

Nitrate Removal from Drinking Water by Using Commercial Nanofiltration

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The aim of the present work was to investigate the efficiency of commercial nanofiltration: NF90 (Dow-Film Tec) in reducing nitrate concentration from water. Salt rejection was studied using KNO_3 , NaNO_3 and K_2SO_4 . The influence of the operating pressure, feed concentration and temperature were studied. The influence of sulfate on the retention of KNO_3 salt was also examined. To examine the influence of the nature of associated cation on nitrate retention, the retentions of two nitrate salts, KNO_3 and NaNO_3 were compared. The experiment results show that nitrate retention increases sharply by increasing the pressure from 4 to 8 bars and becomes stable at higher pressures but decreases by increasing temperature and also by increase in sulfate ion and nitrate salts concentrations. The retention of KNO_3 was always lower than that of NaNO_3 .

Key Words: Nanofiltration, Nitrate retention.

INTRODUCTION

Iran is located in a zone with an average annual rainfall of less than one-third of the average global annual rainfall. Furthermore, the location and time of distribution of the rainfalls are inappropriate and so, major parts of the country are dry and have the problem of supply drinking water¹.

In Tehran, due to a decrease in the number of high quality water resources, it occasionally becomes necessary to draw out lower quality waters. Such reserves are mostly polluted and contain nitrate concentrations up to 150 mg L^{-1} .

One of the methods of purifying water in order to provide healthy and high quality drinking water from ground waters with such nitrate contents is nanofiltration (NF)².

The rejection of ions by NF membranes is rather complicated. Although numerous models have been proposed to delineate and predict solute

rejection by nanofiltration, experimental tests of the models with various NF membranes have shown that none could adequately predict the nanofiltration performance³⁻⁵. In fact, all real membranes have distinctive surface characteristics and pore size distribution, which make prediction of ionic retention complicated. Thus, experimental test is still the easiest mean to know the phenomena responsible for the performance of the commercial nanomembrane in ions retention.

The objective of the present work is to investigate and explain the rejection of nitrate ions as a function of operating pressure and solution characteristics by NF90.

EXPERIMENTAL

The experiment was carried out on a pilot plant operating in a batch recirculation mode, in which both permeate and concentrate were recycled directly to the feed tank to ensure a constant feed concentration. The nanofiltration (NF) module was equipped with a composite spiral-wound membrane of standard size (2540).

The experiments were conducted with potassium salts (KNO_3 , K_2SO_4) and sodium salt (NaNO_3) added to tap water. The effect of the pressure was studied over the range of 5-10 bar. The concentration influence was studied for concentrations 50, 100, 150, 200, 250 and 300 mg L^{-1} (NO_3^-) and the effect of sulfate was observed for two concentrations 50 and 200 mg L^{-1} (SO_4^{2-}). These values were selected in agreement with the ions concentrations in natural waters.

The temperature for all experiments was 22 °C and the pH was above 6. The recirculation flow was fixed at 780 L h^{-1} .

Samples of permeate were collected after 1 h of filtration. Retentions (R) were calculated as percentage by comparing the concentration of ions both in the permeate (C_p) and in the feed water (C_f) as follows:

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

Nitrate and sulfate concentrations were determined by standard methods (4500 NO_3^- nitrogen E. Cadmium reduction method and 4500- SO_4^{2-} sulfate E. turbidimetric method).

RESULTS AND DISCUSSION

Influence of pressure: Fig. 1 shows the nitrate retention vs. the applied pressure for the nitrate concentration of 150 mg L^{-1} . As can be seen, nitrate retention increased sharply by raising pressure from 4 to 8 bars and became stable at higher pressures. This result is in agreement with that obtained by Ratanatamskul *et al.*⁶ and Xu and Leburn⁷.

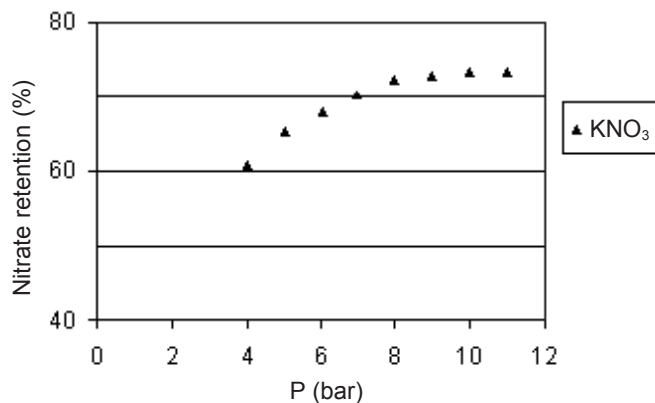


Fig. 1. Nitrate retention as a function of pressure for $150 \text{ mg NO}_3^- \text{ L}^{-1}$

In the experiment with KNO_3 solution, K^+ cations have small ionic radius (0.124 nm) and high diffusivity⁸ ($1.957 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$); so they can enter membrane pores. Some of them will remain in the pores due to surface forces of the membrane. With an increase in pressure, these surface forces remain constant, hence, the amount of K^+ ions passing through the pores and subsequently NO_3^- (for the electric balance in the solution) will not have a remarkable change. But because flux of the solvent (water) has increased, eventually the amount of nitrate detention has increased. When this pressure goes beyond a certain extent, the pressure of the solvent can itself cause the cations absorbed in the pores to come off and take them away, which will lead to a decrease in nitrate retention.

Consequently, nitrate retention increases strongly by increasing the pressure from 4 to 8 bar and become stable at higher pressure.

Effect of nitrate concentration on nitrate retention: The effect of nitrate concentration on nitrate retention is shown in Fig. 2. As can be seen, an increase in KNO_3 concentration causes a slight decrease in nitrate retention. This result is not in agreement with that obtained by Baticle *et al.*⁹ and Xu and Lebrun⁷. These researchers have reported that by increasing the pressure, nitrate ions retention decreases drastically due to shielding phenomenon. As a matter of fact, an increase in cation concentration leads to an increase in the formation of a cation layer on the surface of the membrane, thus reducing its effective charge. Consequently, the repulsion between the membrane and the nitrate ions is reduced and the nitrate ions go through the membrane more easily; thus their retention decreases. In this experiment, the result shows that for NF 90 this decline is slight, indicating that the shielding phenomenon is not greatly involved in ion transfer through this membrane. This result is consistent with previous investigations^{10,11}.

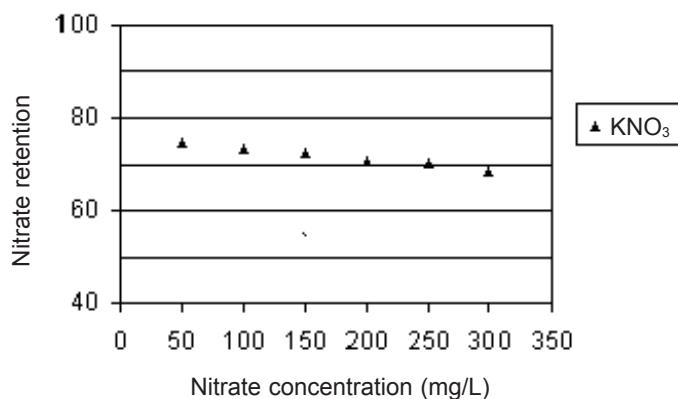


Fig. 2. Concentration effect on nitrate retention (pressure = 8 bar)

Effect of sulfate concentration on nitrate retention: The concentration of nitrate ions was remained constant (100 mg L^{-1}) while the concentration of sulfate was changed (Fig. 3) when the effect of sulfate concentration on nitrate retention was investigated. The results show a strong decrease in nitrate retention when the concentration of added sulfate increases. This result concurs with those obtained by Tsuru *et al.*¹² and Choi *et al.*¹³.

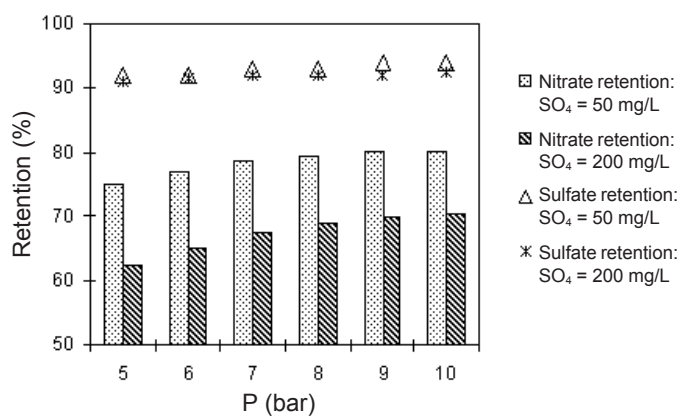


Fig. 3. Sulfate concentration effect on nitrate retention for $100 \text{ mg NO}_3^- \text{ L}^{-1}$

The phenomenon could be related to the increase in the amount of potassium ions in the solution. In other words, by increasing the quantity of these cations, screening of the negative charges of the membrane is increased and so nitrate ions retention decreases. However, in this case, as described in the previous section, this interpretation is not adequate to describe the meaningful reduction of nitrate ions retention.

As can be seen in Fig. 3, the retention of sulfate ions is very high and by increasing the quantity of added K_2SO_4 , sulfate retention still remains high while nitrate ions retention decreases sharply. The high retention of the sulfate ions could be caused by their double negative charge and their size¹⁰. On the other hand, their hydration energy (1090 KJ mol^{-1}) is stronger than that of nitrate ions² (306 KJ mol^{-1}). This causes the sulfates to pass through the membrane with more difficulty. Therefore, by increasing the sulfate concentration, the nitrates pass through the membrane in larger amounts to establish the electroneutrality on both sides of the membrane and thus nitrate retention decreases.

Influence of associated cation on nitrate retention: As shown in Fig. 4, nitrate retention in the case of $NaNO_3$ is higher than in that of KNO_3 . The reason⁸ for this phenomenon is that the transfer of Na^+ ions is more difficult than that of the K^+ ions because of their different Stokes radii (0.183 and 0.124 nm, respectively). Thus, the Na^+ ions are retained more by the membrane than the K^+ ions. Logically, the stronger retention of Na^+ leads to the stronger retention of nitrate to establish electroneutrality on both sides of the membrane.

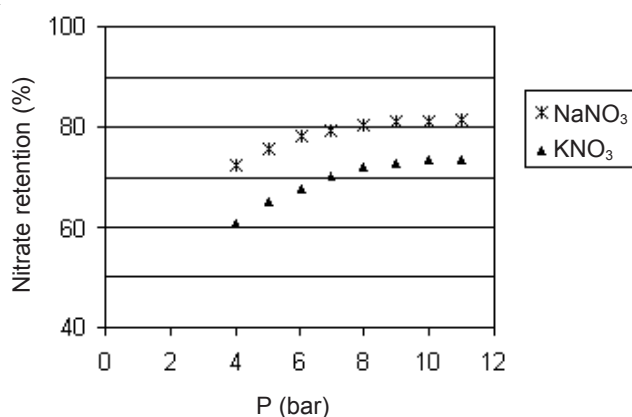


Fig. 4. Influence of associated cation on the nitrate retention for $150 \text{ mg NO}_3^- \text{ L}^{-1}$

Effect of temperature on nitrate retention: Fig. 5 shows the effect of temperature on nitrate retention. The results show that an increase in temperature leads to a decrease in nitrate retention. This phenomenon can be attributed to a decrease in the kinematics viscosity of the solution by increasing the temperature. Decreasing the kinematics viscosity of solution leads to an increase in osmotic pressure and the permeability of the solvent and the solute, consequently, the nitrate retention decreases¹⁴.

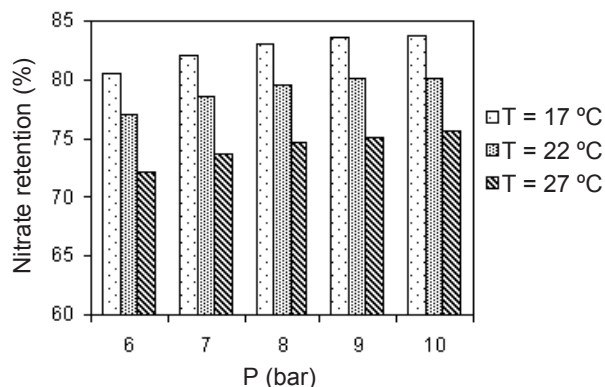


Fig. 5. Temperature effect on nitrate retention for $100 \text{ mg NO}_3^- \text{ L}^{-1}$

Conclusion

In this study, the effects of pressure, concentration, sulfate and associated cation on nitrate retention by commercial nanofiltration (NF 90) were investigated. The experiment confirmed that retention increases with pressure. In fact, nitrate retention increases strongly by increasing the pressure from 4 to 8 bars and becomes stable at higher pressures. The influence of nitrate concentration on nitrate retention was observed and the results show that an increase in KNO_3 concentration leads to a slight decrease in nitrate retention.

The influence of sulfate on the retention of nitrate was investigated. The concentration of nitrate ions was maintained constant (100 mg L^{-1}) and the effect of sulfate was observed for two concentrations 50 and 200 mg L^{-1} (SO_4^{2-}). The results show a strong decrease in nitrate retention when the concentration of added sulfate increases. This behaviour can be attributed to an increase in the quantity of potassium ions present in the solution and thus to an increase in the screening of the negative charges of the membrane by these ions. However, in this case, this interpretation is not adequate to describe the significant reduction in nitrate retention. Actually, sulfate ions are highly rejected, so by increasing sulfate concentration, the nitrate transfer through the membrane is increased to establish the electroneutrality on both sides of the membrane; thus nitrate retention decreases.

The influence of associated cation on nitrate retention was observed and the results show that the nitrate retention in the case of NaNO_3 is higher than in KNO_3 . Finally, the influence of temperature on nitrate retention was examined at: 17 , 22 and 27 °C . The results show that an increase in temperature leads to a decrease in nitrate retention.

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