Case Study: Pilot Plant for Nitrate Removal in Groundwater Using Ion Exchange and Biophysical Treatment of the Recirculating Regenerant

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Abstract
Health concerns regarding microbial contamination on the one hand and brine disposal regulations on the other limits the application of both biological and physico-chemical techniques for nitrate removal from polluted inland groundwater. In the current work, a pilot plant consisting of a combined system of ion exchange (IX) and advanced biophysical treatment of a recirculating regenerant was tested at the Tzur Moshe well for nitrate removal from groundwater with minimal brine discharge and chloride addition to the product water. Using a feed water composing 21.5±1.4 mg NO_3^--N/L, 83.6±7.3 mg/L Cl^- and 35.3±6.6 mg/L SO_4^{-2}, optimal IX operation was found to be at a service cycle length of 500 bed volumes (BV). Product water nitrate concentrations (7.4±1.4 mg/L as N) met regulations while minimizing both Cl^- addition to the treated water (1.03 meq Cl added per meq NO_3^--N removed) and waste brine production (0.2% of the water volume treated). The TOC in the product water was slightly higher (1.5±0.5 vs. 1.3±0.4 mg/L) than the well water and before disinfection the bacterial count was 10-700 cfu/ml. Spent regenerant was first treated in a sequential batch denitrification bioreactor (SBR) followed by ozonation for polishing. The SBR unit was operated at 8 hour cycles and achieved complete nitrate removal with nitrate removal rates of 2.25±0.4 g $N/L_{reactor}/d$ and a low average ethanol to nitrate mass ratio of 1.68±0.18. An ozone dose of 3 to 5 mg/L brine allowed for efficient recycling of the denitrified regenerant by removing suspended solids by foam fractionation. In spite of the low brine blow-down, DOC in the recycled regenerant brine after more than a year of continuous operation was maintained at relatively low levels of 61.0±11.6 mg/L.

Keywords
Nitrate removal; ion exchange; bioregeneration; SBR; ozonation; brine recycling

INTRODUCTION

Excessive nitrate concentration is a major cause of closing potable water wells throughout the world. Treatment options of nitrate bearing waters involve nitrate separation and/or reduction to N_2. Separation is the most common strategy and includes technologies such as reverse osmosis (RO), ion exchange (IX) and electrodialysis (ED). These technologies are cost effective, reliable and safe, but they become impractical in locations where brine disposal is either too expensive or restricted, particularly at inland sites. The other employed option is direct biological denitrification, heterotrophic or autotrophic where nitrate is transformed into harmless nitrogen gas and no brine is produced. However, application of this technology requires extensive post treatment due to health concerns associated with exposure of drinking water to bacteria, nitrite and residual organics. In many places, the low acceptance of biologically treated drinking water by the regulators limits the application of these technologies. Catalytic non-biotic nitrate reduction using metals or hydrogen has also been suggested as a brine free nitrate removal strategy. However, such methods may release nitrite, ammonia and toxic metal catalysts to the product water.

Several alternative strategies attempt to combine physico-chemical technologies with biological technologies in order to avoid the downsides of each separate technology. Ion exchange (IX) combined with biological removal of the nitrate in the spent brine for regenerant recycling is one such method. As compared with conventional IX regeneration, it is possible to reach a significant reduction in brine waste volume and salt requirement. Another advantage of a combined physico-chemical and biological process is the separation between the feed water and the biological treatment step that dramatically reduces the microbial contamination risk of the product water. The concept of IX and bioregeneration is not new (van der Hoek *et al.*, 1988; Clifford and Liu, 1993). Until now, work conducted on such combined systems has been on a research level only with several problems, particularly the poor quality of recycling regenerant brine that contains high DOC, high suspended solids, and bacterial contamination. This can lead to IX resin fouling, reduced IX capacity and treated water bacterial contamination due to bacterial growth on the resin. The present study focused on long term operation of a pilot scale combined ion exchange and bio-regeneration process for nitrate removal from groundwater, with special emphasis on minimal waste brine production, minimal chloride addition to the product water, and minimizing DOC accumulation in the recycled regenerant.

METHODOLOGY

The main elements of the 25 m^3/d system consisted of four IX columns, a sequential batch reactor (SBR) and an ozonator as pictured in Fig. 1. A functional description of ion exchange and bioregeneration steps for nitrate removal is given below.

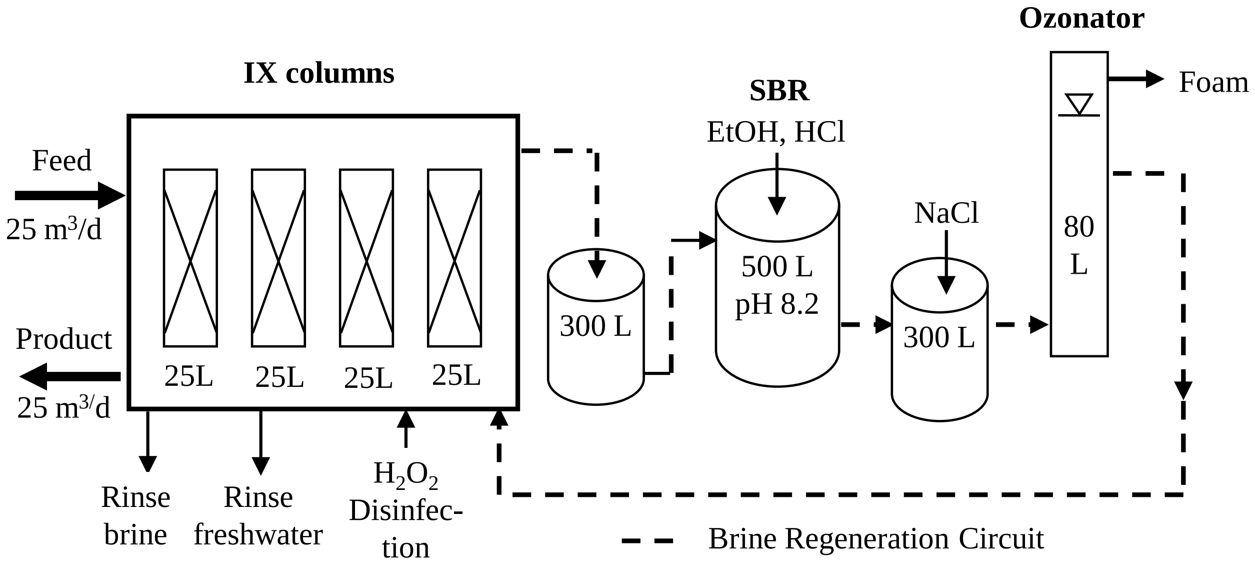

Figure 1. Schematic diagram of 25 m^3/day Pilot Plant for nitrate removal from groundwater.

Ion exchange for nitrate removal

The 25 liter IX columns were equipped with appropriate screens at column top and bottom to prevent resin loss. A conical inset at the IX column bottom was installed to ensure even drainage during absorption and minimize dead spaces during regeneration and disinfection. Each column was filled with 17 liters of resin (A-520E, Purolite, Bala Cynwyd, PA; 17 liters = 1 bed volume, BV). Multiple column operation was staggered and regeneration was carried out in sequential fashion. Full capacity operation was reached when three of the four IX columns operated simultaneously in absorption cycle and one column in regeneration cycle. IX columns were operated in the following sequence:

Absorption (Service) Cycle. The IX columns treat well water removing nitrate ion and replacing it with chloride ion. During the absorption cycle, the main water pump delivered contaminated well water from the feed water tank to the IX columns inlet manifold. The columns operated in down flow mode. The length of a column run was 500 BV (8.5 m^3) over 24 hours or about 21 BV per hour (350 L/hr). At the end of the absorption cycle, excess column water was drained and purged by forced air displacement (blower) to product water stream. This minimized dilution of brine regenerant.

Regeneration Cycle. Treated regenerate (after denitrification and polishing) produced by the ozone reactor was pumped through an exhausted IX column in upflow mode during regeneration. The column regeneration cycle was run at 3.5 BV per hour (60 L/hr) for 5 hours producing a volume of 300L. At the end of the regeneration period, the remaining regenerant in the column was purged by forced air displacement to the spent regenerant tank (regenerant + nitrate). This ensured maximal regenerant recovery and minimal production of high saline waste brine.

Column disinfection and flushing. Following regeneration, the column was disinfected in a two-step fashion. First the column was slowly filled (1 L/min) with 0.3% H_2O_2 disinfectant in down flow mode. This began column disinfection and the transition from saline conditions to potable water salinity. After column filling, the disinfectant and remaining brine was slowly drained at 1 L/min. This high saline waste brine was disposed by truck. After slow drainage the column was filled again with 0.3% H_2O_2 disinfectant this time from the bottom of the IX column to ensure H_2O_2 contact with resin and all parts of the IX column. H_2O_2 remained in the column for 1 hour for adequate disinfection. The top valve of the column remained open to allow for O_2 gas release. The column was emptied of H_2O_2 by air purge and the low saline H_2O_2 waste solution was discharged to sewage. The column was then flushed with 1 BV of well water in upflow mode that was also discharged to sewage.

Bioregeneration of spent regenerant

For regeneration of the spent regenerant, the pilot plant contained a sequential batch reactor (SBR) for denitrification (removal of nitrate), SBR effluent tank and ozonator. The SBR reactor tank had a total volume of 500 liters (diameter 72 cm; height 123 cm) and a working volume 450 liters (sludge settling volume of 150 liters + 300 liters working volume for spent regenerant). The SBR was equipped with mechanical mixer for intermittent mixing, ORP and pH electrodes and control units (Alpha 190 pH/ORP controller, Eutech Instruments Pte Ltd, Singapore) for ethanol and HCl dosing, respectively. The effluent tank for SBR effluent holding had a total volume of 400 liters and a conical bottom for excess biomass sedimentation. The ozonator had a total volume of 80 liters (diameter 24 cm; height 178 cm) and the working volume was 70 liters. Ozonator was equipped with ORP electrode and recirculation pump with Venturi for ozone injection. The bioregeneration circuit in the pilot was designed to treat (denitrify) up to three spent regenerant batches per day (full capacity). The number of batches treated per day determined how many columns worked simultaneously and ultimately determined the pilot plant's product water flow and water composition. Bioregeneration was operated in the following sequence:

SBR operation. 300 liters of spent regenerant from column regeneration were first pumped to the SBR. During the first 90 minutes of the SBR's react period, no ethanol/phosphate solution was given to the SBR reactor. This was to utilize any reduced compounds for denitrification left over from the previous batch. In pilot operation, the required ethanol amount for denitrification was divided into smaller dosages and spaced out over the remaining react time. About 80 to 90% of the required ethanol amount was divided into 3 equal parts and given after 90, 180, and 300 minutes. Additional 10% dosages were given only if the ORP did not fall below -200 mv. pH increases due to denitrification were neutralized by HCl addition. When the ORP reached -250mv, the SBR was put into settling mode (no mixing) for a short period and then discharged to the effluent tank. This was to ensure that sludge with good settling characteristics developed in the reactor. The Cl^- concentration of the regenerant was corrected in the effluent discharge tank by conductivity measurement (set point of 60 mS/cm; Alpha 190 conductivity controller, Eutech Instruments Pte Ltd, Singapore) and adding a 20% NaCl solution.

Ozone reactor operation. The ozone reactor operated during IX column regeneration. Just before the start of a column regeneration cycle, the ozone reactor was turned on with ancillary oxygen production 0-6 L/min, Air Sep model Topaz, Buffalo, NY) and ozone generator (CD 12, ClearWater Tech, LLC., San Luis Obispo CA). The ORP in the ozone reactor was set at +500 mv and was first maintained for 5 minutes to kill bacteria that may have proliferated between cycles. Following initial startup, denitrified SBR effluent was fed from the tank by pump to the ozonator. The ORP in the ozone reactor was kept stable at a given value by increasing/decreasing power (15 to 100%) of the ozone generator and increasing/decreasing SBR effluent flow (0.6 to 1.5 liter/min).

Analysis

Nitrate, nitrite, chloride and sulfate concentrations were determined by ion chromatography (761 Metrohm ion chromatograph equipped with 150 mm MetrosepA Supp5 column and precolumn, Metrohm AG, Herisau Switzerland) using an eluent containing 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. Total Organic Carbon (TOC) concentration was determined by a TOC-VCPH analyzer (Shimadzu, Kyoto, Japan). DOC concentration was determined by performing TOC analysis on samples filtered through 0.22 µm syringe filter. Turbidity was determined using a Hach 2100Q turbidometer (Loveland, CO). Alkalinity was measured using the potentiometric method with the end-point pH selected at 4.5 (APHA, 1995). Heterotrophic plate count (HPC) was performed according to the spread plate method (APHA, 1995).

RESULTS AND DISCUSSION

Pilot plant product water quality

Due to agricultural concerns associated with irrigation with reclaimed water use, the chloride concentration in potable water and domestic wastewater receives high attention by regulators in Israel. The addition of chlorides to the treated water is a significant inherent problem of the IX process that uses chloride as the exchanged ion for nitrate. The addition of chlorides to the treated water during IX operation is expected to be higher than a theoretical 1:1 molar exchange ratio of nitrate with chloride, because sulfate ions are also exchanged and because of possible insufficient rinsing of the resin with freshwater after the IX column.

In an effort to minimize chloride addition to the product water, previous work was carried out to determine the length of the IX service cycle of a nitrate selective resin when nitrate in the feed water is absorbed onto the resin (Klas *et al.*, 2016). In short, it was found that at short service cycle lengths both nitrate and sulfate are exchanged for chloride resulting in high chloride concentrations in the product water. Extending the IX service cycle of the nitrate selective resin (Purolite A-520E) resulted in sulphate breakthrough much earlier than nitrate. In addition, sulphate already adsorbed was released back to the treated water as sulfate was exchanged with the more favorable nitrate. Maximizing “sulfate dumping” by increasing the IX service length reduced chloride addition to product water and lessened sulfate build up in the regenerant, but at a price of higher nitrate concentrations with fluctuations in the product water. An example of wide variations in nitrate concentrations throughout the service cycle is given in Fig. 2 when the pilot plant was initially operated with one column a day at a service cycle of 500 BV. When the pilot plant was at full capacity with staggered simultaneous operation of three columns, variations in the concentration of nitrate in the product water were attenuated and always below the standard of 10 mg/L as N-NO_3.

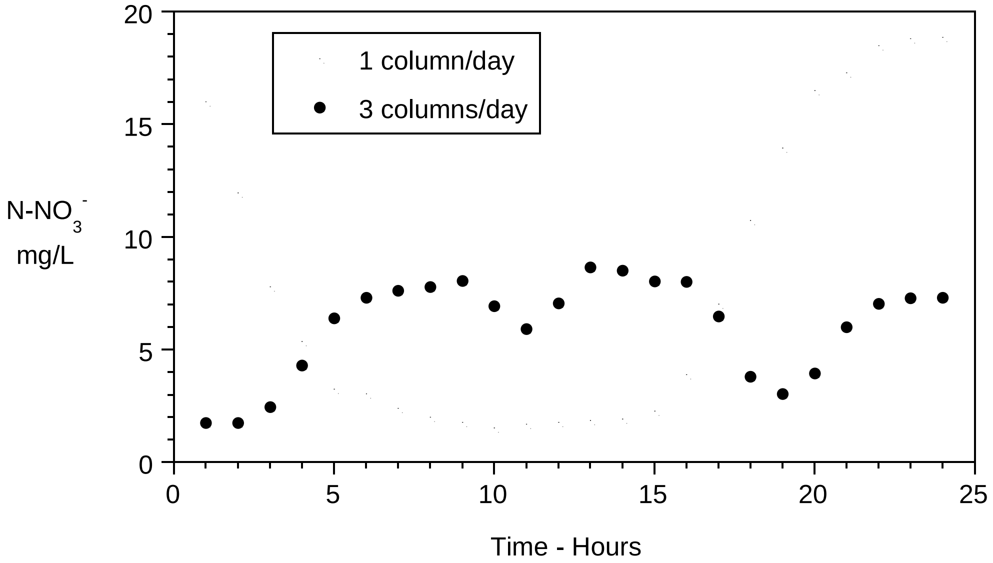

Figure 2. Product water nitrate concentration during 24 hour sampling period for single and multiple column operation at the pilot plant.

In the final six months of pilot plant operation, three columns were operated in service cycle simultaneously (total flow of 25 m^3/d), while one column was in regeneration mode. The average results over this period are given in Table 1. The chloride addition to the product water was slightly higher than the theoretical 1:1 chloride to nitrate molar exchange ratio (1.03:1) limiting local agricultural concerns associated with irrigation.

Table 1. IX product water versus well water quality final 6 month average data (n = 32)

		Well Water		Product Water		
Parameter	unit	Average	STD	Average	STD	Change
Chloride	mg/L	83.6	7.3	120	7	+36.4
Sulfate as SO_4^{-2}	mg/L	35.3	6.6	21.3	5.5	-14.0
Nitrate as N-NO_3^-	mg/L	21.5	1.4	7.4	1.4	-14.1
Nitrite as N-NO_2^-	mg/L	0	0	0	0	0
Alkalinity	mg/L as $CaCO_3$	164	4	167	5	+3
Calcium	mg/L as $CaCO_3$	232	22	220	22	-12
Hardness	mg/L as $CaCO_3$	286	26	264	24	-22
TOC	mg/L	1.3	0.4	1.5	0.5	0.2

A reduction in sulfate concentration was observed in the product water due to absorption during the IX service cycle (incomplete sulfate dumping). Consequently, sulfate was found to build up in the regenerant (see below). As expected calcium, hardness and alkalinity remained largely unchanged in the product water. A slight increase in TOC was observed suggesting that the resin remained relatively free of organics from the recycling regenerant brine. In addition, absorption tests showed that the exchange capacity of the IX resin remained the same after a year of operation. The bacterial count of product water before disinfection was low, 10-700 cfu/ml.

Bioregeneration of the spent regenerant

Spent regenerant was first pumped into the SBR unit for denitrification. The SBR unit operated in 8 hour cycles and achieved complete nitrate removal. The average concentration N-NO_3^- of the spent regenerant was 375±25 mg/L and the total amount denitrified per batch was 113±8 g. During denitrification, ethanol (the electron donor) was dosed in aliquots according to ORP monitoring and control and resulted in very low biomass yields (approximately 1L waste biomass/d). ORP values at the beginning of the batch were between -150 to -200mv, rising to -90 to -125mv by the time of the first ethanol dosage at 90 min. after reactor filling. ORP values of -125 to -175mv were subsequently observed during the denitrification process. The end of denitrification was signified by the sharp drop in ORP to values below -200 mv and the effluent was discharged when the ORP reached -250mv. Based on the settling volume of the SBR reactor (150 L), the volumetric denitrification rate was calculated to be 2.25±0.2 g $N/L_{reactor}/d$.

Over a short period of time (about 100 SBR cycles or 1 month at full capacity) the composition of the recycling regenerant solution changed significantly before reaching steady state concentrations (Fig. 3). The change in chemical composition was first due to the high concentration of alkalinity in the form of bicarbonate ions (HCO_3^-) released during denitrification of the spent regenerant. Secondly, as mentioned above, sulfate absorbed onto the resin from the well water was desorbed to the regenerant during column regeneration and built up in concentration. While the amount of Cl^- lost to the product water during IX was compensated to 13 - 15 g/L by adding HCl and NaCl to the regenerant solution, the concentrations of alkalinity and sulfate reached about 15 g/L and 7 g/L, respectively. No adverse effects of sulfate and alkalinity build up in the recirculating brine on the IX process or the amount of nitrate removed were observed due to the much stronger affinity of the resin to nitrate and chloride. Sulfide formation during biological denitrification was observed, but controlled by accurate ethanol dosing.

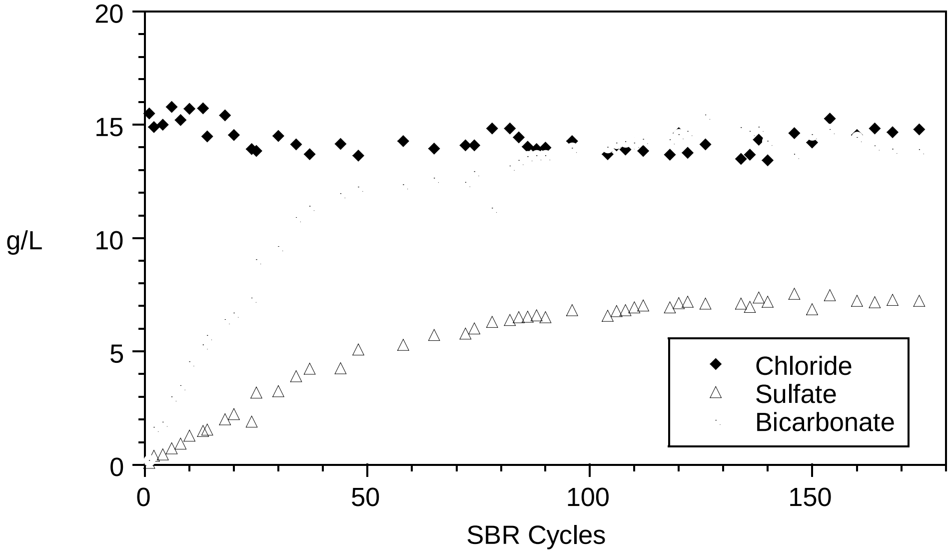

Figure 3. Change in the composition of the recycling regenerant solution.

The resulting denitrified SBR effluent was turbid (30 to 40 NTU) and could not be used directly in column regeneration. Ozonation was found to dramatically reduce turbidity in the denitrified SBR effluent to 2.8±1.0 NTU and enhanced filterability with simple operation. Batch ozonation tests were used to initially determine the retention time necessary to complete turbidity removal under continuous flow conditions (Fig. 4). During ozonation, the suspended solids causing the effluent's turbidity were converted into an easily collectable foam that constituted about 0.3% of the treated brine on a mass basis. Typical ozone demand was about 3 to 5 mg O_3 L/brine. However, when ethanol was significantly over or under dosed during denitrification due to malfunction or inadequate control, ozone demand increased up to ten fold in order to oxidize residual nitrite or sulfide concentrations. In addition, ozonation may cause the formation of bromate, however, none was detected in the product water.

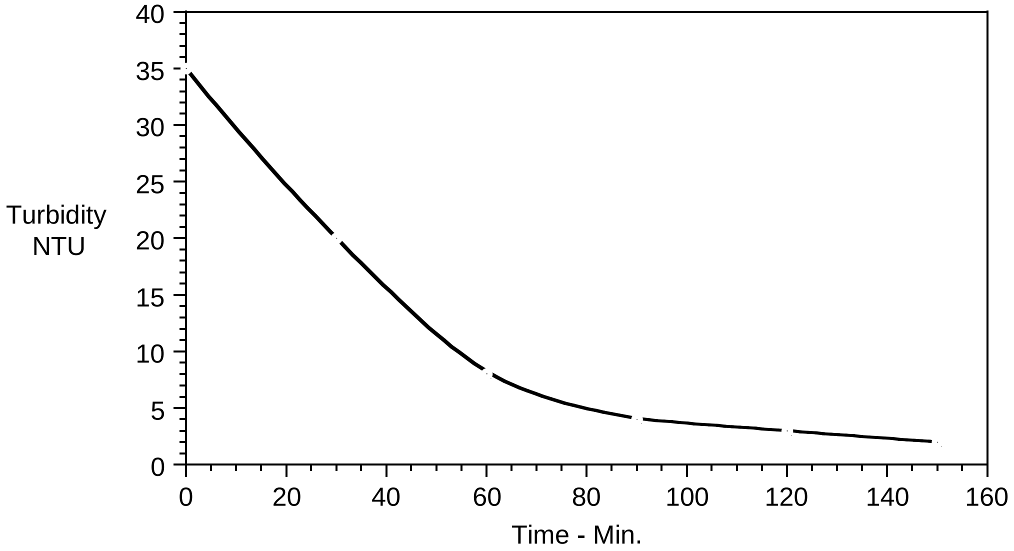

Figure 4. Reduction of SBR effluent turbidity by ozonation.

DOC in the recycled regenerant after more than a year of continuous operation was maintained at relatively low levels of 61±11 mg/L suggesting that ozonation breaks down a significant amount of the residual organic compounds originating from biological denitrification. As mentioned before, the remaining DOC did not interfere with IX resin exchange capacity, however, it was necessary to maintain a rigorous disinfection program to prevent bacterial growth and contamination throughout the system.

Wastewater from the combined ion exchange and biophysical treatment system were identified from four sources: 1) production of excess regenerant due to the addition of chemicals, 2) 1st disinfection wastewater, 3) 2nd disinfection wastewater, and 4) column flush wastewater. Due to high salt content, wastewaters from excess regenerant production and 1st disinfection required disposal by truck. The remaining wastewaters from 2nd disinfection and column flush had EC meeting regulations and were disposed to sewage. Product water recovery from the pilot plant was 99.4% with 0.2% high salt content wastewaters disposed by truck (high EC) and 0.4% disinfection and rinse wastewaters disposed to sewerage.

CONCLUSIONS

A combined process for nitrate removal from groundwater consisting of ion exchange and recycling of the regenerate brine in a closed loop was tested for over a year under field conditions at the Tzur Moshe well. The goals of the process were to minimize IX waste brine production, DOC accumulation in the recirculating brine, and minimize Cl^- addition to the product water for agricultural use. IX product water average chloride addition was 36.4 mg/L (molar exchange ratio of Cl^-/NO_3^- of 1.03) and the average product water nitrate concentration of 7.4 mg/L as N met local regulations. Product water DOC slightly increased. A denitrifying SBR and ozonation reactor integrated in the brine recycle loop produced a high quality regenerant and was efficient with respect to electron donor usage and waste brine production. About 3.5% of the regenerant was lost per cycle, i.e. about 0.2% of total water treated, mainly during rinsing of the regenerated IX resin with freshwater and excess regenerant produced from the addition of chemicals. In spite of this low level of blow-down, steady state regenerant DOC was maintained at relatively low levels. Although relatively complex, the system operated automatically and reliably for a small water treatment plant and compliance with health and environmental regulations.

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