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Preparation and characterization of a PVA/PSf thin film composite membrane after incorporation of PSSMA into a selective layer and its application for pharmaceutical removal

Fatemeh Medhat Bojnourd, Majid Pakizeh*

Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, P.O. Box 9177948974, Mashhad, Iran

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ABSTRACT

A thin film composite (TFC) membrane was synthesized by coating a layer of poly (vinyl alcohol) (PVA) cross-linked with Glutaraldehyde on a polysulfone (PSf) ultrafiltration support membrane. The effect of the incorporation of polyelectrolyte poly (4-styrenesulfonic acid-co-maleic acid) (PSSMA) into the PVA matrix at concentrations of 0% to 3% was investigated. The TFC membranes were characterized by field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), attenuated total reflection Fourier transform infrared (ATR-IR) spectroscopy, contact angle and zeta potential measurements. The rejection rates were measured for Na_2SO_4, $MgSO_4$ and NaCl salts and cephalexin, amoxicillin, ibuprofen and povidone iodine (PVP-I) pharmaceuticals. The effect of molecular weight and size, hydrophobicity, and electrical charge of the pharmaceuticals on the rejection of the TFC membranes was also investigated. It was found that incorporation of PSSMA into the PVA layer could increase membrane pure water flux (PWF). The results revealed that the addition of 1% PSSMA (TFC1) increased PWF from 6.8 to 14 l/m^2 h and showed comparable rejection rates for all membranes. For this sample, rejections of 99%, 97.7%, 93.8% and 74% were obtained for cephalexin, amoxicillin, PVP-I and ibuprofen, respectively. The effects of pH, transmembrane pressure and feed concentration on pharmaceutical separation performance were also studied. The rejection of ibuprofen increased from 74.1% to 97.2% after an increase in pH from 7 to 9. Near 100% rejection for cephalexin and amoxicillin and 80% for ibuprofen at a 20 ppm feed concentration showed the ability of the membrane for efficient pharmaceutical removal at low concentrations. An increase in transmembrane pressure increased the rejection of ibuprofen and PVP-I. For cephalexin and amoxicillin, a plateau occurred in the range of 97–99%.

1. Introduction

The worldwide consumption and production of pharmaceuticals for healthcare is continually increasing. Moreover, the release of pharmaceuticals into the water, from the sources such as domestic effluent and factory discharge, influences the ecosystem and human health [1]. Pharmaceuticals are potential bioactive chemicals which are specifically designed, produced and used with the purpose of affecting living cells [2,3]. As a result, their release into the environment can have unforeseen adverse effects on ecological species [4]. The concentration of pharmaceuticals is currently not regulated in many drinking water directives worldwide, but they have been recommended for maximum removal using new and existing treatment techniques [5]. The World Health Organization has suggested that a sustainable solution for prevention of the entry of pharmaceuticals into the water environment should be achieved by the application of more efficient wastewater treatment systems [6].

Existing treatments include coagulation-flocculation, adsorption, oxidation and advanced oxidation (i.e. ozone, UV), biological treatment and membrane separation [7,8]. Among these techniques, pressure-driven membrane processes such as reverse osmosis (RO) and nanofiltration (NF) are promising alternatives for removal of pharmaceuticals. They are also suitable for retrieval and retreatment of antibiotics and other valuable pharmaceutical compounds from waste [5,9–11].

Polyamide thin-film composite (TFC) membranes fabricated by interfacial polymerization of amine and acyl chloride monomers on the porous support membranes have been used as RO and NF membranes for pharmaceuticals removal [12]. The hydrophobic polyamide active layer, which is suitable for rejection of salts, facilitates passage of non-ionized hydrophobic organic solutes and insufficient removal rates have been observed for some pesticides, pharmaceuticals and endocrine-disrupting compounds [13–15]. In addition, polyamide membranes

* Corresponding author.
E-mail address: pakizeh@um.ac.ir (M. Pakizeh).

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have low chemical resistance to chlorine attack, which shortens their use life in water recycling applications. A decrease in the rejection of pharmaceuticals has been reported by exposure of various types of polyamide membranes to hypochlorite solution [16,17]. Some studies have modified the surface of the commercially-available polyamide membranes to target pharmaceuticals removal [18–20]. However it is essential to exploit TFC membranes with high chemical stability in which the polyamide layer has been replaced with a more hydrophilic one.

Poly (vinyl alcohol) (PVA) is one of the best candidates for the formation of a membrane selective layer because it is water soluble, biodegradable, inherent hydrophilic, has good film-forming properties and excellent thermal, mechanical and chemical stability. It has been applied as a barrier layer for the preparation of TFC NF membranes. Many studies on NF membranes with a PVA selective layer have focused on desalination performance. Gohil et al. [21] prepared TFC NF membranes with a barrier layer of PVA cross-linked with maleic acid (MA) on a porous polysulfone (PSf) support. The effects of parameters such as PSf, PVA and MA concentration and curing time on membrane performance (flux and rejection of inorganic salts) have been studied. The optimum membrane showed 22.8% and 83.8% rejections for NaCl and $MgSO_4$ respectively and a pure water flux (PWF) values less than 300 l/m^2d at 150 psi. Jahanshahi et al. [22] prepared a PVA TFC membrane by dip-coating and crosslinking with glutaraldehyde (GA). The membrane exhibited a PWF of 69.0 l/m^2h and NaCl and $MaSO_4$ rejections of 25.0% and 72.0%, respectively. Peng et al. [23,24] fabricated a TFC NF membrane by depositing an ultra-thin and defect-free PVA layer on a PSf ultrafiltration support membrane through a multi-step coating procedure and a new *in situ* crosslinking technique. They found that the pure water permeability and salt rejection of the composite membrane correlated strongly with the extent of crosslinking in the PVA film.

Recent studies have shown that incorporation of polyelectrolytes has improved the performance of NF membranes in terms of water permeability and rejection rates, because polyelectrolyte-modified membranes have higher surface charge densities [25]. The incorporation of polyelectrolyte poly (sodium-p-styrene-sulfonate) into the PVA matrix of the TFC membrane was studied by Liu et al. [26]. The results revealed that the modified TFC membrane showed increased water flux, but the NaCl rejection decreased from 70% to less than 50%. In addition, the molecular weight cut-off increased from 1350 to 3800 Da as a result of the decline in the extent of crosslinking of the skin layer.

The current study was undertaken to develop a TFC membrane with a PVA selective layer and improve its water permeability and selectivity by incorporating polyelectrolyte poly (4-styrenesulfonic acid-co-maleic acid) (PSSMA) and increasing the crosslinking of the selective layer. The TFC membranes were characterized using different methods. They were also tested for their removal rates of salts and pharmaceuticals. To the best of our knowledge, there has been no report on the application of a PVA/PSf TFC membrane for pharmaceuticals removal from water. The selected pharmaceuticals were cephalexin, amoxicillin, ibuprofen and povidone-iodine (Betadine®), popular in human medical care as antibiotics, analgesics and disinfectant compounds. The structure and physicochemical characteristics of the selected pharmaceuticals are shown in Table 1. This study is the first to report on povidone-iodine (PVP-I) removal by a membrane process. This disinfectant kills germs for medical purposes but also inactivates microorganisms in wastewater treatment systems, which can cause system failure and decreased treatment efficiency [27]. Preventing of the entry of povidone-iodine into a biological treatment system is necessary and membrane separation appears to be an appropriate choice.

2. Experimental

2.1. Materials

PSf (Ultrason 6010) was supplied by BASF (Germany) as a polymer for preparation of the support membrane. Di-methyl formamide (DMF; Merck) was used as a solvent and sulfuric acid (Merck; 98%) as a catalyst. PVA (86–88% hydrolysis, Mw 130,000 g/mol), PSSMA (Mw 20,000 g/mol) and GA (50% solution) as crosslinking agent were purchased from Sigma-Aldrich. NaCl, $MgSO_4$ and Na_2SO_4 salts (Merck) were of analytical grade and used as model solutes to determine the salt rejection characteristics of the resultant TFC membranes. Pharmaceutical powders were kindly supplied by Daana Pharmaceutical Company (Iran). Deionized (DI) water was used to prepare the aqueous solutions and to soak and rinse the membrane samples during experiments.

2.2. Preparation of TFC membrane

The asymmetric support membranes were prepared by phase inversion as explained elsewhere [21]. The PSf solution (16% w/w) was prepared in DMF under constant stirring for a dissolution period of 15 h. The solution was kept at room temperature for 4 h for removal of air bubbles. Afterwards, the homogeneous solution was cast at a thickness of 175 μm on a glass plate for characterization and on non-woven polyester for permeation testing using an adjustable casting bar (Neurtek 2281205). The glass plate with the cast solution was kept for 10 s in ambient conditions and then the support was immersed in a distilled water bath for at least 24 h for removal of most of the solvent. The PSf ultrafiltration (UF) support membrane was removed from the bath, rinsed with DI water and surface dried under an intense nitrogen gas stream for few seconds just before coating.

PVA powder was dissolved in DI water at 90 °C under stirring for about 8 h. PSSMA powder was also dissolved in DI water at ambient temperature under stirring for about 8 h. The PVA solution was cooled to room temperature and the PSSMA solution was added under continuous stirring for 12 h to prepare the coating solution. The aqueous coating solution contained 1.0% (wt) PVA and 0% to 3% (wt) PSSMA. The coating procedure was as follows [22]: The substrate (porous PSf membrane and non-woven polyester) was immersed in coating solution for 5 min. The excess solution was removed by holding the substrate in a vertical position until a uniform dry surface was observed. The membrane was then immersed in 4% (wt) aqueous solution of GA as a cross-linker and 0.5% (wt) H_2SO_4 as catalyst for 20 s. The prepared membrane was finally heat-cured at 100 °C for 3 min. The resultant TFC membrane was washed thoroughly with DI water and stored wet until use. Membranes prepared with PSSMA contents of 0%, 1%, 2% and 3% (wt), hereinafter are referred to as TFC0, TFC1, TFC2 and TFC3, respectively.

2.3. Membrane characterization

2.3.1. Scanning electron microscopy and field emission scanning electron microscopy

To investigate the morphology of prepared membranes, various analytical methods were utilized. The topography of the surface and cross-sections of the PSf support and TFC membranes was observed with a scanning electron microscope (SEM; LED 1450 VP; Germany) and a field emission SEM (FESEM; Tescan; Czech Republic). For cross-sectional observation, the membranes were prepared by cryogenic fracturing after immersing in liquid nitrogen.

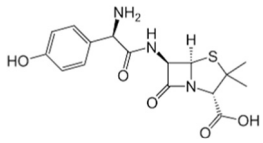
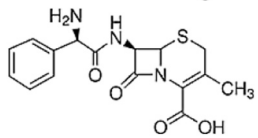
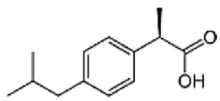
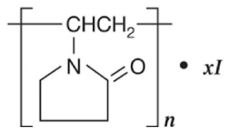
2.3.2. Attenuated total reflection infrared spectroscopy

The functional groups and bonds on the near-surface region of the TFC membrane were analyzed using attenuated total reflectance infrared (ATR-IR) spectroscopy. The ATR-IR spectra of the prepared membranes were recorded on a Thermo Nicolet Nexus 100 ATR-IR coupled to a ZnSe crystal at a 45° operating angle.

2.3.3. Atomic force microscopy

Atomic force microscopy (AFM) images were obtained using an

Table 1
Physicochemical properties of the pharmaceuticals.

Pharmaceutical	Molecular structure	Mw (Da)	pK_a	Log D (pH = 7)	r_s (nm)
Amoxicillin		365.4	2.4 7.4 9.6	−2.21	0.49
Cephalexin		347.4	2.56 6.88	−2.40	0.47
Ibuprofen		206.3	4.4	1.21	0.34
Povidone-iodine		10,000–40,000	–	–	–

Data were collected from Refs. [28–35].

Easyscan 2 Flex instrument (Nanosurf; Switzerland). The surface roughness parameters of the membranes were calculated from the AFM images by the system software.

2.3.4. Contact angle measurement

The sessile drop contact angle method of DI water OCA15 plus a goniometer (DataPhysics; USA) was used for measuring membrane sample contact angles. The data was reported as the mean value of three samples, which were taken as averages of the left and right plateau contact angles at three sites for each sample.

2.3.5. X-ray diffraction

The crystal structures of the composite membranes were observed using X-ray diffraction (XRD; Brüker AXS D8; Germany) at 2θ angles between 10° and 80°.

2.3.6. Zeta potential measurement

The surface zeta potential of the composite membranes at neutral pH was calculated by streaming potential measurements, which were carried out in 0.001 mol/l KCl aqueous solution at 25 °C employing a streaming potential analyzer (Anton Paar; Austria).

2.4. Membrane testing experiments

Membrane separation performance in terms of PWF and solute rejection rate was evaluated using the cross-flow permeation test. All permeation tests were conducted using the circulation model at a constant temperature of 25 °C and pressure of 8.0 bar unless otherwise specified. A cross-flow filtration apparatus was used with a circular filtration cell having an effective membrane area of 0.00138 m^2. All circular TFC membrane coupons loaded in the filtration cell were pressured at 9.0 bar with DI water for at least 3 h to reach a stable PWF before each test.

The PWF (l/m^2h) was calculated as:

$$PWF = \frac{V}{At} \tag{1}$$

where V is permeate volume (l), A is membrane area (m^2) and t is permeation time (h).

Solute rejection (R) was calculated as:

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100 \tag{2}$$

where C_P and C_F are the solute concentration in the permeate and feed streams, respectively.

The concentrations of Na_2SO_4, $MgSO_4$ and NaCl were obtained through conductivity measurements of the aqueous solution using an electrical conductivity meter (Extech EC-400; USA). The concentrations of amoxicillin, cephalexin, ibuprofen and PVP-I were determined from their UV absorbance values at 229, 263, 265, and 288 nm, respectively, measured using a UV–visible spectrophotometer (Optizen POP; Mecasys; South Korea). The detection limit was about 0.2 ppm for cephalexin, ibuprofen and PVP-I and 0.5 ppm for amoxicillin. The filtration system was operated for the individual pharmaceutical or salt solutions in separate runs. This approach permitted quantification by UV absorption or electrical conductivity analysis. For each pharmaceutical, after compaction with DI water, the system was operated and stabilized for at least 2 h after replacing the feed with pharmaceutical solution and prior to sample collection for analysis.

3. Results and discussion

3.1. Characterization of TFC membranes

SEM and FESEM micrographs of the porous PSf support membrane and PVA/PSSMA composite membranes are provided in the Supplementary Information (SI; Fig. 1S). The structure of the PSf membrane with asymmetric morphology and a distinct PVA layer with an approximate thickness of 1 μm (cross-section) are shown in Fig. 1Sa and Sb.

The porous surface of the PSf support membrane and TFC3 membrane (containing 3% PSSMA) are shown in Fig. 1Sc and Sd, respectively. In the TFC3 membrane, the homogenous surface with perfectly-distributed PSSMA indicates that the PSSMA polymer chains were evenly distributed within the PVA matrix in the skin layer and the cross-linked PVA layer formed successfully on the substrate surface.

The chemical groups of the membranes surface were identified using ATR-IR. The reaction of PVA with GA and PSSMA and the schematic network structure of the TFC membrane are shown in Figs. 1 and 2, respectively. During TFC1 to TFC3 membrane preparation, cross-linking between the −OH groups of PVA and −COOH groups of PSSMA

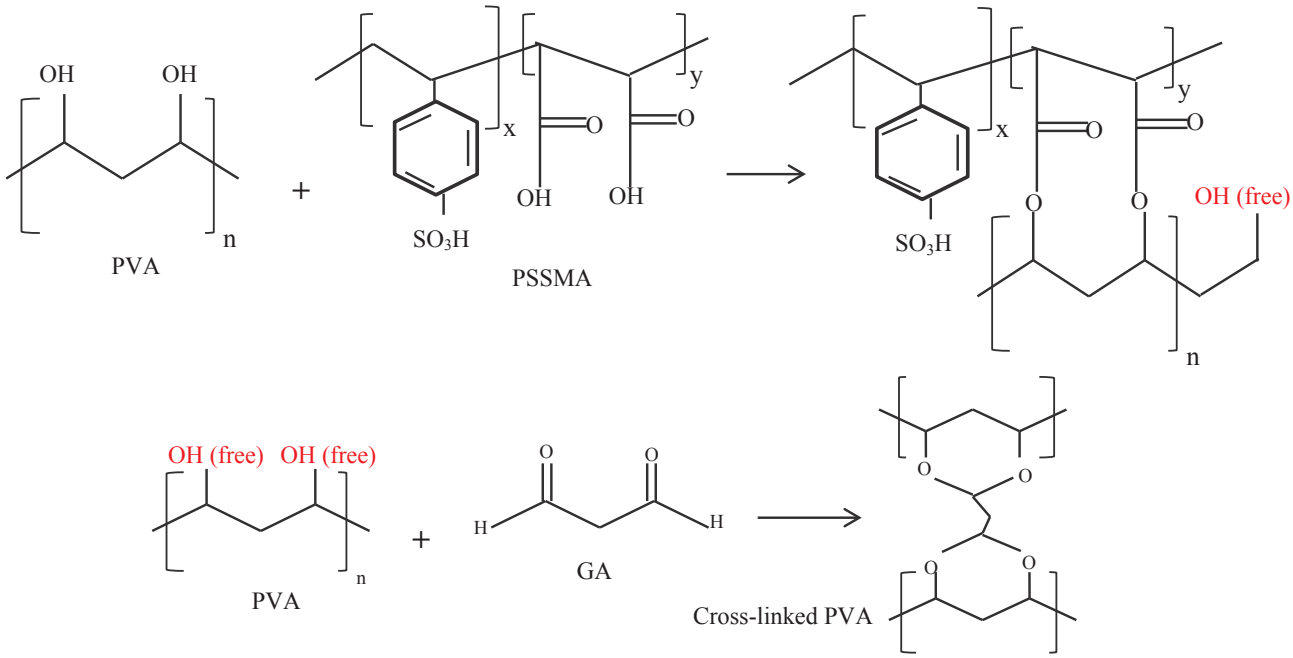


Fig. 1. Reactions of PVA with GA and PSSMA.

occurred [36]. In addition, free hydroxyl groups in the PVA matrix cross linked with GA and a polymeric network was formed on the membrane selective layer. Fig. 3 presents the normalized spectra of the TFC membranes at different PSSMA contents. The peaks in the spectra of all TFC membranes clearly illustrate the presence of PVA, PSSMA and GA.

Absorbance in the 3200–3600 cm^{-1} range can be attributed to −OH stretching in the PVA polymer chain and pendent −COOH groups of PSSMA. It is also related to the hydrogen bond between the −OH of

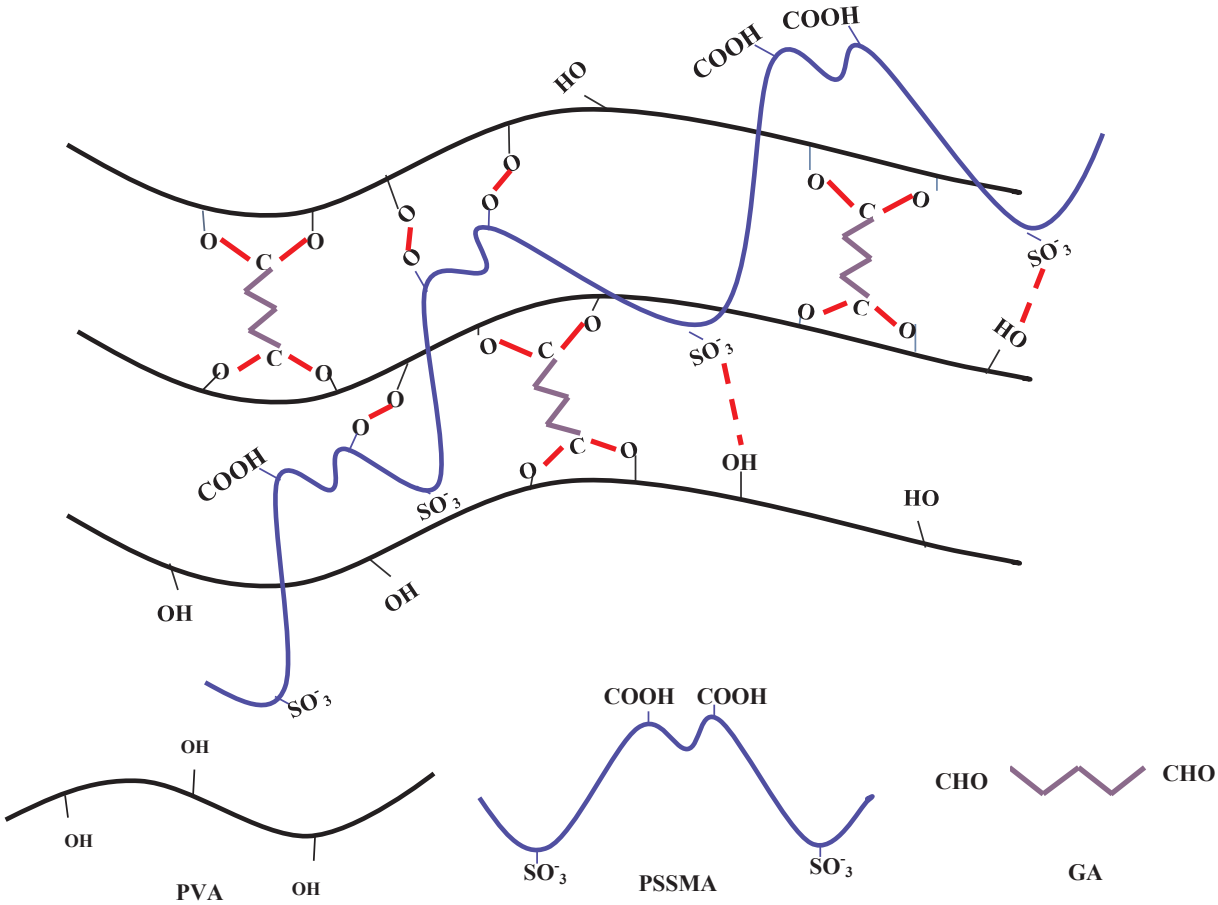


Fig. 2. Schematic polymeric network surface structure of TFC membrane.

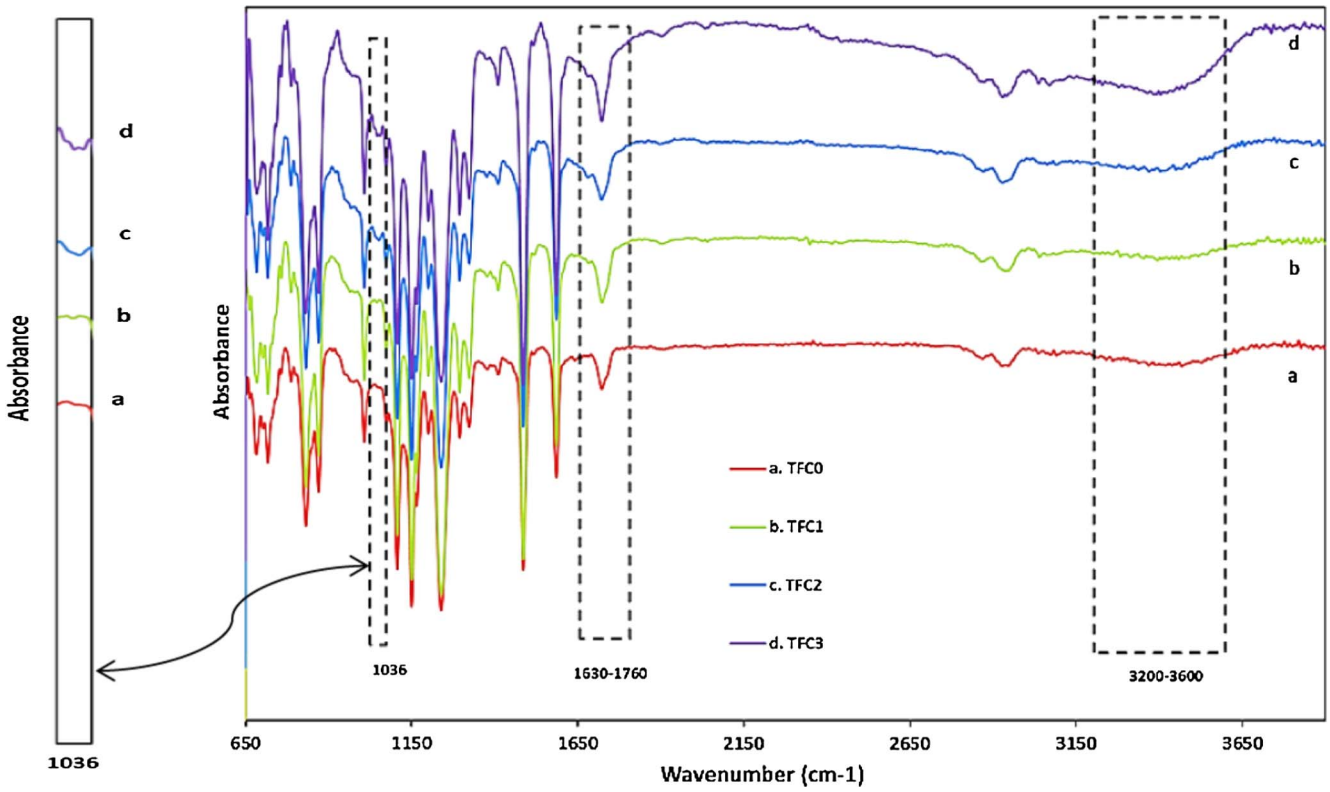


Fig. 3. ATR-IR spectra for the surfaces of TFC membranes, TFC0 (a), TFC1 (b), TFC2 (c) and TFC3 (d).

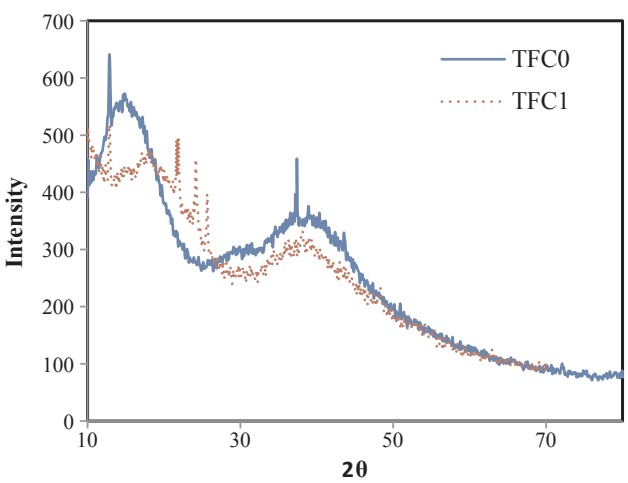


Fig. 4. X-ray diffraction spectra for TFC0 and TFC1.

PVA and $-SO_3H$ of PSSMA, but this cannot be identified separately because of the overlap of the OH–OH and SO_3H–OH bands [36]. The intensity of this band decreased as the extent of crosslinking increased due to the decrease in the number of –OH groups [23]. The spectra of the TFC1 and TFC3 membranes (Fig. 4d and f) show the weakest and strongest peaks at 3200–3600 cm^{-1}, respectively. These relate to the extent of crosslinking in the samples and unreacted –OH groups. The strong peak at 1630–1760 cm^{-1} denotes the –C–C=O–C– groups in the PVA–GA cross-linked film and stretching of the –C=O– bond in the –C=O–O–C– groups in PVA cross-linked with dicarboxylic acid (MA groups). The intensity of this peak is also an indicator of the extent of crosslinking [23,24].

Fig. 3 shows that the intensity of the strong peak at 1630–1760 cm^{-1} for the TFC1 and TFC3 membranes was higher than for other membranes. The strong peak in this region and weak –OH group peak suggest that appropriate crosslinking has been achieved on the TFC1 upper layer. For the TFC1, TFC2 and TFC3 spectra, there is a weak absorbance band at 1630–1760 cm^{-1}. Peng et al. [24] claimed that two peaks at this region were observed because of incomplete crosslinking of the –C=O– groups. The second band is very weak for TFC1, but for TFC2 and TFC3 it is more clear, which indicates more unreacted C=O– groups in the TFC2 and TFC3. The incorporation of PSSMA into the skin layer of the TFC1 membrane increased the crosslinking between the PVA chains because of existing MA groups. However, this incorporation increased the unreacted C=O– groups and –OH groups in the TFC2 and TFC3. The small band at about 1036 cm^{-1} for TFC1 to TFC3 arises from the stretching vibrations of SO_3^- in the PSSMA polymer chain [26]. The intensity of the band in this region increased from TFC1 to TFC3, which illustrates the increase in the PSSMA content in the PVA layer.

The membrane surface topography was characterized using AFM measurement. The root mean square roughness (RMS) and peak-to-valley distance (R_{pv}) of the membrane surfaces are listed in Table 2. Three-dimensional AFM images of the TFC membranes are provided in the SI (Fig. 2S). The membrane surface hydrophilicity was evaluated by measuring the contact angle between the membrane surface and the air–water interface. The contact angle measurements are also listed in Table 2.

It was found that the membranes had smooth surfaces with small roughness parameters. The RMS of the composite membrane for TFC1 increased slightly in comparison with that for TFC2, but the R_{pv}

Table 2
RMS, R_{pv} and contact angle values of the TFC membranes.

Membrane	RMS	R_{pv}	Contact angle (°)
TFC0	0.81	7.301	61.06 ± 0.34
TFC1	0.86	5.735	60.77 ± 0.28
TFC2	0.79	7.934	57.05 ± 0.82
TFC3	0.89	5.972	55.32 ± 1.25

decreased. It appears that the addition of PSSMA resulted in a relatively smoother surface for TFC1. For TFC2, the RMS of the composite membrane decreased slightly, but the R_{pv} increased. For TFC3, the RMS increased, but the R_{pv} decreased.

A slight decrease was obtained in the surface contact angle of TFC1 in comparison with TFC0. The decreasing trend continued to TFC3, which had the lowest contact angle of the four studied membranes. Because the roughness parameters are relatively similar, it can be concluded that the decrease in contact angle was a result of the chemical natures of the membrane surfaces and not their morphology. It was suggested that the addition of PSSMA, having solfunate and carboxyl groups, decreased the surface contact angle and increased the membrane surface hydrophilicity.

The crystalline properties of the PVA film are shown in the XRD results in Fig. 4. The extent of crosslinking controlled the crystallinity of the film and affected TFC membrane performance [23]. The peak at about $2\theta = 19^\circ$ is characteristic of crystalline regions of PVA. From XRD analysis, it is evident that for the TFC1 membrane with a PSSMA content of 1%, the characteristic PVA peak is nearly flat and has dispersed into several small peaks. This suggests that the incorporation of PSSMA destroyed the semi-crystalline structure of the PVA film because of the excess crosslinking and separation of the PVA chains. This result has been confirmed by Peng et al. [24]. They showed that the characteristic peak of the PVA TFC membrane with 40% crosslinking had declined and separated into several small peaks in comparison with that at 10% crosslinking.

The membrane surface charge was determined by measuring the surface streaming potential. The calculated zeta potentials of the composite membranes at pH 7.0 are presented in Fig. 5. As seen, the surface of the composite membrane into which PSSMA was incorporated became more negatively charged. The absolute value of the surface zeta potential at pH 7.0 increased from 8.6 mV for the TFC0 sample to 13.4, 22.8 and 25.8 mV for the TFC1, TFC2 and TFC3 samples, respectively. The slight negative surface charge of TFC0 was caused by the presence of hydroxyl groups [22]. The increase in the negative surface charge of composite membranes TFC1, TFC2 and TFC3 can be attributed to the existence of ionizable sulfonate and unreacted carboxyl groups from the incorporated PSSMA.

3.2. Membrane permeation properties

3.2.1. PWF and salt separation performance

The PWF of the prepared membranes was determined at 8 bar operating pressure after compaction. As shown in Fig. 6, the incorporation of PSSMA had a positive effect on membrane permeability. The PWF of the membranes increased as the PSSMA content of the PVA solution increased. It appears that the improved permeability of the TFC1 (1% PSSMA) can be attributed to the change in the crystallinity and hydrophilicity of the membrane surface. The incorporation of PSSMA with its carboxyl and sulfonate groups increased the hydrophilicity and crosslinking as shown in the characterization results. An increase in crosslinking (less polymer network packing) and increased surface hydrophilicity resulted in higher permeability. The same behavior has been reported by Peng et al. [24]. For the PVA TFC membranes, increased crosslinking caused higher permeability because of lower polymer packing.

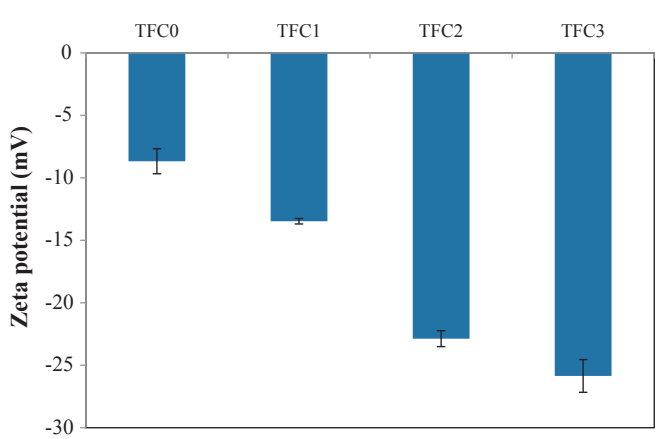


Fig. 5. Surface zeta potential values of the TFC membranes measured using 0.001 M KCl aqueous solution at pH 7.0 and 25 °C.

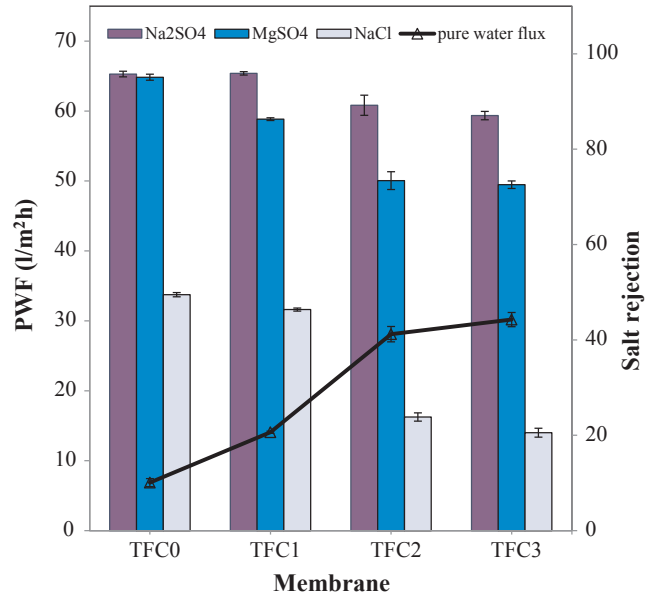


Fig. 6. PWF and Salt rejection of TFC membranes (C_F = 2000 ppm, Δp = 8.0 bar and T = 25 °C).

At higher concentrations of PSSMA, the number of PSSMA chains between the PVA chains increased and opened up the PVA polymeric network. This is confirmed by the incomplete crosslinking results from the ATR-IR spectra. The skin layer of the TFC2 and TFC3 membranes consisted of a partially-degraded polymer network and an increase in PWF was achieved.

Fig. 6 shows the salt rejection characteristics of the composite membranes for Na_2SO_4, $MgSO_4$ and NaCl at 2000 ppm feed concentrations. It is apparent from the figure that an increase in PSSMA content in the coating solution decreased the rejection of all salts except for Na_2SO_4 by TFC1. From TFC0 to TFC1, the rejection of Na_2SO_4 increased slightly from 95.7% to 96.3%, the rejection of $MgSO_4$ decreased considerably from 95% to 86.3% and the rejection of NaCl decreased from 49.5% to 46.4%.

Both size exclusion and Donnan effect affected the rejection of electrolytes by charged membranes [25]. For each TFC membrane with a negative surface charge, the rejection for sulfate salts were greater than that for chloride salts because of the higher charge density and smaller size of the anions. For the anionic part, the rejection of electrolytes depended on the cationic charge density and rejection decreased as the positive charge density increased [37]. The change in the behavior of salt rejection can be explained in terms of changes in the membrane surface charge and surface structure caused by incorporation of PSSMA. The increased surface charge increased the Donnan effect for TFC1. On the other hand, increased crosslinking caused looser packing, but a defect-free polymer network structure for the selective layer of the TFC1. Consequently, for salts with the same anionic parts (Na_2SO_4 and $MgSO_4$), the rejection of Na_2SO_4 increased but the rejection of $MgSO_4$ decreased from TFC0 to TFC1 due to the large size of the ionic Na^+ and higher positive charge density of Mg^{2+} [37]. Furthermore, for NaCl, the decrease in rejection from TFC0 to TFC1 was low, indicating that the positive Donnan effect to some extent compensated

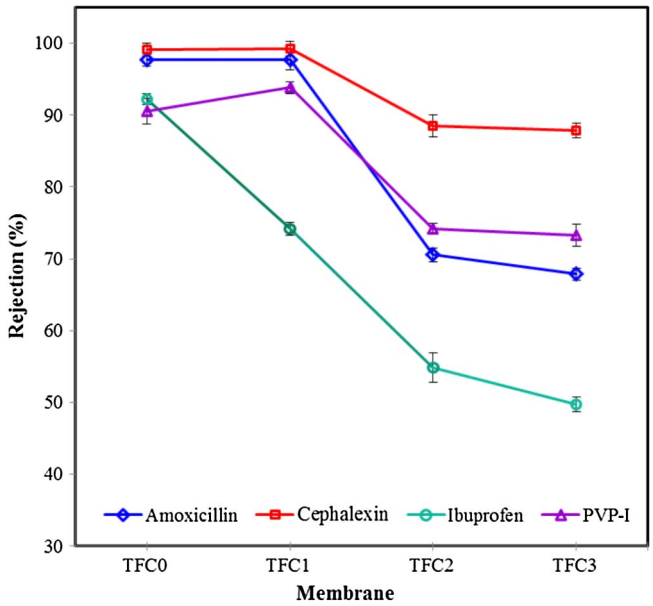


Fig. 7. Pharmaceutical rejections of TFC membranes (C_F = 50 ppm, Δp = 8.0 bar, pH = 7.0 and T = 25 °C).

for the negative size exclusion effect. For TFC2 and TFC3, an incompletely crosslinked surface structure and degraded polymer network negatively influenced size exclusion. The decline of salt rejection for TFC2 and TFC3 was due to the negative impact of the looser structure, which overcame the positive effect of the higher surface charge.

3.2.2. Pharmaceuticals separation performance

The rejections of the TFC membranes for pharmaceutical aqueous solutions are shown in Fig. 7. For TFC0 with a PVA crosslinked selective layer, the rejection of pharmaceuticals was 99.1%, 97.7%, 92.1% and 90.5% for cephalexin, amoxicillin, ibuprofen and PVP-I, respectively. The rejection of pharmaceutical solutes by NF membranes was affected by micropollutant nature and membrane properties. As a result the pharmaceutical solute was rejected by the NF membranes through one or a combination of three basic mechanisms: (i) size exclusion (sieving, steric effect); (ii) charge exclusion (electrical, Donnan) and; (iii) physicochemical interactions between the solute, solvent and membrane [38]. A separation order of cephalexin > amoxicillin > ibuprofen > PVP-I was observed.

The rejections of the cephalexin, amoxicillin and ibuprofen solutes were in the order of their molecular weights, while for PVP-I with the highest molecular weight, the lowest rejection was achieved. PVP-I contains tightly-bound iodine which reacted with the polymer end groups and loosely-bound iodine complexes in the matrix of the polymer as shown in the SI (Fig. 3S) [32]. This loosely-bound iodine was intricately in equilibrium with the I_3^-, I_2, and I^- in the PVP-I solution. The absorption spectrum of the solution for PVP-I (288 nm) was affected by these small iodine species [39]. As a result, although the polymer complex almost completely rejected because of its huge molecular size, the iodine species passed through the membrane, increasing UV absorbance value of permeate and the rejection decreased.

The dissociation constant (pK_a) of a solute is important for the rejection of organic micropollutants and determines the charge of the solute in relation to the feed pH. Compounds are identified as ionic or neutral, depending on the pK_a. Under experimental conditions (pH = 7), the ibuprofen was negatively charged, whereas the cephalexin and amoxicillin were neutral. However, by assuming a small surface charge on the TFC0 membrane, it can be understood that the size exclusion mechanism governs solute separation by the PVA/PSf membrane.

Hydrophobic interaction between the pharmaceutical molecules and membranes may also affect solute permeability. The hydrophobic properties for dissociative systems is represented by log D (Table 1) for different pH values and is defined as the ratio of equilibrium solubility for both ionized and non-ionized forms of a component in two immiscible solvents [40].

The hydrophobicity of ibuprofen decreased at the applied pH; however, the log D of ibuprofen was still higher than those for cephalexin and amoxicillin. But hydrophobic adsorption was not considered as a removal mechanism, because ibuprofen is negatively charged under operating conditions. This has been confirmed by Nghiem et al. at pH conditions higher than 4 [40].

For TFC1, the addition of PSSMA increased crosslinking and produced a relatively looser, but defect-free, polymer network structure for the selective layer. As a result, the rejection of amoxicillin and cephalexin (bigger compounds), which had almost the same size ($r_s \geq 0.47$ nm) and molecular weight (Mw ≥ 347 g/mol) were nearly unchanged when compared to TFC0. The rejection of ibuprofen, with its smaller size (r_s = 0.34 nm) and molecular weight (Mw = 206 g/mol), decreased considerably. Although TFC1 had a greater negative surface charge than TFC0, the rejection reduction showed that the charge exclusion of ibuprofen at the pH of the feed solution (pH = 7) did not compensate for the looser structure of the TFC1. It can be seen that the PVP-I rejection increased from TFC0 to TFC1. As mentioned, the PVP-I solution was composed of a polymer complex and anionic iodine compounds which affect UV absorbance of the solution. The polymer complex was completely rejected because its high molecular size and the small anionic iodine compounds (I_3^- and I^-) were influenced by the negative surface charge of the TFC1 membrane with their high charge densities and the rejection slightly increased.

The rejections of all solutes by TFC2 and TFC3 decreased because of their open surface structures caused by incomplete crosslinking and a degraded polymer network. These reductions were greater for TFC1 to TFC2 because of the uniform and somewhat greater cross-linked structure of TFC1 in comparison with TFC2 and TFC3. The TFC1 sample showed comparable rejection rates and high PWF values, so it was selected for further study on the effects of operating conditions on the membrane performance in the next sections.

3.2.3. Influence of feed pH, feed concentration and applied pressure

It is possible to improve the separation performance of the membranes by varying the treatment conditions. Because the pharmaceuticals had different pK_a values, they could be changed from cations to anions by changing the pH value. To investigate the effect of pH on rejection by the TFC1 membrane, experiments were carried out with feed solutions of cephalexin, amoxicillin and ibuprofen at different pH values (2, 7 and 9). The effect of feed pH on separation of the pharmaceuticals is shown in Fig. 8a.

The rejection of all three pharmaceuticals increased as the pH increased from 2 to 9. The rejection of cephalexin, amoxicillin and ibuprofen increased from 87.3%, 86.7% and 54.9%, at pH 2 to nearly 100%, 100% and 97.2% at pH 9, respectively. As an amphoteric electrolyte molecule, in aqueous solutions cephalexin can act as a base (proton acceptor) or acid (proton donor) according to the active groups present in the cephalexin molecule. The molecule is positively charged below a pH of 2.56 and negatively charged above a pH of 6.88. At 2.56 < pH < 6.88, the molecule becomes net neutral [41]. Because amoxicillin has three pK_a values, it can change from a cation to anion (with a charge of −2) with a change in pH. Amoxicillin is mainly a cation below a pH of 2.4 and is mainly an anion at a pH above 7.4 [11]. Ibuprofen is a neutral species at a pH below its pK_a value (pH 4.9). Above this pK_a value, ibuprofen attains a negative charge.

The negative charge of the TFC1 membrane is likely due to the presence of hydroxyl groups, ionizable sulfonate groups and unreacted MA groups. The TFC1 surface increased with an increase in pH because the degree of ionization of weak poly acids (PSSMA) increased with an

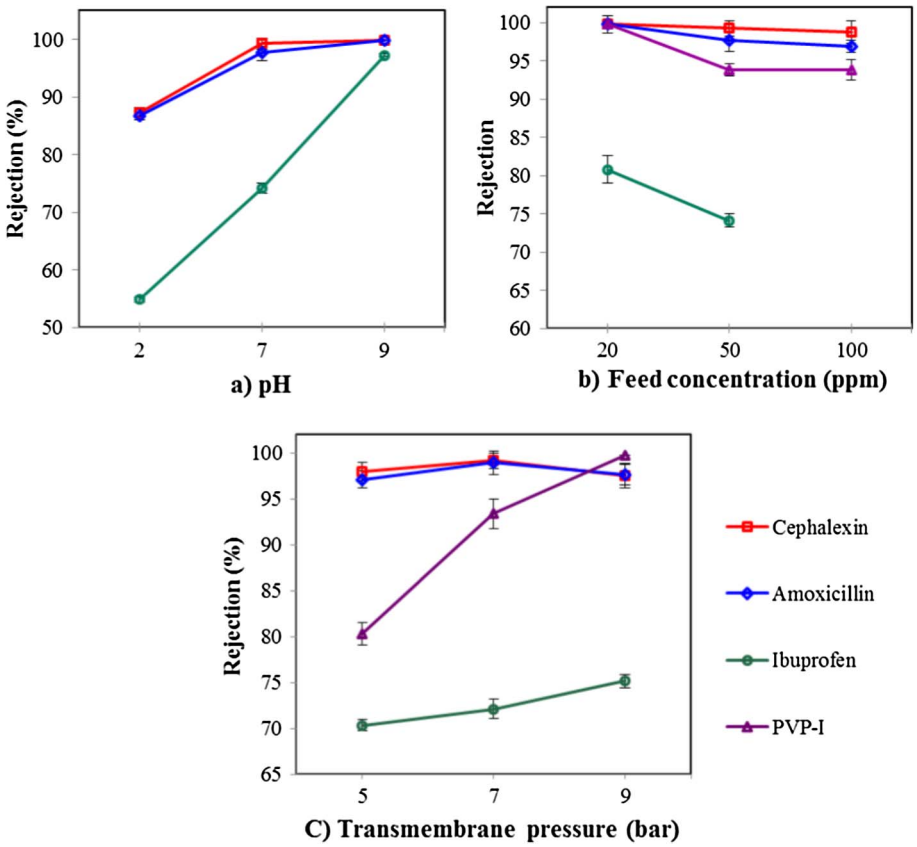


Fig. 8. The effect of pH (a), feed concentration (b) and transmembrane pressure (c) on pharmaceuticals rejections of TFC1 membrane (pH = 7, C_F = 50 ppm, Δp = 8.0 bar and T = 25 °C unless otherwise specified in each figures).

increase in pH. An increase in the number of highly-ionized, unreacted MA occurred at a pH of 9 relative to pH of 2 on the membrane surface [42]. Fig. 4S schematically shows these conditions.

As a result, at a pH of 2, cephalexin and amoxicillin had positive charges and were attracted to the membrane surface, which decreased their rejection rates (86% rejection for both). This concept was called "charge concentration polarization" by Verliefde et al. [43]. For ibuprofen, a 54.8% rejection was observed at a pH of 2. Bellona et al. stated that, at feed pH values below pK_a, ibuprofen is predominately removed by adsorption [44]. It has been hypothesized that, although adsorption can cause initial rejection, the adsorbed solute can partition and diffuse across a membrane, which will reduce rejection considerably by partitioning into permeate for such a small molecule over long-term operation.

At a pH of 9, all the solutes attained negative charges. On the other hand, the membrane surface had a higher negative charge, so the rejections increased. The change in the rejection for ibuprofen from 54.8% to 97.2% was the greatest. This could be due to changes in the effective pore size of the membrane with a change in pH [45]. At lower pH values, the membrane pores are larger in the absence of electrostatic repulsion between the active groups on the membrane surface. At higher pH values, the strong electrostatic repulsion between these groups causes membrane swelling, which shrinks the pores in the surface layer. As a result, at lower pH values, there is less steric hindrance and a low rejection rate [43].

The influence of feed concentration on the rejection of pharmaceuticals is presented in Fig. 8b. Because the solubility of ibuprofen in water at 25 °C was less than 100 ppm (based on supplier data), experiments for ibuprofen were carried out at 20 and 50 ppm of feed solutions. The figure shows that, for amoxicillin and cephalexin with a predominant size exclusion mechanism, the effect of feed concentration was negligible. But for ibuprofen and PVP-I (containing small anionic iodine compounds) with an involved charge exclusion mechanism, higher rejections were achieved at lower concentrations. The increase in feed concentration increased the solute concentration at the membrane surface and retention was lower for low molecular weight solutes [46]. For PVP-I, the rejection decreased with a decrease in feed concentration at 20–50 ppm and remained nearly constant at 50 to 100 ppm. Dilution of PVP-I increased small iodine-containing species due to weakening of the ionic link of I_3^- and the carrier polymer [32]. As a result, a higher concentration of PVP-I did not necessarily produce a higher concentration of iodine species. There were fewer small iodine-containing species and more PVP-I complex macromolecules that were retained completely and the rejection rate remained constant.

Fig. 8c shows the changes in the rejections of all pharmaceuticals when the pressure increased from 5 to 9 bar. For cephalexin and amoxicillin, the rejection rates showed a plateau at about 97% to near 100%. For ibuprofen and PVP-I, the rejections increased as the transmembrane pressure increased. These different trends were also observed for NF (SR2 and SR3) membranes for the removal of tetracycline by Zazouli et al. [29]. In their work, the results showed that increasing the pressure from 7.5 to 12 bar increased the rejection of tetracycline by the SR2 membrane, while for the SR3 membrane, the rejection rate plateaued at 95–98%. It has been suggested that, for the SR3 membrane, separation was controlled by the size exclusion mechanism. For the TFC1 membrane, cephalexin and amoxicillin separation was mainly based on size exclusion and a charge exclusion mechanism was involved in ibuprofen and PVP-I removal. The increase in the rejections of ibuprofen and PVP-I could be explained by the increase in PWF with an increase in pressure, but the solute flux was not affected to the same extent. Rejection then increased because the concentration of solutes declined in the permeate flow.

4. Conclusion

The PVA TFC membranes containing PSSMA in the PVA layer were successfully fabricated and characterized by FESEM, AFM, ATR-IR, XRD, contact angle and zeta potential measurement. The rejection rates

by the membrane samples was studied for three inorganic salts (Na_2SO_4, $MgSO_4$ and NaCl) and four pharmaceuticals (cephalexin, amoxicillin, ibuprofen and PVP-I). The results indicate that adding 1% PSSMA to the PVA layer considerably improved the permeate flux and produced comparable rejection rates for most solutes. The addition of 1% PSSMA with its different functional groups resulted in a looser and defect-free polymer network with a higher surface charge. As a result, the retention of salts occurred primarily from the combination of size and charge exclusion mechanisms.

For the pharmaceuticals studied at pH 7, cephalexin and amoxicillin recorded the highest rejection rates with a predominant size exclusion mechanism. For negatively charged ibuprofen at pH = 7 charge exclusion involved. For PVP-I, the rejection rate was influenced by the iodine species in PVP-I solution which affected UV absorbance. The polymer complex almost completely retained because of its huge molecular size but the small iodine species passed through the membrane.

The effect of pH, transmembrane pressure and feed concentration on the rejections of pharmaceuticals was also investigated. The rejection rate for ibuprofen increased considerably with an increase in the pH of the feed solution due to the higher surface charge and lower effective pore size of the membrane at higher pH values. The effect of transmembrane pressure and feed concentration on cephalexin and amoxicillin was negligible, but the rejection rates of ibuprofen and PVP-I were influenced by changes in the transmembrane pressure and feed concentration. These results can be attributed to the specific mechanisms involved for each compound.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.09.054.

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