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Zhang, Jianhua, Weston, G, Yang, Xing, Gray, Stephen and Duke, Mikel (2020) Removal of herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) from saline industrial wastewater by reverse osmosis and nanofiltration. Desalination, 496. ISSN 0011-9164

Removal of herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) from saline industrial wastewater by reverse osmosis and nanofiltration

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Abstract

Conventional reverse osmosis (RO), a novel temperature-swing RO (TSRO), and tailored nanofiltration (NF), were investigated to target the removal of the chlorophenoxy broad-leaf herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) from saline (HCl-rich) wastewater at pH between 1-2. Batch concentration by RO at 17.5 bar using BW30 and SW30 membranes showed similar performance, where BW30 showed rejections of 95.3% for MCPA and 25.9% for acid, but initial flux of 13 L.m^{-2}.h^{-1} declined by 82% upon reaching 80% volume recovery. For the novel TSRO using BW30 and swing temperature of 40-45°C based on MCPA solubility tests, the significant flux decline was avoided while showing similar MCPA rejection, but with slightly higher acid rejection of 37%. Pilot scale NF using NF270 and NF90 membranes showed decreased rejections of both MCPA and acid. The NF270 showed rejections of 71.3% for MCPA and 16.8% for acid. But despite lower MCPA rejection~~ than RO (and NF90)~~, ~~was sufficiently high~~its high flux up to 80% volume recovery could be used with RO or other treatments to ~~potentially~~ meet MCPA discharge requirements~~ at high flux to 80% volume reduction~~. RO and NF are therefore suitable for MCPA removal from saline (HCl-rich) wastewaters, but novel temperature swing RO process offers potential to achieve higher MCPA rejection simultaneously to higher overall flux at practical volume recoveries.

Keywords: Reverse osmosis, nanofiltration, herbicide, industrial wastewater

1. Introduction

Herbicides are chemicals that are widely utilised for crop protection in agriculture, but in turn have resulted in the presence of their residues in various environments [1]. One of the popular types are chlorophenoxy herbicides, which are used widely for the control of broad-leaved weeds. Since 1970s, the potential for chlorophenoxy herbicides to cause certain forms of cancer in humans has come under increasing scrutiny [2]. Belonging to the chlorophenoxy compounds, 2-methyl-4-chlorophenoxyacetic acid (MCPA) is a brown powder and has been extensively employed in farmlands to control broad-leaf weeds since 1945 [3]. The structure and basic properties of MCPA are shown in **Figure 1** [4]-[5]. Although there is no clear evidence that MCPA is a carcinogen, ingestion of MCPA can result in serious and sometimes fatal sequelae [2, 6, 7]. MCPA may be associated with increased risk of non-Hodgkins lymphoma (NHL), Hodgkin’s disease (HD), leukemia, and soft-tissue sarcoma (STS) [7, 8]. In commercial applications MCPA is usually esterified with 2-ethylhexanol (or octanol) or neutralized with an amine. Generally, the amine form has a lower vapour pressure and thus presents less risk for drift contamination of non targeted crops. The ester form is more lipophilic and is better able to penetrate waxy leaf cuticles.

MCPA properties

- Chemical formula = $C_9H_9ClO_3$
- MW = 200.62 g.~~/~~mol^{-1}
- Solubility in water = 825 mg.~~/~~L^{-1} @ 23°C

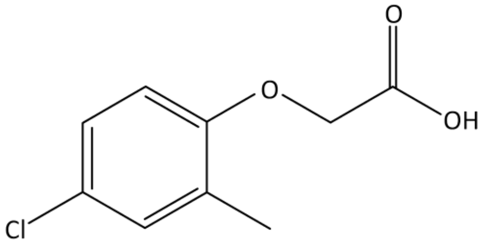

Figure 1: Molecular structure and basic properties of 2-methyl-4-chlorophenoxyacetic acid (MCPA) [4]

MCPA compounds in the environment will be in the acid form, as MCPA (acid or amine) dissociates in water. The solubility of MCPA in water is 825 mg.~~/~~L^{-1} at 25 °C [4, 9], and its octanol-water partition coefficient is low and pH dependent [10]. MCPA does not readily degrade in sterile buffer solution at pH 5 - 9 [11] and its biodegradation in anaerobic aquatic systems is negligible [12]. Meanwhile MCPA was shown to degrade in rice paddy water in the dark totally by aquatic microorganisms in 13 days [13]. Despite this, chlorophenols and chlorocresols could form by photolysis from MCPA degradation, which could cause unacceptable tastes in drinking-water [13, 14].

Attempts have also been made to treat wastewaters containing MCPA. For example, MCPA in ~~the~~ agricultural wastewater can be treated by constructed wetlands [15], which requires a large area. Quiñones, et al. found that ozonation could achieve 99% removal of MCPA in 30 min [16], in which the ozone concentration was 5 mg~~/~~.L^{-1} at the inlet. Adsorption by MgAl-layered double hydroxides and photochemical transformation were also tested effectively in treatment of MCPA [17, 18]. However, these conventional methods in combination with advanced oxidation and adsorption are not effective for removing herbicide residues, as they may also generate toxic by-products [1, 19-23].

Membrane processes working on the basis of size exclusion may also be considered. Since the majority of herbicide compounds have molecular weights greater than 200 Da and sizes in the range of ions (close to 1 nm), reverse osmosis (RO) and nanofiltration (NF) are the most appropriate pressure-driven membrane processes for pesticide removal from contaminated water sources. RO and NF have been widely used in water treatment and wastewater reclamation/reuse applications to achieve high removals of dissolved solids such as regulated organic and inorganic compounds [24-29]. Chian et al. found RO membranes could effectively remove pesticides, including chlorinated hydrocarbons, organophosphorous compounds, and miscellaneous pesticides in 1970s [30]. It was found that cross-linked polyethylenimine and cellulose acetate (CA) membranes showed high pesticide removals and resistance to acidity. NS-100 membrane (cross-linked polyethylenimine membrane) achieved 97.8% removal of atrazine, in comparison with 84.0% removal by CA membrane. In 1980s, nanofiltration (NF) membranes [31] and ultra-low pressure RO membranes (ULPRO) [32] were produced commercially. NF membranes are able to reject divalent and multivalent ions, and usually have relatively low rejection to sodium chloride. Furthermore, NF also has good rejection to uncharged dissolved organic compounds and high specific water fluxes, which could be an excellent choice for treatment of the pesticide-polluted waters [1]. ULPRO has been used at full scale for pesticide and other organic micro-pollutants rejection because of its low energy consumption and construction cost [32, 33].

Despite this progress, it has been demonstrated that neutral organics and organic acids with molecular weights much larger than the reported molecular weight cut-offs of the membrane could still permeate through the membrane [34]. MCPA removal from wastewaters using RO and NF has not been considered. More specifically, the removal of MCPA residuals in wastewaters associated with its production are yet to be explored. The manufacturing process for the ester involves heating the acid and alcohol to an elevated temperature with a catalyst, and under vacuum. Liquid ring vacuum pumps are typically used, and the liquid ring water can become contaminated with small but significant amounts of MCPA acid and ester. This is a waste stream that is difficult to dispose of by conventional means.

In this study, vacuum pump wastewater containing MCPA from Tri-Tech Chemical Co Pty Ltd, Australia was treated by NF and RO membranes. Since MCPA is an organic acid, it is necessary to verify whether the NF and RO membranes are able to remove it efficiently. Furthermore, the vacuum pump wastewater is low in pH (high HCl concentration) and high in total dissolved solid (TDS), and could cause serious membrane fouling at high water recovery. Therefore, the unique approach in this work to use NF and RO to remove MCPA from this real industrial wastewater must take into consideration the low pH and high TDS solution environment, and impacts to separation from cleaning. Since MCPA solubility is expected to be a function of temperature, an innovative temperature swing RO (TSRO) approach was also tested to minimise MCPA fouling of the RO membrane. More fundamental effects governing removal and membrane fouling such as species specific osmotic pressures, membrane charge/effective pore size and MCPA dissociation will also be considered as part of this novel investigation into RO and NF of the saline, low pH, MCPA-rich industrial wastewater.

2. Experimental

2.1 MCPA analysis method development

In order to rapidly and accurately analyse MCPA in industry samples containing other organics and within the low pH solution environment, an analytical method had to be developed. In this method, MCPA concentration in the feed was measured by a Hach® UV-Vis at the wavelength of 226 nm, which was determined to be the strongest peak during sample scanning. The HCl solution (pH = 1.88) was used as the blank sample and for all dilutions, which was similar to the pH of the actual feed water. An ~~’analysis~~ ‘analysis standard’ stock MCPA solution was prepared by dissolving MCPA (99.6%, Sigma®) into HCl solution (pH=1.88) that was maintained at 40°C using a water bath and shaking for 3 hours, before cooling to room temperature (20°C), and then filtering through a 0.45 µm filter to remove the solid residual. The MCPA concentration in the analysis standard stock solution was determined by ~~the~~ total organic carbon (TOC) measurement (Shimadzu, TOC V with TNM-1 unit), which can be converted into MCPA concentration by:

$$C_{mcpa} = \frac{TOC \times D \times M_{mcpa}}{N \times M_{carbon}} \qquad (1)$$

where C_{mcpa} is the MCPA concentration in the sample (mg.L^{-1}), *TOC* is the total organic carbon measured by the TOC machine ~~measured in~~(mg.L^{-1}~~,~~), D is the dilution factor (-), and M_{mcpa} and M_{carbon} are the molecular weights of MCPA (200.62 g.mol^{-1}) and carbon (12.0 g.mol^{-1}), and N is the number of carbon molecules in each MCPA molecule (9).

Four standard solutions were prepared by diluting the analysis standard stock solution by 10, 20, 40, or 50-fold with the HCl solution (pH=1.88), and the MCPA concentrations of the standards were determined by the TOC method. The concentration calibration curve was constructed, in which the concentration was plotted against the light absorbance at the wavelength of 226 nm (ABS@226nm). This lead to a linear correlation between light absorbance (au) and MCPA concentration (in mg-MCPA.L^{-1}) of 0.04261 au per mg-MCPA.L^{-1} with an r^2 of 0.9995. The industry samples were diluted 20-fold before the MCPA measurement by the UV-Vis method. The conductivity and pH of the feed and permeate were measured by a Hach® handhold meter (Q60).

2.2 MCPA solubility test

MCPA solubility is expected to be altered by temperature, so the solubility of MCPA in the low pH solution as a function of temperature needed to be determined to establish the separation process operation conditions for the novel TSRO concept process. Approximately 0.08 g MCPA was mixed with 50 mL acidified ~~DIW~~ DI water (HCl pH = 1.88) in a conical flask as a ‘solubility test’ stock solution, which was pre-dissolved in a shaking water bath at 45°C for 48 hours. The temperatures in the water bath were then varied to 35°C, 22°C, 8.3°C and 4.5°C by adding ice. Disposable syringes and 0.45 µm filters used for sampling and removing the undissolved solid were matched to be at the same temperature by immersion in the same water bath. The temperatures of the five total solubility test stock solutions were measured, and then 5 mL sample was withdrawn by the syringe and filtered directly into the 20 mL acidified DIW. The concentration of the MCPA was determined by the TOC method, which was converted to MCPA concentration by **Equation 1**.

2.3 Reverse osmosis (RO) and nanofiltration (NF) operation – bench scale test

The bench scale reverse osmosis (RO) and nanofiltration (NF) experimental setup is shown in **Figure 2**. The membrane module was a Sterlitech® Sepa CFII which was made of stainless steel and able to accommodate flat sheet membranes with active permeation area of 140 cm^2. In the experiments, RO membranes BW30 and SW30, and NF membrane NF270 from Dow Filmtec® were purchased and used to treat the vacuum pump wastewater from the industry site. All the membrane pieces were cut from Dow Filmtec® 2540 (2.5 inch) membrane elements. The operating conditions are shown in **Table 1.** Uniquely, the NF270 test was conducted at lower feed pressure due to its higher relative flux compared to RO.

The feed flowrate in all tests was set at 800 mL~~/~~.min^{-1} which resulted in a cross flow velocity of 0.2 m.~~/S~~s^{-1}. Permeate flux, *J* (L.m^{-2}.h^{-1}), was determined by calculating the weight change of the permeate measured by the balance over time, divided by the active permeation area. All new membranes were subjected to challenge testing with NaCl solution (0.1 wt%) for at least 2 h before the wastewater tests to check membrane integrity ~~check~~ and obtain a baseline for membrane flux. NaCl concentration of the feed and permeate was measured using electric conductivity.

Table 1: Summarised operation feed pressure and temperature conditions for bench tests on RO and NF membranes with 140cm^2 active permeation area. CW = clean water test with 1,000 mg.L^{-1}~~0.1wt%~~ NaCl solution, WW = waste water test, TS = temperature swing test (temperature of operation to be confirmed by experiments).

Parameter	Unit	Test						
		BW30			SW30		NF270	
		CW	WW	WW(TS)	CW	WW	CW	WW
Feed pressure	~~Bar~~bar (g)	17.5	17.5	16.7	17.5	17.5	5.0	5.0
Membrane temperature	°C	22-25	22-25	TBC	22-25	22-25	22	22
Feed flow rate	mL~~/~~.min^{-1}	800	800	800	800	800	800	800

~~In the challenge tests, o~~Only RO membrane samples that achieved a minimum ~~salt~~ EC rejection of 99% based on **Equation 2** during the integrity test were considered as intact membrane and used for the following tests. Wastewater testing was commenced on the verified new membranes. ~~The~~ Any suspended solid in the wastewater was removed by a 0.45 µm filter. 3 L of this pre-filtered wastewater was used in each test, and the overall volume recovery was set to 80% operating using batch concentration at a constant feed pressure. The MCPA concertation in the waste water feed was observed to vary from 100 mg.~~/~~L^{-1} to 500 mg.~~/~~L^{-1} depending on the sample taken from the site. Tests were repeated at least three times and found to vary within 10%.

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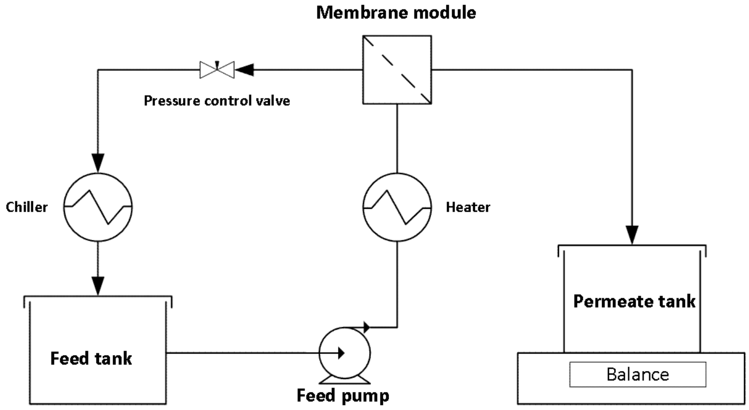

Figure 2. Schematic diagram of the experimental setup

The innovative ~~temperature swing RO (~~TSRO~~)~~ tests were conducted by activating the chiller and heater components as shown in **Figure 2** to alleviate the membrane fouling at high volume recovery by changing MCPA solubility in the wastewater prior and post the membrane module. The swinging temperatures were set from the MCPA solubility tests. The test conditions are shown in **Table 1**. The selection of swing temperatures will be determined by the low pH solubility temperature experiment.

2.4 Nanofiltration (NF) pilot plant operation

The NF pilot tests were conducted for NF270 membrane, but also on the tighter pore size NF90 type, using intact spiral wound Dow® 2540 elements (active area = 2.6 m^2). The setup was similar in operation to the schematic in **Figure 2**, but without facilities to heat and cool. Another difference was the technique to measure flux, which was determine from in-line flow meters connected to the feed and reject sides of the membrane (flux determined from the difference between these two flow rates). Before the tests, both membrane were tested with tap water (TOC ~~≈~~ $\sim$3 $mg.L^{-1}$, conductivity ~~≈~~ $\sim$80 $\mu S.cm^{-1}$) to set up the flux baseline for each membrane. The filtration feed pressures were set at 4.7 and 6.5 bar for NF270 and NF90 membranes respectively. In the pilot tests, wastewater of 200 litres was used as the feed, which was pre-filtrated by a microfiltration membrane (pore size = 0.1 µm) and circulated through the NF membranes with feed flow rates of 7.5 to 7.8 $L.min^{-1}$.The targeted total volume recovery by batch concentration at constant pressure operation for both membrane was set at 80%. For NF270 membrane, the filtration pressure was set to the same pressure as used in the tap water test. For the NF90 membrane, the filtration pressure was set to the same as used in the tap water test initially, but increased to 9.4 bar due to low permeate flow (0.3 L.min^{-1}). Tests were repeated at least three times and found to vary within 10%.

Following filtration, the NF270 membrane in the pilot test was cleaned and tested again to verify if the cleaning method was effective. The cleaning method involved a tap water rinse to flush out the residual on the feed side and then 1,000 mg.~~/~~L^{-1} NaOH solution was circulated for 3 h with the pressure regulating valve fully open.

2.5 Calculations from RO and NF testing results

Membrane rejection to the MCPA, EC or acid (as H$^+$) was calculated by:

$$R = \left(1 - \frac{C_p}{C_f}\right) \cancel{\times 100\%} \qquad (2)$$

where R is the rejection (expressed as %), and C_p and C_f are the concentrations of solute in the permeate and feed respectively.

The ~~water~~ volume recovery was calculated by:

$$V\cancel{W}_r = \frac{m_p}{m_f} \qquad (3)$$

where ~~Wr~~ Vr is the ~~water~~ volume recovery (expressed as %), m_f is the initial mass of the feed, and m_p is the accumulated mass of the permeate. The calculation assumes a liquid density of 1 kg.L^{-1}.

In order to determine the influence of osmotic pressure on total flux, a method adopted previously [35] was followed, which first estimates the osmotic pressure from the known concentrations of components in solution, then calculates the effective pressure drop across the membrane, then in turn the effective (pressure normalised) flux. First, the osmotic pressure, π (bar) of the solution for individual solutes was calculated by:

$$\pi = iMRT \qquad (4)$$

where *i* is the dimensionless van't Hoff factor of the solute, *M* is the molarity of the salt in solution (mol.L^{-1}), *R* is the university gas constant (0.08315 L.bar.mol^{-1} K^{-1}) and *T* is the system temperature (K). In this study the two components in solution are HCl and MCPA. Considering the relatively dilute solution, the van't Hoff factor for HCl was set to 2 assuming complete dissociation into H^{+} and Cl^{-}~~^{1}~~ expected for this mineral acid. Concentration of HCl (mol.L^{-1}) was therefore estimated to be equal to H^{+}, which was calculated from the standard pH relationship:

$$[H^{+}] = 10^{-pH} \tag{5}$$

For MCPA this is more complicated due to its dissociation as a function of pH, however considering the pH of the solutions was always much less (i.e. pH = 1.95 for the feed solution) than the reported pK_a range measured by prior researchers of 2.9 to 3.4 at room temperature [36, 37], it can be assumed MCPA is mostly (>90%) in molecular (undissociated) form ~~this was simplified in 'worst case' maximum osmotic pressure where MCPA fully dissociated in acid form~~ and thus the van't Hoff factor of 1~~2~~ was ~~also~~ used.

The determine the effective pressure, $p_{effective}$ (bar), of the system was then calculated by:

$$p_{effective} = p_{total} - \left(\pi_{tot,conc} - \pi_{tot,perm}\right) \tag{6}$$

Where p_{total} is the applied gauge pressure (bar) when operating at ambient permeate pressures, $\pi_{tot,conc}$ and $\pi_{tot,perm}$ is the sum of all component osmotic pressured determined by **Equation 4** for the final concentrate, and permeate, respectively.

Specific flux, J_S (L.m^{-2}.h^{-1}.bar^{-1}), which normalises the flux, *J*, produced from the RO and NF experiments according to both applied and osmotic pressures, can then be calculated according to:

$$J_S = \frac{J}{p_{effective}} \tag{7}$$

Final specific fluxes were calculated by **Equation 7**. However initial specific fluxes were also calculated simply by substituting $\pi_{tot,conc}$ with the total osmotic pressure calculated for the feed solution ($\pi_{tot,feed}$) in **Equation 6**.

3. Results and discussion

3.1. MCPA ~~measurements~~solubility in HCl as a function of temperature

The solubility of MCPA in acidified ~~DIW~~ DI water is shown in **Figure ~~4~~3**. It can be seen that when the temperature is lower than 20°C (solubility = 322 mg.L^{-1}) or higher than 33°C (solubility = 898 mg.L^{-1}), the solubility of MCPA ~~does not change very~~remains stable much with temperature at pH 1.88. However, changing the temperature from 20°C to 33°C leads to a more than doubling of the MCPA solubility in the acidified DI water~~W~~. With these results, the operating conditions for the temperature swing process concept were established in RO.

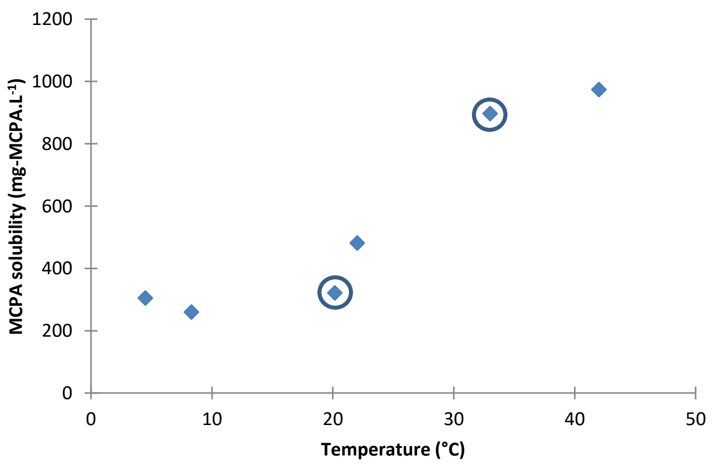

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Figure ~~4~~3: MCPA solubility ~~at different temperatures~~vs temperature at ~~(~~pH = 1.88~~)~~. The circled points indicate the solubility step change where the corresponding temperatures were used for the temperature swing process

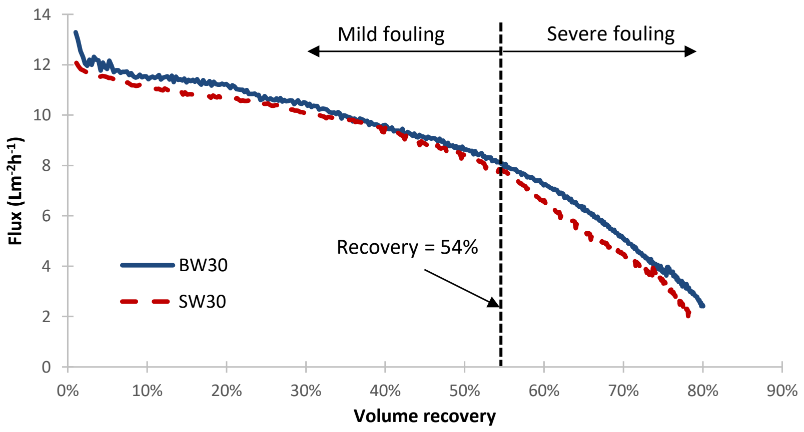
3.2. RO bench scale tests

3.2.1 Conventional RO using BW30 and SW30 for MCPA removal

Prior to feeding with wastewater to the separate BW30 and SW30 tests, the flux and rejection from clean water (0.1 wt% NaCl solution, pH 6.5) was carried out for 2 hours at 17.5 bar(g) feed pressure at room temperature of 22°C - 25°C to confirm membrane integrity. NaCl rejections based on electrical conductivity (EC) measurement were confirmed at >99% for both membranes, while BW30 and SW30 fluxes were stable (<10% change) and recorded at 57 L.m^{-}

[illegible] SW30 membrane is, because ~~SW30 has a~~ of the greater degree of cross-linking ~~and lower membrane permeability than BW30,~~ resulting in lower flux than BW30 under the same operation conditions [38].

Testing then commenced with RO of the industry water containing MCPA, with the flux results shown in **Figure ~~5~~4**. The membranes were assumed clean at low volume recovery (< 1%) of the MCPA wastewater tests, since the feed was pre-filtered and the MCPA was far from saturation in the circulated feed (Initial MCPA analysis result of 132 mg.L^{-1} shown in **Table 2**). In **Figure ~~5~~4**, it can be seen that the initial fluxes of the clean BW30 and SW30 membranes were 13.3 L·m^{-2}·h^{-1} and 12.0 L·m^{-2}·h^{-1}, respectively. The flux difference between both membranes was about 10%, which is less than the difference (30%) between membrane types in the NaCl ~~challenge~~ integrity tests. The reduced flux difference was proposed to be due to the increased domination of interaction between the solute and membrane due to the presence of more complicated solution (rich in MCPA and HCl) and membrane properties such as surface charge and energy (solute-membrane affinity) associated to other membrane systems [39-41]. The presence of MCPA (including in dissociated form) at low pH due to HCl therefore appears to have become dominating for membranes with similar salt rejection features, which would otherwise have quite different water permeabilities. Therefore analysis of the influences from MCPA and HCl will now be considered.



(b) ~~Wastewater tests (conductivity = 4.38 mS.cm^{-1}, pH = 1.95)~~

Figure ~~5~~4: Flux vs. volume recovery from conventional RO bench ~~membrane~~ test ~~s (pressure = 17.5 bar (g), temperature = 22-25°C)~~using BW30 and SW30 membranes on wastewater sample with initial EC = 11.4 mS.cm^{-1} and pH = 1.95. Operating pressure = 17.5 bar(g) and temperature = 22-25°C

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The measured feed and permeate properties are shown in **Table 2**. Both RO membranes showed similar rejection to ~~total dissolved solid (TDS, ≈60% estimated by the EC)~~EC (~60%), TOC (>93%) and MCPA (>95%). It can be seen that both membranes rejected H^+, ~~which led to~~indicated by a pH decrease on the feed/concentrate side (H^+/acid rejections of 25.9% and 20.6% for BW30 and SW30 respectively). Since high MCPA rejection (>95%) was achieved, it suggests the MCPA and MCPA ion (~~-~~$MCPA^-$~~-~~) were retained on the feed/concentrate side. At volume recovery of 80%, the MCPA concentration should have increased 5-fold to 658~~7.5~~ mg/L if it did not precipitate. However, the measured MCPA concentrations for both membranes shown in **Table 2** were only about 430 mg/L ~~-~~on the concentrate side (3.2-fold increase). It also can be found from **Table ~~2~~ 3** that the H^+ concentration increased about 2.8-fold based on the pH value~~ (calculated and shown in **Table 3**)~~. The dissociation of MCPA to $MCPA^-$ and H^+ is represented by:

$$\mathrm{MCPA} \rightleftarrows \mathrm{MCPA}^- + \mathrm{H}^+, \qquad (8)$$

The equilibrium ~~is~~ for acid dissociation is therefore represented by:

$$\mathrm{K}_{\cancel{\mathrm{d}}\mathrm{a}} = \frac{[\mathrm{MCPA}^-][\mathrm{H}^+]}{[\mathrm{MCPA}]} \qquad (9)$$

Or for the monoprotic MCPA:

$$\mathrm{pK_a} = \mathrm{pH} - \log\frac{[\mathrm{MCPA}^-]}{[\mathrm{MCPA}]} \qquad (10)$$

Formatted: Tab stops: 13.75 cm, Left where ~~K_d~~ K_a (or pK_a) is the acid dissociation constant. Using a reported value of pK_a of 3.13 at room temperature (22°C -26°C) [37], our pH is much lower than this value and thus MCPA is predominantly in molecular (undissociated) form. Therefore with increasing H^+ (declining pH) from RO concentration, more MCPA is forced into molecular form (**Equation 8**) which will lead to decreasing solubility at the given temperature. More specifically, using **Equation 10**, the ratio of $MCPA^-$ to MCPA at pH 1.95 of the feed is 6.6%. After concentrating the sample, at pH 1.5 this ratio decreases to 2.3%. ~~The concentration of MCPA should therefore increase by greater than 2.8 times, since the deprotonated MCPA ($MCPA^-$) concentration will not decline in the concentrate and the K_d should be constant at given temperature. Thus, the solubility of MCPA should decline.~~ It is also supported by the on-set of severe fouling occurring after the volume recovery of ~~0.54~~54% (see **Figure 4~~5b~~**), where the MCPA concentration is estimated to b~~y~~e 286 mg.L^{-1}, which is slightly lower than the measured solubility of 321 mg.L^{-1} at 20ºC and pH =1.88. Therefore, the H^+ rejection of RO membrane enhanced the fouling issues due to MCPA precipitation on the membrane surface.

Table 2: pH, EC and MCPA concentrations ~~Properties~~ of initial feed ('Feed 1') used in conventional RO bench test together with the ~~,~~ final collected permeate and concentrate ~~in RO testing~~at the end of the batch run shown in **Figure 4**. MCPA rejection calculated from **Equation 2** using initial feed and final permeate values. Operating feed pressure = 17.5 bar (g) and temperature = 22-25°C.

Sample		pH	EC (mS.cm^{-1})	MCPA (mg.L^{-1})	MCPA Rejection (%)
Feed 1		1.95	11.4	132	
BW30	Permeate	2.08	4.38	6.2	95.3
	Concentrate	1.50	38.9	428	

SW30	Permeate	2.05	4.58	5.9	95.5
	Concentrate	1.49	37.0	426	

The RO membrane flux decline during filtration shown in **Figure** ~~5b~~ 4 can be caused by an osmotic pressure increase (as the concentration increases in the circulated feed as shown in **Table 2**) and by membrane fouling. Theoretically, membrane fouling would cause a faster flux decline than the concentration induced (rising osmotic pressure) flux decline alone [28, 39], as fouling occurs in the presence of concentration increase. In order to estimate the significance of concentration induced flux decline (rise in osmotic pressure difference between the concentrate and permeate), the pH and MCPA concentration values for the tests reported in **Table 2** were used to quantify the osmotic pressures and effective pressures as shown in **Table 3**.

Table 3: Calculated HCl concentration (**Equation 5**), and ~~O~~osmotic pressure (**Equation 4**) ~~calculations~~ for HCl, MCPA and total for initial feed ('Feed 1') and final permeate and concentrates from RO tests ~~based~~ using~~on~~ pH and MCPA concentration data presented in **Table 2**. Effective pressure calculated from **Equation 6**. Operating ~~F~~feed pressure = 17.5 bar~~-~~(g) and temperature = 22-25°C used for osmotic and effective pressure calculations.

Sample		[HCl]	π HCl (bar)	π MCPA (bar)	π_{tot} (bar)	$p_{effective}$ (bar)
Feed 1		0.011	0.55	0.016~~3~~	0.57~~8~~	-
BW30	Permeate	0.0083	0.41	0.00~~2~~1	0.41	16.3
	Concentrate	0.032	1.55~~60~~	0.052~~10~~	1.6~~7~~0	
SW30	Permeate	0.0089	0.44	0.001	0.44	16.3~~2~~
	Concentrate	0.032	1.59~~60~~	0.052~~10~~	1.70	

The osmotic pressure of the feed solution was calculated to be 0.5~~8~~7 bar which is only 3.2~~3~~% of the applied pressure of 17.5 bar(g), with HCl playing the most significant role~~, even in assuming worst case maximum osmotic pressure of fully dissociated MCPA (van't Hoff factor in **Equation 4** is equal to 2)~~. After reaching 80% volume recovery, the effective pressure drop of 16.3 bar was only 7% lower than the total applied pressure drop for both BW30 and SW30 tests. This suggests that flux is not significantly influenced by bulk solution osmotic pressure difference due to concentrating HCl and MCPA, even at 80% volume recovery. However from **Figure ~~5b~~4**, it can be found the fast flux decline commenced at about 54% volume recovery for both membranes, where the fluxes of BW30 and SW30 were 8.2 $L \cdot m^{-2} \cdot h^{-1}$ and 7.7 $L \cdot m^{-2} \cdot h^{-1}$. Therefore, for volume recovery up to 54%, dominant flux decline mechanism is due to mild fouling, potentially due to operation below MCPA solubility as discussed earlier. After 54% volume recovery, the fouling was more severe due to this finding where MCPA is more likely to precipitate. In comparing BW30 to SW30, it can be found that the flux difference between both membranes reduced by 10% at volume recovery of 1%, to a 6% difference at volume recovery of 54% as the feed concentration increases in **Figure ~~5b~~4**. Hence, mild fouling had more influence on the flux of BW30 than that of the SW30. However, as the volume recovery increased beyond 54% where fouling significantly increased, the flux difference between BW30 and SW30 were enlarged from 6% at volume recovery of 54%, to a 45%

difference at the water recovery of 80%, where the fluxes of BW30 and SW30 membrane are 3.1 $L \cdot m^{-2} \cdot h^{-1}$ and 2.1 $L \cdot m^{-2} \cdot h^{-1}$, respectively. If considering the recommended application of BW30 membrane for brackish/wastewater treatment and SW30 membrane for seawater desalination, the phenomena can be explained. The brackish water and wastewater are normally higher in hardness/fouling potential and lower in salinity, in comparison with seawater [42, 43]. Therefore, there is relative less flux stability requirement for BW30 with increasing salinity than that of SW30. Thus, in **Figure ~~5b~~4**, BW30 has a faster flux decline than that of SW30 in the mild fouling area. However, in the severe fouling area (**Figure ~~5b~~4**), the BW30 showed a better performance than that of SW30, which may relate to its development for use in low salinity/high organics applications.

The proposed rejection of H^+ could be further supported by the operation below the isoelectric point (IEP) of the membrane. Typical IEPs for BW30 and SW30 membrane lie between pH 4 and 5 [44, 45]. Thus operating below the IEP as in our case would lead to a positive surface charge. This would facilitate attraction and diffusion of larger negatively charged Cl^- ions, while restrict diffusion of the smaller, yet positively charged, H^+ counter ions. By hindering only the smaller ion, this led to relatively low overall HCl rejection as observed by EC rejections lower than the typical >99% NaCl rejections of these membranes observed earlier during benchmarking at pH 6.5. However, due to the strong positive charge, there may be enhanced concentration polarisation of H^+ that would enhance the osmotic pressure difference observed at the membrane surface and also enhance the MCPA fouling by the mechanism proposed above. This may be due simply to flux induced polarisation, but also more severely by fouling induced polarisation, which could relate to the major differences in fouling rates observed after 54% volume recovery as a result of MCPA.

In the tests, SW30 and BW30 showed similar performance for MCPA removal under the same conditions, but SW30 was inclined to be slightly more fouled at high volume recovery. Therefore, BW30 was selected for the temperature swing tests.

3.2.2 Temperature swing RO (TSRO) with BW30 at bench scale for MCPA removal and reduced fouling

The TSRO test results of flux graphed with time is shown together with volume recovery in **Figure ~~6~~5**. The RO feed was heated to about 40 - 45°C before entering the module, and the returned concentrate was cooled down to 22 - 24°C in the feed container following **Figure 2**. The feed was topped up twice during the test as marked on the figure with 2.0 L ~~and~~ then 1.5 L. It can be seen from **Figure ~~6~~ 5** that flux decline occurred with increasing recovery. Furthermore, it also can be seen from the results that when recovery twice returned to previous values as a result of top up dilution, the fluxes at those recoveries were similar. For example, the first time volume recovery reached ~~0.30~~30%, flux was 15 L·m^{-2}·h^{-1}. When it returned to ~~0.30~~30% after the first top up, flux was 12 L·m^{-2}·h^{-1}. Also, when volume recovery was ~~0.50~~50%, flux was 12 L·m^{-2}·h^{-1} before any top up, 12 L·m^{-2}·h^{-1} after the first top up and 12 L·m^{-2}·h^{-1} after the second top up. This is strong evidence that performance ~~wasn't~~ was not lost over the test time as a result of significant irreversible fouling.

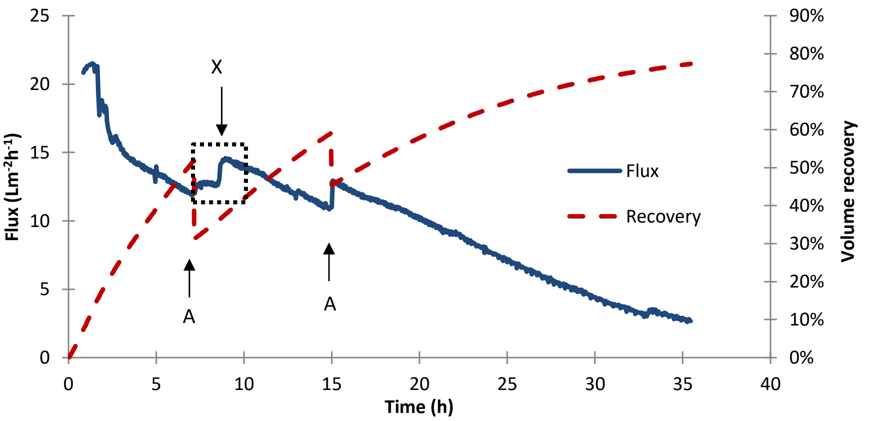

Figure ~~6~~5: Flux and volume recovery vs. time from TSRO bench test using ~~for~~ BW30 membrane on wastewater sample with ~~-~~initial EC = 11.3 mS.cm^{-1} and pH = 1.95. Operating ~~(~~pressure =16.7 bar(g). ~~, t~~Temperature of solution in ~~in the~~ feed/concentrate container = 22 - 24ºC and in ~~, temperature of~~ feed entering RO ~~flowing into the~~ module = 40 -45ºC). Events marked with 'A' represent top ups, and with 'X' represents starting heating to set temperature conditions.

Commented [MD3]: Updated figure

Table 4 shows the MCPA concentration, pH and EC together with separation performance of BW30 membrane during the ~~temperature swing~~TS–RO experiments. Compared to the performance of conventional RO (no temperature swing) in **Table 2**, the TSRO performance of the BW30 membrane only varied slightly. The similarity to conventional room temperature

RO MCPA rejection (**Table 2**) is consistent with literature finding little effect to rejection in the range of 20ºC to 40ºC for antibiotic compounds amoxicillin (365.4 g.mol^{-1}) and ampicillin (349.4 g.mol^{-1}) tested down to pH = 3, where RO provides high rejections to non-ionised organics with molecular weight range of 200-400 g.mol^{-1} [46]~~.~~. Therefore, it is possible to alleviate the MCPA caused membrane fouling by operation in TSRO mode. However, from **Figure ~~6~~5**, it can be found that the membrane flux overall was higher than the conventional ~~constant~~ room temperature ~~conventional~~ RO, but still declined by about 88% from 21.3 Lm^{-2}h^{-1} to 2.6 Lm^{-2}h^{-1} when reaching ~~0.80 water~~80% volume recovery. Despite the calculated bulk solution osmotic pressure difference being too low to be the reason for flux decline at the final recoveries, the increased concentration of MCPA and H$^+$ at the membrane surface appears to be limiting flux (~~HCl~~ H$^+$ rejection calculated to be 36.9%). Thus, it would be preferred if the membrane is able to retain just the MCPA, but allows salts (HCl) to pass through. This is potentially achieved by NF membrane, which will be shown in the next section.

Table 4: pH, EC and MCPA concentrations of initial feed ('Feed 1') used in TSRO bench test using ~~Performance of~~ BW30 membrane together with the final collected permeate and concentrate at the end of the batch run shown in **Figure 5**. Total osmotic pressure calculated from addition of HCl and MCPA osmotic pressures using **Equation 4**, effective pressure using **Equation 6** and MCPA rejection using **Equation 2**. Operating feed pressure ~~when operating in TSRO mode. Applied pressure for effective pressure calculation~~ = 16.7 bar(g) and ~~. T~~temperature ~~for osmotic pressure calculations~~ = 45ºC (used for effective feed and osmotic pressure calculations).

Sample	pH	EC (mS.cm^{-1})	MCPA (mg.L^{-1})	π_{tot} (bar)	$p_{effective}$ (bar)	MCPA Rejection
Feed 1	1.95	11.3	134	0.61~~3~~		94.8%
Permeate	2.15	6.3	7.1	0.38	15.5~~4~~	
Concentrate	1.54	35.8	419	1.6		

3.2.3. NF bench scale test using NF270 membranes to reject MCPA and pass HCl

Integrity testing with clean 1,000 mg.L^{-1} NaCl solution gave ~~Table 5 shows the b~~benchmark salt rejection during NF bench scale testing at 5.0 bar using the NF270 membrane to 80% volume recovery ~~using NaCl in DI water~~. Based on EC of feed and permeate, it can be found that only 15% salt was rejected at water recovery of 80% by the NF270 membrane, based on the electrical conductivities of solutions measured in the permeate and feed sides.

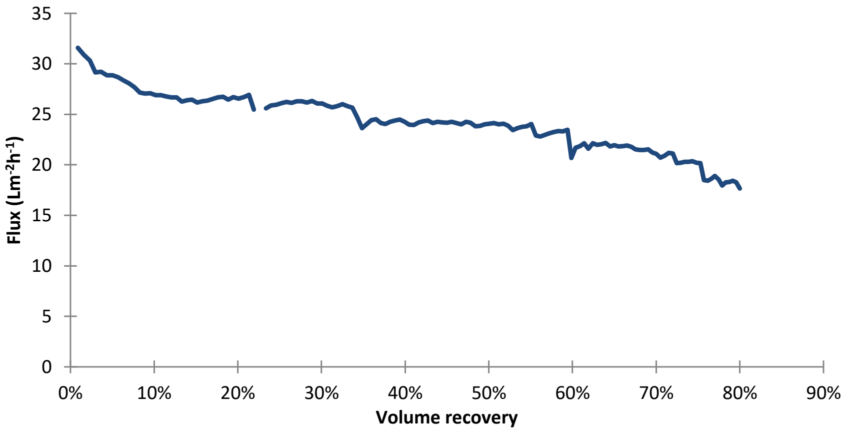

Figure ~~7~~6. Flux vs volume recovery from conventional NF bench test ~~Flux vs water recovery~~ using ~~in~~ NF270 ~~test~~ membrane on wastewater sample with initial EC = 37.1 mS.cm^{-1} and pH = 1.24. Operating feed pressure~~(pressure~~ = 5.0 bar(g) and ~~,~~ temperature = 22°C.~~)~~

Commented [MD4]: Updated figure

The properties of the feed and permeate are listed in **Table 5~~6~~**. It can be found that the MCPA concentration in the received feed sample was 3.4-fold greater than the feed samples used for the RO tests and would have been a more challenging wastewater to treat. ~~With~~ After concentration to ~~0.80~~80% ~~water~~ volume recovery, the permeate pH was 1.28 which increased only 0.04 pH units compared with the feed pH, which is less than the permeate pH increase of 0.1 - 0.2 pH units when the RO membranes were used. Therefore, the MCPA solubility on the feed side (concentrate side) in NF process would theoretically decline less than that of the RO process at the same volume recovery. However, the MCPA rejection also declined from around 95% in RO tests to 61.3% in the NF270 membrane test. The osmotic pressure in the case of the

NF270 showed little difference between the feed and the permeate, due to the passage of HCl through the membrane (H^+/acid rejection 8.8%).

A prior on the rejection of perfluorochemicals by a range of NF membranes including NF270 found decreasing pH of 5-6 to 2.8 led to the 90% rejection cut-off occurring below 300 g.mol^{-1} being raised to 500 g.mol^{-1}. Rejections of the perfluorochemicals with MW as low as 263 g.mol^{-1} were around 70% [47]. This correlates with our findings with lower pH of 1.28 and MCPA with MW of 200.62 g.mol^{-1}, where MCPA rejection was 61.3%. The isoelectric point of NF270 membrane is at pH 5.2 [48], becoming increasingly positive in charge with declining pH to 4. This suggests the membranes in our work tested to pH as low as 1 would have a positive charge, similar to the RO membranes as discussed earlier. Uniquely for NF270 over the other reported supplier membranes, the skin layer exposed to the solution is made of polyamide material that have dissociable carboxylic and amine groups giving it the ability to have a positive or negative charge depending on the pH. They concluded that at acidic pH, the membrane has weaker charge and ions can pass the membrane whereas uncharged organics like glucose are retained due to their size which correlates to our observed findings of H+ vs. MCPA rejections when operating in strong acid conditions.

In considering more fundamental mechanisms that governed organics separation in NF, another study using a NF270 membrane for trace organic compound removal at pH 8 found lower rejections for neutral and positively charged organics compared to negatively charged organics [49]. At their higher pH, the membrane was negatively charged since it was above the IEP of pH 5.2. The higher rejection behaviour (>80%) of the negative charged organics was therefore correlated to electrostatic repulsion between them and the membrane surface, while positively charged and neutral organics which lower rejections (<80%) were based on size exclusion. For example simazine, the hydrophilic neutral organic with MW of 201.7 g.mol^{-1} similar to MCPA, showed similar rejection of 70-80% in their tests, while some hydrophobic neutral organics with higher MW showed even lower rejections. Their proposed theories correlated with our findings, where MCPA at our operation pH should be mostly in molecular (unionised) form as discussed earlier and is therefore likely to follow the less rejecting size exclusion mechanism. Even the small proportion of negatively charged dissociated MCPA would be attracted to the positively charged membrane and follow the same size exclusion rejection mechanism.

Table ~~6~~5: pH, EC and MCPA concentrations ~~Properties of the feed and permeate~~of initial feed ('Feed 2') used in conventional NF bench test using NF270 membrane together with the final collected permeate at the end of the batch run shown in **Figure 6**. Total osmotic pressure calculated from addition of HCl and MCPA osmotic pressures using Equation 4 and MCPA rejection using **Equation 2**. Operating feed pressure = 5.0 bar (g) and temperature = 22°C (used in osmotic pressure calculations).

Sample	pH	EC ($mS.cm^{-1}$)	MCPA ($mg.L^{-1}$)	π_{tot} (bar)	MCPA Rejection (%)
Feed 2	1.24	37.1	439	2.9	61.3
Permeate	1.28	28	170	2.6	

3.2.4 NF pilot scale using NF270 and NF90 membranes to reject MCPA and pass HCl

The bench testing was then scaled up to pilot testing. Prior to introducing the wastewater to the NF pilot for the separate tests on NF270 and NF90 membranes, clean water (tap water) was used to measure reference clean water flux. Feed pressure and operating temperature of NF270 membrane was 4.6 bar(g) and 18°C respectively, while feed pressure and operating temperature of NF90 membrane was 6.5 bar(g) and 20°C respectively. Stable water fluxes of around 35 $L.m^{-2}.h^{-1}$ were observed for both membranes over the 70 minutes of operation. Waste water was introduced after clean water flux testing.

Figure ~~9~~ 7 shows the flux results during pilot NF operation on the MCPA industry wastewater. The sudden drop at the very beginning of the run was due to displacement of tap water with the industry wastewater within the rig to a volume recovery of about ~~0.02~~2%. From then, the fluxes changed with time and volume recovery for the MCPA industry wastewater. It took 2.9 hours for the NF270 to reach the target ~~0.80~~80% volume recovery, while it took 6.3 hours for NF90 to reach only ~~0.65~~ 65% volume reco~~reco~~very, so ~~were~~ the test was aborted due to low flux.

It can be seen that the at volume recovery of 2%, the initial stable flux of NF270 membrane was 25 $L.m^{-2}.h^{-1}$, while the NF90 membrane showed a lower flux of 9.2 $L.m^{-2}.h^{-1}$ despite operating at higher pressures. The increase in pressure for the NF90 run at 16% volume recovery to 9.4 bar only slightly increased flux to 12 $L.m^{-2}.h^{-1}$, but was actioned to improve the production of the membrane. Meanwhile, the flux of NF270 declined to about 14 $L.m^{-2}.h^{-1}$ at 80% volume recovery. This correlated to the flux decline in the benchtop test which operated similarly, but with ~~at around~~about 10% higher pressure.

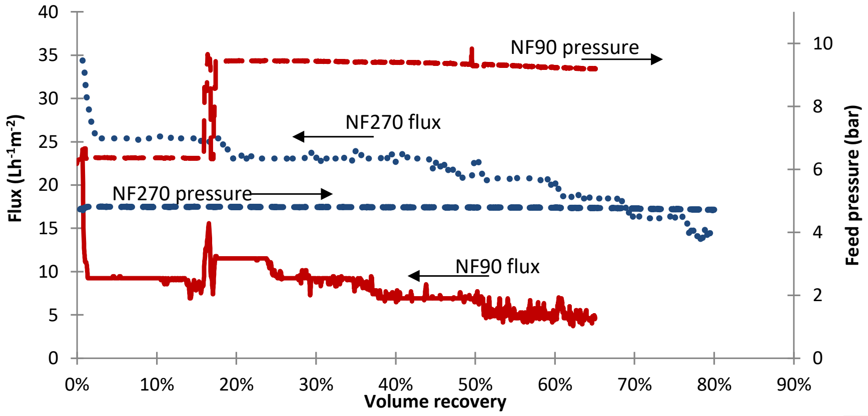

Figure ~~9~~7: Flux and feed pressure vs volume recovery from conventional NF pilot test using ~~Industry wastewater NF test flux of~~ NF90 and NF270 membrane on wastewater sample with initial EC = 26.6 mS.cm^{-1} and pH = 1.11. Operating ~~vs water recovery and time (~~temperature both tests = 20°C.~~)~~

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The analytical results of the feed and permeate are shown in **Table** ~~7~~6. Compared with the feed EC, the concentrate EC increased only by 6.7% using NF270 membrane at 80% volume recovery, and the concentrate EC using the NF90 membrane increased 20.7% at volume recovery of 65%. Therefore, the volume recovery will have more influence on the NF90 flux than that of NF270, due to the greater osmotic pressure increase on the concentrate side of the NF90 membrane. This is correlated to H^+ (acid) rejection, which was 16.8% for the NF270 and

25.9% for the NF90 membranes. The calculated effective pressure for NF90 was 43% lower than the total applied pressure, thus supporting this claim that NF90 operation was more significantly influenced by concentration than NF270 (effective pressure only 6% lower than total applied pressure). Furthermore, the pH on the concentrate side of the NF90 membrane reduced more than that of NF270, which will lead to MCPA precipitating at lower volume recovery when compared to filtration with NF270 membrane based on **Equation 9**. However, the rejection of NF90 membrane to MCPA based on Equation 2 was 94%, which is higher than that (71%) for NF270 membrane in the pilot test and similar to the RO membrane performance in the benchtop tests. The performance difference of NF270 membrane between the benchtop test and the pilot test was due to the MCPA concentration difference in the feeds.

Table ~~7~~6: pH, EC and MCPA concentrations ~~Analytical results of the concentrate, feed and permeate. Total applied pressure and recovery achieved as shown in **Figure 9**. Total pressure of 9.4 bar(g) used to calculated effective pressure for NF90.~~of initial feed ('Feed 3') used in conventional NF pilot test using NF270 and NF90 membranes together with the final collected permeate and concentrate at the end of the batch run shown in **Figure 7**. Total osmotic pressure calculated from addition of HCl and MCPA osmotic pressures using **Equation 4**, effective pressure using **Equation 6** and MCPA rejection using **Equation 2**. Operating feed pressure = 4.7 bar(g) for NF270 and 9.4 bar(g) for NF90, and temperature both tests = 20ºC (used for effective feed and osmotic pressure calculations).

Sample		pH	EC ($mS.cm^{-1}$)	MCPA ($mg.L^{-1}$)	π_{tot} (bar)	$p_{effective}$ (bar)	MCPA Rejection
Feed 3		1.11	26.6	165	3.8	-	
NF270	permeate	1.19	25.6	47.3	3.2	4.4~~5~~	
	concentrate	1.16	28.5	473	3.4~~5~~		71.3%
NF90	permeate	1.24	21.3	11.3	2.8	5.7~~8~~	
	concentrate	0.89	32.1	447	6.3~~4~~		93.2%

The flux comparison of a new NF270 membrane and the used membrane post cleaning is shown in **Figure ~~10~~8**. It can be found that after the cleaning, the flux of NF270 was fully recovered. The analytical results from the post-clean test are shown in **Table ~~8~~7**. When compared with the results in **Table ~~7~~6**, no obvious variation was found. The pH change between feed and permeate was less significant, correlating to 0.0% rejection of H^+ (acid). The cleaning test has shown that treatment to 80% volume recovery in batch mode doesn't benefit from a cleaning routine within the time frame of operation (order of hours) in the present study. This could be translated to single pass continuous operation to 80% recovery, where membrane permeability (or in a continuous setup with constant flux which shows pressure rise over time due to gradual fouling) would be important to monitor in further longer term studies that is needed to determine plant clean-in-place strategy.

However prior studies indicate degradation in the MCPA rejection over years of operation with cleaning could be expected, reporting decrease in organics rejection when new (unfouled) NF270 membranes were exposed to pH 11 and 12 solutions of NaOH for the accumulated equivalent of 3 years of NF operation with cleaning [49]. The lost performance was attributed to altered membrane properties responsible for membrane rejection, and uniquely to organics governed by size exclusion as was concluded for MCPA in our present work. Despite this, our one-off cleaning event of [49]circulating 1,000 mg.L^{-1} NaOH solution (pH = 12.4) for 3 hours showed no impact to flux or MCPA rejection. Further, the impact of NaOH cleaning solution to alter membrane properties could be mitigated by the presence of the fouling layer. Operation of a plant for several years with cleaning would be needed to confirm long term MCPA rejection degradation.

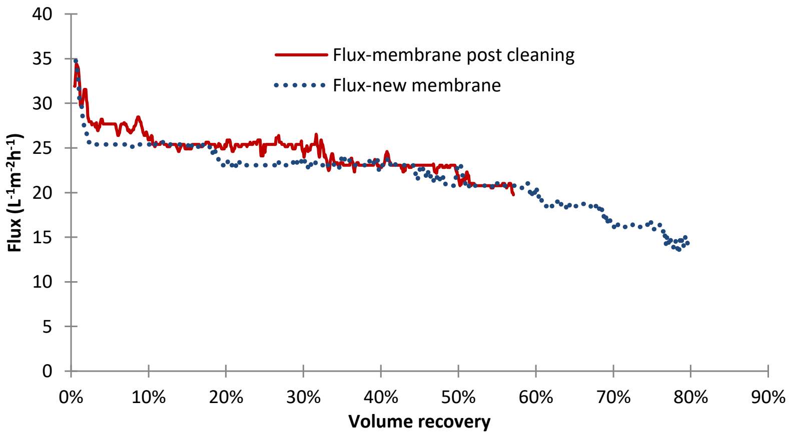

Figure ~~10~~8: Flux vs volume recovery from conventional NF pilot test using ~~Flux comparison between~~ new ~~New membrane~~(~~-~~data from **Figure ~~9~~7**) ~~,~~and ~~used~~ post cleaned NF270

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membranes (cleaned with 1000 mg~~/~~.L^{-1} NaOH solution) on wastewater sample with initial EC = 26.9 mS.cm^{-1} and pH = 1.09. ~~Post~~ Operating feed pressure ~~cleaned test feed pressure~~ = 4.7 bar(g) and, ~~T~~temperature = 20°C. ~~New membrane data from **Figure 9**.~~

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Table ~~8~~7: pH, EC and MCPA concentrations of initial feed (‘Feed 3’) used in conventional NF pilot test using post-cleaned NF270 membrane together with the final collected permeate and concentrate at the end of the batch run shown in **Figure 8**. Total osmotic pressure calculated from addition of HCl and MCPA osmotic pressures using **Equation 4**, effective pressure using **Equation 6** and MCPA rejection using **Equation 2**. Operating feed pressure = 4.7 bar(g) and temperature = 20°C (used for effective feed and osmotic pressure calculations). ~~Analytical results of the concentrate, feed and permeate from post-cleaning pilot test (NF270 membrane)~~

Sample	pH	EC (mS/cm)	MCPA (mg/L)	π_{tot} (bar)	$p_{effective}$ (bar)	MCPA Rejection
Feed 3	1.09	26.9	173	4.0		71%
Permeate	1.09	20.2	49.3	4.0	4.8	
Concentrate	1.10	24.4	386	3.9~~4.0~~		

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~~The NF pilot testing results showed that selecting the correct membrane depends on site specific practical constraints. For example, NF90 can reject 94% of the MCPA (or >95% with RO as shown in **Table 2**) but flux is considerably lower even at higher operating pressure, leading to cessation` of operation at 0.65 recovery. Substantially more feed volume was able to be treated at higher fluxes using NF270, reaching the target 0.80 water recovery but with around 70% MCPA rejection. Depending on the MCPA treatment requirement (volume and concentration reduction), it’s possible that a combination of membranes could achieve a site’s treatment goal. For example, if the 70% rejection of MCPA (reducing to < 50 mg.L^{-1}) could meet not sewer discharge requirements for the site, it could work in conjunction with another NF or RO membrane pass.~~

3.3 Comparison of membrane performance

All the membranes were compared in terms of the specific flux as determined by **Equation 7,** and presented in **Table ~~9~~8**. For reference, the clean water specific fluxes were also included. Looking first at clean water specific fluxes, we can see them increase as a function with the 'openness' of the membrane (i.e. in order of SW30, BW30, NF90 and NF270). The operation at higher temperature for BW30 TSRO showed a slightly higher specific flux as expected due to increased diffusion through the membrane. Looking at the initial specific fluxes of the waste water samples, a similar trend can be observed. However the TSRO concept (RO membrane operating at 43 ºC) showed about double the initial specific flux of conventional BW30 operation supporting the conclusions made earlier where this novel process could be a viable for high flux and high MCPA rejection. The final specific fluxes showed significant reductions compared to their initial specific flux counterparts for all tests except the NF270, which was only slightly lower due to the reduced rejection of acid and the associated MCPA fouling. The NF90 pilot test showed similar initial specific fluxes to the TSRO process, declining less as shown by the final specific flux due to not reaching the target 80% volume recovery. Therefore it could be concluded that combining temperature swing with NF90 at higher applied pressure could lead to much higher fluxes with high MCPA rejections pending further study, however the NF270 is clearly an effective membrane in terms of specific flux under standard operation setup at lower pressure, as long as lower MCPA rejection meets the site requirements.

Table ~~9~~8: Summary of initial and final specific fluxes ~~(L.m^{-2}.h^{-1}.bar^{-1})~~ across all membrane tests carried out in this work for MCPA separation from wastewater. Clean water for BW30, SW30 and bench NF270 tests was 1000 mg/L NaCl solution, and tap water for NF90 and NF270 pilot tests. See relevant figure/table for operating conditions for the specific run.

	Test						
	SW30	BW30	BW30 TSRO	NF90 pilot	NF270 bench	NF270 pilot	NF270 pilot post-clean

Relevant Figure~~/Table~~	Fig 4~~5~~	Fig 4~~5~~	Fig 5~~6~~	Fig ~~8&9~~7	~~Tab 5 &~~ Fig ~~7~~6	Fig ~~8&9~~7	Fig 8~~10~~
~~Water~~ Volume recovery achieved (wastewater)	~~0.80~~80%	80%~~0.80~~	80%~~0.80~~	65%~~0.65~~	80%~~0.80~~	80%~~0.80~~	~~0.~~57%
Clean water specific flux (L.m^{-2}.h^{-1}.bar^{-1})	2.6	3.5	4.0	5.9	NA	6.7	NA
Initial specific flux (L.m^{-2}.h^{-1}.bar^{-1})	0.74	0.77	1.3	1.6	6.7	5.7~~8~~	5.8~~9~~
Final specific flux (L.m^{-2}.h^{-1}.bar^{-1})	0.12	0.16	0.16	0.56~~7~~	NA	3.4	4.2

3.4 Practical considerations for membrane suitability and treatment targets

Choosing the correct membrane to meet a treatment objective is important for the end user. The RO and NF testing results showed that selecting the correct membrane will depend on site specific treatment requirements. For example, NF90 can reject 94% of the MCPA (or >95% with RO as shown in **Table 2**) but flux is considerably lower even at higher operating pressure, leading to cessation of operation at 65% volume recovery. Substantially more feed volume was able to be treated at higher fluxes using NF270, reaching the target 80% volume recovery but with around 70% MCPA rejection. A treatment target of < 10 mg.L^{-1} may comply with MCPA discharge requirements to a municipal sewer network with associated waste water treatment systems in operation, however the actual treatment target for discharge needs to be considered with respect to specific local regulations. For example, if the 70% rejection of MCPA (reducing to < 50 $mg.L^{-1}$) does not meet sewer discharge requirements for the site, it could work in conjunction with another NF or RO membrane pass, or other treatment operations, to meet the requirements.

The other practical consideration for long term operation is the operating pH. The manufacturer pH range for continuous operation of the NF membranes used in our work is specified as 3-10 which does not cover our pH range being consistently <3. Despite this, our use of the same membrane in the pilot plant over the project year showed no signs of performance loss both in terms of MCPA rejection and acid rejection (from pH measurements). Further, NF membranes that are officially resistant to pH as low as 1 are commercial and also a major focus of researchers [50, 51]. Therefore for future consideration, the field longevity of our tested membranes (Dow Filmtec BW30, SW30, NF90 and NF270) could be studied as well as the possibility for similar flux and rejection performance for membranes officially rated to this low pH range.

4. Conclusion

RO and NF membranes were successfully tested in removing MCPA from the industrial wastewater. It was found that:

- Dow Filmtec SW30 and BW30 membranes used in conventional RO setup showed the same performance for MCPA rejection (>95%), reducing it from 132 mg/L in the feed to <10 mg/Lin the permeate product. However, compared with SW30, BW30 showed better resistance to fouling but was more sensitive to salt concentration increase. Flux declined by about ~~82% and~~ 80% for both the SW30 and BW30 membranes at the target ~~at~~ 80% volume recovery ~~for the SW30 and BW30 membranes respectively~~;
- Osmotic pressure calculations indicated that even concentrating up to ~~0.80~~80% volume recovery, the effective pressure was only 7% lower than the total applied pressure and thus the bulk solution properties could not be responsible for the significant flux decline. Flux decline was therefore attributed to MCPA fouling but also H^+ surface concentration polarisation;
- An innovative temperature swing operating mode for RO (TSRO) was able to effectively supress fouling effectively for BW30 membrane by increasing MCPA solubility and lowering subsequent feed MCPA saturation during filtration. This method could be a novel means to remove MCPA and obtain high flux simultaneously to high MCPA rejection;
- NF90 membrane pilot membrane testing showed similar MCPA rejection to the RO membranes (reducing it from 165 mg/L in the feed to 11 mg/L in the permeate), but experienced flux decline because of osmotic pressure increase;
- NF270 pilot membrane testing showed the lowest MCPA rejection of between 63% and 71% both at bench and pilot scale (reducing it from ~170 mg/L in the feed to <50 mg/L in the permeate). MCPA rejection was attributed to size exclusion mechanism since MCPA was mostly in unionised form. NF270 ~~, but it~~ also showed best acid/salt (HCl) passage, fouling resistance and achieved target 80% volume recovery at practical fluxes. The lower rejection may still be sufficient to reduce MCPA but may need to work in conjunction with RO or other further treatment to reduce below discharge requirements;
- Post the NaOH cleaning, the wastewater flux of NF270 membrane had been fully recovered and showed minimal impact to MCPA removal. However the benefit (and schedule) of cleaning and potential degradation of the membrane needs to be considered over longer term operation; and

- Analysis of specific fluxes to account for operation and osmotic pressure differences showed the potential benefit of the novel temperature swing concept in terms of higher fluxes with high MCPA rejections, but also the possibility for NF90 to be used at higher pressure in the temperature swing process to further enhance fluxes while simultaneously achieving high MCPA rejections.

Based on these findings, NF270 in conventional setup was recommended but consideration must be made to the higher expected MCPA concentration in the permeate. For high MCPA rejection, RO can be used, but to achieve high volume recoveries the novel TSRO concept shows potential as it overcomes the significant flux decline issue with conventional RO. In all future cases, future work should consider cleaning strategy and long term performance. Also, despite no observed impact to membrane performance in the very low pH condition, membranes which are officially rated to the very low pH condition should be considered if the current types do not last in practical use.

Acknowledgements

The authors would like to acknowledge the financial support from Tri-Tech Chemical Pty Ltd (TTC) and the Research Connections grant from Australian Government Department of Industry, Innovation and Science Entrepreneurs' Programme (Grant no. RC54587). The assistance on the project from Dr Lining Ding and Tam Fam at TTC is also greatly appreciated.

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