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Selective nitrate removal from groundwater using a hybrid nanofiltration–reverse osmosis filtration scheme

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HIGHLIGHTS

- A hybrid NF/RO filtration scheme for nitrate removal is proposed and tested.
- Production of low salinity brines allowed to be discharged to sewerage systems.
- The new scheme can be applied in single or double NF stage modes prior to RO step.
- Appropriate NF membranes for the process should reject Cl^- better than NO_3^-.
- The results show the process to be both technically feasible and energy efficient.

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ABSTRACT

A novel and potentially cost effective filtration scheme for removal of nitrate from groundwater, characterized by production of low salinity waste brine that can be easily discharged to sewerage systems and high product-water recovery, is proposed. The inherent preference of particular NF membranes for rejecting chloride and sodium over nitrate ions is utilized in a preliminary NF stage to remove Na^+, Cl^+, Ca^{2+} and Mg^{2+} to a side stream. In a second stage, RO is applied to remove NO_3^- and the RO permeate is mixed with the side stream of the NF stage to create product water low in nitrate, yet with a balanced composition consisting all the required species and minerals. The number of NF stages depends mainly on the rejection efficiency of the NF membrane. Based on Israeli regulations for both drinking water and required composition of brines discharged to the sewage, a treatment scheme composed of a single and double NF stages followed by RO is shown to reach water recoveries of 91.6% and 94.3%, respectively. Each NF stage raises the energy cost by approximately 0.5 cent/m^3 product water. However, this cost is easily paid back by the inherent additional advantages of the combined scheme, i.e., less water treated by the RO, significant increase in total recovery ratio, no need in re-mineralization of the product water and minimization of calcium carbonate precipitation potential on the RO membrane. The principles for process design are described, making the specific treatment scheme proposed here easily adjustable to other regulatory requirements and other water characteristics. A provisional patent has been filed.

1. Introduction

Increase in nitrate concentrations is observed in ground waters around the globe, mostly resulting from intensive application of fertilizers. In Israel, nitrate concentrations exceeding the 70 mg/L (~16 mg NO_3^--N/L) standard is the main reason for closure of wells in the coastal aquifer, with an annual water loss of ~24 million m^3. Application of advanced treatment technologies is required to reduce nitrate concentrations from 90–120 to below 60 mg/L in a cost effective and efficient fashion [1].

Advanced physical–chemical treatment techniques such as reverse osmosis (RO), ion exchange and electrodialysis are known to be effective for removing nitrates. However, all three methods produce waste concentrates (brines) containing high concentrations of nitrate, as well as other ions. In many inland places, local regulations regarding discharge of brines to the sewage system limit the application of physical–chemical technologies. In Israel, the threshold sodium and chloride concentrations for disposal to the sewage are 230 and 430 mg/L, respectively [2]. Treatment facilities installed for NO_3^- removal from drinking water in Israel are mainly based on separation by electrodialysis and RO, due to the relative simplicity and proven reliability of these methods [3]. On top of brine production, another drawback of membrane

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technologies is the potential for chemical fouling of the membrane. To minimize chemical fouling, operation with low water recovery ratios or the use of chemicals (antiscalants) is practiced [4]. Biological denitrification, the alternative treatment method, does not produce waste brine but requires an intensive post-treatment step to remove potential water contamination by organic matter and bacteria. Moreover, health concerns and public acceptance constraints limit the application of biological treatment of drinking water [5–7].

Nanofiltration (NF) is a promising technology which has been reported suitable for groundwater treatment. It is defined as a process with characteristics between RO and ultrafiltration and comprises a variety of membrane types with different retention efficiencies for either mono- and multivalent ions [8]. The main advantage of NF over RO is operation under lower pressures and higher recoveries [9]. The use of NF technology was extensively reported for water treatment processes as a sole treatment stage [8–14] or in combination with RO [15–17]. However, with respect to NO_3^- removal all of these processes, in their current development stage, are still limited by the aforementioned drawback associated with production of concentrated brines and the accompanied disposal issue.

A novel filtration scheme is presented for removal of nitrate from groundwater, accompanied by the production of low concentrated waste brine and high recovery. The methodology is based on an inherent preference of particular NF membranes for removing chloride and sodium over nitrate ions [18]. This membrane selectivity is utilized for removing a relatively high fraction of the chloride and sodium ions to a side stream in a preliminary stage prior to a main stage in which nitrate is removed by RO. The side stream of the NF stage is then mixed with the product water after nitrate has been removed from it in the RO step. As a result, the salinity of the waste brine is relatively low and can be discharged to the sewage according to local regulations. Moreover, the nitrate-rich brine contains relatively low Na^+ and Cl^- concentrations and can thus be used for irrigation purposes. The various alternatives for process design such as the NF membrane type, the number of NF stages and the recovery ratio of each filtration stage depend mainly on the planned usage of the waste brine and on the local regulations for both brine and product water. These aspects, along with other considerations related to the proposed process are exemplified in this paper on a specific nitrate-contaminated groundwater and brine discharge according to local Israeli regulations. However, the principles for process design are described in a manner enabling the suggested treatment scheme to be easily adjusted to other discharge criteria and/or water characteristics.

2. Description of the proposed treatment scheme

The combined system consists of a NF step followed by RO filtration. The NF step can be applied in single- or double-stage modes, according to the removal efficiency of the NF membrane, as discussed in Section 4. The suggested single and double NF stage treatment schemes are illustrated schematically in Figs. 1 and 2, respectively. Fig. 1 also demonstrates concentrations of Cl^- and NO_3^--N together with percentages of feed water (Q) and pressures in the different stages of the process. These numbers are based on specific feed water characteristics (Zur Moshe well), Israeli regulations and calculations elaborated later in this work.

The NF stage serves as a selective barrier for passage of nitrate to the permeate water over the passage of other monovalent ions (e.g. chloride and sodium). It also rejects Ca^{2+}, SO_4^{2-} and HCO_3^- ions to a large extent thereby reducing the precipitation and scaling potential of (mainly) calcium-based precipitants in the following RO stage. Additionally, it reduces the amount of water needed to be treated by RO. In the RO step, nitrate and the remaining ions are rejected and removed as brine with relatively low salinity. The concentrated stream from the NF step is mixed with the product water emerging from the RO step (i.e. RO permeate), thus re-mineralization of the product water is unnecessary.

3. Materials and methods

3.1. Experimental setup

A bench scale nanofiltration system operating in cross-flow mode with a flat sheet membrane cell was used for all membrane tests. The total membrane surface area was 48 cm^2. Water was recirculated from the feed tank over the membrane cell with an applied inlet pressure of 8 bars and cross flow rate of 10 L/min. Water temperature was maintained constant at 24 °C. Six different NF membranes were tested: DL and DK (GE Osmonics), NF90, NF245 and NF270 (Dow) and TS80 (Trisep). For each membrane test, permeate and retentate were collected for further analysis throughout the whole process. The final NF recovery ratio was 70%. RO filtration was not tested experimentally. All experiments were carried out with real groundwater brought from the Zur Moshe well located on the coastal aquifer of Israel. The main groundwater quality parameters are shown in Table 1.

3.2. Analyses

Nitrate and chloride were measured using ion chromatography (761 Compact IC, Metrohm). Calcium, magnesium and sodium were measured with ICP-OES spectrometer (iCAP 6000 series, Thermo Fisher Scientific). Conductivity and pH were measured with standard lab conductivity and pH meter (MeterLab). Alkalinity was measured according to Standard Methods (Method 2320). Estimation of precipitation potential of minerals was done using the PHREEQC software (USGS).

3.3. Mass balance for determining the adequate recovery ratio for each filtration stage

The selection of the recovery ratio to be applied in each filtration stage is imperative for successful process design. Maximization of product water recovery, minimization of waste brine, minimization of water volume to be treated in further steps (second NF stage, if applied, and RO), salinity of the waste brine, nitrate concentration in the product water and reduction of chemicals dosing – all are strongly affected by the recovery ratio of the different filtration stages. Operating the preliminary NF stage with a minimal recovery ratio can meet most of these goals. NF with a lower recovery ratio produces less saline NF permeate, thus also reducing the salinity of both the RO feed stream and the resulting waste brine. However, operating the NF with a lower recovery ratio produces a higher volume of NF retentate contaminated with nitrate and raises the nitrate concentration in the product water. The RO recovery ratio controls both the total process recovery ratio and the TDS concentration in the final brine. Therefore, optimal recovery ratios in both the NF (first stage NF in the double NF scheme) and RO steps should be pre-determined in order to meet regulations of both product water and waste brine to be discharged to the sewage. The effect of the recovery ratio of the second NF step on the various process considerations (relevant only to the double NF scheme) is less prominent and was thus fixed at 90% during the following preliminary process design calculations.

Eq. (1) [19] can be used to asses specific ion concentrations in permeate or retentate of NF for a given recovery ratio: