	0	0
Nitrate + Sulfate	RO at 50 psi	6.8	33	110	0	0
Nitrate + Chloride	RO at 50 psi	7.6	32	0	109	0
Nitrate + Alkalinity	RO at 50 psi	8.9	34	0	0	272
Nitrate + Sulfate + Chloride + Alkalinity	RO at 50 psi	8.7	33	101	104	269
Nitrate	RO + Carbon block at 50 psi	8.1	37	0	0	0
Nitrate + Sulfate	RO + Carbon block at 50 psi	7.5	33	106	0	0
Nitrate + Chloride	RO + Carbon block at 50 psi	7.6	33	0	108	0
Nitrate + Alkalinity	RO + Carbon block at 50 psi	8.8	34	0	0	267
Nitrate + Sulfate + Chloride + Alkalinity	RO + Carbon block at 50 psi	8.8	33	100	103	267
Nitrate	RO + Carbon block at 40 psi	Not measured	34	101	0	0
Nitrate + Sulfate	RO + Carbon block at 40 psi	Not measured	31	0	94	0
Nitrate + Chloride	RO + Carbon block at 40 psi	Not measured	32	0	0	269
Nitrate + Alkalinity	RO + Carbon block at 40 psi	Not measured	30	94	54	274
Nitrate + Sulfate + Chloride + Alkalinity	RO + Carbon block at 40 psi	Not measured	34	101	0	0

Table D-9: Conductivity and temperature summary for experiment 5-4-1. Feed water: deionized water spiked with nitrate (23 mg NO_3^--N/L) and alkalinity.

Feed water alkalinity (as $CaCO_3$)	**Treatment**	**Conductivity (µS/cm)**			**Temperature (°C)**		
		Feed water	**Product water**	**Reject water**	**Feed water**	**Product water**	**Reject water**
0	RO	134	16	185	23.5	23.9	23.9
41	RO	182	19	272	23.2	24.1	24.2
82	RO	259	16	339	23.2	24.2	24.2
123	RO	314	17	404	23.0	24.1	24.1
164	RO	364	18	467	23.2	24.2	24.2
205	RO	407	23	528	23.4	24.3	24.3
246	RO	459	26	590	23.4	24.3	24.4
0	RO + Carbon block	134	10	183	23.5	23.9	23.9
41	RO + Carbon block	182	13	280	23.2	24.1	24.0
82	RO + Carbon block	259	17	338	23.2	24.2	24.1
123	RO + Carbon block	314	17	405	23.0	23.9	24.0
164	RO + Carbon block	364	18	464	23.2	23.9	23.9
205	RO + Carbon block	407	20	524	23.4	24.4	24.4
246	RO + Carbon block	459	22	605	23.4	24.3	24.3

Table D-10: Product and reject water characteristics for experiment 5-4-1. Feed water: deionized water spiked with nitrate (23 mg NO_3^--N/L) and alkalinity.

Feed water alkalinity (as $CaCO_3$)	**Treatment**	**pH**			**Nitrate concentration (mg NO_3^--N/L)**		**alkalinity (as $CaCO_3$)**	
		Feed water	**Product water**	**Reject water**	**Product water**	**Reject water**	**Product water**	**Reject water**
0	RO	7.8	7.1	7.2	3	36	0	0
41	RO	8.0	7.6	8.0	3	33	6	48
82	RO	8.3	9.3	8.3	1	33	8	82
123	RO	8.4	8.8	8.3	2	33	8	130
164	RO	8.5	8.6	8.5	2	32	10	172
205	RO	8.5	8.7	8.6	2	32	14	218
246	RO	8.5	9.2	8.6	2	33	14	258
0	RO + Carbon block	7.8	7.1	7.9	1	38	0	0
41	RO + Carbon block	8.0	7.0	8.0	2	34	4	50
82	RO + Carbon block	8.3	6.7	7.9	1	34	6	80
123	RO + Carbon block	8.4	6.9	8.1	2	34	6	122
164	RO + Carbon block	8.5	7.1	8.2	2	33	8	168
205	RO + Carbon block	8.5	7.8	8.4	2	31	8	206
246	RO + Carbon block	8.5	8.9	8.6	2	33	14	266

Table D-11: Conductivity and temperature summary for experiment 5-4-2. Feed water: a composition of nitrate 23 (mg NO_3^--N/L), sulfate 68 (mg/L as SO_4^{2-}), chloride (76 mg/L as Cl^-), and different alkalinities in deionized water.

Feed water anion composition in DI water	**Feed water alkalinity (as $CaCO_3$)**	**Treatment**	**Conductivity (µS/cm)**			**Temperature (°C)**		
			Feed water	**Product water**	**Reject water**	**Feed water**	**Product water**	**Reject water**
Nitrate + Alkalinity	1	RO	134	40	181	22.4	23.1	23.1
Nitrate + Alkalinity	42	RO	190	12	287	22.3	23.3	23.3
Nitrate + Alkalinity	62	RO	212	12	318	22.3	23.2	23.3
Nitrate + Alkalinity	82	RO	264	13	355	22.7	23.6	23.6
Nitrate + Sulfate + Alkalinity	1	RO	321	62	410	22.9	23.8	23.9
Nitrate + Sulfate + Alkalinity	42	RO	371	14	479	23.0	23.5	23.6
Nitrate + Sulfate + Alkalinity	62	RO	382	14	496	22.7	23.1	23.1
Nitrate + Sulfate + Alkalinity	82	RO	413	15	533	22.3	22.9	23.0
Nitrate + Chloride + Alkalinity	1	RO	400	92	495	22.1	22.8	23.0
Nitrate + Chloride + Alkalinity	42	RO	448	18	590	22.9	23.4	23.4
Nitrate + Chloride + Alkalinity	62	RO	473	21	618	22.8	23.2	23.4
Nitrate + Chloride + Alkalinity	82	RO	493	20	653	22.8	23.1	23.1
Nitrate + Alkalinity	1	RO + Carbon block	134	10	185	22.4	23.0	23.0
Nitrate + Alkalinity	42	RO + Carbon block	190	9	283	22.3	23.4	23.4
Nitrate + Alkalinity	62	RO + Carbon block	212	9	317	22.3	23.2	23.1
Nitrate + Alkalinity	82	RO + Carbon block	264	10	350	22.7	23.6	23.6
Nitrate + Sulfate + Alkalinity	1	RO + Carbon block	321	12	422	22.9	23.8	23.6
Nitrate + Sulfate + Alkalinity	42	RO + Carbon block	371	11	487	23.0	23.8	23.9
Nitrate + Sulfate + Alkalinity	62	RO + Carbon block	382	12	493	22.7	23.2	23.1
Nitrate + Sulfate + Alkalinity	82	RO + Carbon block	413	13	528	22.3	23.0	23.0
Nitrate + Chloride + Alkalinity	1	RO + Carbon block	400	16	514	22.4	22.9	22.9
Nitrate + Chloride + Alkalinity	42	RO + Carbon block	448	15	584	22.9	23.2	23.2
Nitrate + Chloride + Alkalinity	62	RO + Carbon block	473	16	613	22.8	23.4	23.4
Nitrate + Chloride + Alkalinity	82	RO + Carbon block	493	17	647	22.8	23.2	23.2

Table D-12: Product water characteristics for experiment 5-4-2. Feed water: a composition of nitrate 23 (mg NO_3^--N/L), sulfate 68 (mg/L as SO_4^{2-}), chloride (76 mg/L as Cl^-), and different alkalinities in deionized water.

Feed water anion composition in DI water	**Feed water alkalinity (as $CaCO_3$)**	**Treatment**	**Product water pH**	**Product water concentration (mg/L)**			
				Nitrate	**Sulfate**	**Chloride**	**Alkalinity**
Nitrate + Alkalinity	1	RO	6.6	6	0	0	1
Nitrate + Alkalinity	42	RO	7.8	2	0	0	6
Nitrate + Alkalinity	62	RO	8.5	1	0	0	6
Nitrate + Alkalinity	82	RO	8.8	1	0	0	7
Nitrate + Sulfate + Alkalinity	1	RO	6.7	9	0	0	1
Nitrate + Sulfate + Alkalinity	42	RO	9.1	2	0	0	6
Nitrate + Sulfate + Alkalinity	62	RO	8.6	2	1	0	7
Nitrate + Sulfate + Alkalinity	82	RO	8.5	2	0	0	8
Nitrate + Chloride + Alkalinity	1	RO	7.5	10	0	0	1
Nitrate + Chloride + Alkalinity	42	RO	9.2	2	0	0	5
Nitrate + Chloride + Alkalinity	62	RO	8.9	2	0	0	6
Nitrate + Chloride + Alkalinity	82	RO	8.9	2	0	0	7
Nitrate + Alkalinity	1	RO + Carbon block	7.1	1	0	0	1
Nitrate + Alkalinity	42	RO + Carbon block	8.1	1	0	0	4
Nitrate + Alkalinity	62	RO + Carbon block	7.5	1	0	0	6
Nitrate + Alkalinity	82	RO + Carbon block	7.6	1	0	0	6
Nitrate + Sulfate + Alkalinity	1	RO + Carbon block	7.8	1	0	0	1
Nitrate + Sulfate + Alkalinity	42	RO + Carbon block	7.8	1	0	0	4
Nitrate + Sulfate + Alkalinity	62	RO + Carbon block	8.0	1	0	0	5
Nitrate + Sulfate + Alkalinity	82	RO + Carbon block	7.9	1	0	0	7
Nitrate + Chloride + Alkalinity	1	RO + Carbon block	6.5	2	0	0	1
Nitrate + Chloride + Alkalinity	42	RO + Carbon block	7.5	2	0	0	4
Nitrate + Chloride + Alkalinity	62	RO + Carbon block	7.9	2	0	0	6
Nitrate + Chloride + Alkalinity	82	RO + Carbon block	7.5	2	0	0	7

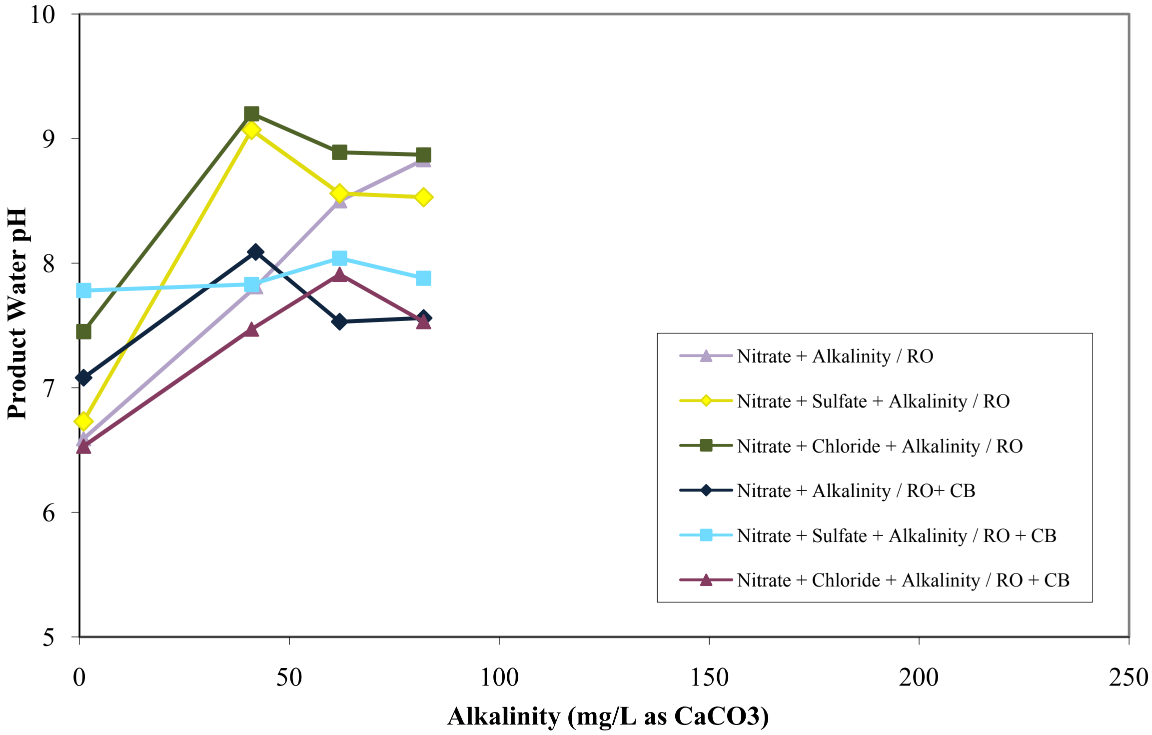


Figure D-3: Comparison of product water pH using RO and RO + carbon block. Feed water: a composition of nitrate 23 (mg NO_3^--N/L), sulfate 68 (mg/L as SO_4^{2-}), chloride (76 mg/L as Cl^-), and different alkalinities in deionized water. Experiment 5-4-2.

Table D-13: Reject water characteristics for experiment 5-4-2. Feed water concentration of nitrate, sulfate, and chloride: 23 (mg NO_3^--N/L), 68(as SO_4^{2-}), and 76 (as Cl^-) mg/L, respectively (in spiked deionized water).

Feed water anion composition in DI water	**Feed water alkalinity (as $CaCO_3$)**	**Treatment**	**Reject water pH**	**Reject water concentration (mg/L)**			
				Nitrate	**Sulfate**	**Chloride**	**Alkalinity**
Nitrate + Alkalinity	1	RO	6.9	31	0	0	1
Nitrate + Alkalinity	42	RO	8.1	33	0	0	58
Nitrate + Alkalinity	62	RO	8.5	33	0	0	80
Nitrate + Alkalinity	82	RO	8.5	33	0	0	104
Nitrate + Sulfate + Alkalinity	1	RO	6.0	29	100	0	1
Nitrate + Sulfate + Alkalinity	42	RO	8.7	31	97	0	56
Nitrate + Sulfate + Alkalinity	62	RO	8.4	31	95	0	84
Nitrate + Sulfate + Alkalinity	82	RO	8.6	32	97	0	102
Nitrate + Chloride + Alkalinity	1	RO	7.5	28	0	106	1
Nitrate + Chloride + Alkalinity	42	RO	8.4	32	0	106	56
Nitrate + Chloride + Alkalinity	62	RO	8.4	31	0	107	90
Nitrate + Chloride + Alkalinity	82	RO	8.5	31	0	106	102
Nitrate + Alkalinity	1	RO + Carbon block	7.4	32	0	0	1
Nitrate + Alkalinity	42	RO + Carbon block	8.5	33	0	0	54
Nitrate + Alkalinity	62	RO + Carbon block	8.3	32	0	0	80
Nitrate + Alkalinity	82	RO + Carbon block	8.4	33	0	0	104
Nitrate + Sulfate + Alkalinity	1	RO + Carbon block	7.2	32	97	0	1
Nitrate + Sulfate + Alkalinity	42	RO + Carbon block	8.1	32	100	0	58
Nitrate + Sulfate + Alkalinity	62	RO + Carbon block	8.4	31	95	0	82
Nitrate + Sulfate + Alkalinity	82	RO + Carbon block	8.4	31	97	0	102
Nitrate + Chloride + Alkalinity	1	RO + Carbon block	6.2	31	0	106	1
Nitrate + Chloride + Alkalinity	42	RO + Carbon block	8.2	34	0	107	56
Nitrate + Chloride + Alkalinity	62	RO + Carbon block	8.4	31	0	106	80
Nitrate + Chloride + Alkalinity	82	RO + Carbon block	8.7	31	0	105	104

Table D-14: Conductivity and temperature summary for experiment 5-4-3. Feed water: a composition of nitrate 23 (mg NO_3^--N/L), sulfate 68 (mg/L as SO_4^{2-}), chloride (76 mg/L as Cl^-), and different alkalinities in deionized water.

Feed water anion composition in DI water	**Feed water alkalinity (as $CaCO_3$)**	**Conductivity (µS/cm)**			**Temperature (°C)**		
		Feed water	**Product water**	**Reject water**	**Feed water**	**Product water**	**Reject water**
Nitrate + Alkalinity	1	139	45	178	23.9	24.7	24.7
Nitrate + Alkalinity	8	150	7	226	23.9	24.3	24.8
Nitrate + Alkalinity	21	165	7	250	24.5	25.0	25.1
Nitrate + Alkalinity	41	190	7	283	24.4	25.0	25.0
Nitrate + Sulfate + Chloride + Alkalinity	1	559	105	721	24.3	24.9	25.0
Nitrate + Sulfate + Chloride + Alkalinity	8	569	20	763	24.6	25.1	25.0
Nitrate + Sulfate + Chloride + Alkalinity	21	580	17	774	24.5	25.2	25.2
Nitrate + Sulfate + Chloride + Alkalinity	41	620	18	829	24.6	25.3	25.3

Table D-15: Product water characteristics for experiment 5-4-3. Feed water: a composition of nitrate 23 (mg NO_3^--N/L), sulfate 68 (mg/L as SO_4^{2-}), chloride (76 mg/L as Cl^-), and different alkalinities in deionized water.

Feed water anion composition in DI water	**Feed water alkalinity (as $CaCO_3$)**	**Product water pH**	**Product water concentration (mg/L)**			
			Nitrate	**Sulfate**	**Chloride**	**Alkalinity**
Nitrate + Alkalinity	1	5.7	6	0	0	1
Nitrate + Alkalinity	8	6.5	1	0	0	2
Nitrate + Alkalinity	21	6.9	1	0	0	5
Nitrate + Alkalinity	41	7.0	1	0	0	6
Nitrate + Sulfate + Chloride + Alkalinity	1	6.0	12	0	5	1
Nitrate + Sulfate + Chloride + Alkalinity	8	6.7	2	0	1	3
Nitrate + Sulfate + Chloride + Alkalinity	21	7.1	2	0	0	6
Nitrate + Sulfate + Chloride + Alkalinity	41	7.5	2	0	0	7

Table D-16: Reject water characteristics for experiment 5-4-3. Feed water: a composition of nitrate 23 (mg NO_3^--N/L), sulfate 68 (mg/L as SO_4^{2-}), chloride (76 mg/L as Cl^-), and different alkalinities in deionized water.

Feed water anion composition in DI water	**Feed water alkalinity (as $CaCO_3$)**	**Reject water pH**	**Reject water concentration (mg/L)**			
			Nitrate	**Sulfate**	**Chloride**	**Alkalinity**
Nitrate + Alkalinity	1	5.6	38	0	0	1
Nitrate + Alkalinity	8	7.4	38	0	0	20
Nitrate + Alkalinity	21	7.7	41	0	0	36
Nitrate + Alkalinity	41	8.0	37	0	0	60
Nitrate + Sulfate + Chloride + Alkalinity	1	5.5	35	97	106	1
Nitrate + Sulfate + Chloride + Alkalinity	8	7.4	40	96	106	18
Nitrate + Sulfate + Chloride + Alkalinity	21	7.8	40	94	105	36
Nitrate + Sulfate + Chloride + Alkalinity	41	8.2	32	97	106	60

Table D-17: Conductivity, temperature, and pH summary for experiment 5-5. Feed water GW2.

Treatment	**Conductivity (µS/cm)**			**Temperature (°C)**			**pH**		
	Feed water	**Product water**	**Reject water**	**Feed water**	**Product water**	**Reject water**	**Feed water**	**Product water**	**Reject water**
RO + Partice filter + Carbon block	790	26	954	14.8	17.5	16.6	7.8	6.7	7.6
RO + Carbon block	790	29	959	14.8	18.0	17.0	7.8	7.0	7.8
RO + Particle filter	790	30	968	14.8	18.1	17.2	7.8	7.0	7.7
RO	790	31	970	14.8	18.2	17.2	7.8	7.2	7.8
Particle filter + Carbon block	795	790	NA	16.0	17.2	NA	7.8	8.0	NA
Carbon block	795	790	NA	16.0	17.5	NA	7.8	8.0	NA
Particle filter	795	790	NA	16.0	17.4	NA	7.8	8.0	NA

NA = not applicable