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Enhanced nanofiltration rejection of inorganic and organic compounds from a wastewater-reclamation plant's micro-filtered water using adsorption pre-treatment

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Abstract

Adsorption pre-treatment to enhance the nanofiltration (NF) removal of inorganic ions, dissolved organic carbon (DOC) and organic micropollutants (OMP) from microfiltered (MF) wastewater was investigated using NF 90 membrane (contact angle 79% and molecular weight cut off value of 90-200 Da). The NF showed greater rejection for divalent cations (Ca²⁺, Mg²⁺) and anions (SO₄²⁻) compared to monovalent cations (Na⁺, K⁺) and anions (Cl⁻,

NO_3^-). The degree of total DOC removal was: GAC adsorption + NF (86%) > an ion exchange resin (Purolite) adsorption + NF (81%) > NF operation alone (72%). GAC + NF removed biopolymers and hydrophobic substances almost completely and the highest percentage of LMW neutral substances. In contrast, Purolite + NF almost completely removed humic substances. The degree of membrane fouling order was: LMW neutrals > building blocks > biopolymers > hydrophobics > humics. Adsorption pre-treatment reduced membrane fouling and increased solution flux, the outcome being better with GAC compared to Purolite. Of the 10 MOPs in the MF water, seven were rejected >90% by NF without any pre-treatment. Conversely, Purolite and GAC pre-treatments rejected >90% of all OMPs.

Keywords: Wastewater treatment; Organic micropollutants; Nanofiltration; Adsorption pre-treatment; Water quality

Highlights

- Adsorption pre-treatment enhanced NF rejection of DOC/salts/organic micropollutants
- Adsorption pre-treatment reduced membrane fouling and increased water flux.
- Fouling impact: LMW neutrals>building blocks> biopolymers> hydrophobics > humics.
- NF treatment enhanced permeate water quality for its use as irrigation water.

1 Introduction

Increasing shortage in water resources worldwide, occurring at the same time as the world's population continues to expand are of serious concern. Industrial activities, and intensive agriculture, combined with challenging climatic conditions such as prolonged drought is forcing many countries to explore alternative sources of water. Wastewater reclamation and

reuse offers an opportunity to solving some aspects of this problem [1]. However, wastewater generally contains pollutants such as heavy metals, inorganic salts, dissolved organic matter and organic micropollutants (OMP) (including pharmaceutical and personal care products, endocrine disruptors, pesticides, and industrial by-products) [2,3]. Elevated exposure to heavy metals can cause damage to the human body, such as reduced mental and central nervous function, lower energy levels and compromised blood composition, lungs, kidneys, liver, and other vital organs' functions [4]. High concentrations of dissolved organic matter (DOC) in water can cause colour, taste, and odour problems, as well as provide a substrate for bacterial growth and lead to disinfectant by-product formation which can adversely affect people's health [5]. Some OMPs are known to be toxic to freshwater invertebrates (such as daphniids), fish, mussels, and human embryonic cells even at very low concentrations [6]. Excessive salts/ions (particularly Na^+) can undermine plant growth when the water is used for irrigation [7-9]. For these reasons, wastewater needs to be reclaimed by reducing the concentrations of a diverse range of pollutants to safe limits.

There are many methods by which to treat wastewater for reuse. Of these, membrane separation technologies such as reverse osmosis (RO) and nanofiltration (NF) are two of the most widely used technologies [10]. Many hundreds of RO-based water reclamation plants are in operation worldwide [11]. Both RO and NF are based on solution-diffusion as the major transport mechanism, requiring high hydraulic pressures and using similar membrane materials [1]. They are designed to remove dissolved chemical constituents. NF removes many of the same solutes as RO but at lower removal efficiency. However, NF membranes feature (negatively) charged functional groups [12]. Consequently, the selectivity of NF for monovalent and bivalent anions is very different [7,8,13]. Compared to RO membranes, NF membranes have higher water permeability and can be operated at lower pressures, thus reducing the specific energy consumption and treatment-related costs. NF was tested in this study to investigate whether the currently used RO process in many countries can be replaced by

the NF process (or used as the first process prior to RO) and achieve an equivalent quality of permeate water.

Despite the usefulness of NF technology, several challenges including membrane fouling, contaminant permeation, energy consumption, and disproportionate rejection of useful divalent cations (Ca^{2+} , Mg^{2+}) beset this process [1,8,10]. For example, Chang et al. [7] compared NF with RO and reported that the measured sodium adsorption ratio (SAR) (a ratio relating the concentration of Na^+ to Ca^{2+} and Mg^{2+} , when it exceeds a certain value affects plant growth if the water is used for irrigation) increased from 1.81 to 4.67 when NF was used to reclaim secondary wastewater effluent, whereas it dropped from 1.81 to 0.72 when RO was employed for the reclamation process. The impact of some of these problems can be reduced by having a pre-treatment step prior to the NF process [1,14]. Woo et al. [15] reported that a powdered activated carbon (PAC) adsorbent added prior to a submerged membrane bioreactor/NF integrated process mitigated membrane fouling, increased water flux, and resulted in a better permeate quality. PAC adsorption prior to NF also reduced membrane fouling during NF treatment of biomass lignocellulosic hydrolysate [16]. However, flocculation and PAC adsorption pre-treatment prior to NF only slightly improved DOC removal and filtration flux compared to NF without pre-treatment of a biologically treated sewage effluent, although foulant concentration decreased [17]. NF has also been employed to remove OMPs [18] but, unlike in the case with DOC, it has been less used with adsorption pre-treatment.

There are many adsorbents other than the previously used PAC that can be employed in the pre-treatment process to remove large number of pollutants including DOC and OMPs. Imbrogno et al. [19] reported that combining ion exchange resin adsorption with NF mitigated membrane fouling caused by humic acid and reduced flux decline. In our earlier studies, it has been shown that granular activated carbon (GAC) and/or ion exchange resins can efficiently

remove heavy metals, OMPs, DOC, and inorganic salts from wastewater and RO concentrate water [3,20-23]. Some of these adsorbents could be used in the pre-treatment phase to enhance the removal of the various pollutants, reduce membrane fouling, and increase flux in NF. In this study the objective was to determine the effect of pre-treatment of microfiltered (MF) wastewater using two adsorbents (GAC, Purolite ion exchange resin) that have contrasting properties for removal of different fractions of DOC, inorganic salts, and 10 OMPs by NF and how membrane fouling was affected. Biofouling is a major long-term operating issue for NF and reverse osmosis. It is important to minimise or eliminate this at the early stages of operation by removing the organic precursors such as DOC before they enter NF. Biofouling leads to drop in permeate velocity, selectivity, and membrane service life. It also increases cleaning frequency and operation cost of chemicals and electricity [24]. This is the reason it is important to remove DOC through adsorption pre-treatment before MF treated water enters NF. The economic benefit from reduced biofouling would cover a major part of the adsorption pre-treatment cost. A recent study showed that the adsorbents that were used can treat 2800 bed volumes of water before requiring regeneration [25] meaning the costs of pre-treatment is not high.

To the best of our knowledge, no previous studies have reported the effect of adsorption pre-treatment on simultaneous removal of different fractions of DOC, OMPs, and inorganic salts from the same feed solution. It will be insightful to compare the efficiencies of DOC and OMP removals from the same feed solution, considering that OMPs are very small constituents of DOC (concentration 10,000 times less than that of DOC). Another innovative feature of this study is the use of two adsorbents, GAC and Purolite ion exchange resin, which have contrasting adsorption properties to remove different constituents of DOC [20,26]. This could lead to: firstly, different NF performance; and secondly, possibly different groups of MOP, DOC fractions, and inorganics removal. The adsorption pre-treatment process was

conducted in a continuous dynamic operation mode which is more suitable for practical treatment plants than the static batch mode generally used in previous studies.

2 Materials and methods

2.1 Feed solution and NF membrane

Microfiltered (MF) water from a water reclamation plant located in Sydney, Australia, which treats domestic sewage and stormwater was used as feed water in this study. The physicochemical properties of the water are presented in Table S1 (Supplementary data). The feed water contains a large concentration range of inorganics and organics including 10 MOPs (concentrations presented later in the paper). A preliminary experiment with five NF membranes (NF 90, NF 270, NP 30, NF TS 80, NF Duracid) showed that NF 90, with the highest water contact angle and among membranes with the lowest molecular weight cut off value (MWCO), had the highest conductivity and DOC rejection. It was therefore selected for use in subsequent experiments. The NF 90 membrane was made from polyamide TFC and supplied by Sterlitech Corporation, WA, USA. The MWCO value of the membrane ranged from 90 to 200 Da [18,19]. The zero point of charge (ZPC, the pH at which the net surface charge is zero) of the membrane was 3.5 [19], indicating that the membrane is negatively charged at the pH of the MF water (6.5-7.5).

2.2 NF membrane water contact angle measurement

The NF membrane contact angle provides information on the hydrophilicity/hydrophobicity of the membranes. In general, a membrane is considered hydrophilic if the contact angle is less than 90° and hydrophobic if it is greater than 90° [27]. The smaller the contact angle the greater the membrane hydrophilicity. Contact angle was measured using a Sessile drop Theta

Lite Tensiometer (Model TL100) which is a compact computer-controlled video-based instrument. In this method, a water droplet is placed with a syringe on the membrane surface and the image of the change in angle formed by the droplet surface and membrane surface is recorded by a computer program for 10 sec. The contact angle is measured via the intersection of the liquid/solid interface by taking the average of the change in the angle during this period.

2.3 NF measurement

A known quantity of MF wastewater (2-3.5 L) was recirculated using a magnetic drive pump through the membrane (Fig. 1). The transmembrane pressure was maintained at 2-5.5 bar by adjusting the valve at the discharge of the pump. The NF unit was fitted with a rectangular cross flow cell with an effective membrane area of 68 cm². A cooling/heating unit was connected to the feed solution by submerging coils to maintain a temperature of 25 ± 1⁰C. Permeate was continuously collected and at the end of the operation a subsample was chemically analysed. The NF rejected solution was continuously transferred to the feed solution. When the experiment ended the feed solution containing the reject solution was also analysed.

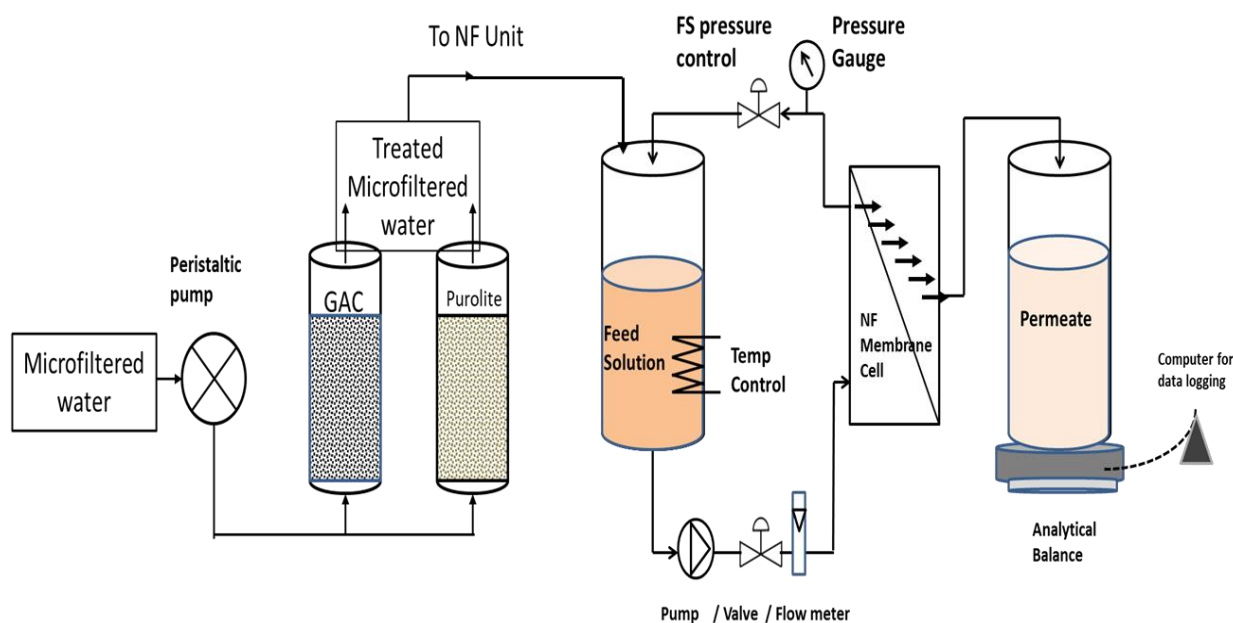


Fig. 1. Schematic of NF operation

2.4 Pre-treatment with fixed-bed column adsorption

Adsorption pre-treatment prior to NF was conducted using cylindrical fixed-bed glass columns packed with 96 g of GAC or 146 g Purolite anion exchange resin to a height of 60 cm to reduce the concentrations of DOC, inorganic salts, and OMPs in the MF water so that the efficiency of the subsequent NF could be increased. These adsorbents were selected due to their strong ability to remove different DOC fractions and OMPs [26]. Their physical and chemical properties are presented in Table S2 (Supplementary data). The MF treated wastewater from the water reclamation plant passed upward through the columns at a filtration velocity of 9.46 m/h using a peristaltic pump. The bottom and top of the columns were fitted with stainless steel mesh so that a uniform flow was generated. Above the top mesh, glass beads were placed to keep the adsorbent intact. The effluent from the columns served as the feed solution for NF operation.

2.5 Chemical analyses

The pH and electrical conductivity of the NF feed solution (FS) and permeate were measured using a manual Multi Portable pH and conductivity meter (HQ 40d, HACH USA), respectively. Concentrations of inorganic anions and cations in the MF and NF waters were measured with an Inductively Coupled Plasma Optical Emission Spectrometry instrument (ICP-OES, Perkin Elmer OPTIMA 7300 DV ICPOES Instruments, USA). DOC and its fractions were measured using a liquid chromatography-organic carbon detection unit (LC-OCD) (DOC-Labor Dr. Huber, Germany) [3]. LC-OCD separates the sample into five fractions of organic carbon with different molecular weight ranges and chemical polarity. Two major fractions are observed: firstly, the hydrophilic chromatographable organic carbon (CDOC) that elutes from the column, and secondly, non-chromatographable organic carbon, which is the hydrophobic organic carbon (HOC) fraction that binds irreversibly to the hydrophobic solid phase of the column. CDOC is further fractionated into four major fractions: biopolymers (>20,000 g/mol), humic substances (1200–500 g/mol), building blocks (weathering product of humic substances) (500–350 g/mol), and low molecular weight (LMW) organics (<350 g/mol) [8,28-30]. The difference between DOC and CDOC is assumed to be the hydrophobic fraction [29]. The OMP concentrations were determined by first solid phase extraction (SPE) followed by liquid chromatography/tandem mass spectroscopy. The details have been documented elsewhere [3].

3 Results and discussion

3.1 Membrane contact angle

The NF 90 membrane had a contact angle of 79° which indicates that it has low hydrophilicity. Other researchers have also reported high contact angle values of $63-65^{\circ}$ for this membrane and stated that the membrane is moderately hydrophobic (weakly hydrophilic)

compared with hydrophilic NF 270 membrane with 30° contact angle [31,32]. The difference in contact angle is due to differences in the polymer composition and morphology of the membranes' active layers. Gryta et al. [33] reported that the higher contact angle of NF 90 compared to NF 270 was due to the rougher top layer in the former membrane and smoother top layer in the latter. Contact angle generally increases with membrane roughness in addition to hydrophobicity [27]. Xu et al. [32] stated that NF 90 had the highest contact angle of 63° out of the three NF membranes tested and called it the most hydrophobic. They also found this membrane had the highest roughness (63 nm) as measured by atomic force microscopy.

3.2. Rejection of inorganic ions with and without adsorption pre-treatment

Three types of feed solutions were used for NF operation: i) MF water, ii) MF water after GAC pre-treatment, and iii) MF water after Purolite resin pre-treatment. The overall inorganics rejection was inferred from the conductivity of NF permeate compared to that of MF water used for NF operation (Table 1). The conductivity of untreated feed solution was $976 \mu\text{S}/\text{cm}$ and after NF operation the permeate conductivity was reduced to $240 \mu\text{S}/\text{cm}$, which is a reasonably high 75% rejection. However, when the adsorption pre-treatments were applied to the feed solution the NF permeate conductivity declined further, with higher percentage rejections (80%, 87%). This is partly due to the adsorption of inorganic ions on the adsorbents, which is higher for the ion exchange resin, Purolite, compared to GAC. The reason for this was the higher number of surface electric charges in the former [3] and hence higher rejection for Purolite adsorbent.

Inorganic ions are rejected by charged membranes mainly by two mechanisms, namely, charge effect (electrostatic forces) and sieving effect (steric interactions) [34]. The negatively charged NF membrane rejected more divalent cations (Ca^{2+} , Mg^{2+}) and anions (SO_4^{2-}) than monovalent cations (Na^+ , K^+) and anions (Cl^- , NO_3^-) for both with and without

adsorption pre-treatments (Table 2). The rejection percentage was larger for the divalent cations than the monovalent cations due to higher charge on the divalent cations leading to greater electrostatic attraction to the negatively charged membrane [8,13,35]. Anions with the same charge as the membrane are repelled by the membrane and hence rejected more than the cations, and as in the case of cations, the higher charged anion, sulphate was rejected more than the monovalent chloride anion. However, to maintain electroneutrality on the permeate side some anions need to pass through the membrane and maintain Donnan equilibrium during the NF operation [34]. This is achieved by the monovalent anions (Cl^-) undergoing less repulsion by the negatively charged membrane and having less hydration energy which makes them easier for their transfer across the membrane [8,12,36,37]. Hydrated anions are larger in size than the un-hydrated ones and the water surrounding the anions need to be removed at least partially for their penetration through the membrane pores. Between the cations, Ca^{2+} and Mg^{2+} , there was not much difference in the rejection values, but between the anions, the difference was large, and it followed the order, $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. The highest rejection of SO_4^{2-} is due to its higher charge and highest hydration energy [38]. Chloride and NO_3^- have the same charge, but the former was rejected more, probably, because it has a higher hydration energy [38,39]. Adsorption pre-treatment slightly increased the rejection of the divalent cations and anion, SO_4^{2-} , but substantially reduced the rejection of NO_3^- .

Table 1. NF conductivity rejection behaviour with and without adsorption pre-treatment of MF water at 2 bar applied pressure

	MF-Untreated	MF-Purolite pre-treated	MF-GAC pre-treated
Initial/final conductivity of FS, $\mu\text{S}/\text{cm}$	976/1590	925/1650	910/1521
Final conductivity of permeate, $\mu\text{S}/\text{cm}$	240	121	178
% Conductivity rejection*	75.4	86.9	80.4
FS/Permeate volume, ml	2000/883	2500/1145	2500/1200
% FS volume conversion**	44.2	45.8	48
NF operation duration, h	16.5	17.4	16.3

*(1-permeate conductivity/initial feed conductivity) x 100, **permeate volume/initial feed volume x 100

Table 2. Inorganic ions rejected by NF with and without pre-treated MF feed solution

Cations						
	Ca ²⁺ mg/L	K ⁺ mg/L	Mg ²⁺ mg/L	Na ⁺ mg/L	FVF*	Sodium adsorption ratio (SAR)
MF water as NF feed	23.9	14.8	17.6	112		4.22
NF permeate	2.34	3.97	1.32	34.3		4.43
NF-treated feed	40.3	21.6	33.3	184	1.79	5.17
Rejection (%)	90	73	93	70		
GAC-treated water as NF feed	22.4	14.3	17.1	109		4.20
NF permeate	1.40	4.61	0.85	36.0		5.90
NF-treated feed	30.2	17.4	22.7	133	1.92	4.43
Rejection (%)	94	68	95	67		
Purolite-treated MF water as NF feed	23.7	15.5	18.5	116		4.32
NF permeate	0.67	2.45	0.35	18.5		4.54
NF-treated feed	41.5	24.6	31.6	188	1.85	5.33
Rejection (%)	97	84	98	84		

$$SAR = \frac{Na^+}{\sqrt{0.5*(Ca^{2+}+Mg^{2+})}}$$

where $\overline{Na^+}$, $\overline{Ca^{2+}}$, and $\overline{Mg^{2+}}$ concentrations are expressed as milliequivalents/L. *FVF: Initial volume of feed solution (FS)/Final volume of FS

Anions			
	Cl ⁻ mg/L	NO ₃ ⁻ mg/L	SO ₄ ²⁻ mg/L
MF water as NF feed	195	8.9	65.1
NF permeate	64	3.8	1.5
NF-treated feed	326	6.9	111
Rejection (%)	67	57	98
GAC-treated water as NF feed	192	9.3	62
NF Permeate	64	8.0	0.0
NF-treated feed	234	9.5	86
Rejection (%)	67	14	100
Purolite-treated MF water as NF feed	206	8.0	71
NF permeate	30	4.9	0.0
NF-treated feed	329	12	121
Rejection (%)	85	39	100

3.3. Irrigation quality of NF permeate water

Electrical conductivity, Na^+ concentration, sodium adsorption ratio (SAR), and Cl^- concentration are important water quality parameters affecting crop production if the permeate water is used for irrigating crops [7-9,40]. Water with high conductivity causes physiological drought (which makes plants unable to compete with ions in the soil solution and water, which affects the crop) [40]. The MF water had high conductivity value (Table 1) which is above the critical value of $650 \mu\text{S}/\text{cm}$ for very sensitive crops [8]. In contrast, the NF-treated water (permeate) with or without pre-treatment had values ($\leq 260 \mu\text{S}/\text{cm}$) much lower than this critical value. NF treatment without adsorption pre-treatment reduced the conductivity of MF water by 75%. Pre-treatments with GAC and Purolite marginally added to the overall performance with reductions of 80% and 87%, respectively.

Of the cations, only Na^+ is generally considered to reduce the quality of irrigation water. Excess Na^+ causes hazards to soils and crops. Continuous use of irrigation water with Na^+ concentration $> 69 \text{ mg}/\text{L}$ could be hazardous to crops including very-sensitive crops [41]. MF feed water had Na^+ concentration ($112 \text{ mg}/\text{L}$) higher than this critical concentration (Table 2). NF treatment reduced the Na^+ concentration to much lower values ($34.3 \text{ mg}/\text{L}$) or a 69% reduction. This reduced by 83% with Purolite pre-treatment. GAC did not give any further reduction.

In addition to Na^+ alone, Na^+ imbalance in irrigation water can have a substantial impact on crop production. When irrigation water has high Na^{2+} content relative to the Ca^{2+} and Mg^{2+} contents, water infiltration in soils decreases [40]. SAR is a measure of this imbalance and if its value is higher than 8 the water is considered unsuitable for sensitive crops [8]. The feed water had values (4.22) much below this value and therefore the quality of water was good even without NF (Table 2). The SAR values slightly increased after NF treatment because NF selectively allowed more monovalent ions (Na^+) to pass through the membrane than divalent ions (Ca, Mg). However, the values are still lower than the critical

value for sensitive crops. Gündoüdu et al. [9] also reported that NF caused unbalanced removal of Na, Ca, and Mg from a membrane bioreactor (MBR) effluent feed, increasing the SAR value of the NF permeate. Adsorption pre-treatment had no significant influence on SAR of NF-treated water.

Chloride is the major anion of concern in irrigation water. A Cl^- concentration above 175 mg/L is hazardous to Cl-very-sensitive crops and above 350 mg/L to moderately sensitive crops [8]. In this study, the Cl^- concentration in feed MF water (195 mg/L) can be hazardous to very sensitive crops if irrigation practice continues with the use of this water. By contrast, NF-treated water (64 mg/L - a 67% reduction of Cl concentration) is very safe with respect to even Cl-very-sensitive crops. Purolite pre-treatment followed by NF reduced the Cl concentration to 30 mg/L (or an 85% reduction). Gündoüdu et al. [9] reported that concentrations of Cl, and Na, electrical conductivity and SAR in NF 90 permeate obtained from treating industrial wastewater were similar to those of RO permeate, whereas the permeates from NF 270 and TR 60 had values for these parameters nearly 5-30 times higher than the RO permeate. This shows that NF treatment can sometimes be employed instead of the RO process to produce good quality water for irrigation, provided that a suitable NF membrane such as NF 90 is employed.

Of the four water quality parameters assessed, with the exception of SAR, all the other parameters (Na, Cl, conductivity) in the MF feed solution had concentrations higher than those considered hazardous to very sensitive/or sensitive crops. By contrast the concentrations of all four parameters in NF treated water were well below the hazard levels. Therefore, it would not be necessary to apply costly adsorption pre-treatment to remove these hazardous chemicals. However, these pre-treatments are necessary to remove organic contaminants as discussed later in the paper.

Though the MF water is suitable without any treatments for moderately sensitive and tolerant crops, its continuous use for a long period can cause adverse effects even on moderately sensitive crops, especially those cultivated in saline and sodic soils (high Na soils) which already amply supply these elements to crops. It is estimated that 23% and 37% of the cultivated soils in the world are saline and sodic, respectively [42].

Shanmuganathan et al. [8] reported that Na and Cl concentrations and SAR values of permeates from a biological treated sewage effluent using three NF membranes were much higher than those from a RO membrane. They suggested that a blend of 'NF permeate-RO permeate after NF pre-treatment (a two-stage system)' at a ratio of 50:50, made the water suitable for irrigation. A similar blending here, of MF water and NF treated water at appropriate ratios, can produce irrigation water suitable even for very sensitive crops. Such a blending will reduce the volume of MF water requiring treatment with NF, with reduced operation cost. The concentrations of Na⁺ and Cl⁻ and conductivity in the water produced at different blending ratios are presented in Table 3, along with the optimum ratios for the water to be suitable for irrigating any type of crop, regardless of their sensitivity to these chemicals, even in problem soils (sodic and saline soils). The results show that a 1:1 ratio of MF to NF water volumes is satisfactory to prevent Na⁺ and conductivity hazards and 4:1 is sufficient to prevent Cl⁻ hazard. Adsorption pre-treatment had no significant effect on the optimum ratios.

Table 3. Water quality parameter values obtained by blending different ratios of MF feed and NF permeate volumes. Water with values shaded in green are suitable for irrigation of all crops (including very sensitive ones – conductivity < 650 $\mu\text{S}/\text{cm}$; Na^+ < 69 mg/L; Cl^- < 175 mg/L)

No adsorption pre-treatment

	(MF:NF ratio)					
	9:1	8:2	7:3	6:4	5:5	4:6
Conductivity ($\mu\text{S}/\text{cm}$)	902	829	755	682	600	534
Na^+ (mg/L)	104	96	89	81	73	66
Cl^- (mg/L)	184	169	156	143	130	116

GAC pre-treatment

	(MF:NF ratio)					
	9:1	8:2	7:3	6:4	5:5	4:6
Conductivity ($\mu\text{S}/\text{cm}$)	896	816	737	657	569	497
Na^+ (mg/L)	104	97	89	82	74	66
Cl^- (mg/L)	184	169	156	143	130	116

Purolite pre-treatment

	(MF:NF ratio)					
	9:1	8:2	7:3	6:4	5:5	4:6
Conductivity ($\mu\text{S}/\text{cm}$)	891	805	720	635	542	463
Na^+ (mg/L)	103	93	84	75	65	56
Cl^- (mg/L)	179	162	146	129	113	96

3.4. Rejection of organics and membrane fouling with no adsorption pre-treatment

The MF feed water used for NF treatment mainly contained hydrophilic DOC (95%) with very small amounts of hydrophobic DOC (5%) (Table 4). Of the hydrophilic fractions, humics (34%) and LMW neutrals (40%) constituted the major fractions. The NF membrane was able to remove a high percentage of all DOC fractions, the removals being not widely

different, i.e. 64%-84% (Fig. 2). However, the amounts rejected were larger for humics, LMW and building blocks than for biopolymers and hydrophobics due to their higher concentrations in the original feed solution (Table 4). Although the percentages of the different fractions rejected were not much different, the mechanism of rejection is different. Humics, being negatively charged [29], were rejected by the negatively charged membrane by electrostatic repulsion, i.e. exclusion [35,43]. Consistent with this electrostatic repulsion, this fraction is the only one whose concentration increased in the feed solution after the NF-rejected solution entered the feed solution (Table 4). The concentration of this fraction in the feed solution after NF was more than double that of the initial feed solution concentration. Other researchers also have reported that negatively charged organic substances were mostly rejected by negatively charged NF membranes due to the electrostatic repulsion mechanism [35,43,44,45].

The smallest size building blocks and LMW fractions of DOC (< 500 Da) were also largely rejected by the membrane. However, the mechanism of rejection is considered to be mainly adsorption of the molecules of these fractions inside the membrane pores and valleys in the rough membrane surface [13,46,47] whose sizes are nearly the same as those of many molecules in these low molecular weight fractions. The adsorptive forces are probably hydrogen bonding of the membrane surface/water molecules attached to the membrane, and the hydrophilic LMW/building blocks molecules, in addition to π - π bonding and van-der-Waal forces. These fractions are not rejected by the membrane like the humics, because the retentate concentration did not increase after the NF operation (Table 4). Biopolymers were also adsorbed by the same forces, but the sites of adsorption are possibly on the membrane planer surface instead of inside the pores, due to their larger size (> 20,000 Da). The rejection of the hydrophobic DOC with a much smaller feed concentration is most likely due to hydrophobic adsorption interaction between the molecules in this fraction and the membrane which is the least hydrophilic/moderately hydrophobic [47]. As in the case of fractions other

than humics, this fraction's retentate concentration was also less than that of the original FS concentration, thus supporting the adsorption mechanism of rejection (Table 4).

During NF operation, the membrane undergoes fouling mainly due to deposition of organic compounds and colloidal substances, inorganics scales, and biofouling [32]. Membrane fouling decreases the lifespan of membrane and reduces the flux with time during the NF operation. In the current study the deposition of colloidal substances is negligible because the NF feed solution was pre-treated with microfiltration which is expected to have removed the colloidal particles. Biofouling was not possible because the NF operation lasted only a short time, thus preventing any microbes from growing on the membrane. However, the continuous deposition of organics on the membrane can promote biofouling in the long-term. Therefore, an investigation of organic fouling by DOC is important and this is studied here.

The foulant amount was determined using a mass balance calculation by subtracting the amount of DOC in the permeate and in the rejected solution from the DOC in the original feed solution. A similar calculation was used by Yangali-Quintanilla et al. [18] for assessing the degree of fouling of a NF membrane by DOC. Of the DOC fractions, humics produced the least membrane fouling (0.002 mg C/cm²), despite having one of the two fractions with the highest concentrations in the feed solution (Table 4). This is because this fraction was rejected back into the feed solution without adsorbing onto the membrane. The rejection of the other fractions occurred mainly by adsorption onto the membrane which caused membrane fouling [43,47]. The amount of fouling caused by these fractions is proportional to their respective feed solution concentrations: LMW neutrals (0.045 mg C/cm²) > building blocks (0.029 mg C/cm²) > biopolymers (0.013 mg C/cm²) > hydrophobics (0.005 mg C/cm²).

3.5 Rejection of organics, membrane fouling, and flux with pre-treatment

Pre-treatment with both adsorbents enhanced DOC removal by NF (Fig. 2). Total DOC removal by GAC adsorption + NF is the highest (86%), followed by Purolite adsorption + NF (81%) and then NF operation alone (72%). The highest percentage removal by GAC + NF is due to the complete removal of biopolymers and hydrophobics, and the highest percentage removal of LMW neutrals (Fig. 2). Though Purolite + NF almost completely removed the humics, the total percentage of DOC removed is less than that of GAC + NF. The enhanced rejection of all fractions when NF feed was pre-treated with the two adsorbents is due to adsorptive removal of a high percentage of these fractions by the adsorbents. It is interesting to observe that GAC and Purolite almost completely removed the hydrophobics and humics, respectively, even prior to the NF operation. Therefore, NF did not have to make any provision for the removal of these fractions. However, for the fractions which were not completely removed by these adsorbents, NF helped in additional removal. For example, NF removed a large percentage of humics after GAC adsorption, and building blocks of DOC after Purolite adsorption. The complete removal of humics by Purolite is due to electrostatic attraction forces between the negatively charged humics and positively charged Purolite. Complete removal of hydrophobics by GAC is due to hydrophobic interactive forces. These mechanisms and the relative amounts adsorbed by the two adsorbents are discussed in detail in our earlier reports [3,26].

The adsorption pre-treatments removed large amounts of all DOC fractions (approximately a total of 60%) (Fig. 2) causing the marked reduction in membrane fouling (0.000 - 0.007 mg C/cm² compared to 0.002 – 0.045 mg C/cm² without pre-treatment) (Table 4). GAC pre-treatment adsorbed all hydrophobics (Fig. 2) and therefore the fouling caused by this DOC fraction in this pre-treatment was zero (Table 4). On the other hand, Purolite pre-treatment adsorbed all humics of DOC resulting in zero fouling caused by this fraction. DOC is an organic precursor for subsequent biofouling which leads to a drop in permeate velocity, selectivity, and membrane service life. Further, biofouling increases cleaning frequency and

operation cost in terms of chemicals and electricity [24]. Reducing organic fouling by removing DOC through adsorption pre-treatment before the MF effluent passes to NF can minimise the intensity and frequency of these problems. The expected economic benefit derived from the anticipated reduction in biofouling would increase the membrane service life and for the most part would cover the cost of adsorption pre-treatment.

Consistent with the reduction of membrane fouling, the solution flux in the NF operation increased when adsorption pre-treatments were used (average flux (L/m².h), NF alone 7.9, Purolite + NF 9.7, GAC + NF 10.9) (Fig. 3). GAC produced a much greater increase in flux than Purolite which was due to less membrane fouling by DOC (Table 4). Flux declined over time because of the increase in membrane fouling [43,47,48].

The improvement of flux after pre-treatment was less significant after 15 hours (Fig. 3). The reason being that as time progressed the adsorbents became increasingly saturated with DOC and less efficient in further removal of DOC, thereby allowing more DOC to reach and deposit on the NF membrane and reduce flux. To alleviate this problem, the adsorbents can be rejuvenated and reused whenever this happens by desorbing the adsorbed DOC, and by backwashing the NF membrane [43]. Another method of sustaining a favourable pre-treatment effect and alleviate fouling is to use a larger quantity of adsorbents (deeper columns) so that DOC removal can occur effectively for a prolonged period.

Fig. 2. Removal of DOC fractions by (A) GAC and Purolite pre-treatments and (B) pre-treatments followed by (f.by) NF

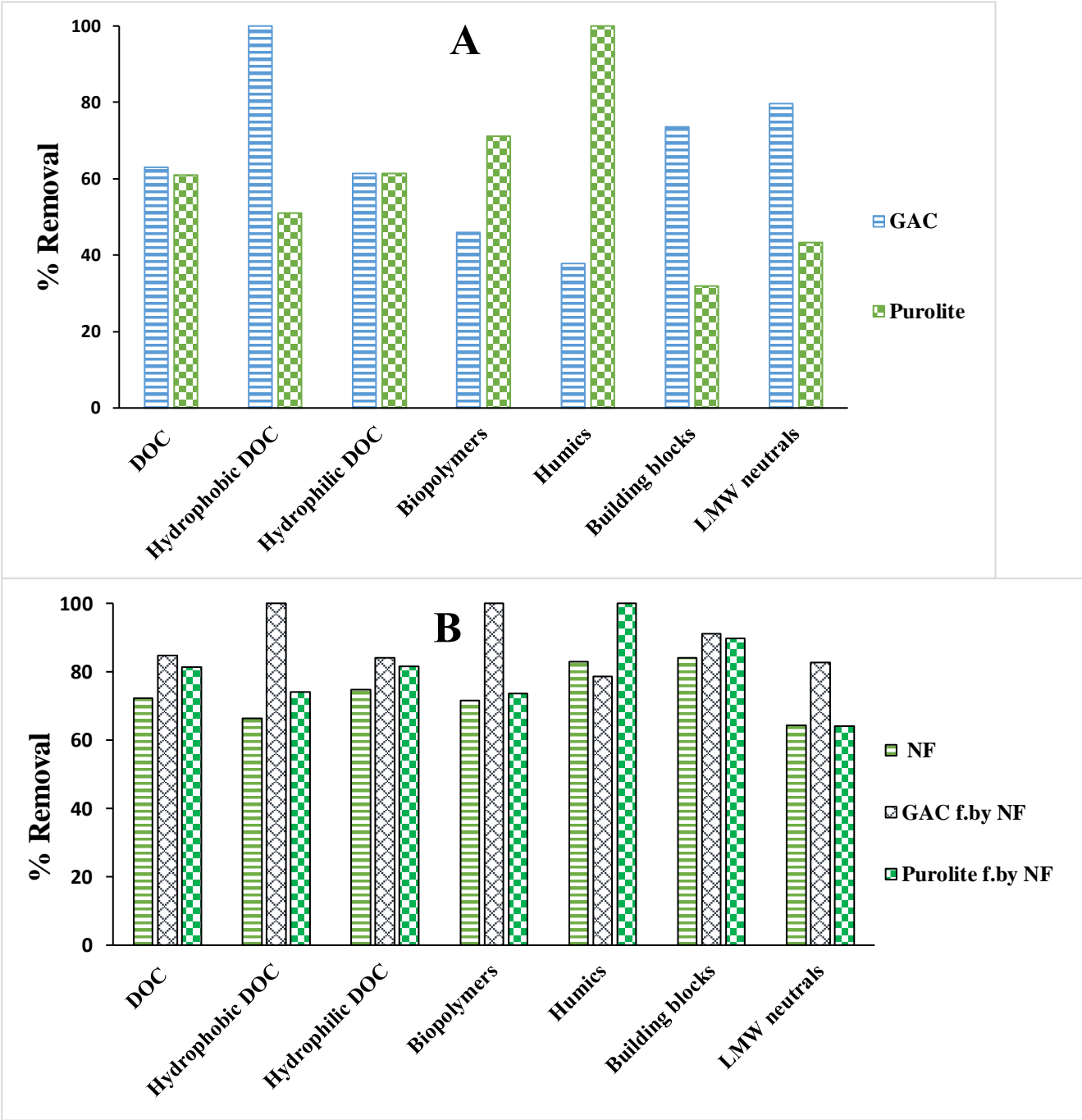


Table 4. Effect of NF with and without adsorption pre-treatment on membrane fouling**Without pre-treatment**

	DOC	Hydrophobic DOC	Hydrophilic DOC	Biopolymers	Humics	Building blocks	LMW neutrals
MF-wastewater (FS), $\mu\text{g C/L}$	7240	301	6939	597	2374	1178	2786
NF-permeate, $\mu\text{g C/L}$	2015	101	1755	170	405	187	993
FS after NF operation, $\mu\text{g C/L}$	8491	225	8266	256	5464	511	2300
Membrane fouling (mg C/cm^2)	0.096	0.005	0.093	0.013	0.002	0.029	0.045

Feed solution (FS) initial vol. 2.2 L; FS final vol. 0.85 L; Permeate 1.1 L; Effective membrane area 68 cm^2

$$\text{Fouling calculation} = \frac{(\text{Total DOC FS} - \text{Total DOC FS after NF operation} - \text{Total DOC Perm}^*)}{\text{Effective membrane area} \times 1000}$$

With GAC pre-treatment

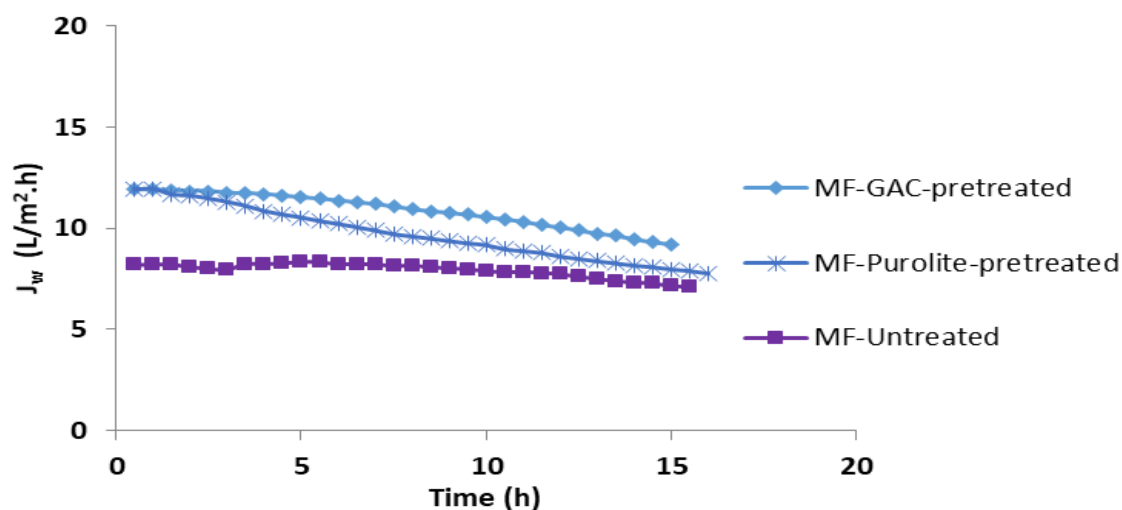
	DOC	Hydrophobic DOC	Hydrophilic DOC	Biopolymers	Humics	Building blocks	LMW neutrals
NF- permeate, $\mu\text{g C/L}$	1100	0	1100	0	510	105	483
FS after NF operation, $\mu\text{g C/L}$	3500	0	3500	301	2008	429	640
Membrane fouling (mg C/cm^2)	0.012	0.000	0.012	0.006	0.007	0.001	0.000

FS initial volume 2.5 L; FS final vol. 1.3 L; Permeate 1.2 L; Effective membrane area 68 cm^2

With Purolite pre-treatment

	DOC	Hydrophobic DOC	Hydrophilic DOC	Biopolymers	Humics	Building blocks	LMW neutrals
NF-permeate, $\mu\text{g C/L}$	1358	78	1280	158	0	122	998
FS after NF operation, $\mu\text{g C/L}$	4100	200	3900	20	0	1500	2175
Membrane fouling (mg C/cm^2)	0.014	0.001	0.014	0.003	0.000	0.003	0.006

FS initial volume 2.5 L; FS final volume 1.1 L; Permeate 1.145 L; Effective membrane area 68 cm^2

**Fig. 3.** Flux behaviour of NF membrane with and without adsorption pre-treatment of MF water

3.6. Organic micropollutants rejection

Of the 10 OMPs detected in the MF water, seven were >90% rejected by NF without any pre-treatment (Table 5, 6). This is a notable difference in the degree of rejection between OMPs and DOC fractions, the percentage of rejection of the latter was less than the former.

The four negatively charged OMPs in the MF water, diclofenac, gemfibrozil, ibuprofen, and naproxen, were >90% rejected by electrostatic repulsion from the negatively charged NF membrane, regardless of their molecular weights. Others also reported this mechanism of rejection of negatively charged OMPs by negatively charged NF membranes [44,49]. Diclofenac which has the highest molecular weight of all OMPs (296 g/mol, Table 5) in MF would also have been rejected by the size exclusion mechanism. Two other OMPs which were >90% rejected by NF were triclosan and trimethoprim having neutral charge. Their high rejection is possibly due to size exclusion because their molecular weights (290 g/mol) are much higher than the MWCO of NF 90 membrane (approximately 200). In addition, the highly hydrophobic triclosan (log Kow 4.76) might have adsorbed to the moderately hydrophobic membrane which helped in the rejection. Adsorption of OMPs on organic materials deposited from the feed solution on the membrane during the NF operation is also a possibility [50]. The other neutrally charged OMPs, saccharin and benzotriazole, with the lowest molecular weights of 183 and 119 g/mol (Table 5), did not have very high rejection (88% and 35% rejection, respectively) because some of them might have passed through the membrane pores. Diuron with a molecular weight of 233, which is within the range of the MWCO values of the membrane, also had a lower rejection rate of 77% probably because some of these molecules would have passed through the membrane's larger sized pores.

Purolite pre-treatment followed by NF rejected >90% of all the 10 OMPs (Table 6). The three OMPs which were rejected at relatively lower percentages by NF-only treatment

(benzotriazole, saccharin, and diuron) were 89%-99% removed by adsorption onto Purolite prior to NF treatment (Table 6). This would have helped the overall removal of these OMPs by NF after the pre-treatment. Pre-treatment with GAC also enhanced the rejection of benzotriazole, saccharin, and diuron by NF. This enhancement is due to the adsorption of these OMPs on GAC prior to NF operation.

Differences in the degree of adsorption by GAC and Purolite are observed for two OMPs, namely benzotriazole and diclofenac. GAC adsorption removed higher percentage of diclofenac (high logKow) than Purolite, but the opposite is the case with benzotriazole (low logKow) (Tables 5 and 6). This is due to GAC being hydrophobic having higher affinity to hydrophobic OMPs (high logKow) and Purolite being hydrophilic having higher affinity to hydrophilic MOPs (low logKow).

Table 5 Properties of OMPs and their concentrations after NF, GAC and Purolite (PU) treatments.

OMP*	Molecular weight (MW, g/mol)	Charge pH 7.4	Log Kow, pH 7	Log D ^a , pH 7.5	MF water (ng/L)**	After NF treat. (ng/L)	After GAC treat. (ng/L)	After PU treat. (ng/L)	After GAC f. by NF treat. (ng/L)***	After PU f. by NF treat. (ng/L)
Benzotriazole	119	0 ^a	1.44	-	2020	1310	500	26	117	20
Carbamazepine	236	0 ^{ab}	2.45 ^{de}	2.23	191	8	100	0	7	<4
Diclofenac	296	- ^{ab}	4.5-4 ^{ef}	1.48	54	<4	5	13	<4	<4
Diuron	233	0 ^a	3.49 ^a	2.7	70	16	4	4	<4	<4
Gemfibrozil	250	- ^{ab}	4.77 ^g	1.51	76	<4	7	6	<4	<4
Ibuprofen	206	- ^{ac}	3.5-4.5 ^{bef}	1.44	38	<4	14	15	<4	<4
Naproxen	230	- ^{bc}	3.2 ^{fh}	0.16	188	<4	<4	<4	<4	<4
Saccharin	183	0 ^a	0.91	0.45	131	16	<10	14	<10	<10
Triclosan	290	0	4.76	5.19	48	<4	13	11	<4	<4
Trimethoprim	290	0 ^{abd}	0.91 ^{ei}	1.1	136	<4	20	<4	<4	<4

*OMP- Organic micropollutant;

**Limit of quantification 4 ng/L for all OMPs except 10 ng/L for saccharin;

***f.by: followed by

^aCalculated with Advanced Chemistry Development (ACD/Labs) Software V9.04 for Solaris; ^bShanmuganathan et al. [2]; ^cHajibabania et al. [50]; ^dTernes and Joss [51]; ^eYang et al. [52]; ^fSerrano et al. [53]; ^gWesterhoff et al. [54]; ^hYangali-Quintanilla et al. [18]; ⁱU.S. National Library of Medicine (<http://chem.sis.nlm.nih.gov/chemidplus/rn/52-53-9>).

Table 6. Removal of OMPs as a percentage (%) of their concentrations in MF

OMP	By NF alone	By GAC alone	By Purolite alone	By GAC + NF	By Purolite + NF
Benzotriazole	35	75	99	94	99
Carbamazepine	96	48	>98	96	>98
Diclofenac	>93	91	76	>93	>93
Diuron	77	94	94	>94	>94
Gemfibrozil	>95	91	92	>95	>95
Ibuprofen	>90	63	61	>90	>90
Naproxen	>98	>98	>98	>98	>98
Saccharin	88	>92	89	>92	>92
Triclosan	>92	73	77	>92	>92
Trimethoprim	>97	85	>97	>97	>97

4. Conclusions

The NF membrane rejected more divalent cations (Ca^{2+} , Mg^{2+}) and anions (SO_4^{2-}) than monovalent cations (Na^+ , K^+) and anions (Cl^- , NO_3^-) whether GAC or Purolite adsorption pre-treatments were used or not. The NF treatment reduced Cl, Na, and electrical conductivity of the MF water and rendered the permeate water more suitable for irrigation of crops. However, SAR slightly increased because of the uneven rejections of Na, Ca, and Mg. Nevertheless, this increase in SAR is much below the level considered to cause serious damage to crops, if the permeate is used for irrigation.

Adsorption pre-treatment enhanced DOC removal by NF. Total DOC removal by GAC adsorption + NF is highest (86%), followed by Purolite adsorption + NF (81%) and then NF operation alone (72%). Highest percentage removal by GAC + NF is due to the complete removal of biopolymers and hydrophobics, and highest percentage removal of LMW neutrals. In contrast, Purolite + NF completely removed the humics. The enhanced rejection of all fractions when NF feed was pre-treated with an adsorbent is due to the removal of a high percentage of these fractions by the adsorbent.

Of the DOC fractions, humics produced the least membrane fouling, despite having one of the two fractions with the highest concentration in the feed solution. The amount of fouling caused by the other fractions is proportional to their respective feed solution concentrations: LMW neutrals > building blocks > biopolymers > hydrophobics. Adsorption pre-treatment greatly reduced fouling. Consistent with the reduction of membrane fouling, the solution flux in the NF operation increased when adsorption pre-treatments were used, with GAC producing a higher increase in flux than Purolite.

Of the 10 MOPs detected in the MF water, six were >90% rejected by NF without any pre-treatment. Conversely, Purolite and GAC pre-treatments rejected >90% of all the MOPs.

Overall, the study confirmed that adsorption pre-treatment using suitable adsorbents can greatly increase the NF rejection of salts, DOC and OMPs from wastewaters.

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SUPPLEMENTARY DATA

Enhanced nanofiltration rejection of inorganic and organic compounds from a wastewater-reclamation plant's micro-filtered water using adsorption pre-treatment

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Table S1. Chemical properties of micro-filtered water used in the study

Property	Measurement unit	Range
Conductivity	mS/cm	0.9-1.2
Dissolved organic carbon (DOC)	mg/L	4.5-6
Sodium adsorption ratio (SAR)	-	4.22-5.33
pH	-	6.5-7.5
Cl ⁻	mg/L	190-200
F ⁻	mg/L	1-1.5
NO ₃ ⁻	mg/L	8.9-9.3
PO ₄ ⁻³	mg/L	Nil
SO ₄ ⁻²	mg/L	62-71
Na ⁺	mg/L	109-112
K ⁺	mg/L	14-16
Mg ⁺²	mg/L	17-18
Ca ⁺²	mg/L	22-24

Table S2. The physico-chemical properties of Purolite and GAC

	Purolite A502PS*	GAC
Type and structure	Polystyrene cross-linked with divinylbenzene	Coal based (MDW/4050CB)
Functional group	R-(CH ₃) ₃ N ⁺	-
Ionic form (as shipped)	Cl ⁻	-
Exchange capacity (eq/L)	0.85	-
Moisture retention (%)	66-72	Maximum 2
Particle size (mm)	0.425 – 0.600	0.42-1.68
Surface area (m ² /g)	21	-
S _{BET} ** (m ² /g)	-	1000

* <https://www.purolite.com> > assessed 11 September 2019

** S_{BET}- Surface area (Brunauer, Emmet and Teller isotherm)