

INVESTIGATION OF CIPROFLOXACIN REMOVAL FROM AQUEOUS SOLUTION BY NANOFILTRATION PROCESS

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Received: 15/01/2016

Accepted: 17/03/2016

Available online: 19/04/2016

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ABSTRACT

This study investigated the removal of ciprofloxacin (CIPRO) from aqueous solution at a concentration of 10 mg l⁻¹ and the permeate flux behavior during dead-end stirred-cell filtration system using six type of commercially available loose and tight NF membranes (NP010, NP030, NF90, NF270, CK3001 and DS-5DK). The rejection of CIPRO and permeate flux value were evaluated according to the effects of different parameters such as volume reduction factor (VRF), membrane type, transmembrane pressure (TMP) and pH. Contact angle and SEM measurements were also performed for the analysis of the pollution occurring in the pores and on the surfaces of the membranes. Filtration experiments for all membranes used indicated that the flux reached the steady state at VRF 3. CIPRO rejection was found to vary especially with both pH and membrane tightness. Despite the fact that, the loose NF membranes showed poor and variable CIPRO removal, the highest rejection was obtained with NF90 tight membrane at the original pH value (pH 5.65) and 10 bar of applied pressure. NF90 membrane achieved 98.3% TOC, 98.9% COD, 96.9% TDS and 95.7% E_c rejections at 24.39 l m⁻² h⁻¹ permeate flux at the predefined operating conditions.

Keywords: Antibiotics, Nanofiltration membranes, Removal of ciprofloxacin, Permeate flux, Retention mechanism

1. Introduction

Ciprofloxacin (CIPRO) is the second generation antibiotics in a group of drugs called fluoroquinolone which are active against gram-positive and gram-negative bacteria. It is used to fight against human and veterinary diseases as well as to treat different types of bacterial infections (Vasconcelos *et al.*, 2009; Jiang *et al.*, 2012; Jiang *et al.*, 2013a; Rakshit *et al.*, 2013; Zaviska *et al.*, 2013; Zhou and Jiang, 2015). This antibiotic acts by inhibiting essential enzyme function for DNA production (Le-Minh *et al.*, 2010); it has been identified among the top ten of high priority pharmaceuticals associated to the water cycle in general and as a key priority substance for an EU project on the elimination of pharmaceutical residues from point sources in the healthcare sector (Jiang *et al.*, 2012).

CIPRO has a high aqueous solubility under various pH conditions and a higher stability in soil and wastewater systems (Jiang *et al.*, 2013a). Due to its high wastewater-sludge partition coefficient ($\log k_d \sim 4$), 79-92 percent of the initial concentration was removed in a wastewater treatment plant (WWTPs) by sorption onto sludge (De Witte *et al.*, 2009; Martin *et al.*, 2012). However, literature shows that its predominant removal mechanism in treatment plant was attributed to significant adsorption to sludge and/or flocs rather than biodegradation (Le-Minh *et al.*, 2010; Jiang *et al.*, 2013a). In light of its zwitterionic characteristics, it can be concluded that the adsorption of fluoroquinolones on activated sludge was mainly affected by the electrostatic repulsion rather than hydrophobic interaction (Genç *et*

al., 2013). Concentrations of CIPRO in wastewater effluents and surface water were observed to range from ng to mg l⁻¹, with measured concentration near drug manufacturing plants as high as 50 mg l⁻¹ (i.e. 0.15 mM) (Rakshit *et al.*, 2013). CIPRO has a molecular weight of 331.4 g mol⁻¹. CIPRO concentrations between 0.7 and 124.5 µg l⁻¹ in hospital effluent (Jiang *et al.*, 2012; Genç *et al.*, 2013), between 249 and 405 ng l⁻¹ in wastewater treatment plants have been reported (Zaviska *et al.*, 2013). CIPRO was found in wastewater treatment plant effluents at concentrations of 313-568 ng l⁻¹ and up to 124.5 µg l⁻¹ in hospital sewage water (De Witte *et al.*, 2009). Although, the presence of trace levels (ng l⁻¹) of CIPRO in wastewater effluents, receiving waters and drinking water sources led to negative impacts on ecological and human health (Comerton *et al.*, 2008; Vasconcelos *et al.*, 2009; Wu *et al.*, 2013), effective removal of this compound from discharge streams to the environment becomes an important issue (Sun *et al.*, 2011).

A number of promising wastewater treatment technologies have been used for removing CIPRO from wastewater, such as sorption and adsorption (Wu *et al.*, 2010; Jiang *et al.*, 2013a; Rakshit *et al.*, 2013; Genç *et al.*, 2013; Wu *et al.*, 2013), membrane separation (Sun *et al.*, 2011; Zaviska *et al.*, 2013; Urtiaga *et al.*, 2013), ozonation, oxidation and other photocatalytic degradation processes (De Witte *et al.*, 2009; Vasconcelos *et al.*, 2009; De Witte *et al.*, 2010; Jiang *et al.*, 2012; Jiang *et al.*, 2013b; Zhou and Jiang, 2015). Notwithstanding the differences between degradation mechanisms of these oxidation processes, the by-products formed may be the same, or at least, similar to each other (Vasconcelos *et al.*, 2009). Since mineralization is evaluated to be not cost effective, advanced oxidation processes focus on partial degradation. However, degradation products can be more toxic than the parent compound or they can still have the same features as the parent compound (De Witte *et al.*, 2010).

Nanofiltration (NF) and reverse osmosis (RO) processes are proper for the effective removal of a variety of micropollutants such as pharmaceuticals, personal care products, endocrine disrupting compounds and hormones (Comerton *et al.*, 2008; Kimura *et al.*, 2009; Urtiaga *et al.*, 2013; Sadmani *et al.*, 2014). Nevertheless NF process which is more economical than RO due to its lower operating pressures which will lead to less energy consumption (Swamy *et al.*, 2013; Ravikumar *et al.*, 2014) has shown more effective removal for low-molecular-weight compounds, predicting their rejection has posed challenges due to the fact that multiple mechanisms including adsorption, steric-hindrance effects, and electrostatic effects can be involved in this concurrently controlled removal (Shah *et al.*, 2012).

This study examined and compared the rejection of CIPRO as a function of membrane type having well-characterized pore sizes of NF membranes with dead-end filtration system in laboratory scale. Some of the membranes used in this study were not examined in the literature previously for the removal of CIPRO from water. Experiments were conducted with three loose (NP010, NP030, CK3001) and three tight (NF90, NF270, DS-5DK) NF membranes which have different molecular weight cut off (MWCO). The effects of the membrane type and the main operating parameters (VRF, pH and TMP) on CIPRO rejection and the permeate flux were examined. Finally, the fouling on pores and the surface of NF membrane was characterized by contact angle and SEM measurements, respectively.

2. Materials and methods

2.1. Aqueous Solutions

Prior to experimental studies, the aqueous solutions were prepared by spiking CIPRO at a concentration of 10 mg l⁻¹ with laboratory-grade Milli-Q pure water at pH 7. Unlike other studies reported in the literature, in this study higher CIPRO concentration in the feed was used to easily monitor the performance of each membrane for their CIPRO rejection in a short period. CIPRO with a purity higher than 99 percent was obtained from the Sanovel, pharmaceutical company in Turkey. This commercially available product contains no more than 0.2 percent by weight of the by-product contaminant fluoroquinolonic acid. The solubility of CIPRO is pH-dependent, ranging from 6.19 g l⁻¹ at pH 5 to 0.15 g l⁻¹ at pH 7 at 37 °C. Values for acid dissociation constants - pK_{a1} and pK_{a2} - of CIPRO are 5.90±0.15 and 8.89±0.11, respectively. The cationic form CIPRO⁺ predominates due to protonation of the amine group in the piperazine moiety when the solution pH is below 5.90 as shown in Figure 1. When the solution pH

is above 8.89, the anionic form CIPRO⁻ prevails due to loss of a proton from the carboxylic group. When solution pH is between 5.90 and 8.89, the zwitterionic form CIPRO⁰ resulting from the charge balance of the two groups mentioned above is the dominant species (Genç *et al.*, 2013). The physico-chemical properties of CIPRO were summarized in Figure 1.

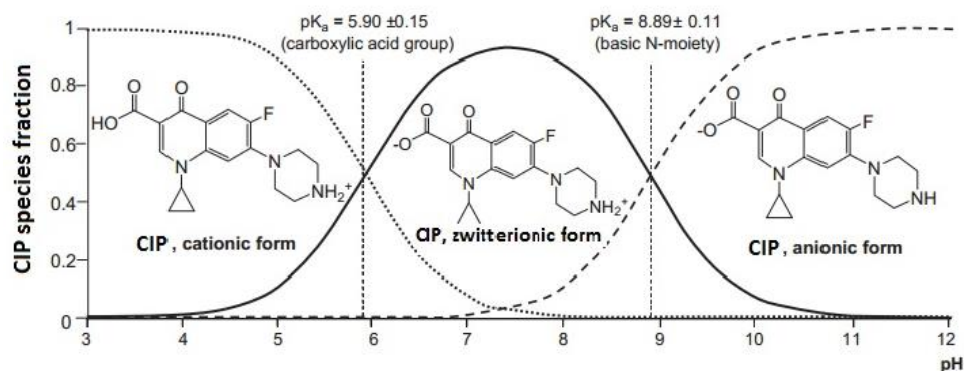
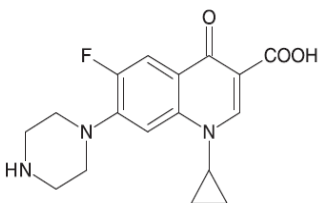


Figure 1. Molecular structure of CIP and its ionic forms as a function of pH, pK_a values (Genç *et al.*, 2013)

Table 1. Physico-chemical properties of Ciprofloxacin (CIPRO) used (Vasconcelos *et al.*, 2009; Jiang *et al.*, 2012; Rakshit *et al.*, 2013; Zhou and Jiang, 2015)

Use	Structural formula	Chemical formula	Dissociation constant pK _a (25 °C)
Antibiotic B Antibiotic use in chemoprevention		C ₁₇ H ₁₈ O ₃ N ₃ F	6.09-8.74
Appearance	Molecular weight (g mol ⁻¹)	Water solubility (mg l ⁻¹)	Log K _{ow}
White crystalline	331.35	30	0.28

d_c (nm)=0.826 (Zhou and Jiang, 2015)

d_c =Effective diameter of organic component in water, ($d_c=0.065MW^{0.438}$)

2.2. Membrane characterization

Six different loose and tight NF membranes with high pressure including NP010, NP030, NF90, NF270, CK 3001 and DS-5DK were selected for this study and their detailed specifications were listed in Table 2. These membranes were chosen because they represent different molecular weight cut off values and inorganic and organic compound rejection performances. NP010 and NP030 membranes were hydrophilic polyethersulfone (PES) membranes that were obtained from Microdyn-Nadir, polyamide thin film composite (PTFC) membranes (NF90, NF270) were purchased from Dow Film Tech., and cellulose acetate membranes of CK 3001 and thin film composite membranes of DS-5DK were also obtained from GE Osmonics.

The hydrophilicity and hydrophobicity of surfaces of the membranes were measured by contact angle measurements which were carried out using an Attension Theta Lite Optical Tensiometer. Scanning electron microscope (SEM) was also used for determination of membrane surface morphologies using a

JEOL Aqueous JSM-6060 LV microscope. SEM photographs were taken at different magnifications (in the range of x400–5000).

2.3. Membrane filtration system and set-up

A dead-end filtration system (Aqueous HP4750 Stirred cell, Sterlitech Corporation, USA), made of stainless steel 316 with an inner diameter of 49 mm and an effective membrane area of 14.6 cm^2 , was used for all the filtration experiments. The volumetric capacity of the feed tank is 300 mL in which there is a stirrer with a stirring rate of 350 rpm. The pressure was set at 7–10–15 bar by nitrogen gas and the temperature was maintained at room temperature ($22 \text{ }^\circ\text{C} \pm 1$). Filtration processes were operated at the concentration mode, which means that permeate solution was not returned into the feed tank and the retentate became concentrated by accumulating in the feed tank. The volumetric flow rate of the permeate solution collected in a beaker was measured by an electronic balance (Precisa XT2220M–DR) and recorded by a computer. Afterwards, the permeate fluxes were calculated using RsKey Ver.1.34 software (A&D Comp. Ltd., Japan). Initially, experiments were carried out until the volume reduction factor (VRF) value of 6 was reached for all the membranes used. Then, in the experiments conducted with tight membranes filtration experiments were performed until VRF 3 wherein the flux reached a steady state. Before starting the experiments, all NF membranes were passed through pure water at maximum pressure values given in literature for each membrane until when flux reached a constant. Removal of CIPRO at different operating conditions and water matrices by utilizing commercially available different NF membranes was examined in the laboratory set-up showed schematically in Figure 2.

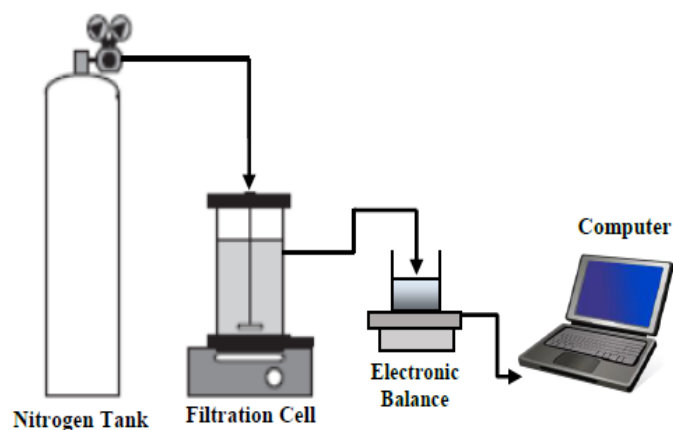


Figure 2. Experimental set-up of membrane system

2.4. Analytical Procedure

The total amount of removed organic substances in withdrawn aqueous-phase samples, was determined by measuring the total organic carbon (TOC). Total carbon was analyzed using a carbon analyzer (Teledyne Tekmar, aqueous Torch) in a measurement range of 30.000 mg l^{-1} , detection limit of $50 \text{ } \mu\text{g l}^{-1}$ and accuracy of maximum 1.5 percent. A high temperature catalytic oxidation method was applied at $750 \text{ }^\circ\text{C}$, which equipped with a high pressure NDIR detector. In all the analyses, three repeated measurements were taken for each sample, and the standard deviation was always below 1.5 percent. The average value of TOC concentration was reported. The COD was measured according to “Standard Methods for the Examination of Water and Wastewater” (APHA, 2005) by means of 5220 C-Closed reflux titrimetric method. Temperature, conductivity, TDS and pH were analyzed with the desktop multiparameter with Hach HQ440d (Hach-Lange GmbH).

Table 2. General properties of the membranes used

Trade name	Manufacturer	Membrane materials	MWCO (Da)	pH	MgSO ₄ Na ₂ SO ₄ Rejection (%)	Pure water flux or permeability (25 °C)	Maximum Pressure (Bar)	Maximum Temperature (°C)	Reference
NP 010	Microdyn-Nadir	Hydrophilic polyethersulfone	1000	0-14	25-55 Na ₂ SO ₄	> 200 L m ⁻² ·h ⁻¹	40	95	(Ince <i>et al.</i> , 2010)
NP 030	Microdyn-Nadir	Hydrophilic polyethersulfone	400	0-14	80-95 Na ₂ SO ₄	> 40 L m ⁻² ·h ⁻¹	40	95	(Ince <i>et al.</i> , 2010)
NF 270	Dow Film Tech	Polyamide	200-400	2-11	99.2 MgSO ₄	13.3-18.6 L m ⁻² ·h ⁻¹ bar ⁻¹	41	45	(Dolar <i>et al.</i> , 2011; Shah <i>et al.</i> , 2012)
DS-5DK	GE-Osmonics	Thin Film Composite	150-300	2-10	96 MgSO ₄	5.4-6.1 L m ⁻² ·h ⁻¹ bar ⁻¹	41	50	(Hesampoura <i>et al.</i> , 2010; Bennani <i>et al.</i> , 2012,
NF90	Dow Film Tech	Polyamide	200-400	2-11	99 MgSO ₄	6.4 L m ⁻² ·h ⁻¹ bar ⁻¹	-	-	(Dolar <i>et al.</i> , 2011; Shah <i>et al.</i> , 2012)
CK 3001	GE-Osmonics	Hyrophobic cellulose acetate	2000	2-8	94 MgSO ₄	3.01 L m ⁻² ·h ⁻¹ bar ⁻¹	-	-	(Acero <i>et al.</i> , 2010)

2.5. Technical Analysis

NF experiments were conducted at concentration mode, where permeate streams were collected in a separate unit and not returned into the feed water reservoir, whereas retentate was accumulated in the feed cell. VRF was calculated using Eq. (1).

$$VRF = \frac{V_f}{V_c} \quad (1)$$

where V_f and V_c are the initial volume of the feed and the final volume of the concentrate, respectively.

The permeate fluxes (J) were calculated by measuring the permeated water volume through the membrane and using Eq. (2).

$$J(\text{L/m}^2 \text{ h}) = \frac{1}{A} \frac{dV}{dt} \quad (2)$$

where A is the effective membrane filtration area (m^2), V is total volume of the permeate (m^3) and t is filtration time (h), respectively (Can Doğan *et al.*, 2015).

The rejection performance (R) of each NF membrane on the basis of TOC which is a water quality parameter was derived from the following equations:

$$R (\%) = \left(1 - \frac{C_p}{C_R} \right) \times 100 \quad (3)$$

where C_p is the TOC concentration in permeate (mg l^{-1}) and C_R is the TOC concentration in the cell after the filtration (mg l^{-1}) (Can Doğan *et al.*, 2015).

For the purpose of determining the amount of adsorbed CIPRO onto the membrane surface and into the membrane pores, the adsorption percentage (AP) was calculated by the Eq. (4) (Acero *et al.*, 2010):

$$AP = \frac{(C_f V_f) - [(C_p V_p) + (C_r V_r)]}{(C_f V_f)} \times 100 \quad (4)$$

Adsorbed mass which was defined as the amount of solute adsorbed per unit membrane area onto the membrane surface and into the membrane pores was calculated using Eq.(5):

$$M_{\text{ads}} = \frac{(C_f V_f) - [(C_p V_p) + (C_r V_r)]}{A} \quad (5)$$

where C_f , C_p and C_r are the feed, permeate and retentate TOC concentrations (mg l^{-1}); V_f , V_p and V_r are the feed, permeate and retentate volumes (m^3), respectively (Yoon *et al.*, 2006).

3. Results and discussion

3.1. Effect of VRF and membrane type on TOC rejection

The first step in the filtration experiment was the filtration of distilled water with each clean membrane (NP010, NP030, CK3001, NF90, NF270, DS-5DK). In the following step, prepared aqueous solution with a concentration of 10 mg l^{-1} was subject to filtration until VRF 6 at a pressure of 10 bar, $\text{pH}=5.65$ (original pH) and room temperature ($22 \pm 1 \text{ }^\circ\text{C}$) using the general properties of membranes which were already described in Table 2. The flux values in Figure 3 obtained for different VRF values were 91.83 , 23.67 , $18.37 \text{ L m}^{-2} \text{ h}$ for loose NP010, NP030, CK3001 membranes and $23.88 \text{ L m}^{-2} \text{ h}^{-1}$, $65.70 \text{ L m}^{-2} \text{ h}^{-1}$, $38.46 \text{ L m}^{-2} \text{ h}^{-1}$ for tight NF90, NF270, DS-5DK membranes, respectively. The maximum flux value was reached with NP010

loose membrane having a pore size of 1000 Da MWCO and the maximum flux decline during the filtration was observed at a rate of 51.25% for NF90 membrane.

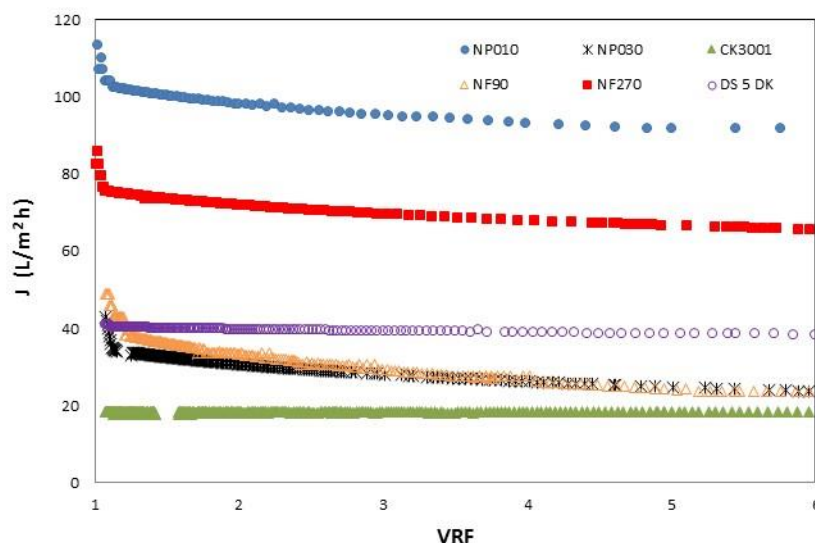


Figure 3. The flux decline as a function of VRF for different loose and tight NF membranes during the filtration of CIPRO aqueous solution (TMP: 10 bar, pH: 5.65, temperature 22 ± 1 °C)

As it can be observed from Figure 3, the permeate flux decreased drastically for NP010 and NF270 membranes until the VRF value reached 1.07-1.13 and for NP030 and NF90 membrane until the VRF value reached 1.15-1.20, then it slightly decreased until VRF 3 for all four membranes. Although, Acero *et al.*, (2010) determined that adsorption is not the prevailing mechanism for micropollutant retention with NF membranes, the amounts of CIPRO adsorbed per unit membrane area were calculated for tight NF membranes as 10.4, 6.5 and 8.8 mg cm⁻² with NF90, NF270 and DS-5DK membranes and the adsorption percentages were obtained as 7.2%, 4.5% and 6.1%, respectively. Adsorption values for the loose membranes were at negligible levels. There was not any change in the flux values obtained against VRF for CK 3001 and DS-5DK membranes. Slight decrease of J value followed by an almost constant values for higher VRF was a consequence of the causes of membrane fouling such as cake layer formation, pore blocking or the partial adsorption of CIPRO onto the membrane. The small decrease in J indicated that low fouling effects occurred with the selected membranes except NF90. It can be concluded that the higher decline of flux for NF90 membrane resulted from the formation of cake and concentration polarization occurring on the membrane surface in a short time due to the smaller size of the membrane pores. Similar results have been reported in literature (Yoon *et al.*, 2006, Acero *et al.*, 2010, Gönder *et al.*, 2011).

The TOC rejections were given in Figure 4 as a function of membrane type during the filtration of CIPRO from aqueous solution for VRF 3 and VRF 6 at original pH and 10 bar of applied pressure. TOC rejections obtained on loose NP010, NP030 and CK 3001 membranes were 18.5%, 15.4% and 36.2% for VRF 3, however, during the filtration experiments, removal efficiencies increased up to 26.7%, 37.5% and 70.5% for VRF 6, respectively. On the other hand, TOC rejections on tight NF90, NF270 and DS-5DK membranes obtained from polyamide material were 98.5%, 95.1% and 97.4% for VRF 3 and they increased up to 99.7%, 97.2% and 99.0% for VRF 6, respectively. Since NP010 membranes have both hydrophilic properties and large pore structures, they achieved low TOC rejections although they have high flux value. The flux value for NP030 membrane was lower, however higher TOC rejection was obtained due to its smaller pore size compared to the one for NP010. Due to its hydrophobic properties, flux values obtained for CK3001 membrane were too low despite its large pore structure. Despite the fact that the flux value of the CK 3001 membrane was lower than that of the NP010 and NP030 membranes, TOC rejections increased up to the level of 70% at VRF 6 because of its hydrophobic characterization. It is known from the literature that higher material retention was observed under concentrate mode in the loose

membranes during the experiment-(Nghiem *et al.*, 2007). This could be explained by the fact that, the rejection on the surface of the loose membranes was higher at VRF 6 compared to VRF 3 like it happened for CK3001 membrane. Cake layer formation functioned as a secondary membrane on the membrane surface at higher VRF value prevented the penetration of pollutants which eventually resulted slow flux decline and lower membrane fouling as reported by Gönder *et al.*, (2011). Comerton *et al.* (2008) also emphasized that molecular weight was not much effective in removal of micropollutans due to large MWCO in loose membranes and there was not a significant correlation between the properties of the compound and the rejection. When TOC rejections were studied, tight polyamide membranes (NF90, NF270 and DS-5DK) showed higher performance than all loose membranes used. In the experiments conducted with tight membranes, it was observed that removal efficiencies did not change considerably with the increasing VRF values although TOC concentration in the retentate was much higher for VRF 6 compared to the one for VRF 3. This case explained the size exclusion occurred due to the small pore structure and having dense surface film on the top of a porous sub-layer, which possibly blocked diffusional transport across the membrane (Yoon *et al.*, 2006; Yüksel *et al.*, 2013). In accordance with these results, the optimum VRF value was determined as 3.

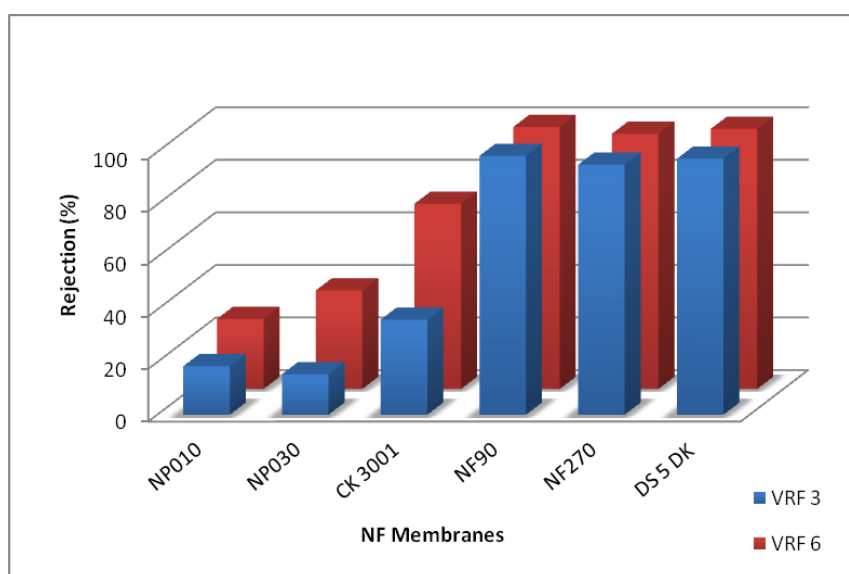


Figure 4. Evaluation of TOC rejection as a function of membrane type during the filtration of CIPRO aqueous solution for different VRF (TMP: 10 bar, pH: 5.65, temperature 24±1°C)

3.2. Effect of operating conditions on rejection

Rejection of solutes on NF membranes will be affected by solute properties (molecular weight (MW), molecular size, dissociation constant (pK_a) and octanol-water partition coefficient compounds ($\log K_{ow}$)), membrane properties (molecular weight cut-off (MWCO), pore size, surface charge, hydrophobicity-hydrophilicity and surface morphology), feed composition (pH, ionic strength, hardness and the presence of organic matter) and also operating conditions. In addition, solutes can be rejected on NF membrane by one or a combination of three basic mechanisms including size exclusion (sieve steric effect), charge exclusion (electrical, Donnan), and physico-chemical interactions between solute, solvent and membrane (Yoon *et al.*, 2006; Acero *et al.*, 2010; Dolar *et al.*, 2011; Sun *et al.*, 2011; Vergili, 2013). Moreover it is also reported in the literature that size exclusion in tight membranes and charge exclusion and physico-chemical interaction in the other membranes were more effective mechanisms in membrane filtration (Dolar *et al.*, 2011).

In the second part of the study, effects of different pressure and pH operating conditions on COD, TDS and E_c removal efficiencies were investigated with TOC rejection for the selected VRF 3 value by utilizing tight membranes, with which the best removal was achieved.

3.2.1. Pressure

The most critical factor in operating a membrane process is the applied pressure. To investigate whether the concentration polarization and fouling exist, experiments with varying TMPs were carried out. Filtration experiments were performed at different pressure values (5, 10, 15 bar) with tight NF90, NF270 and DS-5DK membranes for which the best removal efficiency was achieved at $22 \pm 1^\circ\text{C}$, original pH and VRF 3. The flux values obtained at different pressures for each membrane were given in Figure 5 while the TOC rejections were given in Figure 6. Generally, the increase in applied pressure leads to an increase in both the initial and final flux values based on Darcy's law (Gönder *et al.*, 2011). While this was observed for DS-5DK membrane, flux increase was not observed with the increasing applied pressure for the other two tight NF membranes.

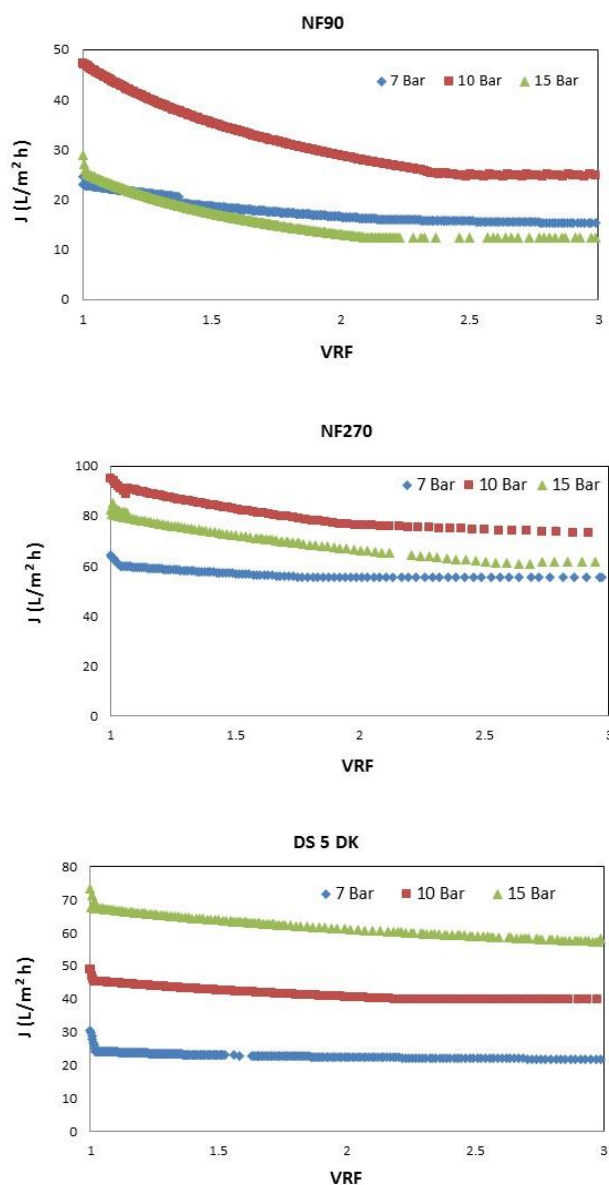


Figure 5. The flux decline as a function of VRF for different transmembrane pressures during the filtration of CIPRO sample solution (pH: 5.65, temperature $24 \pm 1^\circ\text{C}$)
NF90 (b) NF 270 (c) DS-5DK

According to Figure 5, it was determined that the higher flux values were obtained at 10 bar for NF90 and NF270 membranes, however, higher flux value was determined for DS-5DK membranes at 15 bar. During

the experiments, the highest permeate flux decline was observed as the VRF increased with NF90 membrane at 10 and 15 bar. This was because, an increase in applied pressure could also contribute to membrane fouling that resulted from concentration polarization with flux decline as reported by Kaya *et al.*, (2010). Then, more pollutants accumulated and cake layer formed onto the membrane surface. Although, flux values increased in parallel to the pressure increase in DS-5DK membrane, it was observed that intermediate blocking and fouling were present for all applied pressures until VRF 1.2. Later, the flux value stayed constant for all 3 pressure values.

It was demonstrated in Figure 6 that maximum TOC rejections were obtained at 10 bar for each three membrane and were found to be 98.7%, 91.2% and 97.1% for NF90, NF270 and DS-5DK membranes, respectively. When a comparison was made between the membranes, the maximum efficiency was achieved with NF90 membrane with 98.9% COD, 96.9% TDS and 85.7% E_c at 10 bar applied pressure as it was given in Table 3. When COD and TDS removal efficiencies determined in this study were compared, the results obtained were similar to those obtained by Swamy *et al.* (2013) and Ravikumar *et al.* (2014). In addition, the decline of the flux from $47.24 \text{ L m}^{-2} \text{ h}^{-1}$ down to $21.43 \text{ L m}^{-2} \text{ h}^{-1}$ which was about 55 percent meant that there was more fouling in the pores and on the surface of NF90 membrane where size exclusion was effective for the removal of CIPRO with a molecular weight of $331.35 \text{ g mol}^{-1}$. Nghiem *et al.* (2007) determined in their study that the main retention mechanism of the organic matter in filtration with negatively charged NF90 membranes was size exclusion. Another experimental study was conducted by Comerton *et al.* (2008) with different micropollutants where the dominant mechanism in the NF270 membranes was physico-chemical interaction with charge exclusion. However, in the filtration experiments conducted with NF270 membrane, it can be stated that the results were due to the concentration polarization occurred on the surface of the membrane and the membrane fouling which was also reported by Nghiem *et al.*, 2007. This is due to the fact that there was no electrical interaction between membrane and the hydrophilic structure CIPRO which was present at water in uncharged state at original pH value.

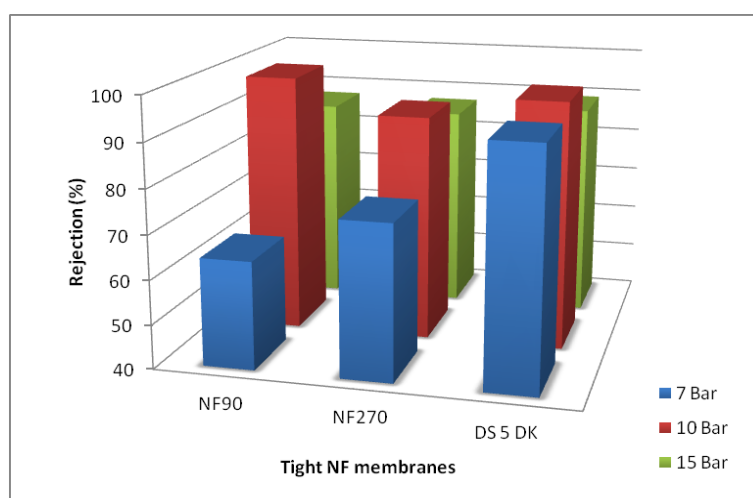


Figure 6. Effect of the TMP on TOC rejection for sample solution with different tight NF membranes for VRF 3

3.2.2. pH

Generally, the reason for pH to significantly affect the removal mechanism in the membrane filtration is the fact that membrane surface charge and properties of the compounds change with pH (Nghiem *et al.*, 2005; Yoon *et al.*, 2006; Shah *et al.*, 2012). Solubility changing with the pH of the solution, charge, dissociation constant (pK_a), polarity, dipole moment and hydrophobicity expressed as the octanol-water partition coefficient compounds ($\log K_{ow}$) are important physico-chemical properties that affect the rejection of the compounds and the membrane flux (Yoon *et al.*, 2006; Nghiem *et al.*, 2005; Vergili, 2013).

The log K_{ow} value was found to be the best parameter to describe the hydrophobic adsorption of the solutes to the membrane (Comerton *et al.*, 2008). pK_a value of the solute is an important parameter in the rejection of organic micropollutants, and it determines the charge of the solute in relation to the feed pH (Vergili, 2013). As defined in the literature, despite the low log K_{ow} value (0.28) and hydrophilic property of CIPRO, the general characteristics of which were given in Table 2, its adsorption to membrane surface occurs very little, and the main rejection mechanism (beside the size exclusion) depends on membrane materials and solution pH which makes the study of CIPRO rejections at different pH values important.

Table 3. Membrane performances of sample water matrix at different transmembrane pressures for VRF 3 (Feed solution TOC: 7.99 mg l⁻¹; COD: 39.6 mg l⁻¹; pH: 5.65;

TMP (Bar)	NF90				NF270				DS 5 DK			
	Permeate pH	R (%)			Permeate pH	R (%)			Permeate pH	R (%)		
		COD	TDS	Ec		COD	TDS	Ec		COD	TDS	Ec
7	5.95	76.3	58.9	58.4	6.1	77.1	45.3	46.8	6.3	95.6	64.4	65.1
10	6.3	98.9	96.9	85.7	6.4	93.6	77.7	78.2	6.3	97.3	81.5	81.0
15	6.2	87.5	83.4	81.3	6.3	85.8	60.9	63.8	6.2	91.2	60.2	58.5

To determine the optimum pH value with the tight membranes with which the best rejection was achieved at 10 bar applied pressure where the maximum rejection was obtained, synthetic aqueous solutions were subjected to filtration until VRF 3. The solutions were prepared at four different pH values (3, 5.65, 7.5 and 11), in which ionic structure of CIPRO varies. The flux values obtained for each membrane were given in Figure 7. For NF90 membrane, the flux values obtained were close to each other except for pH 3. The numbers were 9.18, 24.39, 21.47 and 21.84 l m⁻² h⁻¹ for pH 3, 5.65, 7.5 and 11, respectively. However, in this study, when utilizing NF90 membrane for filtration, the reason of permeate flux decrease of hydrophilic CIPRO, which is in cationic form in the solution at pH 3 can be attributed to the fouling occurring in the pores and onto the surface of the membrane resulting due to the opposite charge effect. As a result of this fouling, cake formation occurred onto the membrane surface and the flux decreased. Lower flux decline was observed on NF270 and DS-5DK membranes. High permeate fluxes were obtained on NF270 membrane with a large pore size such as 94.19 l m⁻² h⁻¹, 73.0 l m⁻² h⁻¹, 58.83 l m⁻² h⁻¹, and 93.97 l m⁻² h⁻¹ at pH 3, pH 5.65, pH 7.5, and pH 11, respectively. Fluxes reached steady states for DS-5DK membranes at the values of 28.46 l m⁻² h⁻¹, 39.68 l m⁻² h⁻¹, 29.82 l m⁻² h⁻¹ and 46.16 l m⁻² h⁻¹ for pH 3, 5.65, 7.5, and 11, respectively.

TOC rejections given in Figure 8 showed that, the rejections at original pH values on three membranes were very much higher than the rejections at the other pH values. Urase *et al.*, (2007) and Vergili (2013) determined that under suitable operating conditions, almost same rate of drugs was removed on the tight membranes and generally a removal efficiency of above 95 percent was obtained. In this study, TOC rejection was found to be above 90 percent for each three membrane at original pH value. The TOC rejections obtained at different pH values showed once more that not only the size exclusion mechanism but also physico-chemical interaction and electrostatic exclusion are also effective mechanisms for NF membranes. TOC rejections being below 70 percent for all the membranes at pH values (pH 7.5 and 11), where CIPRO was charge-free or negatively charged, supported this fact. Low retention of negatively charged CIPRO on NF membranes at high pH values can also be explained with the increase of the number of negatively charged groups of the membrane surface as the pH value increased and electrostatic repulsion occurred. It was also reported by Yoon *et al.*, 2006 and Zazouli *et al.*, 2009. When a general evaluation was made in terms of TOC removal, the maximum removal was obtained with NF90 membrane with 98.3% at original pH, and the minimum efficiency was observed with NF270 membrane with 91.2%. Similar results were obtained in the literature; Shah *et al.*, (2012) showed that NF90 membrane exhibited rejection greater than >90% for two antibiotics (sulfamethoxazole and carbadox), whereas loose NF270 membrane exhibited lower rejection between 52 and 100%.

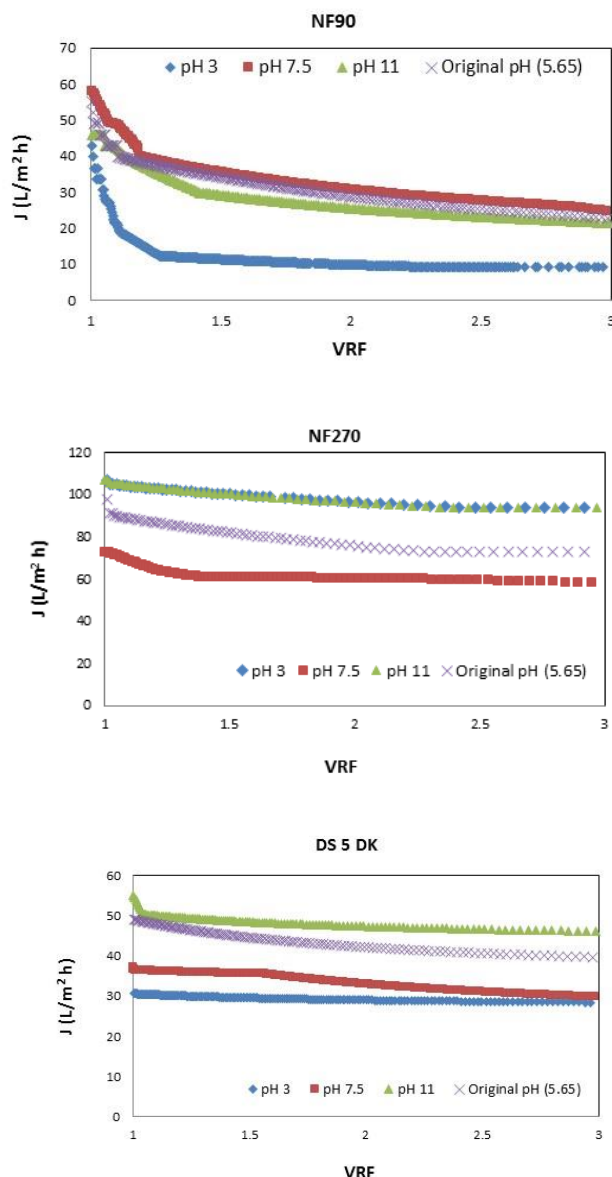


Figure 7. The flux decline as a function of VRF for different pH during the filtration of CIPRO sample solution (TMP: 10 Bar, temperature $24 \pm 1^\circ C$) (A) 90 (b) NF 270 (c) DS-5DK

Removal efficiencies of COD and inorganic quality parameters from CIPRO sample solutions were given in Table 4 for each membrane at different pH values. It was clearly seen from these values that the rejections of other parameters changed based on pH like it was for TOC rejection.

CIPRO solution, which is in cationic form at original pH value, had more interaction with negatively charged NF90 membrane as a result of which removal efficiencies of some parameters reached at maximum levels such as 98.9% COD, 96.9% TDS and 95.7% E_c rejections. Besides, along with the 78.2% COD and 74.7% TDS and 76.3% E_c removals, rejections of CIPRO on NF90 membrane at pH 7.5 where it was in charge-free form in aqueous solution were in minimum levels. When the filtration mechanism at pH 11 was examined, it was seen that negatively charged CIPRO compound in aqueous solution which was purified from proton, moved away from the membrane and COD removal efficiency reached to 84.8%, solely because of the electrostatic repulsion. Yoon *et al.* (2006) also put emphasis on the rejection of uncharged trace organics on NF membranes that is influenced by steric hindrance, while the rejection of polar trace organics could be explained by electrostatic interactions with the charged membranes.

Removal efficiencies were very much lower for NF270 membrane than NF90 membrane at all pH values, wherein COD, TDS and E_c parameters were 93.6%, 88.7% and 88.2% respectively, at original pH value. Rejections of COD and inorganic quality parameters decreased down to a level of 60 percent in case positive charge distribution increased in the aqueous solution of CIPRO at pH 3 for NF270 membranes. This result is same with that obtained by Nghiem *et al.*, (2005) defining that salt (conductivity) retention also dropped dramatically as the electrostatic repulsion decreased at isoelectric point below pH 4 in loose NF270 membrane. In the experimental study, while the removal rate was 25% at pH 3.5-4, this rate increased up to 100% at pH 10 in the removal of sulfamethoxazole with NF270 membrane (Nghiem *et al.*, 2005). As for NF90 membrane, removal efficiencies obtained at pH 7.5 and 11 were also at low levels for NF270 membrane. Besides rejections increased slightly due to the electrical repulsion at pH 11, where CIPRO was purified from proton.

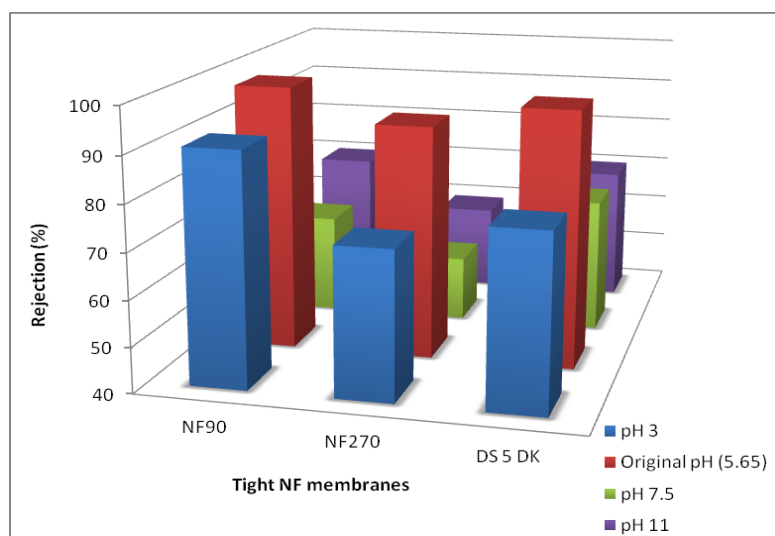


Figure 8. Effect of pH on TOC rejection coefficient for sample solution with different tight NF membranes for VRF 3

The situation was slightly different in DS-5DK membrane. While the maximum COD removal was observed with the rate of 97.3% at original pH value, 91.3% TDS and 90.5% E_c rejections were obtained at pH 3 where positively charged CIPRO released proton in aqueous solution.

Table 4. Membrane performances of sample water matrix at different pH for VRF 3 (Feed solution TOC: 7.99 mg l⁻¹; COD: 39.6 mg l⁻¹; pH: 5.65; TDS: 66.9 mg l⁻¹; Conductivity: 139.8 μ S cm⁻¹)

Feed pH	NF90				NF270				DS 5 DK			
	Permeate pH	R (%)			Permeate pH	R (%)			Permeate pH	R (%)		
		COD	TDS	<i>Ec</i>		COD	TDS	<i>Ec</i>		COD	TDS	<i>Ec</i>
3	3.7	93.2	89.7	89.3	3.2	62.5	58.7	57.0	3.7	83.8	91.3	90.5
5.65	6.3	98.9	96.9	95.7	6.4	93.6	88.7	88.2	6.3	97.3	85.5	86.2
7.5	6.2	78.2	74.7	76.3	6.7	55.6	60.0	60.4	8.2	73.0	79.7	78.1
11	10.2	84.8	84.2	84.0	10.4	67.3	69.8	72.0	10.7	74.9	77.9	78.1

When the effect of pH was examined by discussing the inorganic quality parameters in DS-5DK membrane, it was concluded that pH parameter was not that much effective in the rejection of inorganic quality parameters and the main mechanism was the size exclusion. Zazouli *et al.*, (2009) determined in their study that the removal of neutral substances was mainly driven by the size exclusion, while for charged substances no systematic trends were observed, however; electrostatic interaction was a more dominant parameter in explaining the membrane rejection in the negatively charged compounds.

3.3. Membrane separation performance

In order to determine the pollution in the surface of the NF90, NF270 and DS-5DK tight membranes with which the best removal was achieved, contact angle measurements were performed at 10 bar applied pressure and different pH values for VRF 3. Moreover, the pollution occurring on the membrane pores at 10 bar and original pH value was determined with SEM analysis for three tight membranes.

Contact angles were measured by a sessile drop method called the water droplet method based on measuring the contact angles between the water droplet and the membrane surface. As the contact angle increases, hydrophobicity of the membrane increases. It is stated in the literature that hydrophobic membranes are more sensitive to pollution compared to the hydrophilic membranes (Yoon *et al.*, 2006; Cho *et al.*, 1999). In the experiments conducted with the clean membranes passed through pure water prior to the experimental study, the contact angles of the contaminated membranes were measured three times repetitively and the average values thereof were given in Figure 9.

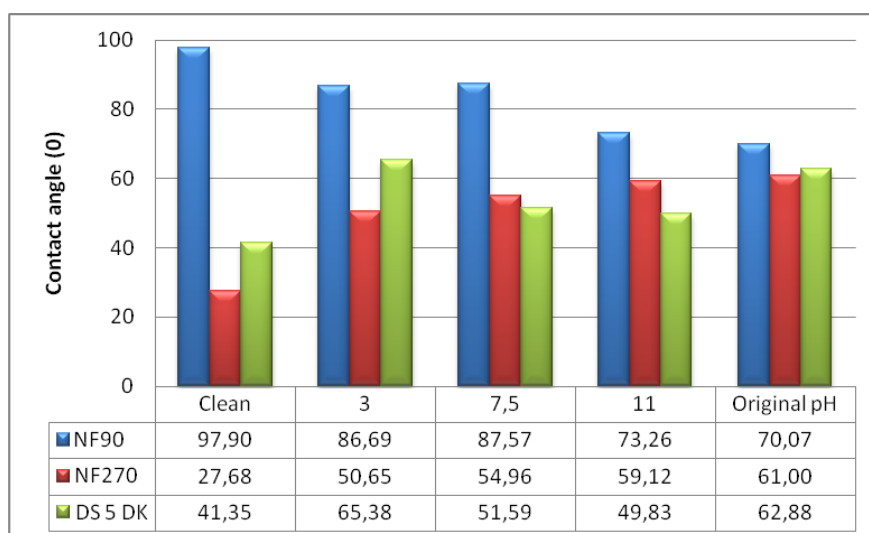


Figure 9. The contact angle results for all clean and fouled membranes (VRF 3, TMP: 10 Bar, temperature $22 \pm 1^\circ\text{C}$)

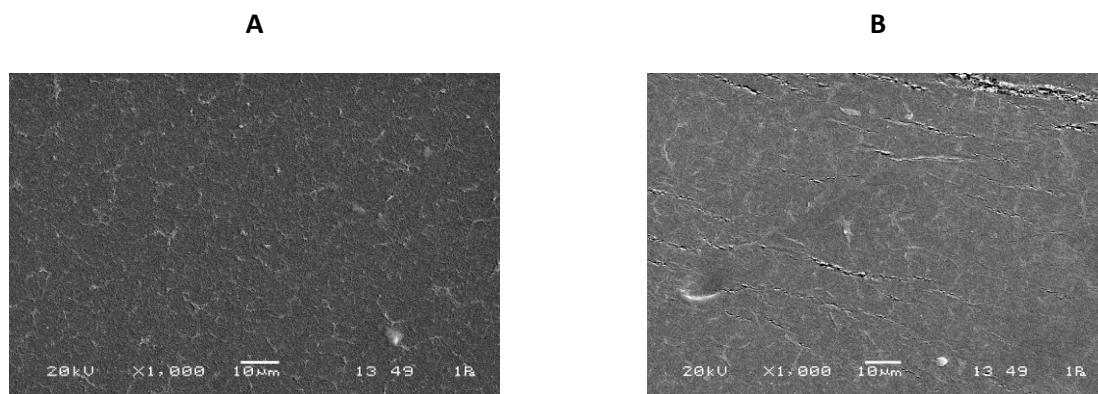
In the clean membranes, the membrane with the maximum contact angle was NF90 while the membrane with minimum contact angle was NF270 which has a large pore size. As a result of the contact angle measurements performed in clean and fouled membranes, contact angle values were lower in dirty NF90 membranes compared to the clean membranes while a reverse situation was observed in NF270 and DS-5DK membrane. Accordingly, low contact angle values of the NF membranes may be attributable to the presence of a large number of $-\text{OH}$ groups on the membrane surface. The low contact angle values of the NF90 membranes showed that the membranes were all hydrophilic. The contact angle of NF90 membrane, which was 97.9° in the clean membrane, decreased down to 70.1° . Accordingly, it can be deduced that the fouling resulted from inorganic matters and the hydrophilicity increased after the fouling. The contact angle, which was 27.7° in the clean membrane, increased up to 61.0° for NF270 membrane at the same operating conditions while it increased from 41.4° up to 62.9° for DS-5DK membrane. As it is known that there is a direct proportion between hydrophobicity and contact angle (Vergili *et al.*, 2013), it can be concluded that the hydrophobic property is dominant and these latter two membranes are more sensitive to pollution.

The pollution occurring onto the membrane pores were examined conducting SEM analysis in clean and fouled membranes for a more detailed examination of the pollution under operating conditions. SEM images of typical surface morphologies of all the NF membranes were shown in Figure 10.

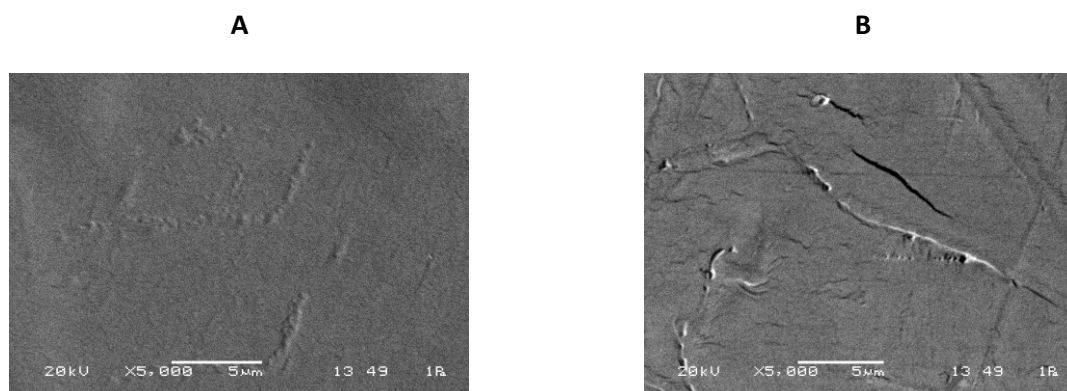
The images showed that the surface of the NF90 membrane is heterogeneous and uneven without any crack. The coating and roughness with many modules are effective in the membrane surface. NF270

membrane has a relatively homogeneous surface and there are some grooves on the surface which may be due to the very delicate and flexible character of the membrane. The surface of DS-5DK membrane is also homogeneous and continuous without any crack and has a much smoother surface than the others. Zhang *et al.* (2003) determined that the membrane surface properties were found to be correlated with membrane fouling. When the membranes used in this study were compared, it was observed that tight NF90 membranes are very rough and appear to consist of several layers. As defined in literature, according to Comerton *et al.*, (2008), this is likely attributed to the roughness of their surfaces which are more prone to fouling in comparison to the smooth surface of the NF270 and DS-5DK membranes.

NF90



NF270



DS-5DK

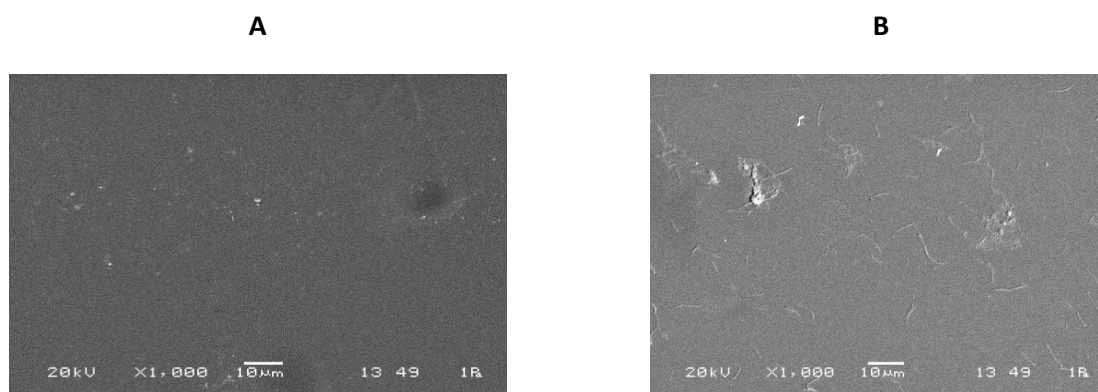


Figure 10. SEM images of typical surface morphologies of the NF membranes
Cleaned membrane (A) Fouled membrane (B)

4. Conclusions

In this study, the removal efficiency of CIPRO from aqueous solution at a concentration of 10 mg l⁻¹ was investigated by utilizing six different commercial NF membranes while studying also the effect of various operating conditions. When TOC rejections were examined, better removal efficiencies (≥90%) were obtained with tight membranes (NF90, NF270 and DS-5DK) when compared to the loose ones. Rejection of CIPRO by the 'loose' NF membrane was poor and variable, which showed that the membrane pore size was large relative to the compound size. Despite the decrease in the flux value, the maximum removal efficiencies with NF90 membrane were obtained with 98.9% COD, 96.9% TDS and 95.7% E_c along with 98.3% TOC rejection for determined operating conditions such as room temperature, original pH of 5.65, 10 bar applied pressure at VRF 3. According to the experimental studies conducted at different pH values, it was concluded that beside the size exclusion, the most effective operating parameter in the filtration of CIPRO (found in aqueous solution) with NF membranes is pH. The reason of this is the fact that in the membrane filtration processes, pH affects the physico-chemical interactions between solute and generally negatively charged membrane surface.

Acknowledgement

This work was supported with a scientific research by [Kocaeli University] under Grant [number: BAP 2011/071] and [number: BAP 2014/043].

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