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Rejection of Caffeine and Carbamazepine by surface coated PVDF hollow-fiber membrane system

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Abstract

This research investigates surface coated ultrafiltration (UF) polyvinylidene fluoride (PVDF) hollow fiber membrane for the removal of organic micropollutants (OMPs) in water. Coating of PVDF membranes with Poly (1-phenylethene-1,2-diyl) - Polystyrene solution through physical adsorption was carried out under two modes, 'dipped' and 'sprayed'. The performance of the coated membrane in the rejection of model organic micropollutants, caffeine and carbamazepine spiked in deionised water (at 300 $\mu\text{g/L}$ and 500 $\mu\text{g/L}$), correlated with the coating methods used. Dipped coated membrane showed a better removal of recalcitrant hydrophobic carbamazepine compared to the 'sprayed' coated membrane; while for both methods of coating, removal of caffeine was relatively insignificant. Inferably, hydrophobic interaction and size exclusion may be the major removal mechanism involved in the rejection by the coated membranes. The coating layer potentially enhanced reduction of pore size with resulting effect on membrane permeability and providing more sites for possible hydrophobic interaction.

1.0 Introduction

Organic micropollutants (OMPs) represent a wide spectrum of chemicals used in products that are consumed regularly in one form or the other. They are mostly discharged with wastewater into the environment, and are not efficiently removed by conventional treatment systems^{1,2}. Consumption of water containing a mixture of organic micropollutants over a prolonged period of time can pose a major severe health risk; therefore removal of OMPs in water and wastewater treatment can deliver positive impact on human and environmental health^{3,4}. The most important concerns about OMPs in the aquatic environment arises from the incompetence of conventional water and wastewater treatment systems in removing most of the pollutants⁵. **Although biological waste water treatment may remove most OMP, trace concentrations still remains. Therefore there is a need for innovative biological systems such as Membrane Bioreactors to remove OMPs at trace level concentrations.** Recently, significant amounts of OMPs have been detected in the discharge from municipal wastewater treatment plant (WWTP)^{6,7} and advanced treatment processes such as high pressure membrane filtration (Nanofiltration - NF and Reverse osmosis – RO) have been reported to be capable of removing a reasonable range of these compounds. Membranes predominantly remove pollutants in waste streams through sieving effect; however, with regards to removal of OMPs other separation phenomena come into play, which involve interactions between membrane surface and the pollutant as well as the solution chemistry of the waste stream. These phenomena may include charge interactions, sorption to membrane (adsorption and absorption) and sorption to fouling layer⁸⁻¹¹.

Low-pressure membrane filtration systems (Microfiltration-MF and Ultrafiltration–UF) have better ‘industrial presence’ at municipal level compared to high pressure membrane filtration (Nanofiltration-NF and Reverse osmosis- RO) due to the relatively lower capital and operation

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3 cost, and suitability for adaptation into conventional treatment processes ^{12,13}. However, earlier
4
5 studies suggest that low-pressure membrane systems are not capable of removing most OMPs
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7 compared to high pressure membrane filtration mainly because the **sieving ability** and other surface
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9 properties of the membrane materials involved are obviously not suitable in retaining most OMPs,
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11 which are usually small in molecular weight and are present at low concentration in water ^{13–15}.
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13 Nevertheless, some specific OMPs could be removed by tight UF membranes ^{13,16,17}.
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20 Some recent studies in membrane material technology are focused on improving membrane
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22 performances by functionalizing surface properties of membranes through surface modifications.
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24 Surface properties of membranes play a major role in the performance of the membrane especially
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26 in the flux decline, fouling phenomena as well as the overall selectivity of the membrane. In most
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28 cases, the main focus of surface modification of polymeric membranes involves management of
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30 desired interactions between membrane surface and solution components that contribute
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32 significantly to membrane fouling. The other aim is to improve the selectivity and/or formulate
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34 novel separation functions ^{18–21}.
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41 A variety of methods and techniques have been employed to modify the surface properties of
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43 polymeric membranes, most of which involves the use of complex processes and chemical routes.
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45 Frequently reported methods of surface modification available on commercial scale include coating,
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47 blending, grafting, chemical, composite and combined methods ^{19,22–25}. Surface grafting and
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49 blending are two common and most effective modifications used, which provides a more stable
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51 modification (physical and chemical stability) during the operation and cleaning process of the
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53 membrane ²⁶; however, on an industrial application they are considered complicated and costly.
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55 Grafting techniques used to initiate grafting may involve covalent bonding of single polymers or a
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3 mixture of polymers ²⁷ in a complicated chemical synthesis procedures including plasma,
4 photochemical or high-energy radiation (UV photo, electron beam etc.), enzymatic reactions ^{19,25}.
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6 Blending is achieved when two (or more) polymers are physically mixed together during membrane
7 preparation to obtain a desired functional property. This allows the preparation and modification of
8 the membrane to be achieved in a single step. However, membranes produced via this method
9 suffers from relatively low mechanical strength and contains a large quantity of blended additives
10 that do not contribute to the membrane functions.
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22 Coating through physical adsorption onto membrane surfaces by dipping is suitable for large scale
23 industrial production. Coating involves the formation or deposition of a functional thin film layer
24 that non-covalently adheres to the surface of the membrane ²². Surface coating is the simplest way
25 to improve the surface properties of an already prepared polymeric membranes. However, there is
26 the problem of instability of the coated layer which could be removed during the operation and
27 cleaning process because of the relatively weak physical adsorption interaction between the coating
28 material and the membrane surface ^{23,25,28}. Coating materials that can achieve stronger bonds are
29 potentially able to ameliorate this problem.
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43 While most applied surface modification studies have aimed at improving the fouling resistance
44 and selectivity of polymeric membranes, very little work has been done on investigating the
45 potential of surface modification of low-pressure membranes in the removal of OMPs. Therefore,
46 this research work will focus on evaluating the stability and efficiency of the physical adsorption of
47 the coating on the low-pressure UF PVDF membrane surfaces as well as the filtration performance
48 by measuring the membrane's ability to achieve enhanced removal of model organic
49 micropollutants (MOMP), which are commonly reported OMP in municipal waste streams; namely
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caffeine which has high water solubility and recalcitrant carbamazepine with relatively high hydrophobicity, in deionised water. Based on the experimental results and membrane surface characterisations, possible removal mechanism for the MOMP studied are analysed and proposed.

2.0 Experimental Methods

2.1 Materials

Surface modifications were conducted on commercially available ultrafiltration PVDF membranes (Hangzhou Microna Membrane, China), supplied as hollow fiber membranes and fabricated to suit the laboratory membrane modules, with nominal pore size of 0.02 μm , and inner and outer diameter of 0.9mm and 1.5mm, respectively.

Poly (1-phenylethene-1,2-diyl)-Polystyrene (average M_w 35,000) and density of 1.06 g/mL at 25°C, Carbamazepine (Carb, $\geq 98\%$ purity) and Caffeine (Caf, 99% purity) were purchased from Sigma-Aldrich Ltd and used as received without further purification. The physicochemical properties of Carb and Caf are shown in Table 1.

Table 1 Physicochemical properties of selected model organic micropollutants⁸ (MOMP).

MOMP	Water Solubility (mgL^{-1})	Log K_{ow}
<i>Caffeine</i> Stimulant	<i>18.7 at 16°C</i>	<i>-0.13</i>
<i>Carbamazepine</i> Anticonvulsant	<i>Insoluble</i>	<i>2.67</i>

2.2 Surface coating by polymer based material

Polystyrene coating solution of 5g/L concentration was prepared using acetone as solvent and allowed to shake for over 12h at 23°C to ensure complete dissolution and mixing of the polystyrene in the solvent. Two methods of surface coating was done; spraying and dipping methods (Figure. 1). The spraying procedure is as follows; surface of PVDF plain membranes were ‘sprayed’ using a hand pressurised sprayer placed at a distance of 12-15cm until the whole surface is completely wetted by the solution. Afterwards, the the solvent was allowed to dry, leaving the coated material physically adsorbed onto the surface of the membrane and forming a thin film on the surface. In the dipping procedure, raw PVDF membranes were immersed in the polystyrene solution and allowed to dry for 2-3h as the solvent evaporates and the polystyrene also forms a thin film layer on the membrane surface ^{29,30}. The coating procedure terminates once solvent evaporates, therefore coating is independent of rate of dipping but on the concentration of the coating solution. This method is similar to that reported by Lee et al. ²⁹ where multifunctional polymer coatings were produced through a simple dip coating of objects in an aqueous solution of coating material. Plain and coated membranes were then used for surface characterization and then fabricated into membrane modules to be used in the filtration experiments

Figure 1. Experimental protocol for surface modification and filtration tests

2.3 Ultrafiltration System

The schematics of the laboratory ultrafiltration setup is depicted in Figure 2. The filtration unit is a dead-end filtration setup which consist of a 10 liters volume feed tank, a membrane module (length of approximately 220mm and effective surface area of 34cm²), a peristaltic pump as suction pump with a vacuum pressure gauge to measure pressure across membrane (Transmembrane pressure - TMP), a reactor tank (4L) with the membrane module submerged into it.

Each experiment was performed with plain and modified membranes previously soaked in deionised water for 24 h in order to allow saturation of dry membrane pores and surface before filtration. Stock solutions of Caffeine and Carbamazepine were prepared in pure methanol and ethylacetate, respectively. Deionized water was spiked with the pollutants at 300 µg/L and 500 µg/L concentrations, and allowed to mix well. The pH in the reactor ranged from 6.7 to 7.1. The same concentration was maintained in the reactor tank and feed tank at the start of filtration experiment with average filtration time of 120 mins. The operating parameters for filtration is examined and the retention of pollutants as well as performance of coated membranes is observed. Equation (1) shows the removal obtained as a measurement of the efficiency of the membrane¹⁵.

$$R = \frac{C_f - C_p}{C_f} \times 100 \quad (1)$$

Where R is the removal (%) and C_p and C_f are concentrations of MOMP in the permeate and feed stream respectively. C_f is concentration in the feed after OMPs dosing at the beginning of the test and the permeate concentration C_p is the average permeate concentration obtained after the system has reached equilibrium, which is usually after 60mins of filtration.

Figure 2. Schematic representation of the laboratory ultrafiltration set up.

2.4 Analytical Methods

2.4.1 Water sample analysis

Solid phase extraction (SPE) sample preparation was done using the Chromabond Easy 6 mL, 500 mg SPE cartridges purchased from Hilchrom limited. The extracted samples were analyzed using the GCMS Perkin Elmer Clarus 500 Gas chromatograph; Clarus 560D Mass spectrometer with Elite Series GC capillary column $30\text{m} \times 0.25\text{mm} \times 0.25\mu\text{m}$. GC conditions were as follows; Caffeine - $1\mu\text{L}$ autosampler injection with oven conditions at 70°C initial temperature hold for 2mins and ramped to 280°C at 15°C per minute; Carbamazepine - $1\mu\text{L}$ autosampler injection with oven conditions at 50°C initial temperature hold for 1min, ramped to 180°C at 10°C per minute hold for 7mins, ramped to 220°C at 10°C per minute and then hold for 3 mins - Selected Ion Recording (SIR) MS scan mode with EI source was used since the samples contained single components³¹. Each sample and calibration standards were analysed thrice and the quantification was done using respective calibration standard curve

2.4.2 Membrane surface analysis

Scanning electron microscopy (SEM) characterization was performed to examine the membrane pore size, pore distribution and roughness. The JEOL JSM-7100F Field Emission Scanning Electron Microscope (operating at 5KV) equipped with an Energy Dispersive X-ray Detector was used. The SEM samples of plain and coated membranes were mounted on aluminium sample holders and then coated with gold before SEM analysis. Selected images from the SEM analysis were further analysed to obtain data on the pore size and pore distribution. For each type of membrane (i.e., plain, sprayed and dipped) an average of 20 SEM images from various locations on the membrane were analysed and the area of each micrograph analysed was $\sim 150\mu\text{m}^2$. Image analysis was performed using suitable image analysis software - Image J to obtain the data on the pore size and pore distribution³². Data on the thickness of coating layer was also obtained through the analysis. While analysing the selected SEM images, it was assumed that the representation is homogenous for all the membranes in individual modules.

Water contact angle measurements by the sessile drop method using the Kruss drop shape analyser – DSA25S were used to characterize the membrane surface hydrophobicity. The static contact angles were obtained immediately after dropping deionised water on the membrane surface. At least 7 measurements were repeated at different locations of each membrane surface.

2.4.3 MOMP molecular model analysis

The molecular weight (MW) is the most used parameter in characterizing the size of molecules, however, studies have shown that (MW) may not give a direct measurement of the size of the molecules^{8,33,34}. This becomes very important as size exclusion mechanism is been considered in solute-membrane interaction. The molecular length and width can be measured as geometric descriptors³⁴ which gives a good indication of the molecular size. Molecular length is the distance

between the two farthest atoms, while the molecular width and depth are measured by projecting the molecule perpendicularly to the plane of the length axis.

Molecular volume can give transport characteristics of molecules. The geometric indicators mentioned were determined using suitable molecular model analysis package – Avogadro software and results compared with earlier studies⁹. Molinspiration Property Calculation Services, a web based cheminformatics tool (www.molinspiration.com) was used to obtain information on the molecular volume of the MOMP. The molecular size and dimensions of MOMP are shown on Table 2. From the geometry shown, both pollutants have almost the same width size, but carbamazepine molecule is shown to have more length, depth and volume.

Table 2 Molecular properties - size and dimensions of MOMP

MOMP	Molecular Length <i>nm</i>	Molecular Width, Depth <i>nm</i>	Molecular Volume <i>nm</i> ³	Molecular Weight (g/mol)
Caffeine	0.98	0.70, 0.18	0.17	194.19
Carbamazepine	1.20	0.73, 0.58	0.22	236.27

3.0 Results and discussion

3.1 Membrane characterisation

Polystyrene as a surface coating material acts as a hydrophobic surface with a contact angle (CA) to water of approximately 85°³⁵ and its particles have a relatively rough surface because of their soft interface consisting of loosely bound and dangling polymers³⁶. Furthermore, polystyrene as a hydrophobic material can provide efficient anchorage onto hydrophobic PVDF membrane surface as well as forming a functional coating layer³⁷. In this experimental work the coating show good

and stable physical adsorption of coating material to the surface of PVDF membrane. The effect of the various coating regime on the hydrophobicity, pore size and distribution are shown to influence the performance of the membrane.

3.1.1 Effect of surface coating on membrane surface roughness and hydrophobicity

Images observed from the SEM (Figure 3a-f.) show that more coating layer is achieved in the 'dipped' coating compared to the 'sprayed' coating. The thickness of the coating layer measured are in the range of 0.05 μ m - 2 μ m and 6 μ m -10 μ m for the 'sprayed' and 'dipped' membranes, respectively. It could also be observed that while the membrane surface roughness increased in the coated membranes compared to the plain membranes, more irregularity in the coating thickness and surface of the active layer were observed in the dipped coating than the 'sprayed' coating, hereby increasing possible sorption site on the membrane surface for the dipped coated membranes. Physical adsorption onto membrane surface by dipping is suitable for the formation or deposition of a functional layer that adheres to the surface of the membrane^{22,24}. Kochan et al.³⁸ reported similar results with surface modification of PES ultrafiltration membranes by polyelectrolyte using layer-by-layer deposition technique to reduce the pore size (MWCO) of the membrane, consequently obtaining a better rejection performance by converting the membrane with open structure to a membrane with denser active layer.

Since Polystyrene is a hydrophobic coating material in this study, the coated surface is expected to remain hydrophobic. Contact angle (CA) measurements (Figure 3 g-i) show increase in hydrophobicity in the 'sprayed' and 'dipped' coating compared to the plain membrane (> 29%

increase) , with the latter recording higher contact angle measurements (Table 3). The CA measurements for the ‘sprayed’ showed a slightly lower range in results compared to the ‘dipped’, indicating a more uniform and homogenous coating layer with smoother morphology. Sorption of pollutants to the membrane surface through hydrophobic interaction/adsorption is expected to increase since coating layer and resulting surface roughness provides more sorption sites.

Figure 3. SEM Images of surface of plain(A) and modified membranes – ‘sprayed’ (B) and ‘dipped’ (C); all at x 50,000 magnifications; Contact Angle measurements by sessile drop methods Plain (D) and modified membranes – ‘sprayed’ (E) and ‘dipped’ (F)

Table 3. Static contact angle measurements

Membrane type	Static Contact angle measurement
Plain	71.93 ± 2.3
‘Sprayed’	92.50 ± 1.6
‘Dipped’	96.80 ± 5.7

3.1.2 Effect of surface coating on membrane pore size and distribution

The changes in the surface structure of membranes after modification can be monitored through the changes in the pore size and pore size distribution in response to the surface modification (Figure 3. and Figure 4). As can be observed the surfaces of the membranes were affected by the coating with the pore been evidently reduced in size and number (Figure 4). Also, the coating material – Polystyrene is expected to stay mostly on the surface of the membrane without significant deposition into the wall of the pores since its molecular size is 0.018μm³⁹ which is close to (or greater than) the nominal pore size of the plain membrane. The Image analyses show that the plain membranes has an nominal pore size of 0.016μm while the ‘sprayed’ and dipped membrane showed an nominal pore size of 0.011μm and 0.013μm, respectively (Table 4). The plain membrane showed a wider pore distribution compared to the sprayed and dipped membrane which generally have more pore size lower than the average pore size of the plain membrane (Figure 4). This may indicates a prospective improvement in the performance in the rejection by sieving effect in the modified membranes since 19 -31% reduction in the nominal pore size was achieved through the modification.

Surface coating by dipping is the simplest way to improve the surface properties of an already prepared polymeric membranes. The coating modification occurs mainly in most cases, around the surface of the membrane, excluding the wall of the pores inside the membrane. This is due to the limited diffusion ability of the coating material into the membrane pores²⁵. The membrane structure is also seen from SEM images, to be stable and uncompromised after the coating procedure.

Figure 4. Pore size distribution of the plain (A) and modified - ‘sprayed’ (B) and ‘dipped’(C) membrane obtained from SEM image analysis.

Table 4 Nominal pore size and pore distribution of plain and modified membranes

	Plain membrane	Modified membrane	
		‘sprayed’	‘dipped’
Nominal pore size (μm)	0.016	0.011	0.013
Pore size standard deviation	± 0.010	± 0.012	± 0.009

3.2 Operation conditions of coated membrane system

The dipped coating produced about 200% increase in TMP during filtration, while the pure water permeability (PWP) decreased by 63% compared to the plain membrane, while the ‘sprayed’ coating showed little increase in TMP and 33% decrease in PWP compared to plain membranes (Table 5). This is due to the effects of the coating. Average transmembrane pressure (TMP) across the membrane during filtration of synthetic wastewater is shown to be influenced by the method of coating (Figure 5.). Average TMP of 219 mBar with corresponding flux of 24 L/m²hr and PWP of

117 L/m²hrBar is shown to be reasonable compared to operating conditions of UF and NF system of similar studies and typical industrial scale water treatment application (Table 5). The flux was observed to be consistent throughout the filtration time depending on the type of membrane used, and no fouling was observed. However, it must be noted that the water matrix (Deionised water) and operating time (120 mins) used in this study is far from ideal situations as other constituents in feed of real surface water and wastewater could impact on the operating conditions causing significant changes in filtration process.

Figure 5. Average Transmembrane pressure for the plain and modified membranes for experiments with carbamazepine and caffeine respectively; Plain (A) and (B); ‘Sprayed’ (C) and (D); ‘Dipped’ (E) and (F).

Table 5 Average TMP and computed flux for the plain, ‘sprayed’ and ‘dipped’ membrane during UF filtration compared to similar studies with wastewater.

	Plain	‘Sprayed’	‘Dipped’	UF ¹³	NF ¹³
Pure water permeability, PWP (L/m ² .hr.Bar)	317	212	124	70.5	7.6

Average TMP (mBar)	76	90	219	6000	30000
Flux Computed (L/m ² /hr)	24	19	25	423	228

3.3 Removal of MOMP in deionised water filtration experiment

The performance of the coated membranes in the removal of model organic micropollutants (MOMP) was dependent on the method of surface coating as well as the physicochemical properties and concentration of the MOMP. It was found that membranes modified by ‘dipped’ coating method performed better than membranes modified by ‘sprayed’ coating especially for carbamazepine. The percentage removal of caffeine at concentrations 300µg/L and 500µg/L in the plain and modified was less than 20% (Figure 6.), while with the carbamazepine, more than 20% removal was achieved with the dipped membrane achieving greater than 50% removal (Figure 6.). The high retention achieved by the ‘dipped’ coating can be attributed to the greater number of sorption sites, smaller pore sizes and greater surface roughness compared to the ‘sprayed’ coating. UF systems are usually incapable of removing caffeine and carbamazepine at trace concentrations as studies show relatively low percentage of removal compared to NF/RO systems¹³. This is consequent to the molecular weight (and/or dimensions) of the compounds being smaller than the pore size range of UF membrane. However, adsorption is reported to be the predominant removal mechanism in UF compared to size exclusion.^{15,40–42}

Correlation between the hydrophobic interaction/adsorption and the compound’s octanol-water partitioning coefficient (Log K_{ow}), solubility and the membrane pure water permeability was shown to be evident in recent studies⁴⁰. Hydrophobic interaction between OMPs and membrane surface also affects the adsorption phenomena. Hydrophobicity of OMPs, which is a function of octanol–

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3 water partition coefficient ($\log K_{ow}$), and the hydrophobicity of the membrane surface, determined
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5 by contact angle measurements⁴³, both promoted interaction and adsorption of hydrophobic OMP
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7 onto the hydrophobic membrane surfaces. Generally compounds with relatively high
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9 hydrophobicity ($\log K_{ow} > 2.5$) are expected to adsorb onto solid phases rather than being soluble in
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11 water. Hydrophobic OMPs are therefore expected to adsorb onto the hydrophobic membranes
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13 surfaces by hydrophobic interactions. In this study, carbamazepine has a higher $\log K_{ow}$ compared
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15 to caffeine, and coupled with the 'dipped' membrane having a higher surface hydrophobicity (Table
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17 3), this has contributed to the higher removal of Carbamazepine in dipped membranes observed.
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24 Size exclusion mechanism is mostly observed with uncharged (neutral) OMPs as studies show a
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26 correlation between rejection of uncharged OMPs and their molecular weight, volume and/or width
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28^{44,45}. Suggested explanation for the trend observed in this study is that Caffeine with smaller
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30 molecular dimensions and volume and high water solubility compared to carbamazepine (Table 1
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32 and 2) is likely to pass through the coated membranes. Although both pollutants' molecular length
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34 (and/or width) are smaller than the nominal pore size of coated membranes, comparison between the
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36 molecular length of both pollutants and the pore size distribution of the coated membranes suggest
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38 that carbamazepine with molecular length of 1.2 nm (0.0012 μ m) is likely to be retained more than
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40 caffeine, as supported by the filtration results which show a higher removal of carbamazepine. Also,
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42 the shape of the pores may have been altered by the surface modifications which can also affect the
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44 removal phenomena as studies show that pore geometry can affect the selectivity of UF membranes;
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46 slit-shaped pores seen to perform better than cylindrical pores³³. Although the pore geometry is not
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48 studied in this work.
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In general, comparison between percentage removal in all membrane types for Carbamazepine is greater than Caffeine at both concentrations except for the plain membrane at 500 μ g/L concentration where the percentage removal is fairly similar. The molecular shape and volume (Table 2) of the pollutants may have also influenced their removal by size exclusion. Both pollutants are uncharged implying that charge interaction between the compound and the charged coated membrane surface is minimal. While hydrophobic adsorption contributes to removal, it must be noted that membrane fouling can be escalated by the hydrophobicity of the membrane affecting membrane operating conditions⁴⁶. Nghiem et al.¹⁴, while using 'loose' NF to filter pharmaceuticals including carbamazepine, reported poor and variable OMP removal rates and concluded that changes in solution chemistry parameters such as pH has great influence on the removal rate by affecting the charges of targeted compounds, and the ionic strength of the organic micropollutants.

Figure 6. Removal of Caffeine and Carbamazepine in single-component filtration test by plain and modified membranes from MOMP: (a) at concentrations of 300 μ g/L; (b) at concentrations of 500 μ g/L ('Sprayed' and 'Dipped')

It must also be emphasized that the synthetic waste stream used was Deionized water containing only single components of pollutant at a time. The results might be significantly different in a real wastewater matrix. Other water matrices will be studied in the future work. A recent relevant study in a nanofiltration laboratory test of using membranes with pore size of 0.002 μ m to filter selected pollutant including carbamazepine spiked at trace concentrations into water treatment plant effluent was able to achieve only 31-39% removal⁴⁷. This was due to the effects of electrostatic interaction based on the solution chemistry, charge of pollutants and surface charge of the membranes⁴⁷.

A plot of percentage removal against PWP (Figure 7) shows the effect of PWP on the removal efficiency. The plain membrane with the highest PWP recorded lowest overall removal of the MOMPs while the 'dipped' coated membrane with significantly lower PWP recorded higher removal of hydrophobic carbamazepine at both concentrations. This phenomenal has posed questions for researchers trying to understand the impact of membrane micro-structure (or pore characteristics) on the trade-off between the selectivity and permeability for UF membranes^{33,34}. Membrane with smaller pores are likely to have lower permeability and better selectivity and vice versa. The major challenge will be how to achieve a balance between these two crucial parameters for membrane performance.

Figure 7. % Removal against membrane PWP (Plain-317 , Sprayed-212 and Dipped-124)

3.4 Possible removal mechanism by modified membrane surface

The removal of organic micropollutants (OMP) is governed by different parameters based on the membrane characteristics, aqueous media/solute characteristics, operating conditions, membrane fouling as well as OMP characteristics^{8,48–50}, but generally membranes are designed to work as a physical barrier (semi-permeable) that rejects components greater than its pore size while allowing water to permeate through it. However, studies have shown that other significant physicochemical phenomenal activities occur during membrane processes out of which sorption is considered one of the major phenomena contributing to removal of pollutants in membrane processes^{9,40}.

Removal mechanism such as size exclusion, charge interaction, hydrophobic interaction/adsorption as well as fouling mechanism of membranes has been altered through various surface modification methods in earlier studies^{18,19,22–25}. Loose UF membranes have also been surface modified to enhance the selectivity by making the pore sizes smaller after modification and/or adding charged coating materials to improve selectivity by charge repulsion^{18,38}. In this study,

the coated surface has properties suitable for promoting hydrophobic interaction/adsorption of hydrophobic pollutants as well as rejection by size exclusion (Figure 8.). Sorption of pollutants to the membrane surface through hydrophobic interaction/adsorption is expected since coating layer and resulting rough morphology provides more sorption sites^{9–11,13,17}. Although, Polystyrene can be used as a surface charge regulator and so it is mostly charged in aqueous solution⁵¹; however, the MOMP studied are both uncharged in deionised water^{13,47}, therefore charge interaction between the surface of the coated membrane and the MOMP are not expected to contribute to their removal in the filtration test.

Figure 8. (A) Representation of coating of membrane surface by polystyrene showing hydrophobic anchorage; (B) Schematic representation of the possible removal mechanisms coated membrane.

4.0 Conclusions

Surface modification of polymeric membranes is usually performed to improve surface properties of membranes so as to enhance fouling resistance as well as improve desired and relevant removal mechanism of pollutants. Physical adsorption of hydrophobic polystyrene as a facile and suitable way to enhance surface characteristics of the PVDF UF membrane has been demonstrated in this paper. Reasonable removal of recalcitrant carbamazepine by coated membrane was observed while removal of hydrophilic caffeine was relatively low. Hydrophobic interaction/adsorption and size exclusion are suggested to be an influence in the removal by the coated membrane since carbamazepine with larger molecular size, volume and higher Octanol-Water Partition Coefficient-Log K_{ow} showed higher removal rates especially at higher concentrations. Filtration experiments show an overall better removal of MOMP in modified membranes compared with plain unmodified membranes. Effectively, the coated UF membrane exhibited some NF characteristics in regards to the removal of trace organic micropollutants without any significant corresponding change in operating conditions that the coating may have impacted. TMP during filtration of MOMP increased from 76 to 90 to 219 mBar for plain, sprayed and dipped, respectively. Similarly, a slight decrease in flux 24, 19 to 25 L/m²hr for plain, sprayed and dipped, respectively. This research therefore, suggests that physical adsorption of functional polymers is a simple and efficient way to modify the surface of polymeric membranes for water filtration application. Further investigations into the use of better coating material to address the problem of fouling alongside organic micropollutants removal is recommended.

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For Table of Contents Only/Abstract Graphic

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60