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Identification, Quantification and Removal of Pharmaceuticals and Endocrine Disrupting Compounds from Water Using Customized PDMS Membrane

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Abstract

This study concentrates on the identification and quantification of three pharmaceutical compounds (ibuprofen, naproxen and diclofenac) and an endocrine disrupting compound (17α-ethinylestradiol) in wastewater effluents collected from Adelaide Wastewater Treatment Plant and Greenway Pollution Control Plant, London, ON, Canada. For sample preparation, both solid-phase extraction and liquid-liquid extraction techniques were followed and GC-FID and LC-MS were used for sample analysis. Although the target pharmaceuticals were present in the wastewater samples at concentrations in a range of 0.29-8.98 µ/L, 17α-ethinylestradiol was not detected.

For eradicating or removing the above-mentioned organic compounds from water, organic solvent nanofiltration (OSNF) membrane was used in this study. Different types of OSNF membranes were prepared where commercially available PTFE ultrafiltration membrane as well as laboratory-made polysulfone ultrafiltration membranes served as the base supports, and poly (dimethylsiloxane) as the thin active layer. A thin film composite membrane was also prepared using a base support made of a mixture of polysulfone and multi-walled carbon nanotubes and a thin active layer top constituted from interfacial polymerization between m-phenylenediamine and trymesoyl chloride. For membrane characterization, Scanning Electron Microscopy (SEM) and Atomic Force Microscoopy (AFM) were performed. The performance of the membranes was studied by monitoring permeability along with the removal capacity using a dead-end filtration system, under a pressure range of 5~30 bars. A commercially available polyimide membrane, DuraMem, was exploited to compare the membrane performance. The 2.5% PTFE/PDMS (RTV 615) membrane showed the highest performance by removing 95~97% 17α- ethinylestradiol, 70% ibuprofen, 65% naproxen and 65% diclofenac. Hansen’s Solubility Parameter theory was adopted to explain the removal mechanism of pharmaceutical compounds, while size exclusion theory explained the removal of the synthetic estrogen by OSNF.

Keywords

Wastewater effluent, pharmaceutically active compounds, endocrine disrupting compounds, organic solvent nanofiltration, PDMS, polyimide.

Co-Authorship Statement

Unless otherwise indicated Ambareen Atisha outlined the research objectives, conducted the experiments, and analyzed the data. Ambareen Atisha also wrote the thesis and the manuscripts that are being prepared for publication. The Supervisor, Dr. Ernest Kwesi Yanful, reviewed every chapter of the thesis. Dr. Wojciech Kujawski, as a co-author, provided the use of the Scanning Electron Microscopy and Atomic Force Microscopy. He also provided guidance, aided in the interpretation of data, and reviewed the manuscripts.

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List of Abbreviations and Symbols

µD – Micro Debey

µg/L – Microgram per liter

µm – Micrometer

A – Androsterone

AC – Activated Carbon

A^o - Angstrome

AOP – Advanced Oxidation Process

BPA – Bisphenol A

BSTFA - Trifluoroacetamide

C-18 - A cartridge for solid - phase extraction

CH_2N_2 - Diazomethane

CNT – Carbon Nanotube

CSA – Camphor Sulfonic Acid

DCF – Diclofenac

DCM – Dichloromethane

Desal-5 - A commercial nanofiltration membrane

DHT – Dihydrotestosterone

DI – Deionized water

DMAc – Dimethylacetamide

DMDCS – Dimethyldichlorosilane

DMF – Dimethylformamide

E1 – Estron

E2 - 17β-estradiol

E3 - Estriol

EDCs - Endocrine Disrupting Compounds

EE2 - 17α-ethinylestradiol

fN – CNT – Nitrogen doped functionalized Carbon Nanotubes

fP – CNT – Phosphorous doped functionalized Carbon Nanotubes

g/mol – Gram per mole

GC-FID – Gas Chromatography-Flame Ionization Detector

GO – Graphene Oxide

H_2O_2 – Hydrogen per oxide

H_2SO_4 – Sulfuric Acid

HNO_3 – Nitric Acid

HPDMS – Hydroxyl terminated polydimethylsiloxane

IBP - Ibuprofen

IDL – Instrumental Detection Limit

IPA – Isopropyl alcohol

LC-MS – Liquid Chromatography – Mass Spectrometry

LLE – Liquid Liquid Extraction

M20 – Hyflux InoCep M20 membrane

MCL - Maximum Contaminant Level

MCM-41 – A mesoporous silica

MDL – Method Detection Limit

MF – Micro Filtration

mg/L – Milligram per liter

$MgSO_4$ – Magnesium Sulfate

mm – Millimeter

MnO_2 – Manganese dioxide

MPa – Mega Pascal

MPD – m-phynylenediamine

MPF-50 – A commercial nanofiltration membrane

MWCNT – Multiwalled Carbon Nanotube

N - Norgestrel

NaCl – Sodium Chloride

NF - Nanofiltration

NF270 - A commercial nanofiltration membrane

NF70 - A commercial nanofiltration membrane

NFPES10 – A commercial nanofiltration membrane ng/L - Nanogram per liter

NH_2 - A cartridge for solid - phase extraction

nm - Nanometer

NMP – N- methylpyrrolidone

NPR - Naproxen

NSAIDs - Nonsteroidal Anti-inflammatory Drugs

NTR-7250 – A commercial nanofiltration membrane

OASIS HLB – A cartridge for solid - phase extraction

OSNF – Organic Solvent Nanofiltration

PAHs – Polyaromatic Hydrocarbons

PAN - Polyacrylonitrile

PDMS - Polydimethylsiloxane

PE – Polyester

PEG – Polyethelene glycol

PES – Polyethersulfone

PFBB - Pentafluorobenzyl bromide

PhACs - Pharmaceutically Active Compounds

PHMS – Polymethylhydrosiloxane

PPD – p-phynylenediamine

PRP – Piperazine

PSF – Polysulfone

PTFE – A commercial ultrafiltration membrane

PVA – Polyvinyl alcohol

RO – Reverse Osmosis

RTV 615 – A silicon kit

SDS – Sodium dodecyl sulfate

Si_3N_4 – Silicon nitride

Si-O – Siloxane

SPE – Solid Phase Extraction

SPSF – Sulfonated Polysulfone

SWNT – Single-walled Nanotube

SYLGARD 184 – A silicon kit

T - Testosterone

TAOS – Tetraethylorthosilicate

TEA – Trimethylamine

TEOS – Tetraethoxysilane

TFAA - Trifluoroacetic anhydride

TFC – Thin Film Composite Membrane

THF – Tetradydrofuran

THM – Trihalomethane

TiO_2 – Titanium dioxide

TMC – Trimesoyl Chloride

TMSH - Trimethylsulphonium hydroxide

Tr – Trenbolone

UF – Ultra Filtration

UV – Ultraviolet

VTG – Vitellogenin

WWTP – Wastewater Treatment Plant

ZrO_2 – Zirconium dioxide

ZrO_2/Al_2O_3 – a tubular asymmetric membrane

Chapter 1

1 Introduction

The incidence of emerging or recently recognized pollutants in our water resources is of great concern to the health and safety of the consuming public. These contaminants are defined as low molecular weight, synthetic or naturally occurring compounds, not commonly monitored in the environment. Wastewater effluents from municipal treatment plants [1, 2], hospital effluents [3, 4], industrial as well as livestock wastewater [5] are common sources of trace contaminants in the environment; they are present usually in the µg/L range or less. Most trace contaminants are anthropogenic, created in extensive quantities for many purposes, for example, as pharmaceuticals, pesticides, refrigerants, dye carriers, propellants, pigments, dielectric fluids, preservatives, heat transfer media, degreasers & lubricants [6]. Along with contributing to the prosperity of the world and preventing many diseases, these synthetic organic compounds create an environmental menace due to a combination of physiochemical and toxicological properties [6]. Being continuously introduced in the environment along with their presence at small concentrations may cause potential negative impact on drinking water supplies, human health and ecosystem behavior [7, 8]. Furthermore, this may also result in the introduction of by-products and metabolites of these chemicals into the environment, creating even more damaging conditions than the parent compounds [6]. Dispersion, aggregation and volatility are the major characteristics of the trace contaminants leading to a further division into different groups covering pesticides, pharmaceutically active compounds, persistent organic compounds and endocrine disrupting chemicals [9]. A particular attention has been paid to pharmaceuticals and endocrine disrupting compounds since they may function at very low concentrations (ng/L range) [10].

Pharmaceutical compounds along with their metabolites are publicly denoted as pharmaceutically active compounds (PhACs) [11]. According to Bush [12], the most commonly detected pharmaceuticals in water are anti-inflammatories and analgesics (acetylsalicylic acid, ibuprofen, diclofenac and paracetamol); antidepressants (benzodiazepines); antiepileptic (carbamazepine); lipid-lowering drugs (fibrates); β-blockers (atenolol, metoprolol and propranolol); antiulcer drugs and antihistamines (famotidine and ranitidine); antibiotics (β-lactams, chloramphenicol, fluoroquinolones, imidazole derivatives macrolides, penicillin, quinolones, sulfonamides and tetracyclines) and other substances (amphetamines, barbiturates, cocaine, methadone and other narcotics). Pharmaceuticals like cyclophosphamide, erythromycin, naproxen and sulfamethoxazole can persist in the environment for a year whereas clofibric acid lingers on for several years, being biologically active through accretion [8]. According to some researchers, it is currently not clear whether the presence of PhACs through exposure to multiple compounds at a very low levels could invoke an increased toxic or synergistic effects [13]; however, [14] validated that a mixture of pharmaceuticals at ng/L range can lead to physiological and morphological effects on human embryonic cells. Moreover, the catastrophic consequences on the population of vultures in India and Pakistan due to the use of the anti-inflammatory drug, diclofenac [15], has made the researchers to extend their studies and analysis regarding the effects of PhACs in aquatic environment. The target PhACs selected for this study are ibuprofen (IBP), naproxen (NPR) and diclofenac (DCF). These are known as nonsteroidal anti-inflammatory drugs (NSAIDs) widely used over the world and possess analgesic and antipyretic activities.

Endocrine disrupting compounds (EDCs) are another major group of emerging pollutants with estrogenic/ androgenic action, comprised of a wide band of compounds with multifaceted roles that are dissimilar in their forms [9, 16-22]. EDCs are highlighted for impeding the reproductive systems of wildlife and humans through imitating the biological activity of natural hormones, subjugating the hormone receptors, or restricting the transport and metabolic processes of natural hormones [23]. Although EDCs exist at very low concentrations in the aquatic environment, they pose a threat to water quality and are believed to lessen fertility and intensify the manifestation of breast, ovarian and tubular cancer [9, 24]. Natural estrogens, such as estron (E1); 17β-estradiol (E2) and estriol (E3); natural androgens, such as testosterone (T), dihydrotestosterone (DHT) and androsterone (A); artificial synthetic estrogens or androgens, such as 17α-ethinylestradiol (EE2), norgestrel (N) and trenbolone (Tr); phytoestrogens as well as other industrial compounds like bisphenol A, nonyphenol etc. comprise the broad class of EDCs [17]. Among all of these EDCs, EE2 has been selected for this study because it possibly demonstrates the sturdiest estrogenic effect, about ten times higher than that of natural hormones, interferes with the development of living organisms and should be considered as the EDC of the greatest concern [6, 25-27].

Very few protections and monitoring guidelines for EE2 and pharmaceuticals have been proposed so far; the identification of EE2 is rather complex due to the absence of strict protocols specific to EE2 [28]. Consequently, the evolution of low-cost technique for recognition of PhACs and EDCs, especially for EE2 and its estrogenic activity in wastewater is still an emergent and thought-provoking research area [17, 28]. Since existing conventional wastewater treatment plants (e.g., activated sludge) have not been demonstrated to effectively remove this estrogen, enhanced, innovative and highly sensitive analytical and bio-analytical technologies are needed to detect their low concentration in complex matrices such as wastewater [17, 28]. Under these circumstances, nanofiltration (NF) and reverse osmosis (RO) membrane techniques have become more prevalent and are receiving increasing attention because of their supreme performance in removing micro-pollutants from waste water [17, 28-30]. Having pore sizes between 0.2 and 0.4 nm [28, 31], the NF membrane can remove most trace micro pollutants [6, 17, 22, 32-34]. The low operating pressure (10-50 bar), high flux rate, high retention of multivalent anions, relatively low investment, low operating and maintenance costs and environmental friendliness along with delivering high quality effluent demonstrate NF as an attractive option for treatment of organic contaminants.

On the other hand, Organic Solvent Nanofiltration (OSNF), one of the most recent membrane techniques, has been known to have very high potential to escalate the concentration of dilute species from low molecular weight solvents [35]. This technique affords the recycling of organic solvents at lower energy when paralleled to conventional processes [35, 36]. Molecules of 200-1,000 g/mol in several organic solvents have been successfully separated using OSNF membranes [37]. Most OSNF membranes are asymmetric and integrally skinned, they might be free-standing and made of polyimides (PI) or composites with a thin active layer on a porous support. Recently the potential for using polydimethylsiloxane (PDMS) has been verified in cases of nanofiltration, pervaporation and vapor permeation [38]. It has been suggested that the highly hydrophobic PDMS can be utilized for the preparation of OSNF membranes with high flux, high selectivity and excellent removal capacity of most organics [39]. A free standing PDMS membrane is much thicker when matched to the active layer of the thin film composite membranes. Therefore, composite PDMS membranes, with a selective, defect-free membrane film of sub-micrometer size thickness over a porous support could serve better in terms of permeability. The PDMS composite membranes on a variety of porous supports, like polysulfone, polyethersulfone, polyetherimides, polyimides, polyacrylonitriles, polyesters, ceramics etc., have been described in a number of scientific studies [40]. Stafie et al. [41] used polyacrylonitrile/PDMS (PAN/PDMS) composite membranes for separation of hexane from mixtures of oil/ hexane and PIB-hexane. Dutczak et al. [37] manufactured composite capillary PDMS membranes to determine the permeance of toluene, whereas Vankelekom et al. [42] made a polyacrylonitrile-polyester/PDMS (PAN-PE/PDMS) composite membrane for the same purpose.

1.1 Scope and Objectives

To the best of our knowledge, OSNF membranes have only been used, so far, in gas permeation and pervaporation; they have not yet been utilized in removing trace organic components from water. The scope of the present work is to prepare, characterize and evaluate the efficiency of a custom made PDMS membrane for the removal of PhACs and EE2. However, it was important to first evaluate the presence of the PhACs and EE2 in the wastewater effluents in the study area (London, ON, Canada). Thus, the first part of this research work covers the testing of wastewater effluents collected from different wastewater treatment plants in London, ON to identify and quantify the presence of the specific compounds. For analytical determination and quantification, sensitive analytical methods based on enrichment steps, chromatographic separation and necessary derivatization were investigated.

The specific objectives of the study were to:

- Identify and quantify the presence of selected PhACs (ibuprofen, naproxen, and diclofenac) and 17α-ethinylestradiol in the effluents from Wastewater Treatment Plants (WWTPs) in London, Ontario, Canada.

- Prepare a customized PDMS Composite Nanofiltration Membrane, and evaluate its efficiency in removing ibuprofen, naproxen, diclofenac and 17α-ethinylestradiol from water.

- Compare the characteristics and efficiency of the PDMS membrane with a Thin Film Composite (TFC) membrane and a commercially available OSNF membrane.

1.2 Outline of the thesis

The thesis consists of the following five chapters:

- Chapter 1 gives a brief introduction of the research work along with the scope and objectives.

- Chapter 2 provides a review of pertinent literature to highlight several aspects of research conducted on the presence of pharmaceuticals and EE2 in the aquatic environment, different methodologies used to synthesize thin film composite and organic solvent nanofiltration membranes along with their performance criteria.

- Chapter 3 discusses the materials and methodologies used in the study, including collection of wastewater samples; preparation of samples for analytical investigation, such as solid-phase extraction, liquid-liquid extraction and derivatization; development of necessary analytical methods to run samples on liquid chromatography/mass spectrometry and gas chromatography/flame ionization detector; preparation of different kinds of OSNF and TFC membranes along with characterization and permeability performance evaluation.

- Chapter 4 presents and discusses the results obtained from the experiments.

- Chapter 5 is the concluding chapter; it provides a summary of the whole work with further recommendations.

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Chapter 2

2 Literature Review

The removal of pharmaceuticals and endocrine disrupting compounds through the municipal wastewater treatment plants have been found to be neglected [1-6] resulting in ~80% of the total load of these active compounds being discharged into surface waters [7]. This chapter reviews the literature regarding the occurrence of pharmaceuticals and estrogenous compounds in the aquatic environment, their conventional removal technologies, nanofiltration and the methods of preparation and performance of different types of nanofiltration membranes.

2.1 Occurrence of 17α-ethinylestradiol (EE2) in the aquatic environment and its removal

17α-ethinylestradiol (EE2) is used in almost all modern formulations of combined oral contraceptive pills, medicines for the (i) menopausal and postmenopausal syndrome, (ii) physiological replacement therapy in deficiency states, (iii) treatment of prostatic cancer and breast cancer in postmenopausal women, and (iv) osteoporosis, and other ailments [8-10]. In the hormonal birth control, it is usually present in the form of a combination medication including a form of progesterone or progestin. EE2 is a nonpolar and hydrophobic organic compound with low volatility and is resilient to biodegradation [11]. It is a derivative of 17β-estradiol (E2) and is defined by an aromatic ring with hydroxyl group at the C-3 and an ethinyl group at C-17 (Figure 2.1); this ethinyl group is responsible for its resistance to biodegradation unlike other endogenous estrogens [12]. Therefore, EE2 has a longer persistence in the environment with a dissipation time in the order of 20~40 days in the river system as a result of its lowest biodegradation efficiency as well as insufficient removal in wastewater treatment plants [12, 13]. The physiochemical characteristics of the molecule are summarized in Table 2.1

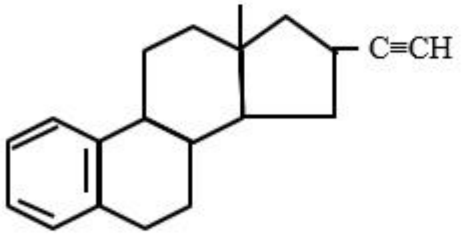

Figure: 2.1 – Chemical Structure of 17α-Ethinylestradiol (EE2)

Table 2.1: Physiochemical Properties of EE2 [12, 14, 15]

Chemical Formula	$C_{20}H_{24}O_2$
Molecular weight (g/mol)	296.4
Molecular width (A^o)	5.7
Molecular length (A^o)	11.9
Molecular volume (A^{o3})	881.1
Dipole moment (μD)	2.64
Water Solubility (mg/L)	4.8
Log K_{OW}	3.67
Vapor Pressure (mm Hg)	6 x 10^{-9}
Henry's Law constant (atm-m^3/mole)	7.94 x 10^{-12}

While EDCs move in the environment from innumerable disseminated points, several researchers have shown that the most likely source of EDCs in the aquatic environment is the discharge of municipal and/or industrial effluents along with the runoff from agricultural production and irrigation return waters, such as pesticides and animal husbandry hormones and medicines [1, 16, 17]. It has been detected that the release of large amounts of expired medicines from households as well as in waste from hospitals and pharmaceutical companies upsurge the concentration EE2 along with mestranol and diethylstilbestrol in the environment [14]. A substantial part of the endogenous estrogens is emitted from human and animal bodies through urine as glucuronides and sulfates complexes; thus, occurs their presence in municipal wastewater [1, 14, 18]. Nevertheless, these can be quickly cleaved and metabolized into an active form or parent compound due to microbial deconjugation in the course of transport and treatment in a Water Treatment Plant resulting at concentrations up to sub nanograms per liter levels [1, 19, 20]. EDCs' presence and main distribution in the environment is illustrated in Figure 2.2.

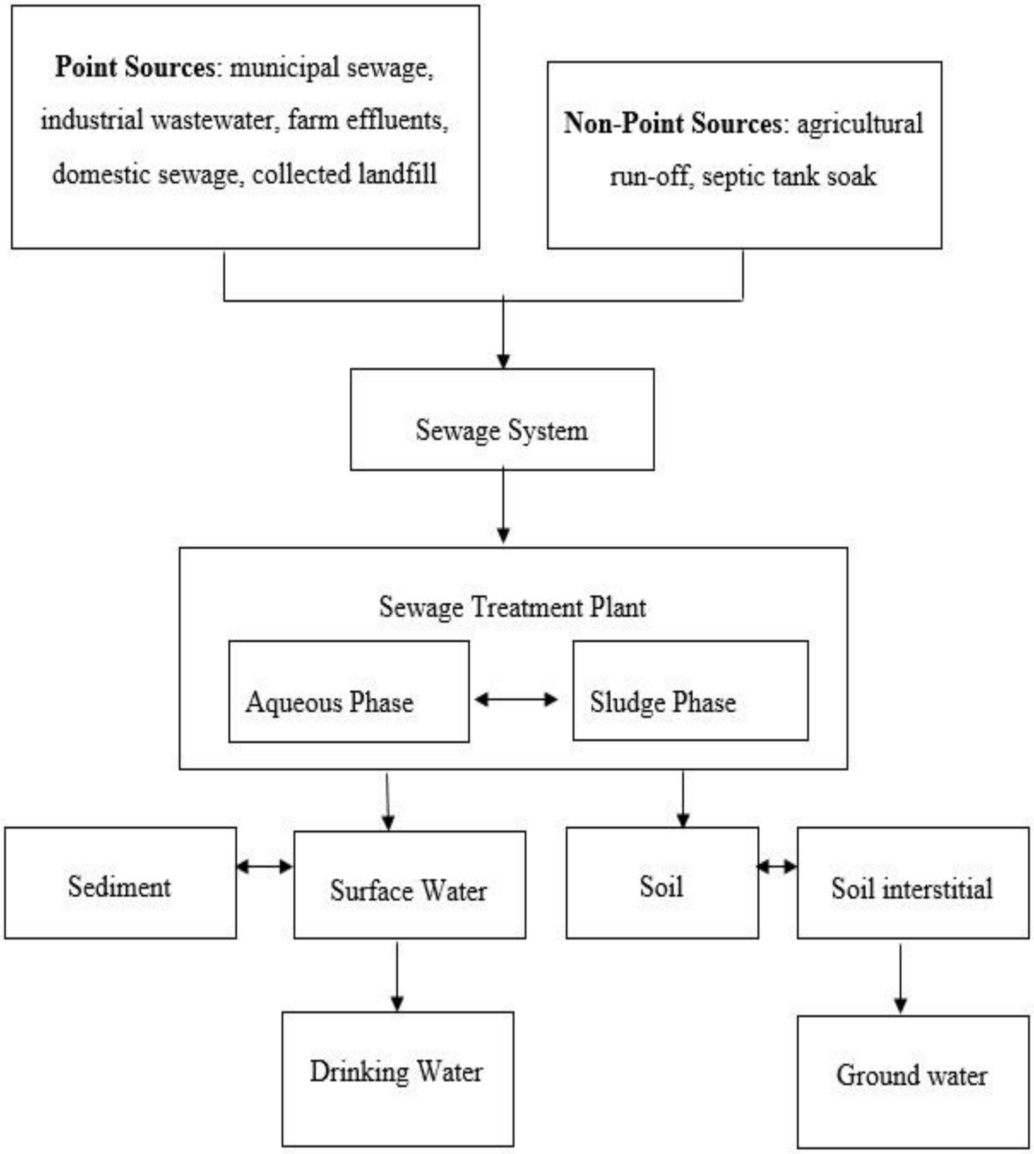

Figure 2.2: EDCs' distribution in the environment [21, 22]

In human body, EE2 has revealed one to two times higher binding affinity to the estrogen receptor (ER) than E2, whereas up to five times higher binding affinity in some fish species [23]. When compared to naturally produced E2, the higher receptor affinity designates EE2 as a more potent estrogenic compound, even though at extremely low (ng/L) concentrations, in case of stimulating an estrogenic response [19, 24-27]. Researchers have found that 50 ng/L E1, 54 ng/L E2 and 21.7 µg/L E3 are responsible for sex change in fish whereas only 6 ng/L of EE2 is adequate enough for 100% alteration of male fish into female [28] through the development of rare testes, making of an egg protein precursor usually created in female fish, low circulation of sex hormone levels as well as dropping gonad size [29-31]. Concentrations of EE2<10 ng/L can completely shut down the egg production in fishes [32] and persuade vitellogenin (VTG) production in male zebrafish, Japanese medaka and rare minnow [33]. Even EE2 < 1 ng/L in water could have a clear contribution to the reproductive end point of fishes [32].

Because of the increased awareness of the risks involved with EE2, the removal of this synthetic estrogen from water and wastewater to levels that do not pose any health risk have been given considerable attention by public health officials. Traditional methods/ conventional wastewater treatments favorably remove more hydrophobic, larger molecular weight (MW) compounds leaving behind the more hydrophilic smaller compounds. One research study done in Europe revealed that a 14-hour hydraulic contact time with activated sludge removed approximately 85% of 17β-estradiol, estriol and mestranol whereas the removal of estron was even less [14]. In another research work, conventional treatment was able to remove about 60~70% of 17β-estradiol [34]. After assessing six waste water treatment plants (WWTPs) in Rome, Baronti et al. [35] found that an average removal of 87% E2, 61% E1, 85% EE2 and 95% E3 was possible through activated sludge treatment. Again, a study on a number of WWTPs in Canada revealed that a full scale municipal wastewater treatment plant removed 74.9% EE2, 93.2% E1 and 83.3% E2 [36]. Although conventional treatment methods have been found to be quite effective in removing EDCs up to a certain extent from wastewater, researchers have noticed that a very low concentration of these chemicals in the downstream effluents is still a major concern [17]. Furthermore, it has also been observed that the concentration of these micropollutants in the treated wastewater is often higher than that in the influent due to the transformation of biologically inactive conjugated estrogens into free forms by some enzymes present in a specific ecosystem [14]. Given the increasing difficulty in meeting maximum contaminant levels (MCLs), researchers are trying to recover the outmoded treatment methods. Several procedures including physical, chemical and biological treatment processes are being used to clean up wastewaters depending on the type and extent of contamination. Innovative, highly sensitive analytical and bio-analytical methodologies are continuously being investigated to detect the low concentration of these contaminants in complex matrices like wastewater [21, 22, 37, 38]. Photolysis, Ultra Violet (UV) irradiation, oxidation, hydrolysis, and reverse osmosis are some of the physico-chemical transformation processes that EDCs undergo [39, 40]. Rapid filtration (88%), chlorination and coagulation/ sedimentation can remove 20~40% of E1, E2 and EE2 from drinking water [18]. On the other hand, activated carbon (AC) made from carbonaceous material such as wood, bark, coal, bone and solid petroleum residue is a relatively inexpensive material with an enormous surface area, typically 1, 000 m^2/g and is mostly used to remove trace amounts of EDCs from water in the form of both powdered (5~100μm) and granular form (0.6~0.9mm) [22]. Irradiating water with UV light is another attractive alternative to chemical treatment methods. EDCs are more effectively degraded utilizing UV/H_2O_2 (hydrogen per oxide) advanced oxidation in comparison to direct UV photolysis treatment [17]. Another strategy to remove EDCs can be the implementation of Manganese dioxide (MnO_2) as an oxidative removal substrate. MnO_2 is a well-known solid phase oxidant and can remove ~81.7% of EE2 due to its adsorption capacity and catalytic properties [1]. Besides, a further technique, Fenton’s oxidation, is cost effective, non-toxic and has homogenous catalytic nature [41]. Furthermore, several researchers have also used Titanium dioxide (TiO_2) nanowires to treat water and wastewater [17]. However, even after these treatments, some compounds might continue to be present in drinking water due to their low biodegradability, high chemical stability, and high water solubility and reduced propensity for sorption.

2.2 Pharmaceutically Active Compounds in aquatic environment and their removal

Most of the pharmaceutical compounds possess a molecular mass less than 500 Da [42]; they are polar molecules with more than one ionization group and the degree of ionization and their characteristics are dependent on the pH of the medium [43].

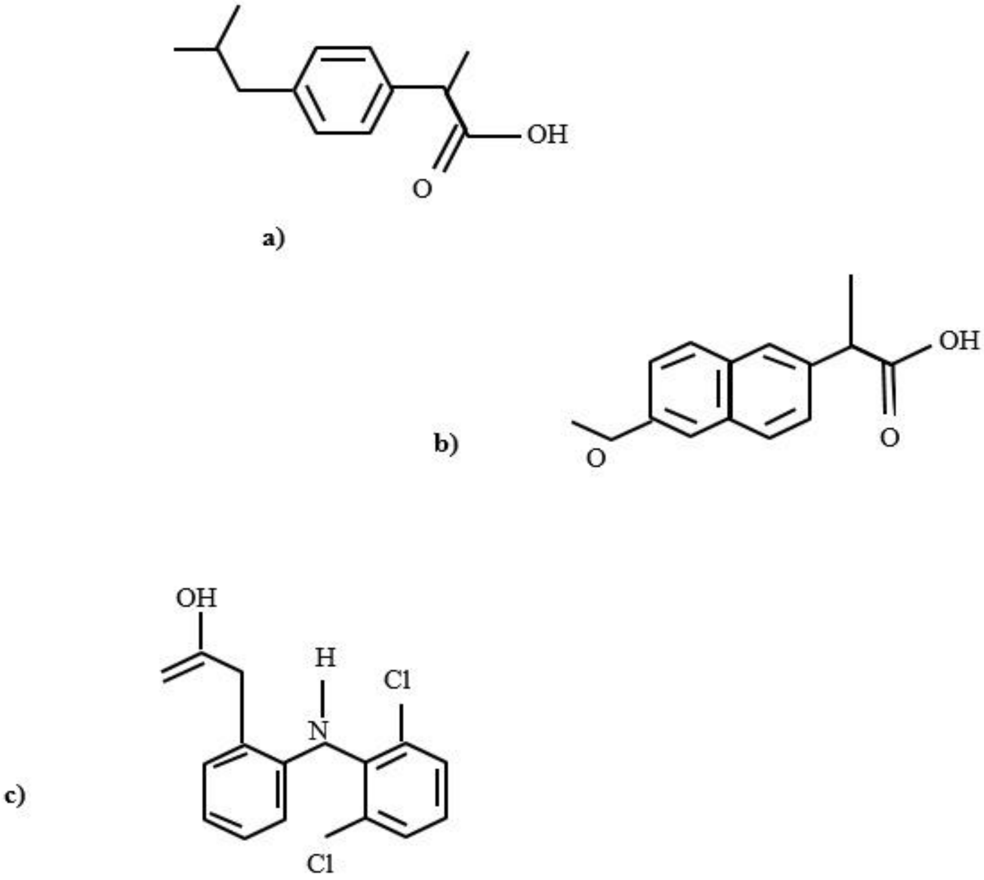

Figure: 2.3 Chemical Structure of a) Ibuprofen b) Naproxen c) Diclofenac

Table 2.2: Physiochemical Properties of Ibuprofen, Naproxen and Diclofenac

	Ibuprofen	Naproxen	Diclofenac
Chemical Formula	$C_{13}H_{18}O_2$ [44]	$C_{14}H_{14}O_3$ [44]	$C_{14}H_{11}NCl_2O_2$ [45]
Molecular weight (g/mol)	206.30 [44]	230.3 [46]	296.2 [45]
Water Solubility (mg/L)	<1 [45]	15 [46]	2.37 [45]

pKa	4.91 [44]	4.15 [44]	4.15 [44]
Log K_{oW}	4.13-4.91 [44]	3.18-3.24 [44]	4.51 [44]
Vapor Pressure (mm Hg)	1.86 X 10^{-4} [47]	1.89 X 10^{-6} [48]	6.14 X 10^{-8} [47]
Henry's Law constant (atm-m^3/mole)	1.5 X 10^{-7} [44]	3.39 X 10^{-10} [44]	4.73 X 10^{-12}[44]

Figure 2.4 shows different possible pathways through which pharmaceuticals could enter water. Different types of pharmaceutical compounds can be disposed into the sewage system from different sources like hospitals, personal consumption, livestock, and aquafarming mainly in two ways: through inclusion in normal rubbish tips and via human or animal feces or urine. The sewage is then led through WWTPs and afterwards move into the water systems. Here a wide selection of these compounds and their metabolites have been detected making compound and more complex mixtures exhibiting synergetic effects [49-52].

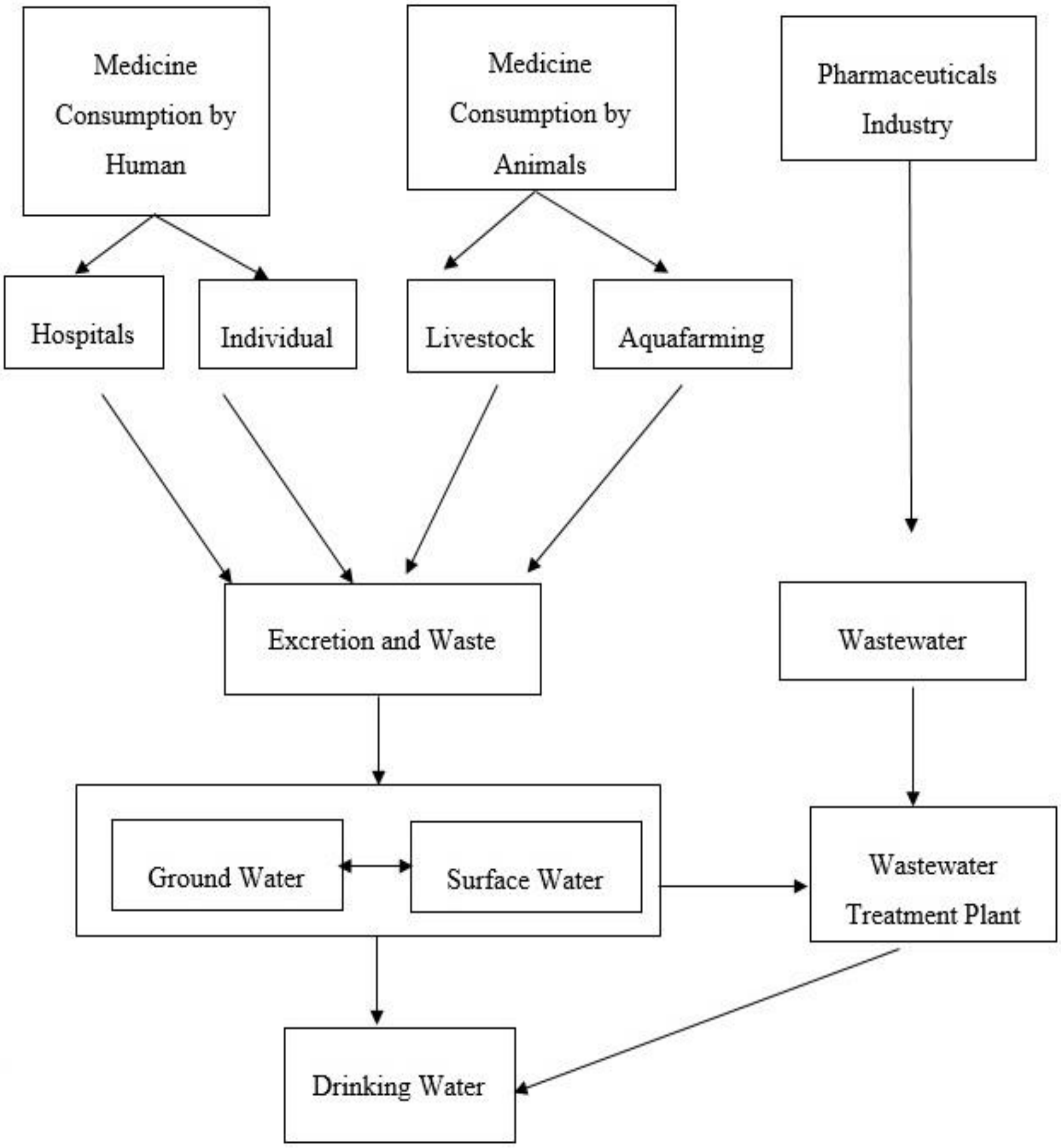

Figure 2.4: Pharmaceuticals dissemination in the environment [43]

As stated in recent research [53-57], some of the pharmaceuticals (e.g.- β-blockers, analgesics, antacids, antibiotics, antidepressants, antipyretics, lipid-lowering drugs, stimulants and tranquilizers) are not entirely removed by conventional WWTPs due to their complex molecular structure and/or low molecular weight [2, 50, 58] and thus have been detected in surface and ground water of different regions of the world. According to Carballa et al. [59] although some pharmaceuticals can be removed in primary treatments by adsorption; ibuprofen (IBP), naproxen (NPR), sulfamethoxazole and iopromide remain in the water and subsequent biological treatment can eliminate only 30-70% of the anti-inflammatories. Heberer [60] reported that WWTPs are not at all effective in removing diclofenac (DCF); at least five sub products are generated during chlorination of DCF and the degree of mineralization attained is significant [61]. Following the study of Petrovic et al [62], Table 2.3 summarizes the concentrations of some of the pharmaceutical compounds detected in wastewaters of various WWTPs before and after treatment. The variation in concentrations of the compounds before and after treatment confirms the inability of conventional WWTPs to completely remove a number of pharmaceutical compounds. The removal degree varies from 1 to 80%.

Table 2.3: Detection of Pharmaceuticals in the Influent and Effluents of WWTPs [62]

Compounds detected	WWTPs influent (ng/L)	WWTPs effluent (ng/L)	% Removal
Ketoprofen	451	318	29.49
Naproxen	99	108	-9.09
Ibuprofen	516	266	48.45
Diclofenac	250	215	14.0
Acetaminophen	10194	2102	79.38
Bezafibrate	23	10	56.52
Clofibrate	72	28	61.11
Gemifibrozil	155	120	22.58
Carbamazepine	420	410	2.38
Ranitidine	188	135	28.19

Azithromycin	152	96	36.84
Metronidazole	80	43	46.25
Sulfamethoxazole	590	390	33.90
Trimethoprim	1172	290	75.26
Atenolol	400	395	1.25
Sotalol	185	167	9.73
Propanolol	290	168	42.07

Conventional treatment methods have been found to be inefficient in the complete removal of pharmaceutical compounds from water [43]. Conventional Activated Sludge can remove ~45% IBP, ~0.1% NPR and ~35% DCF [43]. The degree of removal varies with different factors, such as type of treatment process, hydraulic retention times, solid retention times as well as the physicochemical properties of the compounds. Since most of the PhACs are not degraded to the desired levels through biodegradation [43], research is being focused on the development of new technologies for the safe destruction of micro pollutants. Advanced oxidation processes (AOPs) have been found to be quite successful in removing refractory, toxic and organic pollutants that are not treatable by conventional technologies [43]. However, it is not clear if compounds are completely mineralized or not; intermediate products might cause possibly greater adverse effects on human and ecological system [63]. Moreover, the operational cost, when using hydrogen peroxide (H_2O_2) is a barrier. Heterogeneous photo catalysis is another procedure that has been utilized as a removal technology for PhACs [64]; however, this technology is found to be quite expensive and shows low quantum yield of light adsorption along with low efficiency [64]. Additionally, secondary operations are required for the purpose of recovering catalysts after use. Ozonation can remove 30-80% IBP, 65-100% NPR and ~96% DCF; nevertheless, the ozonation products formed are currently unknown. In general, higher doze of ozone is required for complete removal of organic contaminants which is very expensive [16]. Besides, ozone is unstable and cannot be stored and therefore, it must be generated on site [65]. Although Membrane Bioreactor can remove almost >99% of PhACs from water [66], competences of diverse microbial population in the eradication of selected pharmaceuticals and optimization of design and operating settings are crucial for the success of this methodology [67].

2.3 Nanofiltration

Nanofiltration (NF) is a pressure-driven membrane process placed between ultra-filtration (UF) and reverse osmosis (RO) with respect to size discrimination. Recently, NF and RO removal mechanisms are becoming more and more popular because of their utmost importance in eliminating micro-pollutants [21, 22, 68, 69]. In microfiltration (MF) and UF membranes, pore sizes are 100 to 10,000 times larger than the size of micro pollutants and therefore UF and MF are not effective in removing organic contaminants [16, 70]; whereas in RO and NF, a transmembrane pressure is applied to force the water transport through “pores”, thereby retaining the contaminants on the membrane by charge and size interactions [34]. Although RO will achieve almost complete removal due to a tighter membrane structure than in the case of NF, the lower operating pressure (10-50 bar), higher flux rate, high retention of multivalent anions, relatively low investment, low operation and maintenance costs and environmental friendliness make NF as a more enhanced option than RO [21, 34, 38, 71]. NF membranes have pore sizes between 0.2 and 0.4 nm [21, 72] and can eradicate most of the trace micro pollutants including natural hormones, a wide variety of pesticides, phthalate, polycyclic aromatic hydrocarbons (PAHs), trihalomethanes (THMs) and their precursors [14, 16, 22, 34, 73, 74]. Achievement of high quality effluents including extremely low concentrations of organic compounds and the removal of microbes and viruses without chemical disinfection is one of the remarkable advantages of membrane processes, when compared to the conventional treatment ones [22]. Therefore, they are being used progressively for treatment by both water and wastewater industries, thereby offering a valuable tool to concentrate and recover a variety of organics [21, 75].

2.3.1 Thin Film Composite (TFC) Membranes

Thin film composite (TFC) membranes have been shown to be excellent candidates for a wide variety of separation applications, particularly in water and wastewater treatments [76] with high permeability under ultralow pressure [77]. TFC membranes can be used for separation of polyvalent ions and chemicals with molecular weight within a range of 100 and 1,000 [77]. Most of the available commercial NF membranes are TFC membranes formed through interfacial polymerization (IP), an established technique in which a polyamide (PA) active layer is synthesized on a polymeric support layer. The ultra-thin layer of TFC membranes are fabricated through IP of two monomers [78, 79] that are usually dissolved in immiscible solvents like water and hydrocarbon solvents [71, 76, 80-82]. The IP occurs in the interface between the two phases in two steps: first, the support is impregnated with an aqueous polyfunctional amine solution; and then it is put into interaction with an organic solvent containing a polyfunctional acid chloride [76, 79]. An ultra-thin (tens of nm to several µm) dense layer (top selective layer) is formed on a support porous substrate [71, 80, 82] and each of the layers can be independently adjusted and controlled to attain the anticipated solute separation rate and water permeability of the NF membrane [76, 77]. The ability to develop extremely thin layers of barrier materials from almost any conceivable chemical combination makes TFC technology a great success. Along with that, this method offers an excellent mechanical strength and compression resistance of the resulted material [76].

2.3.2 Synthesis of Thin Film Composite (TFC) Membranes

The performance of a membrane is determined by pore dimensions, thickness, roughness, hydrophilicity/hydrophobicity, cross-linking and functional bonds [76]. Since the productivity flux and membrane thickness are inversely proportional to each other, the synthesis of the thin membranes is of ultimate significance.

The development of dense membrane structure and hence the performance of the membrane are usually reliant on the porous support layer. The support of a TFC membrane, which is usually MF/UF membrane, is developed through the phase inversion method, in which a film of concentrated polymer is cast on an appropriate substrate and successively submerged into a non-solvent bath [77, 79, 83-85]. Thus, the interchange of solvent and phase separation takes place in the casting film. Usually, polysulfone (PSF) is proved to be the most appropriate polymer to form the substrate layer by many researchers [76, 81, 85-87] because of its availability, ease in processing and stability against thermal, mechanical, chemical and bacterial occurrence [81]. PSF is a rigid, amorphous, transparent polymer with high molecular weight and is soluble in a number of organic solvents, such as ethylene chloride, dimethylformamide (DMF) and N-methylpyrrolidone (NMP) [88]. Despite the excellent properties and broad usage in water purification, biochemistry, gas separation and drug extraction, PSF membranes have the major disadvantage of high hydrophobicity. This is an issue that renders PSF membranes easily susceptible to fouling [83, 88]. As a result, the flux through the PSF membranes declines and the rejection of contaminants, such as heavy metals, natural organic matter, salts, bacteria and viruses, becomes low [83]. One approach to increase the membrane’s hydrophilicity is the use of PSF and polyethersulfone (PES) with some modifications that find a compromise between hydrophobicity and hydrophilicity and localize the hydrophilic materials in the membrane pores increasing flux and reducing fouling [88]. Graft polymerization, plasma treatment, physical pre-adsorption of hydrophilic components to the membrane surface, surfactant modification, self-assembly of hydrophilic nanoparticles and membrane nitrification are some of the modification processes [88]. On the other hand, sulfonation, carboxylation and nitration are techniques by which the membrane polymers get modified before the preparation of membranes [88]. Song et al. [77] added sulfonated polysulfone (SPSF) into the porous PSF substrate to improve the hydrophilic property and binding capacity of the NF membrane. Membrane with PSF/SPSF blended support modified the asymmetric membrane structure with a higher permeability than that with PSF structure and could be successfully used in separating polyvalent ions, softening underground water, and purifying wastewater under low pressure with a wide pH range [77]. Several researchers have found that the blend of carbon nanotubes (CNTs) and PSF resulted in a new composite membrane with improved properties [89, 90]. According to Choi et al. [84], CNT/PSF composite membranes are more hydrophilic with smaller pores than pure PSF membranes. In that work, multi-walled carbon nanotube (MWCNT)/PSF blend composite membrane was fabricated through phase inversion method, using water as a coagulant [84]. MWCNTs were surface-modified with concentrated nitric acid (HNO_3) and sulphuric acid (H_2SO_4) (1:3 vol%) because acid-treated MWCNTs are known to have carboxyl groups on their surfaces showing easy dispersion in organic solvent, NMP [84]. Exactly 0.5%, 1%, 1.5%, 2% and 4% of MWCNTs were added with 20% PSF in NMP. Celik et al. [91] synthesized MWCNT/PES blend membranes through phase inversion method and produced more hydrophilic membranes with higher flux than the pristine PES membranes. Along with that this membrane showed less membrane fouling caused by natural water. The CNTs used were functionalized through reflux with 3:1 (v/v) HNO_3:H_2SO_4 and the solvent used was NMP. With an increase in MWCNT in the blend material, the flux increased; 2% MWCNT in 20% PES decreased 64% more of foulant than on bare PES membranes [91]. The work of Yokwana et al. [83] focused on the fabrication of nitrogen and phosphorous doped carbon nanotubes (fN-CNTs and fP-CNTs) and PSF blend membranes. They also used phase inversion method to prepare a membrane made with 15% PSF dissolved in dimethylacetamide (DMAc) and CNTs, and functionalized by a refluxing procedure. The purpose of using fP-CNTs and fN-CNTs was to improve hydrophilicity, thermal stability, water uptake and surface charge. Research showed that doped CNTs lead to the formation of “finger-like” structures that resulted in better membrane porosities and pore sizes. Ionita et al. [92] utilized graphene oxide (GO) to make a PSF-GO composite membrane through phase inversion method. In that process, DMF was used to dissolve 20% PSF and later GO was added to the homogenous polymer solution. Ethanol was used as the non-solvent where the PSF-GO solution, cast on a glass plate, had been immersed to complete the phase inversion method.

The principal concept of the IP is to select the correct partition coefficient of the monomers in the two-phase solution along with setting the appropriate diffusion speed which gives the ideal degree of densification of the ultra-thin layer [71]. The widely-used monomers are m-phynylenediamine (MPD) in aqueous phase and trimesoyl chloride (TMC) in organic phase. This combination has been commercially utilized to fabricate the TFC membrane [76, 78]. Xie et al. [93] indicated MPD concentration of 1.5-2% as optimum for ideal membrane performance and suggested that higher MPD concentration resulted in thicker barrier layer and lower membrane performance [93]. On the other hand, lower MPD concentration causes less diffusion of the amine to the organic phase, creating a thinner, less rough and defective layer with lower permeability and lower selectivity [94]. Meihong et al. [71] studied the development of TFC-NF membranes through IP of 0.2% piperazine (PRP) in DI water and 0.26% TMC in hexane and their performance for the removal of sulfate ions from concentrated aqueous salt solution. The support used for this IP was commercially available microporous PSF. Song et al. [77] synthesized the active skin layer by reaction between polyamine (p-phenylenediamine (PPD), MPD or PRP) in deionized (DI) water and TMC in hexane. Under ultra-low pressure (0.3 MPa), the membranes showed higher selectivity with reasonable flux rates for polyvalent ions than for monovalent ions [77]; PPD/TMC & MPD/TMC showed higher selectivity and lower permeability than PRP/TMC. Jeong et al. [95] reported the formation of mixed matrix RO membranes through the IP of nanocomposite thin films on porous PSF supports. The thin film was fabricated using 2% MPD and 0.1% TMC in n-hexane; the aqueous nanocomposite membranes were made by dispersing 0.004-0.4% of synthesized zeolite nanoparticles in the hexane-TMC solution. The purpose of selecting super hydrophobic, negatively charged, molecular sieve zeolite particles was hypothesized to provide preferential flow paths for water permeation while maintaining high solute rejection through combination of steric and Donnan exclusion [95]. The loading of zeolite into the TFC membranes affected the permeability of membranes; with a rise in zeolite loading, a growth in permeability was observed. Qiu et al. [96] prepared RO composite membrane with extra thin separation layer through IP of 2% MPD and 0.3% TMC on PSF support. The permeability and salt rejection capacity of TFC membranes depended highly on the concentrations of the monomers [96], especially MPD. Qui et al. [96] tried some phase-transfer catalyst so that monomers could diffuse to the phase interface and allow chemical reaction to proceed. The concept behind this was that the presence of phase transfer catalyst can transfer the complex compound of one monomer to the other phase in which the other monomer is dissolved and, as a consequence, both monomers could collide with each other in the same phase [96]. Cetyltrimethylammonium bromide was used as a phase transfer catalyst and it was found that when the concentration of MPD was low, it had notable consequence on both salt rejection and flux. The reason behind this improvement in IP yield was the introduction of hydrophobic functional groups that showed one kind of ionic surfactant, the effect of electrostatic exclusion helped the salt rejection and the introduction of ionic surfactant changed the binding energy between support layer and top layer that eventually influenced the property of the membrane. Qui et al. [96] also experimented the addition of isopropyl alcohol (IPA) and phenol to the MPD aqueous solution before the IP. The reason behind was that since alcohols and phenols are hydrophilic reagents, their addition to the monomers in water phase causes the hydroxyl to react with acylchloride of TMC changing the physico-chemical properties of composite membranes, forming structure of ester and thus improving the flux. Addition of IPA and phenol increased 2.5 times the initial flux with fairly constant rejection [96]. Hermans et al. [79] used a simplified method in which the phase inversion step and impregnation with the amine monomer were accomplished instantaneously by accumulating the amine to the coagulation bath before the cast polymer was immersed in it [79]. PSF-UF membranes were cast by phase immersion method (PSF in NMP) and then immersed in aqueous amine solution with 2% MPD, 2% trimethylamine (TEA) and 0.1% sodium dodecyl sulfate (SDS) whereas the organic solution was represented by 0.1% TMC (w/v) in n-hexane. The research showed that without compromising with membrane performance, the simplified method was able to reduce the required PSF concentration (16 and 18% PSF) compared to the traditional IP technique (20% PSF). The addition of TEA and SDS together had a positive impact on both water permeability and membrane selectivity. Ghosh et al. [81] dissolved 18% PSF in NMP to prepare the porous support; prepared the aqueous amine solution by dissolving 2% MPD, 2% TEA and 4% camphor sulfonic acid (CSA) in DI water and organic solution by dissolving 0.1% TMC in n-hexane [81]. Seman et al. [97] used Bisphenol A (BPA) as aqueous solution and TMC in n-hexane as organic solution to create thin film on asymmetric commercial membrane NFPES10. With an increase in BPA concentration, the thickness of the membranes increased exhibiting lower permeability. Barona et al. [78] synthesized TFC membrane by incorporating single-walled nanotubes (SWNT) in a polyamide matrix to increase the hydrophilicity and thus pure water flux. Commercial PSF-UF membranes were used as support, 2% (w/v) MPD served as aqueous monomer and 0.1% TMC (w/v) with 0.05%, 0.1% and 0.2% (w/v) SWNT in n-hexane acted as organic monomer in their research work [78]. The addition of 0.59 wt% SWNT in the membranes increased the pure water flux a 1.5-fold magnitude compared to that of a TFC membrane without SWNT [78].

Drazevic et al. [98], on the other hand, examined the effect of coating layer on the performance of TFC membrane. They layered commercial NF membrane NF270 with polyvinyl alcohol (PVA) layer and found that the coating resulted in an increase of 5 to 30% in the rejection of hydrophobic solutes and a decrease of 6 to 50% in the rejection of hydrophilic solutes [98]. PVA has been proved to have enormous prospective as an NF membrane material due to its numerous amounts of hydroxyl groups on the membrane surface revealing a polar character [86]. Peng et al. [99] synthesized a composite NF membrane by coating commercial PSF-UF membrane with 0.1wt% PVA, cross-linked with maleic acid (MA) to get 20% cross-linking degree. Gohil and Ray. [86] prepared a TFC membrane with 17% porous PSF as base support and 1% PVA, cross-linked with 0.2% (w/w) MA as the barrier layer [86]. Maphuta et al. [87] prepared CNT impregnated polymer composite membranes with PVA barrier layer to separate oil from water.

2.3.3 Separation Performance of Thin Film Composite (TFC) Membranes

Jeong et al. [95] carried out the permeability and separation performance of TFC membranes, synthesized with MPD, TMC and zeolite nanoparticles, in a high pressure chemical resistant stirred-cell (HP-4750). When the amount of zeolite nanoparticles was increased in the TFC membranes, the permeability increased from $2.1 \pm 0.1 \mathrm{x} 10^{-12}$ $\mathrm{mPa}^{-1}\mathrm{s}^{-1}$ to $3.8 \pm 0.3 \mathrm{x} 10^{-12}$ $\mathrm{mPa}^{-1}\mathrm{s}^{-1}$ [95]. Yokwana et al. [83] utilized a cross-flow membrane testing unit with an effective membrane area of 18.30 cm^2 for permeability and selectivity tests of functionalized doped CNT/PSF NF membranes. Although 0.3% fN-CNT/PSF showed the maximum flux of 84.7 $\mathrm{L.m}^{-2}.\mathrm{h}^{-2}$, 0.5% fN-CNT/PSF showed the highest rejection of magnesium sulfate ($MgSO_4$) (95%) [83]. The TFC membrane prepared with 0.2% aqueous PRP and 0.26% TMC in hexane exhibited a water permeability coefficient of 75 $\mathrm{L.m}\text{-}^{2}.\mathrm{h}^{-1}$ MPa with 67% rejection of sodium chloride (NaCl) and 98% rejection of $MgSO_4$ at 1 MPa [71]. Song et al. [77] found that when the support of the TFC membranes prepared with MPD/PPD/PRP and TMC was PSF/PSF alloy substrate, there was an amplification in the permeability of the membranes. For MPD/TMC membranes, this increase was 4.0 to 6.1 $L.m^{-2}.h^{-1}$; for PPD/TMC, the rise in flux was from 2.8 to 4.0 $L.m^{-2}.h^{-1}$; whereas an increase from 8.0 to 13.2 $L.m^{-2}.h^{-1}$ was visible for PRP/TMC membranes [77]. In case of MWCNT/PSF blend membranes, at a pressure of 4 bar, maximum pure water flux of ~21 m^3/m^2-day was observed when 1.5 wt% MWCNT was used [84]. Qiu et al. [96] found that the concentrations of MPD and TMC in TFC membranes significantly impact the pure water flux and rejection capacity of the membranes. When the TMC concentration raised from 0.05 to 0.4% (w/v), there was a 20% decrease in water flux; whereas with an increase of MPD concentration from 0.8 to 2.4% (w/v), the flux dropped ~34% [96]. Hermans et al. [79] synthesized TFC membrane via a simplified method and indicated that with 2.5% MPD in coagulation bath and 18% PSF, at 15 bar, membrane permeance was 4 $L.m^{-2}.h^{-1}.bar^{-1}$ and $MgSO_4$ rejection was 99%. The TFC membrane prepared by Gohil and Ray [86] achieved 22.8% and 83.8% rejection of NaCl and $MgSO_4$ respectively. Table 2.4 gathers the permeability and rejection capacity of chosen TFC membranes.

Table 2.4: Permeability and Separation Performance of TFC Membranes

Membranes	Flux ($L.m^{-2}.h^{-1}$)	Rejection of NaCl (%)	Rejection of $MgSO_4$ (%)	Reference
MPD/TMC	19	96	-	[96]
MPD/TMC	5-7	-	95-97	[100]
MPD/TMC	42	99.8	-	[101]
MPD/TMC	60	95	-	[102]
MPD/TMC	25.8	96.4	-	[103]
MPD/TMC	82	95.3	-	[104]
PRP/TMC	5-20	-	85-95	[77]

PPD/TMC	2-5	-	92-99	[77]
PIP/TMC	75	67	98	[71]
0.3% fN-CNT/PSF	84.7	31.6	92.6	[83]
0.3% fP-CNT/PSF	72.6	32.3	93.3	[83]
0.5% fN-CNT/PSF	51.3	33.5	95	[83]
MPD/TEA/SDS	33.75	-	99	[79]
PSF/PVA/MA	12.5	-	90	[86]
NTR-7250 (commercial)	62.5	50	98	[71]
Desal-5 (commercial)	47.1	50	96	[71]
NF-70 (commercial)	72	70	98	[71]

2.4 Organic Solvent Nanofiltration (OSNF) Membranes

Another type of NF is the organic solvent nanofiltration (OSNF) which is an energy efficient separation process showing high potential in different branches of industry [105]. The OSNF is proficient at separating molecules of 200-1,000 g/mol in several organic solvents [105]. According to literature, most of the OSNF membranes are asymmetric and integrally skinned, and made of polyamides (PI) or composites consisting of a thin poly(dimethyl siloxane) (PDMS) separating layer on various types of supports, such as: PES [106, 107]; PSF [108, 109], polyamide [110], polyimide (PI) [111], polyacrylonitrile (PAN) [112], cellulose acetate [113, 114], polytetrafluoroethylene [115], ceramic porous support [116-118], polyethylene-perforated metal support [119] etc. Chemical, thermal and mechanical stability are the general requirements for the supporting layers [120]. Along with that, strong adherence of the support layer to the top layer as well as high porosity are also important criteria [120].

2.4.1 Poly (dimethyl siloxane) PDMS

Poly (dimethyl siloxane) (PDMS) is known to be the most commonly used hydrophobic material with elastic behaviour, resistance to high temperatures, light degradation and chemical attack that has been efficaciously applied for the preparation of membranes used in different purposes [121, 122]. PDMS is a biocompatible, cheap and easy to use [123] elastomer with an inorganic siloxane (Si-O) backbone and organic methyl groups attached to the silicon atoms [122, 124]. Its non-polar, hydrophobic nature makes PDMS susceptible to swelling in the presence of alkane and aromatic solvents [125]. PDMS is highly soluble in non-polar solvents; thus to make it chemically stable, the cross-linking of PDMS is necessary and various applications, such as- electrical/optical devices [126], anticorrosion [127], anti-fouling material [128] as well as biomedical applications [129, 130] have found cross-linked PDMS to be very suitable. To attain the chemical stability, it is necessary to create a three-dimensional cross-linked network by reacting the functional vinyl end groups on the linear PDMS chains with a multifunctional cross-linker in the presence of a catalyst [121, 124, 125, 131]. Since the addition of hydrosilation has been normally utilized for the synthesis of cross-linked PDMS materials [132, 133], the rate of hydrosilation, the vinyl group of the PDMS, the number of Si-H groups on the cross-linker, the concentration of the cross-linker as well as the type and molecular structure of the catalytic complex are of important concern. For vinyl terminated PDMS, according to Esteves et al. [121], the most credible reaction is the β-addition of a silicon hydrogen to the vinyl bond (Eqn 2.1).

$$\text{R-Si-H} \quad + \quad \text{CH}_2\text{=HC-Si-R} \xrightarrow{\text{Heat and catalyst}} \text{R-Si-CH}_2\text{-CH}_2\text{-Si-R} \ldots\ldots\ldots\ldots\ldots \text{(2.1)}$$

According to Stein et al. [134], the hydrosilation reaction, in the presence of a platinum catalyst, continues in three phases: the induction period, a rapid exothermic regime and finally a post-curing stage. In the induction period, the active species of the catalysts are formed; during the rapid exothermic regime, most of the products of the hydrosilation reaction are formed whereas in the post-curing stage, the hydrosilation reaction ensues very slowly or ends [121]. The performance of PDMS membranes depends on the terminal group, PDMS to cross-linker ratio, cross-linking density, PDMS chain length etc. [108]. The degree of cross-linking of the silicone network is a very important factor in the characteristics of the NF membranes [135]. During the synthesis of PDMS membranes, the optimization of inter-chain bonding of PDMS oligomers depends on two main factors: a) the chemical curing agents and catalysts b) the cross-linking temperature. Simpson et al. [100] noted that the rate of polymerization is linearly proportional to the catalyst concentration. Berean et al. [123] studied the effect of cross-linking temperature on the permeability of PDMS membranes and found that an optimal temperature of 75^{o}C resulted in membranes with the highest gas permeation. Dutczak et al. [105] showed that adjusting the viscosity of the PDMS coating solution highly affects the quality of the PDMS layer in a composite membrane and a better control of viscosity can be accomplished at a temperature around 50^{o}C.

2.4.2 Preparation of Organic Solvent Nanofiltration Membranes with PDMS

Literature reports several methodologies to synthesize composite PDMS membranes, for example, filling the pores of a support layer with an active PDMS layer [117], dip-coating [136] and pressing [137]. During the dip-coating process, the spreading velocity of the PDMS solution as well as the dip-coating time plays an important role in PDMS film thickness. The thickness increases with an increase in PDMS concentration as well as with a dipping time. Stafie et al. [112] prepared a composite membrane with PAN as a support and PDMS as the selective top layer for the recovery of hexane from oil/hexane and PIB/hexane mixtures [112]. As PDMS, RTV615 consisting of a vinyl-terminated pre-polymer with high molecular weight (RTV A) and a cross-linker having several hybrid groups on shorter PDMS chains (RTV B) with a ratio of 10:1 had been used [112]. Pt-catalyzed hydrosilylation reaction caused the curing of PDMS membrane that resulted in a densely cross-linked polymer network. The PAN support was dip-coated in 5 and 7 wt% pre-cross-linked PDMS-n-hexane solution. The pre-cross-linking was done at 60^{o}C for 3 hours. Then the membrane was dried in air for 10 minutes and the final cross-linking was performed for 4 hours at 65°C. Membranes made with 5% (w/w) PDMS showed coating layer with defects due to the low viscosity, whereas 7% (w/w) PDMS coating provided a much better quality top-layer [112]. In another study, Stafie et al. [135] studied the influence of cross-linker amount of 6.5, 9.1 and 16.7% corresponding to the pre-polymer cross-linker ratio of 10:0.7, 10:1 and 10:2 respectively on the membrane swelling and permeation properties [135]. The research found that hexane permeability through the PAN/PDMS composite membrane synthesized at a pre-polymer/cross-linker ratio of 10:0.7 was higher than that of the ratio of 10:2 and 10:1; the apparent viscosity inside the membrane and higher membrane swelling were the reasons for the difference in permeability [135]. Dutczak et al. [105] investigated the preparation of composite capillary membranes consisting of commercial Hyflux InoCep M20 α-alumina support with tailor-made PDMS (RTV 615) top layer. A 15% PDMS solution was diluted up to 3.75% as lower PDMS concentration is vital to preparing a thin selective layer of the membrane [105]. Moreover, the low concentration PDMS solution was pre-crosslinked to get a higher viscosity as low viscosity PDMS solution produced defected top-coat. Dutczak et al. [105] also found that, to prepare a good PDMS composite membrane, the pore size of the support should be small, otherwise the coating solution intrudes significantly into the pores of the supports and blocks the pores which eventually decreases the permeability of the membrane [105, 120].

Dobrak-Van Berlo et al. [122] studied the importance of solvent parameters (such as viscosity, molar volume) and solvent-membrane interaction parameters (such as swelling) and difference in surface tension in both NF and pervaporation (PV) by preparing both unfilled and filled membranes from 10% PDMS solution. The PI support layer was prepared from a PI solution containing 15 wt% PI, 2 wt% H_2O, 62.25 wt% NMP and 20.75 wt% tetrahydrofuran (THF). This solution was cast on a polypropylene non-woven support with a casting knife; after casting, the solvent was allowed to evaporate for 30 secs and then the membrane was immersed in water at room temperature. Subsequently, the membrane was immersed in para-xylenediamine/methanol (1:10, w/v) mixture for 24 hours for the purpose of cross-linking the PI and then rinsed with methanol. These membranes were furthermore treated through solvent-exchange procedure. To coat this PI support, a 10% pre-cross-linked PDMS solution (RTV 615A and B, pre-polymer and cross-linker in a 10:1 ratio) in hexane was used. For zeolite filled PDMS membrane, 15 wt% of silicate zeolites was used in the PDMS solution. This assimilation of zeolite lessened swelling and enhanced retention capacity of the membrane [122]. In this study, for dense PDMS and PI membranes the transport mechanisms were investigated using a wide range of solvents and pressures [122].

Madaeni and Hoseini [138] fabricated a series of membranes with PES as support and PDMS as active layer for the separation of ethylene from nitrogen. The PDMS used was Sylgard 184 silicone elastomer, consisting of polymer base and hardener. The polymer base consisted of dimethylsiloxane, dimethyl vinyl terminated, dimethyl vinylated and trimethylated silica as well as tetra (trimethylsiloxy) silane while the hardener consisted of dimethyl methylhydrogen siloxane tetramethyl tetravinyl cyclotetrasiloxane. The asymmetric PES support was synthesized by a phase-inversion method using NMP and dimethylsulfoxide as solvents. PDMS (base: hardener = 10:1), dissolved in n-hexane, was used to top-coat the PES support and left at room temperature for several days for drying. Madaeni and Hoseini [138] found that lower concentration of the support polymer created wider pores and less tight membranes; on the other hand, dense PDMS coating layer resulted in lower nitrogen permeability. The best performance for ethylene permeance was achieved for membranes prepared from 20 and 22% PES, 9% coating solution and 35-50 µm thickness [138].

Wei et al. [139] prepared cross-linked PDMS/ceramic composite membranes by the conventional dip-coating method. Here tubular asymmetric ZrO_2/Al_2O_3 membranes were used as ceramic supports and blend cellulose acetate MF membrane was used as a polymer reference membrane [139]. Exactly 10wt% α,ω-dihydroxypolydimethylsiloxane was dissolved in n-heptane with tetraethoxysilane (TEOS)/PDMS weight ratio 0.1 and 0.2wt% dibutyltin dilaurate catalyst was used as the coating solution. The supports were pre-wetted with water before dipping into polymer for the fact that since the pores of the supports were filled with water, the penetration of coating solution into the pores was significantly reduced and that improved the permeability. This study supported the work of Vankelecom et al. [120]. They also found that composite membranes prepared with higher molecular weight PDMS exhibited higher separation and lower permeate flux.

Li et al. [113] prepared PDMS composite membranes by top-coating pre-wetted cellulose acetate MF membranes with α,ω-Dihydroxypolydimethylsiloxane, cross-linking agent Tetraethylorthosilicate (TAOS) and catalyst dibutyltindilaurate in a ratio of 10:1:0.2 in n-heptane. The membrane was initially cross-linked at room temperature for 2 hours and then finally at 60^{o}C for 4 hours. These membranes showed remarkable high permeate flux for ethanol [113].

Jadav et al. [140] used a mixture of hydroxyl terminated polydimethylsiloxane (HPDMS) and polymethylhydrosiloxane (PHMS) in n-hexane (HPDMS:PHMS=10:1) with dibutyltindilaurate as the catalyst to prepare the polymer solution [140]. For free-standing PDMS membrane, the PDMS concentration used was 20% whereas for composite membrane, a diluted PDMS concentration (0.05-5%) was used to top coat PSF support [140]. Cross-linking was finalized by putting the membranes in an oven at 80^{o}C for 1 hour. The neat PDMS membranes showed non-porous, dense, relatively smooth surfaces; on the other hand, when the coating was done with dilute PDMS solution, more polymer could penetrate the porous support, making the membrane structure loose upon decreasing its thickness and exhibiting larger crystalline domains on the surface of the composite PDMS membranes [140]. These polymer clusters or crystals could be produced with defects showing high permeability of water and methanol but low selectivity [140]. Kim et al. [141] used three types of supports, such as-non-woven fabric, PSF-UF membrane, non-woven fabric treated with polyethylene glycol (PEG, MW=10,000) aqueous solution to prepare PDMS composite membranes and compared the removal capacity of toluene. The study found that the membranes with PEG-treated non-woven fabric support layer showed the best performance in toluene removal. Since water soluble PEG had been used as a clogging medium, the PDMS intrusion in the pores was prevented increasing the toluene flux over the other two types of membranes [141].

The incorporation of filler-like nanoparticles into polymer matrix and then coating with PDMS is a recent trend in membrane technology that has been used to improve the gas separation performance. Jomekian et al. [142] incorporated MCM-41, both unmodified and modified with dimethyldichlorosilane (DMDCS) nanoparticles in 20% PSF to prepare a MCM-41/PSF nanocomposite membrane; N,N-dimethylacetamide (N,N-DMAc) had been used as a solvent. The mixture of MCM-41/PSF was cast on a glass plate with a casting blade and the support was prepared using the phase-inversion method [142]. Exactly 5, 7 and 30 wt% PDMS was dissolved in n-hexane and the MCM-41/PSF support was dip-coated with a given PDMS solution. Final cross-linking was done in an oven at 100^{o}C for 24 hours. Scanning Electron Microscopy (SEM) images showed that the mixture of unmodified MCM-41 and PSF created unfavorable voids between polymer matrix and inorganic material whereas MCM-41 modified with DMDCS ensured higher dispersion in PSF resulting in no distinct voids between two phases [142]. PDMS coating on the membrane surface controlled the permeation and ideal selectivity of membrane through the concentration of coating solution [142].

To prevent the pore intrusion, several techniques have been applied by researchers: some found that filling the support pores with a non-solvent [143, 144] for the coating polymer or with a solvent [145] before applying the coating solution could reduce the pore intrusion. Another way is to fill the pores with high viscosity materials [146]. Some authors suggested the casting of top layers from a concentrated solution to form a gel as soon as the support is contacted for limiting the penetration [147]. Vankelecom et al. [120] tried pretreatment of support layers by combining different solvent exchange steps (IPA, n-hexane and water) before applying a selective layer on the support. PSF, PAN and Zirfon (PSF membranes containing Zirconium dioxide, ZrO_2 fillers) membranes were used as supports whereas RTV 615A and RTV 615B were used as prepolymer and cross-linker (RTV A: RTV B=10:1) respectively in the study. PDMS concentrations ranged between 10 and 20% (v/v) that was pre-cross-linked for 30 minutes at 70^{o}C. Final cross-linking was done at 150^{o}C for 1 hour. Pervaporation with 6 wt% aqueous ethanol or t-butanol solutions was done to evaluate the performance of these membranes [120] and it was found that water in the pores of the supports was perfect to coat with PDMS dissolved in hexane [120] to reduce intrusion. Jomekian et al. [142] showed that higher PDMS concentration (30 wt%) prevented the undesirable penetration of PDMS during dip-coating into pores of supports and thus showed remarkable increase in selectivity of gases.

2.4.3 Performance of Organic Solvent Nanofiltration Membrane

Stafie et al. [112] tested performance of PDMS membranes through a dead-end filtration system. According to their study, the solution-diffusion model described the hexane transport through the membrane and both the flux and solute retention depended on the applied transmembrane pressure and feed concentration. The permeability of hexane decreased with an increase in oil concentration in the oil/hexane feed [112]. Table 2.5 summarizes the performance of PAN/PDMS composite membranes for various oil/hexane feed concentrations.

Table 2.5: Performance of PAN/PDMS Composite Membranes for Various Oil/Hexane Feed Concentrations [109]

Transmembrane Pressure (bar)	Hexane Flux (L.m^{-2}.h^{-1})			
	Pure hexane	8% w/w (oil/hexane)	19 % w/w (oil/hexane)	30 % w/w (oil/hexane)
1	4	-	-	-
2	8	2.5	-	-
3	12	5	-	-
4	16	7.25	2.5	-
5	20	8.5	5	1
6	24	11	6	2
7	27.5	12.5	7.5	4

In another study [74], it was found that, PAN/PDMS composite membrane with the pre-polymer/cross-linker ratio of 10/0.7 showed the highest hexane permeability of 4.5 L.m^{-2}h^{-1}bar^{-1}. Table 2.6 shows the hexane permeability of some of the OSNF membranes.

Stafie et al. [135] also studied the hexane permeability of PAN/PDMS for various PIB-1300/hexane feed concentrations (Table 2.7).

Dutczak et al. [105] performed the permeation experiments in a custom-made cross-flow high pressure permeation set up equipped with an HPLC pump that could pressurize the set-up up to 40 bar. It was found that the composite capillary membrane developed in this study M20/55 (where M20 represents Hyflux InoCep M20 support and 55 represents the viscosity in mPa-s of 3.75% PDMS solution) showed the highest toluene permeance of 1.6±0.11 L.m^{-2}.h^{-1}.bar^{-1} [105]. Vankelecom et al. [148] prepared a polyacrylonitrile-polyester/PDMS (PAN-PE/PDMS) composite membrane with toluene permeance of 1.2 L.m^{-2}.h^{-1}.bar^{-1} whereas a commercial silicon-based membrane, MPF-50 (Koch) had a toluene permeance of 1.3 L.m^{-2}.h^{-1}.bar^{-1} [149]. The use of PDMS membranes for separation of ethanol from an aqueous solution is of great importance. Table 2.8 provides an overview of pervaporation data for the separation of ethanol from dilute aqueous solution with PDMS membranes.

Table 2.6: Hexane Permeability of Chosen OSNF Membranes [60, 78-80]

Membrane	Permeability of Hexane (L.m^{-2}.h^{-1}.bar^{-1})	Reference
PAN/PDMS	4.5	[135]
Pebax Composite Membranes	3-4.9	[150]
D membrane from Osmonics	1.6	[151]
MPF-50	1.52	[152]

Table 2.7: Performance of PAN/PDMS Composite Membranes (Pre-polymer/Cross-linker ratio 10:0.7) for Various PIB-1300/Hexane Feed Concentrations [135]

Transmembrane Pressure (bar)	Hexane Flux ($L.m^{-2}.h^{-1}$)		
	Pure hexane	8% w/w (PIB-1300/hexane)	19 % w/w (PIB-1300/hexane)
1	-	-	-
2	9.5	4	-
3	14	n/a	1.25
4	19	10	n/a
5	n/a	13	5
6	n/a	n/a	6
7	31	20	8.5

Table 2.8: Separation of Ethanol from Water with PDMS Membranes

Membranes	Mass % of Ethanol in Feed	Permeation Flux ($L.m^{-2}.h^{-1}$)	Separation Factor	Reference
PDMS/CA	5	4927	8.3	[113]
PDMS/ceramic	5	6064	8.9	[139]
PDMS/PVDF	10	3411	31	[153]

PDMS-PS/PESF	10	493	6.2	[154]
PDMS/PS	8	1005	6.4	[155]

2.5 Concluding Remarks

Trace contaminants like PhACs and EDCs along with their degradation by-products have been increasingly detected in the aquatic environment. Because of the rapid development of sensitive analytical techniques, it has become possible to identify the trace amounts of these emerging contaminants in the environment. Nevertheless, despite their unidentified influence on human health and environment, there is, at present, no legitimately controlled maximum tolerable concentration of these chemicals in the environment.

Since conventional wastewater treatment plants are not efficacious in thorough elimination of the trace contaminants from urban wastewater, more effective and precise treatment procedures are essential. AOPs, in the recent years, have shown quite effective removal efficiency for PhACs and EDCs; nevertheless, the investigation of their fate and transformation along with the by-products during these removal techniques are still largely unknown.

A number of studies have identified nanofiltration technique as an established remedial procedure for emerging contaminants from water and thin film composite nanomembranes are dominating representatives for this category. Interfacial Polymerization has been known as a proven concept for the preparation of thin film composite nanofiltration membranes where an ultrathin selective layer is formed through interfacial cross-linking between reactive monomers over a porous support layer. Commonly, polysulfone (PSF), which is a rigid, transparent and high molecular weight polymer, has been extensively utilized to form the support layer of a TFC membrane. Whereas, aqueous m-phynylenediamine (MPD) and trimesoyl chloride (TMC) in n-hexane are the most widely used monomers. The combination of PSF-MPD-TMC membranes were able to achieve a NaCl rejection of 95~99.8% and $MgCl_2$ removal of 95~97% with a flux of 5~82 $L.m^{-2}.h^{-1}$. The infusion of functionalized multi-walled carbon nanotubes with the PSF polymer matrix often produced an improved flux.

Organic solvent nanofiltration membrane is another emerging pressure-driven separation methodology having a number of advantages like flexibility and ease of production. Mostly, the OSNF membranes are asymmetric and integrally skinned; free-standing or composites comprising of a thin poly (dimethyl siloxane) (PDMS) separating layer on different types of supports, such as polysulfone, ceramic acetate, polyacrylonitrile, polyethersulfone etc. The terminal group, PDMS to cross-linker ratio, cross-linking density and temperature, PDMS chain length, viscosity of PDMS solution etc. are some of the factors affecting the characteristics of the OSNF membranes. Composite PDMS membranes synthesized in different studies have been used for gas permeation, separation of phase-transfer agent, solvent-deoiling, homogeneous catalyst recovery etc.

2.6 References

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Chapter 3

3 Materials and Methods

This chapter discusses the materials and methods used in this study: the chemicals and instruments utilized for the detection of ibuprofen (IBP), naproxen (NPR), diclofenac (DCF) and 17α-ethinylestradiol (EE2), developed methodologies for the purpose of preparation, and characterization and evaluation of membrane performance.

3.1 Chemicals and Reagents

HPLC-grade (≥99%) hexane and methanol were purchased from Sigma Aldrich, Canada. Reagent grade dichloromethane and toluene were purchased from Caledon Laboratories Ltd. For analytical determination, reference compounds for ibuprofen, diclofenac sodium salt, naproxen and 17α-ethinylestradiol (≥98%) were purchased from Sigma Aldrich, Canada. Anhydrous N,N-Dimethylformamide (99.8%), Polysulfone pellets (average M.W.~35,000), Trimethylsilyl-2,2,2-trifluoro-N-(trimethylsilyl) acetamide (BSTFA) (99.6%) and Multi-walled Carbon Nanotubes (6-9 nm x 5 µm, > 95% carbon) were also purchased from Sigma-Aldrich, Canada. For solid-phase extraction, Hypersep C18 cartridges were purchased from Thermo Scientific, Canada. PTFE laminated membranes (0.1 micron, non-woven polyester backer, 47 mm diameter) were purchased from Sterlitech Corporation, USA. ACS grade sulfuric acid and nitric acid were obtained from VWR Analytical, Canada.

General Electric PDMS RTV 615 kit was purchased from Momentive Performance Materials. The silicon kit comprises two components: a) a vinyl terminated pre-polymer (RTV 615A) and b) a Pt-catalyzed cross-linker (RTV 615B) containing a polyhydrosilane component.

SYLGARD 184 silicone elastomer kit, purchased from Sigma Aldrich, Canada, comprises of two parts: a polymer base and a hardener. The polymer base has a specific gravity of 1.05 g/cm^3 at 25^{o}C and a viscosity of 500 mPa-s; it is a viscous, colorless liquid comprised of dimethylsiloxane, dimethylvinilterminated, dimethyl vinilated and trimethylated silica as well as tetra (trimethylsiloxy) silane [1]. The hardener with a specific gravity of 1.03 g/cm^3 at 25°C and a viscosity of 110 mPa-s, consisted of dimethyl methylhydrogen siloxane tetramethyl tetravinyl cyclotetrasiloxane.

Laboratory grade water was obtained with a Barnstead Easy Pure UV 45 Ultrapure water purification system (Barnstead, IOWA, U.S.A.).

3.2 Collection of Wastewater Samples

All glassware, supplies and containers were solvent rinsed three times each with acetone, hexane and methanol. To analyze pharmaceutically active compounds (PhACs), wastewater effluent samples were collected over a six-month period, from August 2015 to January 2016, from two WWTTPs: Greenway Pollution Control Plant and Adelaide Wastewater Treatment Plant, in London, ON, Canada. Whereas, to analyze EE2, effluent samples were collected from Adelaide Wastewater Treatment Plant in London, ON, Canada. Triplicate grab samples were collected in both cases in clean and dry amber bottles. The samples were immediately filtered through 0.45 µm filters purchased from Whatman. For the analysis of PhACs, the samples were acidified to pH=1.95 with hydrochloric acid (HCl); on the other hand, EE2 analysis did not require any acidification. Subsequently the samples were stored at 4°C until further processing. Samples were processed within 24 hours of collection.

3.3 Sample Preparation

Analytical stock solutions of IBP, NPR, DCF and EE2 of 1 mg/mL were prepared in methanol and stored at -18°C. To prepare calibration curves, standards of different concentrations were prepared by diluting the stock solution in methanol. Synthetic samples with specific concentrations of pharmaceuticals and EE2 were prepared by spiking the desired amount of stock solution in Milli-Q water.

3.4 Extraction and Derivatization of Sample

Because of the very low concentration of EE2 and PhACs in water samples, pre-concentration by solid phase extraction (SPE) or liquid-liquid extraction (LLE) is required before LC-MS or GC-MS analysis [2-4]. C-18, Oasis HLB and NH_2 are the common types of cartridges used in SPE [2, 4, 5] whereas dichloromethane (DCM) has been used as the solvent for LLE.

3.4.1 Solid-phase Extraction

In this study Hypersep C18 (6 mL, 500 mg bed) cartridge has been used to perform the SPE of EE2 (Figure 3.1). Total SPE procedure was carried out in 5 steps: i) conditioning, ii) loading, iii) drying, iv) elution and v) reconstitution. For the purpose of conditioning, 12 mL of methanol was initially passed through the cartridge at -3 in Hg (~11 kPa), followed by 12 mL of deionized (DI) water at -5 to -8 in Hg (~20 kPa). The sample was then percolated through the cartridge at 1~2 drops/ sec at 20 kPa. The cartridge was subsequently allowed to dry for 5-60 minutes, depending on the type of elution solvents. Furthermore, a flow of hexane was allowed to go through the cartridge. Afterwards, elution took place by passing 15 mL of elution solvents at a rate of 1-2 drops/ sec at 20 kPa. Finally, reconstitution was performed by completely drying the collected volume with gentle flow of N_2 and adding 100 µL of methanol for LC/MS analysis.

Figure 3.1: Solid-Phase Extraction of Water Sample using Hypersep C-18 Column

3.4.2 Liquid-liquid Extraction

According to U. S. Environmental Protection Agency (EPA) Method 625, liquid-liquid extraction (LLE) with DCM followed by gas chromatography/mass spectrometry (GC/MS) analysis can be used for the determination of extractable organic pollutants in water. In the present study, to extract IBP, NPR and DCF, the LLE technique was used; whereas to do a comparison of extraction for EE2, both LLE and SPE were performed. To do a successful LLE, 50 mL of the samples were extracted with 50 mL of dichloromethane (Sample: DCM = 1:1), three times, by using a separatory funnel. The collected DCM extract was then evaporated using a BÜCHI Rotavapor®; here the water bath was maintained at 45°C (±2°C), until the remaining extract was about 1 mL. The extract was then moved to a 2-mL vial and completely dried with N_2. In case of EE2, a reconstitution was done by adding 100 µL of methanol. This 100 µL extract was then analyzed on LC/MS. In the case of IBP, NPR and DCF, to be compatible with GC analysis, a sample derivatization was required to make the compounds more volatile [4, 6-9].

Figure 3.2: BÜCHI Rotavapor used to evaporate the sample obtained after LLE

3.4.3 Derivatization

The core tenacity of analytical derivatization is to increase the volatility of the analytes by reducing the polarity of carboxylic (COOH-) or phenolic (OH-) functional groups, thereby increasing the thermal stability. In literature, acidic pharmaceuticals containing carboxylic moieties were found to be derivatized by silylation with N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA), acylation with trifluoroacetic anhydride (TFAA), and benzylation with pentafluorobenzyl bromide (PFBB), or methylation with trimethylsulphonium hydroxide (TMSH) or diazomethane (CH_2N_2) [10-13]. In this study, samples were derivatized using pyridine (50 µL) and BSTFA (50 µL) at 70^{o}C for 40 minutes.

The different sample preparation schemes for the analysis of EE2 and PhACs in wastewater and synthetic water are shown in Figure 3.5.

3.5 Analytical Methods

The reported low concentrations and small molecular weight (296.4 g/mol) of EE2 present challenges in its analysis in complex matrices such as sludge and wastewater [14, 15]. Along with that, lack of restrictive strategies to regulate the release of new compounds, by-products and pharmaceuticals into water and wastewater makes the analysis of EE2 even harder [14]. Improved and advanced analytical and bioanalytical techniques comprised of highly sensitive instrumentation are therefore needed [9, 16].

The most extensively used analytical technique for detection of EE2 has been found to be gas chromatography coupled with mass spectrometry (GC-MS) [6, 9, 16, 17]. Lately, the use of liquid chromatography coupled with mass spectrometry (LC-MS) has become more convenient than GC-MS due to its higher sensitivity, selectivity, simplicity, and the absence of derivatization steps [3, 4, 8, 9].

The analytical measurements for EE2 were performed using an Agilent 6230 TOF-LC/MS (Figure 3.3). Liquid chromatographic separation was carried out at room temperature using a Zorbax Eclipse Plus C18 (2.1 x 50 mm; 1.8 µ) Rapid Resolution High Through Column. For the separation of EE2, a programmed gradient was applied using water with 0.1% formic acid (A) and 0.1% formic acid in 90% acetonitrile (B) as solvents. The initial composition of the mobile phase was 70% A and 30% B. This level was held for 3 minutes and then was changed within 10 minutes to 40% A and 60% B. Next, within 1 minute, B became 100% and this condition maintained for 3 minutes. In the next 1 minute, A and B went back to the initial condition (70% and 30% respectively) and this continued for the next 7 minutes. The flow rate of the mobile phase was 0.256 mL/min. The injection volume was 75 µL and the column temperature was 35°C. Mass spectrometric measurements were performed with an electrospray ionization source operated in the positive ionization mode. High purity N_2 was utilized for de-solvation and nebulization.

Figure 3.3: Agilent 6230 TOF-LC/MS used for EE2 Analysis

Separation and detection of the pharmaceutical compounds was done using an Agilent 7890A GC-FID system (Figure 3.4). The GC-FID was equipped with a DB-5 column (30 m x 320 µm x 0.25 µm). Hydrogen was used as a carrier gas at 2.5 mL/min. N_2 was used as a make-up gas with a flow of 20.5 mL/min. Samples (1 µL) were injected in split less mode with a pressure pulse of 30 psi for 1.4 minutes. The injector was set as 250°C. The oven temperature was programmed as shown in Table 3.1. The FID was set at 310 °C.

Table 3.1: Oven Temperature Program for GC analysis of Pharmaceuticals

Rate °C/min		°C	Hold Time (min)	Run Time (min)
	0	60	1.5	1.5
Ramp 1	20	120	0	4.5
Ramp 2	4	160	0	19.5
Ramp 3	12	300	3.8	30

Figure 3.4: Agilent 7890A GC-FID System used for PhACs Analysis

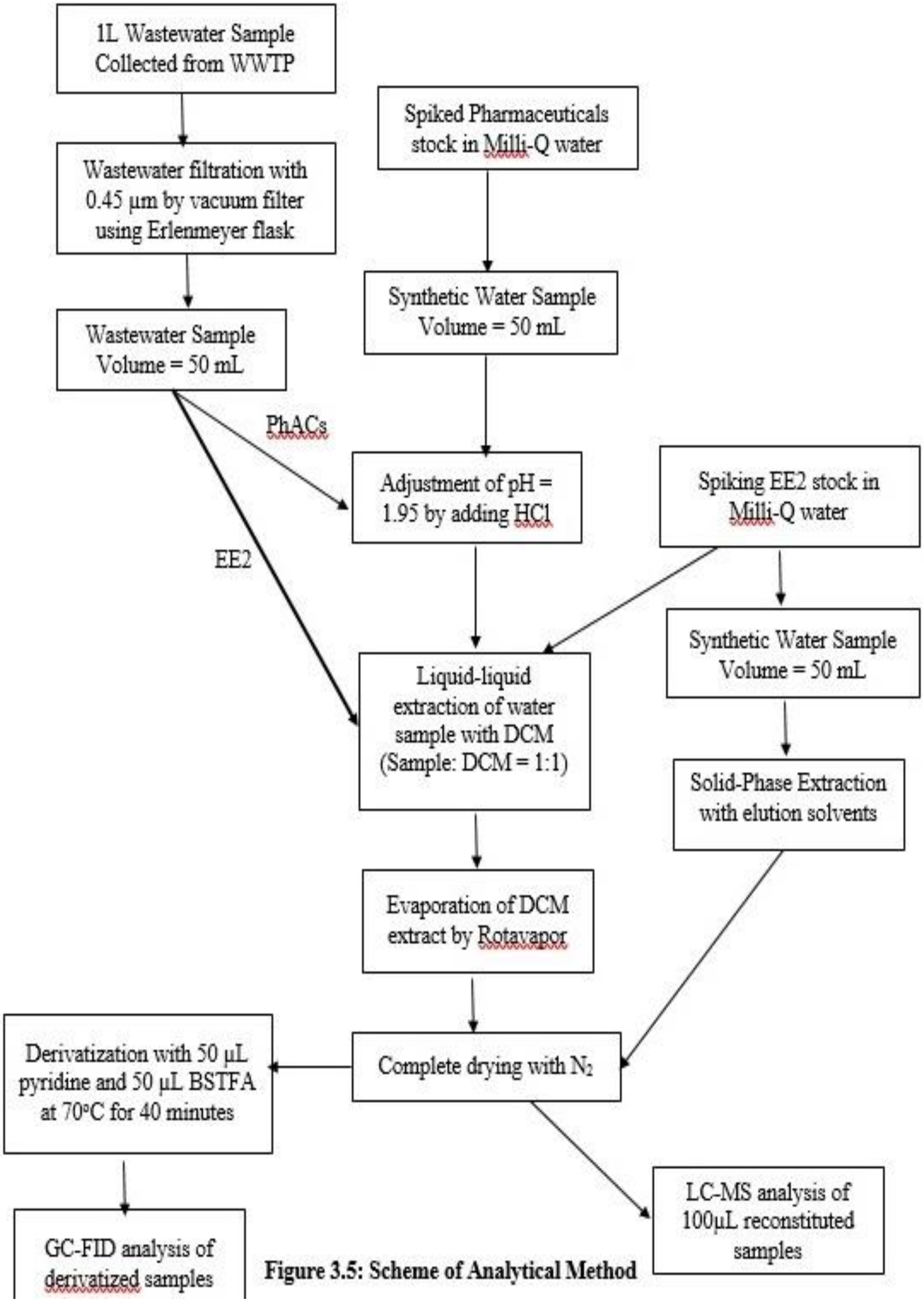

Figure 3.5: Scheme of Analytical Method

3.6 Method Validation

Sample extraction is a significant step; extraction recoveries of target compounds were calculated for spiked WWTP effluent and synthetic water samples at 3 concentration levels: 2.5, 5 and 10 µg/L. For the WWTP effluents, recoveries were determined relating the concentrations attained to the primary or initial spiking levels. In each case, samples were analyzed in triplicates. As the WWTP effluents included target compounds, blanks or un-spiked samples were analyzed and the measured concentrations were subtracted from those of the spiked samples. The method detection limit (MDL) for each compound was estimated from its concentration in spiked water samples after subjecting it to either SPE or LLE and reported as the minimum detectable concentration the compound with a signal to noise ratio of 3. The instrument detection limits (IDL) was calculated from the injection of a standard solution consecutively diluted until a concentration was reached that matched to a signal to noise ratio of 3.

3.7 Preparation of Membranes

Several batches of membranes were prepared in this study to establish the reproducibility of the performance of the membranes (see Appendix). Two principal types of membranes were prepared: a) Organic Solvent Nanofiltration (OSNF) membranes and b) Thin Film Composite (TFC) membranes. The OSNF membranes were prepared from RTV 615 and SYLGARD 184, using both commercially available PTFE ultrafiltration membrane and laboratory-made polysulfone (PSF) support as the base. In the case of TFC membranes interfacial polymerization was performed on a PSF support using m-phenylenediamine (MPD) and trymesoyl chloride (TMC) with multi-walled carbon nanotubes (MWCNTs).

3.7.1 Preparation of OSNF Membranes

3.7.1.1 Preparation of the PDMS Coating Solution with RTV 615

To prepare the PDMS coating solution, 5 g of RTV 615 pre-polymer (RTV-A) was dissolved in toluene to make a concentration of 15% (w/w). The mixture was placed on a magnetic hot plate stirrer at a speed of 450 rpm and the temperature of the solution was brought to 60^{o}C. At this point, the cross-linker, RTV-B (0.5 g) was added (RTV-A: RTV-B = 10:1) to the solution under continuous stirring. This reaction was continued at 60^{o}C in anticipation of the viscosity of the solution to be ~45 mPa-s. The viscosity was measured using Brookfield DV-II+ Pro, Programmable Viscometer. At this stage, toluene was added to dilute the concentration of RTV 615 down to 7.5%. The reaction again continued until the viscosity reached ~45 mPa-s. After that, toluene was added again to obtain final concentrations of RTV 615 of 5% and 2.5%, each with a viscosity of ~45 mPa-s. Once the desirable concentration and viscosity were achieved, the reaction was stopped by putting the solution into the ice-bath. Following the same procedure, another batch of PDMS solution was prepared using hexane as the solvent.

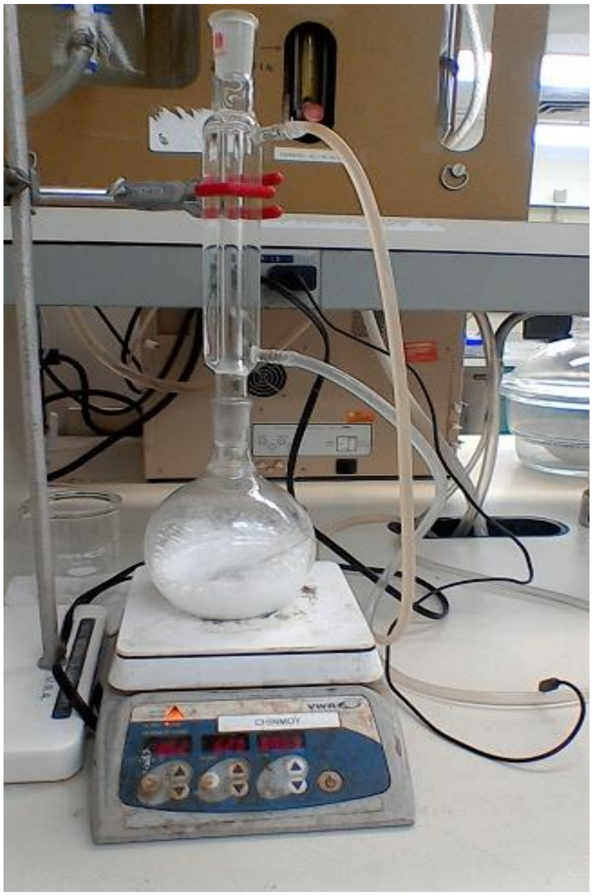

Figure 3.6: Preparation of PDMS Coating Solution using RTV 615: the mixture was continuously stirred and heated at 60^{o}C to get a homogeneous cross-linked solution

3.7.1.2 Preparation of the PDMS Coating Solution with SYLGARD 184

A 20% PDMS solution was prepared using SYLGARD 184 and hexane. The base and the hardener were mixed at a ratio of 10:1 [1] in hexane at 80^{o}C. The solution was stirred continuously, maintaining the same temperature. Following the procedure in Section 3.7.1.1, the solution was diluted to 7, 5, 3.1, 2 and 1% SYLGARD 184.

3.7.1.3 Preparation of the PSF Support

In this case, a PSF support was first prepared using the phase-inversion technique. Exactly 20% (w/w) polysulfone (PSF) was dissolved in N,N'-dimethylformamide (DMF) to produce the casting solution [18]. This solution was cast on a clean glass-plate with a custom-made doctor-blade with a 200-µm slit. This liquid film was kept in air for about one minute to evaporate the solvent and then immersed in DI water to complete the phase-inversion method. After 24 hours, the porous substrate was collected, dried in air and thus was ready to be used as a support.

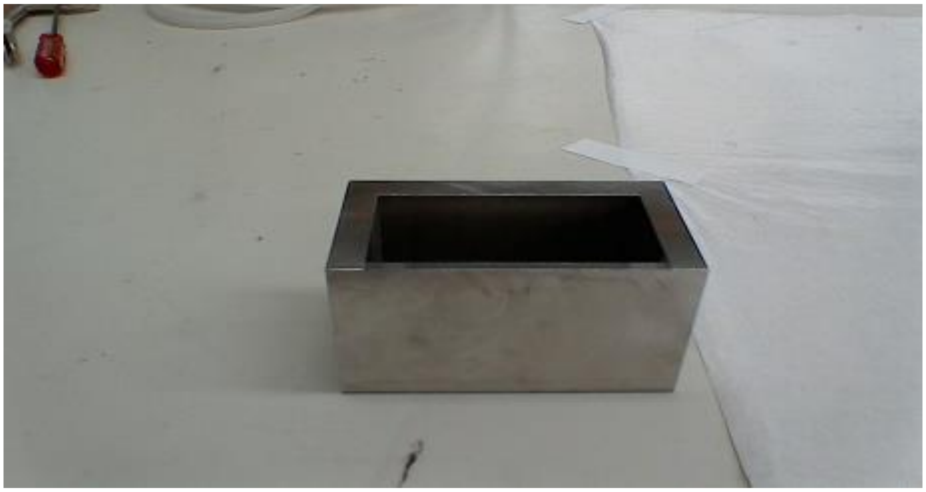

Figure 3.7: Custom-made Doctor Blade used to cast 20% PSF support membrane

3.7.1.4 Preparation of the Composite PDMS Membrane with RTV 615

Composite PDMS (RTV 615) membranes were prepared by using both commercially available PTFE membranes and the PSF supports prepared in this study. Both PTFE and PSF supports were dipped in the pre-crosslinked 7%, 5% and 2.5% PDMS solution made with toluene and hexane respectively for 30 secs. They were then taken out of the solutions very quickly with a tweezer by keeping track of time for consistent results. The coated membranes were then dried in air for 30 minutes to evaporate the solvent from the surface. Finally, the membranes were dried in an oven at 60°C for 4, 6 and 8 hours to complete the cross-linking reaction; the membranes were ready to use for the rejection and permeation tests (Figure 3.8) after the final cross-linking.

Figure 3.8: 2.5% PTFE/PDMS (left) and 2.5% PSF/PDMS (right) membranes prepared in lab. The shiny surfaces prove the cross-linked PDMS layer on the supports.

3.7.1.5 Preparation of the Composite PDMS Membrane with SYLGARD 184

Commercially available PTFE membranes were dipped in pre-cross-linked 7, 5, 3.1, 2 and 1% Sylgard 184 PDMS solutions for 30 seconds and then dried in the fume hood for 30 minutes. The PDMS-dipped membranes were then dried in the oven at 80°C for 4, 6, 8, 10, 12 and 18 hours to complete the cross-linking reaction.

3.7.2 Preparation of Thin Film Composite Membrane

For the purpose of uniform dispersion of MWCNTs in the PSF matrix, the MWCNTs were first modified. For the modification, 1 g of raw MWCNTs was soaked in 100 mL solution of 3M HNO_3: H_2SO_4 (1:3, v/v) and then was sonicated with a probe sonicator for 1 h. After that, the solution was refluxed at about 400 K for 12 hours following the study of Vatanpour et al. [19]. Then the solution was diluted with 2L of DI water and filtered through a 0.45µm filter. The modified MWCNTs were rinsed with DI water until a pH of ~7 was attained and were then put in the oven for complete drying.

Asymmetric MWCNT/PSF support was prepared via phase-inversion technique [19, 20]. Exactly 20% (w/w) PSF was first dissolved into N,N'-dimethylformamide (DMF) to produce the casting solution [18] and then was left overnight to get rid of air bubbles. Dried and modified MWCNTs were then added to this polymer mixture to get a 1% MWCNT in the PSF support; the mixture was first stirred on a mechanical stirrer for 4 hours and then sonicated for 30 minutes to get a good dispersion. Next, the solution was cast on a clean glass plate with the doctor blade, left in air for 1 minute and then immersed in DI water for 24 hours to complete the phase inversion technique.

The active skin layer on the support was prepared by interfacial polymerization following the protocol of Xie et al. [21]: a 2% (w/v) m-phynylenediamine (MPD) solution was prepared in DI water. The MWCNT/PSF support was immersed in this MPD solution for 10 minutes and then the excess MPD solution was drained off. A rubber roller was used to remove the surplus MPD solution from the support. After that, the support was immersed in 0.1% trimesoyl chloride (TMC) in n-hexane solution for 10 secs, washed with 100 mL n-hexane and finally put in oven at 80°C for 10 minutes (Figure 3.9).

Figure 3.9: TFC membrane prepared on a support made with 0.1% modified MWCNTs and 20% PSF; the active skin layer is the result of the interfacial polymerization between 2% MPD and 0.1% TMC

3.8 Characterization of Membranes

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to characterize the laboratory made OSNF membranes in the study. Morphology of the prepared membranes was examined using the Scanning Electron Microscopy apparatus (Quanta^{TM} 3D FEG SEM, FEI Company, USA). Membranes for SEM imaging were prepared by immersing a sample of membrane in liquid nitrogen for several minutes. Frozen sample was subsequently fractured, sputtered with a thin layer of gold and subsequently analyzed with SEM technique. The gold layer contributed to improve conductivity of the sample surfaces and to achieve better quality of the data. Surface and cross section of membranes were scanned at various magnifications from 100 to 50,000. AFM technique was applied using a NanoScope MultiMode SPM System and NanoScope IIIa Quadrex controller, Veeco, Digital Instrument, UK. Surface analysis containing roughness determination was done by AFM images by tip scanning (tapping mode). Roughness of the surface (scanning sample size 5um x 5um) was shown as RMS - root mean squared roughness. During the measurements, silicon nitride (Si_3N_4) probes NP-1 (spring constant provided by the manufacturer (Veeco) 0.58 Nm-1) was applied. All tests were done under ambient conditions of temperature.

3.9 Separation Performance of Membranes

The filtration experiments were carried out using a stainless steel dead-end filtration system (HP4750, SterliTech Corp., USA). The schematic diagram of the filtration system is presented in Figure 3.10. The cell consists of a cylindrical stainless steel vessel with detachable end plates. A membrane sample was positioned at the end of the cell held by a porous stainless steel disk. The active area of the membrane inside the module was 14.6 cm^2 with a feed capacity of ~290 mL. The system was pressurized with compressed nitrogen gas. Each membrane was pre-compacted with DI water at a pressure of 5-30 bar until a constant flux was obtained. The flux through the membrane was calculated by the following equation:

$$\boldsymbol{J = \frac{V}{A.T}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.1)}$$

Where J is the permeate flux ($Lm^{-2}h^{-1}$), V is the permeate volume (L), A is the membrane area (in m^2) and T is the permeation time (h). The permeate volume was measured using a graduated cylinder.

The pH of the feed solution was maintained at ~7.5. IBP, NPR and DCF with pK_a values of 4.91, 4.15 and 4.15 respectively are deprotonated at pH 7.5 [22]. An initial volume of 270 mL feed with desired concentrations of pharmaceutical compounds was then passed through the membrane at 20-30 bar until a permeate of 120 mL and a corresponding retentate of 150 mL were collected. In the same manner, a feed of ~270 mL with desired concentrations of EE2 was passed through the membrane to get a permeate of ~120 mL. The volume of permeate was measured with a graduated cylinder. The concentrations of pharmaceuticals in feed, permeate and retentate were analyzed using GC-FID; while those of EE2 in feed, permeate and retentate were analyzed by LC-MS. The retention of pharmaceuticals and EE2 was calculated using Eq (3.2):

$$\boldsymbol{R} = \frac{\mathbf{C_F - C_p}}{\mathbf{C_F}} \cdot \mathbf{100} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.2)}$$

Where, R is the % retention, C_F is the concentration of solutes in feed and C_P is the concentration of solutes in permeate. A mass balance was calculated using Eq. (3.3) by measuring the concentrations of the three pharmaceutical compounds and EE2 in the feed, permeate and retentate.

$$\text{Mass balance (\% recovery)} = \frac{\boldsymbol{V_R}.\mathbf{C}_{\boldsymbol{R}} + \boldsymbol{V_P}.\boldsymbol{C_P}}{\boldsymbol{V_F}.\mathbf{C_F}} \cdot \mathbf{100} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.3)}$$

Where, V_R is the retentate volume, C_R is the retentate concentration, V_P is the permeate volume and V_F is the feed volume.

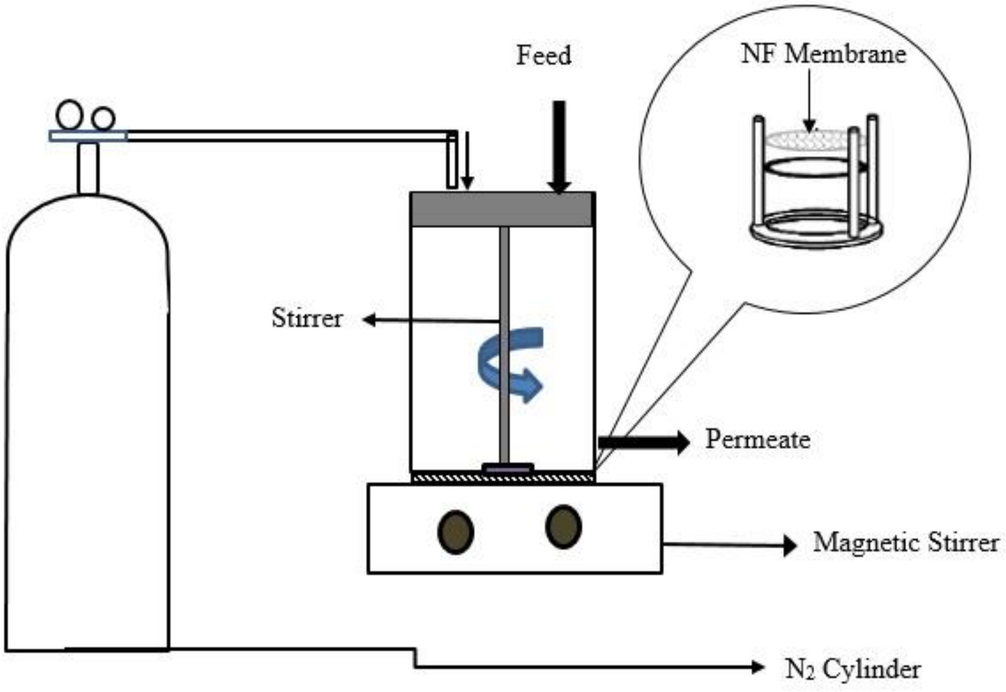

Figure 3.10: A Schematic Diagram of the Dead-End Filtration Set-Up

3.10 References

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Chapter 4

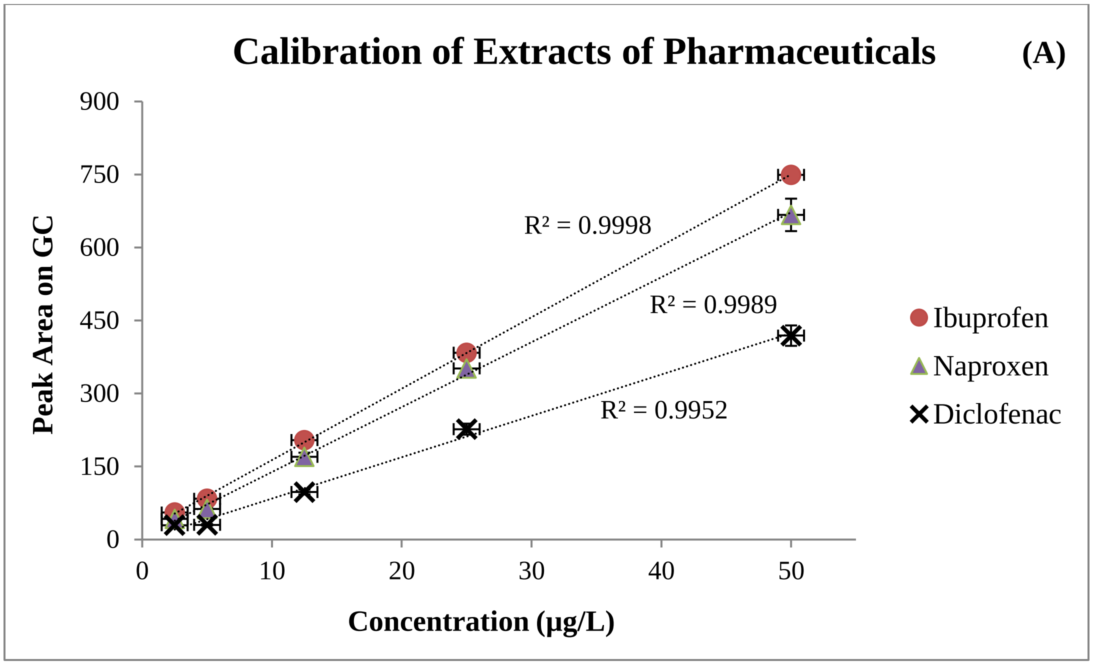
4 Results and Discussion

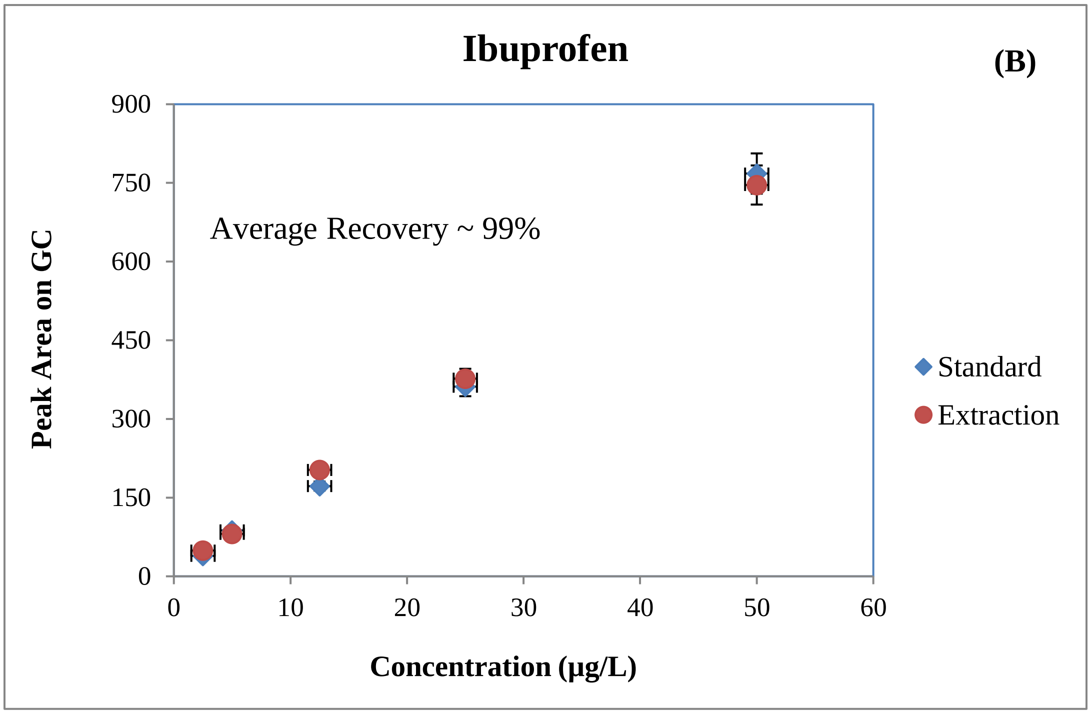
This chapter presents and discusses the results of the experimental work carried out in the study.

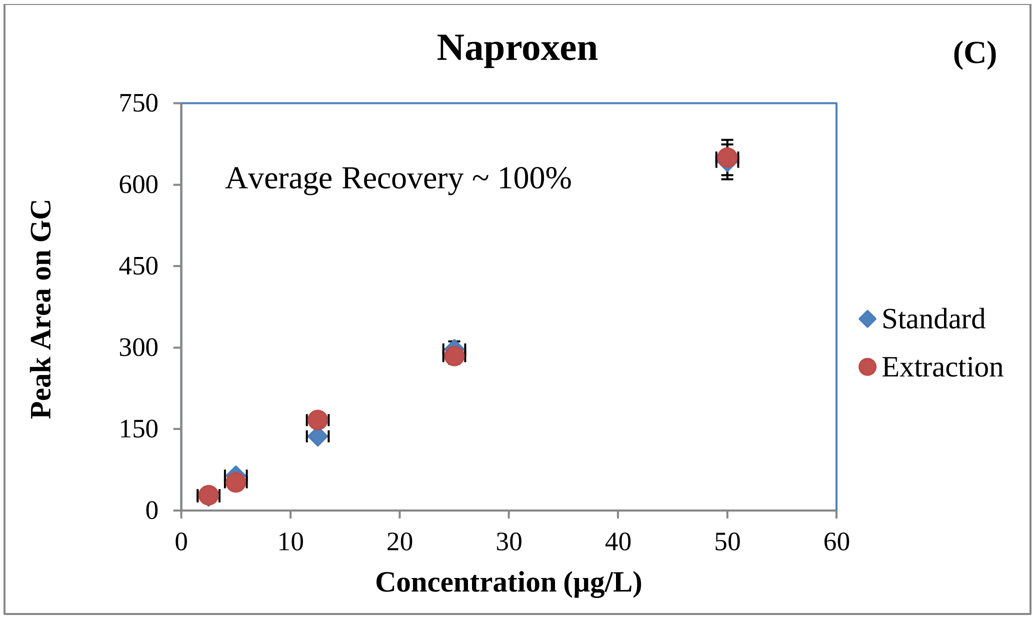
4.1 Extraction Recovery

4.1.1 Recovery of Extracted PhACs

Five-point calibration curves were generated for ibuprofen (IBP), naproxen (NPR) and diclofenac (DCF) within a concentration range of 1.25-50 µg/L using linear regression; the curves gave very good fits (R^2>0.99) between peak area of the gas chromatographs and concentration (Figure 4.1A). The efficiency of the liquid-liquid extraction (LLE) was evaluated using recovery experiments. Recovery achieved for IBP, NPR and DCF ranged from 80 to 100% (Figure 4.1B, 4.1C, 4.1D). Compound recoveries were tested with water samples having pH between 1.95-3.6 and it was found that a pH of 1.95 showed the maximum recovery. The Method Detection Limit (MDL) for IBP, NPR and DCF was 0.1 µg/L.


Calibration of Extracts of Pharmaceuticals
(A)
Peak Area on GC
0
150
300
450
600
750
900
0
10
20
30
40
50
Concentration (µg/L)
R² = 0.9998
R² = 0.9989
R² = 0.9952
Ibuprofen
Naproxen
Diclofenac


Ibuprofen
(B)
Peak Area on GC
0
150
300
450
600
750
900
0
10
20
30
40
50
60
Concentration (µg/L)
Average Recovery ~ 99%
Standard
Extraction



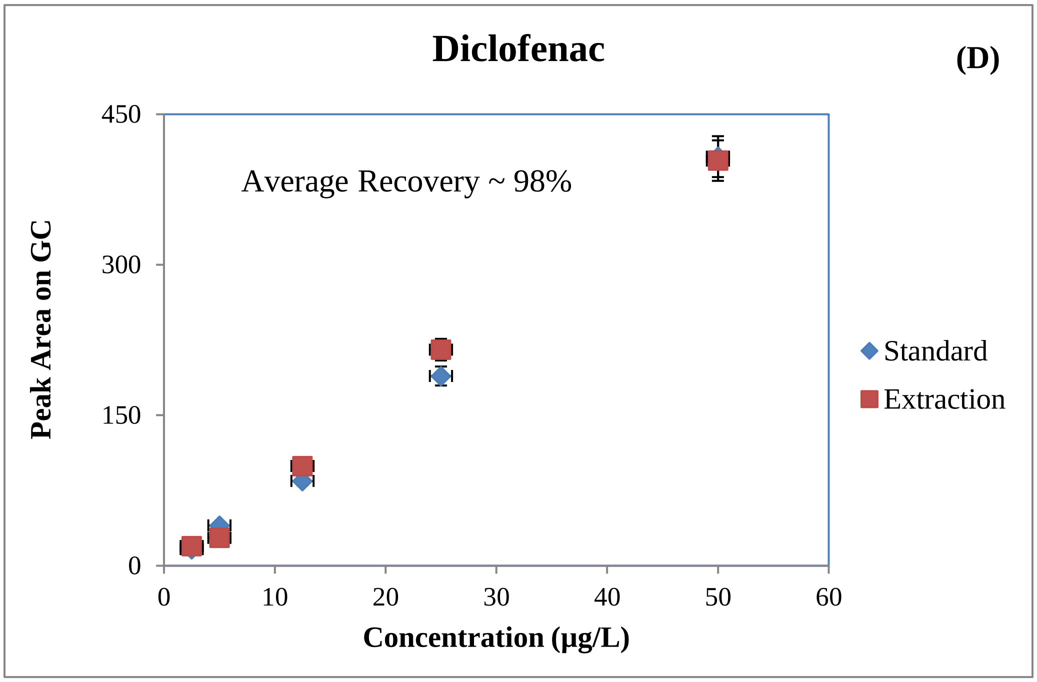


Figure 4.1: Recovery of ibuprofen, naproxen and diclofenac by Liquid-liquid Extraction. Figure 4.1A represents calibration curves obtained from LLE extracts of IBP, NPR and DCF. Figures 4.1 B, 4.1C and 4.1D represent the comparison between standards and extracts of IBP, NPR and DCF respectively.

4.1.2 Recovery of Extracted EE2

As in the case of the extracted PhACs, five-point calibration curves were also generated for EE2 using linear regression analysis and over concentration ranges of 0.019-0.3 mg/L and 0.625-10 mg/L.; the curves gave very good fits (R^2>0.99) (Figure 4.2A & 4.2B). As most of the estrogenic compounds are moderately hydrophilic, polar solvents such as methanol and dichloromethane are widely used in their extraction [1-6]. The recovery of EE2 by SPE was tested for methanol, ethyl acetate, acetonitrile and dichloromethane and it was found that methanol gave the highest recovery of EE2 at 75% (Figure 4.3). Recovery achieved for EE2 through LLE was ~50%. MDL for EE2 was 50 ng/L.

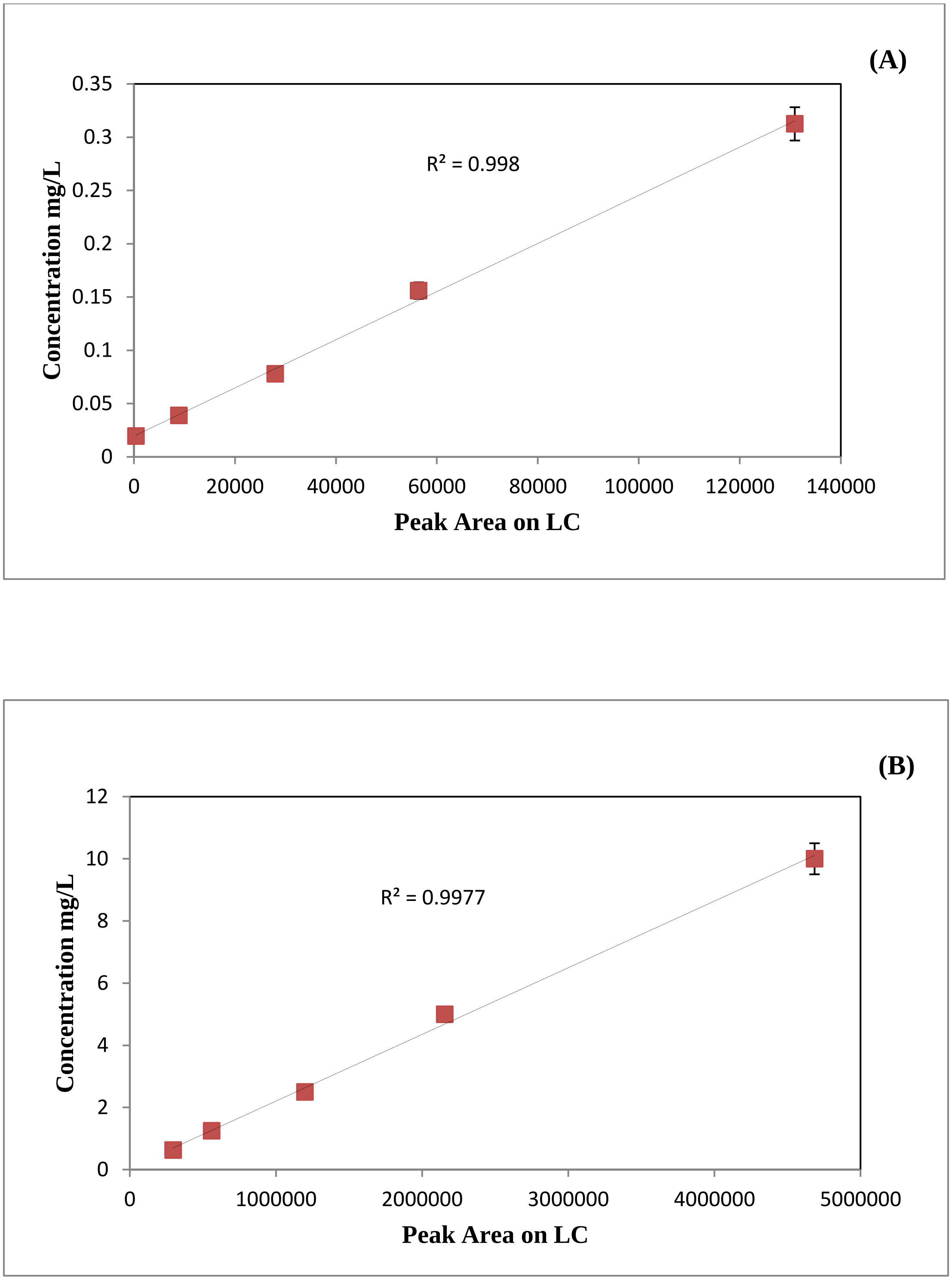


Figure 4.2: Calibration curves for EE2; A) Standards ranging from 0.019 to 0.3 mg/L (Top); B) Standards ranging from 0.625 to 10 mg/L (Bottom)

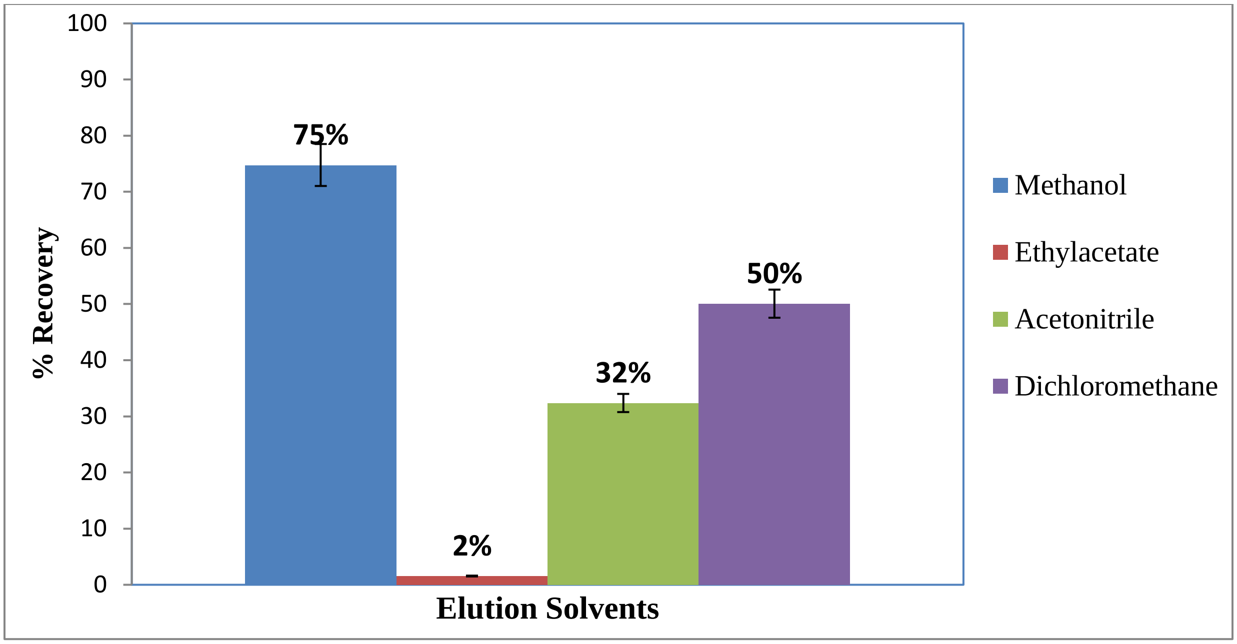


Figure 4.3: Recovery of EE2 during solid-phase extraction using methanol, ethyl acetate, acetonitrile and dichloromethane as elution solvent. Methanol shows 75% recovery which is the highest among other elution solvents.

4.2 Concentrations of IBP, NPR, DCF and EE2 in Wastewater Effluent

There are six wastewater treatment plants (WWTPs) in London, Ontario, all operated by the City of London and located along the Thames River. The estimated population size served by the Adelaide WWTP is 85,183; while that of the Greenway WWTP is 175,517 based on census data and the sewersheds. The Greenway plant receives about 60% of the flow generated in London as well as the thickened sludge from all the satellite plants for processing in centrifuges and for incineration. The Greenway facility also receives wastes from three major hospitals, food processing plants, platers, etc. The Adelaide plant receives sewage from the north-east part of the City which is mainly residential and commercial. To eradicate solids in these WWTPs, screens and settling tanks are used. Solids that fail to pass through the screens are removed and landfilled, whereas suspended solids are removed in large settling tanks during “Primary Treatment”. In the case of “Secondary Treatment”, bacteria and other micro-organisms are grown and aid in the removal of organic material and transformation of ammonia to nitrate. This process takes place in the aeration section in the presence of oxygen. The effluent from the aeration tank is passed to a final tank; here suspended sludge (waste solids and bacteria) settle out by gravity and are removed. In order to remove phosphorous, chemicals are utilized. Subsequently, the sludge is pumped to centrifuges, dewatered and incinerated. To end with, for the purpose of disinfection, ultra-violet light is used and the disinfected water is then released to the Thames River.

Figure 4.4 shows a schematic diagram of the Activated Sludge Process used in WWTPs in London, ON and Table 4.1 shows the capacity, actual flow and sludge production of the WWTPs.

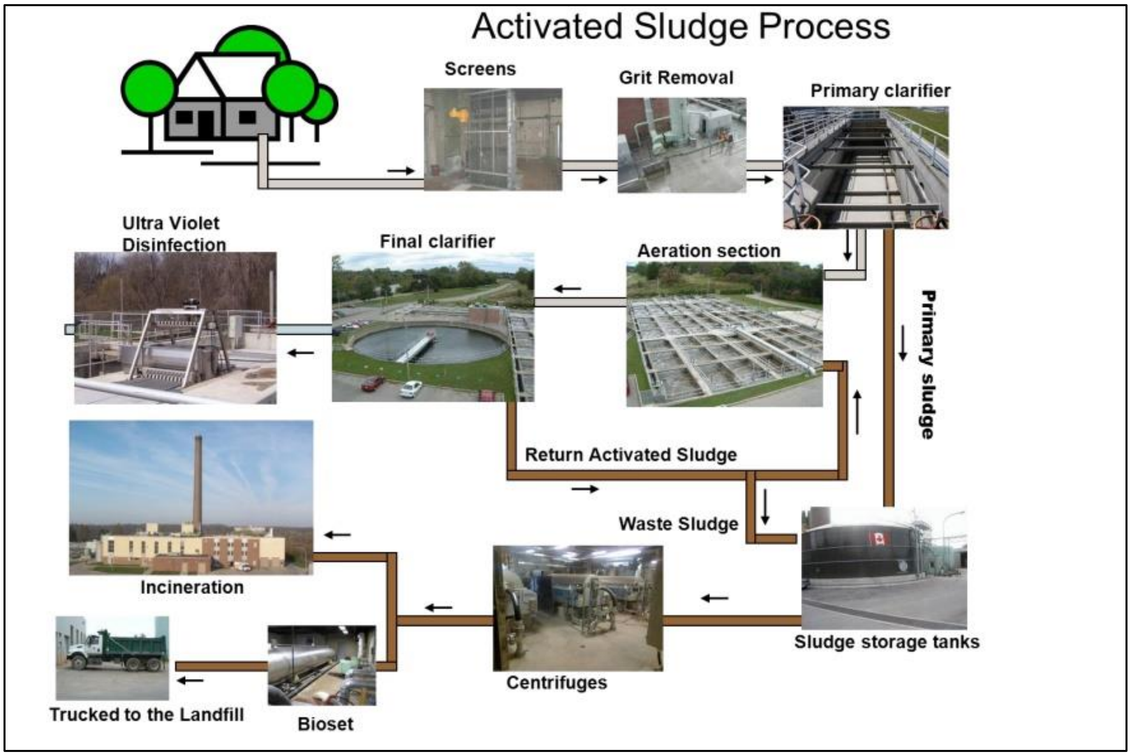


Figure 4.4: Different steps of Activated Sludge Process followed in treating wastewater in different WWTPs in London, ON. (City of London, March 2013)

Table 4.1: Capacity, Actual Flow and Sludge Production of the WWTPs in London, Ontario (City of London, March 2013)

WWTP	Capacity (m^3/day)	2013 Actual Flow (m^3/day)	Sludge produced average day (m^3) (normalized to 3% solids)
Adelaide	36,400	25,800	325
Greenway	152,175	129,900	1,180
Oxford	17,250	9,900	101
Pottersberg	39,100	27,000	216
Southland	564	286	1
Vauxhall	20,900	15,800	111
Total	266,389	208,686	1,934

It has been reported that NPR exists in WWTP influents in the range of 1.14-52.9 µg/L [7], in the effluents in the range of 0.1-5.09 µg/L [7-10] and 0.01-0.1 µg/L in surface waters [9, 11, 12]. For IBP, concentrations in WWTP influents and effluents are 3.73 – 603 µg/L and 1.3-10.16 µg/L [7, 10]. According to Tixier et al. [10], the effluent of a WWTP in Switzerland showed the existence of DCF to be 0.99 µg/L. Santos et al. [13] analyzed a number of influent and effluent wastewater samples collected from four different WWTPs located in Seville city, Spain. According to this study, the mean amount of IBP, and NPR in effluent wastewater was in the range of 4.13-10.16 µg/L and 1.64-2.74 µg/L, respectively. Yang et al. [14] reported 220 ng/L of DCF and 11 µg/L of IBP in the primary effluent of an advanced wastewater reclamation plant in Gwinnett County, Georgia, U.S.A. Wastewater effluents collected from Beggen, Luxembourg, showed maximum concentration of IBP and DCF to be 359 and 78 ng/L, respectively [15]. Metcalfe et al. [16] collected influent and effluent samples from 18 sewage treatment plants in 14 municipalities in Canada. The concentrations of IBP and NPR ranged 1- 24.6 µg/L and 7.2 - 33.9 µg/L respectively in the effluent samples. DCF, on the other hand, was found in only one WWTP influent at a concentration of 1.3 µg/L [16].

An analysis was done by Ternes et al. [17] on different STP effluents in Canada, Brazil and Germany. The results indicated an EE2 concentration of 9 ng/L in the effluents of Canada which is higher than that of in Germany (1 ng/L). Wastewater samples collected from Cornwall WWTP, Ontario, Canada, contained 9.8 ng/L of EE2 [18]. In one research work by Fernandez et al.[19] it was shown that EE2 was the most recurrently spotted synthetic estrogen in municipal effluents in Western Canada; nevertheless, its concentration was as low as 5 ng/L with some irregular occurrences of up to 178 ng/L. Research done on the effluent of the municipal WWTP in Brandon, Manitoba, Canada, indicated the presence of EE2 at a concentration of 7.63 ng/L after UV-treatment [20]. In a study of WWTPs in Calgary, Alberta, Chen et al. [21] reported an EE2 concentration of 8.5 ng/L. Lishman et al. [22] studied the occurrence of pharmaceutical and personal care products along with estradiol and estron in 12 Ontario Municipal WWTPS discharging into the Thames River; however, EE2 was not included in that study. Another survey conducted on the effluents of several STPs in Germany showed EE2 concentrations of 3-13 ng/L, while river waters revealed a maximum concentration of 1.6 ng/L [23]. Some river water samples collected from Italy showed E1, E2 and EE2 concentrations of 0.04-1.5 ng/L [24] whereas in the UK, the EE2 concentrations in river waters were in the range of 0.4 to 3.4 ng/L [25]. EE2 has been detected in drinking water (Germany) at a concentration of 0.5 ng/L [26]. Table 4.2 shows EE2 concentrations in WWTPs influents, WWTPs effluents and in surface water in a number of countries.

Table 4.2 Concentrations of EE2 in influents and effluents of WWTPs as well as in surface water [18, 27]

Country	EE2 concentration (ng/L)
France	Influent: 4.9-7.1 Effluent: 2.7-4.5 Surface water: 1.1-2.9
USA	Influent: 0.1-4.3 Effluent:<0.02-0.76 Surface water:<0.02-0.52
Italy	Influent:<1.6 Effluent:<1.1 Surface water:<0.4-1.0
Ontario, Canada	Influent: 5.7 (The City of Cornwall WWTP) Effluent: 9.8 (The City of Cornwall WWTP) Surface water: 2.2 (Ottawa River)

Tables 4.3 and 4.4 show the amount of IBP, NPR, DCF and EE2 identified in the wastewater effluents of Greenway and Adelaide Treatment Plants during this research work over a period of 6 months.

Table 4.3: IBP, NPR and DCF in Greenway Pollution Control Plant

Date of sample collection	IBP (µg/L)	NPR (µg/L)	DCF (µg/L)
31-Aug-15	0.66	2.09	0.45
18-Sep-15	<LOD	1.22	0.45
31-Oct-15	2.26	1.46	0.49
20-Nov-15	3.63	8.98	0.73
08-Dec-15	2.78	4.78	1.23
29-Jan-16	3.31	5.09	1.04

Table 4.4: IBP, NPR, DCF and EE2 in Adelaide Wastewater Treatment Plant

Date of sample collection	IBP (µg/L)	NPR (µg/L)	DCF (µg/L)	EE2 (µg/L)
31-Aug-15	1.88	2.85	0.29	<DL
17-Sep-15	0.98	1.42	0.47	<DL
30-Oct-15	2.37	2.14	0.52	<DL
21-Nov-15	<LOD	3.62	0.48	<DL
07-Dec-15	2.85	3.64	0.46	<DL
31-Jan-16	3.32	2.98	0.42	<DL

It can be seen that the occurrence of IBP in the effluent of Greenway Pollution Control plant varied between 0.66 to 3.63 µg/L; whereas the concentration ranged between 0.98 to 3.32 µg/L in case of Adelaide Wastewater Treatment Plant. The presence of NPR in the effluents of both WWTPs varied from 1.22 to 8.98 µg/L. On the other hand, the amount of DCF determined in the effluents of Greenway ranged between 0.45 and 1.23 µg/L and, in the case of Adelaide, it was between 0.29 and 0.52 µg/L. Therefore, it can be concluded that the results support quite well what has been reported in literature [8, 11, 28, 29]. Nonetheless, the pattern of usage as well as the removal efficiency of these drugs may also fluctuate throughout the year, resulting in variability in the concentrations of PhACs within the watershed. It should be noted that in our research, we did not find any EE2 in the Adelaide WWTP effluent; this could be explained by the fact that EE2 might be below the detection limit (MDL 50 ng/L) of the LC-MS method used in this study.

4.3 Preparation of PDMS Coating Solution

The preparation of thin membranes is of utmost importance because the thickness of the membranes controls the flux through it. A good quality composite membrane is fabricated only when the PDMS coating solution has well-defined properties, like adequate concentration and viscosity. It has been found that a higher concentration and higher viscosity of the coating solution make the PDMS layer thick, whereas a lower viscous solution results in high pore intrusion and defects [30]. To make a thin, selective layer, the viscosity of the PDMS solution should be high and the concentration low [30]. Therefore, it is desirable to pre-cross link the PDMS solution containing lower concentration [31]. Dutczak et al. [30] used a 3.75% (w/w) PDMS toluene solution with a viscosity of 55 mPa-s to prepare a composite capillary membrane that showed the highest toluene permeance and low pore intrusion. For that purpose, in this study, first a 15% PDMS coating solution was prepared, pre-crosslinked and eventually was diluted to get concentrations of 7.5%, 5% 2.5 % when using RTV 615 and 7, 5, 3.1, 2 and 1% when using SYLGARD 184 as PDMS. It has been found that the PDMS solutions of concentrations 5~7.5% resulted in membranes that were very tight and almost impermeable. On the other hand, concentrations as low as 1.85-2.5% with a viscosity of ~45mPa-s formed the best membranes. Figure 4.5 shows the difference in permeability between 2-2.5% PDMS membranes, due to a difference in viscosity of the coating solution. When the viscosity of the PDMS solution was increased from 20 mPa-s to 45 mPa-s, the permeability of the membrane almost doubled. These results support the study of Dutczak et al. [30].

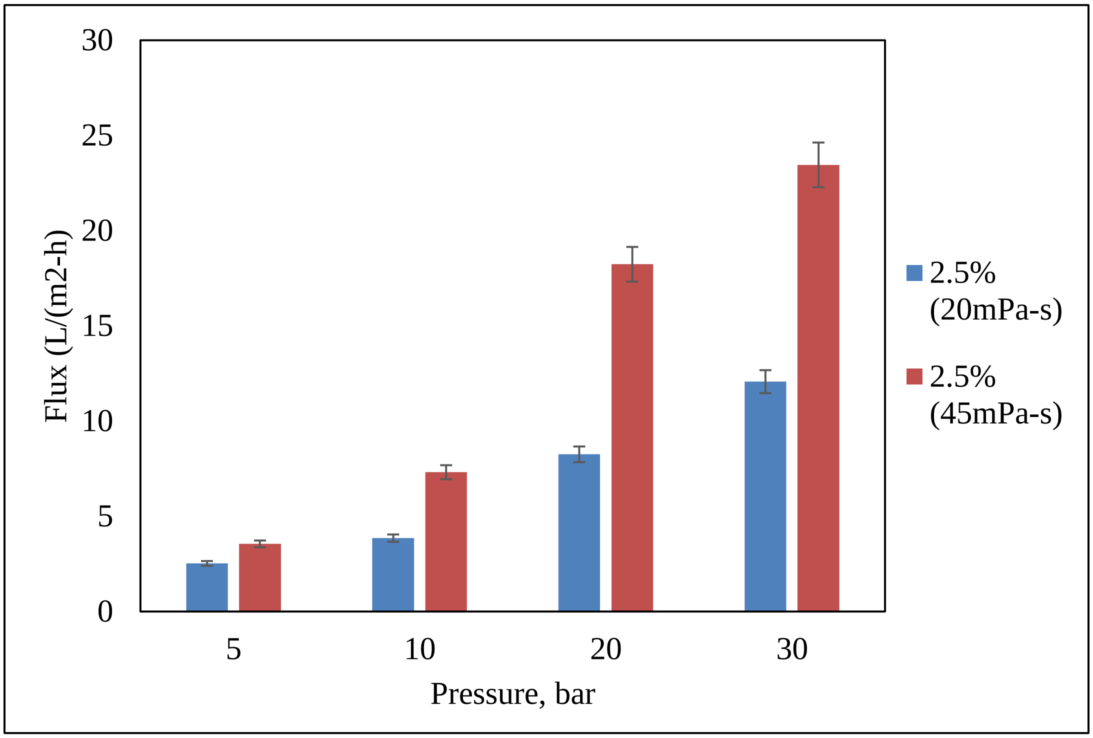


Figure 4.5: Difference in membrane permeability due to change in viscosity of PDMS coating solution. Higher viscosity causes higher permeability.

The pre-crosslinking temperature was maintained at 60°C following the study of Dutczak et al. [30] because if the temperature is below 50°C, the viscosity stays below 20 mPa-s for more than 300 min. This was also proved in trial experiments in our work.

The cross-linking temperature in the oven was maintained at 60°C and the time for cross-linking was optimized to be 4 hours for RTV 615. It has been found in this study that the more the cross-linking time exceeds 4 hours for RTV 615, the tighter the membrane becomes and the lower the permeability. Figure 4.6 shows the volume of permeate monitored for three 1.85% PDMS (RTV 615) membranes (cross-linked at different temperatures) when the pressure was 10 bar. It can be seen that the maximum volume of permeate (96 mL) was achieved when the membrane was cross-linked for 4 hours whereas a cross-linking of 8 hours gave the minimum permeate volume (15 mL) at the end of ~90 minutes.

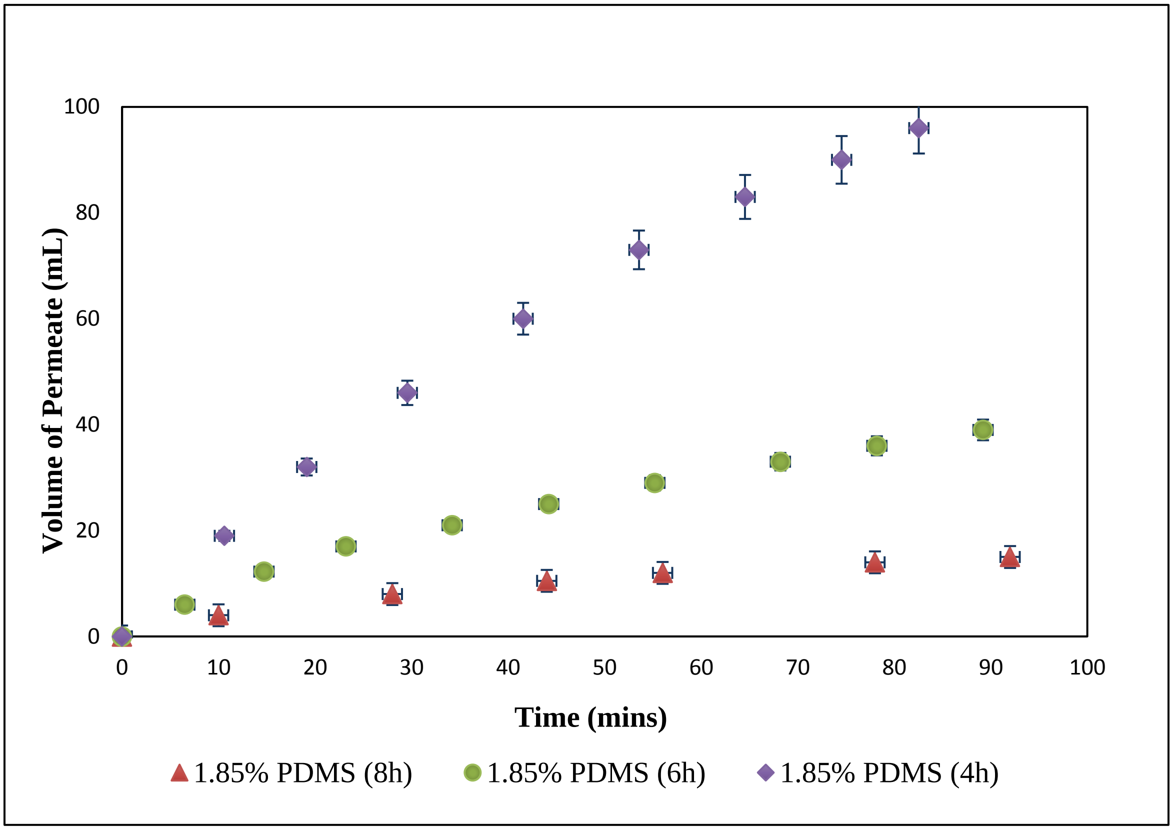


Figure 4.6: Comparison of Permeate Volume at Different Cross-linking Temperature

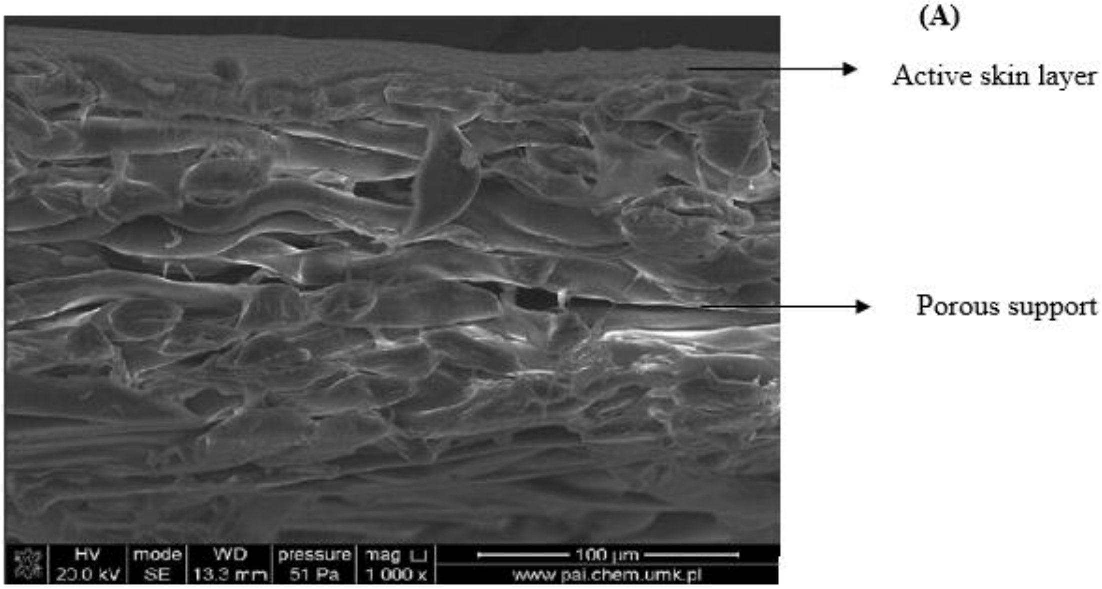
However, in case of SYLGARD 184, the cross-linking process took a longer period, ~18 hours. This might be due to the usage of 10 gm clips of SYLGARD 184. The package contained pre-measured base and hardener (10:1) from the supplier, which gave inconsistent cross-linking throughout the study period.

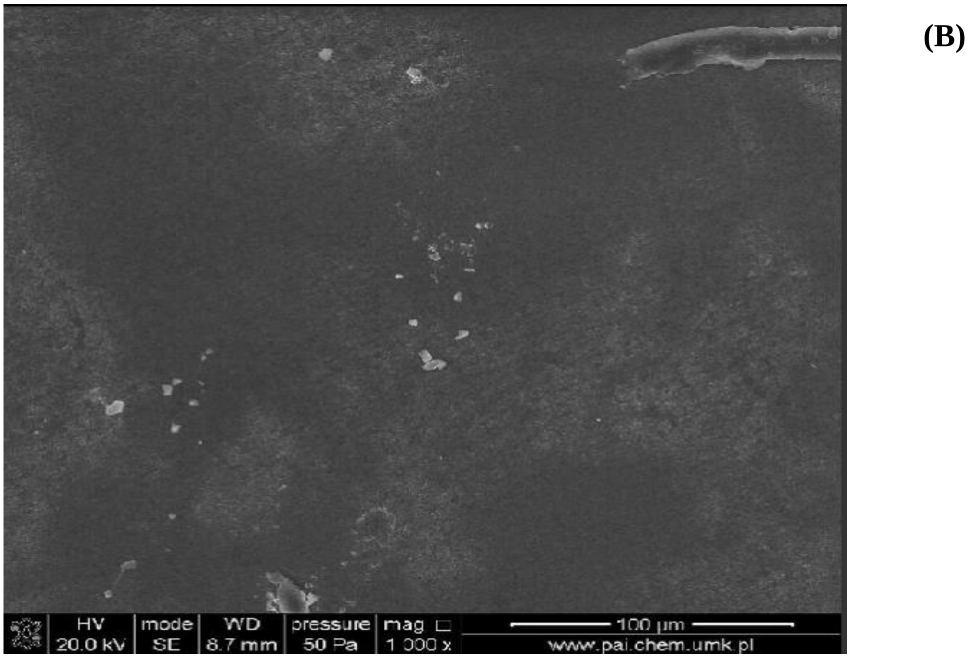
4.4 Characterization of NF Membranes

4.4.1 SEM Characterization

Figure 4.7 shows the SEM photomicrographs of 2.5% PTFE/PDMS composite membrane. Figure 4.7A presents the cross-section and it is evident from the SEM image that the PDMS top layer is tightly and properly cast on top of the PTFE support. Figure

4.7B and 4.7C show the top surfaces of PTFE/PDMS membranes made from coating solutions with viscosity ~45 mPa-s and 15 mPa-s respectively; the polymer clusters or crystals on the top surface in Figure 4.7c is formed due to the low viscosity of the PDMS (~15 mPa-s).





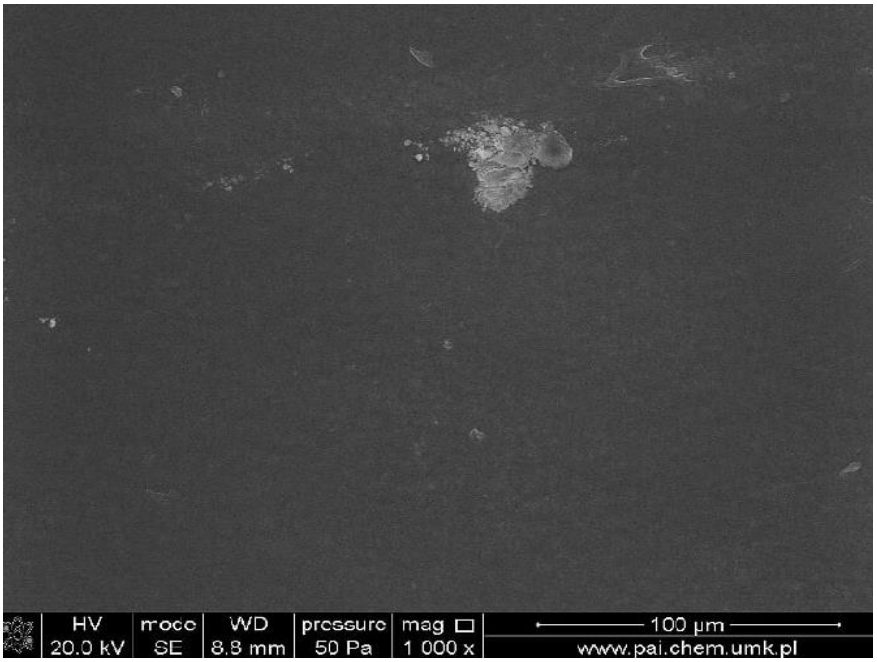
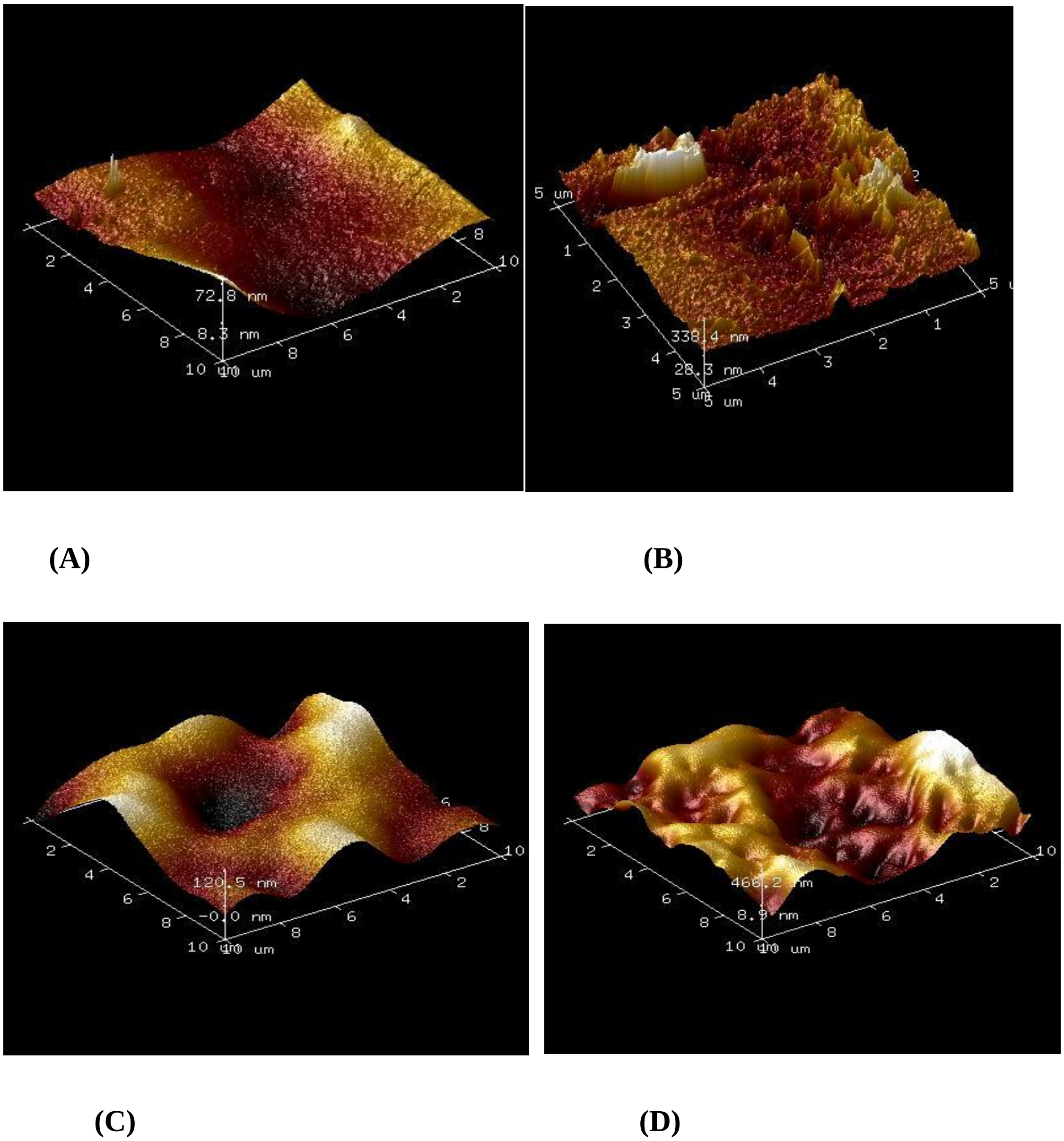


Figure 4.7: SEM photographs of 2.5% PTFE/PDMS composite membrane: a) cross-section (~45 mPa-s); b) top surface (~45 mPa-s); c) top surface (~15 mPa-s)

4.4.2 AFM Characterization

Figure 4.8 shows the AFM photographs of three PTFE/PDMS membranes and a thin film composite (TFC) membrane: Figure 4.8A represents PTFE/PDMS prepared with PDMS (RTV 615) solution with a viscosity of ~45 mPa-s; this membrane was not compacted under pressure. Figure 4.8B shows a TFC membrane prepared with 2% MPD, 0.1% TMC and 0.1% CNT on a 20% PSF support. It has been stated by researchers that the introduction of hydrophilic functional groups into the surface of CNTs enhances the dispersion of CNTs into a particular polymer matrix [32]. The use of functionalized carbon nanotubes could increase the hydrophilicity and surface charge of the membrane's top layer which eventually enhances the property of NF membranes by providing better resistance to fouling and improved salt rejection [32]. In Figure 4.8B, the dispersed MWCNTs is clear in PSF matrix showing very good bonding of the acid modified MWCNTs in the PSF matrix. Figure 4.8C represents a used PTFE/PDMS membrane with PDMS 45 mPa-s whereas Figure 4.8D shows a PTFE/PDMS membrane prepared with a PDMS solution of ~15 mPa-s, used. It is clearly evident that the membrane prepared with a lower viscosity PDMS solution shrinks more than that prepared with a more viscous PDMS solution.



(A) **(B)**

(C) **(D)**

Figure 4.8: SEM images of different NF membranes: A) 2.5% PTFE/PDMS (unused, not compacted); B) 2% MPD, 1% TMC and 0.1% MWCNT on 20% PSF support; C) 2.5% PTFE/PDMS (viscosity ~45mPa-s); D) 2.5% PTFE/PDMS (viscosity ~15mPa-s).

4.5 Permeability Performance of NF Membranes

4.5.1 Permeability Performance of PTFE/PDMS (RTV 615)

The filtration performance of composite PTFE/PDMS membrane in water has been investigated including the effect of transmembrane pressure. Figure 4.9 presents the effect of the operating pressure (5, 10, 20 and 30 bars) on the volume of permeate passing through a PTFE/PDMS composite membrane with PDMS concentration of 2.5%, having a viscosity of ~ 45 mPa-s. The volume of permeate increased with increasing pressure, which indicates no compaction of membrane occurred over the applied pressure range. Figure 4.10 represents the flux of 2.5% PDMS (45 mPa-s) at different pressures.

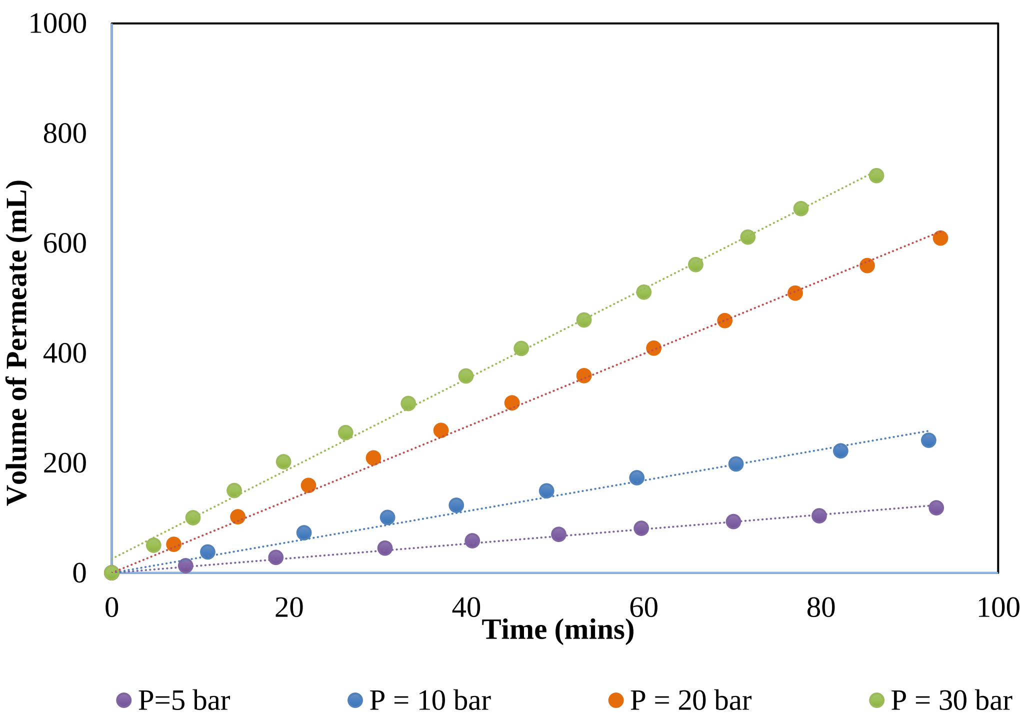


Figure 4.9: Influence of Pressure on volume of permeate for 2.5% PTFE/PDMS (RTV 615) Membrane

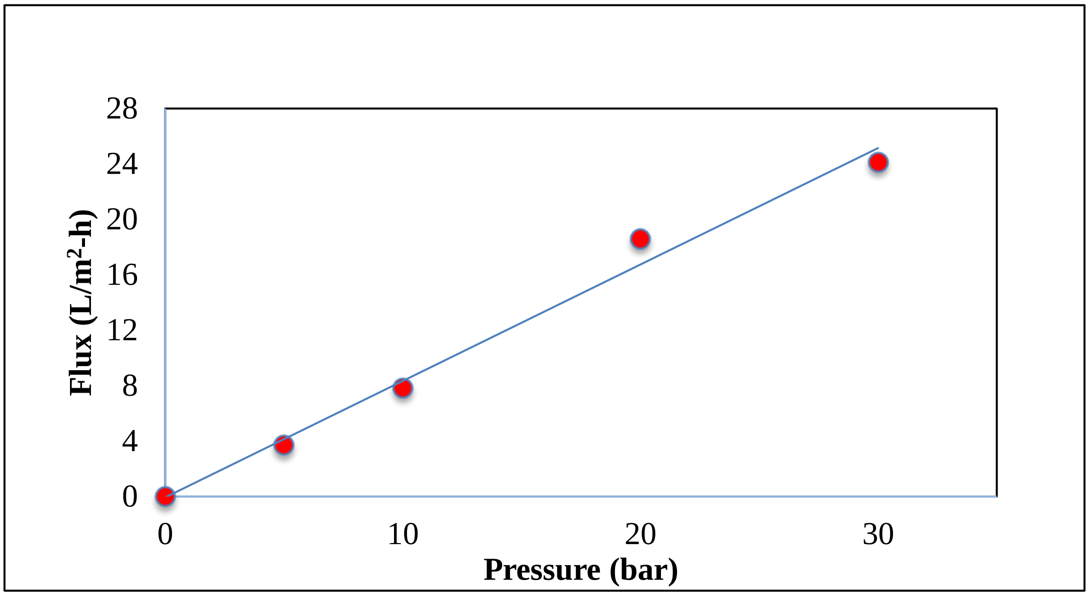


Figure 4.10: Flux at different pressures for 2.5% PTFE/PDMS (RTV 615) membrane. With an increase of pressure, flux increases.

The permeability of the 2.5% PTFE/PDMS membrane was compared with that of DuraMem, a commercially available OSNF membrane, prepared with modified polymer. Figure 4.11 shows the influence of pressure (10, 20, 30 & 40 bars) on flux for DuraMem, over a period of 2.5 hours. The results show that this membrane was also not compacted over the applied pressure range. Figure 12 reflects the flux through DuraMem membrane at different pressures. and if compared with Figure 4.10, it can be seen that the flux through the laboratory made PTFE/PDMS is higher than that of the commercially available DuraMem membrane.

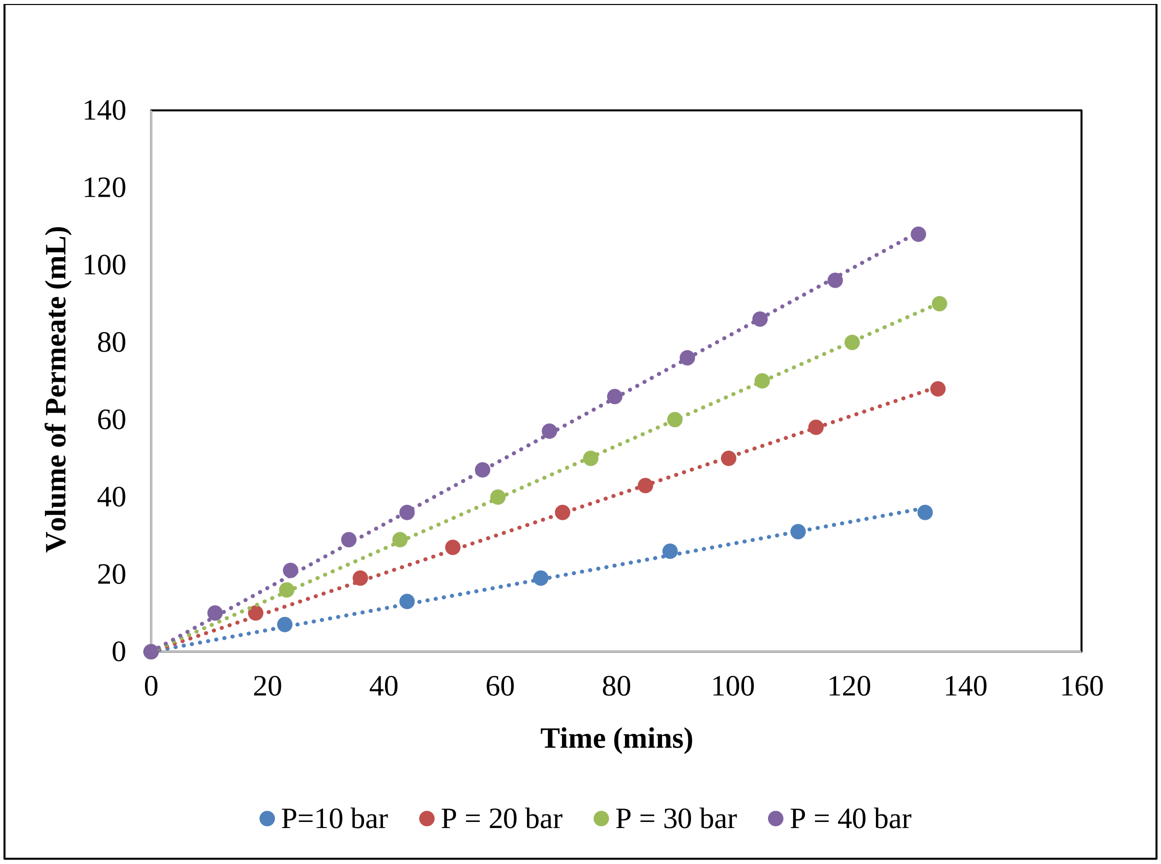


Figure 4.11: Influence of Pressure on Flux for Commercial DuraMem Membrane

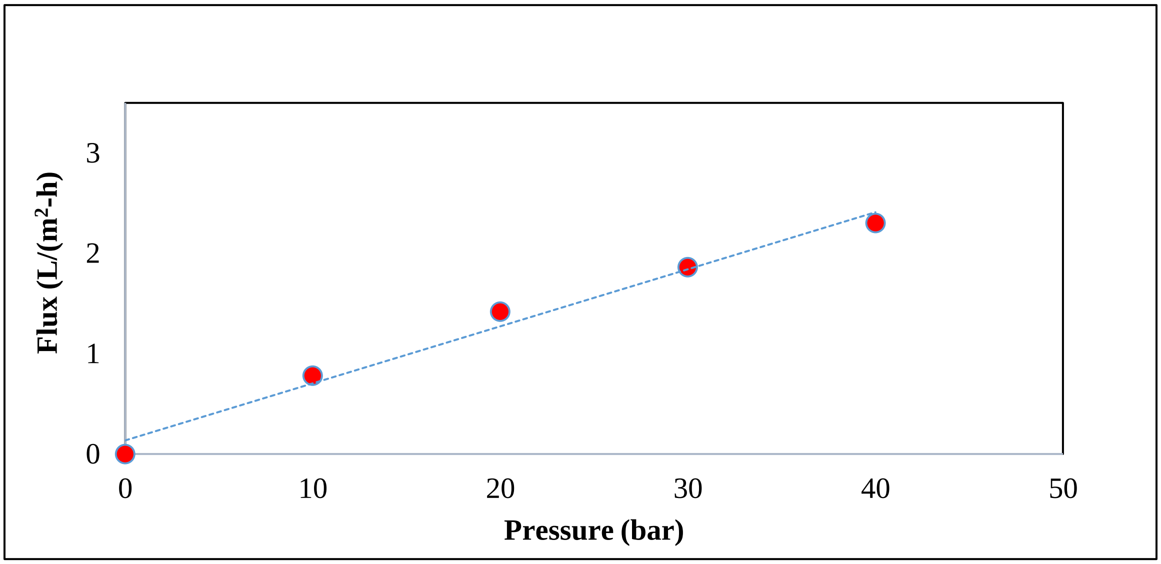
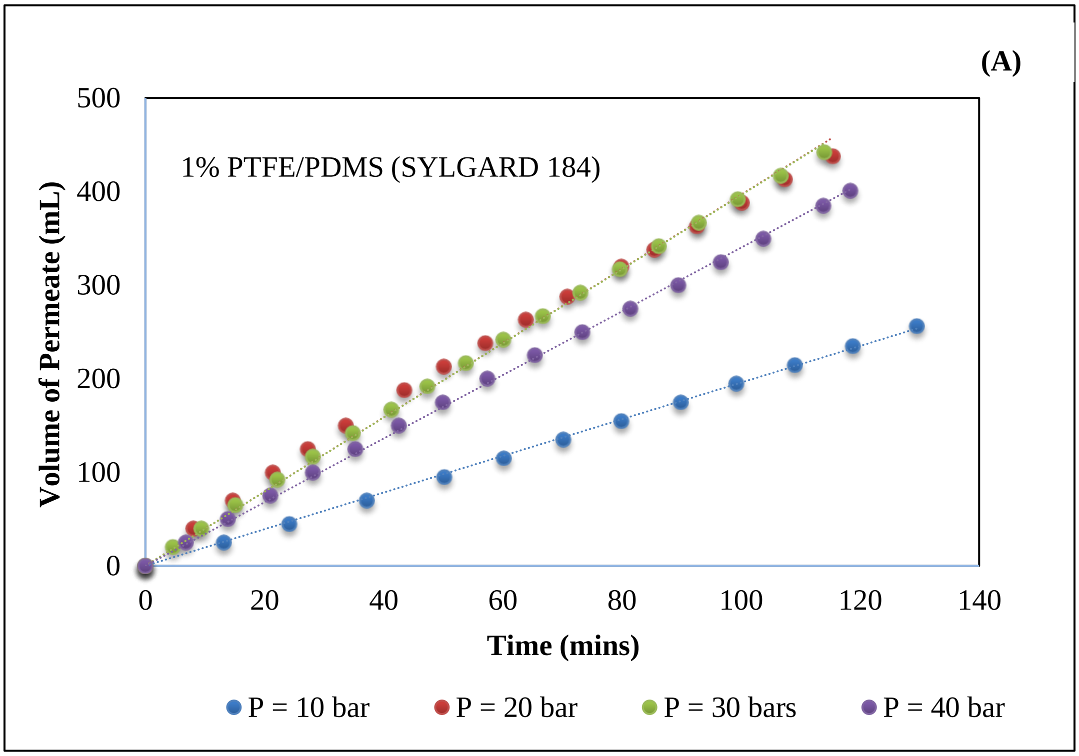
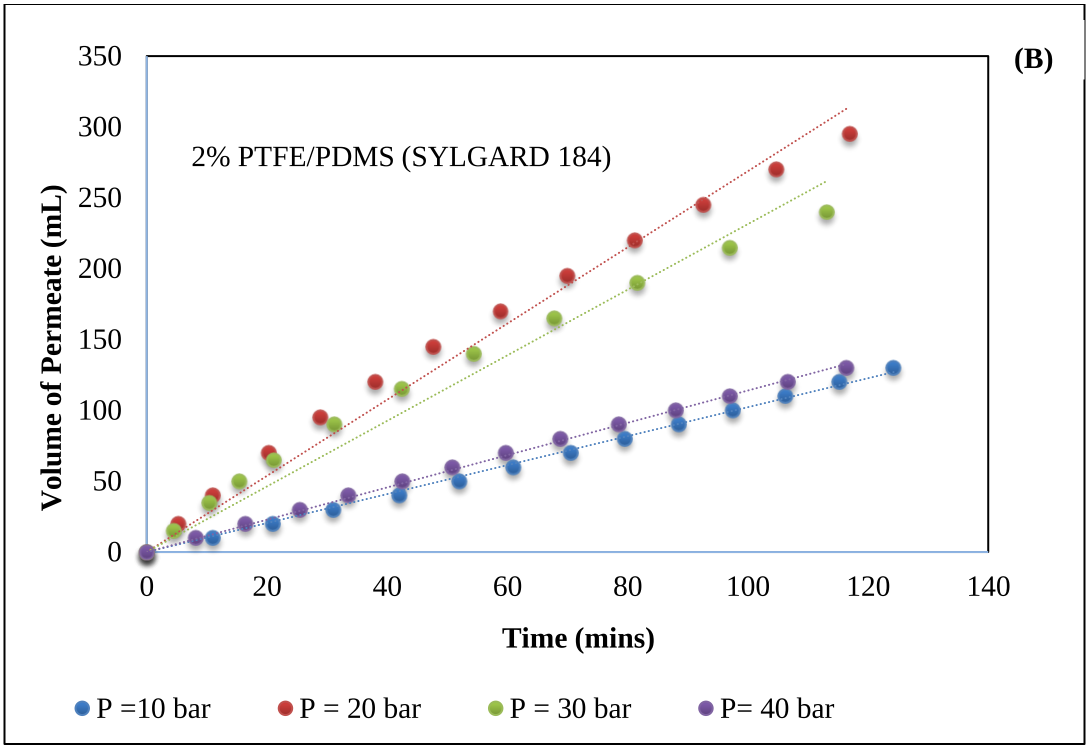


Figure 4.12: Flux at different pressures for commercial DuraMem membrane

4.5.2 Permeability Performance of PTFE/PDMS (SYLGARD 184)

When the PDMS solutions were prepared from SYLGARD 184 (15%, 7%, 3.1%, 2%, 1%), it was found that 15% and 7% resulted in very tight NF membranes whereas 1% (Figure 4.13.A), 2% (Figure 4.13.B) and 3.1% (Figure 4.13.C) solutions were successfully tested to check the permeability at 10, 20, 30 and 40 bars. It is evident from Figure 4.13 that with a decrease in PDMS concentration, permeability increases; 3.1% gives the lowest permeate volume (120 mL) and 1% shows the highest permeate volume of 450 mL after 2 hours of operating.





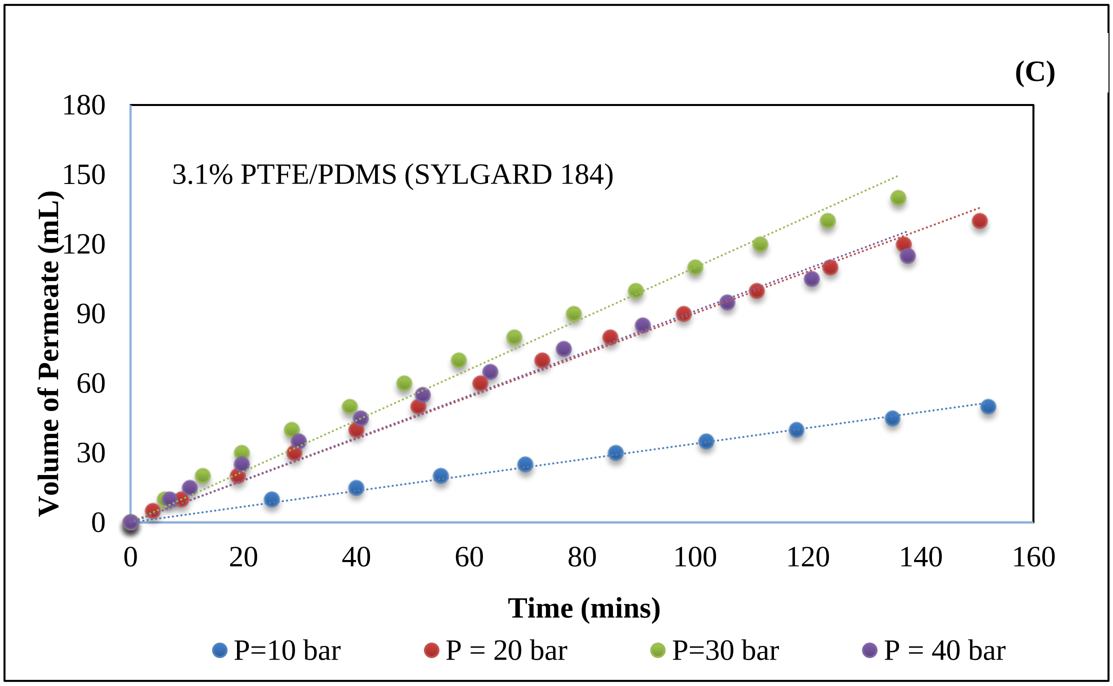


Figure 4.13: Influence of pressure on flux for SYLGARD 184 PTFE/PDMS membrane: A) 1% PTFE/PDMS; B) 2% PTFE/PDMS; C) 3.1% PTFE/PDMS

The SYLGARD 184 PTFE/PDMS was compacted when the applied pressure exceeded 30 bars; the result was consistent when the Flux versus Pressure values for 3.1, 2 and 1% SYLGARD 184 PTFE/PDMS membranes were compared (Figure 4.14). Nevertheless, in this case also, the permeability was lower than that of the PTFE/PDMS made from RTV 615. Thus it can be stated the PTFE/PDMS composite membrane prepared from 2.5% RTV 615 with a viscosity of ~ 45 mPa-s (Figure 4.10) showed the highest flux among all the OSNF membranes.

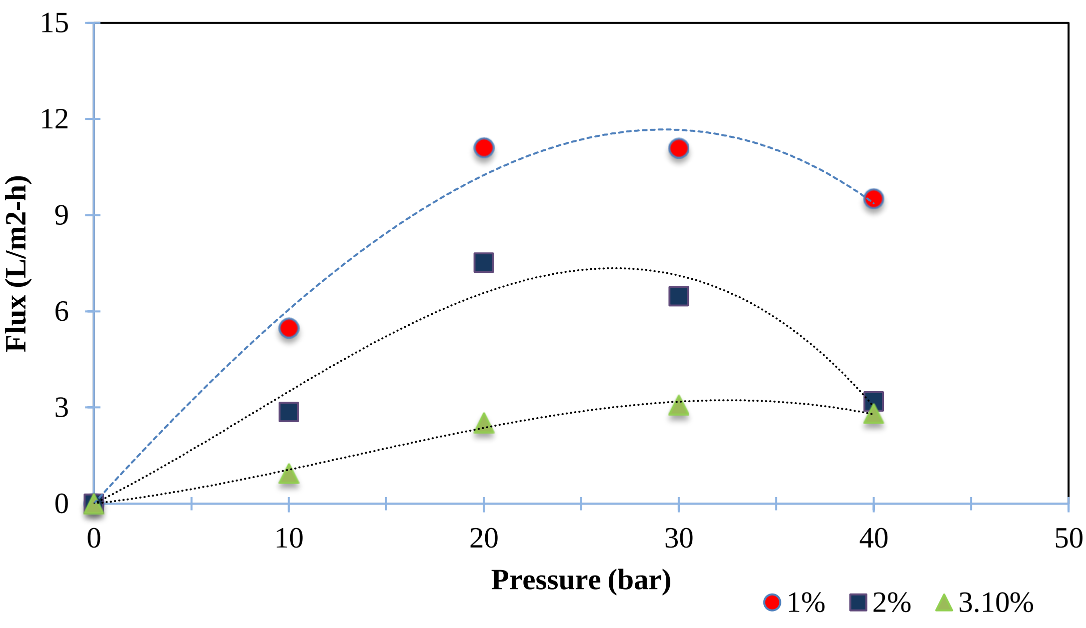


Figure 4.14: Flux (mL/min) at different pressures for 3.1%, 2% and 1% PTFE/PDMS membrane made from SYLGARD 184.

4.6 Removal of PhACs using different types of NF Membranes

The transport mechanism of organic solutes through NF and RO membranes has attracted the attention of several researchers. It is very important to understand the retention mechanism of the trace contaminants in the nanomembrane as well as their chemical characteristics and environmental fate in order to design a suitable treatment system. The separation through the nanomembrane can be achieved by physical selectivity (charge repulsion, size repulsion, size exclusion or steric hindrance) or chemical selectivity (solvation energy, hydrophobic interaction or hydrogen [33-41]. Size exclusion is an important phenomenon showing that suspended particles larger than the pore sizes of the membrane get trapped on the surface of the membrane as wastewater passes through. This can be compared to sieving phenomenon except that neither the solute has uniform size nor the membranes possess uniform pores [36, 37, 42]. Pore size, molecular size and pure water flux are found to be useful for predicting solute retention. When the membrane pores are larger than the size of trace contaminants, surface diffusion becomes faster than sorption diffusion [35, 36]. Another important removal mechanism is adsorption and subsequent sorption diffusion which is the initial stage in the transport mechanism of organic molecule using NF. Measurement of the hydrophobicity is done through LogK_{ow} i.e. partitioning between octanol and water. Trace contaminants with high LogK_{ow} or high hydrogen bonding capacity get adsorbed to the membrane surface [36]. The capability to form hydrogen bonding with hydrophilic groups of membrane polymer regulates the water flow through the membrane, whereas adsorption caused by hydrogen bonding can lessen water infiltration [36]. Compounds with no hydrogen bonding capacity are reported to exhibit significant adsorption and negligible water flux drop whereas compounds with high hydrogen capacity promotes significant drop in flux [36]. The electrostatic and steric hindrance have significant involvement in the solute retention, which is a function of the ratio of charge density of membrane to ionic concentration, solute radius to pore radius of membrane as well as relative mobility between cations and organic anions [36]. In other words, it can be revealed that pH and ionic strength can be expected to be influential factors in the retention of organic molecules. Various researchers have reported an increase in the rejection of negatively charged organic solutes owing to electrostatic repulsion among the negatively charged membrane and the negatively charged organic solute [38, 43-46]; however, organics that are positively charged show reduced retention on negative membranes [36]. At high pH, the adsorption is lower because of charge repulsion [37]. With a variation in pH, the zeta potential of the membrane diverges from positive to negative along with dissociation of the functional groups of membrane polymers taking on positive or negative charge fractions [33, 36]. When the NF membranes are considered to be “tight”, then the rejection of polar trace contaminants might be dominated by a size exclusion/steric hindrance mechanism [47].

There is a general lack of good understanding of the fundamental transport mechanisms for both solute and solvent in the OSNF system, through dense or porous structure [48, 49]. According to some researchers, the solution-diffusion process is the mechanism of transport through OSNF [50-52]. This model describes the transport mechanism through a polymer film as a composition of three main steps: sorption, diffusion and desorption [49]. Whereas others have advocated a convective mechanism, based on several specific fluid dynamic laws, as the explanation for transport through porous media [53-55]. Soltane et al. [49] invoked the Hagen-Poiseuille Law as the most likely explanation, wherein it is assumed that the membrane is made of cylindrical pores. Besides, the Spiegler-Kedem-Katchalsky model is a hybrid model in which the membrane is considered to be a “black box” and the solvent and solute fluxes are expressed separately [56]. Soltane et al. [49] worked specifically on solute transport processes in OSNF mechanism by describing solvent-membrane affinity, solvent-solute affinity and solute-membrane affinity; they predicted through the concept of solubility parameter theory by Hansen. According to Hansen’s solubility parameter theory, the solubility parameter describes the density of cohesive energy and comprises three different types of interactions: hydrogen bonding interaction (δ_H), polar interaction (δ_P) and dispersion interaction (δ_D) [57]. The total solubility parameter δ_T, can be expressed as:

$$\delta_T^2 \ = \ \delta_H^2 + \delta_P^2 + \delta_D^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (4.1)$$

The more comparable the solubility parameters of two molecules are, the more imperative is their affinity and the more they can be conjointly soluble. In consequence, the absolute difference in solubility parameter of two molecules allows for the evaluation of a qualitative assessment of the strength of their attraction. If δ_A and δ_B are solubility parameters of molecules A and B respectively, then the absolute difference in their solubility parameter is $|\delta_A - \delta_B|$; the higher the $|\delta_A - \delta_B|$ value, the lower their mutual affinity [49].

In the present study, OSNF with a PTFE support and a 2.5% PDMS top-coating has been used to assess the retention capacity of the membrane for IBP, NPR and DCF from aqueous media. The solubility parameters for the pharmaceutical compounds, water and PDMS membrane are given in Table 4.5. Since an established universal model for the solute transport in OSNF membrane does not exist, an experimental approach by Soltane et al. [49] was followed in this study to analyze the effects of solute sorption/ diffusion through the PDMS membrane. For the purpose of a better understanding of solute transport through PDMS membranes, various interactions such as, solvent membrane affinity, solvent-solute affinity and solute membrane affinity were considered.

Table 4.5: Solubility parameters of pharmaceutical compounds, water and PDMS

Compounds	Solubility Parameter δ (MPa)$^{1/2}$	Reference
IBP	20.9	[58]
NPR	23.4	[58]
DCF	27.79	[59]
Water	47.81	[57]
PDMS	16.42	[57]

Figure 4.15 illustrates the rejection capacity of the 2.5% PDMS membrane for the study pharmaceuticals, IBP, NPR and DCF. The results show that this particular PDMS membrane was able to reject 64% IBP, 65% NPR and 70% DCF. The graph also includes the values of solute - membrane affinity (on top) and solute-solvent affinity (at the bottom)

for each of the pharmaceuticals. According to this graph, DCF has the lowest solute membrane affinity, 11.37 MPa^{½} while IBP has the highest value, 4.48 MPa$^{½.}$ According to Soltane et al. [49], the solute membrane affinity seems to have a significant effect on the separation mechanism: the higher the interaction, the lower the rejection. This supports rejection results in the present study: DCF showed the highest rejection when compared to IBP and NPR. Then again, the higher the affinity of the solute with the solvent, the more significant the rejection of the solute is: this is also supported by our results since IBP has the lowest solute-solvent affinity and the lowest rejection.

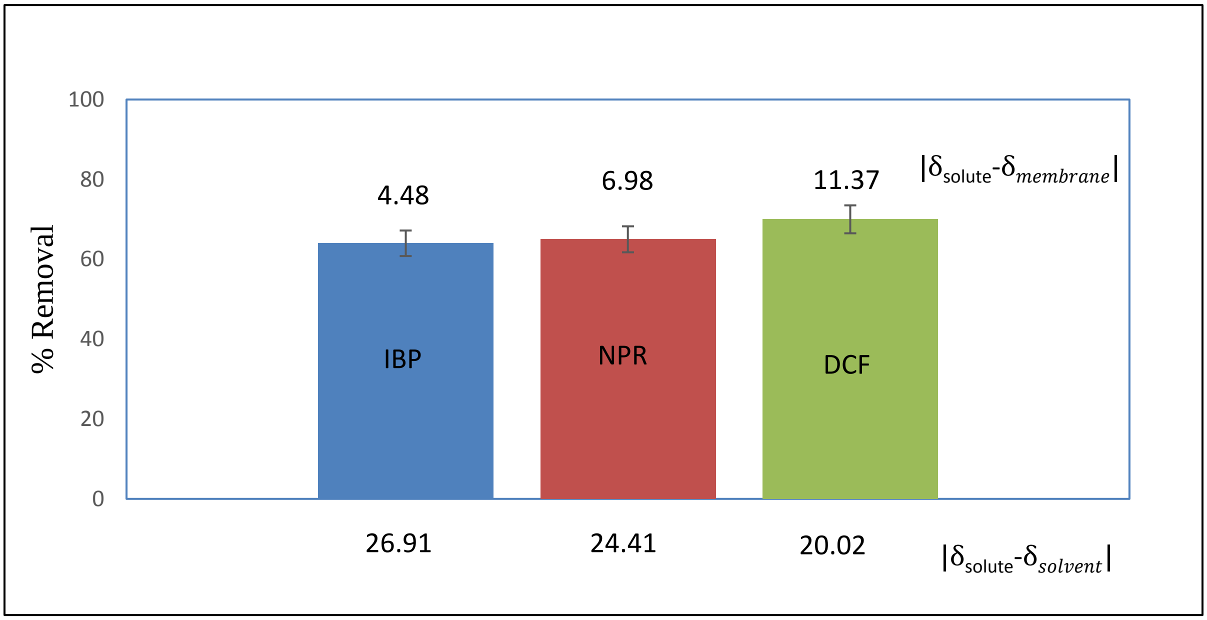


Figure 4.15: % Removal of pharmaceuticals by 2.5% PTFE/PDMS (RTV 615) membranes

Another set of experiments were performed to see the effect of base support of a 2.5% PDMS membrane on removal efficiency of IBP, NPR and DCF. The first membrane contained 2.5% PDMS active layer on commercially available PTFE support and the second membrane possessed 2.5% PDMS active layer on a laboratory made 20% PSF support. From Figure 4.16, it can be seen that change of support did not greatly affect the removal efficiency of the membrane. That means the composite membrane, prepared in the laboratory by casting PSF support and top-coating with PDMS solution was as efficient as the composite membrane prepared by using commercially available PTFE support. Figure

4.17A and 4.17Bb show the similarity in structure of a commercial PTFE support along with a hand- cast PSF support.

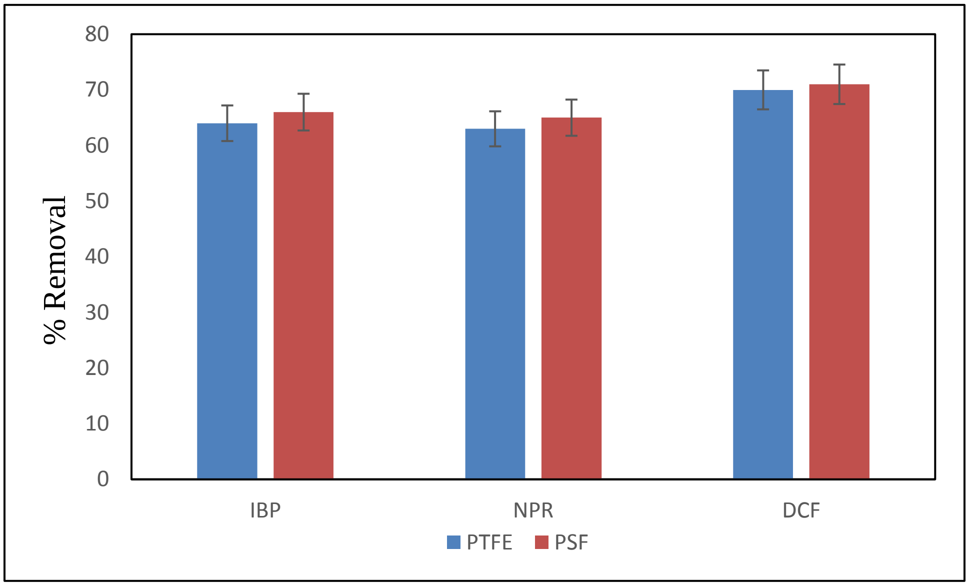
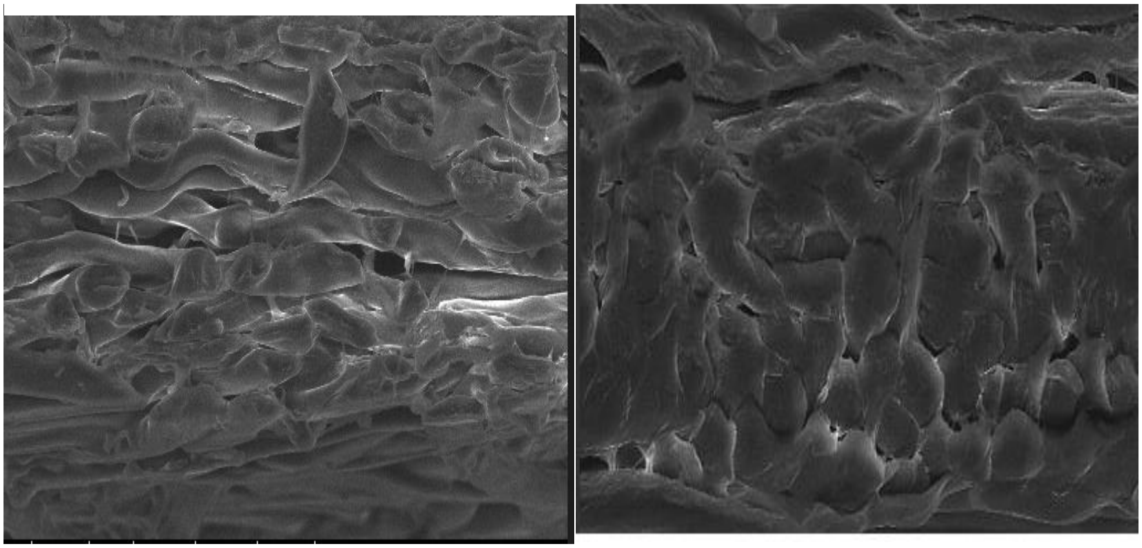


Figure 4.16: Comparison of pharmaceutical removal capacity of 2.5% PDMS membrane having PTFE and PSF support



(A) **(B)**

Figure 4.17: SEM of (A) Commercial PTFE support (left); B) PSF support cast in lab (right)

The TFC membrane prepared in lab with 2% MPD, 0.1% TMC and 0.1% CNT on a 20% PSF support was also used to check the removal capacity for IBP, NPR and DCF and it was found that IBP was removed 60%, NPR 56% and DCF 66%. In literature, it has been mentioned that commercial NF membranes are able to remove ~ 99% of PhAcs; however, the actual composition of those NF membranes are not mentioned anywhere.

PTFE/PDMS membranes prepared with 3.1%, 2% and 1% SYLGARD 184 were used for removing pharmaceuticals and it was found that 3.1% PTFE/PDMS showed the lowest removal efficiency whereas 2% PTFE/PDMS performed the best (Figure 4.18).

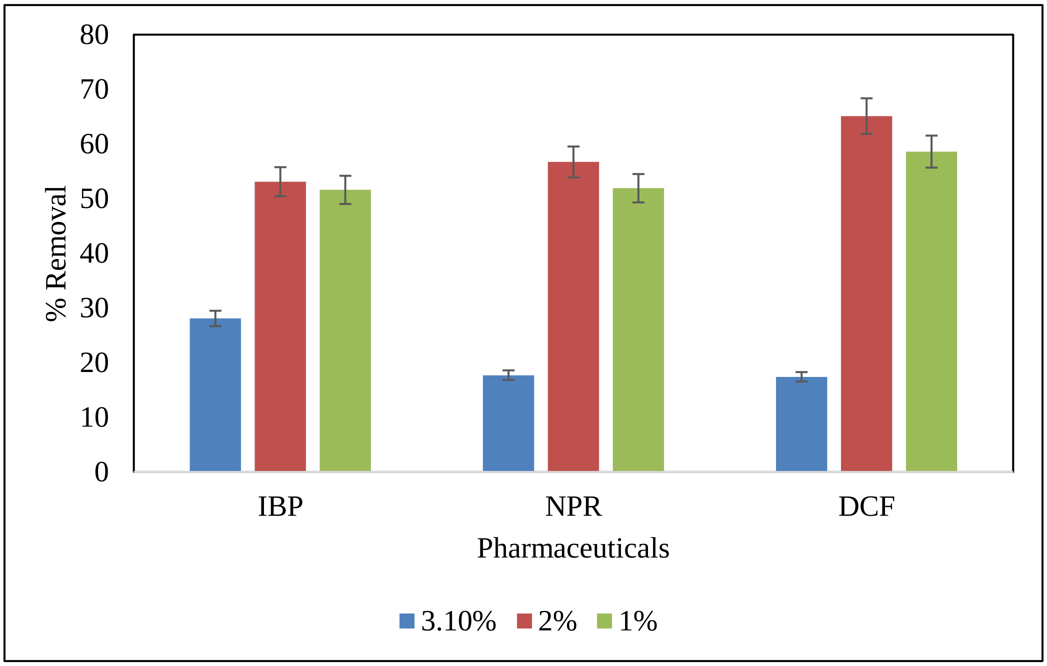


Figure 4.18: Removal efficiency of 3.1%, 2% and 1% PTFE/PDMS (SYLGARD 184) membranes

When commercial DuraMem membrane was used, the removal for IBP, NPR and DCF was 48.6%, 45.4% and 58.12%, respectively. Thus it can be seen that the 2.5% PTFE/PDMS (RTV 615) is better than the Commercial DuraMem membrane from the perspective of both permeability and removal of pharmaceuticals. Figure 4.19 shows a comparison between the four types of membranes used in this study for the removal of IBP, NPR and DCF. It is clear that the composite PTFE/PDMS prepared with RTV 615 gives the best result among all the membranes. Therefore, the PTFE/PDMS (RTV 615) membrane was subsequently used to evaluate the rejection capacity of EE2 in the next section. In all cases, the mass recovery of pharmaceutical compounds was found to be between 93~100%.

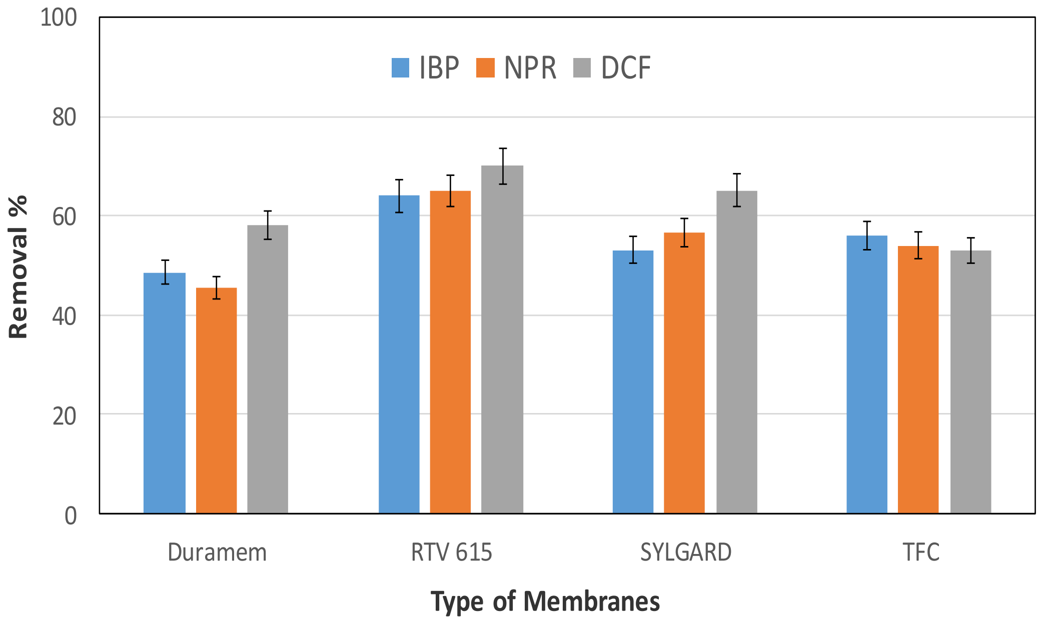


Figure 4.19: Comparison of removal efficiency of IBP, NPR and DCF: DuraMem, PTFE/PDMS (RTV 615), PTFE/PDMS (SYLGARD 184) and TFC

4.7 Removal of EE2 using PTFE/PDMS Membranes

Researchers have found that low molecular weight volatile compounds usually face low retention on NF membranes and branched and complex molecules get rejected by RO membranes [36, 37]. As the molecular weight of EDCs vary between 268 and 315 g/mol [37], they are found to be too small to be retained on MF or UF membranes and are expected to show higher retention on NF and RO membranes [37]. Neutral organic solutes have been known to be rejected by steric hindrance effect/ size exclusion between the solutes and the membrane polymeric matrix [21, 60-63]. According to Nghiem et al. [45], natural steroid hormones are known to partition onto the membrane and successively diffuse through the membrane polymer which results in lower removal of trace contaminants when compared to that through size exclusion mechanism. EDCs with

LogK_{ow} > 2.5 are anticipated to interact with the membranes by hydrophobic interactions [37].

Most of the available commercial NF membranes are thin-film composite (TFC) membranes where an ultra-thin (10 nm to several µm) dense layer (top selective layer) is formed on a bottom porous substrate by interfacial polymerization [64-68]. TFC-S, TFC-ULP, TFC-SR1, TFC-SR2 are some examples of commercial polyamide on polysulfone membranes that were found effective in removing estrone [33, 49] and estradiol [36]. Bodzek and Dudziak [69] used two types of flat membranes-NF polyamide and NF cellulose in conjunction with coagulants and found removals of almost 94% EE2, 92% estradiol & estron and 82% estriol. NF90, another commercial NF membrane, succeeded in removing approximately 90% of EE2 whereas a different membrane, NF200, could remove ~75% EE2 [70]. Estrone, estradiol, testosterone and progesterone were almost completely retained on NF270 and NF90 in a research work by Ngheim et al. [36]. EE2 rejection of about 90% and 98% retention of progesterone were observed by using NF200 by Koyunchu et al. [71]. In another study, NF 270 showed the highest retention of micro pollutants when a synthetic urine sample was tested [46].

In the present study two identical PTFE/PDMS membranes were used to check EE2 removal efficiency; both were prepared with 2.5% PDMS (RTV 615) solution having a viscosity of ~45 mPa-s cast on a commercial PTFE membrane. For Membrane 1, a feed concentration of 66 µg/L and for Membrane 2 a feed concentration of 19 µg/L were used. In both cases, triplicate samples were analyzed for accuracy. It was found that the removal efficiency of 2.5% PTFE/PDMS (RTV 615) membrane ranged between 95~97% (Table 4.6). The removal mechanism can be explained by size exclusion theory- both the EE2 and the PTFE/PDMS membrane have neutral surface and since EE2 has a small molecular weight, it gets trapped on the surface of the PDMS membrane. As a result, almost 3-5% of EE2 remained in the permeate solution when the feed solution is passed through a dead-end filtration system.

Table 4.6: Removal of EE2 with 2.5% PTFE/PDMS Composite Membrane

2.5% PTFE/PDMS (RTV 615)	Feed (µg)	Permeate (µg)	% Removal
Membrane 1	18.05	0.55	97%
Membrane 2	5.28	0.27	95%

4.8 Conclusions

After analyzing the wastewater effluents from Adelaide Wastewater Treatment Plant and Greenway Pollution Control Plant, over a period of six months, it has been found that samples contained IBP, NPR and DCF in very small concentrations, 0.66 ~ 3.63 µg/L, 1.22 to 8.98 µg/L and 0.29 to 1.23 µg/L respectively, supporting the previous research works. The presence of EE2 in the effluents of Adelaide Wastewater Treatment Plant could not be detected, considering the concentration was below the detection limit of the analytical instrument.

While preparing PTFE/PDMS composite membranes using RTV 615, it could be concluded that the process of pre-crosslinking was necessary to get a PDMS solution of low concentration and high viscosity because PDMS solutions with higher concentrations and lower viscosity declined the permeability of the membranes. The optimal condition was, therefore, pre-crosslinking of a 2.5% PDMS (RTV 615) solution at 60^{o}C until a viscosity of ~45mPa-s is achieved. The most appropriate duration of final cross-linking was found to be 4 hours. However, when SYLGARD 184 was used as PDMS solution, the final cross-linking time extended up to 18 hours.

Along with PTFE/PDMS (RTV 615) and PTFE/PDMS (SYLGARD 184), a commercial OSNF membrane, DuraMem, was also tested for membrane permeability as well as removal efficiency of PhACs. It has been found that all of the membranes showed a linearity between flux and pressure within a pressure range between 5~30 bars. Besides, a TFC membrane was prepared and tested as well to check its pharmaceutical removal efficiency. It was found that 2.5% PTFE/PDMS (RTV 615, viscosity ~45 mPa-s) showed the best performance in case of both permeability and removal efficiency of IBP, NPR and DCF. Therefore, this membrane was tested for rejection of EE2 and was found that the membrane could successfully remove 95-97% EE2.

The retention mechanism of OSNF for pharmaceuticals has been explained by solution-diffusion mechanism based on Hansen’s Solubility Parameter Theory; whereas EE2 was considered to be removed through OSNF following size exclusion mechanism of NF membranes.

4.9 References

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Chapter 5

5 Summary and Conclusions

The incomplete removal of pharmaceutically active as well as endocrine disrupting compounds through conventional wastewater treatment plant results in their occurrence in the aquatic environment. Even a very small amount of these compounds may have potential negative impacts on human and ecosystem health. For example, long term exposure to EE2 in the aquatic environment may result in the creation of female-specific protein in male fish, introduction of gonopodia in female, lower sperm count as well as incidence of intersexuality. On the other hand, the absence of strict procedures precise to these trace contaminants along with insufficient protections and monitoring guidelines has made analysis of these compounds very important.

In this work, wastewater effluents were collected from two major wastewater treatment plants in London, ON, Canada: Adelaide Wastewater Treatment Plant and Greenway Pollution Control Plant. Necessary sample preparations were made and individual analytical methodologies were developed to analyze the collected effluents for the identification and quantification of ibuprofen (IBP), naproxen (NPR), diclofenac (DCF) and 17α-ethinylestradiol (EE2) on GC-FID and LC-MS. It was found that the wastewater effluents contained IBP in the range of 0.66-3.63 µg/L, about 1.22 to 8.98 µg/L of NPR and DCF within a limit of 0.29 to 1.23 µg/L. However, the presence of EE2 in the effluent was below the detection limit (50 ng/L) of the LC-MS.

Although physico-chemical transformation processes like photolysis, ultra violet irradiation, oxidation, ozonation and hydrolysis are being used to treat water contaminated with trace amounts of PhACs and EE2, it is possible that the compounds are not completely mineralized forming intermediates and by-products due to their low biodegradability, high water solubility, elevated chemical stability and decreased tendency for sorption. In this study, a novel approach has been presented for the removal of PhACs and EE2 from water using organic solvent nanofiltration (OSNF) membranes. OSNF membrane technology is an energy competent separation process that has been successfully used to remove molecules of 200-1,000 g/mol in several organic solvents. OSNF membranes are asymmetric, integrally skinned, or composites containing a thin poly (dimethyl siloxane) (PDMS) layer on a porous support. In this study, instead of using an organic solvent, the OSNF was used in aqueous media.

As a part of the removal of PhACs and EE2, in this study, customized composite PDMS membranes were prepared using both commercial PTFE ultrafiltration membrane and laboratory made polysulfone (PSF) ultrafiltration membrane as base support; RTV 615 and SYLGARD 184 served as PDMS solutions to create an active skin layer on the polymeric supports. Along with that, a thin film composite (TFC) nanomembrane was also synthesized where the base support was made with a homogeneous mixture of PSF and multi-walled carbon nanotubes (MWCNTs) and the thin active layer on top of the support was prepared through interfacial polymerization between m-phenylenediamine (MPD) and trimesoyl chloride (TMC). These lab-made composite membranes were subsequently investigated for the purpose of membrane performance and removal of IBP, NPR, DCF and EE2. Furthermore, a commercially available polyimide membrane (DuraMem) was also investigated to compare the performance of the lab-made membranes. The following conclusions are made, after all the experimental works:

- Pre-crosslinking of a 2.5% PDMS (RTV 615) solution at 60^{o}C with a viscosity of ~45mPa-s served the as best method to prepare the thin active layer of a composite PDMS membrane. PDMS solutions with higher concentrations resulted in tighter membranes with little to no permeability. Moreover, a viscosity lower than ~45 mPa-s reduced the permeability of the membranes.

- The optimum condition of the composite PDMS (RTV 615) membranes for final cross-linking was 60^{o}C in the oven for 4 hours. With an increase in cross-linking time in the oven, the membranes became tighter and the flux through the membranes decreased.

- SYLGARD 184 as a PDMS solution required longer cross-linking period (~18 hours). The use of 10 g clip package from the supplier consisting of a pre-measured hardener and base (10:1) might cause the requirement of longer and inconsistent cross-linking.

- Flux was measured through the membranes in a dead-end filtration system at different pressures: 5, 10, 20 and 30 bars and all of the membranes showed a linearity between flux and pressure; that means no compaction of membranes was observed within this pressure range. However, at 40 bar, the composite PTFE/PDMS (SYLGARD 184) showed a compaction and reduction in permeability.

- Hydrodynamic permeability coefficient of water through the TFC membrane as well as that of a commercially available polyimide membrane, DuraMem, was also determined.

- Comparing the permeability of all of the membranes, it was found that 2.5% PTFE/PDMS (RTV 615, ~45 mPa-s) showed the highest permeability.

- All of the membranes were tested to check their efficiency for the removal of IBP, NPR and DCF. PTFE/PDMS (RTV 615) was able to remove 70% IBP, 65% NPR and 65% DCF. The removal efficiency of PTFE/PDMS (SYLGARD 184) for IBP, NPR and DCF was 53%, 57% and 65% respectively. On the other hand, the TFC membrane was able to remove 60% IBP, 56% NPR and 66% DCF. Along with that, DuraMem was found able to successfully remove 49% IBP, 45% NPR and 58% DCF. Therefore, it was observed that composite PTFE/PDMS (RTV 615) showed the highest removal capacity for IBP, NPR and DCF.

- Composite PDMS membranes prepared with both commercially available PTFE and laboratory made PSF base support did not show any major difference in permeability and pharmaceuticals removal efficiency.

- Since 2.5% PTFE/PDMS (RTV 615) showed the best performance among all other membranes, this membrane was solely tested to see its retention capacity for EE2 and it was found that it removed ~95-97% of EE2.

- The retention mechanism of pharmaceutical compounds by composite PDMS membranes is explained here through Hansen’s Solubility Parameter theory, comprised of solute-membrane affinity, solute solvent affinity and solvent-membrane affinity. The absolute difference between the solubility parameters of two molecules explains the strength of attraction between them; the higher is the difference, the lower is the mutual strength. The removal of EE2 is explained through size exclusion mechanism.

5.1 Contribution of Thesis

OSNF has been established as an auspicious and high potential separation process in organic solvent permeation due to flexibility, ease of production and less energy requirement over the past decade [1-4]. However, in aqueous media, the use of this promising technology has not yet been practiced. The present study offers a new area of research on the application of OSNF membranes in removing trace organic contaminants from water. Several batches of OSNF membranes were prepared using two different types of polymers in this study to establish the reproducibility of the performance of the membranes (see Appendix). Comparison of the lab-prepared OSNF membranes with a commercial polyimide membrane shows slight superiority of the lab prepared membranes with respect to permeability and removal efficiency of trace contaminants from water. While the presence of EE2 in waterbodies is currently considered a threat to aquatic life, this novel technology has been shown in the present study to successfully remove this endocrine disrupting compound from water.

5.2 Future Recommendations

In this research work, all the experiments were carried out with synthetic water to evaluate the performance of the OSNF membranes. Therefore, the next step would be to utilize wastewater samples to verify if it affects the performance. Moreover, the effect of fouling on transport of organic micro-pollutants needs to be studied. Since this work initiates the application of OSNF for the purpose of water treatment, further research would be required to explore its applicability to different types of solutes in water. In literature, till date, the mechanism of transport and separation phenomena for OSNF membranes are not well understood. Therefore, detailed research would be necessary to enhance the understanding of the mechanisms of transport of solutes through OSNF.

5.3 References

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Appendix

List of OSNF Membranes Prepared in this Study:

Types of Polymers	Solvent	% of Polymers	# of Batches	# of Membranes
RTV 615	Toluene	20%	2	10
RTV 615	Toluene	15%	2	10
RTV 615	Toluene	7.5%	2	10
RTV 615	Toluene	5%	3	15
RTV 615	Toluene	2.5%	5	25
RTV 615	Toluene	1.85%	5	25
RTV 615	Hexane	2.5%	2	10
RTV 615	Hexane	1.85%	5	25
SYLGARD 184	Hexane	20%	4	12
SYLGARD 184	Hexane	15%	3	6
SYLGARD 184	Hexane	12%	3	12
SYLGARD 184	Hexane	10%	3	12
SYLGARD 184	Hexane	7%	3	12
SYLGARD 184	Hexane	5%	3	12
SYLGARD 184	Hexane	3.1%	5	15

SYLGARD 184	Hexane	2%	5	15
SYLGARD 184	Hexane	1%	5	15
SYLGARD 184	Hexane	0.5%	1	2

List of TFC Membranes Prepared in this Study:

PSF	MPD	TMC	MWCNT	# of Batches	# of Membranes
20%	-	-	-	10	50
15%	-	-	-	5	25
20%	2%	0.1%	-	4	20
20%	2%	0.2%	-	4	20
20%	2%	0.1%	1% (modified)	2	6
20%	2%	0.1%	0.5% (modified)	2	6
20%	2%	0.1%	0.1% (modified)	2	6
20%	2%	0.1%	0.5% (unmodified)	2	6
20%	2%	0.1%	0.1% (unmodified)	2	6
20%	2%	0.1%	1% (unmodified)	2	6

Curriculum Vitae

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Publications	1.Thin Film Composite and Solvent Resistant Nanofiltration Membrane: A Critical Review of Methodology for Fabrication

Atisha, Ambareen; Wojciech Kujawski, Ernest K. Yanful

(Submitted to “Separation & Purification Technology’)

2. Application of Customized Nanofiltration Membranes for the Removal of Ibuprofen (IBP), Naproxen (NPR), and Diclofenac (DCF) from Wastewater Effluents

Atisha, Ambareen; Mark Barnards, Wojciech Kujawski, Ernest K. Yanful

(Submitted to “Desalination”)

3. Removal of EE2 with Customized PDMS Composite Membrane from Water

Atisha, Ambareen; Mark Barnards, Wojciech Kujawski, Ernest K. Yanful

(Submitted to “Desalination”)