Impact of Operating Parameters on the Nitrate Removal by Nanofiltration

Ali Rıza Dinçer*, Tarık Uçar**

Department of Environmental Engineering, Namık Kemal University, Çorlu, Tekirdağ, Turkey.

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Abstract: The removal of NO$_3^-$ from synthetic water has been studied using two different nanofiltration (NF) membranes (GE Osmonics DK and, GE Osmonic DL). Nitrate removal efficiencies of two different nanofiltration membranes investigated by means of a lab-scale membrane module in synthetic nitrate solutions that have different concentration. The impact of principle working parameters, for example, NO$_3^-$ concentration, pH, and pressure and permeate flux of both membranes, was examined.

The outcomes demonstrated that the dismissal of NO$_3^-$ and the flux rate for all membranes (DK and DL) expanded directly with the trans-membrane pressure and diminished with the NO$_3^-$ concentration. Nitrate rejection rate for the DL membrane was between approximately 23% and 30%. Under the same pressure (6 bar), the DK membrane generated a higher nitrate rejection rate (42%-55%) than the DL membrane. And also, rejection levels for 12 bar pressure achieved by DK have been in range of 63-69%, while DL gives the lowest rejection in the range of 29-30%.

The wide range change of the pH from 4 to 11 of the feed did not alter nitrate rejection very much for DK and DL membranes. Nitrate rejection for DL and DK membranes decreases by increasing feed concentrations and filtration time.

Key words: Nanofiltration, Synthetic water, Nitrate removal, DK and DL membranes

1. Introduction

Nanofiltration is a pressure driven separation process that is situated between ultrafiltration and reverse osmosis, reaching a molecular weight cut-off (MWCO) around 300g/mol. Nanofiltration membranes have a dense active membranes that contains charged functional groups on its surface. [1]

The segregation conduct should be the consequence of double strengths: a worldwide surface (friction, electrostatic) which holds the solute in the pore and a worldwide convective drive coordinated towards the retentate which relies on upon the applied pressure. In parallel arrangements, surface drive relies on upon the

Corresponding author: Ali Rıza Dinçer, Department of Environmental Engineering, Namık Kemal University, Çorlu, Tekirdağ, Turkey.
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hydration energy of the related cation and also membranes solute electrostatic cooperations. In ternary blends, we underscored the impact of solute-solute interactions (Donnan effect) [2,3,4]. For uncharged molecules, sieving or size exclusion is most responsible for separation; for ionic species, both sieving and electrostatic interactions are responsible for separation [5]. A suitable NF membrane for nitrate removal must have tight porous structures and be negatively charged [6].

Nanofiltration membranes are efficacious for the generation of high-quality drinking water that can be used for the removal of inorganic contaminants (like nitrates, hardness, arsenic, fluorides and heavy metals) and organic contaminants (like trihalomethanes, pesticides, and natural organic matter) [7,8,9]. This technology also proposal the great advantage of lower operating expense than reverse osmosis. Low cost membrane materials have also contributed to its spread, making it less expensive than the other process. Since reverse osmosis cannot be used for fractional and/or selective demineralization, nanofiltration is more appropriate for producing drinking water directly without the need for remineralization [10]. The European Community established an MCL of 50 mg NO₃⁻/l (11.3 mg NO₃⁻-N/l) and a recommended level of 25 mg NO₃⁻/l [11]. The maximum admissible nitrate concentration for drinking water is fixed at 50 ppm [12].

Nitrates are monovalent and thus not expected to be rejected to a large extent by nanofiltration membranes. However, they have been used by a number of researchers as model species to study rejection mechanisms [13,14]. Van der Bruggen et al. found a significant nitrate removal (76%) with the NF70 membrane (Dow/Filmtc), which is to be expected from a nanofiltration membrane with tight pores. For tight nanofiltration membranes, size exclusion can provide an additional ion rejection [15,16]. The material utilized for nanofiltration membranes creation is natural in nature and most nanofiltration membranes are different membranes thin-membranes composites of natural polymer. The membranes are made of many different materials, mostly from polymers such as aromatic polyamides, polysulfones, polyethersulfones, substitutedpoly (vinyl alcohols), poly (acrylonitrile), poly (phenylene oxide), as well as from different modifications of them [17]. The membranes are accepted to be permeable, with an average pore diameter of 2nm [18]. DK and DL membranes had similar morphologies. Both of them showed a highly porous structure which exhibited great tortuosity, offering important flow resistance. The separation mechanism of these membranes involves steric and electrical (Donnan) effects [19]. Nanofiltration membranes have private characteristics: high retention coefficient for neutral molecules with a molecular mass(Mm)~300 Da, which is equivalent to a pore diameter of app. dₚ=1nm [20].

The GE Osmonic D-Series family of proprietary, thin film, nanofiltration, and flat-sheet membranes are portrayed by an approximate sub-atomic weight cut-off 150-300 Dalton for uncharged organic molecules. Multiple anions are preferentially rejected by the membrane while monovalent ion rejection is dependent upon
initial concentration and composite membrane systems to operate at applied pressures below those of RO systems. DK sheets are ideal for industrial water applications such as sodium chloride diafiltration and metals recovery. The DL designation is commonly used for acid and alcohol removal, antibiotic concentration, BOD/COD removal, cheese whey desalting, dextrose treatment, dye concentration, ethylene glycol treatment, detergent and heavy metal removal, plating waste polysaccharide desalting, sugar fractionation [21].

The performance of the tested membranes have been measured in terms of permeate and nitrate rejection under different operation conditions. This study aims at contributing to identification and a better understanding of the mechanism of nitrate particle move in nanofiltration and at underlining the conceivable uses of this procedure in the treatment of dirtied waters.

This exploration work was completed with the accompanying destinations: (1) to explore the ability of nanofiltration membranes (DK and DL) for nitrate removal from synthetic waters. (2) to investigate the influence of different operating parameters such as membrane type, initial feed concentration, applied pressure, feed pH, operating period on nanofilter membrane performance. Membrane process performance was evaluated by measuring filtration flux and percentage rejection of nitrate.

2. Materials and Methods

Fig.1 demonstrates a schematic diagram of the experimental set-up used for the study of the impact of pH, pressure, and concentration and operation time. The experimental work consists in evaluating the performances of the nanofiltration process by comparing two membranes for the nitrate removal from synthetic waters. The experimental setup included a feeding tank, a high-pressure pump for producing trans-membrane pressure and feeding, and three pressure gauges. The active volume of the feed tank was 5.0 litre. Both penetrate and concentrate has been recycled to the feed tank except for the sample withdrawn for nitrate analysis. Re-circulating the concentrate and the penetrate streams into the feed tank kept up constant concentration of the feed.

The membrane pressure and volumetric stream rate were balanced using the concentrate (reject) outlet valve. Pressure over the membrane can be varied from 2 to 12 bar with manuel valves. There were two pressure gauges of 0-1500 kPa range. One was installed at the highest point of the feed tank for measuring the pressure of the tank and additionally the inlet pressure of the membrane and the other was installed for measuring the outlet pressure of the membrane. There is a by-pass before feed inlet to recycle extra feed to the tank. The operating pressure is controlled by a back pressure regulator and monitored with a pressure gauge. The pumps (SEKO KS1D038A for 12 bar operating pressure and DENG YUAN TYP-2500N for 2-6 bar operating pressure) have been used to supply the operating pressure and feed circulation.
The nanofiltration (NF) experiments have been performed by using two types NF membranes: DK series and DL series. Flat sheet membranes have been used with an active surface of 42 cm². Table 1 shows the characteristic of the two membranes. All chemicals used were analytical reagent grade or higher quality. All solutions were prepared with deionized water and stored at 4°C until use. Nanofiltration efficiency was fundamentally measured as far as permeate flux and % rejection of nitrate. A synthetic solution of sodium nitrate (NaNO₃, MERCK) has been prepared and used as the feed solution. The pH of the solution was balanced by either HCl or NH₃ at 4, 6.8 and 11, separately. Before starting experiments, an initial sample was taken from the sustain tank and analyzed. During the experiments, samples were taken from the permeate stream at various pressure.

Table 1. Characteristic of nanofiltration membranes (www.sterlitech.com)

<table>
<thead>
<tr>
<th>Membrane* %</th>
<th>Material</th>
<th>MWCO</th>
<th>Size</th>
<th>MgSO₄ rejection</th>
<th>MgSO₄ rejection</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK</td>
<td>Polymer</td>
<td>150-300</td>
<td>CF042</td>
<td>96</td>
<td>Negative</td>
<td>2-11</td>
</tr>
<tr>
<td>DL</td>
<td>Polymer</td>
<td>150-300</td>
<td>CF042</td>
<td>98</td>
<td>Negative</td>
<td>2-11</td>
</tr>
</tbody>
</table>

MWCO: represents moleculer weight cut-off*: manufacturer (GE Osmonics, Thin film, YMDKSP4205, YMDLSP4205)

After every run feed, the feed tank was loaded with refined water and the membrane was cleaned by flushing at higher stream rate. Membranes’ cleaning is typically vital with a specific goal to recover the flux reduced by fouling and reuse similar membranes for various experimental runs. No chemical cleaning has been performed.

The removal efficiency (R) was calculated by the following equation.

\[ \%R = \left( \frac{C_o - C_e}{C_o} \right) \times 100 \]

Where:

- \( C_o \): Nitrate concentration in permeate (mg/l).
- \( C_e \): Nitrate concentration in feed water (mg/l).

Flux rate represents the volume of liquid passing through specific area of membrane at certain operating pressure during a period of time.

\[ J_w = \frac{\Delta V}{\Delta t \cdot S} \]

where:

- \( J_w \): flux rate (l/m².h)
- \( S \): represent the surface membrane area (m²)
- \( \Delta t \): time of filtration (h)
∆V: volume of water (l)

A schematic diagram of the test set-up is appeared in Figure 1. The principle parts of the set up can be separated into following:

(1)- Feed tank (5.0 l)
(2)- Feed pump
(3) - (7) Pressure regulation valves
(4) - (6) Barometer
(5) Nanofiltration module (CF042)
(8)- Permeate beaker

All experiments have been performed at room temperature (around 25°C) and each test has been repeated twice. Because of the little membranes region, the permeate stream was low, in this manner the permeate samples were gathered each 30 minutes time slot.

Nitrate concentrations the samples have been determined by a spectrophotometric method by using a AQUAMATE spectrometer. WTW-pH 3210 model pH meter has been used to measure pH values of samples. All the experimental results are obtained when the steady state is achieved. All measurements are performed according to standard methods relevant to water and wastewater. The feed cross-flow rate and the applied
pressure have been adjusted through changing the by-pass and outlet valves. After each experiment finished and when the feed solution was changed, the membrane has been rinsed with deionized water.

3. Results and Discussion

Removal efficiency is one of the most important characteristics of membrane; that’s depended on the feed water characteristics, membrane characteristics and applied pressure. Removal efficiency, represent the ability of membrane to reject nitrate from feed water. The behavior of nitrate separation under different operating conditions needs to be analyzed to get a proper understanding of the problem.

3.1. Effects of nitrate concentration on nitrate rejection rate at the different trans-membrane pressure

Fig.2 shows the effect of nitrate concentration on nitrate rejection rate at the different trans membrane pressure. Experiments have been carried out for NaNO₃ solutions with concentrations in the range of 30-150 mg NO₃⁻/l with the different membranes (DK and DL). In this step, the experiments were carried out at different pressure 2, 4 and 6 bars.

Nitrate rejection for DK and DL membranes decreases with increasing feed concentrations. Nitrate was removed 38-46% and 13-15 % from synthetic feed waters containing between 30 and 150 mg/l NO₃⁻ concentrations for DK and DL membranes (for 2 bar transmembrane pressure). Besides, in general maximum nitrate rejections both DK and DL membranes were obtained at 6 bar transmembrane pressure under all feed concentrations. The maximum rejection (30% DL and 55% DK for 6 bar) were observed at the lower feed concentration (30 mg/L NO₃⁻) and the minimum rejection (23% DL and 42% DK for 6 bar) were observed at the higher feed concentration (150 mg/L NO₃⁻).

Increasing of solutes at the membrane surface results in a higher solute concentration gradient across the membrane and thus, a greater solute transport through the membrane and a lower observed solute rejection. Another intriguing point which can be seen is that at higher pressure and higher concentration both DL and DK not gives appealing nitrate dismissal productivity. With low concentration, the impact of the screen is extremely feeble, the aversion of anions is essential and it prompts high retention. It can be demonstrated that the nitrate retention ascends with an expansion in the pressure for both membranes. This can be clarified by the influence of the pressure on the permeate flux furthermore its impact on concentration polarization.

DK may have higher charge limit than DL membrane. Since DL is closer to UF, the higher pressure may drive some monovalent particles to go through the membranes. Nitrate dismissal for DL membrane was 10-30% and that for DK membrane 40-60%.
3.2. Effect of filtration time on nitrate removal efficiency at varying transmembrane pressure

Fig. 3 shows the rejection of nitrate as a function of filtration time and transmembrane pressure for both membranes at a feed nitrate concentration of 30 mg/l, a pH of 6.8 and a temperature of 25°C. The nanofiltration experiments have been conducted under four different transmembrane pressures (2, 4, 6 and 12 bars). The cross flow filtration pressure was controlled by a valve after cells (Fig.1).

The impact of connected pressure on nitrate rejection is appeared in Fig.3 which demonstrates that the dismissal increases with an expansion in the applied pressure for both DL and DK membranes. The NO$_3^-$ rejection efficiency of DL membrane has been found to be lower than those of DK membrane. Initial range of nitrate rejection for 30 minutes filtration time was 15-45 % for DL and 47-69 % for DK membranes. After half past one hour of operation, the final ranges were 14-40% for DL and 45-63% for DK, accordingly. The result in this study has been confirmed by [22,23,9,4,2]. It can be seen that the nitrate rejection rate for DK membrane decreased from 63% to 45% with the decrease of operating pressure from 12 to 2 bar for 1.5 h operation time. When pressure decreased from 12 to 2 bar, nitrate rejection rate for DL membrane decreased from 40 to 14%.
for 1.5 h operation time. Depending on the operating conditions, the rejection of nitrate for DK membrane was in the range between 69% (for 30 min) and 63% (for 90 min) for transmembrane pressure higher than 12 bar. A high diffusive transport of salts through the membrane compared to convective transport is the reason for low retention at low pressure. With an increasing pressure, convective transport becomes more important than the diffusive transport and therefore solute retention increases.

Based on these results, it can be suggested that the NO₃⁻ rejection efficiency of both membranes was affected positively with increasing transmembrane pressure and negatively with filtration time.

![Fig. 3. The effect of filtration time on rejection of nitrate (%) at the different transmembrane pressure (pH=6.8, 30 mg NO₃⁻/l).](image-url)
3.3. Filtration time on nitrate removal efficiency at different initial nitrate concentrations

Fig. 4 shows the rejection of nitrate ions as a function of filtration time and initial nitrate concentrations for both membranes with an applied pressure of 6 bar and a temperature 25°C. It is found that, for both membranes DK and DL, an increase of initial nitrate concentration causes a decline in nitrate rejection efficiency. That drop becomes relatively weak during filtration time for both membranes. Another intriguing point which can be seen is that at higher concentration, neither DL and nor DK gives attractive nitrate rejection efficiency. Nitrate has been removed 43-57% and 26-30% from synthetic feed waters containing between 30 and 150 mg/l NO$_3^-$ concentrations for DK and DL membranes for 30 min. filtration time, respectively. Nitrate dismissal for DL membrane was 24-29% and that for DK membrane 39-54 for 90 minutes filtration time. The nitrate removal efficiency of DK membrane was better compared to DL membrane.

At the point when the pressure is more noteworthy, the screen impact increments and the capability of the membranes weakness. As an outcome, the repulsion between the membrane and the NO$_3^-$ anions diminishes; the last cross the membranes all the more effortlessly, in this manner pulling the cations with them to maintain electroneutrality, and retention is diminished. With low concentration and low filtration time, the impact of screen is extremely powerless, the repugnance of anions is vital and it leads to high retention. Generally, whereas ionic concentration increases, retention, and flux, decreases due to Donnan exclusion effect [12,17].
3.4. Effect of pH on nitrate removal efficiency

The impact of pH on the nitrate rejection for both membranes, at a nitrate concentration of 60 mg/l, a temperature of 25 °C and a trans membrane pressure of 6 bar, is depicted in Fig.5. The pH of the feed was controlled by addition of HCl or NH₃ solution. Three different pH values were investigated which were 4, 6.8, and 11.

The initial pH can affect membrane surface charge, hydrophilicity, porosity and the speciation of solutes [24]. The skin layer of NF membranes is generally made from hydrophilic amphoteric polymers, for example, polyamide, which possesses dissociable carboxylic (-COOH) and amine groups, exhibiting positive or negative surface charge dependent on pH [25,26]. Figure 5 shows that the nitrate removal efficiency decreases slightly with increasing pH. It can be seen that there was no much difference between the rejections at different
pHs. Nitrate retention depended on membrane, and was mostly pH independent [27]. The lowest retention was observed with DL membrane, which is the loose membrane.

The DK membrane demonstrated a higher nitrate rejection if compared with the DL membrane in all the range of pH researched. The results indicate that a decrease in pH from 11 to 4, the removal percentage of nitrate increases from 48% to 55% (for DK membrane). For the DL membrane the nitrate rejection increases 26% to 31% when the pH of solution decreases from 11 to 4. The higher nitrate rejections were observed up to pH 4 for both of membranes. For acid pH, the retention of nitrates slightly increases when the pH decreases.

The positive charge of the membranes develops when the pH decreases and the Na⁺ particles are increasingly dismisses by the NH₃⁺ groups of the membrane. As the cation and the anion can’t act freely, NO₃⁻ also rejected to keep up the electroneutrality. This charge impact is hence added to the steric exclusion phenomenon and the maintenance increases [2].

The results presented in Figure 5 show a minimum of nitrate ion retention for an estimation of pH equivalent to 11 around. The expansion of NH₃ also leads to neutralization of the membrane charge by the NH₄⁺ ions and in this manner to a decrease of the membrane-anions aversion. This can be explained by the lack of electrostatic repulsion between the membrane and solute at pH 11.
3.5 Effect of transmembrane pressure on permeate flux

Figure 5 demonstrates the impact of applied pressure (at a fixed feed concentration) on the permeate volume flux and it can be seen that the permeate volume flux for both of filters increases linearly with increasing applied pressure, which indicates that there may be negligible concentration polarization in the membrane cells. With increase in operating pressure, the driving force across the membrane increases, leading to an enhancement of permeate flux [28]. Experiments have been conducted to study the effect of pressure ranging from 2-12 bar at pH: 6.8. Permeate flux is one of key factors for evaluating the performance of membranes, which reflects the amount of permeate and product rate and is a factor demonstrating the membrane’s efficiency. It demonstrates that both the NF membranes (DL and DK) provide linear permeate increase with pressure which is like that reported in literature [29,30]. The maximum flux rate was obtained at 12 bar (DL: 128.57 l/m².h and DK: 90.48 l/m².h) and minimum flux rate was obtained at 2 bar (DL:33.33 l/m².h and DK:19 l/m².h). The transmembrane pressure used was p=2 bar, which is relatively low. The concentration of nitrate in
feedwater was kept at 30 mg/l. Dismissal by NF membranes increases with pressure, in light of the fact that at high pressure, solvent permeability expands compared to solute [3]. The expanded solvent penetrability with pressure might be the conceivable reason of this. The linearity of the permeate flux with the transmembrane pressure indicates that the concentration polarization phenomenon is not significant for this feed concentration (30 mg/l NO$_3^-$). These results may be explained by low level of NO$_3^-$ concentration in feed solution.

The flux increase rate for membrane DK is about 19, 30.95, 47.62, and 90.48 l/m$^2$.h under operating pressure of 2, 4, 6 and 12 bar, respectively. While for more permeable membrane DL, the corresponding permeate flux rate are 33.33, 48.94, 71.43 and 128.57 l/m$^2$.h, respectively. The foods/industrial water fluxes for the DK and DL membranes were 37.4 l/m$^2$.h for 6.9 bar and 47.6 l/m$^2$.h for 15.17 bar (www.sterlitech.com).

It can be seen from the figure that permeate increasing rate for DL membrane is higher than that for DK membrane. The conceivable explanation behind this is DL is loose membranes contrasted to DK [31,19]. DK may have higher charge limit than DL. So dissolvable transport through DL was easier constrained with DK, while repulsion of nitrate by DK was higher than DL.
4. Conclusions

Two nanofiltration (DK and DL) membranes were investigated for their capacity to remove NO$_3^-$ ion. For both membranes the expulsion for nitrate was affected by the operating conditions, for example, transmembrane pressure, initial nitrate concentration, operation time and pH.

The charge of membrane is significant to membrane performance because charge affects the electrostatic repulsion between the ions or charged molecules and membrane surface. DL and DK were the two different membranes used in the experiments. DK is better than DL in terms of rejection, while DL is better as far as penetrates. It can be demonstrated that the nitrate retention ascends with an expansion in the pressure. This can be clarified by the impact of the pressure on the permeate flux and also its effect on concentration polarization.
The permeate volumetric flux increments linearly with the pressure, so the concentration polarization which leads to a resistance to the transfer through the membrane is not critical. At low membrane pressure, diffusion contributes substantially to the nitrate transport resulting in a lower retention. In this study, increasing transmembrane pressure from 2 bar to 4, 6 and 12 bar has led to an increase in permeates flux both in DK and DL membrane. With increasing membrane pressure, the nitrate transport by diffusion becomes relatively less important, so that nitrate retention is higher. The nitrate removal strictly depends on the ionic composition of the medium.

The retention indeed decreases when the concentration increases. This behaviour has been interpreted by the screening phenomenon of the membrane by the cations which come along with a reduction of the membrane–solution interactions. The DK membrane has a given a NO$_3^-$ retention rate varying between 45% and 69% while the DL membrane allow to reach 13 to 31% for NO$_3^-$ rejection. Rejections ranged from 13% to as high as 69% depending on the membrane type, transmembrane pressure, influent nitrate concentration, pH and filtration time.

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