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Modified Nanofiltration Membranes Performance Improvement for Desalination Applications

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Additional information is available at the end of the chapter

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Abstract

The study focuses on NF membranes modification and performance improvement while desalinating brackish water. The study provides valuable information about flux and rejection changes and relationship with pressure changing before and after modification. Experimental works included in the study investigate modified and unmodified NF membranes performance while filtering synthesized single salt and mixture salt solution at various concentrations (ranged from 1000 ppm to 4000 ppm) and various pressure magnitudes (pressure ranged from 2 to 10 bars). The rejection rates witnessed an increase after membrane modification took place with about 11–30% for magnesium sulfate and sodium sulfate, and 50–60% for sodium chloride and potassium chloride.

Keywords: Nanofiltration, Membrane, Desalination, Modification, UV graft

1. Introduction

Nanofiltration membranes have made noticeable establishment and found a way into many industries since their first introduction in the early 1990s. The major industries in which these membranes are variously applied and served are water and wastewater industries. The characteristics of these membranes determined by high flux, high rejection of salts, and low energy consumption associated with low pressure requirements enabled these membranes to apply significantly and perfectly [1-5]. However, obtaining an improved flux and rejection as well as fouling resistance of NF membranes for various applications are of major interest for

researchers [6]. Technically, surface modification is considerably applied to improve membrane properties in terms of flux, salt rejection, and fouling resistance [6, 7]. In addition, micropollutant removal could also be improved by surface modification [8]. Various modification techniques have been applied for NF membranes by researchers including radical polymerization [9], low temperature plasma [10], pre-oxidation [11], layer-by-layer alternating polyelectrolyte deposition (APD) [12], ionizing radiation [13], and photochemical techniques [14]. However, photochemical grafting techniques (mainly UV-initiated grafting) have been widely used due to their low cost of operation, mild reaction conditions, selectivity to absorb UV light without affecting the bulk polymer, and the possibility of easy incorporation into the end stages of a membrane manufacturing process [15].

Several hydrophilic monomers are commonly used including N-vinyl-2-pyrrolidinone (NVP), 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AA), acrylamide (AAM), and 2-acrylamidoglycolic acid (AAG) for membrane surface modification of which such monomer would be grafted on the membrane surface by UV-initiated graft polymerization [7, 16-19]. Generally, modification process sufficiency is measured by measuring membrane properties and performance after modification. Two common methods are considered and followed for the UV-initiated grafting of membranes: the dip method and the immersion method. For the same support, with the same the monomer concentration and irradiation time, the degree of grafting achieved using the dip method is two to three times higher than with the immersion method. However, in certain cases, membranes modified by the dip method showed lower rejection factors compared to the membrane support and membranes modified by the immersion method [19].

Normally, UV-initiated grafting of polyethersulfone membranes involves two parallel competitive processes, crosslinking and chain scission, that determine the final membrane transport properties [20]. Both mechanisms are very important for any modified membrane where crosslinking and chain scission may affect hydrodynamic resistance and membrane selectivity, respectively. Kaeselev et al. [21] illustrated that the membrane hydrodynamic resistance is increased relatively with crosslinking while the membrane selectivity loss is affected by chain scission in a direct manner. This study focuses on NF membrane performance improvement in terms of flux and rejection for desalination applications via surface modification.

2. Materials and methods

2.1. Materials

NF membrane used manufacturing properties, salts (NaCl, MgSO_4 , Na_2SO_4 , and KCl) used for filtration experiments, chemicals used for modification (acrylic acid and ethylenediamine dihydrochloride), and experiment set-up. One commercial NF membrane denoted as NF-1 was purchased from Amfor Inc. China. A summary of membrane information is given in Table 1. The monomers used in this study were acrylic acid (99% purity, purchased from Sigma-Aldrich, USA) and ethylenediamine dihydrochloride (99% purity, purchased from Frinde-

mann Schmidt chemicals, Germany). In addition, high purity salts including MgSO_4 and NaCl , 99% purity, were purchased from John Kollin, UK.

Membrane	Material	Manufacturer operational data
NF-1	Polyethersulfone (PES)	Operational pressure is 150 psi, temperature is 25°C , and water flux is $100 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and rejection rate is 98% for 2000 ppm of MgSO_4 solution.

Table 1. NF membranes manufacturer characteristics

2.2. Methods

2.2.1. Membrane modification

The membrane was modified using a monomer solution of 4% acrylic acid and 1% ethylene-diamine dihydrochloride (w/v) following the immersion method [7, 22]. The monomer was grafted on the membrane surface using a commercial UV device (LC5) supplied by Hamamatsu, Japan. The membrane was exposed to UV radiation for 5 minutes. The unmodified membrane was marked with a UV time of 0 min. The modification procedure is detailed as followed:

1. Membrane was soaked in ultra-pure water for 24 hours and dried on room temperature for 3 hours.
2. The membrane was placed in a membrane holder where only the membrane surface was exposed to the monomer.
3. The monomer was placed on the membrane surface and left for 15 minutes; then the remaining unabsorbed monomer was removed.
4. The membrane was exposed to the UV light for 5 minutes.
5. The membrane was soaked in NaOH solution (concentration: 1 M) for 5 minutes then washed out with ultra-pure water for 1 minute.

2.2.2. Membrane permeation and rejection

Filtration experiments were performed in a stainless steel cylindrical batch cell (HP 4750), served as a dead-end filtration system (cell volume: 300 cm^3), supplied by Sterlitech (UK). The working pressure in the cell was applied by a nitrogen gas cylinder in the range of 2 to 10 bar for unmodified and modified membranes; the experiments were conducted at room temperature. The membrane active area was 14.6 cm^2 . Membranes were washed with ultrapure water and compacted at 10 bar of pressure for 20 minutes prior to use. No further pretreatment was performed on the membranes, bearing in mind that the manufacturer did not provide certain instructions for preparing the commercial membrane prior to use. A new filter was used for each experiment. Ultrapure water was used with conductivity below $1 \mu\text{S}/\text{cm}$. The system was

flushed with ultrapure water before and after use. Solutions of MgSO_4 , NaCl , Na_2SO_4 , and KCl at four various concentrations each (1000, 2000, 3000, and 4000 ppm) were used as the feed for unmodified and modified membranes to measure their rejection and determine the best performing membranes in terms of rejection. The concentrations of the feed and permeate were measured depending on solution conductivity measurements using a commercial conductivity meter supplied by Martini instruments (Romania).

3. Results

The major findings illustrated and analyzed in this section are concluded in the following two sections.

3.1. Flux

Pure water flux and solution flux (both single and mixture salt solutions) at various pressure magnitudes are highlighted and discussed in this section. The flux observed to be reduced after modification but with less than 30% compared to the unmodified membrane flux.

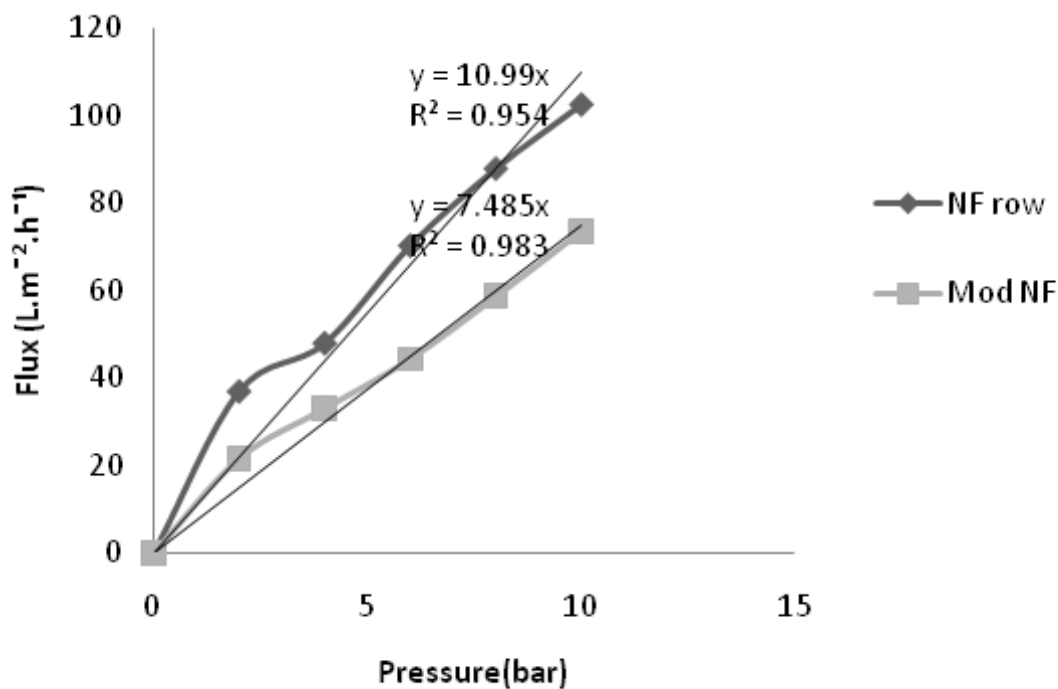


Figure 1. Pure water flux of unmodified and modified membranes

As illustrated in Figure 1, pure water flux for both unmodified and modified membranes was obtained at different applied pressures ranging from 2 to 10 bar. Membrane permeability was defined as the slope of pure water flux versus pressure. Apparently, the pure water flux of the

membrane decreased after modification by about 30%. Accordingly, the permeability had shown some 24% decreasing after modification. Both flux and permeability decreasing is evidently confirming pore size decreasing following the modification process. Membrane permeation decreasing and increasing with membranes modified by UV grafting can be found in the literature. The increase in permeation of modified membranes was observed by Puro et al. [23] when modifying commercial polyethersulfone membranes (NTR7450 Nitto Denko) following the immersion method. The study also demonstrated pore size increasing in some of the modified membranes. In contrast, UV-initiated grafting of membrane pore walls may reduce pore size according to Yu et al. [24]. In their work, they stated that for membranes with small pores, most of the polyacrylic acid may be grafted on the membrane surface, not on the pore walls. Abu Seman et al. [7] observed both mechanisms depending on the degree of grafting, which was related to UV irradiation time and monomer concentration.

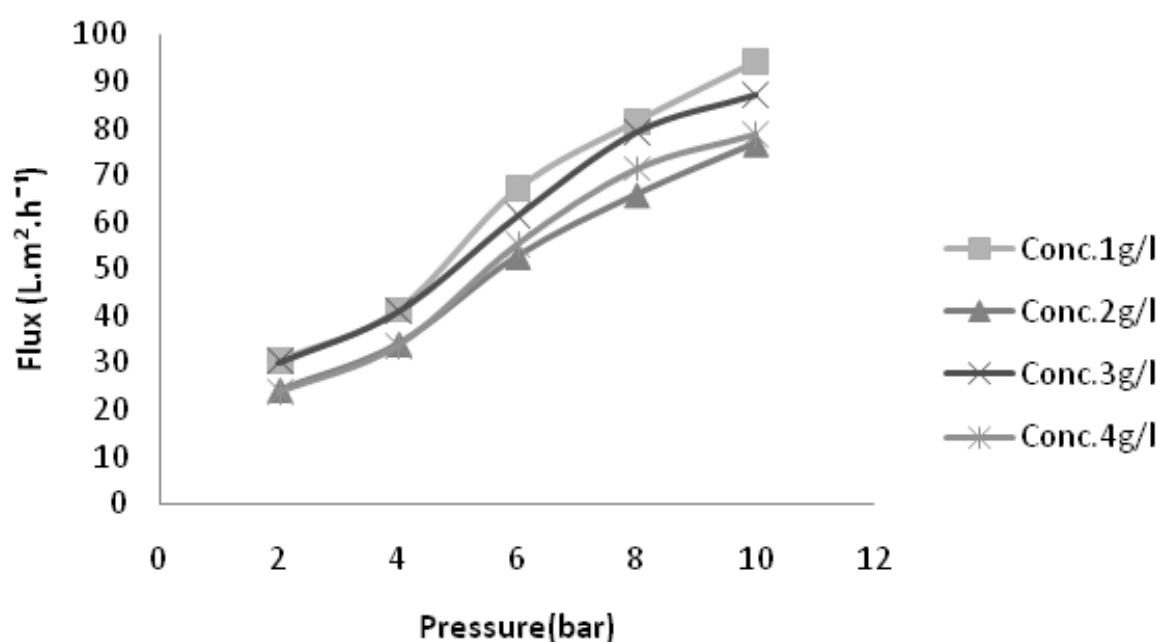


Figure 2. MgSO_4 solution flux for unmodified membrane at various concentrations

Figures 2 and 3 showed the effect of MgSO_4 concentration increasing on unmodified and modified membranes flux. For unmodified membrane the flux decreased with concentration. However, the decreasing for unmodified and modified membranes was 11% and 17%, respectively (flux decreasing from 1 g/L to 4 g/L). The same observations noticed for Na_2SO_4 solution (Figures 4 and 5) but with different percentage (30% and 7% for unmodified and modified membranes, respectively).

For NaCl (Figures 6 and 7), the observations were different, as the flux at 2 and 4 bar pressure for both unmodified and modified membranes decreased with concentration but increased at higher pressure magnitude with concentration.

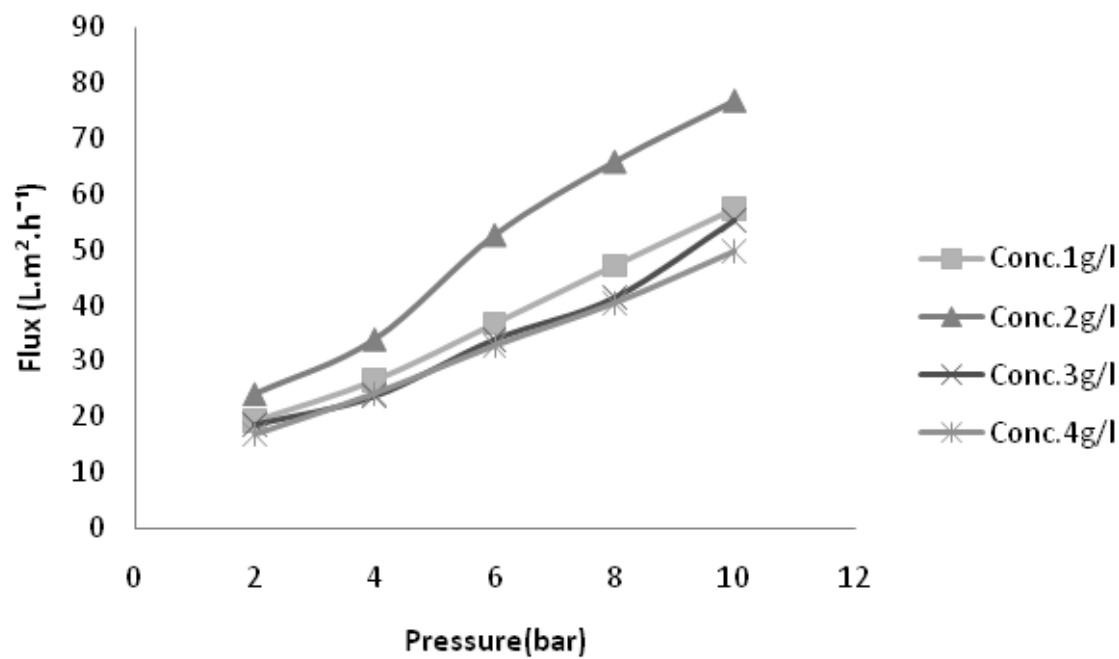


Figure 3. MgSO_4 solution flux for modified membrane at various concentrations

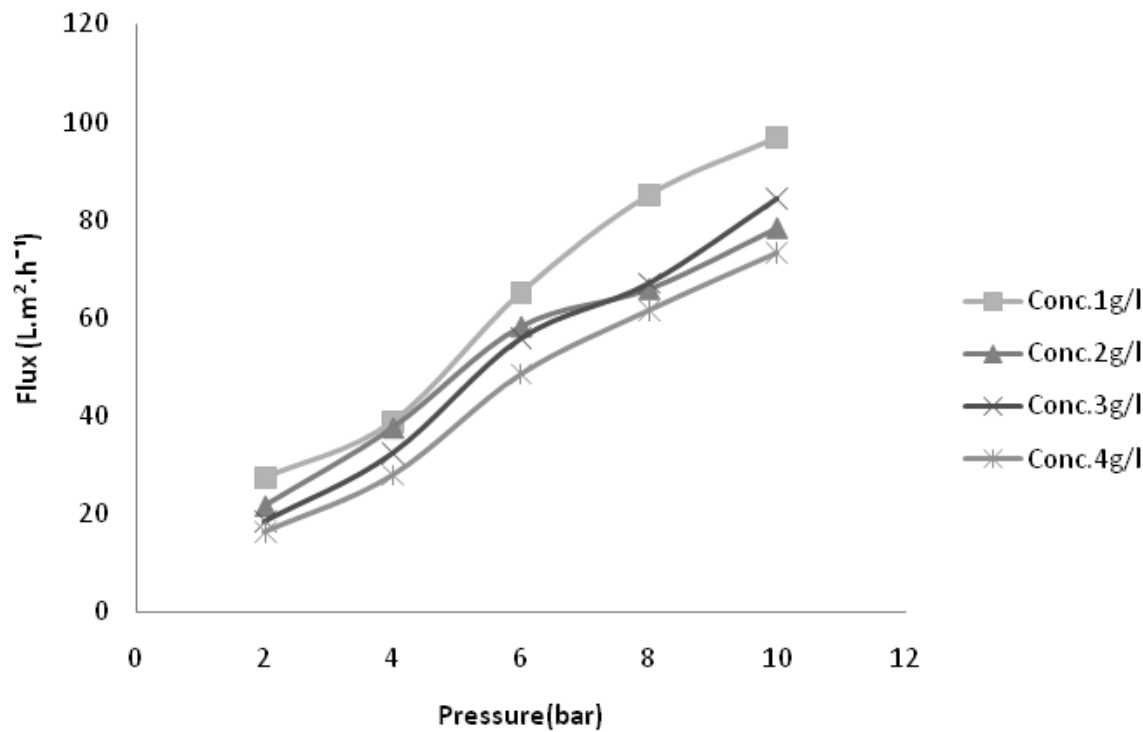


Figure 4. Na_2SO_4 solution flux for unmodified membrane at various concentrations

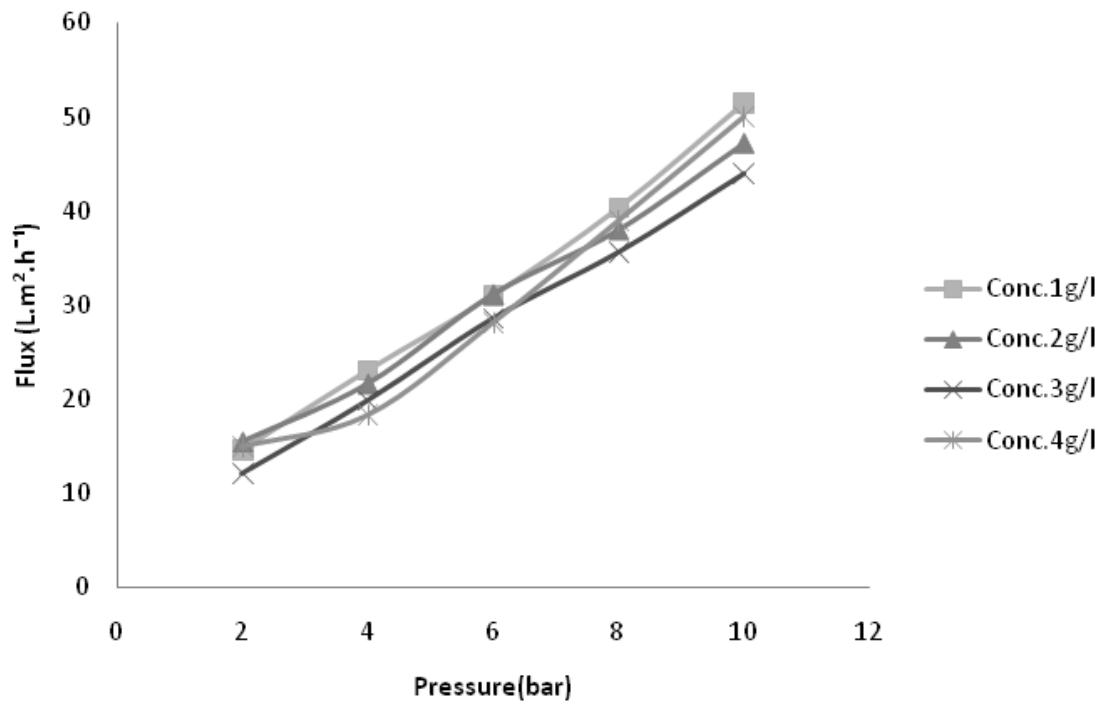


Figure 5. Na₂SO₄ solution flux for modified membrane at various concentrations

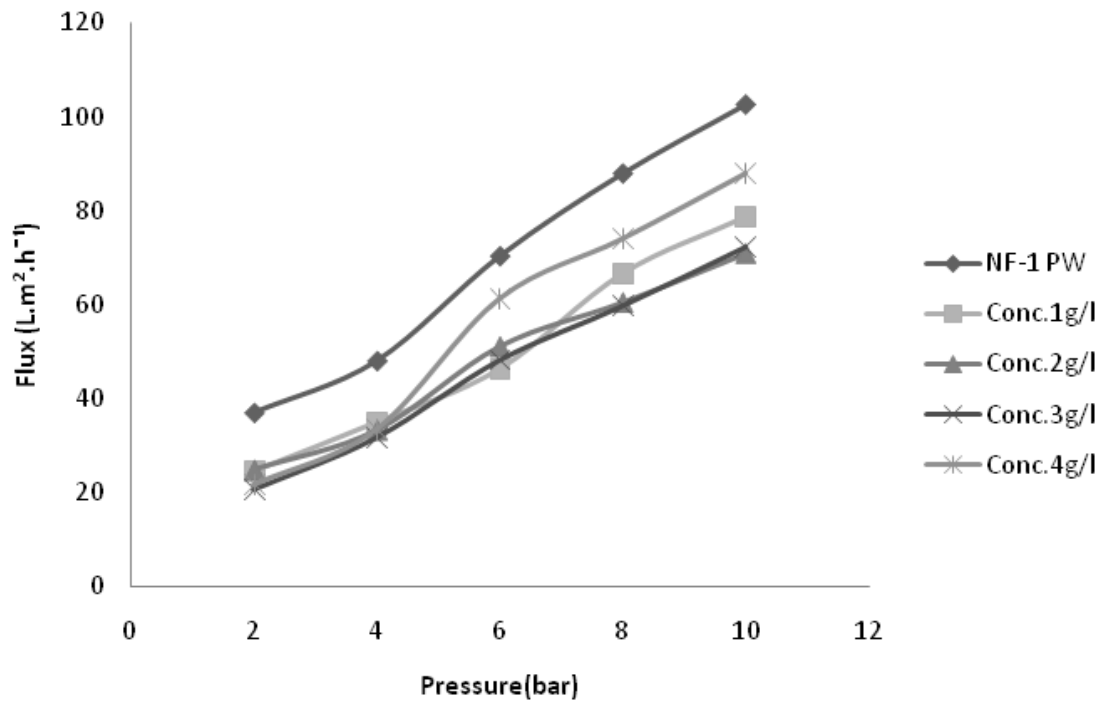


Figure 6. NaCl solution flux for unmodified membrane at various concentrations

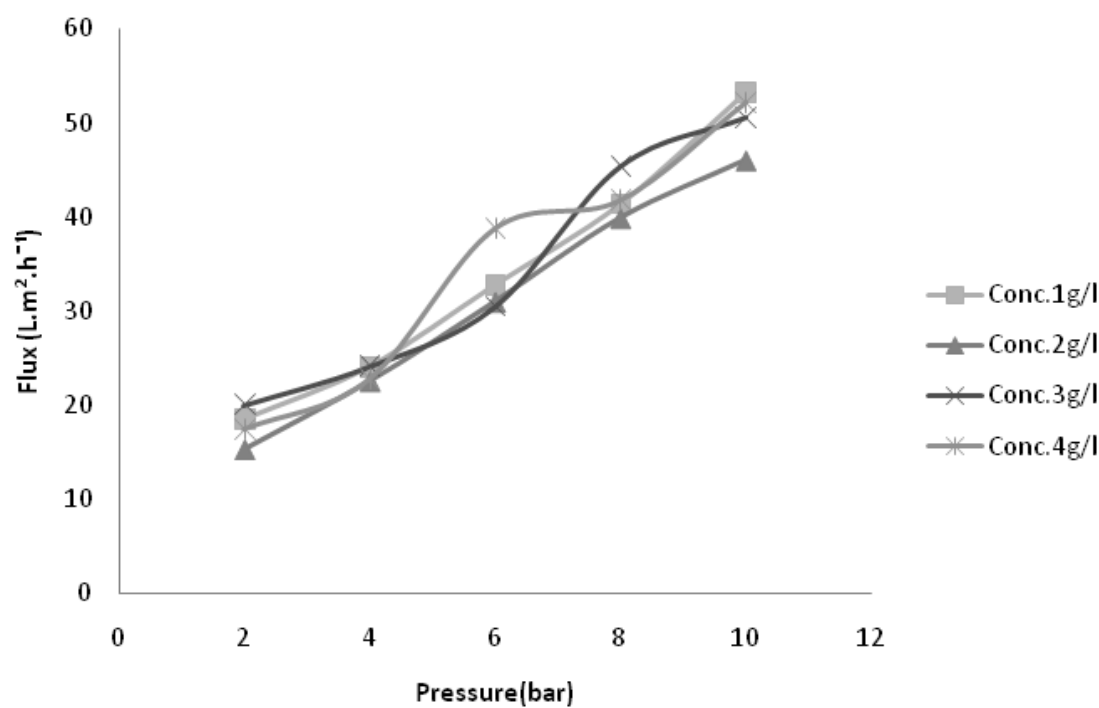


Figure 7. NaCl solution flux for modified membrane at various concentrations

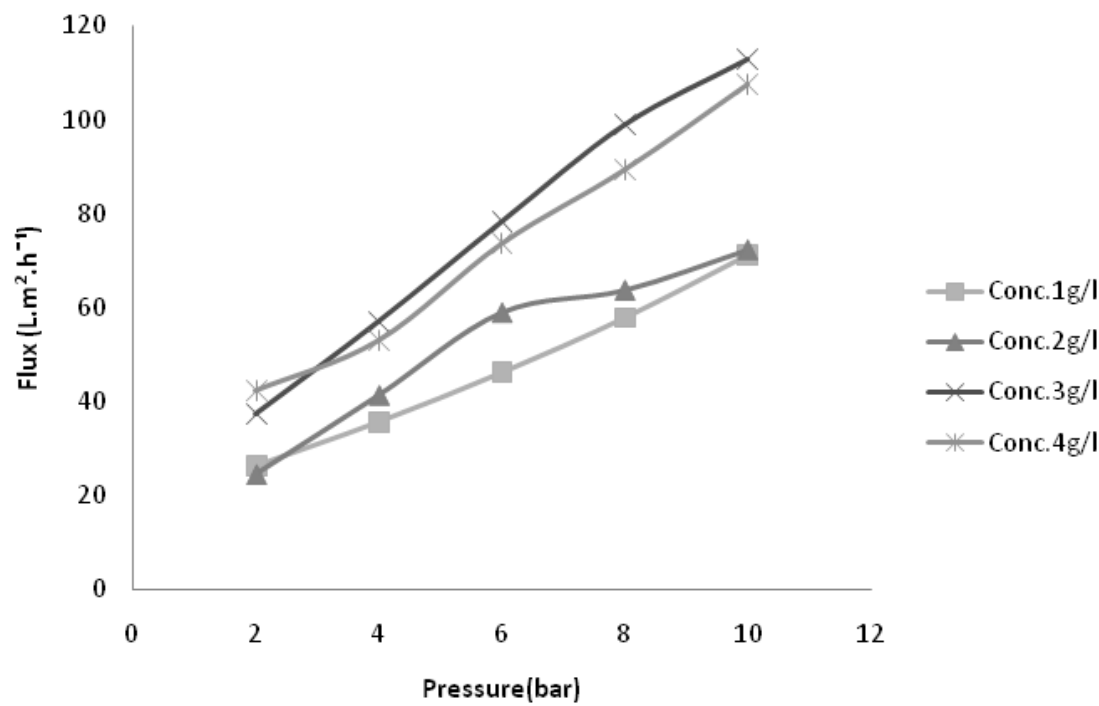


Figure 8. KCl solution flux for unmodified membrane at various concentrations

The same observations noticed for KCl solution (Figures 8 and 9) but with different percentage (55% and 1% for unmodified and modified membranes, respectively). It is worth mentioning that increasing concentrations have much more influence on unmodified membrane than the modified one for all solutions.

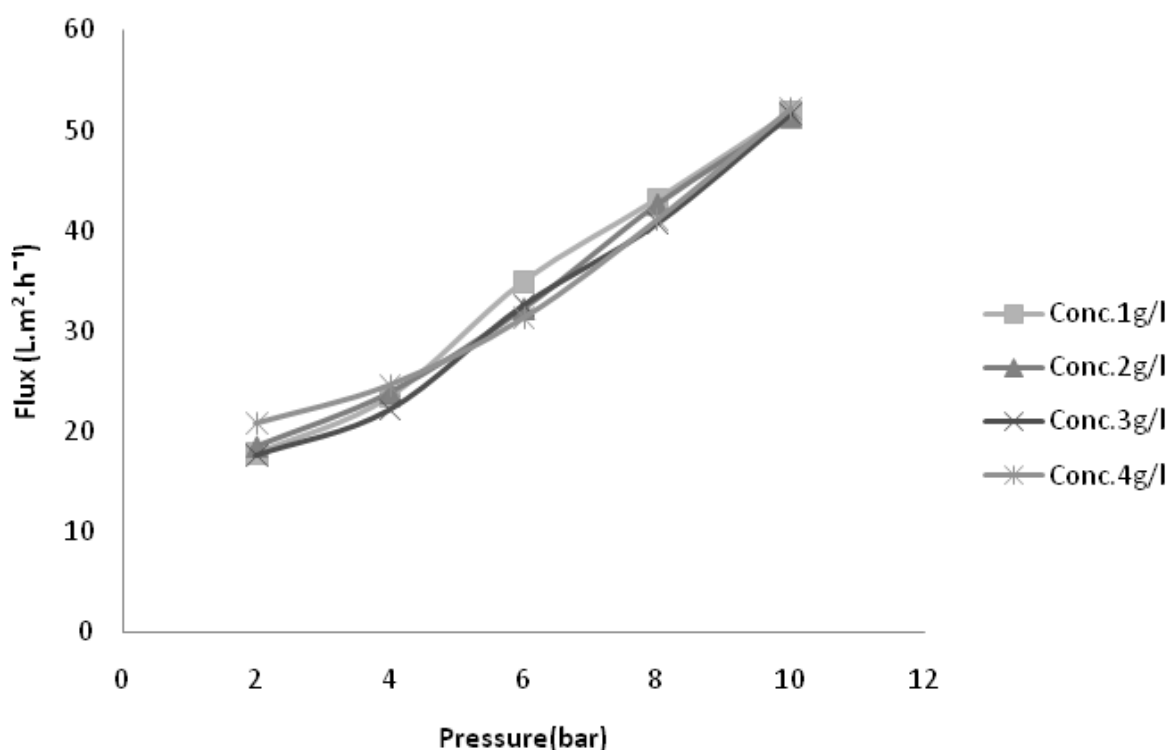


Figure 9. KCl solution flux for modified membrane at various concentrations

It is worth mentioning that flux may decline with time and concentration increasing, as osmotic pressure increased leading to reducing net driving pressure. Such observation is potentially associated with a dead-end filtration system, while for cross-flow system, flux decline may be lesser or may occur with longer time running.

3.2. Rejection

Rejection rates at various pressure magnitudes and for different concentrations are highlighted and discussed in this section. In addition, rejection of both modified and unmodified NF membranes for solutions consisting of a mixture of salts is also included. The rejection rates witnessed an increase after membrane modification took place with about 11–30% for magnesium sulfate and sodium sulfate, and 50–60% for sodium chloride and potassium chloride.

Figures 10 and 11 illustrate membrane rejection for both MgSO_4 and Na_2SO_4 at various concentrations, respectively. MgSO_4 and Na_2SO_4 rejection of modified and unmodified membranes decreased with concentration increase. The rejection observed for modified

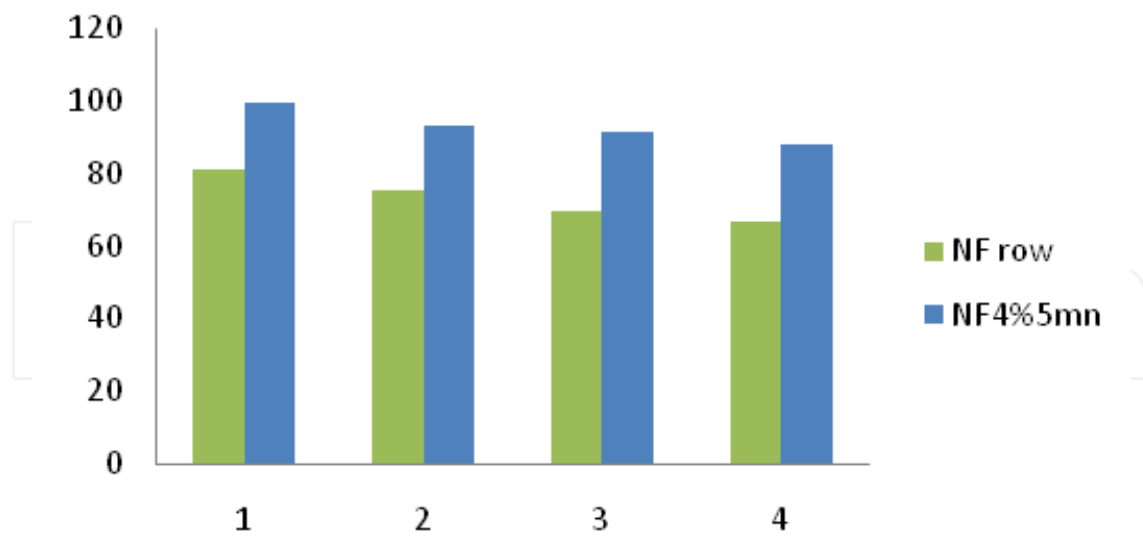


Figure 10. Membrane rejection (unmodified and modified) for MgSO_4 at various concentrations

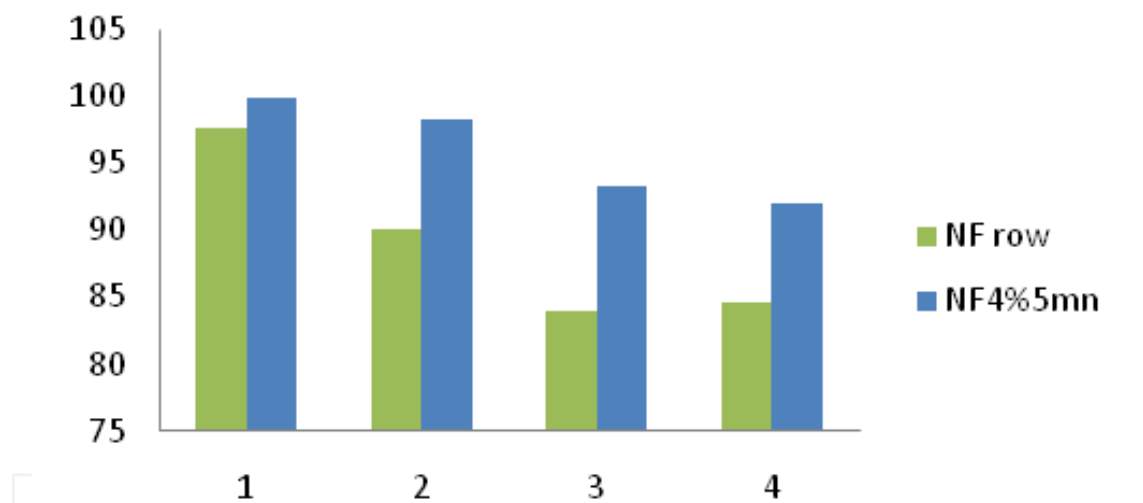


Figure 11. Membrane rejection (unmodified and modified) for Na_2SO_4 at various concentrations

membrane was higher than that observed for unmodified membrane at all concentrations for both MgSO_4 and Na_2SO_4 . However, concentration increasing found to have more influence on unmodified membrane than the modified one. For the modified membrane, MgSO_4 rejection decreased by 12% from 1g/L to 4 g/L while rejection decreased for unmodified membrane with nearly 20%. For Na_2SO_4 , rejection was reasonably decreased for unmodified membrane from 98% to 85% (difference is 13%) while for the modified membrane, the rejection decreased from 100% to 92% (difference is 8% only). This attributes to the fact that pore geometry and size have reasonably changed leading to better rejection as well as lowering concentration increasing effect on the membrane at this concentration range (1–4 g/L) [6, 25].

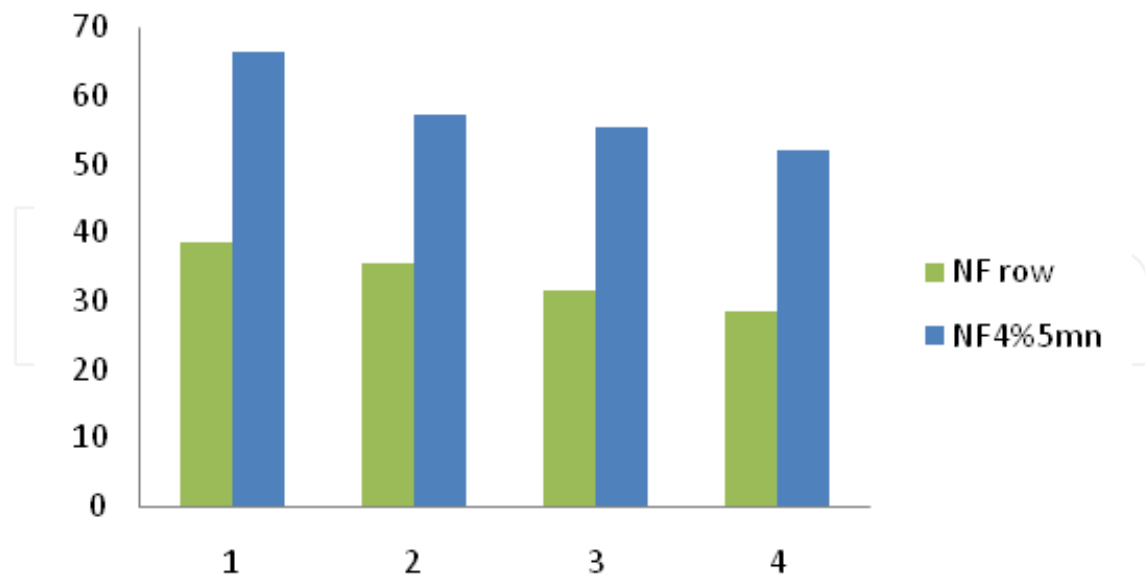


Figure 12. Membrane rejection (unmodified and modified) for NaCl at various concentrations

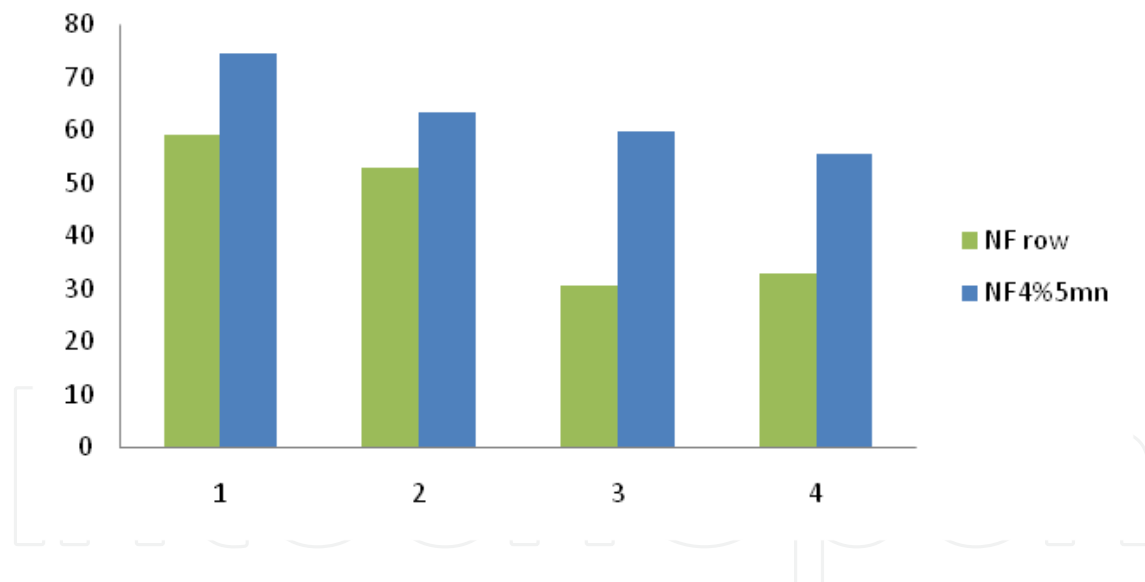


Figure 13. Membrane rejection (unmodified and modified) for KCl at various concentrations

Figures 12 and 13 illustrate membranes rejection for both NaCl and KCl at various concentrations, respectively (concentration range: 1–4 g/L). Two main observations worth concluding: firstly, the significance increase of both NaCl and KCl rejection at all concentrations for modified membrane over unmodified ones (for NaCl, modified membrane had rejection increasing from 39% to 72% in average while for KCl rejection increased from 59% to 75%); secondly, concentration increase had lower influence on both NaCl and KCl rejection for the modified membrane over the unmodified membrane (rejection decreased with concentration

for NaCl and KCl by 26% and 44 % for unmodified and 25% and 22% for modified membrane). Although NF membranes are more vulnerable to chloride ions than sulfate ions, modified membrane seemed to have more consistent performance and less concentration increasing influence in terms of rejection than unmodified membrane. Generally, salt rejection values may suffer some decline with time as applied dissolved solids concentrations increase.

4. Conclusions

A commercial NF membrane was modified via UV-grafted surface modification method to obtain better salt rejection and reasonable flux while desalting brackish water. The study provides valuable information about flux and rejection changes and the relationship with pressure changing before and after modification. Experimental works included in the study investigate modified and unmodified NF membranes performance while filtering synthesized single salt solution at various concentrations (ranged from 1000 ppm to 4000 ppm) and various pressure magnitudes (pressure ranged from 2 to 10 bars). Following the modification, the rejection rates showed an increase with about 11–30% for magnesium sulfate and sodium sulfate, and 50–60% for sodium chloride and potassium chloride. It is worth mentioning that concentration increase was found to have lower effect on membrane rejection after modification.

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