

# Natural organic matter and sulphate elimination from rainwater with nanofiltration technology and process optimisation using response surface methodology

Börte Köse-Mutlu

## ABSTRACT

In the current study, the effect of operating conditions including membrane characteristics and applied pressure on natural organic matter and sulphate removal of nanofiltration (NF) membranes for drinking water production was investigated. Water stress has been increasing all over the world due to population growth, climate change, and pollution; rainwater management stands out as one of the key solutions to this problem. Nanofiltration to treat rainwater stored in a cistern was studied. The objectives were sufficient treatment performance to overcome the taste problem and lower energy consumption. In this regard, three commercial nanofiltration membranes (NP010, NP030, and NF90) were used for the experiments carried out at 6–12 bar operating pressure regarding the response surface methodology. The correlation among the results of experiments and the model parameters were also calculated for all steps. According to the results, the effect of membrane characteristics was more abundant than the effect of the operating pressure. Finally, over 99% of natural organic matter and sulphate were eliminated in the optimum conditions. The results showed that it is possible to obtain treated rainwater with desired qualities, in a non-continuous NF plant operated at the pressure of 6 bar to reuse the rainwater and achieve water sustainability.

**Key words** | nanofiltration, optimisation, rainwater, response surface methodology, reuse, treatment

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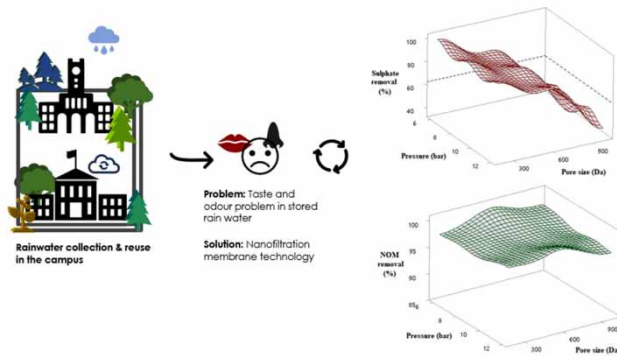
## HIGHLIGHTS

- The applicability of low-pressurised NF for rainwater treatment was investigated.
- Process was optimised using response surface methodology.
- Rainwater was stored in a cistern located on campus.
- The treatment efficiency regarding the removal of natural organic matter and sulphate was measured.
- The taste problem could be eliminated and a pilot-scale non-continuous NF plant was suggested to be installed.

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doi: 10.2166/wst.2020.591

## GRAPHICAL ABSTRACT



## INTRODUCTION

Water resources are gradually decreasing all over the world due to population growth, climate change, and pollution. Nowadays, rainwater stands out as an alternative natural resource that can be easily collected to address limited water resources problems worldwide (UNICEF and WHO 2012; GhaffarianHoseini *et al.* 2016). It is possible to use rainwater as drinking water after a certain level of treatment (Silva *et al.* 2015; Oviedo-Ocaña *et al.* 2018). Additionally, the effective control of rainwater flow helps to close the hydrological cycle in urban areas. There are many examples throughout history of rainwater stored in cisterns being used as drinking water (Antoniou *et al.* 2014; Angelakis 2016; Yannopoulos *et al.* 2017). AbdelKhaleq and Alhaj Ahmed also presented many examples of rainwater harvesting and treatment in some facilities located in sanctuaries in both ancient and modern times in their paper (AbdelKhaleq & Alhaj 2007). The construction of a rainwater harvesting system and installation of a treatment system for the reuse of rainwater was common. However, rainwater may have serious contaminants, contrary to expectation (Jaiyeola 2017; Hamilton *et al.* 2019), as it is affected by airborne particles and pollutants on surfaces in the collection area. Sulphate and organic pollutant contents are especially important (Eriksson *et al.* 2007). In urban situations, the sulphate concentrations have increased because of the increasing fog (Penkett *et al.* 1979; Angrill *et al.* 2017). On the other hand, studies had indicated that the source of the organic matter in rainwater can be due to different causes (Tran *et al.* 2020). While biogenic organic compounds are dominant in rural areas, the anthropogenic compounds

are more abundant in urban areas' rainwater samples (Kawamura & Kaplan 1986; Pantelaki *et al.* 2018). Health authorities generally do not recommend the use of untreated rainwater because of disease risks, and some previous studies have proven the relationship between rainwater consumption and water-borne illnesses (Lye 2002; Heyworth *et al.* 2006; Rodrigo *et al.* 2011). There is a limit for the daily intake of sulphate from water, air, and food. Generally, it is thought that food is the major source. However, in areas with water supply having high levels of sulphate, water may be the major source of intake (Fawell & Mascarenhas 2004). In the literature, it was found that there was a diarrhoea problem in piglets fed with drinking water including sulphate (Cocchetto & Levy 1981; Morris & Levy 1983). It is also reported that humans can face cathartic effects (US DHEW 1962; Chien *et al.* 1968), and these effects can be important for population groups like children and elders that may be more sensitive. On the other hand, organic matter in rainwater can be addressed with the parameter of Natural Organic Matter (NOM). NOM is a complex matrix of organic substances in aquatic ecosystems that are generated as a result of biological, geological, and hydrological cycles (Sillanpää *et al.* 2018). Intrinsically, NOM is not toxic but its presence in water can be hazardous. For instance, it can act as a carrier of toxic pollutants including pesticides and radionuclides (Knauer *et al.* 2017; Santschi *et al.* 2017) and increase their bioavailability through increased solubility (Reid *et al.* 2000). Moreover, Sillanää and colleagues also underlined that NOM tends to form some strong complexes with heavy metals (Matilainen

*et al.* 2011; Tang *et al.* 2014) and it reacts with disinfectants, resulting in the formation of disinfection by-products (DBPs) (Golea *et al.* 2017; Goslan *et al.* 2017). This leads to the creation of carcinogenic compounds (Bond *et al.* 2012; Jiang *et al.* 2017). Besides, the presence of NOM causes the sensorial properties of rainwater to change. Water is naturally considered to be of poorer quality if taste or odour can be perceived (de França Doria 2010), and consumers are suspicious of drinking water with an unpleasant taste or odour. As a result, the concentration of sulphate and organic matter should be reduced, not only for health reasons but also for taste and odour reasons (Shen & Schäfer 2015). Taste disturbance varies according to the nature of the associated cation (WHO 2011) and a sulphate concentration of 25 mg/L is recommended by Turkish Standards as a threshold level for the minimal disturbance of taste (TSI 2005).

The removal of sulphate and NOM from drinking water supplies is becoming a challenging task requiring the application of reliable and highly efficient water treatment technologies. Many methods have been proposed to treat rainwater in the literature. These methods include physicochemical processes such as granular activated carbon (GAC) combined with ultraviolet (UV) disinfection or nanofiltration (NF) (Naddeo *et al.* 2013; Ding *et al.* 2018; Leong *et al.* 2018), chemical processes like chlorination and adsorption (Keithley 2012; Omar *et al.* 2017) and biological processes like biosand filter (Kassim & Hashim 2006). Membrane filtration technologies are gaining preference for rainwater treatment due to their low carbon footprint and low disinfectant consumption (Oosterom *et al.* 2000; Kus *et al.* 2013; Dobrowsky *et al.* 2015; Leong *et al.* 2017). According to the results of a study carried out with raw rainwater collected from a rainwater channel in Sydney and treated using GAC and ultrafiltration (UF) membrane, organic matter concentrations were significantly reduced (Kus *et al.* 2012). On the other hand, Kim *et al.* (2005) investigated the treatability of rainwater by preferring a metal membrane, and found it particularly suitable to treat rainwater due to its high purification efficiencies, but the expected delay in clogging could not be achieved (Kim *et al.* 2005). It is obvious that the treatability of rainwater with membrane processes is a research topic that deserves further examination. Besides, it can be also seen that the treatment studies in the literature using membranes were generally carried out using conventional and classical methods of experimentation. In this method, the researcher has to carry out many experiments in which one of the parameters is varied while the others

remain constant. As this approach can be time-consuming and results in the lack of explanations with a comprehensive mathematical relationship, this ultimately causes poor optimisation of the process concerned. On the other hand, the response surface methodology (RSM), which is a methodology for the design of experiment (DoE), can be applied as an alternative. DoE is a statistical tool to reduce the number of experiments/runs and to ensure that the maximum data can be collected from the performed experiments, and RSM takes a statistical approach where all the variables are varied over a wide range of levels and in turn swiftly manages to eliminate the aforementioned drawbacks of the conventional and classical method (Myers *et al.* 2016; Montgomery 2017). RSM can be practically used by researchers to obtain mathematical models for making some predictions via simulating the membrane processes (Santafé-Moros *et al.* 2005; Xiarchos *et al.* 2008; Jadhav *et al.* 2016).

To sum up, urbanisation has increased the number of impermeable areas in rainwater collection basins, and the leakage and storage of rainwater are restricted (Zhang *et al.* 2015; Li *et al.* 2017). For this reason, it is important to design and construct rainwater collection and storage elements in newly built structures (Sürmeli 2016). Moreover, it must be highlighted that rainwater should go through proper treatment before using it as drinking water (Shen & Schäfer 2015) and researchers argue that the feasibility for this kind of treatment unit can be determined through a detailed analysis of design and operation parameters (Villarreal & Dixon 2005; Mun & Han 2012). Few investigations have addressed the application of the NF membrane, which is a type of pressure-driven membrane having properties in between those of UF and reverse osmosis membranes, in the treatment of rainwater. Some of these studies were exemplified above. Indeed, the NF process benefits from ease of operation, reliability, and comparatively low energy consumption, as well as high efficiency of pollutant removal, and it has given rise to worldwide interest. In this regard, the treatability of rainwater with NF was studied and optimised in this paper with samples taken from the cistern of the new mosque, which was built on campus in Istanbul. Sulphate and NOM removal in NF processes performed at different operating pressures with three commercial membranes (NF90, NP030, and NP010) have been evaluated in terms of potability of the permeate after disinfection. Finally, the technical feasibility of NF at low pressures with a membrane having bigger pore size and higher flux, as a result, was presented within the regard of the models from RSM and fouling analysis.

## MATERIALS AND METHODS

### Reagents, membranes, and rainwater

Three commercial flat sheet polymeric membranes were used in this study. These membranes were subjected to the rainwater treatment after their characterisations. The technical properties of these membranes are given in Table 1. Deionised water (DI water) was preferred for all experiments, and DI water was supplied by using a Milli-Q<sup>®</sup> IQ 7003/05/10/15 system (Germany). The Dionex<sup>™</sup> Combined Seven Anion Standard II was used for the calibration curve preparation to determine the anion concentrations in the samples (Thermo Fisher Scientific, USA) using Ion Chromatography (IC). Metal concentrations in the samples were determined with the calibration curve created by single-element standards manufactured for Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) by Inorganic Ventures (USA). The rainwater was taken directly from the cistern, of which details are explained in the following sections. The characteristics of rainwater are shown in Table 2.

### Rainwater supply and experimental plan

The rainwater was supplied from the cistern located in the garden of a mosque, newly constructed on the university campus. While the volume of the cistern was 278 m<sup>3</sup>, the rainwater collection area was 2,000 m<sup>2</sup>. There were four channels for the rainwater collection in the tetrastoon and a weir in the cistern to remove the excess amount of

**Table 2** | The characteristics of rainwater collected in the cistern

Parameter	Unit	Value
Appearance	–	Clear/Colourless
Odour	–	Odourless
Temperature	°C	17 ± 0.5
pH	–	7.5 ± 0.2
Conductivity	µS/cm	320 ± 0.2
Sodium	mg/L	0.60 ± 0.23
Natural organic matter	mg/L	3.30 ± 0.05
Fluoride	mg/L	0.14 ± 0.07
Chloride	mg/L	5.17 ± 0.16
Nitrite	mg/L	0.18 ± 0.04
Nitrate	mg/L	3.32 ± 0.04
Bromide	mg/L	<0.20
Sulphate	mg/L	66.47 ± 0.49
Phosphate	mg/L	<0.40
Iron	ppm	0.05 ± 0.01
Manganese	ppm	0.05 ± 0.02
Zinc	ppm	<0.02
Cadmium	ppm	<0.001
Chromium	ppm	<0.004
Lead	ppm	<0.02

**Table 1** | The technical properties of membranes

Parameter	Membrane		
	NP010	NP030	NF90
Code	YMNP0104205	YMNP0303001	1121012
Manufacturer	Microdyn Nadir	Microdyn Nadir	Dow Filmtec
Pore size (Da)	~1,000	~500	~200–400
Operating pH range	0–14	0–14	2–11
Salt rejection (%)	35–75 <sup>a</sup>	80–95 <sup>a</sup>	>97 <sup>b</sup>
Applications	Acid, metal, and chemical	Acid, metal, and chemical	Industrial

<sup>a</sup>Tested salt: Na<sub>2</sub>SO<sub>4</sub>.

<sup>b</sup>Tested salt: Mg<sub>2</sub>SO<sub>4</sub>.

rainwater during the heavy storm days. The water sample was taken using clear plastic bottles. The bottle was filled and sealed. The temperature, pH, and conductivity were measured on-site. All on-site measurements were triplicated. Following this, rainwater was characterised prior to the NF experiments to determine the concentration of some metals, anions, and cations (Step-1 in Figure 1). Commercial membranes were also subjected to the characterisation prior to the NF studies (Step-2). NF experiments had been carried out by following the experimental combinations given by RSM (Step-3). The optimum membrane and operating pressure were determined for a feasible rainwater treatment. Finally, to determine the reuse potential of commercial membranes, the four filtration cycles were also carried out using the rainwater at optimum operating pressure (Step-4). The experimental plan is schematically summarised in Figure 1.

### Design of experiments

Minitab 17.0 software was used to design the NF experiments and for data analysis. The experimental plan was

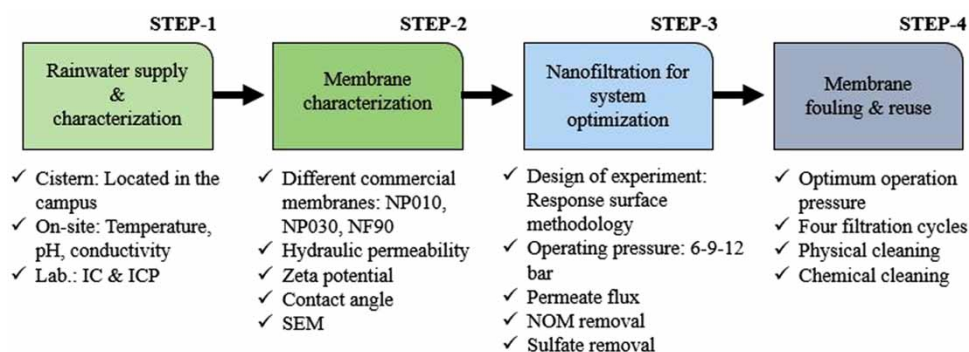


Figure 1 | The experimental plan that was followed in the study.

created according to a central composite face-centered (CCF) design prepared with RSM. The experimental data set including the factors and the levels can be seen in Table 3, where the factor levels are coded from low (-1) to high (+1) at the basic level 0 as centre points. Responses were the permeate flux, NOM removal efficiency, and sulphate removal efficiency. Experiments were carried out with the membrane filtration system explained in detail in the next section. It is important to mention that several preliminary experiments were performed to determine the optimal conditions, and this preliminary data was used further as input range to the factors in Minitab Worksheet. A quadratic approximation was considered to explain the

behaviour of the RSM models of second-order polynomial equation (Equation (1)).

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j \quad (1)$$

where  $Y$  is the predicted response,  $b_0$  is the constant coefficient,  $b_i$  is the linear coefficients,  $b_{ij}$  is the interaction coefficients, and  $X_i$ ,  $X_j$  are the coded levels of the process factors studied. The validity of the quadratic empirical model was tested with the analysis of variance (ANOVA) with the confidence level used as 95%. The insignificant parameters were deleted from the model equations given in the Results and Discussion section and these parameters are presented in Supporting Information (SI). All NF experiments were duplicated.

Table 3 | Experimental data set according to the RSM<sup>a</sup>

Run Order	Pt Type	Blocks	Replicates	Experimental variables (Factors)	
				Pore size (Da)	Pressure (bar)
1	0	1	1	600	9
2	-1	1	2	1,000	9
3	-1	1	3	600	6
4	0	1	4	600	9
5	1	1	5	200	12
6	0	1	6	600	9
7	1	1	7	1,000	12
8	-1	1	8	600	12
9	1	1	9	200	6
10	0	1	10	600	9
11	0	1	11	600	9
12	1	1	12	1,000	6
13	-1	1	13	200	9

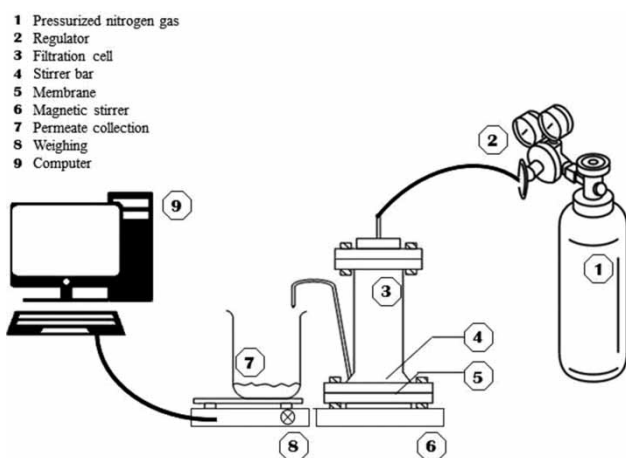
<sup>a</sup>Factors: 2, Replicates: 2, Base runs: 13, Total runs: 26, Base blocks: 1, Total blocks: 1, Cube points: 8, Centre points in cube: 10, Axial points: 8.

### Filtration experiments and the lab-scale system

All filtration experiments including membrane characterization and rainwater treatment were performed with Sterlitech Brand High-Pressured Filtration Cell (HPFC) (HP4750, Sterlitech Coop, USA). The system consists of a filtration cell, a nitrogen gas tank with a regulator, a permeate collection cell, and a computer that records data for the calculation of flux. Schematic representation of the experimental setup and technical properties of the high-pressure filtration cell are given in Figure 2 and Table 4, respectively.

### The determination of hydraulic membrane permeability

NF membrane was subjected to hydraulic membrane permeability (DI water permeability) tests before the rainwater treatment using the HPFC. Prior to each test, NF membranes were conditioned with DI water for 1 h at



**Figure 2** | The schematic presentation of the experimental setup (The technical drawings of HPFC and gas tank were supplied from the supporting files prepared by manufacturers in their official website (Sterlitech 2020) and modified by the author).

**Table 4** | Technical properties of high-pressured filtration cell

Parameter	Value/Information
Membrane size	47–49 mm diameter
Active membrane area	14,6 cm <sup>2</sup>
Max. operation volume	300 mL
Max. operating pressure	69 bar
Permeate line	1/8 inch diameter 316 L stainless steel
Cell	316 L stainless steel
Seal	Nitrile rubber
Magnetic stirrer	Polytetrafluoroethylene (PTFE)

a constant pressure of 14 bar. After that, the hydraulic membrane permeability was measured within the range of 6–12 bar at room temperature (25 °C) and at least three measurements from different membrane samples were averaged. During these experiments, collected permeate mass was measured by weighing with a balance (OHAUS, USA) and Equations (2)–(4) were used for the permeate flux calculation (Mutlu *et al.* 2018).

$$V_p = \frac{M_p}{\rho} \quad (2)$$

$$J_p = \frac{V_p}{(A * \Delta t)} \quad (3)$$

$$L_p = \frac{J_p}{(\Delta P - \sigma * \Delta \Pi)} \quad (4)$$

where  $V_p$  is the volume of permeate (L),  $M_p$  is the mass of permeate (g),  $\rho$  is the density of permeate (g/L),  $J_p$  is the permeate flux (L/m<sup>2</sup>/h<sup>-1</sup>) (can be also presented as LMH),  $A$  is the effective membrane area (m<sup>2</sup>),  $\Delta t$  is the sampling time (h),  $\Delta P$  is the applied pressure (bar),  $\sigma$  is the reflection coefficient,  $\Delta \pi$  is the osmotic pressure difference (bar) (assumed as zero), and  $L_p$  is the permeability (L/m<sup>2</sup>/h/bar).

### The determination of treatment efficiencies

The NF experiments on real rainwater were carried out at different operating pressures using the same HPFC. The initial feed volume was 200 L and the temperature during the operation was 25 ± 1 °C in NF experiments. Permeate flow rates have been measured and permeate flux was calculated as explained previously. When 120 mL of permeate was collected, the permeate samples were stored for further analysis. The instrumental analysis for the determination of sulphate and NOM was carried out as explained below. The removal for each contaminant,  $i$ , has been calculated as follows:

$$R_i = \left(1 - \frac{C_{p,i}}{C_{f,i}}\right) \times 100 \quad (5)$$

where  $R_i$  is the removal of contaminant  $i$  (%),  $C_{p,i}$  is the concentration of contaminant  $i$  in the permeate (mg·L<sup>-1</sup>), and  $C_{f,i}$  is the concentration of contaminant  $i$  in the feed (mg·L<sup>-1</sup>).

### Membrane characterisation techniques and instrumental analysis

After the determination of hydraulic permeability, membranes were subjected to additional characterisation with zeta potential (ZP) and contact angle (CA), and scanning electron microscopy (SEM) analysis, because the surface characteristic of the membrane plays an important role in the permeation and rejection. The top surface morphology of the membranes was observed by using the FEI scanning electron microscope at standard high-vacuum conditions. Polaron sputter coater was used to coat the outer surfaces of membrane samples with gold. The hydrophilicity of the membrane was determined using contact angle measurements. ZPs of clean membranes were determined using an electrokinetic analyser (Anton Paar Surpass, Austria). CAs of clean NF membranes were measured by the KSV Attention Theta Brand contact angle measure instrument (Sweden) using scissile drop mode on dried membranes. A

small droplet of DI water was delivered onto the membrane surface and after waiting 1.5 s, an image of the droplet on the membrane surface was taken. Each ZP and CA of the membrane was measured at a minimum of five different points on the samples in order to calculate the average value.

Raw rainwater and permeate samples were collected for analysis during the NF experiments. Elemental analysis was performed using ICP-OES (3000 DV, Perkin Elmer, USA) and IC (Dionex ICS-3000, USA) for the raw rainwater characterisation. Also, a total organic carbon (TOC) analyser (Shimadzu V-CPN, USA) was used for the determination of NOM concentration in raw and treated rainwater as described in the paper of Pantelaki *et al.* (2018). The sulphate concentration in raw and treated rainwater was determined using IC. At the end of the NF processes, the morphology of the membranes was observed again using SEM (FEI Quanta FEG 250, USA). Before scanning, the surface of the membranes was coated with 3–4 nm gold-palladium (Pd–Au) using the Quorum SC7620 model sputter coating machine (UK) as carried out with clean membranes. All pH determinations were realised with the Fisher Scientific probe (XL Series, USA). All analytical measurements were conducted in triplicate, and the average values with standard deviations are presented in the paper.

### Membrane fouling analysis and determination of reuse performance of commercial membranes

NF runs were also used for the estimation of the fouling property of commercial membranes. The steady-state flux during DI water filtration ( $J_{w,o}$ ) and the steady-state flux during rainwater filtration ( $J_{w,i}$ ) were determined to be compared. The flux reduction ratio (FRR) was calculated as follows:

$$\text{FRR} = \left(1 - \frac{J_{w,i}}{J_{w,o}}\right) \times 100 \quad (6)$$

FRR values of commercial membranes were evaluated regarding the analysis of the foulants observed on the membrane surface after the rainwater filtration. SEM images of used membranes were obtained with this aim. Finally, the four filtration cycles were carried out with a high volume of rainwater to determine the reuse potential of commercial NF membranes. At the end of the first cycle, the membrane was physically cleaned with DI water and the second filtration cycle was started with the same membrane. These applications

were complete after four runs and a chemical cleaning was applied at the end. NaOH was preferred as a model chemical cleaning solution and prepared as described in the paper of Li & Elimelech (2004). The solution (3% v/v) was freshly prepared with DI water right before the experiment.

## RESULTS AND DISCUSSION

### Filtration performances of commercial membranes on rainwater treatment

The characterisation of rainwater used as the feed solution during the NF process is presented in the Materials and Methods Section as Table 2. Rainwater was completely colourless and odourless. The conductivity of rainwater was 320.0  $\mu\text{S}/\text{cm}$  and lower than the conductivity of conventional tap water and the maximum conductivity value (1,017.0  $\mu\text{S}/\text{cm}$ ) reported in the study of Leong *et al.* (2017). On the other hand, the NOM concentration (3.30 mg/L) was slightly higher than for a rainwater sample presented in the literature (Leong *et al.* 2017). The concentrations of fluoride, chloride, and manganese in the rainwater were as expected. Besides, the only anion that had a high concentration when compared to others was sulphate. The sulphate concentration was two times higher than the concentration  $\text{SO}_4^{2-}$  that was originated from asphalt surfaces in the study of Angrill *et al.* (2017), and this can be related to combustion emissions from transportation on the campus. The metal concentrations in the rainwater were negligible.

Clean NF membranes were also characterised before the experiments. The DI water permeability, ZPs, and CAs of three commercial membranes are presented in Table 5. While the highest DI water permeability was obtained with NP010, the lowest value was obtained with NF90. This means that DI water permeability was directly proportionate to the pore size, as expected. Then, the surface properties of the three NF membranes were assessed by measuring the streaming potential, expressed as ZP. While the ZP of NP010 was positive at the pH of rainwater, it was negative for NP030 and NF90. This means that NF90 has more potential to reject anions like sulphate, since the membrane surface and anions were both negatively charged. Finally, the CA values of the clean NF membranes were also investigated to evaluate their hydrophilicity. The highest hydrophilicity can be exhibited by NP030 and NF90 with their lower contact angles when compared to NP010 with a contact angle of 72°.

**Table 5** | The characteristics of clean membranes

Parameter	Unit	Membrane		
		NP010	NP030	NF90
Permeability	L/m <sup>2</sup> /h/bar	15.23 ± 0.2	4.27 ± 0.07	2.91 ± 0.1
Zeta potential	mV	0.69 ± 0.5	-21.90 ± 3.8	-25.90 ± 2.5
Contact angle	°	72.00	58.00	57.00

The characterised membranes were then subjected to rainwater filtration as explained in detail in the Materials and Methods section (Step-3 in this study). The average flux values for rainwater treatment are presented in Figure 3. The rainwater fluxes during NF were lower than DI water flux for all three NF membranes. Rainwater flux increased with the increasing operating pressure, but the pore size was another factor in this study. To understand the individual and combined effect of the pore size and operating pressure on the flux, a unique RSM study was carried out.

The results showed that the flux varied in the range 27.0–118.8 L/m<sup>2</sup>/h and depended on the combination of operating conditions. In a case described in the paper of Pronk and colleagues, the stable flux in a pilot-scale plant for rainwater treatment was 0.47 L/m<sup>2</sup>/h (Pronk *et al.* 2019), which was significantly low when compared to the flux achieved in the study. The full quadratic stepwise analysis, including all linear, quadratic, and interaction effects of pressure and pore size on the response (flux), was used to select significant terms, applying a significance level of 0.05. ANOVA results are shown in the supplementary information as Table S1. The RSM analysis gave a mathematical equation (Equation (7)) for flux as a function of the first-order effects of pressure and pore size, as well as an interaction effect between the two factors. This mathematical relationship will be called 'Model-F' (F for flux) in this

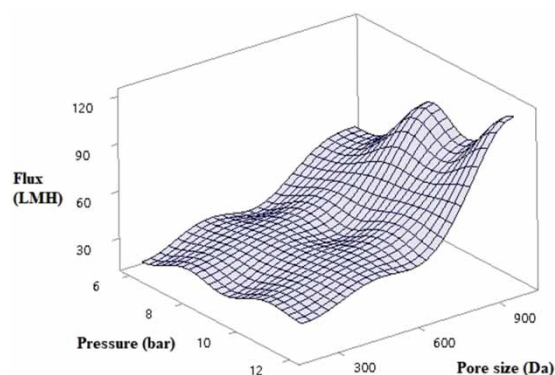
paper, and the R<sup>2</sup> for Model-F was 98.08%.

$$\text{Model-F: } J = 10.7 - 0.1697 * \text{MWCO} + 6.35 * P + 0.000144 * \text{MWCO}^2 + 0.00944 * \text{MWCO} * P \quad (7)$$

where J is the permeate flux (L/m<sup>2</sup>/h), MWCO is the molecular weight cut-off (pore size) of the NF membrane (Da), and P is the operating pressure (bar). The NP010 and NP030 membranes delivered very high permeate flux. This behaviour of these membranes can be explained by a relatively larger pore size allowing more liquid to pass through, the simple reason being that the force applied on the membrane surface increases with an increase in the pressure, resulting in increased driving force across the membrane. Consequently, this phenomenon increases the amount of liquid volume discharged at the permeate side; in turn, creating higher permeate flux. With increasing pressure, flux also increased linearly in this study; however, it was observed that the permeate flux began to decrease after a limit. This result fits with the flux profile obtained by Pino *et al.* (2018). The small decrease in flux with pressure seen in Model-F is probably due to the combined influence of hydrophilicity (please see Table 5) and the fouling under higher operating pressures (Shirazi *et al.* 2010; Buca *et al.* 2018).

### Treatment performances of commercial membranes at rainwater treatment

The NOM and sulphate removal of NF membranes were the second and third responses analysed by response surface methodology, respectively. All responses are also reported in SI. While the sulphate removal varied in the range of 35.43–99.85%, the NOM removal varied in the range of 96.80–100% depending on the combination of the parameters pore size and operating pressure. The removal efficiency with dead-end membrane systems was around 93.9–95.9% in a previous study carried out with several NOM fractions (Pronk *et al.* 2019) and the lowest efficiency

**Figure 3** | Flux profile with varying membrane pore size and operation.



obtained in our study was higher than the maximum value in the relevant study. ANOVA results for these responses related to the removals are shown also in the supplementary information (Table S1). The resulting  $\text{SO}_4^{2-}$  removal model 'Model-S' as a function of pore size and pressure is described by Equation (8). The  $R^2$  value for this model was 99.78%.

Model-S:

$$R_{\text{SO}_4} = 100.83 + 0.02683 * \text{MWCO} - 0.000091 * \text{MWCO}^2 \quad (8)$$

where  $R_{\text{SO}_4}$  is the sulphate removal (%), MWCO is the molecular weight cut-off (pore size) of the NF membrane (Da), and P is the operating pressure (bar). The 3D graph is given in Figure 4 to present the individual and combined effects of the factors on the sulphate removal.

The effect of pressure on sulphate removal during the NF of rainwater was not significant when compared to the effect of the pore size in this study. Al-Zoubi *et al.* (2007) presented similar results from their NF studies carried out with  $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$  salts. The rejections did not change with increasing pressure, especially at operating pressures higher than 6 bar (Al-Zoubi *et al.* 2007). Stable removal efficiencies with changing operating pressure generally prove that the concentration polarization on the membrane surface was slightly abundant. The effect of concentration polarization is to reduce actual product water flow rate and salt rejection versus theoretical estimates. Theoretical estimation was an increasing rejection with increasing operating pressure. Jadhav and colleagues confirmed that the key mechanism of ion rejection was the charge exclusion (2016) and found also that pressure was the most ineffective parameter when compared to characteristics of membranes and feed solution.

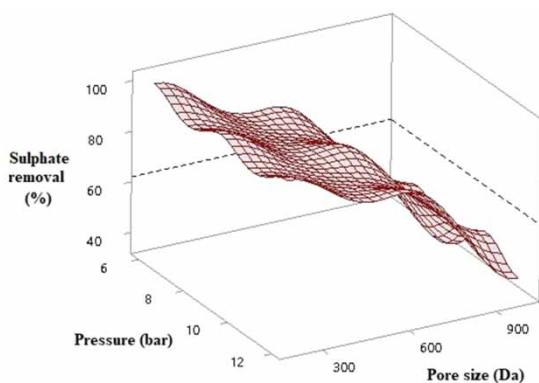


Figure 4 | Sulphate profile with varying membrane pore size and operation (dotted line refers to the required sulphate removal).

The highest sulphate removals were obtained with the NF90 membrane. This result fits the successful rejection of sulphate by NF90 in previous papers in the literature (Krieg *et al.* 2005; Al-Zoubi *et al.* 2007; Pino *et al.* 2018). While the average sulphate removal was 37.81% for the NP010 membrane, it was 82.28% for the NP030 membrane. Then, the average sulphate removal increased and an efficiency of 99.03% was obtained. The increase in the efficiency from 37.81% to 99.03% can be explained by the combined effect of the smaller pore size and more negatively charged membrane surfaces. While the atomic radius of sulphate is 0.242 nm, this value can be 0.38 nm if it is hydrated (Pino *et al.* 2018). Since the pore sizes of NF90, NP030, and NP010 are 0.25 nm, 0.31 nm, and 0.35 nm; respectively, it may be said that the sieving effect is the main mechanism in an environment in which the charged surface is the helper (Bellona & Drewes 2005; Mullett *et al.* 2014). The removal efficiency should be a minimum of 62.3% to have a lower sulphate concentration than the desired, which is 25 mg/L, according to Turkish Standards. Additionally, the resulting NOM removal model 'Model-N' as a function of pore size and pressure is described by Equation (9).

$$\text{Model-N: } R_{\text{NOM}} = 106.73 - 0.000008 * \text{MWCO}^2 + 0.179 * P^2 - 0.000587 * \text{MWCO} * P \quad (9)$$

where  $R_{\text{NOM}}$  is the NOM removal (%), MWCO is the molecular weight cut-off (pore size) of the NF membrane (Da), and P is the operating pressure (bar). The  $R^2$  value for this model was 85.62%. The 3D graph is given in Figure 5 to present the individual and combined effects of the factors on the NOM removal.

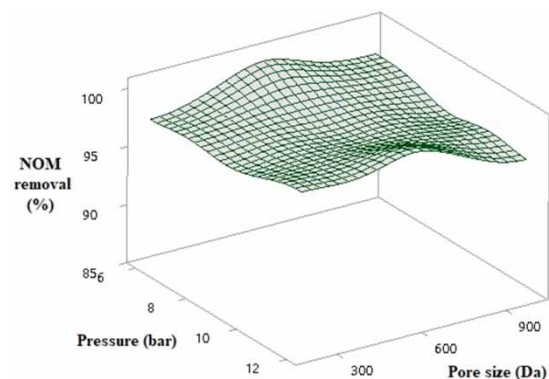


Figure 5 | NOM profile with varying membrane pore size and operation.

As it is mentioned in the literature that the insoluble organic matter in the rainwater has an average pore size of 0.3–1  $\mu\text{m}$  (Holecek *et al.* 2007), all NF membranes could successfully reject the organic matter. The NOM removals were not significantly affected by the pressure and the pore size. The average NOM removal efficiencies of NP010, NP030, and NF90 were 97.27%, 98.06%, and 99.20%, respectively. The results fit the NOM rejection efficiencies obtained in the study of Shen & Schäfer (2015). They had found that the efficiencies with NF90 were higher than the efficiencies with other NF membranes. When the NOM rejection by membranes was evaluated, it can be said that NOM rejection is independent of MWCO, as the molecular size of NOM is significantly larger compared to the membrane pore size (Shen & Schäfer 2015). Only small amounts of NOM could pass through the membrane.

In summary, the NF process, which is a suitable process for obtaining treated rainwater without causing any problem in taste, could be optimised using model results to find the optimum point that meets the required permeate quality and lowers energy consumption. Silva *et al.* (2016) also reported in their studies that the model parameters obtained by independent methods can be used as a predictive tool. The process was optimised by considering the minimum sulphate removal efficiency. According to Model-S, the only important and effective factor was the pore size of the membrane. When Model-S was solved, it was seen that the biggest pore size of the NF membrane should be approximately 800 Da (62.8%  $\text{SO}_4^{2-}$  removal). Since the operating pressure was not a significant factor when compared to the pore size of a membrane, NF processes can be carried out at a low operating pressure like 6 bar. When Model-N was used, the NOM removal was found as approximately 99%. As the final step, the flux was estimated as 36.4  $\text{L}/\text{m}^2/\text{h}$  utilising Model-F. This flux is higher when compared to the permeate flux ( $\sim 12.5 \text{ L}/\text{m}^2/\text{h}$ ) presented in Shen and Schäfer's study carried out at 6 bar with natural waters (Shen & Schäfer 2015). As a result, it can be said that a package NF unit, including two spiral wound 8-inch elements, can be installed on the basement floor of the building and 13 tons of treated water can be supplied in a day with only a 6 hours-long operation.

### The fouling and reuse performances of commercial membranes

To understand the fouling tendencies of used commercial membranes, the flux reduction ratio values (FRR) were calculated as described in Section 2.5 and are presented in

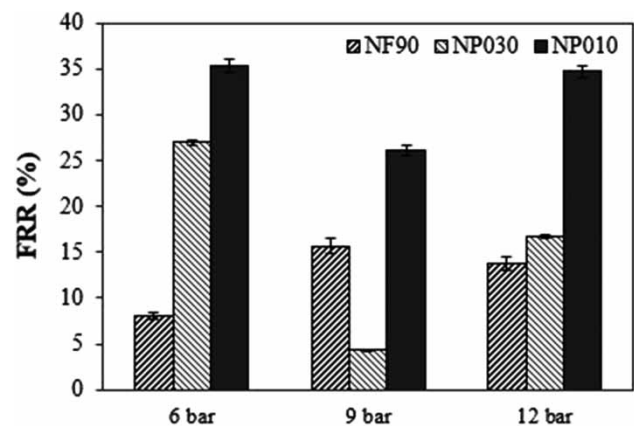


Figure 6 | The FRR values of the commercial membranes on rainwater treatment.

Figure 6. The FRR values of membranes on rainwater filtration varied between 8 and 15.7, 4.4 and 27, and 26.2 and 35.3% for NF90, NP030, and NP010, respectively. Concerning these values, it can be said that FRR values were directly proportional to pore size characteristics of commercial membranes. This result fits the results obtained by Koseoglu-Imer (2013). She also mentioned in her paper that the change of FRR in five different UF membranes manufactured at the laboratory was proportional to the porosity (Koseoglu-Imer 2013). The increase of pore size increased the adsorptive fouling except for the filtration at 9 bar. The effect of operating pressure was negligible. Besides, all membranes were subjected to microscopic investigation after the rainwater treatment to visualise the fouling effects. The SEM images can be seen in Figure 7. The virgin NF90 membrane exhibits the network-like structure typical of a membrane polyamide layer. The SEM image of fouled membrane clearly shows the accumulation of a foulant layer onto the membrane surface. The visual observation of the SEM image indicates that surface adsorption may be the main mechanism for NF fouling. When the shape and surface morphology with minor colloids on the used membranes was evaluated, it can be said that these are indicative of organic fouling. It is also observed that some white crystal substances appear in the fouling layer, which should be sulphate. NP010 membrane, which has the biggest pore size in the membranes used in this study, had less foulant on its surface, in line with its lower treatment efficiencies. NP030 membranes had more foulants on the surface than the foulants on NP010. The highest amount of foulant was seen on the surface of the NF90 membrane. In the case of NF90, the colloids were distributed over the entire membrane surface due to hydrophobic interactions between the

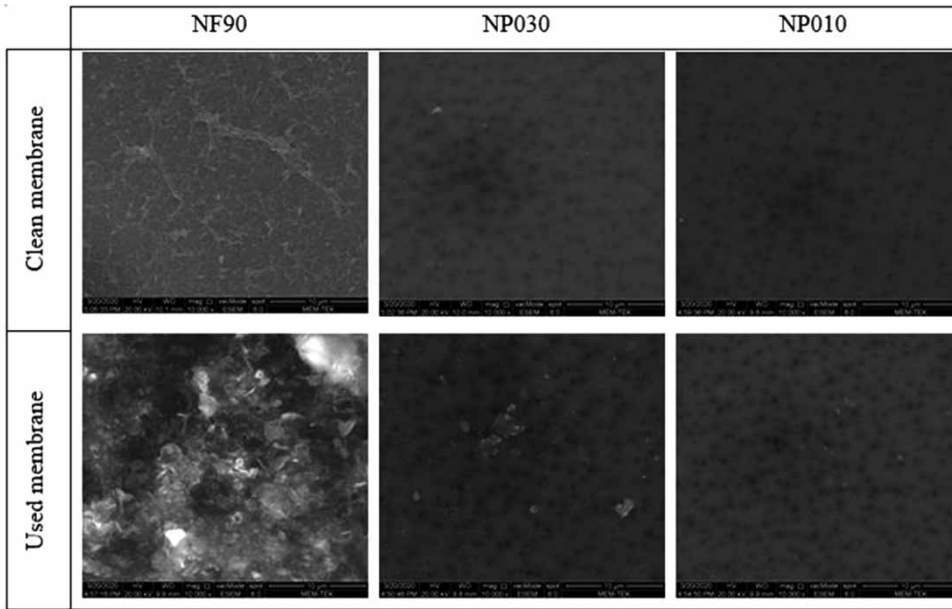


Figure 7 | SEM images of clean and used membranes (10 kX magnification).

colloids and the membrane surface. As a result, valley clogging did not occur.

It is important to prove that the selected membrane will have flux recovery property and a long lifetime during the operation. As explained in Section 2.6, commercial membranes were used four times to see their flux reduction profiles. The flux profiles can be seen in Figure 8. At the beginning of the first cycle, the membrane was conditioned and each cycle included 1.5 h rainwater filtration. At the end of the first cycle, the membranes were physically cleaned

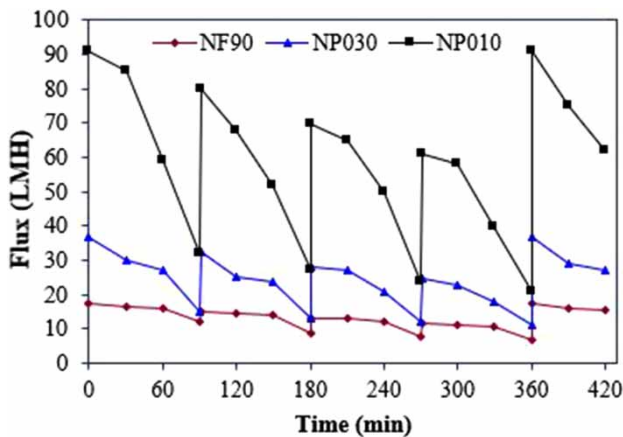


Figure 8 | Flux variation of commercial membranes during cycles of nanofiltration of rainwater.

with DI water and the second filtration cycle was started with the same membranes. After four runs of rainwater filtration, which equals 6 h long NF in a day, the membrane was subjected to chemical cleaning using sodium hydroxide. The aim was to simulate a non-continuous operated plant described in the previous part. It is expected that flux will decline in time because of fouling. This decline could be seen in each cycle continuing 90 minutes. The physical cleaning applied at the end of each 90 minutes helped to increase the flux; however, the initial flux in the second, third, and the fourth cycle was lower than the initial flux value observed in the previous cycle. This means that physical cleaning could not be sufficient to remove all foulants on the membrane surface.

As a result, it seemed that physical cleaning was sufficient to complete the day with a 33% loss of flux averagely for all membranes used during 6 hours. At the 360th minute, membranes were subjected to chemical cleaning. The flux at the 361st minute of the operation was almost equal to the initial flux obtained at the very first minute of the operation day. So, results showed that caustic cleaning was effective at controlling membrane fouling and chemical cleaning could efficiently recover the flux at the end of the day/operation. In good agreement with the literature, high membrane permeability recovery was observed here. However, alkaline cleaning may lead to temporary enlargement of the membrane pores, and it can be said that this

temporary enlargement of the membrane pores due to alkaline cleaning subsequently may result in some notable changes in the rejection of contaminants. For instance, it was reported in the literature that sequential alkaline cleaning caused a decrease in rejection (Liikanen *et al.* 2002; Simon *et al.* 2013). To prefer the use of more dilute alkaline cleaning agent as in this study is suggested.

## CONCLUSION

This study proposed a promising approach for rainwater recycling by the NF treatment process. Elimination of natural organic matter and sulphate from rainwater using NF membrane technology was discussed in this regard. It was seen in the literature that NF can be a suitable process for obtaining treated rainwater without causing any problem in taste. In addition to treatment performances, the membrane fouling was also identified.

RSM was successfully applied for evaluating the importance of operating parameters and approaching the optimal NF process conditions for rainwater treatment. RSM based on CCF design was applied to study the effects of operating parameters including operating pressure and membrane pore size on the NF of rainwater containing sulphate and NOM. From the results of the experiments, the following conclusions can be drawn:

- (1) The more effective factor was the pore size of the membrane, and it was seen that the biggest pore size of the NF membrane should be a minimum of 800 Da. This means that NP010 should not be preferred for rainwater treatment when it is required to meet the health standards. On the other hand, it is not an obligation to prefer a tight NF membrane to prevent the taste problem while rainwater drinking. This means that the feasibility can be enhanced with reasonable decisions in the planning and design steps.
- (2) By considering the removal of natural organic matter and sulphate with maximum allowable concentrations, it could be found that NF processes can be carried out at low operating pressure (6 bar in this study). From the resultant models, it is expected to achieve a NOM removal with a percentage of 99% when the concentration of sulphate is below the limit. In an NF process carried out at an operating pressure of 6 bar with the proper membrane, the flux would be 36.4 L/m<sup>2</sup>/h, which is a relatively high flux compared to the flux values presented in the literature. So, it is possible to

operate a low-risk system concerning occupational health and safety and operational costs by making no concessions to have a sufficient amount of treated water.

- (3) Membrane fouling was further examined based on SEM analyses and membrane cleaning procedures. Considering SEM measurements, it was determined that surface fouling was effective on the flux decline caused by fouling. The amount of the foulants on the membrane surface were not at high levels, and commercial membranes presented high cleanability on long-term rainwater filtration. A diluted alkaline cleaning agent was suggested by the author to prevent commercial NF membranes from pore extensions.

To conclude, rainwater recycling systems can save a large quantity of relatively high-quality water at a reasonable cost although there had been some published results based on the misrepresented operational costs of membrane systems. There is a growing awareness of water-sensitive urban design with water recycling. It seemed important to consider the costs and environmental impacts before choosing a treatment method for that recycling. Membrane processes have better drinking water quality, safe drinking water, and lower environmental impact compared to the other treatment alternatives. Especially regarding the energy demand, NF is known to have a large demand due to the required pressures; however, it was proven in this study that lower operating pressures can be also applied. Generally speaking, NF was found to be a proper method for NOM and sulphate removal from rainwater, and a package NF unit can be easily installed on a university campus for the reuse of water.

## ACKNOWLEDGEMENT

There was no funding provided for this study. The author would like to thank the National Research Center on Membrane Technologies (MEM-TEK) for SEM analysis. Also, the author is thankful to the campus administration for the rainwater supply. The graphical abstract was prepared with the software of Microsoft PowerPoint.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 14 September 2020; accepted in revised form 30 November 2020. Available online 10 December 2020