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Comparison of Membrane-Based Treatment Methods for the Removal of Micro-Pollutants from Reclaimed Water

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Abstract: Dual membrane hybrid systems generally produce reclaimed water for non-potable uses by blending microfiltered biologically treated sewage effluent (BTSE) and reverse osmosis (RO) permeate. This reclaimed water is found to contain a significant amount of micro-pollutants, which possibly cause toxicity effects to aquatic organisms and plants when exposed to it. Therefore, removing such pollutants from the reclaimed water before reaching the community is highly emphasized nowadays. The currently used treatment of the RO treatment of microfiltered BTSE is energy intensive and not cost effective. This paper focuses on less costly and efficient membrane-based hybrid treatment systems such as the microfiltration-adsorption (MF-GAC) hybrid system, Nano filter (NF) and RO in the removal of micro-pollutants from the microfiltered BTSE. Both the MF-GAC hybrid system and NF (with NTR 729HF membrane) removed 70 to 95% of micropollutants from microfiltered BTSE. The removal depends on the hydrophobicity, charge, and size of the micropollutants. RO was excellent in removing more than 90% of pollutants, while MF was inefficient, as the latter primarily depends on the size exclusion mechanism. Based on the finding, it is suggested to treat only a portion of microfiltered BTSE through the MF-GAC or NF membrane before blending with RO permeate to enhance the removal of micro-pollutants from reclaimed water. The development of sustainable hybrid systems for the removal of all micropollutants of different chemical and physical properties is the key for the water reclamation.

Keywords: micro-pollutant; reclaimed water; nanofiltration; submerged membrane hybrid system

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1. Introduction

Biologically treated sewage effluent (BTSE) has progressively been used to produce recycled water as an alternative water resource in many countries (Singapore, Saudi Arabia, Qatar, Namibia, California and Australia) to meet the basic water demands [1]. The dual membrane process is a sustainable treatment solution [2]. In most of the dual membrane treatment plants, microfiltration (MF) or ultrafiltration (UF) is used as the first step to remove particulate and colloids from BTSE, and the reverse osmosis (RO) is used as the second stage [2,3]. RO is used to polish water and to improve the quality of the treated water [3,4].

Regarding the quality of recycled water, the presence of pathogens and chemical contaminants was the main concern in recycled water [5]. In the early 1990s, scientists observed endocrine disruption effects (feminization of male fish) in some fish species when exposed to wastewater effluents, even at trace levels of hormone concentration (a few ng/L) [5]. The micropollutants include pharmaceuticals, personal care products (PCPs), hormones, flame retardants, endocrine disrupting chemicals (EDCs), herbicides, pesticides, and nanomaterials. All of these are widely used by modern society.

They become detrimental to human and animal health when their residues eventually enter and accumulate in the food chain through effluent discharge, reuse of treated sewage and with sludge used in agricultural applications [6,7]. Many micro-pollutants have been reported to be toxic to freshwater invertebrates, fish, mussels, and human embryonic cells [8,9] and have been linked to an array of carcinogenic, mutagenic, and reproductive toxicity risks [10]. Despite their low concentrations in the environment, they can also affect plant growth and development and agricultural activities where reclaimed water is used for irrigation purposes [11,12].

Recycled water is generally a blend of MF/UF permeate mixed with the RO permeate in an appropriate ratio. The Water Reclamation Scheme (WRAMS), operated in Sydney, Australia, produces recycled water, which is a blend of MF permeate and RO permeate. The RO permeate ratio is from half to a fifth of the total product water (i.e., 50–20%) [4]. The recycled water produced at WRAMS is sourced from a larger proportion of BTSE, and the micro-pollutants load in the recycled water is higher [13,14]. The recycled water is sold back to households for various non-potable uses, including watering gardens, lawns and parks, filling ornamental ponds, water fountains and irrigation of parklands [4].

Researchers have studied different treatment methods such as adsorption, membrane filtration, advanced oxidation methods, and different types of biological treatment [15,16] to remove micro-pollutants from feed water. Our previous studies demonstrated that granular activated carbon (GAC) coupled with MF was able to significantly (>90%) remove most of the micro-pollutants from BTSE [17–20]. Rostral et al. [20] demonstrated a positive correlation between the removal efficiency of micro-pollutants and their respective Log K_{ow} (octanol water partition coefficient) values for sorbents such as Xylit, lignite, sand, and GAC. GAC was found to be the most efficient at removing micro-pollutants from on-site sewage treatment facilities. Some studies focused on ozonation techniques to remove such micro-pollutants. However, Ullberg et al. [21] reported that ozonation might produce hazardous by-products. They further recommended GAC filters as a post-treatment to remove hydrophobic compounds, including potentially hazardous micro-pollutants from the wastewater. Khanzada et al. [22] claimed that ozonation techniques are less efficient in removing micro-pollutants compared to activated carbon adsorption, especially for pesticides, industrial chemicals, antibiotics, antidepressants, and surfactants.

Membrane filtration was found to be a promising treatment with excellent removal of micro-pollutants from the feedwater. UF showed a poor removal of micro-pollutants, nano-filtration (NF) exhibited a good removal and RO is excellent (>90%) for a wide range of contaminants [22]. MF (of pore size around 200 nm) and UF (3 nm) membranes reject micro-pollutants primarily by size exclusion, and the permeate quality of both membranes are similar [23]. NF/RO processes are effective and remove the micro-pollutants by various mechanisms such as size exclusion, electrostatic interaction (Donnan effect), hydrophobic interaction, H-bonding, charge, and orientation of the molecule to the membrane, etc. [24–27]. To understand the removal of micro-pollutants by the different type of membranes, it is necessary to study the mechanism driving the removal of micro-pollutants. This helps design more specific and appropriate systems for various water needs.

Therefore, a modification/addition of a treatment process is necessary to enhance the removal of previously ignored micro-pollutants from the BTSE. Very few studies focused on the safe provision of reclaimed water with no or insignificant amounts of micro-pollutants. Therefore, this study aims to find out suitable membrane-based treatment options as the microfiltration-adsorption (MF-GAC) hybrid system, combined the NF and RO process in the removal of micro-pollutants from the microfiltered BTSE to produce environmentally safe reclaimed water. In addition, the current dual membrane system combined MF and RO to produce reclaimed water and is costly, as it requires higher energy for RO. This study further focuses on utilizing membrane-based hybrid treatment systems such as the MF-GAC hybrid system and NF, with less energy consumption, which are cost effective in the removal of micro-pollutants from BTSE.

Detailed experiments were conducted with the above two systems with microfiltered BTSE (MF/BTSE) in a water reclamation plant in Sydney, Australia, and the removal of representative micro-pollutants were measured.

2. Materials and Methods

2.1. Materials

2.1.1. Feed Water

The WTP treats wastewater through a dual membrane system consisting of continuous flow MF and RO with a total capacity of 7.5 ML/d from MF units and a maximum of 2 ML/d from RO units. The pH, conductivity, and sodium adsorption ratio (SAR) of BTSE were 6.8–7.6, 0.52–1.12 dS/cm and 39, respectively. The concentration of dissolved organic carbon was 3.6 to 7.7 mg/L. BTSE contain high concentration of Na^+ and Cl^- ions in the ranges of 81–120 and 150–300 mg/L, respectively. All the BTSE is firstly passed through MF to remove suspended particles (>0.2 µm). A portion of the water filtered through the MF units was passed through the RO units. The MF unit consists of hollow fiber (Memcor) filters with 0.2 µm pores and arranged in three blocks. One block can produce approximately 2.5 ML/d. Two RO modules, each producing 1 ML/d, were used as a post-treatment to improve the quality of the water by reducing salinity. Following filtration, a portion of MF and RO permeate is blended at an appropriate ratio in the water reclamation/blending tank. The proportion of RO in the effluent usually ranges from 20–50%. After blending, the recycled water is sold back to the households for non-potable uses [4] (Figure 1).

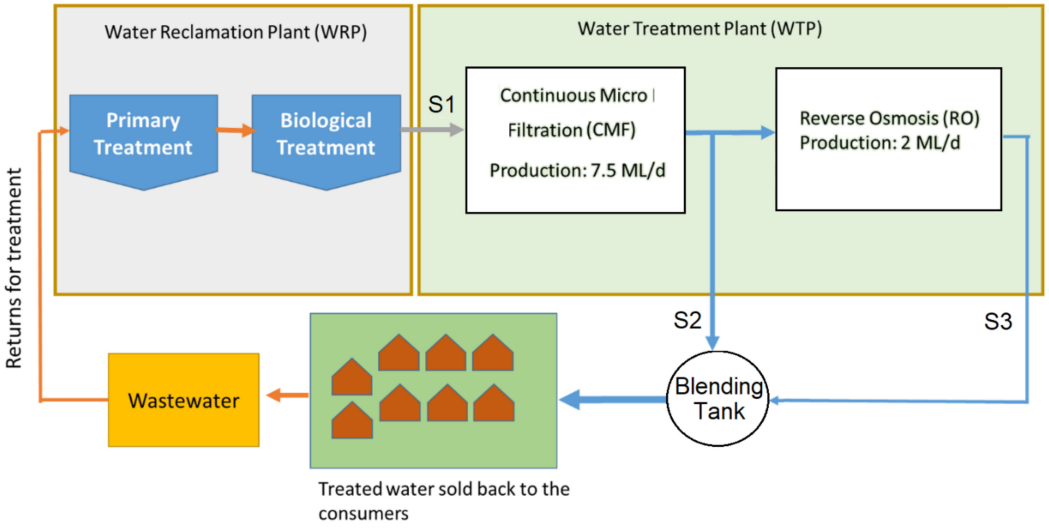


Figure 1. Schematic diagram of a water reclamation plant at Sydney, Australia (modified from [4]).

Figure 1 shows the treatment path of BTSE (S1), microfiltered BTSE (S2), and RO permeates (S3) collected from the WTP. The various effluent was transported to the laboratory and maintained at 20 °C for the experiments. The DOC, conductivity, fluoride, chloride, sulfate, nitrate, calcium, and magnesium contents of the feed were 4.5–7.5 mg/L, 680–1120 µS/cm, 0.7–1.1 mg/L, 132–150 mg/L, 49–51 mg/L, 4.5–6.1 mg/L, 25–35 mg/L, and 10–12 mg/L, respectively.

2.1.2. Membranes

The following membranes were used in this study.

a. Flat sheet membrane module: A flat sheet MF membrane module made up of polyvinylidene fluoride (PVDF) with a nominal pore size of 0.14 µm and surface area 0.2 m^2 was used for the MF-GAC hybrid system. It had 8 vertical membrane sheets with 11 mm gap between any two adjacent membrane sheets. The dimensions

of this membrane are: 11.5 cm (width), 10.5 cm (length), and 22.5 cm (height). It was manufactured by the A3 Membrane Company, Gelsenkirchen, Germany.

b. Nanofiltration (NF): Two hydrophilic NF membranes, NP030 and NTR729HF, were used to assess the performance of NF in removing micro-pollutants. The NP030 (manufactured by Macrodyn®Nadir) was made of polyethersulfone with a molecular weight cutoff (MWCO) 400 Da and Zeta potential of −15 mV at pH 7 [28]. The NTR 729HF, manufactured by Nittto Denko, was made of Polyvinylalcoho/polyamides (Heterocyclic aromatic) with a MWCO 700 Da, and the Zeta potential was −100 mV [29].

c. Reverse Osmosis (RO) membranes: RO membrane (manufactured by Woongjin Chemical) made of polyamides, with MWCO of 100 Da and zeta potential −21 mV [30] was used to investigate the RO removal performance of micro-pollutants from the feed water.

2.1.3. Granular-Activated Carbon (GAC)

Coal-based premium grade (MDW4050CB) GAC supplied by James Cumming and Sons Pty. Ltd., Sydney, Australia was used in the MF-GAC hybrid system. The GAC had an exchange/adsorption capacity of Iodine #1000 mg/g; moisture content 2% max; particle size 300–600 µm; surface area of 1000 ± 50 m^2/g; and average pore diameter of 30 Å. This particle size was selected as it lowers the Trans Membrane Pressure (TMP) development by reducing the membrane-clogging effect [17].

2.2. Methodology

The following treatment methods were employed to compare the removal of micro-pollutants from the feed water.

2.2.1. MF-GAC Hybrid System

The performance of GAC on the removal of micro-pollutants was studied using a MF-GAC hybrid system (Figure 2). The experimental procedure is stated in the previous studies [17,31]. An MF membrane (flat sheet) was submerged in the reactor tank containing 10 L of micro-filtered BTSE. Peristaltic pumps were used control the flow of feed water in and out of the tank. The TMP of the membrane filtration was measured using a pressure gauge. Initially, 20 g of GAC was added to the reactor tank to maintain the GAC dose of 2 g/L. The reactor tank was fed with continuous air flow at 1.5 m^3/m^2 membrane area h (pre-determined), which keeps the GAC particles in suspension. The air flow also produces shear stress across the membrane surface, and this leads to a reduction of fouling of the membrane. The loss of volatile organic compounds (VOCs) due to aeration was neglected as the wastewater used in this study was previously biologically treated and stabilized. The primary purpose of the MF (flat sheet membrane) was to remove particulate GAC [32].

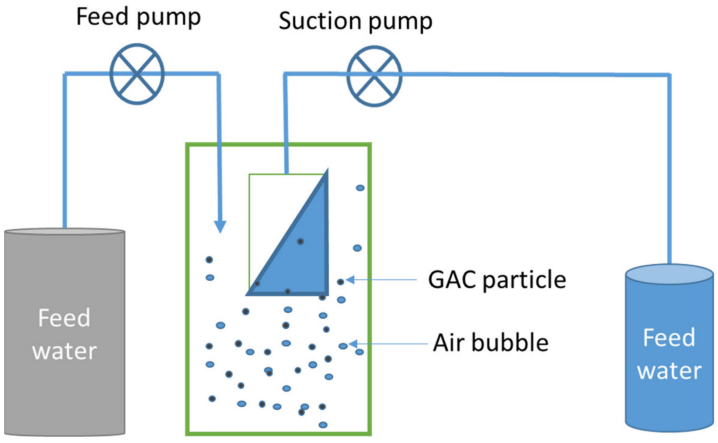
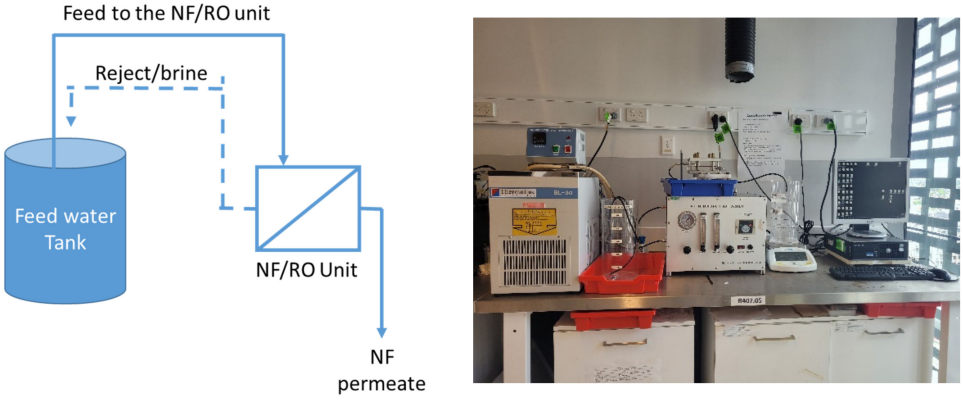


Figure 2. MF-GAC hybrid system (GAC initial dose of 2 g/L).

2.2.2. Nanofiltration

As shown in Figure 3, the filtration unit equipped with NF membranes (NP030 and NTR 729HF; membrane area of 68 cm^2) was used to filter the micro-filtered BTSE [12,19]. A cooling coil was submerged in the feed tank to maintain the feed water temperature constant at 20 °C. The filtration pressure was maintained at 4 bar. The clean water fluxes of NP030 and NTR 729HF were 12 and 62 $L/m^2 \cdot h$, whilst their permeability was 3 and 15.5 $L/m^2 \cdot bar \cdot h$, respectively. The reject was re-circulated to the feed tank.



(**a**) (**b**)

Figure 3. NF/RO membrane filtration unit: (**a**) schematic diagram; (**b**) laboratory set-up.

2.2.3. Reverse Osmosis

A similar experimental setup (Figure 3) was used for the experiment with the RO membrane at the filtration pressure of 40 bar. The clean water flux was maintained to be 23.5 $L/m^2 \cdot h$, whilst its permeability was 0.59 $L/m^2 \cdot bar \cdot h$.

2.2.4. Analysis of Micro-Pollutants

Concentrations of micro-pollutants were extracted using solid phase extraction (SPE) and examined with high performance liquid chromatograph with tandem mass spectroscopy (HPLC-MSMS) and quantified by isotope dilution. Samples (500 mL) were collected in clean glass bottles, stored in the dark (<4 °C) and extracted within 48 h.

Prior to SPE, samples were spiked with 50 ng (50 µL of a 1 mg/L solution) of isotope labelled analogues of all targets' micro-pollutants. Samples were loaded onto pre-conditioned OASIS 500 mg hydrophilic or lipophilic balance cartridges (Waters, Millford, MA, USA) at a rate of 10 mL/min. After completion, cartridges were rinsed with 5 mL of water and dried with a stream of nitrogen. Then, they were stored at 4 °C if not immediately eluted. The elution of target micro-pollutants was conducted from the cartridges with methanol (3 × 2.5 mL) and 1/9 (v/v) methanol/ethyl-tert-butylether (2.5 mL), and evaporated under a stream of nitrogen to approximately 100 µL. The extract was made up to approximately 1 mL with 60% methanol/water (v/v) and transferred to a 2 mL amber auto-sampler vial for instrumental analysis.

Target micro-pollutants were chromatographically separated and quantified using an Agilent (Santa Clara, CA 95051, USA) 1200 series HPLC equipped with a 150 × 4.6 mm, 5 µm particle size, Luna C18 column (Phenomenex, Torrence, CA, USA). Identification and quantification of micro-pollutants were carried out using an API 4000 triple quadrupole mass spectrometer (Sciex/Applied Biosystems, Forster City, CA, USA), which is equipped with a turbo-V ion source employed in both positive and negative electro-spray modes. A binary gradient consisting of 5 mM ammonium acetate in water (A) and 100% methanol at a flow rate of 800 mL/min was used. For electrospray ionization (ESI) positive analyses, the gradient was as follows: 10% methanol held for 0.50 min, stepped to 50% methanol at 0.51 min and increased linearly to 100% methanol by 8 min, then held at 100% methanol

for 2 min. For ESI negative analyses, the gradient was as follows: 10% methanol held for 0.50 min, stepped to 60% methanol at 0.51 min and increased linearly to 100% methanol by 8 min, then held at 100% methanol for 3 min. A 5 min equilibration step at 10% methanol was used at the beginning of each run. An injection volume of 10 mL was used for all methods. Using scheduled multiple reaction monitoring (sMRM), two precursor–product ion transitions were monitored for all analytes, the most abundant used for quantitation.

Calibration was achieved by the construction of a minimum 5-point analyte/ISTD relative response ratio over a concentration range of 0.5–500 ng/mL. Linearity coefficients for all analytes were $\geq$0.99. Limits of Detection (LODs) were defined as the concentration of an extracted analyte giving a signal to noise (s/n) ratio greater than 3. Limits of Quantification (LOQ) were determined as the concentration that gave a peak of an extracted target analyte with a signal to noise ratio (s/n) of >10. For quality assurance and control, laboratory grade water blanks and fortified blanks at 10 and 100 ng/L were extracted with every batch of samples. No analytes were detected in blank samples above the quantitation limit. Recoveries of all target analytes were within 20% of expected concentrations. Solvents, buffer reagents and analytical standards were purchased from Sigma Aldrich (North Ryde, Australia). Isotope labelled internal standards were purchased from CDN Isotopes (PointeClaire, Canada). Water used in analysis was obtained from a Milli-Q purification system (Merck, Damstadt, Germany).

2.2.5. Estimation of Micro-Pollutants in the Reclaimed Water

Since the MF/BTSE is blended with the RO permeate to produce reclaimed water, the concentration of micro-pollutants in the reclaimed water was estimated using the following, Equation (1):

$$C_1V_1 = C_2V_2 \quad (1)$$

where C_1 is the concentration of micro-pollutant in MF/BTSE; V_1 is the volume of the MF/BTSE sample; and C_2 is the concentration of micro-pollutant in RO permeate; and V_2 is the volume of the RO permeate. The upper limit of the concentration range of the respective MP in MF/BTSE was considered for C_1, and the C_2 was considered as 0 assuming the RO achieves 100% rejection for all the micro-pollutants.

2.2.6. Removal Efficiency (%) of Micro-Pollutants

The removal efficiency of the micro-pollutants was calculated relative to the influent concentrations using the following, Equation (2).

$$Removal\ (\%) = \frac{Ci - Ce}{Ci} \times 100 \quad (2)$$

where, Ci = concentration in influent (ng/L) and Ce = concentration in effluent (ng/L).

3. Results

3.1. Micro-Pollutants in the Microfiltered BTSE

The dissolved organic content of the feedwater ranged between 3–7 mg/L. The feedwater was tested for 36 commonly available micro-pollutants in municipal wastewater, out of which 20 micro-pollutants were detected above the LOQ (Table 1). Micro-pollutants that were detected at less than its LOQ (<5 ng/L or <10 ng/L) include Bisphenol A, Simvastatin-hydroxyacid, simvastatin, polyparaben, phenylphenol, paracetamol, dilantin, enalapril, risperidone, atrazine, linuron, omeprazole, clozapine, triamterene, hydroxyzine and diazepam. The micro-pollutant analysis was conducted in triplicate and the linearity coefficients for all analytes were $\geq$0.99.

Table 1. Micro-pollutants in the MF/BTSE and recycled water [17,22,27].

Micro-Pollutants	Class of Micro-Pollutants	Log K_{ow} (pH 7)	Molecular Weight (MW) (g/mol)	Precursor Ion (m/z)	Charge of Molecule	Electrospray Ionization (ESI) Mode	LOQ (ng/L)	Actual Conc (ng/L) in MF/BTSE	Estimated Conc. (ng/L) in Reclaimed Water (Max Limit)
					Positive (+); Neutral (0); Negative (−)				Blending Proportion
									CMF:RO (Mixing Ratio 80:20–50:50)
Ketoprofen	Analgesics	3.12	254	252.80	−	−	5	95.2	47.5–76
Naproxen	Analgesics	3.18	230	228.90	−	−	5	69–313	156–250
Ibuprofen	Analgesics	3.97	206	204.90	−	−	5	38–70	35–56
Gemfibrozil	Lipid regulator	4.77	250	248.90	−	−	5	24–430	215–344
Diclofenac	Analgesic	4.51	296	293.90	−	−	5	8–200	100–160
Triclosan	Anti-microbial agent	5.34	290	286.60	0	−	5	6–90	45–72
Triclocarban	Anti-microbial agent	4.90	316	312.90	0	−	10	12–38	19–30
Atenolol	Beta blocker	0.16	266	267.20	+	+	5	78–186	93–148
Sulfamethoxazole	Therapeutic	0.89	253	254.00	−	+	5	84–114	57–91
Caffeine	Stimulant	−0.07	194	195.00	0	+	10	86–675	337–540
Trimethoprim	Anti-infective	0.91	290	291.10	+/0	+	5	26–229	114–183
TCEP Tris(2-chloroethyl) phosphate)	Flame retardant	1.44	250	284.90		+	10	29–99	49–79
Carbamazepine	Anti-analgesics	2.45	236	237.00	0	+	5	231–541	270–432
Fluoxetine	Anti-depressant	4.10	309	310.00	+	+	5	8–24.7	12–20
Amitriptyline	Anti-depressant	4.92	277	278.20	+	+	5	5–37	18–27
Primidone	Therapeutic	0.91	218	219.20	−	+	5	8–117	58–94
Verapamil	Therapeutic	3.79	454	455.40	+	+	5	8–28	14–22
Simazine	Herbicide	2.18	201	202.00	0	+	5	7–11	5–9
Diazinon	Insecticide	3.81	304	305.10		+	5	10–104	52–83
Diuron	Herbicide	2.68	233	233.02	0		5	35.7–42.8	21–34

The micro-pollutants, naproxen, gemfibrozil, diclofenac, caffeine, trimethoprim, and carbamazepine, were detected at more than 100 ng/L in the MF/BTSE. Carbamazepine was detected at a high concentration, as it was less effectively removed by conventional wastewater treatment systems [33]. There is a possibility that this water could cause toxicity in the zebra embryo due to the levels of micro-pollutants such as diclofenac, diuron, carbamazepine, diazinon, and triclosan, as their Predicted No Effect Concentration (PNEC) are 11.64, 9.41, 53.05, 7.97, and 1.14 ng/L, respectively [34]. The algae toxicity might be due to the concentration of diuron [35], diazinon [36], and triclosan, as their PNEC were 8.00, 10.00, and 1.40, respectively [37]. Carbamazepine could possibly cause invertebrate toxicity (PNEC 25.00) [38].

Based on the review by Orias and Perrodin [39], Gemfibrozil reduces the plasmatic testosterone in the species C. auratus (PNEC 300 ng/L), triclosan affects the biomass of biofilms (PNEC 24 ng/L), trimethoprim might reduce the metabolic activity of D. polymorpha (PNEC 5.8 ng/L), Caffein affects the development of the number of viable offspring of X. laevis (PNEC 0.05 ng/L) and fluoxetine delays the development of R. pipiens species (PNEC 2.9 ng/L). The feedwater analyzed in this study detected the aforementioned micro-pollutants at levels greater than their respective PNEC. In some cases, the LOQs were higher than PNEC of the respective micro-pollutants. Micro-pollutants detected at less than LOQ in the feed water do not necessarily mean that the compound is absent or within safe levels [39].

The reclaimed water supplied to the consumers was detected with a range of micro-pollutants which are greater than PNEC. This might possibly cause several aquatic and environmental toxicity when using reclaimed water, especially for filling ornamental ponds, irrigation, water fountains, and some other water features.

3.2. Removal of Micro-Pollutants by MF

MF bearing a nominal pore size of 0.2 µm was found to only reduce the micro-pollutants by less than 50% except for fluoxetine and triclosan (Table 2). Similar results were reported by Gidstedt et al. [23], who observed less than 55% removal of micro-pollutants by MF (0.2 µm) of wastewater. It was further noticed that there was no removal (0%) of Sulfamethoxazole, which agrees with the observation in this study [14]. Rodriguez-Mozaz et al. [14] reported that MF is not capable of rejecting any micro-pollutants as the MWCO of MF (~300,000 g/mol) is far bigger than that of the size of micro-pollutants (<1000 g/mol). The reduction of micro-pollutants observed in this study could be due to the interaction of the membrane surface with the nature of the micro-pollutants.

Table 2. Removal (%) of micro-pollutants by MF filtration of 0.2 µm pore size.

Micro-Pollutants	Influent (MF Feed) (ng/L)	MF Effluent (ng/L)	Removal (%)
Amtriptyline	19	13	30
Atenolol	104	84	19
Caffeine	73	68	6
Carbamazepine	393	369	6
Diclofenac	164	152	7
Fluoxetine	19	9	53
Gemfibrozil	334	298	11
Ketoprofen	114	95	17
Naproxen	820	522	36
Primidone	29	26	12
Sulfamethoxazole	61	61	0
Triclocarban	81	41	50
Triclosan	91	5	95
Trimethoprim	236	208	12
Verapamil	35	27	23

3.3. Removal of Micro-Pollutants by MF-GAC Hybrid System

The MF-GAC hybrid system was found to reduce the concentration of micro-pollutants by more than 60% for 15 micro-pollutants out of the 18 monitored (Table 3). The micro-pollutants such as gemfibrozil, atenolol and trimethoprim were efficiently adsorbed into GAC and the removals were more than 95%. Micro-pollutants naproxen, ibuprofen, tricloson and carbamazepine were also efficiently removed (90–95%). The remaining micro-pollutants also had large removals from the feedwater after treatment with the MF-GAC hybrid system (70–95%), except primidone, which demonstrated the lowest removal (54%).

Table 3. Removal (%) of micro-pollutants by MF-GAC hybrid system (GAC's initial dosage of 2 g/L).

Micro-Pollutants	Influent Feed Water (ng/L)	Effluent MF-GAC Hybrid System (ng/L)	Removal (%) by MF-GAC
Naproxen	211	19	90.9
Ibuprofen	70	5	92.8
Gemfibrozil	430	16	96.3
Triclosan	90	5	94.4
Diclofenac	131	18	86.6
Triclocarban	38	10	73.7
Atenolol	220	7	96.6
Sulfamethoxazole	114	30	73.7
Caffeine	675	151	77.6
Trimethoprim	229	7	97.0
TCEP	56	10	82.1
Carbamazepine	434	36	91.8
Fluoxetine	20	5	74.6
Amtriptyline	37	5	86.5
Primidone	11	5	54.4
Verapamil	28	5	82.2

The literature explains the removals based on the hydrophobicity of the micro-pollutants, which is typically described by the K_{ow} value (octonol-water partition co-efficient) and acid dissociation constant (pKa) [27,40]. The micro-pollutants having high hydrophobicity had more affinity towards GAC than the micro-pollutants with low hydrophobicity [21]. As shown in Table 3, the micro-pollutants, namely naproxen, ibuprofen, gemfibrozil, and tricloson with Log K_{ow} values > 3.0, were effectively removed (>90%) by the GAC. The primidone and sulfamethoxazole with Log K_{ow} values 0.91 and 0.89, respectively, showed smaller removal of 54% and 73% respectively. The reduced removal can be explained by the lower Log K_{ow} values that have a lower affinity to GAC.

Contrary to the above, micro-pollutants such as atenolol and trimethoprim demonstrated higher removals (97%) despite their Log K_{ow} values (0.16 and 0.89, respectively). A similar observation was made by Liu et al. [41]. They also observed high removal of trimethoprim and the sulfamethoxazone (80–90% and 60–70%, respectively) with the treatment with an artificial composite soil treatment system. Here, the removal is strongly related to sorption. Atenolol having low Log K_{ow} (0.16) showed greater removals by GAC (97%). This could be due to its positive charge. Caffeine with low Log K_{ow} (−0.07) also had a high removal of 78%, as it bears a neutral charge. A similar observation was reported by Jamil et al. [27]

The MF/BTSE contains approximately 85% of low molecular weight (LMW) hydrophilic compounds (humics and LMW neutrals) [32], which may possibly compete with micro-pollutants for GAC adsorption sites. However, the micro-pollutants with higher log K_{ow} can become adsorbed into GAC even in the presence of high load of NOM [42]. This has been clearly demonstrated by the results obtained in this study.

The removal of individual trace organics cannot be described by the GAC adsorption based solely on the log K_{ow}, molecular size, and charge. Removal also depends on a variety

of physical and chemical interactions among trace organics, dissolved organic matter, and GAC, its dosage, temperature, pH, etc. [43,44].

3.4. Removal of Micro-Pollutants by NF

The performance of the two NF membranes, NP030 and NTR729HF, in terms of the removal of selected micro-pollutants, are presented in Table 4. The NP030 and NTR729HF membranes were found to reduce 9 and 11 micro-pollutants, respectively, by more than 50% out of the total number of micro-pollutants detected in the feed water. Comparing NP030 and NTR729 HF, the latter was more efficient at removal.

Table 4. Removal of micro-pollutants by two different hydrophilic NF membranes (NP030 and NTR729HF) at operating pressure of 4 bar.

Micro-Pollutants	NP030			NTR729 HF		
	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Influent (ng/L)	Effluent (ng/L)	Removal (%)
Atenolol	220	76	65.4	83	20	75.5
Sulfamethoxazole	114	80	29.5	174	<5	97.1
Caffeine	675	631	6.5	88	57	34.9
Trimethoprim	229	146	36.2	146	31	78.7
Carbamazepine	434	344	20.7	376	50	86.7
Amtriptyline	37	9	76.8	11	<5	55.4
Primidone	11	<10	>10	26	<5	80.9
Verapamil	28	8	71.3	12	<5	57.3
Diazinon	104	6	94.2	98	<5	94.9
Naproxen	211	47	77.7	84	<5	94.0
Gemfibrozil	430	122	71.6	31	9	72.2
Diclofenac	131	71	46.0	57	<5	91.2
Triclocarban	38	<10	73.7	10	<9	>10
Diuron	43	25	41.8	94	49	47.9
Fluoxetine	20	11	44.7	ND	-	-
Ibuprofen	70	17	76.3	ND	-	-
Triclosan	90	25	72.5	ND	-	-

The removal of micro-pollutants by the NF membrane is governed by two mechanisms, namely size exclusion and electrostatic screening [12,27]. The fundamental mechanism behind the rejection of micro-pollutants by membrane filtration is size exclusion, although the removal by electrostatic repulsion, adsorption due to hydrophobic interactions, and adsorption onto the membrane fouling layer also can play a part [45].

The rejections (%) of micro-pollutants such as sulfamethoxazole, naproxene and diclofenac were much higher (>90%) with NTR729HF than the NP 030 despite the higher MWCO (700 Da) of NTR 729HF compared NP 030 (400 Da). Since these micro-pollutants are negatively charged, the electrostatic interaction between the micro-pollutants and the membrane surface exerts electrostatic repulsions and hinders its passage through the membrane [45]. The zeta potential of the membrane surface of NTR729HF (−100) is higher compared to that of NP030 (−15).

The insight mechanism on the removal of micro-pollutants by the NF cannot preciously be explained, as the removal mechanism pertaining to electrostatic repulsion depends on several factors such as the properties of membrane, the micro-pollutant and the chemical properties of the solution [46]. They further reported that the charge of the micro-pollutant and the membrane determines the distribution of ions on the surface of the membrane. If the micro-pollutant charge is opposite to the membrane charge, there is a possibility to transport the micro-pollutant across the membrane. In case of micro-pollutant and membrane being with the same charge, the membrane will repulse the ions. However, the charge of the micro-pollutant and the membrane surface are highly influenced by the presence of the charge of other compounds and the solution pH [46]. Therefore, considering the other physico-chemical characteristics of the membrane and the properties of the micro pollutants are essential [47,48]. For example, the lower removal of pharmaceuticals was observed by NF/RO membranes with the presence of calcium ions [49].

The performance of NP030 is better in the removal of positively charged micro-pollutants (namely atenolol, amitriptyline, verapamil, fluoxetine) than that of NTR729HF. This can be explained by the size exclusion mechanism of the NF membrane [27,45]. The removal of amitriptyline and verapamil were between 71–76% by the NP030 and 55–57% by the NTR 729HF, as the MWCO of the former is more restrictive. Atenolol was removed 65% by the NP030, and 75% by the NTR729 HF could be due to the size exclusion mechanism. This could be due to the adsorption of the compound on the membrane surface due to several other factors, such as the shape of the molecule, hydrophobic interaction and hydrogen bonding. Fluoxetine showed lesser removal (44%) by NP030, and this may be due to the larger size of the molecule (MW = 309 g/mol). The relation between the rejection and the molecular weight of the compounds agrees with Shirley et al. [50]. Further, the direction of the dipole moment also determines the position of the molecule with respect to the membrane surface in rejecting compounds by NF [51].

The removal mechanism of uncharged compounds (caffeine, trimethoprim, carbamazepine, primidone, diuron, triclosan) cannot be explained by size exclusion nor electrostatic repulsion by the membrane surface. The positively charged or uncharged compounds can reach the membrane surface and become adsorbed onto the polymer matrix more easily compared to negatively charged molecules [52]. Removal could be due to hydrophobic interactions among the compounds, membrane surface or foulants [53]. Caffeine was detected at high concentrations in the feedwater (675 ng/L), and its removal was insignificant by NP030 (6%) and by NTR729HF (35%). The low MW of the compound allowed it to pass through the pores of the membrane (MW = 194 g/mol).

3.5. Removal of Micro-Pollutants by RO

RO membranes are nonporous, and the removal of micro-pollutants occurs through the sorption diffusion mechanism, where the micro-pollutants are solubilized and moved by gradient of the chemical potential [54].

RO demonstrated excellent removal of micro-pollutants from feed water and most of the compounds remained below LOQ (Table 5). The compounds, namely caffeine, carbamazepine, atenolol, and triclosan, detected in permeate, demonstrated more than 92% removal. The micro-pollutant caffeine was left at a higher concentration in permeate (21 ng/L) compared to the rest. The smaller MW of the caffeine (194 g/mol) would have reduced the RO removal rate. This is supported by Dolar et al. [51], as they found the RO rejects the compounds primarily by the size exclusion mechanism.

Table 5. Removal of micro-pollutants by RO membrane at operating pressure of 40 bar.

Micro-Pollutants	Influent (RO Feed) (ng/L)	Effluent (RO Permeate) (ng/L)	Removal (%)
Caffeine	675	21.1	97
Carbamazepine	434	11	97
Gemfibrozil	430	<5	>99
Trimethoprim	229	<5	>98
Atenolol	220	5.11	98
Naproxen	211	<5	>98
Diclofenac	131	<5	>96
Sulfamethoxazole	114	<5	>96
Triclosan	90	7.04	92
Ibuprofen	70	<5	>93
Triclocarban	38	<10	74
Amtriptyline	37	<5	>86
Verapamil	28	<5	>82
Fluoxetine	20	<5	>75
Primidone	11	<5	>53

4. Conclusions

A total of 20 micro-pollutants out of 36 measured were detected at the above LOQ in the reclaimed water. The micro-pollutants naproxen, gemfibrozil, diclofenac, caffeine, trimethoprim, and carbamazepine were detected at more than 100 ng/L. Out of the 20 detected micro-pollutants, about 50% of them were above PNEC levels in the feed water. Therefore, this reclaimed water may not be ecologically safe if living species including plants are exposed to it.

The MF is not effective in removing micro-pollutants (removed less than 20%). NF is effective in rejecting micro-pollutants through electrostatic interactions and size exclusion and most of the micro-pollutants' removal rates were in the range of 70–95%. NTR729HF was more efficient than NP030, as the former had smaller MWCO and higher zeta potential. GAC also efficiently (75–95%) removed micro-pollutants, and the hydrophobic substances demonstrated higher affinity towards the solid surface of GAC. The removal of the micro-pollutant by RO membrane was excellent.

Development of sustainable hybrid systems for the removal of all micro-pollutants of different chemical and physical properties is the key for the water reclamation. In this study, the performance of MF-GAC hybrid system and NF were equally good in the removal of micro-pollutants. Therefore, a portion of the MF permeate (presently in blends of between 70–50%) could be sent to either the MF-GAC hybrid system or NF membrane (NTR 729HF) to further reduce the micro-pollutants in the MF permeate before blending with the RO permeate (Figure 4).

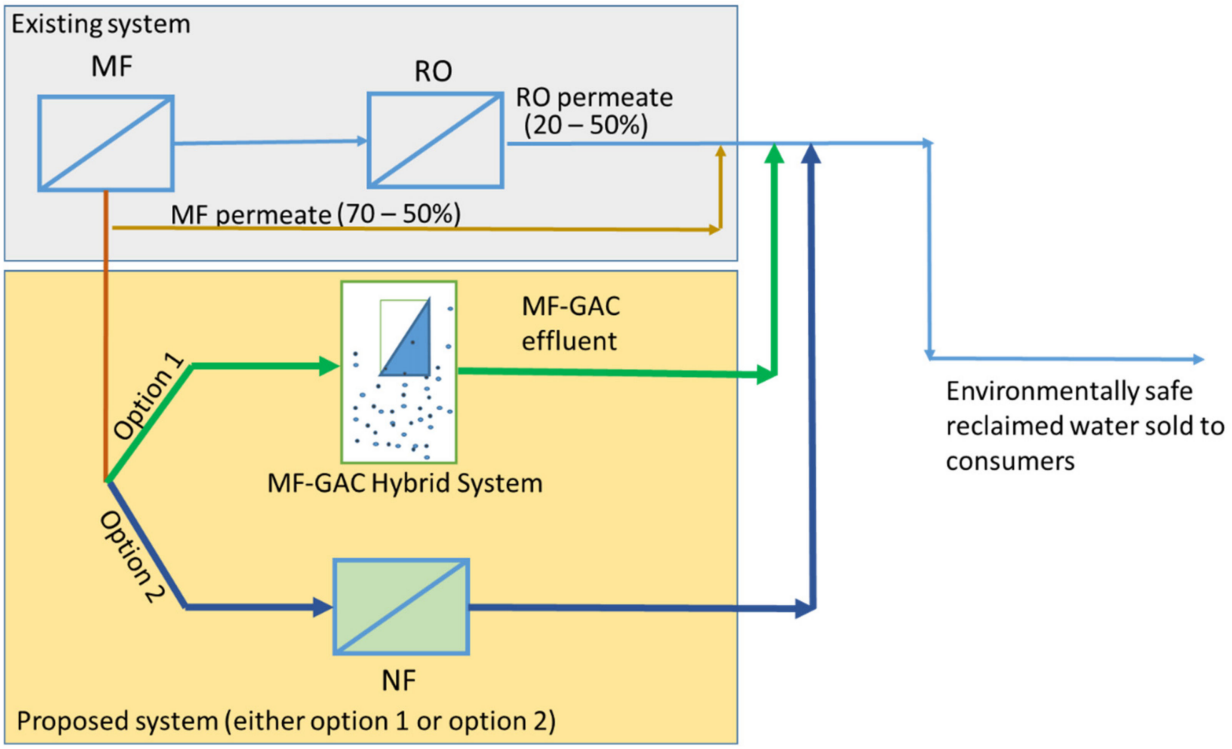


Figure 4. Proposed system for the WTP to produce environmentally safe reclaimed water.

Option 1: Blending of MF, MF-GAC, and RO permeate: Since MF-GAC is effective in reducing micro-pollutants, a portion of the MF permeate could be treated through MF-GAC hybrid system to further reduce the micro-pollutants before it is blended with RO permeate at an appropriate ratio.

Option 2: Blending of MF, NF permeate, and RO permeate: Since the NTR729HF is effective in rejecting micro-pollutants, a portion of the MF permeate can be filtered through NTR729HF, and the permeate can be blended with the RO permeate.

The appropriate blending ratio of MF permeate, either MF-GAC or NF permeate, and RO permeate should be decided based on the water quality parameters and the level of micro-pollutants in the reclaimed water. Therefore, a proper monitoring mechanism should be developed to monitor the micro-pollutants levels in the reclaimed water at regular intervals to ensure environmental safety.

Different low-pressure NF membranes and alternative adsorbents need to be studied to remove the broad spectrum of micro-pollutants (of different charges and molecular weights) to achieve sustainable water reuse.

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