Conductive Ultrafiltration Membrane Fabrication via a Novel Vacuum-Assisted Layer-by-Layer Assembly of Functionalized Carbon Nanotubes

Farah Rahman Omi
A Thesis
In
The Department of
Building, Civil and Environmental Engineering

Presented in partial fulfillment of the requirement
For the Degree of Master of Applied Science (Civil Engineering) at
Concordia University
Montreal, Quebec, Canada.
February 2015

CONCORDIA UNIVERSITY

School of Graduate Studies

This is to certify that the thesis prepared

By: Farah Rahman Omi

Entitled: Conductive Ultrafiltration Membrane Fabrication via a Novel Vacuum-Assisted Layer-by-Layer Assembly of Functionalized Carbon Nanotubes

and submitted in partial fulfillment of the requirements for the degree of

Master of Science (Civil Engineering)

complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Signed by the final Examining Committee:

______________________________ Chair
Dr. Catherine Mulligan

______________________________ Examiner
Dr. A. S. Ramamurthy

______________________________ Examiner
Dr. Govind Gopakumar

______________________________ Supervisor
Dr. Saifur Rahaman

Approved by ____
Dr. Fariborz Haghighat

__________ 2015 ____
Dr. Amir Asif

Abstract

Conductive Ultrafiltration Membrane Fabrication via a Novel Vacuum-Assisted Layer-by-Layer Assembly of Functionalized Carbon Nanotubes

Farah Rahman Omi

Membrane processes are currently used in several ways to purify water and wastewater. Because of their high performance and smaller footprint, membranes are likely to grow in importance as compared to other conventional technologies. Therefore, there is a critical need for development of improved membranes that have higher flux, greater selectivity, and are less prone to fouling. Recently, multiwalled carbon nanotube (MWNT) electrochemical (EC) filter was reported to be extremely effective as a point-of-use technology in achieving complete removal and inactivation of pathogens. In order to scale-up the electrochemical filtration technology to utilize it in a plant-scale centralized water treatment plant, conductive nano-composite ultrafiltration membranes were developed in this project, through incorporating amine and carboxylic functionalized MWNTs (MWNT-NH_2, MWNT-COOH) into polysulfone (PSf) substrates. A novel fabrication method, vacuum-assisted layer-by-layer self-assembly was used for surface modification of polysulfone ultrafiltration membrane.

First, the polysulfone membrane was functionalized with oxygen containing negatively charged functional groups through oxygen plasma treatment. In order to optimize the degree of functionalization of polysulfone membrane with increasing plasma duration, a comprehensive physicochemical characterization of the plasma treated membrane was performed by using ATR-FTIR, XPS, contact angle, EKA and SEM analyses. Water permeability test was also conducted to investigate the differential performance of the plasma-treated membrane with increase in plasma treatment duration. The ATR-FTIR analyses revealed the peaks at specific wavelengths for hydroxyl, carboxyl and carbonyl functional groups, while the XPS results showed an increase in oxygen content of the pristine polysulfone from 18.6% to 30.7%, after being plasma treated.

The contact angle of the plasma-treated membrane dropped down to 44.2° from 68.6° of the pristine membrane and the EKA showed an increase in surface zeta potential from -22.5mV to -42.8mV for varying plasma duration. Based on these analyses, 60s plasma treatment time was set as optimum for further modification of PSf membrane with MWNT.

The MWNT modified PSf membrane was characterized with a SEM that showed the uniform distribution of MWNTs throughout the membrane thickness as well as a linear growth in membrane thickness with increasing number of MWNT bilayers. The water contact angle analyses revealed that the modified membrane became more hydrophobic with increasing number of bilayers. The modified membrane exhibited reasonable permeability, higher conductivity and high antifouling properties due to application of very low DC potential (0V-3V). Due to high conductivity of the MWNT modified membrane an application of 3V DC voltage showed almost 100% inactivation of *E. coli* inactivation suggesting the effectiveness of the MWNT modified polysulfone membrane in controlling the biofouling in electrofiltration system. Moreover, this study showed over 99% degradation of methyl orange during electrofiltration that could contribute to reducing the organic fouling of the modified membrane. Overall, the new MWNT modified polysulfone membrane has huge potential to be used in large scale electrofiltration systems.

Acknowledgments

First of all I wish to express my thanks to almighty Allah, the beneficent, and the most wise for enabling me to complete this study successfully.

I would like to acknowledge and extend my heartfelt gratitude to my supervisor, Dr. Saifur Rahaman, for granting me an opportunity to pursue my graduate studies at Concordia University, as well as for his continuous inspiration and guidance in this research. I really appreciate his vast arena of knowledge, his expertise and his patience during correcting my writing. His encouraging words always cheered me up in difficult times of problem solving.

I highly appreciate my research group members for their support and feedbacks throughout my research work. Very special thanks go to Wen Ma, who inspired me as a friend and always supported me during my study period. I would like to thank Shahidul Islam and Ahmed Bakr, for their generous help during explanation of some difficult concepts with their expertise. Also I would like to thank Adel Soroush for his excellent suggestions and feedback that helped me to solve some of the difficult situations rose during research.

I am thankful to all the undergraduate students who worked with our research group as summer interns, especially Melissa Nielson and Emad Haneef for their help and support during laboratory experiments. I extend my heartfelt gratitude to Gregory Brennan for his super supporting attitude during any difficulties in experimental setup.

I would like to acknowledge Concordia University for their financial support and extensive laboratory facilities for membrane research. Also I would like to acknowledge Mcgill University, NanoQAM lab in Université du Québec à Montréal (UQAM) and École Polytechnique de Montréal for sharing their laboratory facilities with us.

Finally I would like to extend my gratitude to my sister, brother-in-law and my nephew who were always there as my cheerleaders.

Dedication

I dedicate this work to my parents Hafizur Rahman Molla and Monoara Begum, who have taught me the value of hard work and supported me with their words. Their constant love and inspiration has made me what I am today and motivated me to work for my dreams. Also I dedicate this work to all my family members, who has been a great source of encouragement throughout this work.

Finally I would like to dedicate this work to all the readers who believe in the richness of research.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

CNT	Carbon nanotube
SWNT	Single wall carbon nanotube
MWNT	Multiwalled carbon nanotube
MWNT-COOH	Carboxylic acid functionalized multiwalled carbon nanotubes
MWNT-NH_2	Amine functionalized multiwalled carbon nanotubes
EC	Electrochemical
PSf	Polysulfone
PES	Polyethersulfone
JMP	Joint Monitoring Programme
IPCC	Intergovernmental Panel on Climate Change
WHO	World Health Organization
UNICEF	United Nations Children's Fund
FAO	Food and Agriculture Organization
MFC	Microbial fuel cells
PTFE	Polytetrafluoroethylene
PVDF	Polyvinyldenefluoride
LBL	Layer-by-Layer (LBL)
UV	Ultra violet
GA	Glutaraldehyde
PVA	Poly Vinyl Alcohol
EDC	N-Ethyl-N′-(3-dimethylaminopropyl) carbodiimide hydrochloride
NHS	N-Hydroxysuccinimide
MMM	Mixed Matrix Membranes
TOC	Total organic carbon
TiO_2	Titanium oxide nanoparticle
Al_2O_3	Aluminum oxide nanoparticle
ZnO	Zinc oxide nanoparticle
MnO	Manganese oxide nanoparticle
nAg	Silver nanoparticles

$Mg(OH)_2$	Magnesium oxide nanoparticle
LaB_6	Lanthanum Hexaboride
PVP	Polyvinylpyrrolidone
TAP	2, 4, 6-triaminopyrimidine
MWCO	Molecular weight cut-off
NMP	N-methyl-2-pyrrolidinone
MF	Microfiltration
UF	Ultra filtration
NF	Nanofiltration
RO	Reverse osmosis
TEOA	Triethanolamine
BPPO	Brominated polyphenylene oxide
VASA	Vacuum assisted self assembly
PANi	Polyaniline
DBP	Disinfection byproducts
MNP	Metal oxide nanoparticles
ENP	Novel engineered nanoparticles
MIP	Molecularly imprinted polymers
PCL	Polycaprolactone
2CP	2-chlorophenol
NIPAM-*co*-$AAB_{18}C_6$	N-isopropylacrylamide-*co*-acryloylamidobenzo-18-crown-6
PVK	Polyvinyl-N-carbazole
ROS	Reactive oxygen species
LB	Lauria-Botani
ATR-FTIR	Attenuated total reflection-Fourier transform infrared spectroscopy
SEM	Scanning electron microscopy
XPS	X-ray photoelectron spectroscopy
EKA	Electrokinetic analyses
PEG	Polyethylene glycol

1. INTRODUCTION

1.1 Motivation

1.1.1 Water scarcity throughout the world

Access to clean water and sanitation is a global challenge that needs to combat for ensuring basic needs worldwide. As education, health, poverty and hunger are the critical functions of access to the safe water, the world need much strategic plans for sustainable resources. The growing population is proportional to the water scarcity, even worse the number is expected to reach almost 9.6 to 12.3 billion [1] at the end of this century while we have fixed sources of water (97% saline water and 3% fresh water). According to the WHO/UNICEF Joint Monitoring Programme (JMP) for Water Supply and Sanitation report (2012), 780 million people lack access to an improved water source that is approximately one eighth of the world's population [2]. Another report (2014) by Intergovernmental Panel on Climate Change (IPCC) states that, approximately 80% of the world's population suffers serious threats to its water security which is measured by indicators including water availability, water demand and pollution [3]. Food and Agriculture Organization (FAO) estimated 70% of the total water use accounts for agricultural need while approximately 10% water use for industrial and 20% for domestic purpose. Groundwater is the crucial source for the food security and livelihood of the world's population. Also groundwater-fed irrigation contributes more to the drinking water shortage risks than the surface water fed irrigations. The global pollution increment is limiting the access to the safe sources of water, making surface water sources more vulnerable to contamination with questionable applicability that people started depending on the groundwater facilities. The world is extracting 26% [4] of the ground water (compared to the total water abstraction) to serve the domestic, irrigation and industrial purpose of its inhabitants. Wherever available, people are using groundwater as a reliable source of drinking water. Groundwater is subjected to many natural pollution sources as arsenic, nitrate and also contamination occurs due to landfill seepage, excessive use of fertilizers and pesticides etc. Consumption of groundwater is also a concerned issue as the amount of groundwater withdrawal is not recharged form external sources. In the era of concreting, surface water penetration throughout the soil media is neglected and the earth lacks methods of utilizing the natural sources for groundwater recharge. The world requires more alternative sources of safe water and it requires ideas of using the surface water with proper treatment. Industrial processes produce huge quantities of wastewater that can also be a good alternative of usable water if it can be treated up to certain level. Not necessarily the alternative sources need to be used for drinking purpose; it can meet the need of agricultural, household and industrial purpose to an extent. Due to the limited reliable water sources and the sensitivity of unhygienic water towards human health, filtration membrane technology offers the best solution in present days.

1.1.2 Increased stress on water treatment plant

Potable water stress is one of the major environmental stresses of 21st century. According to the FAO report, by 2025 approximately 1.8 million people living in urban areas will have absolute water scarcity, while two-third of the population might be under stressful condition. Another fact is that the water use may increase at a rate which is more than twice the rate of population growth. These facts clearly depict the necessity of alternative sources of water through treating both the surface water and wastewater. Not only wastewater treatment is encouraged for re-use, but also the treatment of wastewater needs to be done for protecting water bodies from unwanted pollution. Every industry that uses water for their production should have facilities for treatment of wastewater or it has to be transported and handled by the aerial treatment plant. In many cases there is no separate storm water collection network and it is often circulated in the central sewerage system. This surface water runoff is then treated with the grey water by considering the same chemical potential with the wastewater. Clearly the amount of clean water use for toilet and sanitation purpose as well as the laundry overwhelms the treatment plants with huge loads. Meanwhile the decentralization of the municipal wastewater treatment plant may play a role is reducing the wastewater stress.

Membrane filtration is gaining popularity for industrial waste water treatment plants because of its smaller footprint and diversity of use. As the shortage of space is a serious consideration for any kind of industry, the membrane modules offers great advantage of minimizing the space requirement as well as an effective treatment option. Also it requires less energy if compared to the conventional thermal separation processes as distillation, sublimation or crystallization. However, a major challenge related to membrane filtration is the membrane fouling that hinders the filtration rate and if the fouling is due to the biofilm growth then the water flux recovery is very difficult. The biofouling is the Achilles heel for any kind of membrane and thus the efforts are being taken by the researchers to develop antifouling membranes. Due to the membrane fouling problem the treatment plants are always challenged with the membrane cleaning and therefore a tradeoff remains between the membrane fouling and the performance lifetime.

1.2 Electrically conductive membrane can be useful for the inactivation of microorganisms and organic matter degradation

Membrane filtration technology offers physical separation of the unwanted particles, colloids, macromolecules and pathogenic microorganisms depending on the pore sizes of different types of membrane. The separation is mostly physical sieving for the microfiltration, ultrafiltration and nanofiltration except the reverse osmosis and forward osmosis membrane separation mechanism is termed as diffusion. Due to the size exclusion and diffusion depending on the membrane properties (pore size, hydrophilicity, hydrophobicity and membrane material); membrane filtration ensures higher rejection of both particulate and microorganisms. Membranes are unavoidably subjected to fouling which may occur due to the attachment of colloidal(clay, floc), biological (bacteria, fungi), organic (oil, polyelectrolyte, humic acid) and scaling by mineral precipitates [5]. Depending on the type of foulant attachment fouling is categorized as reversible (weak attachment, removable with strong shear force or backwashing) and irreversible (strong attachment, not removable with physical cleaning) fouling. The irreversible fouling includes the biofouling and organic matter fouling; both of them are considered as the most complex form of foulant as once they are formed, and it becomes very difficult to remove. The biofouling is referred to as active fouling because of its tendency of continuous growth of microorganisms that increases the biofilm layer thickness ultimately resulting into flux reduction. One of the ways to mitigate bio-fouling is through inactivation of micro-organisms, which prevents them from strongly adhering to the membrane surface as well as from reproducing. Researchers has been studied the effect of incorporating biocidal nanoparticle into membrane matrix such as titanium dioxide (TiO_2) [6], zinc oxide (ZnO) [7], silver nanoparticle (Ag) [8], magnesium hydroxide

($Mg(OH)_2$) [9] and carbon based nanoparticles [10-12] and they found remarkable results of antifouling properties. Aluminum oxide (Al_2O_3) incorporation in polymeric membrane explicitly improved organic matter removal [13] as well as the manganese oxide(MnO) coating on ceramic membrane showed higher rejection of total organic carbon [14]. Another way of controlling fouling is through using conductive membrane where application of DC potential would results in inactivation of microorganisms and degradation of organic matters that cause fouling. Conductive nanocomposite materials have been widely used in fuel cell and batteries, especially the microbial fuel cells (MFCs) used for wastewater treatment. In these systems, conductive nanocomposites can be used as the anode material where they act as electrocatalysts and accelerate the electrochemical reaction. A conductive nanocomposite would be highly effective for the development conductive membranes for the electrochemical filtration system. Conductive polymeric nanocomposites, especially those with carbon nanomaterials, have been closely investigated due to their low cost. In a recent study, Vectis et al.(2011) [15] dispersed multiwall carbon nanotubes (MWNT) on polytetrafluoroethylene (PTFE) filter and found that at very low potentials (2 and 3V) MWNT filters exhibited more than 75% bacterial and 99.6% viral inactivation. In a follow-up study, Rahaman et al. reported complete removal (5.8 to 7.4 log) and significant inactivation of viral particles when 2 or 3V was applied to an electrochemical MWNT filter [16]. In a very recent study Gao et al.(2014) [17] reported higher (>99%) reduction of organic nitrobenzene by sequential reduction oxidation process through the conductive CNT-PVDF membrane. All these studies showed the efficacy of conductive membrane surface in reducing biofilm via inactivation of microorganism as well as in reducing organic fouling through organic matter degradation. Therefore, it is obvious that the development of conductive membranes and their application in electrofiltration system will add new functionality to the membrane industry.

1.3 Layer-by-layer self assembly for surface modification of membranes

Layer-by-Layer (LBL) deposition is a thin film fabrication technique in which films are formed by depositing alternating layers of oppositely charged electrolytes with wash steps in between. The layer-by-layer method has been used in several studies to develop a mechanically and chemically strong membrane [14, 18-20]. It includes dip, spray, and spin coating, and can be followed by curing, which leads to cross-linking. Curing can be accomplished through heating, UV, or chemical means [21], and can lead to a membrane which is more chemically, thermally, and mechanically stable [22]. There are four types of interactions that hold the polyelectrolyte layers with the substrate membrane: electrostatic interaction [14, 19, 23], hydrophobic interaction [24], hydrogen bonding [25-27], and attraction through the van der waal's force [28].

As the name "dip-coating" suggests, a membrane prepared by this method is dipped into a homogeneous polyelectrolyte solution with the coating materials. In the case of a thin film nanocomposite membrane, a polymeric membrane (usually prepared by phase separation) is dipped into a solution containing evenly dispersed nanoparticles. If nanoparticles have been functionalized, this can sometimes be accomplished with cross-linking: Pourjafar et al. reported on a PES/PVA/TiO_2 membrane where phase separation-prepared PES membranes were coated with PVA, which were then dipped into a cross-linking solution containing glutaraldehyde (GA) which was able to link to the TiO_2 nanoparticles [22]. Layer-by-Layer dip-coating depends on the electrostatic interactions between membrane and coating layers and leads to multilayer with monolayer precision [29-32]. Positively and negatively charged polyelectrolyte solutions are coated onto an electrode [29], for membranes its mostly the substrate. LBL coating can be done with metal oxide [14, 19, 30, 33], multiwall carbon nanotubes and [34] silver nanoparticles [35]. A major downside of dip-coating is that it is very time-consuming and therefore it is not attractive at this time for scaling up to an industrial level. Another downside is that, while the films created by dip coating can still be categorized as thin films (<100 nm), they are relatively thick, and this can hinder water permeability.

Spin-coating and spray-coating are gaining popularity as these techniques have some advantages over dip-coating. Spray-coating requires less time, and provides higher control and homogeneity over dip coating. Liu et al. [34] developed CNT-bound polyelectrolyte membrane by spray-assisted layer-by-layer (LBL) technique and reported improved flux and enhanced antifouling properties for commercial polyethersulfone membrane. A number of studies have been performed on development of spray assisted LBL membrane for fuel cell application [36], proton exchange membrane [37] and supercapacitor [38]. Spin coating entails putting a small amount of the solution in the middle of the substrate, and then spinning the substrate at a very high speed, using the centripetal force created by this motion to evenly spread the coating. Also the spin coating technique does not allow the layers to diffuse into one another due to the high air shear and rotational speed in contrast to dip coating [36]. To the best of our knowledge, spin-coating has not been used thus far in nanocomposite membranes for water treatment, however, the possibility of a spin-coated nanocomposite membrane was demonstrated by Jiang et al., in which the authors were able to uniformly coat a silica thin film with LaB_6(lanthanum hexaboride) nanoparticles [39]. Similar improvements of dip-coated membrane modification could be investigated with spin-coated membranes as the latter is more versatile for scaling up.

1.4 Objectives

The objective of this study was to develop conductive membrane through incorporating MWNT onto polysulfone substrate membrane and to demonstrate its application in electrochemical filtration systems to reduce the membrane fouling. Leading steps to reach this objective are detailed below:

1. Plasma treatment of substrate polysulfone membrane to functionalize the membrane surface with oxygen containing functional groups and optimization of plasma treatment time through contact angle measurement, SEM pore size analyses, permeability measurement, XPS analyses and FTIR analyses;
2. Selection of appropriate solution chemistry for N-ethyl-N′-(3-dimethylaminopropyl) carbodiimide hydrochloride(EDC) and *N*-Hydroxysuccinimide(NHS) also named as EDC-NHS initiated amine reactive NHS ester formation on the functionalized polysulfone membrane which creates conjugate stable bond when contacted with nanomaterials with specific functional groups;
3. Selection of conductive nanomaterials ($MWNT-NH_2$ and MWNT-COOH) and their concentration for uniform dispersion in aqueous solutions and optimizing the solution quantity for each layer formation;
4. Evaluating the effect of increasing number of bilayers by analyzing the membrane performance characteristics measured by conductivity, permeability, antimicrobial activity and organic matter degradation ability.

1.5 Organization of the dissertation

This dissertation comprises five sections in a chronological order, which was designed to assist the reader of this paper in understanding without any difficulties. In addition, a reference of publications has also been presented.

Section-1 deals with general introduction of the topics, existing challenges that have been faced and objectives of the study.

Section-2 describes the reviewed literature, which covers the description of membrane technology, different type of membrane characteristics, modification of membrane surface for additional functionality, recent studies of layer by layer self assembly and its application in water filtration, fouling challenges faced by membrane technology and expectation from the developed conductive membrane for water filtration.

Section-3 includes the materials used in this study, methodology of the study and performance investigation techniques. A briefs explanation of the membrane surface characterization techniques and protocols followed during the experiment have been presented here. Also the membrane performance evaluation with consecutive steps is mentioned clearly with reference to ensure the accuracy of protocol.

Section-4 covers the results of the membrane characteristic and performance evaluation with detailed discussion of each finding. The discussion includes comparison of the results with previous research findings and the evidences found in this study.

Section-5 contains conclusions of the current study, and Section-6 addresses the recommendations for further investigations.

2. BACKGROUND AND LITERATURE REVIEW

Membrane filtration theory is contingent on engineering aspects of mechanical and physical sieving through the size exclusion of molecules. Due to its efficiency compared to the conventional water treatment processes (distillation, crystallization etc.); membrane technology is widely used for both industrial and domestic purposes. Though there is an interest going on using inorganic membrane (ceramic membrane, metal oxide membrane etc.), polymeric membranes occupied majority of applications due to their cheap, flexibility in use, variety in material and property and so on. There is a variety of polymeric materials available for ultra filtration membrane preparation including cellulose acetate, cellulose tri acetate, polyacrylonitrile, polyvinyl chloride, polyamide, polysulfone, polyethersulfone, polyimide, polyvinylidenefluoride, etc. Most of these polymers used in membrane present high specific surface area and the membrane modules greatly reduce the size of the plants if compared to the conventional treatment plant. The few factors that define a membrane's effectiveness are permeability, pore structure, selectivity, hydrophilicity, and mechanical stability. Polymeric membranes are favored for their ease of fabrication and their low cost [21], however, their disadvantages are that the polymers most commonly used, namely polysulfone (PSf) and polyethersulfone (PES), are hydrophobic, which can lead to reduced flux and increased fouling. Polymeric membranes also have an inherent tradeoff between flux and rejection, and they have a much lower selective rejection than inorganic membranes such as those made of ceramic, glass, carbon, or zeolites. Furthermore, recently there have been several novel approaches in membrane technology in order to create reactive membranes, including membranes that are antimicrobial, conductive and catalytic. However, they have the major advantage of costing one to three orders of magnitude less than these membranes [40]. Surface pore size, cross-section morphology, skin layer thickness, and hydrophilicity contribute to a membrane's permeability [41] and rejection properties, and in nanocomposite mixed matrix membranes (MMMs), surface modification with nano-sized particles is used to alter these membrane properties. Membrane characteristics such as thermal, chemical, and mechanical stability can also be improved.

Plasma treatment is a method of modifying ultra thin material's surfaces without changing the bulk physical or chemical properties which involves intake of less chemical reagent for the modification [42]. This method of surface modification is easy to control, relatively cheaper and scalable as the modifications are repetitious.

2.1 Different type of nanomaterials used in membrane fabrication

The incorporation of different types of nanoparticles in nanocomposite membranes with various increments in membrane performance will be discussed in this section. Membranes with integrated metal oxide nanoparticles can have increased water diffusion due to the nanoparticles inherent hydrophilicity. Unfortunately, uniform dispersion can be a difficult task because of their very high surface energy and a tendency to agglomerate, which can lead to inhomogeneities in the membrane and inconsistencies in gathered data [43]. Metal oxide nanoparticles have also been extensively used as coating for ceramic membranes in hybrid ozonation-filtration processes [14, 18]. Byun et al. compared the effectiveness of Mn, Ti, and Fe oxide, and determined that the membranes coated with Mn oxide had superior flux recovery and the greatest reduction in total organic carbon (TOC) [14].

The nanoparticle most extensively studied in water treatment membranes is titanium oxide (TiO_2). TiO_2 is super-hydrophilic, anti-bacterial, and has photo catalytic properties. The organic-inorganic composite membranes made with TiO_2 have been shown to have superior permeability, hydrophilicity, mechanical stability, and anti-fouling properties when compared to their purely polymeric counterparts [44]. It is also semi-conductive and often used as a coating on ceramic membranes because of its ability to prevent the growth of biofilm [45, 46]. Membranes with integrated nano-TiO_2 typically use its photo catalytic properties to produce hydroxyl radicals which would oxidize organic materials and prevent membrane fouling [47]. The exact mechanism by which TiO_2 kills bacteria was reported on by Sunada et al [6]. Cao et al. found that the size of TiO_2 size affects the structure and performance of a PVDF/TiO_2 membrane. They found that the antifouling abilities of a nanocomposite membrane with 10 nm TiO_2 particles were remarkably better than a membrane with 28 nm TiO_2 particles [48].

A very popular category of nanoparticle that is often used in membranes is carbon-based nanomaterials, such as carbon nanotubes, graphene, and fullerenes. Carbon nanotubes are the most studied type of carbon nanomaterial, though much of the research that has been done so far on water filtration using carbon nanotubes has been done using coated filters rather than nanocomposite membranes. However, the future of membranes with carbon nanotubes is very bright, as their very large surface area to volume ratio makes them highly antimicrobial, and they have an added advantage of being conductive [49, 50], which allows them to be used in electrochemical filtration systems [15, 16, 51]. There are two types of carbon nanotubes: single-walled nanotubes and multi-walled nanotubes. Multi-walled nanotubes are more commonly used in membranes because they are less expensive and have large surface area. Theoretical results suggest that membranes consisting of vertically aligned carbon nanotubes are very promising for water filtration membranes. Also simulations have suggested that flow through carbon nanotubes should be nearly frictionless. However, the challenges of fabricating such a membrane are still great and have yet to be overcome [47]. Recently, the use of functionalized carbon nanotubes has gained interest as the functional groups improve the solubility, dispersion and optical properties [52].

Another carbon-based nanomaterial commonly used is graphene. Graphene is very inexpensive and has higher chemical stability, strong hydrophilicity, adsorption capabilities, and is photocatalytic. It is generally coated onto membranes using the layer-by-layer technique[53]. It can also enhance the conductivity of polymeric sheets, especially when added with a conductive polymer, such as PANI. [54] Graphene oxide nanosheets, which are sheets of single-atom-thick graphene that have been modified to contain carboxyl, hydroxyl, and epoxide functional groups have exceptional potential in the field of membrane technology [53].

Interestingly, aluminum oxide is one of the lesser studied nanoparticles, surprising due to its superior performance when compared to TiO_2 and ZrO_2 for hydrophilicity, porosity, compaction grade, and flux. However, it does not possess the photo catalytic properties of TiO_2, so may be less versatile. Most of the research that has been done on alumina and alumoxane nanoparticles for membrane technology has been with ceramic membranes [55, 56], as well, there have been a few notable studies regarding polymeric/aluminum oxide nanocomposite membranes. Yu et al. reported in 2011 on a nano-sized Al_2O_3/PVDF membrane that had tripled water flux when compared to the control, while almost no loss of rejection capabilities [57]. Yan et al. have published three successive papers [13, 58, 59] about phase inversion-prepared Al_2O_3/PVDF nanocomposite membranes. The membranes had improved hydrophilicity and anti-fouling properties while the porosity, rejection, and the molecular weight cut-off (MWCO) were not significantly affected [57]. The rejection of organic contaminants was also improved once a steady state was reached [13].

Iron oxide nanoparticles have been shown by Raciny et al. to improve the Cu(II) rejection capabilities of a membrane. Iron oxide nanoparticles have also been used in several reactive membranes due to their interesting magnetic and electrical properties [60, 61].

Zinc oxide is hydrophilic, antibacterial [7], UV resistant, a semiconductor [62], and has a high specific surface area [62, 63]. PVDF/ZnO [64] , PSf/ZnO [63] and PES/ZnO [62] nanocomposite membranes have been created that exhibited highly improved hydrophilicity and permeability. Balta et al. [62] have suggested that zinc oxide is an alternative to TiO_2, as it is considerably cheaper and shows similar improvement to nanocomposite TiO_2 membranes in terms of hydrophilicity and antifouling at a much lower nanoparticle concentration.

Silver is another commonly used nanoparticle for nanocomposite membranes: silver nanoparticles are widely known to be antimicrobial, and there are commercial home water systems currently available which use membranes or filters coated with silver nanoparticles, and these are reported to remove 99.99% of pathogens [8]. They have also been shown recently to improve hydrophilicity in polymeric membranes [65] and change the porous structure of membranes [66]. However, there are considerable problems with the leaching of silver nanoparticles into the membrane's effluent. It's been shown by Basri et al. that the leaching of silver can be lessened by more even dispersion of silver nanoparticles, which can be accomplished by adding polyvinylpyrrolidone (PVP) and 2, 4, 6-triaminopyrimidine (TAP) to the casting solution [67]. Mollahosseini et al. showed that smaller silver nanoparticles led to membranes with higher antibacterial activity [66].

Clay nanoparticles have occasionally been used in mixed matrix membranes because they are naturally abundant and inexpensive [68]. It has been reported that they change the internal pore structure of a membrane, creating long, finger-like pores, increase hydrophilicity, increase thermal stability, and decrease fouling [68, 69].

Zeolites change the porous structure of the membrane [70], but are more commonly incorporated into membranes for gas separation [71, 72]. However, the super-hydrophilicity of ZnO [73] can lead to ultra filtration membranes with improved permeability and rejection [70, 73, 74].

Of the many types of commercially available nanoparticles, only the few mentioned above have been extensively studied for use in membrane technology for water treatment. However, there have been several studies on the lesser used nanoparticles that show great potential. For example, Dong et al. reported that $Mg(OH)_2$ nanoparticles improve the removal *E. coli* removal [9]. Davies et al. reported that magnesium oxide nanoparticles (MnO) are effective for use in ceramic ozonation-filtration membranes [14], and acrylic acid nanoparticles were used by Himstedt et al. to create novel pH-responsive membranes [75]. Many composite nanomaterials have also been studied: Vatanpour et al. reported on an anti-fouling PES membrane with TiO_2-coated MWNTS [76].

Nanoparticles are often blended with one another or functionalized to give them more desirable properties. Specifically, functionalization of nanoparticles allows for homogeneous dispersion and cross-linking with polymers. MWNTs, which are naturally hydrophobic, can be acid-oxidized to make them more hydrophilic, which can improve dispersion in the casting solution as well as the final membrane's hydrophilicity [77]. Razmjou et al. demonstrated a considerable improvement in fouling behavior when they compared PES/non-functionalized TiO_2 to PES/functionalized TiO_2 nanocomposite membranes [78]. Composite nanomaterials such as TiO_2-coated MWNTs for fouling reduction [76] and PANi-coated iron oxide nanoparticles for the removal of toxic metal ions [79] have been explored.

2.2 Preparation and Characteristics of Nanocomposite Ultra filtration Membranes

2.2.1 Mixed matrix membrane

Most polymeric membranes are created by phase separation by the Loeb-Souririjan process. In this process, a polymer solution (known as the casting solution) is spread onto a support layer and subsequently dipped into a non-solvent bath (usually of purified water, though it has been shown by Oh et al. that the non-solvent used can affect the membrane's pore structure [80]). The solvent most commonly used in this process is N-methyl-2-pyrrolidinone(NMP) [81]. A rapid exchange between solvent and non-solvent takes place, and consequently a solid membrane is formed. The resulting membrane is asymmetric and can usually be classified as a microfiltration (MF), ultra filtration (UF), nanofiltration (NF), or reverse osmosis (RO) membrane [5]. For MF and UF membranes, an extremely thin, highly microporous, active layer is formed on a thicker microporous support layer with larger pores. In ultra filtration membranes formed by this process, the support layer is more open and often has finger-like pore structures that stretch from just below the active layer to the underside of the membrane.

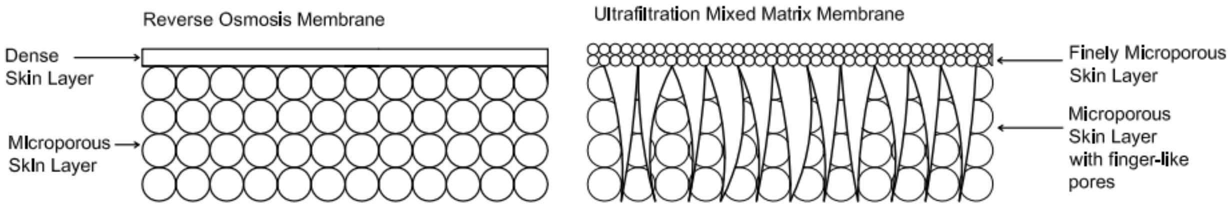

Figure 2.1: Schematic representation of RO and UF membrane

Zimmerman et al. [82] first proposed a composite polymeric/zeolite mixed matrix membrane for gas separation and their theories have since been adapted to create MMMs for water treatment. A modifying chemical that acts as a pore-forming agent [81] is added to the casting solution, and is subsequently incorporated into the polymer matrix, thus justifying the name ‘Mixed Matrix Membrane.’ The casting solution additives are usually derived empirically, and many manufacturers will not reveal their ‘recipe’, for membrane casting has become a carefully determined art. The additives in the past have usually been bulk-sized, however it has been determined more recently that when particles of nano-dimensions are added, the benefits to a membrane’s hydrophilicity, permeability, and anti-fouling characteristics can be much greater. As well, the addition of nanoparticles can change the membrane’s internal pore structure, often enlarging the finger-like voids beneath the active layer [48, 68, 83]. Generally, the polymer concentrations in the casting solution are in the range of 15 – 20 wt.% [5]; the nanoparticle concentrations typically range from 1 – 7 wt.%. However, there have been several cases where ultralow nanoparticle concentrations (as low as 0.01% [73]) have been shown to improve membrane features [62, 73, 76, 77, 84]. Larger quantities of nanomaterials are often found to create unsuccessful membranes because of the agglomeration and sedimentation of nanomaterials [48, 63, 69, 73].

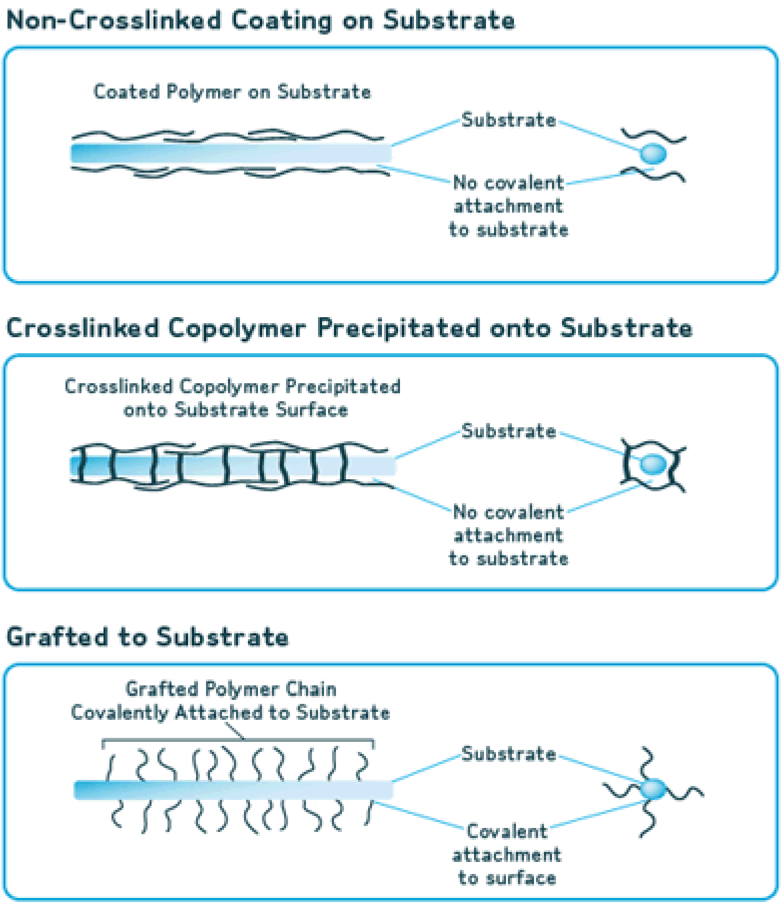

Figure 2.2: Schematic representation showing different types of membrane modification [85]

Nanomaterials can be immobilized in the polymer matrix in one of two ways: either with [85] or without cross-linking. Either of these can occur when nanoparticles are added to the casting solution, but cross-linking can only occur when the nanoparticles have first been functionalized by coating with organic coatings through physical and/or chemical means [78], and/or a 'cross-linker' is added. For example, Wu et al. added triethanolamine (TEOA) to the casting solution in a brominated polyphenylene oxide (BPPO)/MWNT membrane, and the TEOA cross-linked with the MWNTs and the polymer [85]. When no cross-linking occurs, the nanoparticles are simply 'entrapped' in the polymer matrix [47, 86, 87]. It is desirable that the nanomaterials are cross-linked into the matrix because once formed, cross-links are extremely difficult to break. In comparison with covalently bonded and entrapped nanomaterials, there is a far smaller risk of nanomaterials leaching into the effluent and posing environmental hazards.

There are several challenges that exist in the fabrication of mixed matrix membranes. First, due to the high surface energy and strong intra-particle interaction of nanoparticles [88], it is difficult to attain homogeneous nanoparticle dispersion using conventional methods [78] in the casting solution, and thus in the polymer matrix. Additionally, some of the nanomaterials used are hydrophobic and tend to agglomerate in water. Uneven dispersion in the casting solution can also lead to a reduction in antifouling abilities, because the rougher membrane surface that is created favors the attachment of foulants [78]. Another challenge is that the inherent trade-off between permeability and rejection still exists to an extent (though far less than with purely polymeric membranes), and often the rejection capabilities of a membrane are slightly compromised when nanoparticles are added and permeability increases. It should be noted that these two complications can be directly related to one another – uneven dispersion can lead to uneven pores which decrease the membrane's rejection. These problems can sometimes be alleviated by the functionalization of the nanomaterials, or by the addition of another additive in the casting solution [67, 68].

2.2.2 Surface modification of membrane by plasma treatment

Plasma treatment is a reactive surface modification technique where positive and negative ions, electrons, radicals react and collide with the presence of electric potential. Plasma contains these highly excited species that can etch and alter the surface properties of the plasma induced substrate. The surface after plasma treatment attains properties as surface cross linking [89], functionalization [90], surface grafting [91] and long time plasma treatment can lead to surface degradation [92]. Plasma treatment can penetrate to first few molecular layers of the substrate that can cause physical or chemical modification of the surface. The extent of plasma induced modification is dependent of some parameters as precursor gas type, applied radiofrequency (RF) power, system pressure, distance between the plasma source and substrate surface and most importantly treatment time [93]. Usually plasma treatment is done by a wide variety of non-polymerizable gases as Ar, He, N_2, O_2, CO_2, H_2O etc., while the treatment by using the polymerizable gases as vinyl containing monomer (allyl alcohol, allayloamine and acrylic acid) is referred as plasma polymerization [94].

Polysulfone membranes are widely used for microfiltration and ultrafiltration membrane application due to its high mechanical stability and resistance to harsh thermal and chemical conditions. Though polysulfone membrane is hydrophobic in nature, there are investigations that reports improvement on hydrophilicity can be done by chemical means [95]. Also plasma treatment of polysulfone membranes without any noticeable degradation is very promising for modification of hydrophilic membrane [96, 97]. The hydrophilicity is increased with oxygen containing gas (O_2, CO_2 and H_2O) induced plasma through generation of hydrophilic functional groups as hydroxyl, carboxyl and carbonyl groups that are rich in atomic oxygen [96-98].

The wettabilility measured by the contact angle after plasma treatment of polysulfone membrane shows improvement with the increase in plasma treatment time [96]. The change in pore size of the membrane surface after the plasma induction is different for different plasma gases as well as membrane materials. One study on polyethersulfone(PES) membrane used argon plasma and found no visible change on pore size after plasma treatment [99]. Another study of argon plasma on polyvinyldenefluoride (PVDF) membrane shows a subsequent increase in pore size with the increase in treatment time [100].

The permeability of plasma treated membrane also shows variable result with varying plasma parameters (i.e. applied pressure, flow rate, precursor gas, exposure time) and highly depends on membrane material. The argon plasma treatment of PVDF membrane shows an increase in permeability with increasing plasma treatment time form 0 to 120s [100] whereas the CO_2 plasma on polysulfone membrane shows decrease in permeability till 2 minute of exposure time and then it shows increase in permeability after 2 minute plasma [97]. This permeability reduction behavior of polysulfone membrane was further explained by the deposition of treated membrane material into the pore of the membrane in the early stage of treatment (less than 2 min) and then longer treatment time resulted in pore enlargement and water flux(200% increase after 10min plasma) due to the progressive ablation.

The concerned limitation of plasma treatment is the instable nature of the plasma induced surface which limits their long term application. The most accepted hypothesis behind this fact is that the polar functional groups generated by plasma treatment tend to reorient from the topmost layer towards the bulk that is explained as ‘aging’ effect or ‘hydrophobic recovery’ [101]. As the plasma treatment not only generates polar groups but also increase the surface roughness, which also contributes to the surface hydrophilicity. The aging effect occurs due to the random oxidation of the polar groups when exposed to the ambient atmosphere which can be influenced by the external contamination. Longer time plasma is more prone to aging effect as it shows approximately 50% loss of oxygen content while shorter time plasma shows negligible effect [102]. Studies of H_2O plasma treatment on polysulfone membrane shows 100% wettability even after storage in ambient air for 16 month [98].

2.3 Vacuum filtration assisted Layer by layer (LBL) Self Assembly

Layer by layer method has been used widely for last two decades for fabricating composite films for various applications. This technique was developed by Iler in 1966 where he explained alternate negative and positive layers can be deposited into glass like structure which has highly controlled thickness [103]. Although it was pioneered by Iler but the importance of this technology was not realized until Decher and coworkers redeveloped the LBL strategy in early 1990s [103]. As mentioned earlier, LBL is a versatile and elegant method of fabricating ultrathin films depending on the required functionalities of the film. The elementary units of LBL self assembly can be comprised of a variety of material including colloidal particles [104], synthetic polymers [105], block co polymers [106], polymeric microgels [107], biomacromolecules [108], nanocrystals [109], carbon nanomaterials [109] etc. The layer by layer is galvanized by certain interaction forces as electrostatic interactions, coordination bonds [110], hydrogen-bonds [111], halogen-bonds [112], charge-transfer interactions [113], biospecific interactions [114], guest–host interactions [115], cation-dipole interactions [116], and the combined interaction of the above forces. The conventional layer by layer techniques offered so far are dip, spin and spray coating as shown in the Figure 2.3.

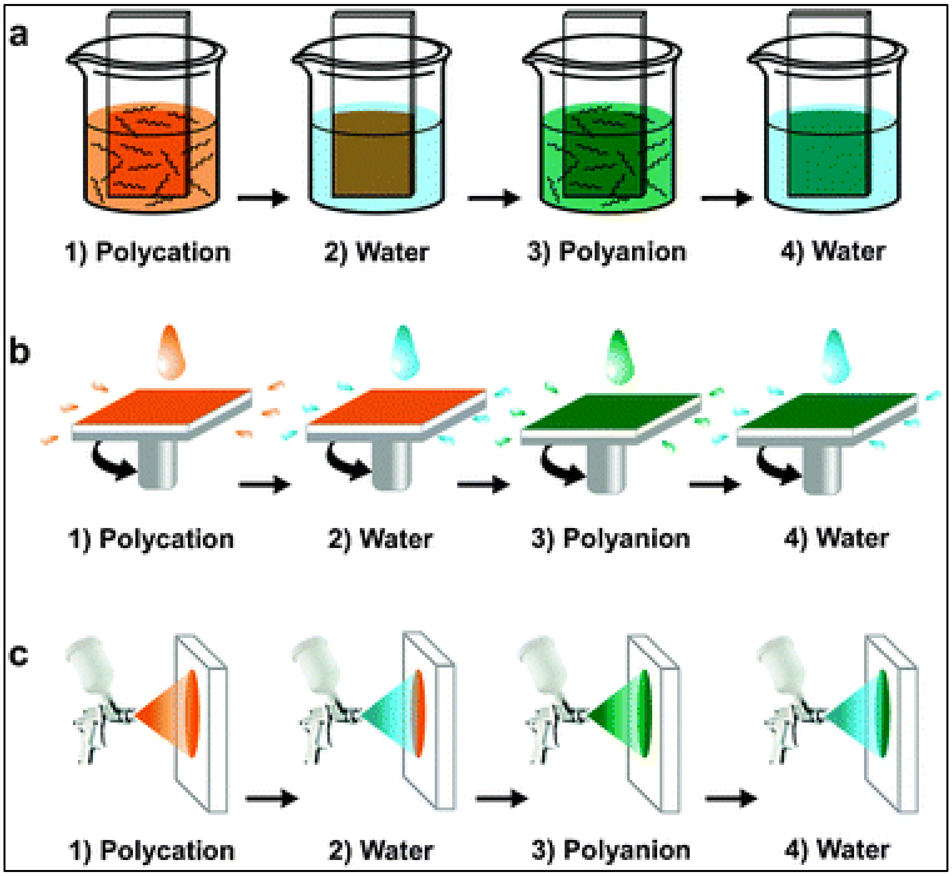

Figure 2.3: Schematic image of Layer by layer self assembly fabrication technique (a) Dip assisted layer by layer, (b) Spin assisted layer by layer and (c) spray assisted layer by layer [117]

Present study offers a novel approach of vacuum filtration assisted layer by layer self assembly for development of a conductive membrane surface. This technique of developing ultrathin film is also called as vacuum assisted self assembly (VASA). VASA are mostly used for manufacturing mechanically stable free standing films of polyelectrolytes or nanomaterials. But in this method the proposed material has to be of high aspect ratio and also should have high dispersibility in the solvent to generate stable dispersion. These requirements limit the choice of materials as in most cases the fibrous material fits in this criteria. The carbon nanotubes are one of the ideal choices for this VASA technique as it has high aspect ratio and can prepare stable dispersions with a wide range of solvents [118]. The films prepared by VASA method can be controlled by the sonication time of the solution, solution volume and the degree of the vacuum[119]. Several work on development of self assembly of cellulose nanocrystal as well as cellulose nanocrystal/ grapheme oxide hybrid films were successfully used the vacuum filtration [119, 120]. These studies present the first attempt for creating free standing, crack free and iridescent films using the VASA by simply controlling dispersibility in aqueous solution. In another study, Compton, Putz, Brinson and Nguyen [121] developed composite graphene oxide/polymer laminate sheets through the VASA method. In another study Liu, Aksay, Choi, Kou, Nie, Wang and Yang [122] successfully used graphene/metal oxide multilayered nanocomposites to generate self assembly for electrochemical or energy storing devices. As carbon nanomaterials show high aspect ratio, huge specific surface area and electrical conductivity, they are widely used for electrochemical or energy storage devices. Although there is several studies of using VASA method for self assembly, emphasis was given more on single layered nanocomposite film rather than layer by layer constructed film.

The LBL technique is very well known for its green chemistry as it requires the water soluble material thus avoiding the use of chemicals for preparing mechanically stable films. Hyder et al. reported vacuum filtration assisted layer by layer technique of MWNT-polyaniline (PANi) nanocomposite free standing electrode development for energy storage [123]. To the best of our knowledge, this study is the first to report vacuum filtration assisted layer by layer self assembly of functionalized MWNT (MWNT-NH_2 and MWNT-COOH) on a functionalized polysulfone support membrane to modify a conductive surface of an ultra filtration membrane. The purpose of developing the conductive surface is to provide electrochemistry driven antifouling property and organic matter degradation properties of the membrane.

2.4 Highly Successful Nanocomposite Membranes for Ultrafiltration

2.4.1 Non-Reactive Membranes

Non-reactive nanocomposite membranes can be defined as a membrane in which the property is enhanced by nanoparticles only through physicals means, namely by hydrophilic enhancements, physical adsorption, changes in membrane morphology, and creation of preferential flow paths by way of molecular sieves.

Nanoparticles are most often used in non-reactive membranes to enhance membrane hydrophilicity. This improves multiple membrane functions, leading to reduced fouling [64, 124, 125] and enhanced permeability. Inorganic and organic fouling can be reduced with increased hydrophilicity because the most significant attractive force that causes foulant deposition is the hydrophobic force [126], and a hydrophilic membrane surface will attract water molecules rather than foulants. Most non-reactive nanocomposite membranes have been created for antifouling purposes [9, 57, 63, 64, 69, 70]. While complete avoidance of fouling is impossible, membranes with incorporated hydrophilic nanoparticles often have fouling that is mostly reversible, and flux can be recovered when the membrane is cleaned. This is usually due to the increased hydrophilicity that prevents fouling adhesion, and can also be due to changes in roughness [57] or repulsive electrostatic forces [70]. In some cases, flux can be recovered almost completely. This was demonstrated by Liang et al., whose ZnO/PVDF membrane recovered almost 100% of its original flux (as opposed to a 78% recovery with a neat PVDF membrane) when 6.7 wt.% hydrophilic ZnO was added to the casting solution [64].

Contrary to the hydrophilic membranes mentioned above, there has been research that suggests that extremely hydrophobic, low surface energy membrane surfaces can also mitigate irreversible fouling. This is especially true in cross-flow systems: on a low surface energy membrane, the Van der Waals force that binds foulants to the membrane surface is very weak, and the shear force created by the transverse flow can potentially wash away these foulants [127].

Membrane surfaces can physically adsorb undesirable compounds, leading to their removal, and this effect can be enhanced by nanomaterials due to their extremely high surface area when compared to bulk materials. Mierzwa et al. and Ghaemi et al. have reported on the effect of the addition of clay nanomaterials into polymeric membranes. The modified membranes demonstrated enhanced removal of organic compounds, and it is hypothesized that adsorption to the internal surface area is the mechanism by which this occurs. It's important to mention that more often than not, the prevention of adsorption is more desirable because adsorption can be synonymous with fouling, especially in terms of biofilm formation. Thus, most of the hydrophilic membranes mentioned above aim to limit adsorption.

General membrane morphology can be altered upon the addition of nanomaterials which can cause a variety of changes: the alteration of pore size and shape can lead to increased permeability, selectivity, or enhanced mechanical, thermal, or chemical strength. Dong et al. reported that adding $Mg(OH)_2$ to PVDF membranes (with poly ethylene glycol as an additive in the casting solution) had the effect of creating a higher number of pores in the membrane surface and almost eliminating the larger pores. They have suggested that the increased number of pores was due to the hydrophilicity of the casting solution and the increased uniformity was due to the increased viscosity of the casting solution. Additionally, more macrovoids could be seen in the membrane cross-section (also attributed to casting solution hydrophilicity). Combined, these factors lead to a membrane with improved permeability and anti-fouling propensity [9]. Clay and zeolite nanoparticles, when added to the casting solution, result in a membrane with long, finger-like voids [68, 70]. It is not clear whether these voids are desirable for fouling characteristics, as Mierzwa et al. found in a recent study; however, the large spaces in the membrane result in a less dense membrane and therefore improved permeability [68].

Changed membrane morphology upon addition of nanomaterials can also improve mechanical strength. This is especially important in reverse osmosis and other high pressure systems, where membranes are subjected to harsh conditions for extended periods of time, and the resulting membrane compaction can lead to irreversible fouling.

One extremely important factor in successful membrane fabrication is nanoparticle concentration. Generally, membrane characteristics will improve with increasing nanomaterial concentration up to an optimal concentration, beyond which performance will diminish. The optimal nanomaterial concentration is entirely dependent on the materials involved: optimal concentrations have been found to range anywhere between 0.1 wt% [73, 79] and 15 wt% [70] and higher. Excessive nanomaterial concentration often causes agglomeration in the casting solution, resulting in a higher frequency of membrane defects, causing more sparse pores, larger pores, low flux, and poor selectivity [73]. Too-high concentrations can also weaken the mechanical stability of the membrane [63] and can result in a more compacted membrane structure which reduces permeability [64].

2.4.2 Reactive Membranes

2.4.2.1 Antimicrobial Membranes

Biofouling of membranes can be reduced by antimicrobial membranes, as the inactivation of bacteria and viruses prevents the growth of biofilm on membrane surfaces. For many years, chlorine has been the most popular antimicrobial product used, however, many pathogens show resistance to chlorine and chlorine produces disinfection byproducts (DBP) that are toxic to humans [128]. Nanoparticles such as CNTs, metal oxides, and silver have been shown to create antimicrobial membranes when incorporated into both polymeric and inorganic membranes. Antimicrobial nanomaterials can be naturally occuring antimicrobial substances (such as silver), metal oxide nanoparticles (MNPs) or novel engineered nanoparticles (ENPs) (such as ZnO, TiO_2).

The mechanism of microbial inactivation by nanomaterial varies greatly depending on the materials involved: interaction between microbial cells and antimicrobial nanomaterials can lead to damage and inactivation of the microbes. The antimicrobial nanomaterials can inactivate microbes by interrupting/disrupting cell membranes (for example, partitioning transmembrane electron transfer), by oxidizing cell components, or by producing a secondary product (such as reactive oxygen species or dissolved heavy metal ions) [8]. As well, photocatalytic production of reactive oxygen species by some nanoparticles inhibits antimicrobial activity; there will be a detailed discussion of this mechanism shortly.

Silver (Ag) ions and Ag-based compounds are well-known for their microbial toxicity at both the bulk and nano-scale; however, the exact mechanism has not yet been definitively determined. Already, commercial home water systems currently available which use membranes or filters coated with silver nanoparticles; these systems are reported to remove 99.99% of pathogens [8]. Several mechanisms for silver's antimicrobial activity have been hypothesized. Li et al. found evidence indicating that silver nanoparticles inhibit bacterial growth and thus kill the cells by destroying bacterial membranous structure. Two other possible mechanisms that explain the antimicrobial activity of silver nanoparticles (nAg) are (i) the penetration of nAg ions inside the bacterial cell leading to DNA damage and (ii) the release of antimicrobial Ag^+ ions by dissolution of nAg particles [8, 129]. While there are many advantages of incorporating Ag nanoparticles into membranes, at this time, researchers doubt its potential for long-term application for commercial purposes due to the unavoidable issue of leaching. Leaching can happen due to physical damage or improper fabrication technique, but it also occurs due to the natural dissolution of Ag^+ ions which is necessary bacterial inactivation. This poses multiple problems: Most importantly, the natural dissolution of silver causes membranes to lose their functionality. As well, health problems can be caused by excessive levels of silver ions in drinking water [130]. It's been shown by Basri et al. that the leaching of silver can be lessened by more even dispersion of silver nanoparticles, which can be accomplished by adding polyvinylpyrrolidone (PVP) and 2, 4, 6-triaminopyrimidine (TAP) to the casting solution [67]. Mollahosseini et al. showed that smaller silver nanoparticles led to membranes with higher antibacterial activity [66].

Carbon nanomaterials such as fullerenes, graphene oxide, and carbon nanotubes also have excellent potential for water treatment membrane technology because of their antimicrobial properties. Fullerenes are currently mostly recognized for their use in biomedical applications while the other carbon nanomaterials mentioned above have proven their efficacy for membrane improvement. Multi-walled carbon nanotubes (MWNTs) generally exhibit less antimicrobial activity than single-walled carbon nanotubes because of their smaller diameters [131]. However, SWNTs appear to perform with reduced antimicrobial capacity when embedded within a polymeric membrane: a study by Zhao et al. suggests that this reduction is due to the polymer wrapping [132]. Furthermore, Kang et al. [133] have suggested that the size of carbon nanotubes (CNTs) is a key factor governing their antibacterial effects. This suggests that the main CNT-cytotoxicity mechanism is the cell membrane damage by direct contact with CNTs. Evidence also suggests that generation of oxidative stress can trigger CNTs' toxicity to microorganisms [133]. Hu et al. have confirmed the antimicrobial activities of graphene oxide and reduced graphene oxide [134], though to the best of our knowledge, these materials have not been used in any membranes specifically for antimicrobial uses. However, they have, very recently, been used in polymeric membranes to dramatically enhance permeability, hydrophilicity, anti-fouling, selectivity, and mechanical strength [135, 136].

As well, naturally occuring antimicrobial peptides and chitosans have been recently engineered into nanoparticles [137, 138]. Studies showed that nano-scale chitosan and peptides exhibit antimicrobial effects towards bacteria, viruses, and fungi [139, 140]. A recent study by Cooper et al. reported on the development of chitosan-polycaprolactone (PCL) nanofibrous membranes to utilise the natural antimicrobial property of chitosan. The modified membrane was prepared by electro-spinning and consisted of chitosan- PCL fibres of 200-400nm diameter [141]. It demonstrated improved bacterial adhesion when compared to the unmodified membranes, greatly improved water flux and 100% removal of 300nm particulate with 25 wt. % chitosan-

PCL membrane [141].

Zero valent iron(Fe^0) nanoparticles have strong bactericidal effect under de-aerated conditions and were found to be effective for the inactivation of a wide range of bacteria [142, 143]. Physical disruption of the cell membranes and the creation of oxidative stress by producing reactive oxygen species are believed to be the mechanisms of antibacterial activity and the Fe^0 nanoparticles show higher antibacterial activity when compared to Ag nanoparticles [142]. Fe^0 nanoparticles are mostly used in permeable reactive barrier for groundwater purification but could potentially replace other nanomaterials used in water filtration membranes due to its lower toxicity to human and its cost effectiveness.

It is important to realize that biofilm formation is a complex problem and there are several factors which control a membrane's anti-biofouling activity: specifically, a membrane's hydrophilicity, its surface charge, and its antimicrobial activity [144]. Liu et al. found that membranes that prevented the adhesion of microbes to the membrane surface were better for preventing fouling than membranes with only anti-bacterial activity, and that the membranes that were most effective in preventing biofouling had were both anti-adhesive and anti-microbial. They also found that membrane hydrophilicity was a worse predictor of bacterial adhesion than was the membrane surface charge. A negative surface charge was most effective for preventing the adhesion of microbial foulants, and they ascertain that hydrophilicity should not be used as the sole factor in predicting a membrane's anti-fouling characteristics, as it so often is [144].

2.4.2.2 Photocatalytic Membranes

The introduction of photo catalytic nanoparticles into membranes can greatly reduce organic scaling [145, 146] and biofouling [45, 147-151], leading to increased long-term water permeability of a membrane. It can also remove NOM from the water being treated, which is of particular importance in MF and UF filtration, which suffer from poor NOM removal due to the extremely small particle size of NOM[152]. Photocatalysis can be achieved with semiconducting materials, and has been described in detail by Likodimos et al [153]. Briefly, when semiconductors absorb a photon of energy greater than their own band gap energy, an electron-hole pair is created. This process needs to be activated by UV or sunlight. These unstable electron-hole pairs will either recombine or react with the surrounding media. Nano-sized photocatalysts are advantageous over bulk-sized materials because both the hole and the electron (as opposed to one or the other, as is the case bulk materials) are available for interaction [21]. The electrons released by the light source bind with oxygen to become superoxide radical anions. Then, the surface of the semiconductor is positively charged, and binds with electrons from the water molecules. A product of this reaction is hydroxyl radicals (-OH). These two compounds destruct materials by oxidation in the water such as organic compounds [151]. Photocatalytic semiconducting materials can also be antibacterial: reactive oxygen species (such as hydroxyl) can damage the cell wall or organism[21] and/or a lipid peroxidation reaction can occur, effectively inactivating cells [151]. The exact mechanism of photo catalytic bacterial inactivation on films was recently reported on by Pulgarin et al.[147]. Titanium oxide nanoparticles are most commonly used for photo catalytic membranes, but zinc oxide [154] and ferric oxide can also be used [21]. Both polymeric [148, 151, 155] and ceramic [45] substrates have been used for this purpose. Though polymeric membranes have all of the advantages discussed earlier, when used in a photo catalytic system, the inevitable long-term outcome is the degradation of the organic compounds in the polymeric membrane [21]. Both mixed matrix membranes and coated membranes have been used in photo catalytic systems [151].

Titanium oxide (TiO_2) is the most studied nanomaterial for its antifouling and biocidal functions as a photo catalytic semiconductor. TiO_2 demonstrates antimicrobial activity by producing reactive oxygen species (such as hydroxyl free radicals) and by forming peroxide under UV-A irradiation via oxidative and reductive pathways [149]. Recent studies have reported on the efficacy of nano-sized TiO_2 particles in killing viruses such as poliovirus 1, hepatitis B virus, herpes simplex virus, and MS2 bacteriophage [8]. Damodar et al. prepared a modified PVDF with 0-4 wt.% TiO_2 in the casting solution and found that the modified membranes had improved permeability, antibacterial properties, photo catalytic properties, and antifouling properties [148].

ZnO nanoparticles also inhibit bacterial growth during biofilm production due to the production of H_2O_2 during photocatalysis [156]. As well, Brayner et al. reported that biofilms became disorganized upon contact with ZnO nanoparticles [157]. Chen et al. reported that the addition of doped silver reduced the ionization energy of acceptors in ZnO, thus, Ag^+ ions could enhance the antimicrobial activity of ZnO. Bai et al. found in their recent research that the hierarchical N-doped ZnO "nut-like" nanostructured material can enhance the photo catalytic activity in comparison to commercial ZnO powder and thus demonstrate strong antibacterial ability under visible light irradiation. These points emphasize the great potential of ZnO nanostructured membranes for water purification [158].

Chae et al. found that carbon nanomaterials also have potential for use in photo catalytic membranes: when testing C_{60} fullerenes, SWNTs and MWNTs, they found that all three types of carbon nanomaterials enhanced degradation of 2-chlorophenol (2CP) (an organic compound), and that a smaller nanomaterial diameter was linked with more enhanced 2CP degradation [159].

Typically, photo catalytic nanoparticles are incorporated into membranes either by (i) the deposition of a coating through a dipping method, or (ii) by the entrapment of nanoparticles into a polymeric matrix through nanoparticle addition to the casting solution [151]. Usually, the bond between TiO_2 and substrate is formed by physical adsorption, electrostatic interaction, or hydrogen bond interaction [160]. None of these bonds are as strong as chemical bonds, so the membranes can have problems with leaching and loss of functionality. Lei et al. successfully created a membrane where the TiO_2 nanoparticles were chemically bonded into a PVA matrix by applying a heat treatment to the modified membrane [160]. PVA is inexpensive and has inherent chemical properties that allow it to form bonds well with TiO_2, making it the ideal polymer for this purpose. The modified membrane exhibited long-term functionality because of its cross-linking.

Photocatalysis in membranes presents some limitations not present in a photocatalysis slurry system. When the nanoparticles are immobilized on/in a membrane, the number of active catalyst sites are reduced, and mass transfer becomes more limited [161]. Thus, some researchers doubt the functionality of a photo catalytic membrane. However, a photo catalytic membrane presents the major advantage of being a one-step process, where further separation of photocatalyst and effluent is not required. Additionally, the fact that the process can be triggered by sunlight gives this one-step the unique opportunity to leave an extremely small environmental footprint, especially if a low pressure membrane system is used.

2.4.2.3 Membranes for Electrochemical Filtration

Electrochemicalfiltration systems can be compared to an electrolytic cell where filtration membranes mostly work as an anode. Specifically, the membrane surface must be conductive, as it have been found by research that a small current run through a filtration system can very dramatically reduce fouling. The reactions that makes the electrochemical filtration system work, are mainly dependent and usually occur in the membrane surface. If membrane nanomaterials and/or polymers are electrically conductive, then the membrane can be used as a electrochemical filtration cell. The chemical reactions can be driven by an externally applied voltage, as in electrolysis, or the voltage can originate from chemical reactions, as occurs in electrochemical filtration. Redox (oxidation-reduction) reactions are the most prominently occuring reactions in this type of filtration process which produce reactive oxygen species (ROS) and thus the microorganisms are believed to be killed or inactivated.

Obviously, carbon nanotubes as conductive nanomaterials were the first candidates for experimentation in the development of conductive membranes. Firstly, there was a idea of dispersing carbon nanotubes onto the support polymeric membrane [10-12]. Thus, the support membrane was expected to show more or less conductive properties due to the conductivity of the CNTs. In their first study, Vectis et al. determined that at very low potentials (2 and 3V) MWNT filters exhibited more than 75% bacterial and 99.6% viral inactivation [15]. In a follow-up study, Rahaman et al. reported complete(5.8 to 7.4 log) removal and significant inactivation of MS2 viral particles when 2 or 3V was applied to an electrochemical MWNT filter [16].

Recently, De Lannoy et al. developed a highly electrically conductive polymeric ultra filtration membrane composed of PVA crosslinked with carboxylated MWNT and succinic acid that showed an electrical resistivity as low as 2.8×10^{-4} Ω m, pure water flux of 1440 L/m^2 h at pressures of 550 kPa, and triple-point initial contact angles as low as 40° with high hysteresis [50].

2.4.2.4 Stimuli-Responsive Membranes

Stimuli-responsive membranes are designed to change their physicochemical properties in response to the change in temperature, pH, ionic strength, light, electric and magnetic fields, and chemical cues. Porous and non-porous stimuli-responsive membranes currently have a large number of applications as sensors, separation processes and drug delivery systems. These membranes are very important for the development of the functional membranes which can show reversible change in polarity or conformation and for these membranes stumuli responsive polymers are considered as the building blocks [162].

Generally, stimuli-responsive membranes can be prepared by casting a blend of stimuli-responsive polymers or by surface modification by grafting of the membranes. Also, molecular recognition gating membranes, which are able to open and close pores using volume phase transition and can recognise specific ions with its receptors, have been introduced in the stimuli-responsive membrane categories which is mainly composed of molecularly imprinted polymers(MIPs). The MIPs have had molecular memory introduced to them, thus it becomes a selective binder of template molecule which can change the mass transfer properties of the membrane [162]. Recently, Liu et al. presented a gating membrane with poly((*N*-isopropylacrylamide-*co*-acryloylamidobenzo-18-crown-6)(poly(NIPAM-*co*-$AAB_{18}C_6$)) copolymer chains as functional gates with a large number of crown ether units which were provided to detect Pb^{2+} ions and treat trace amounts of Pb^{2+} from wastewater [163].

2.5 Potential Risks associated with Nanocomposite Membranes

There are several remaining issues that impede us launching nanomaterials into usage in the environmental engineering industry. Long-term investigations and development stages have been undertaken in the fuel cell, battery, and biomedical fields, and this work has yet to be done with nanocomposite water treatment membranes. Stimuli-responsive nanocomposite materials are gaining popularity in biomedical applications which are operated in a controlled manner to assure minimum risk of exposure. As the nanomaterials used to serve this purpose are mostly engineered nanoparticles (ENPs) and show certain levels of toxicity, care should be taken in advance to determine the fate and transport of the nanoparticles.

Nanomaterials such as single-walled carbon nanotubes exhibit dermal toxicity due to increased oxidative stress on the skin of the exposed workers involved in the manufacture of the nanomaterials [164]. When SWNTs were tested on mice skin, Murray et al. found that free radical generation, oxidative stress, and inflammation were the main causes of dermal toxicity [165]. Long term exposure to MWNTs can also lead to irreversible oncogenic cancerous transformation of human bronchial epithelial cells and tumorigenicity [166].

Acid-functionalized carbon nanotubes have been found to be more toxic than the pristine CNTs when tested in vitro lung tumor cell [167]. The toxicity is also contingent on the size of the nanomaterials: a study by Liao et al. on graphene oxide suggests that the smaller GO shows higher hemolytic activity (abnormal breakdown of red blood cells) while the aggregated GO shows lowest hemolytic activity [168]. Coated nanoparticles can eliminate hemolytic activity: it was found that chitosan-coated GO can nearly eliminate hemolytic activity [168]. Despite the vast research that has been done on the beneficial antimicrobial effects of silver nanoparticles, research has shown that subcutaneous (skin layer beneath the dermis and epidermis) AgNP injections were found to affect the cells in the kidney, liver, spleen, lung tissue, heart tissue and endothelial cells of the blood-brain barrier due to the agglomeration of the NPs [169]. Also long term exposure to nAg can cause argyria, a blue–gray discoloration of the skin and other organs [99].

While the studies mentioned above tested the toxicity of nanomaterials individually, there has been little research on the toxicity of nanocomposite membranes. Ahmed et al. developed water filtration nitrocellulose membranes coated with a nanocomposite containing 97% (wt. %) of polyvinyl-***N***-carbazole (PVK) and 3% (wt. %) of SWNT and performed toxicity test against fibroblast cells (wound healing cells). The results depict non-toxic behavior of fibroblast cells when subjected to PVK:SWNT(97%:3%) -coated membranes as opposed to the toxic behavior of SWNT(3%) coated membranes [170].

Studies on the toxicity of nanomaterials demonstrate a certain level of toxic effects from micro level to higher level organisms. As the use of nanoparticles is increasing in various emerging fields of applications, the membranes that incorporate nanoparticles should pass the toxicity test. In water filtration, toxicity tests should be performed alongside other membrane characterization and usefulness tests. As well, studies regarding the release of nanomaterials from water treatment membranes and their route of exposure, fate, and transport have to be done in a standardized manner to avoid exaggeration due to varying methods and give us an accurate picture of the amount and danger of nanoparticles that could be released by these processes.

2.6 Technical Hurdles and Current Limitations

One of the largest technical hurdle in producing phase separation-produced mixed matrix membranes is the difficulty in the even dispersion of nanoparticles in a polymer matrix due to the tendency of nanoparticles to agglomerate[171]. This is most difficult with hydrophobic nanoparticles such as carbon nanotubes, where the Van der Waal's interaction will attract the carbon nanotubes to each other and cause them to be insoluble and, at worst, undispersable [21, 172]. Functionalization of carbon nanotubes can improve their dispersability, especially when the functionalizing polymer is identical or similar to the polymer matrix into which it is being mixed.

While solutions that do not have perfect dispersion of nanomaterials can still have functionality, they often have reduced mechanical properties [173]. Sonication is the method that is almost always used to disperse nanomaterials in mixed matrix membranes, and optimization of the sonication time and amplitude can improve the dispersion [173]. Additionally, it can be more difficult to disperse higher quantities of nanomaterials because of the increased tendency to agglomerate. Often, when mixed matrix membranes with different nanomaterial concentrations are created and tested in a study, improvements in hydrophilicity and fouling reduction will reach a maximum with one of the mid to higher-level concentrations, then decrease at the highest concentrations [64, 69, 70]. Uneven nanoparticle dispersion is thought to be a main reason behind this.

However, other fabrication routes for nanocomposite membranes also have flaws and limitations .For example, layer-by-layer deposition is becoming increasingly popular because of its high potential to give membranes functionality. However, the coating is usually achieved by dip-coating, which is a highly time consuming process. Briefly, an electrode (the substrate) must be alternately in cationic and anionic solutions, and be soaked in de-ionized water between steps. Each soaking takes between 30 and 60 seconds [29], and due to the extremely thin layer created by each soaking, this must be repeated many times. Even a scaled-up process would be highly time-consuming. Alternatives to the traditional dip-coating are spray-coating and spin-coating, which may be more useful for industrial purposes.

As discussed earlier, nano-coated ceramic membranes have potential for functionality because of their high chemical and mechanical strength. However, their biggest drawback is that they cannot easily be used in formations other than flat sheet membranes, such as hollow fiber membranes, which provide a much higher surface area to volume ratio, necessary in treatment plants which do not have unlimited space. Ceramic membranes can be formed in hollow fiber formations. However, ceramic membranes are usually coated, therefore it would be nearly impossible to coat something in the hollow fiber formation, or to shape a coated flat sheet membrane into a hollow fiber formation.

Another drawback of functionalized nanoparticles is the loss of functionalization with time, especially with silver and copper nanocomposite materials, where the degradation of silver is necessary for the membrane's functionalization [129, 174]. For these membranes to be useful in the long-term in real-world applications, a regeneration process would have to be devised.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1 Chemical Reagents and Membranes

Polysulfone membranes were purchased from SEPRO Membranes (PS20, thickness 165µm) and used as a support membrane for developing conductive membrane. *N*-Ethyl-*N*′-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC, assay ≥ 98%), MES monohydrate (BioXtra, assay ≥ 99% (T)) and *N*-Hydroxysuccinimide (NHS, 98%) were purchased from Sigma Aldridge, St. Louis, USA. Amine and carboxylic acid functionalized multiwalled carbon nanotubes (MWNT-NH_2 and MWNT-COOH) were purchased from Cheap Tubes (99% purity, 8-13 nm diameter and 3-30 µm length). Nonionic surfactant, triton X 100 was purchased from Sigma Aldridge, St. Louis, USA. Reagent grade hydrochloric acid, potassium hydroxide, methyl orange, sodium chloride, and sodium hydroxide were also purchased from Sigma Aldridge.

3.1.2 Glassware and Labware

All glassware (i.e., flasks, vials, bottles, etc.) was cleaned in the laboratory basin following a detergent wash, acetone wash, acid wash, and a minimum of three DI water rinses. The super deionized (DI) water was generated by using Milli-Q filtration setup from Millipore (Molsheim, France) and was used throughout the membrane modification steps.

3.1.3 Bacterial Cells and Nutrients

For antimicrobial tests *E. coli* (Top 10, pGEN-GFP, LVA) were collected from McGill University and LB Broth (Lauria-Botani. Difco^{TM}, Miller), agar (Microbiology grade) and ampicillin were purchased from Sigma Aldridge.

3.2 Methods

3.2.1 Substrate membrane cleaning and plasma treatment of membrane

The polysulfone membranes were cleaned with a solution prepared by mixing 0.5% nonionic surfactant triton X 100 in DI water. The membranes were soaked in the solution for 24 hours and then rinsed for several times with DI water. The clean membranes were air dried with an air knife for 15 min and then placed in a dessicator for 1 hour and prior to plasma treatment. The dry membranes were placed in a plasma chamber (PICO, Diener Electronic GmbH + Co. KG, Ebhausen, Germany), connected to O_2 gas cylinder. Prior to the activation of plasma generator the membranes were allowed to rest on the O_2 gas stream for 10 min in order to eliminate the impurities from the plasma chamber. The flow rate of O_2 gas was maintained to 20sccm which is a function of pressure and thus the pressure remained in a range of 0.8-1.0 mbar. The power used for plasma generation was 100 W and the membranes were treated for 30s, 60s, 90s, 120 and 180s to functionalize the surface with negatively charged functional groups (i.e., carboxyl, carbonyl or hydroxyl groups). After the plasma treatment the O_2 gas was allowed to flow through the plasma chamber for 30 min to avoid any reaction between the remaining free radicals and air [175]. Then the membranes were immediately stored under vacuum condition.

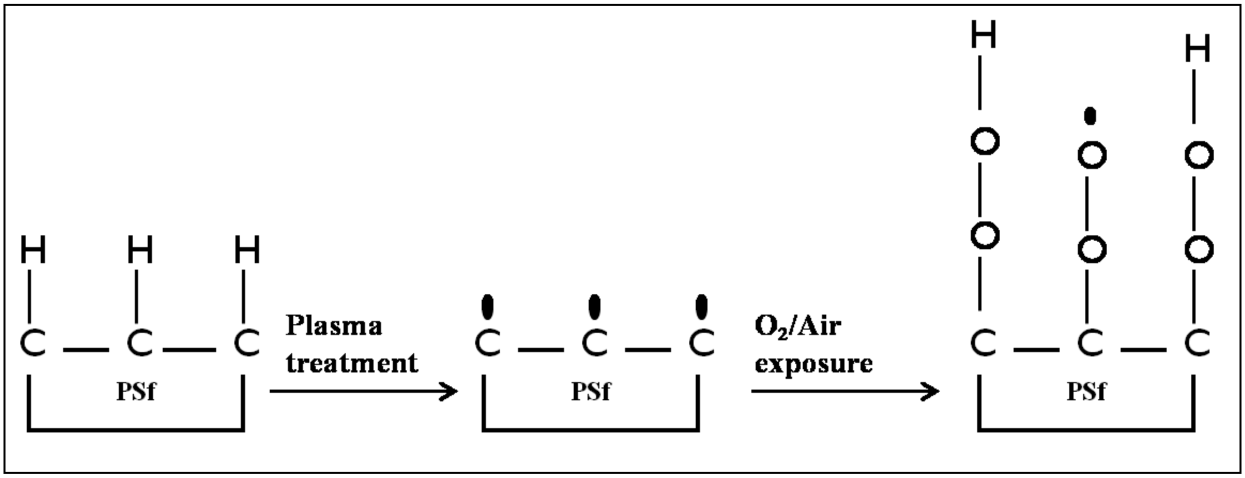

Figure 3.1: Polysulfone surface plasma treatment generates free radicals that eventually convert into negative charged functional groups upon exposure to O_2/air mixture

3.2.2 EDC/NHS cross-linking of the membrane functional groups

The polysulfone develops oxygen containing functional groups after the oxygen plasma treatment. For layer by layer membrane modification, charged surface plays a very important role to initiate the electrostatic interaction. Though the plasma treatment is very efficient for surface functionalization, the stability of these groups is time dependent. Thus EDC/NHS cross-linking was used in this experiment to create the amine reactive esters which facilitates the reaction between the carboxylic functional groups present on the membrane and the MWNT-NH_2. A recently reported protocol by Perreault et al. [176] was used in this study for EDC/NHS cross-linking on the surface of the membrane. The membranes were placed in glass petri dishes and taped with a waterproof tape leaving the active side exposed to air. The membranes were then exposed to a solution of 4 mM EDC, 10 mM NHS, 0.5 M NaCl in 10 mM MES buffer (adjusted pH of 5) for 1 hr. This procedure ensures the activation of amine reactive esters on negatively charged functional groups of the plasma treated polysulfone membranes. Finally, the membranes were rinsed twice with DI water to remove the excess EDC/NHS solution from the membrane.

3.2.3 MWNTs solution chemistry and pH adjustment

For dispersion, DI water is used as the background solution and the multi-walled carbon nanotubes (Positively charged MWNT-NH_2 and negatively charged MWNT-COOH) were added to prepare an electrolyte solution of concentration of 0.05 mg/mL. The suspensions of MWNT-NH_2 and MWNT-COOH were probe sonicated using a Branson 3510 ultrasonic cleaner at 50% amplitude for 3 hours to form stable dispersion. Prepared MWNT solutions were subjected to dialysis against DI water for 24 hours to remove any byproducts and residuals. Figure 3.2 represents the zeta potential of the MWNT-COOH and MWNT-NH_2 solutions with different pH range. During the experiment, MWNT-NH_2 and MWNT-COOH solutions were stable at around the pH range of 2 to 4 respectively, as in the other pH solutions, a concerned amount of aggregation was observed. The pH of the MWNT-NH_2 and MWNT-COOH solutions were adjusted to 2.5 and 3.5, respectively with the aid of 1M, 100mM and 10mM hydrochloric acid consecutively. The pH-adjusted solutions were sonicated for 1 hour prior to use in vacuum filtration assisted LBL assembly. During sonication an ice bath was used to avoid overheating of the solution.

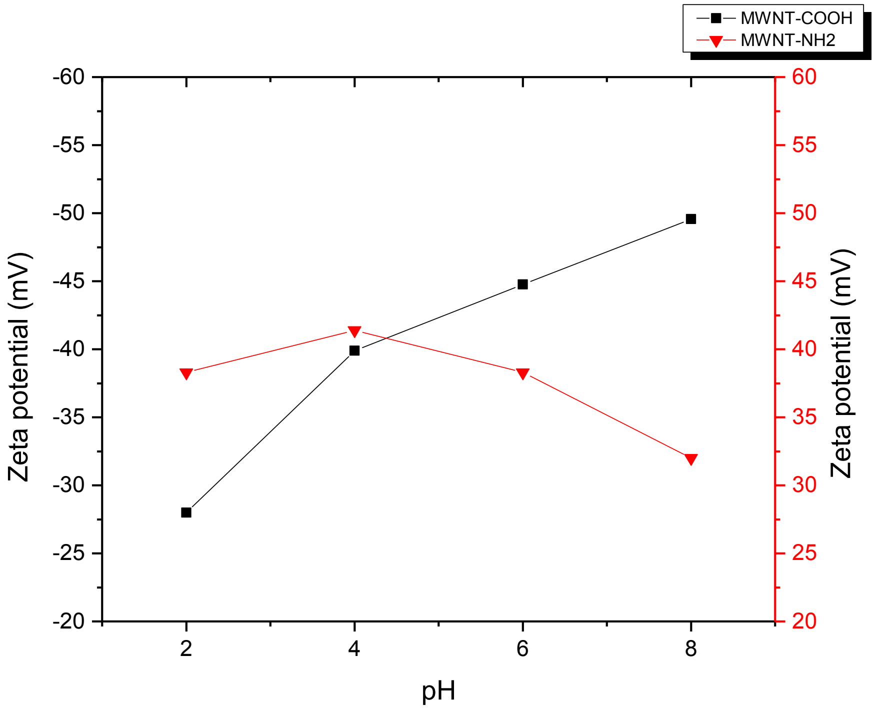

Figure 3.2: Zeta potential of MWNT-COOH and MWNT-NH_2 at different pH.

3.2.4 Vacuum-assisted LBL self-assembly of MWNT-NH_2 and MWNT-COOH

First, an acidic and positively charged MWNT (MWNT-NH_2, pH 2.5) solution was filtered through 47-mm diameter plasma treated polysulfone membrane by using a vacuum filtration apparatus. Due to the vacuum filtration the adsorption of MWNTs occurs by electrostatic interaction that is facilitated by transport of MWNT through convection force. The process continues with the incorporation of another layer of negatively charged MWNT (MWNT-COOH, pH 3.5) through solution filtration onto the membrane, already containing the positively charged MWNT layer. The different pH values of the solutions were chosen to ensure enough effective charge of the positively charged MWNT and negatively charged MWNT solution for electrostatic interaction. After depositing each layer of the positively charged MWNT/negatively charged MWNT, 5mL of DI water was filtered through the membrane to wash away any residual pH solutions. The modified membrane with a desired number of bilayers was finally washed twice with DI water to eliminate the effect of pH solutions on the membrane.

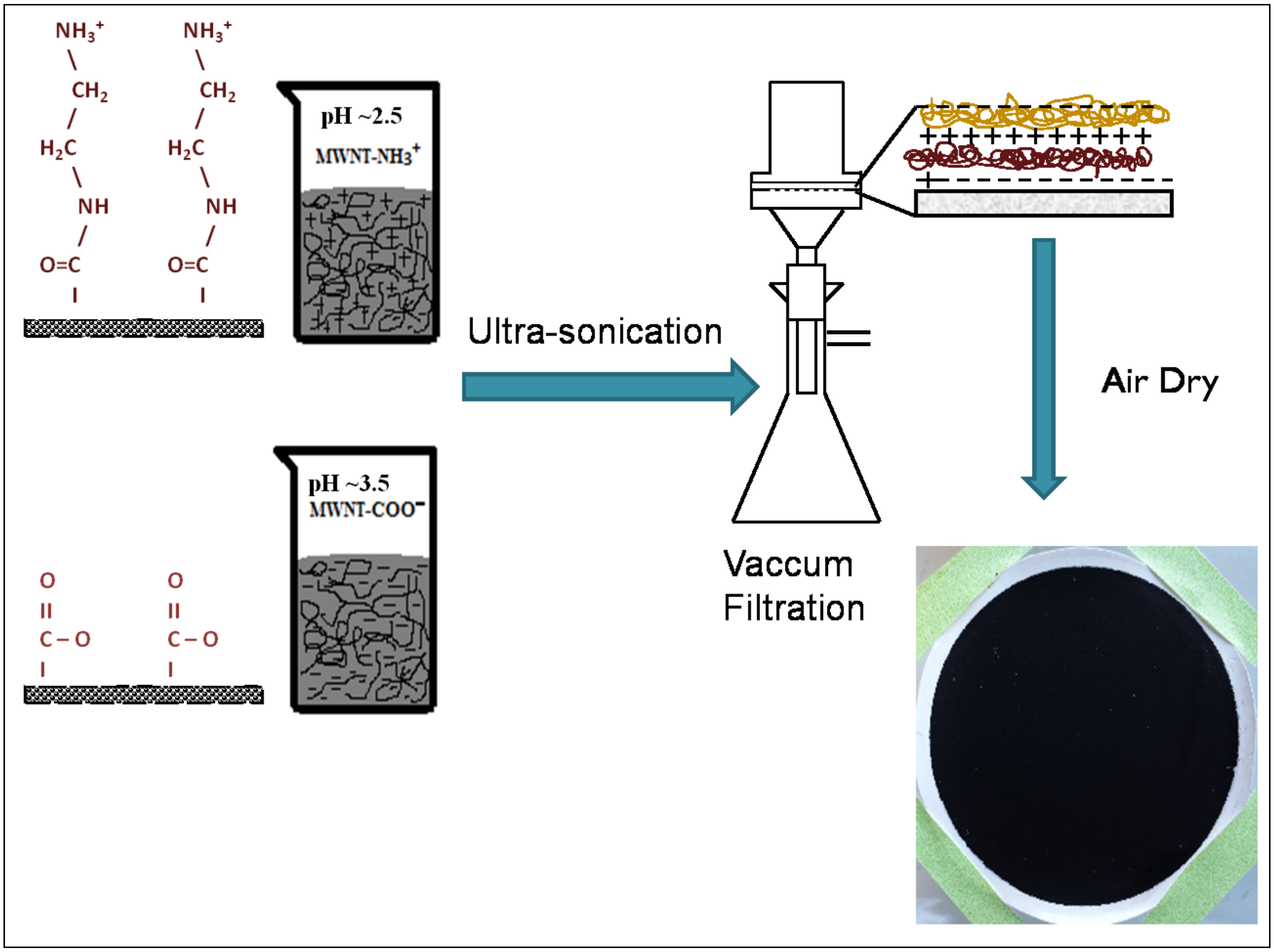

Figure 3.3: Schematic diagram of VF assisted LBL self assembly of CNTs on polysulfone membrane

3.3 Membrane Characterization: Chemical and Morphological

3.3.1 Zeta potential measurements

The zeta potential of the MWNT-NH_2 and MWNT-COOH suspensions as a function of pH was measured by Zeta potential analyzer (Brookhaven Instruments Corp., US). The suspensions for zeta potential analyses were prepared from a very stable dispersed solution (probe sonicated for 3 hours) of MWNTs in DI water and diluted into 0.0001mg/L concentration. The pH values were adjusted to 2, 4, 6 and 8 by using 100mM HCl and 100mM NaOH in order to determine the pH effect on suspension stability.

3.3.2 Scanning electron microscopy (SEM) analyses

Scanning electron microscopy (JEOL, JSM-7600 TFE, Japan) was used to take images of the membrane surface and the cross section of the membrane. The surface images of the modified membrane reveal the tubular structures of the MWNTs. The cross sectional images were taken to verify the fingerlike structures of polysulfone membrane at the bottom and a thin compact layer of MWNTs. Also the uniformity of carbon nanotube layer was verified from the surface morphology of the modified membrane.

3.3.3 Fourier Transform Infrared (FTIR) spectroscopy analyses

Attenuated total reflection-Fourier transform infrared spectroscopy (Nicolet 6700 / Smart iTR, Thermo Scientific, US) was used for a qualitative analyses of the functional groups on polysulfone membrane after plasma treatment. The intensity of the peaks on certain specified wavelengths verify the incorporation of functional groups on the polysulfone membrane.

3.3.4 X-ray photoelectron spectroscopy analyses

X-ray photoelectron spectroscopy analyses (XPS, SK-Alpha, Thermo Scientific, US) was also performed on the plasma treated membrane to observe the change in the percentage of oxygen content after the plasma treatment for different time intervals (i.e., 30s, 60s, 90s and 120s).

3.3.5 Electrokinetic analyses

The electrokinetic analyses (Anton Paar, Graz, Austria) was also performed on the pristine and plasma treated membrane (30s, 60s and 90s) to determine the surface charge of the membranes after being exposed to plasma treatment for different time intervals. The EKA analyses were performed at a pH value of 8.

3.3.6 Contact Angle Measurements

The hydrophobicity of the membranes modified with CNT was compared with that of the pristine and plasma treated PSf membranes by measuring contact angle using a VCA Optima Contact Angle Surface Analyses System (AST Products, Inc., Billerica, MA, USA). In order to measure the contact angle, images were taken in a dynamic mode for a 1μm water droplet on the sample (Figure 3) surface for 2s. The pictures were then analyzed by using software (AST Products, Inc., Billerica, MA, USA) to suit the shape profile of the water droplet on the sample surface for computing the contact angle. For each sample seven consecutive measurements were taken and the average values are reported as representative measurements.

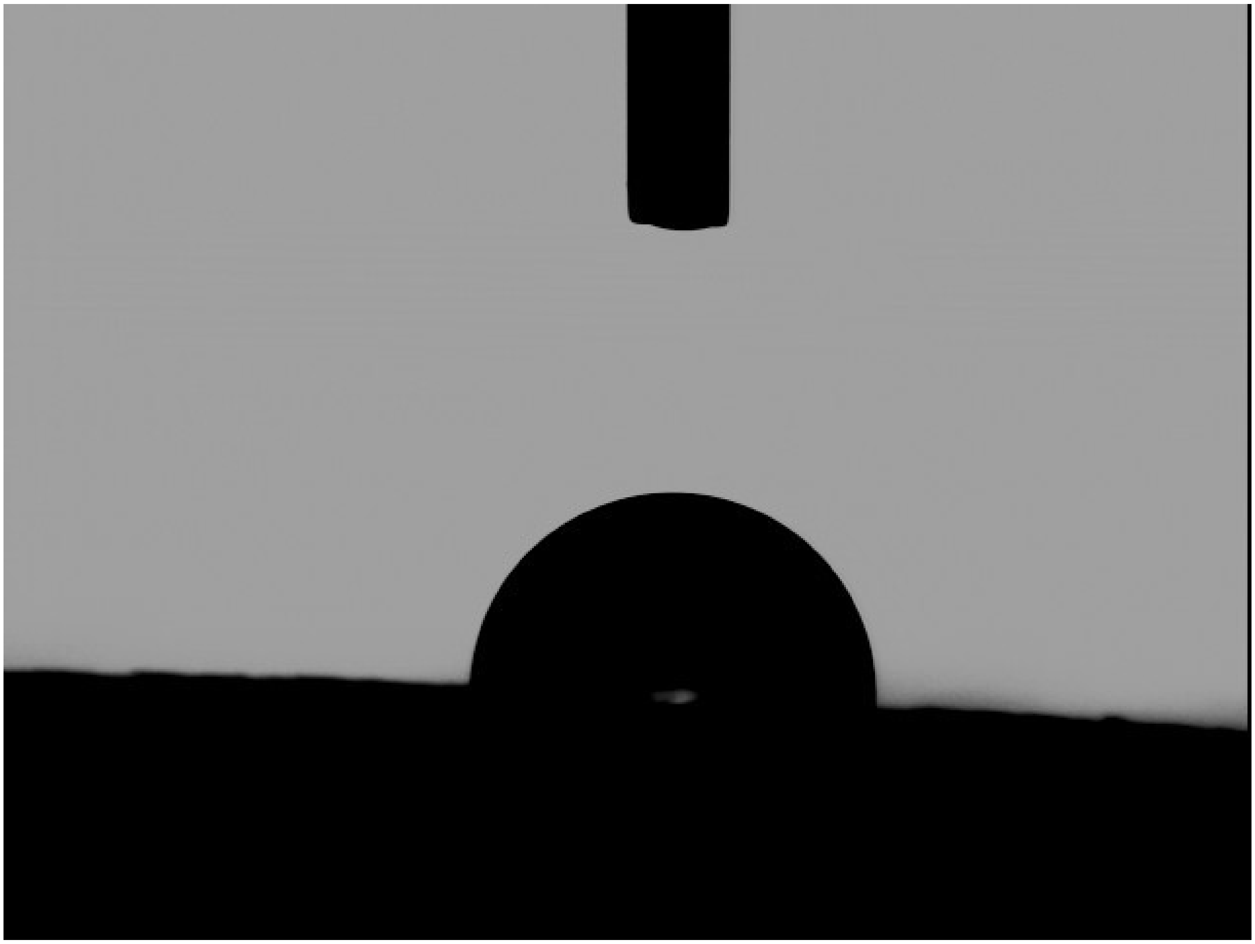

Figure 3.4: Shape profile of 1µl water droplet on membrane surface during contact angle analyses in dynamic mode

3.3.7 Bilayer stability and MWNT leaching studies

The stability of the MWNT layers has been examined by using the protocol of Liang et al [100] where membranes were exposed to harsh physical and chemical stresses. The chemical stress was amplified by immersing the modified membrane for 15 minute in an acidic solution of pH 2 (0.01M HCl), a basic solution of pH 12 (0.01M NaOH) and a saline solution of 5M NaCl. This step was followed by a thorough rinsing with DI water to wash away the extra solutions from the membrane and then the membrane was air dried. The physical stress was applied on the membrane through immersing the membrane in 10 mL DI water and bath sonicated (Branson 8510R-MTH) for 2 minute. After applying the physical and chemical stresses, the membrane contact angles were determined to evaluate the stability of the MWNT layers on modified membranes.

3.3.8 Membrane thickness measurements

The thickness of the modified membrane with MWNT bilayers was measured by using a profilometer (Dektak XT) and verified by determining thickness from SEM images of the cross-sectional view of the membranes (Figure 3.5). The thickness measurements provide an overall idea about the uniformity of MWNT layer. For taking cross sectional SEM images of the membrane, the polysulfone layer was separated from the support layer. Then the membrane was broken by putting it into liquid nitrogen and by pulling it from two sides.

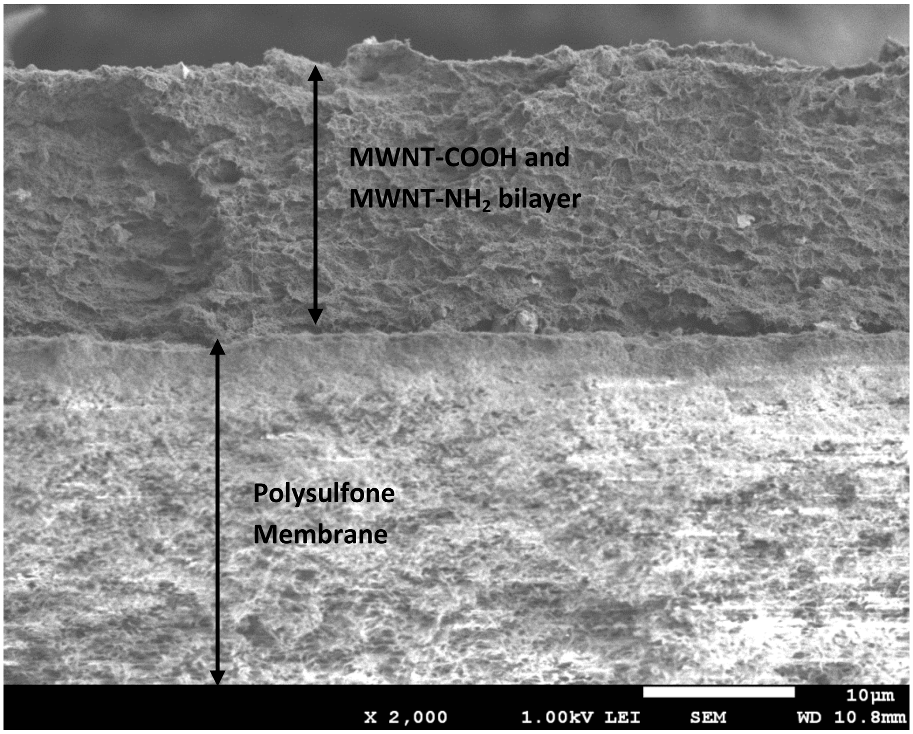

Figure 3.5: Cross sectional SEM image for thickness measurement

3.4 Membrane Performance Evaluation

3.4.1 Electrical conductivity measurements of the membranes

Electrical conductivity of the membranes was measured by two different ways. In both of which the resistivity of the membrane was measured and the conductivity was calculated using the following equation,

Conductivity = 1/ Resistivity

The first method required a modified membrane strip of 1cm x 4cm and a laboratory grade multimeter-voltage (Mastercraft, USA) detector. The probe tips of a multimeter-voltage detector were placed on different spaces of the membrane strip along the length and the resistance values were recorded. The recorded values of membrane resistance were then used to calculate the membrane conductivity. The more accurate measurements were obtained by using the vander pauw method (4-points-4TS, Sigmatone-302, USA). The 4-point probe tip penetrates through the cross-section and provides a value of sheet resistance, which is further multiplied by the thickness of the MWNT layer to obtain the resistivity of the membrane. For each membrane 5 consecutive measurements were taken across the membrane surface and the average value was taken as a representative for that particular membrane.

3.4.2. Membrane permeability measurements

Permeability of the membrane was measured by using an Amicon 10-mL stirred ultrafiltration cell (Amicon 8010, Millipore, Cole Permer, US). The membranes were wet before use. A 2.54cm coupon was cut by using the membrane cutter (Power punch maxi set, Spearhead 130) and precompacted for 30minute under a pressure of 30psi to obtain a steady flow rate. Then to record the pure water flux we operated the stirred cell with DI water at 30psi with continuous stirring of 300rpm. Several measurements were taken within 1h of operation. The permeability for ultrafiltration membrane has been calculated by the following equation[177],

$L_p = J_v / \Delta P$

Where J_v is referred as volumetric filtrate flux (volume flow rate per membrane area) or hydraulic permeability as the solvent is water and ΔP is the transmembrane pressure driving force.

3.4.3 Membrane selectivity determination

Membrane selectivity is a very important property that determines membrane performance. For ultrafiltration membrane it is termed as molecular weight cut off (MWCO) that happens due to the size exclusion of solutes due to their higher molecular weight. The MWCO of the membrane should be lower than the molecular weight of the molecules that are aimed for rejection. In order to determine the membrane selectivity, rejection tests were accomplished by challenging the membrane against polyethylene glycol (M_v 20KD) solution. Briefly, the solutions were prepared at a concentration of 1gL^{-1}(Polymer source, Montreal, Quebec, Canada) and were filtered through the modified membrane via the stirred ultrafiltration cell after precompaction for 30 min. The collected permeation was analyzed for total organic carbon (TOC) using a TOC analyzer (TOC $V_{CPH/CPN}$, Shimadzu corp., Japan). The rejection was then calculated by the concentration of total organic carbon present in permeate and feed solution.

Rejection (%) = $1 - C_{Permeate} / C_{Feed}$

3.4.4 Organic matter degradation using the conductive membrane in an electro filtration unit

In order to determine the efficiency of organic matter degradation, methyl orange was used as a model organic compound in a background solution of 10 mM NaCl. More details about the experimental protocol can found elsewhere Liu and Vecitis [178]. An influent solution of methyl orange with a concentration of 14μM in 10 mM NaCl was prepared to conduct the electrochemical filtration test. The membrane was placed in an electrofiltration unit with active side facing the anode. Then the influent flow rate was set to 1.5 mL min^{-1} and DI water was used to flush the tubing and calibrating the flow rate. After flow rate calibration, the influent was filtered through the modified VF-assisted LBL membranes (5, 10, 15 and 20 bilayer) consecutively at a constant flow rate of 1.5 mL min^{-1} by means of a peristaltic pump (Masterflex, Cole Permer, US). The external wires of cathode and anode of the electro filtration unit was connected to a DC power supply (Agillent, Germany). The effluent was collected and analyzed with an UV-Visible-NIR spectrophotometer (Perkin Elmer, Lambda 750) to determine the concentration of methyl orange from the absorption values at 464 nm.

3.4.5 Bacterial inactivation by using conductive membrane in an electro-filtration cell

Bacterial inactivation experiments were carried out by following the procedure of Vecitis, et al. [15]. Briefly, the procedure includes several steps starting from overnight bacterial culture, then preparing *E. coli* solution for antimicrobial test and finally preparing plates for determining active bacterial cell concentration through plate counting.

For preparing the plates, a nutrient solution containing LB (25mg/L), and agar (15g/L) in DI water was prepared and the solution was autoclaved. After autoclaving, 2 mL of amphicilin (25g/L) was added in the solution and cooled it for 1 h. Then approximately 8-9 ml of solution was poured into each petri dish, left them in the safety cabinet for an hour to be cooled before storing them in a refrigerator (upside down).

In order to prepare the bacterial solution, one single bacterial colony was added in 50 mL autoclaved LB (25g/L) solution containing amphicilin (50 mg/L) and incubated overnight at 37˚C. Then 1ml solution from the overnight bacterial culture was mixed with 50 ml LB solution containing 50 mg/L of amphicilin and the solution was incubated again for 2.5 h at 37.5˚C. Then the bacterial suspension was undergone centrifugation at 15000 rpm for 3 min and after discarding the solution, 20 mL of 0.9% NaCl solution was used for the wash step. The washing of the pellet through centrifugation was done 3 times consecutively followed by subsequent vortex mixing. The optical density of the *E. coli* cell suspension was maintained to 0.3 at 600 nm in order to ensure the cell concentration of 10^6 CFU/mL.

The plate counting method was used for quantifying the cells inactivated through electrochemical oxidation. 3mL of bacterial solution was permeated through the membrane using a vacuum filtration unit. Firstly no voltage was applied through the electrochemical filtration setup for non electrochemical experiments and the sieved bacteria remained on the membrane. For the electrochemical experiments the filtration casing was filled with the isotonic salt solution and a potential difference of 0-3V was applied to electrolyze the system. Then the membrane was taken out of the cell and rinsed with isotonic (0.9% NaCl) salt solution and subsequently sonicated for 7 min in a water bath sonicator. The final solution after the bath sonication was then diluted serially. From the diluted solutions, 200μL solution was spread onto the agar plates and incubated overnight. The number of active cell was determined by counting the number of colonies formed on the agar plate as shown in Figure 3.6.

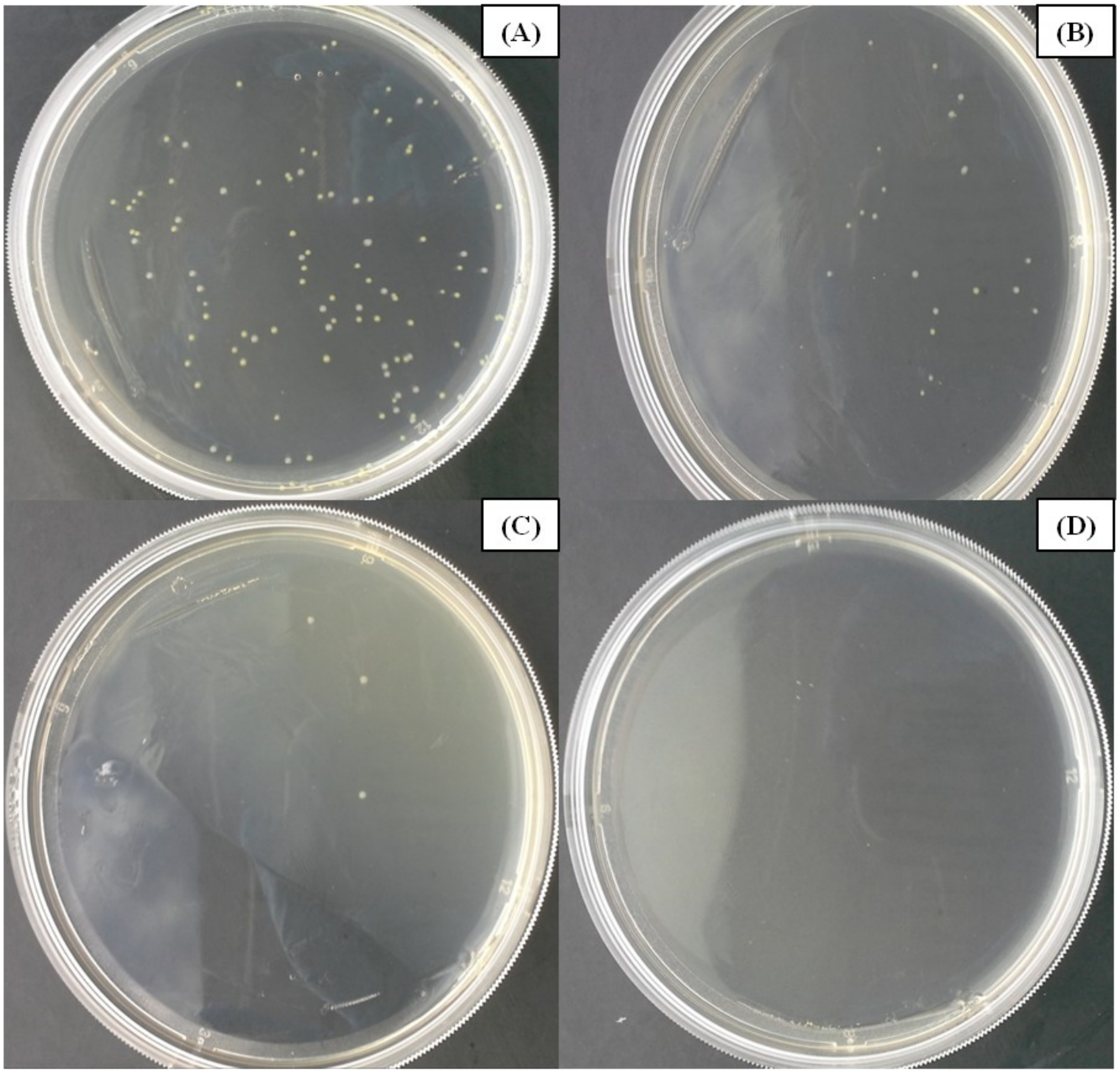

Figure 3.6: Plate counting for (A) 0V, (B) 1V, (C) 2V and (D) 3V electrofiltration membrane for a specific dilution factor

4. RESULTS AND DISCUSSION

4.1 Optimization of O_2 plasma treatment for membrane functionalization

4.1.1 Morphological characterization of membranes

The effect of O_2 plasma treatment on surface morphology of polysulfone membrane was analyzed through scanning electron microscopy (SEM). The SEM images display an increased pore size and pore density with increasing plasma treatment time (Figure 4.1). For each sample 4 images were taken at different location to see the uniformity of the pore size as well as distribution. The average pore diameter of pristine polysulfone membrane was measured be 26.2 nm while the 60s plasma treated polysulfone membrane was measured to be 38 nm. These increased pore size and pore density are attributed to oxygen absorption in the pores and making new pores through surface oxidization of membrane.

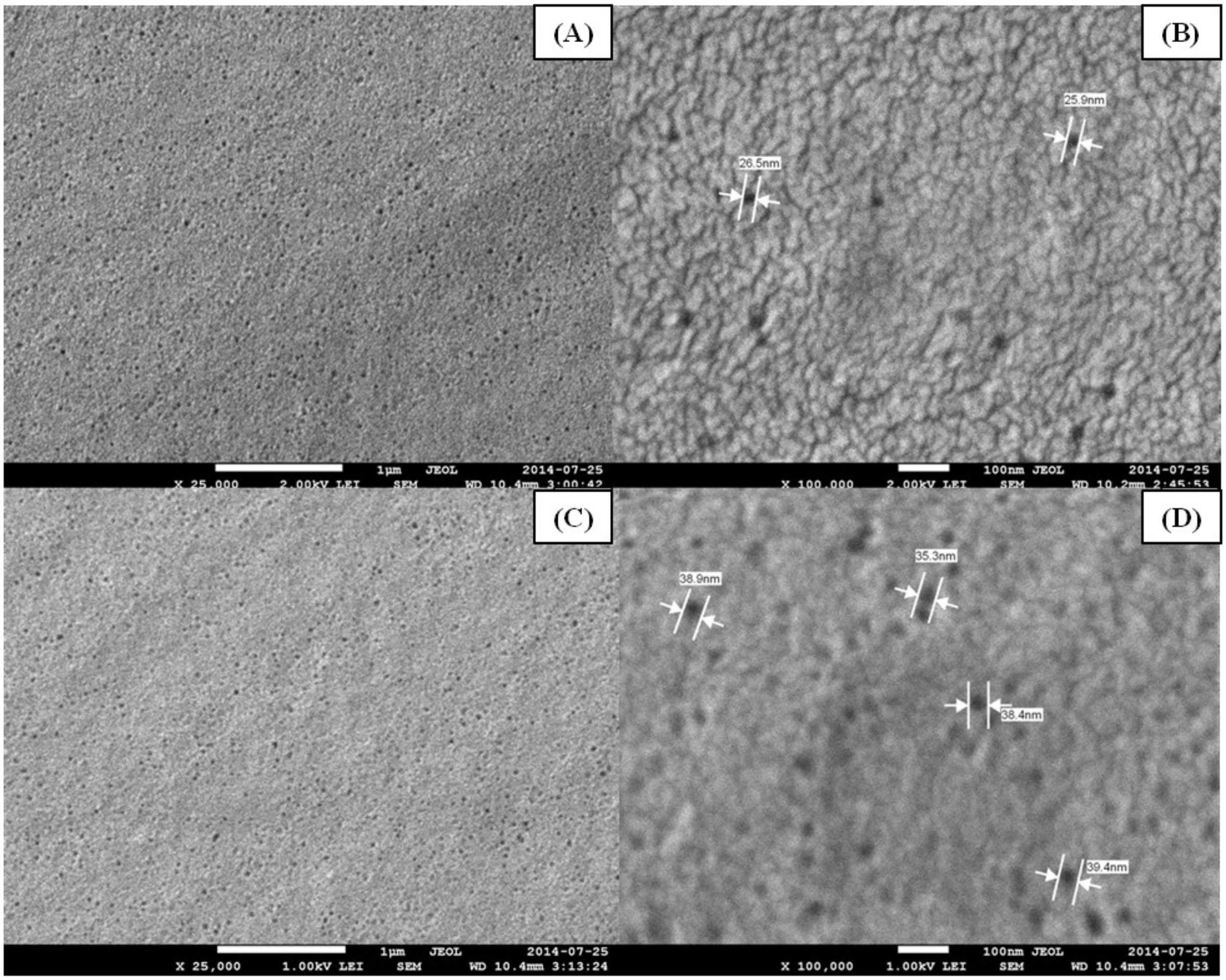

Figure 4.1: SEM images of (A) pristine polysulfone membrane, (B) pristine polysulfone membrane with marked pore diameter, (C) 60s plasma treated membrane and (D) 60s plasma treated membrane with marked pore diameter

4.1.2 ATR-FTIR analyses of membranes

The Attenuated total reflectance- Fourier transform infrared (ATR-FTIR) spectra reveals the chemical changes of pristine polysulfone membrane due to plasma treatment. In general, the pristine polysulfone membrane surface contains different functional groups such as C-C stretch, asymmetric S=O, Symmetric S=O, C=C and C-O-C stretch and after being plasma treated some carbonyl stretch as C=O and acid functional group O-H are expected to appear. Figure 4.2 represents the ATR-FTIR spectra for the pristine and plasma treated polysulfone membranes.

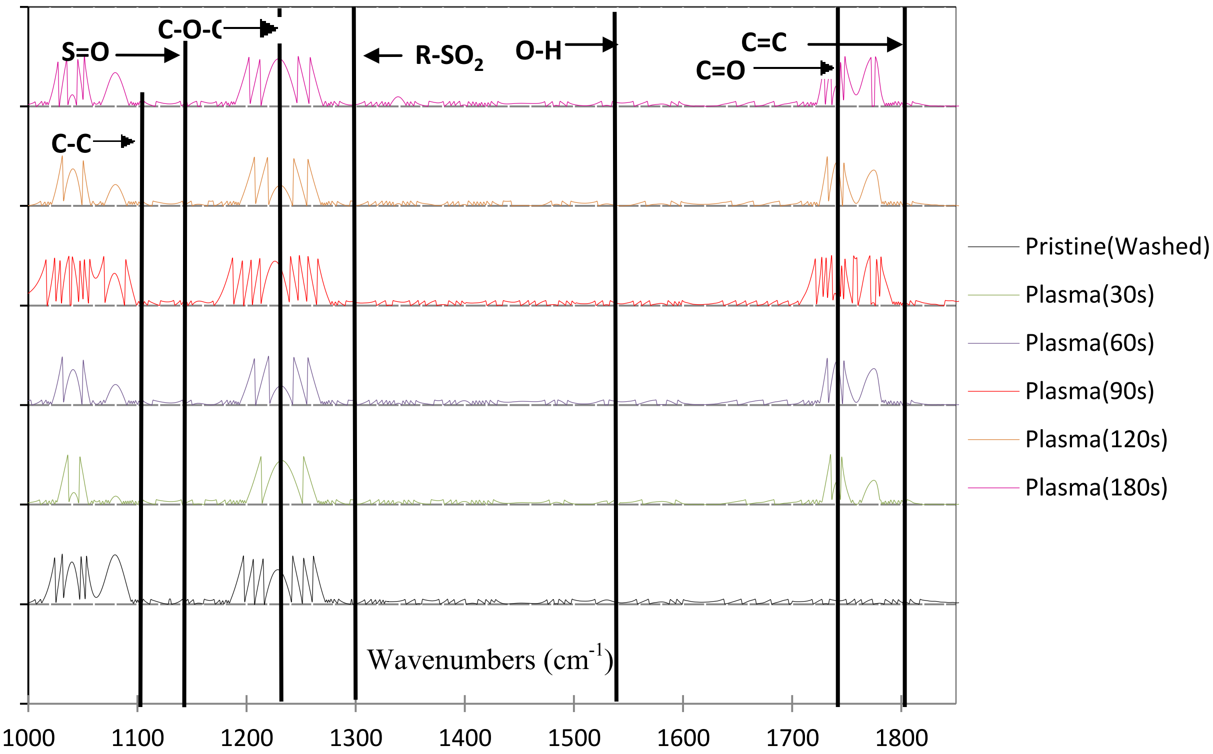

Figure 4.2: Attenuated total reflectance- Fourier transform infrared (ATR-FTIR) spectra for pristine and plasma treated polysulfone membrane with peak identification

The spectra for polysulfone membrane clearly indicates the peaks at 1100 cm^{-1} (C-C stretch), 1300 cm^{-1} (asymmetric S=O stretch), 1232 cm^{-1} (C-O-C stretch), 1800 cm^{-1} (C=C stretch) and 1143 cm^{-1} (symmetric stretch) corresponding to the previously mentioned functional groups. After being O_2 plasma treated carbonyl functional group (C=O) and polymeric O-H bend appear on the spectra at wave frequency of 1740 cm^{-1} and 1540 cm^{-1}, respectively. Generally, with increase in plasma treatment time the peak broadens except some exceptions that might be observed due to the polysulfone membrane heterogeneity even though the polysulfone is resistant to etching with mass losses of 2 mg $cm^{-2}s^{-1}$ for a high energy plasma [179].

Table 4.1: Experimental and literature frequencies for specific functional groups

Specification of membrane	Experimental Frequencies (cm^{-1})	Literature Frequencies (cm^{-1}) [129, 175, 180]	Possible peak assignments
Polysulfone Membrane	1100	1100	C-C stretch
	1300	1294.4, 1300	S=O asymmetric stretch
	1143	1143.5	S=O symmetric stretch
	1232	1232.8,1180	C-O-C stretch
	1800	1800	C=C stretch
O_2 plasma functionalization	1540	1300-1600	Polymeric O-H bend
	1740	1650-1750	C=O stretch

4.1.3 XPS analyses of membranes

X-ray photoelectron spectroscopy (XPS) analyses illustrate the surface composition of pristine polysulfone and the O_2 plasma treated polysulfone membrane as shown in Figure 4.3. The percentage of oxygen content, compared to carbon and sulfur is plotted as a function of plasma treatment time. The plasma etching initiates the degree of functionalization of the membrane surface and as a result the oxygen content increases with increasing plasma duration. The pristine membrane contains an oxygen content of 18.5% while the 30s plasma treated membrane exhibits about 29.5%. There is an increase of 11% after 30s plasma etching compared to that of pristine polysulfone membrane. The curve reaches a plateau after 30s of plasma treatment and continues gradual increment for 60s, 90s and 120s plasma treated membrane. This implies the evolution of carboxyl, carbonyl and hydroxyl groups onto the membrane surface due to the plasma etching.

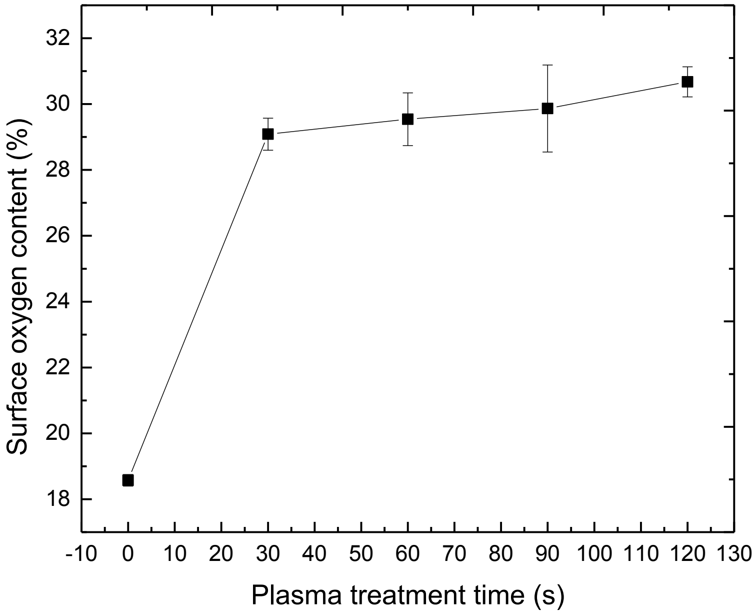

Figure 4.3: Percentage of membrane surface atomic oxygen content compared to sulfur (S) and carbon(C) as a function of O_2 plasma treatment time, analyzed by XPS

4.1.4 Water contact angle / wettability of membranes

The water contact angle of the plasma treated polysulfone membrane decreased with the increase in plasma treatment time (Figure 4.4). The polysulfone membrane has an average contact angle of 68.6, consistent with previously reported observations and the value reduces to 44.2 after being plasma treated for 180s. The change is contact angle is significant up to 90s of plasma treatment time but the values remain almost the same for any further increase in plasma treatment time. The decrease in the contact angle confirms the increase in oxygen functional groups onto the membrane surface. Oxygen containing functional groups increase the membrane hydrophilicity which leads to the gradual decrease in water contact angle (i.e., wettability increases).

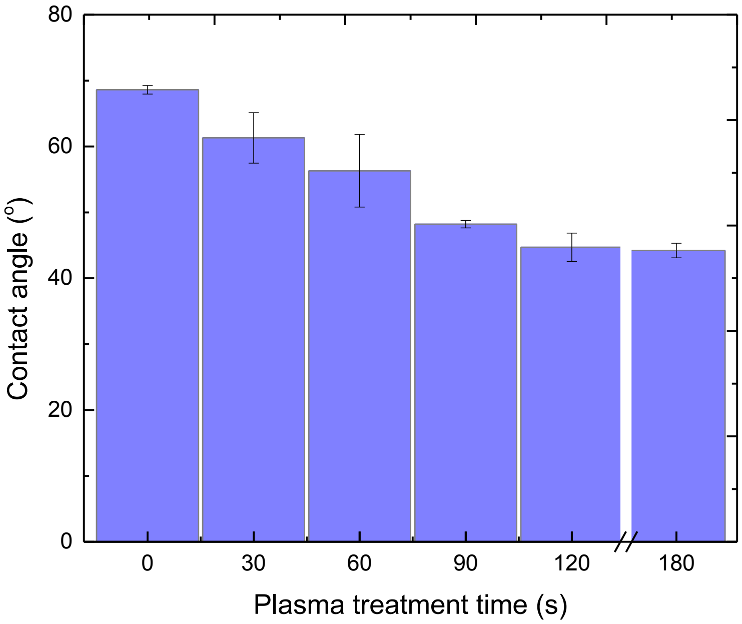

Figure 4.4: Water contact angle for different plasma treatment time duration

4.1.5 Permeability of the plasma treated membranes

The water permeability of the plasma treated membranes is measured in a stirred cell and the values are reported in Figure 4.5. The water flux decreased after 30s of plasma treatment but the values increased with increasing plasma treatment time. Although there are increase in functional groups after 30 s plasma treatment and the membrane has higher hydrophilicity than the pristine membrane, this result seems odd to fit here. Moreover, in most previously reported studies, plasma treatment improves water flux of polymeric membranes [100]. This behavior can be explained by the drying up of membrane during plasma treatment and the wetting time after plasma treatment wasn't enough to observe the effect of membrane hydrophilicity [181]. However, for any further increase in plasma treatment time (e.g., 60 s to 180 s) the water permeability increases due to increase in pore diameters. The increase in water flux is obvious as the values increases from 463 Lmh/bar (for pristine membrane) to 966 Lmh/bar (for 180s plasma treated membrane).

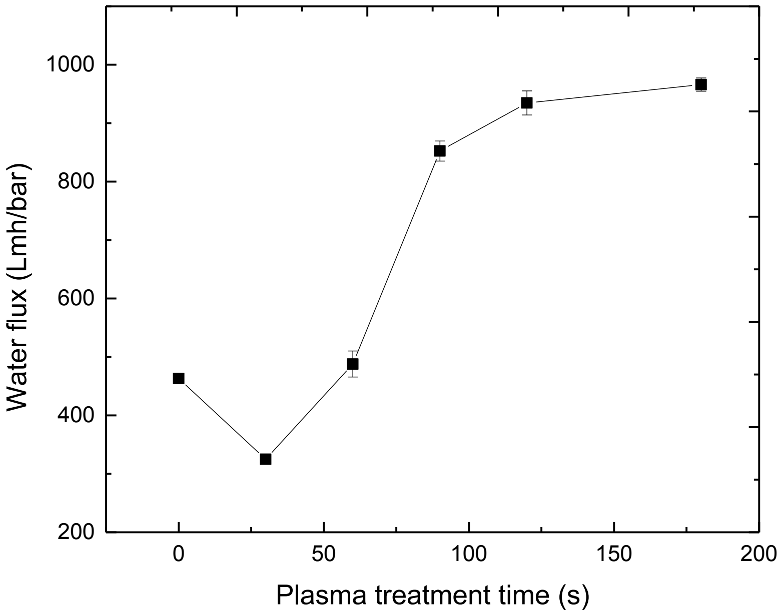

Figure 4.5: Water flux for different plasma treated time

4.1.6 Electrokinetic analyses (EKA) of the membranes

Another method of confirming the evolution of functional groups through plasma treatment is the measurement of zeta potential of the membrane (i.e., the net effective charge on the membrane surface). The isoelectric point of polysulfone membrane is found to be at pH 3 and the membrane surface becomes more negative with increasing pH beyond pH 3 [96]. In order to confirm the oxygen plasma initiated functionalization, electrokinetic analyses of the plasma-treated membrane was performed. The analyses is performed at pH 8 since the oxygen containing functional groups are negative and at this pH the zeta potential is believed to be more negative with increase in plasma treatment time. At pH 8 the pristine polysulfone showed a zeta potential of -22.5 and a sharp increase in zeta potential (-36.28) is observed for the plasma-treated membrane for 30s. The curve soars up steadily for 60s and 90s plasma treatment time and the zeta potential becomes -41.28 and -42.8, respectively. The differential increase in zeta potential confirms the increase in negatively-charged oxygen containing functional groups in the membrane surface.

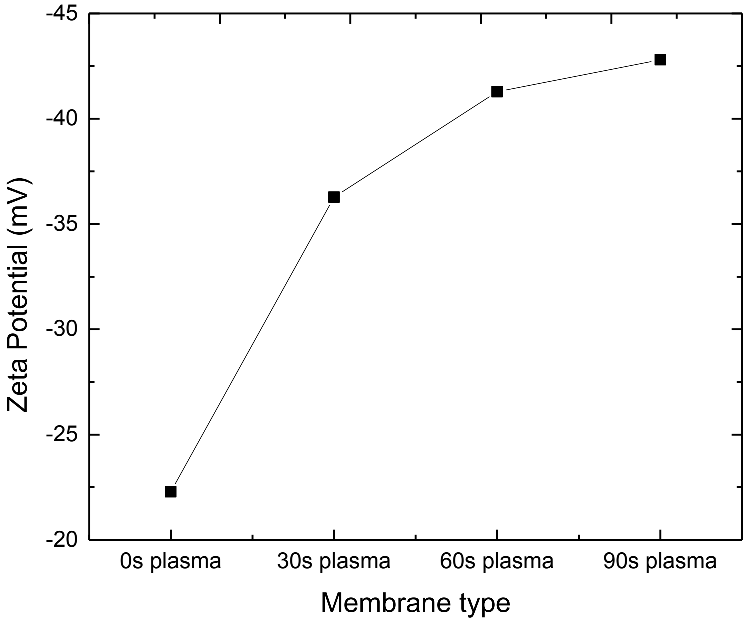

Figure 4.6: Electrokinetic analyses for the plasma treated membrane at pH 8

Based on the analyses performed the plasma treatment time for polysulfone membrane was optimized to be 60 s. Although 30s plasma treatment showed a significant addition of functional groups onto the membrane surface but a decrease in permeability restrained this study to optimize 30s as the plasma treatment time. The higher plasma treatment time is usually not preferred as with increased plasma intensity the top dense layer of polysulfone membrane may get oxidized and therefore, the overall selectivity of the membrane may be compromised with increasing membrane pore sizes.

4.2 Vacuum filtration assisted LBL modified polysulfone membrane characterization

4.2.1 SEM images of MWNT modified membranes

The SEM image (Figure 4.7) clearly depicts the carbon nanotubes on the VF assisted LBL modified polysulfone membrane surface. The modified membrane surface morphology illustrates uniform distribution of carbon nanotubes. However the nanotubes were not horizontally aligned to create atomic layers. It is not possible to differentiate between different functionalized carbon nanotubes in the SEM images but due to the high aspect ratio of carbon nanotubes, the orientation may initiate accumulation and aggregation.

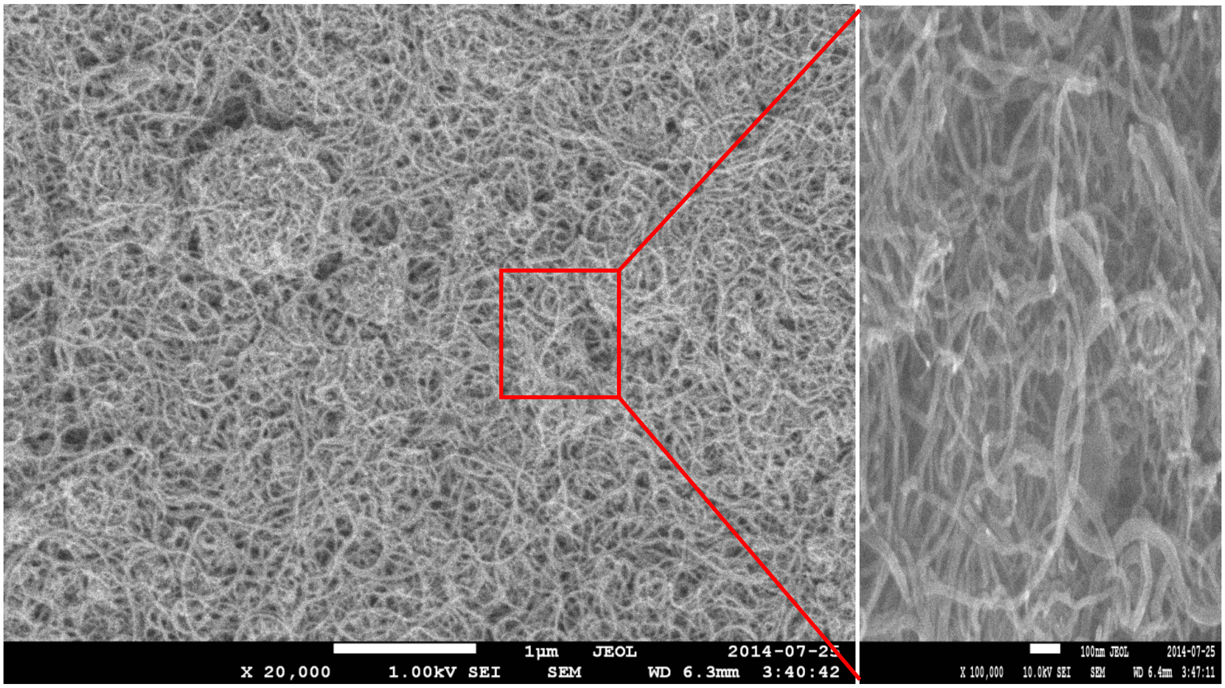

Figure 4.7: SEM images of the MWNT-NH_2/MWNT-COOH modified VF-LBL self assembled membrane

4.2.2 Water contact angle of VF-LBL modified membranes

The contact angle of the modified membranes as a function of surface modification and number of bilayer is presented in Figure 4.8. The 60s plasma-treated polysulfone membrane was used for the surface modification through VF assisted LBL assembly and thus it serves as a control with a contact angle of 56.3˚. The plasma-treated membrane was treated with EDC/NHS solution for converting the unstable oxygen containing functional groups to stable amine reactive ester groups which made the membrane more hydrophilic. The membrane contact angle after the EDC/NHS treatment became 48.1˚, indicating improved hdrophilicity compared to the control, plasma treated membrane. The incorporation of carbon nanotubes through LBL self-assembly made the membrane surface hydrophobic due to the higher hydrophobicity of the carbon nanotubes as it lacks sufficient polar groups to show water affinity. The 5 bilayer MWNT membrane showed a contact angle of 92.8˚ which is almost doubled the contact angle of EDC/NHS modified membrane. With increasing the number of MWNT bilayers the contact angle increased to 102.9˚, 114.3˚ and 116.5˚, respectively for 10, 15 and 20 bilayers, indicating higher hydrophobicity. Although hydrophobic membrane are very prone to fouling[182], the modified membrane will be used in an electrofiltration cell where, applied voltage will be the dominant factor in controlling fouling events.

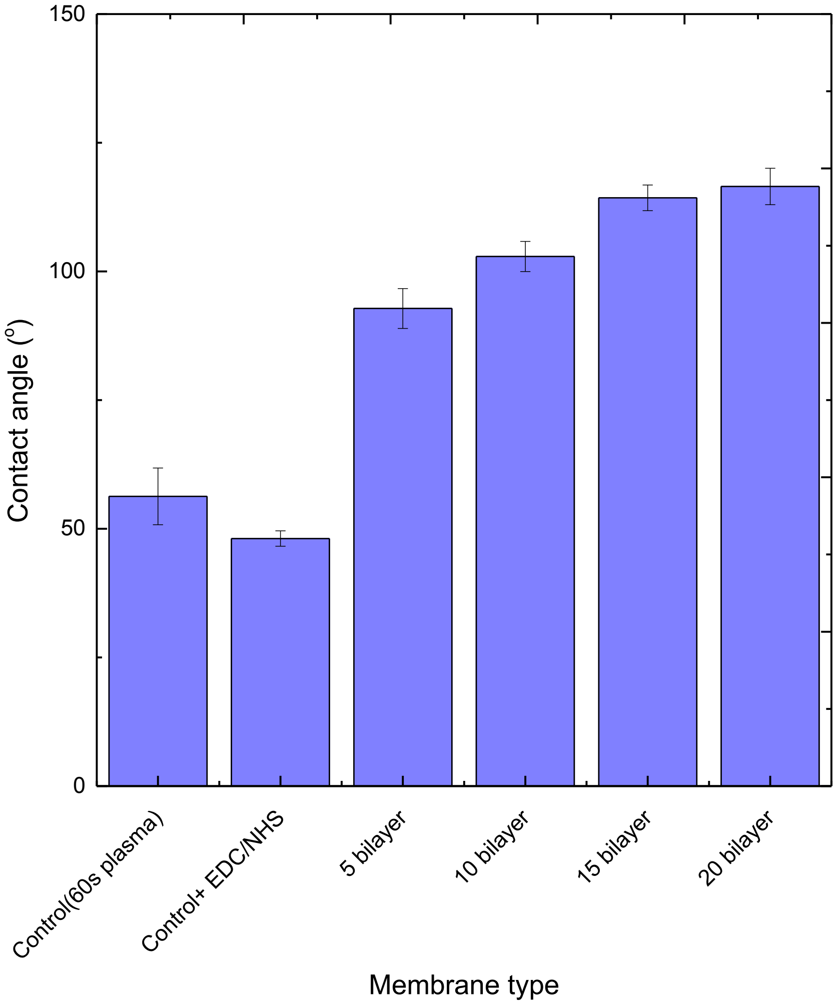

Figure 4.8: Water contact angle for the VF-LBL modified membranes

4.2.3 Thickness of modified membranes

It is expected that incorporating MWNT bilayer will increase the thickness of the modified membrane. The SEM images of the cross section of the modified membranes were taken to analyze the thickness of the LBL film. The SEM images in Figure 4.9 displays uniformity of thickness throughout the membrane cross section and the Figure 4.10 shows a linear increase of MWNT layer with increasing the number of bilayer. The average thickness for 5, 10, 15 and 20 bilayer membrane is 3.02µm, 6.6µm, 10.3µm and 14.3µm, respectively. For a single bilayer the

5, 10, 15 and 20 bilayer membranes display an average thickness of 302 nm, 330 nm, 343.3 nm and 357.5 nm, respectively. The atomic layer of horizontally aligned carbon nanotubes should be around 10-15 nm as the diameter of the nanotubes are 8-13nm. But the average length of the carbon nanotubes is 3-30μm and due to its high aspect ratio it is very difficult to align CNTs horizontally or even vertically. The nanotube curls during the LBL deposition and orient themselves in a different pattern. The orientation of carbon nanotubes makes it nearly impossible to obtain an atomic layer thickness. Therefore, the actual average thickness of a bilayer is significantly higher than the thickness calculated from the atomic layer thickness (i.e., 30 nm).

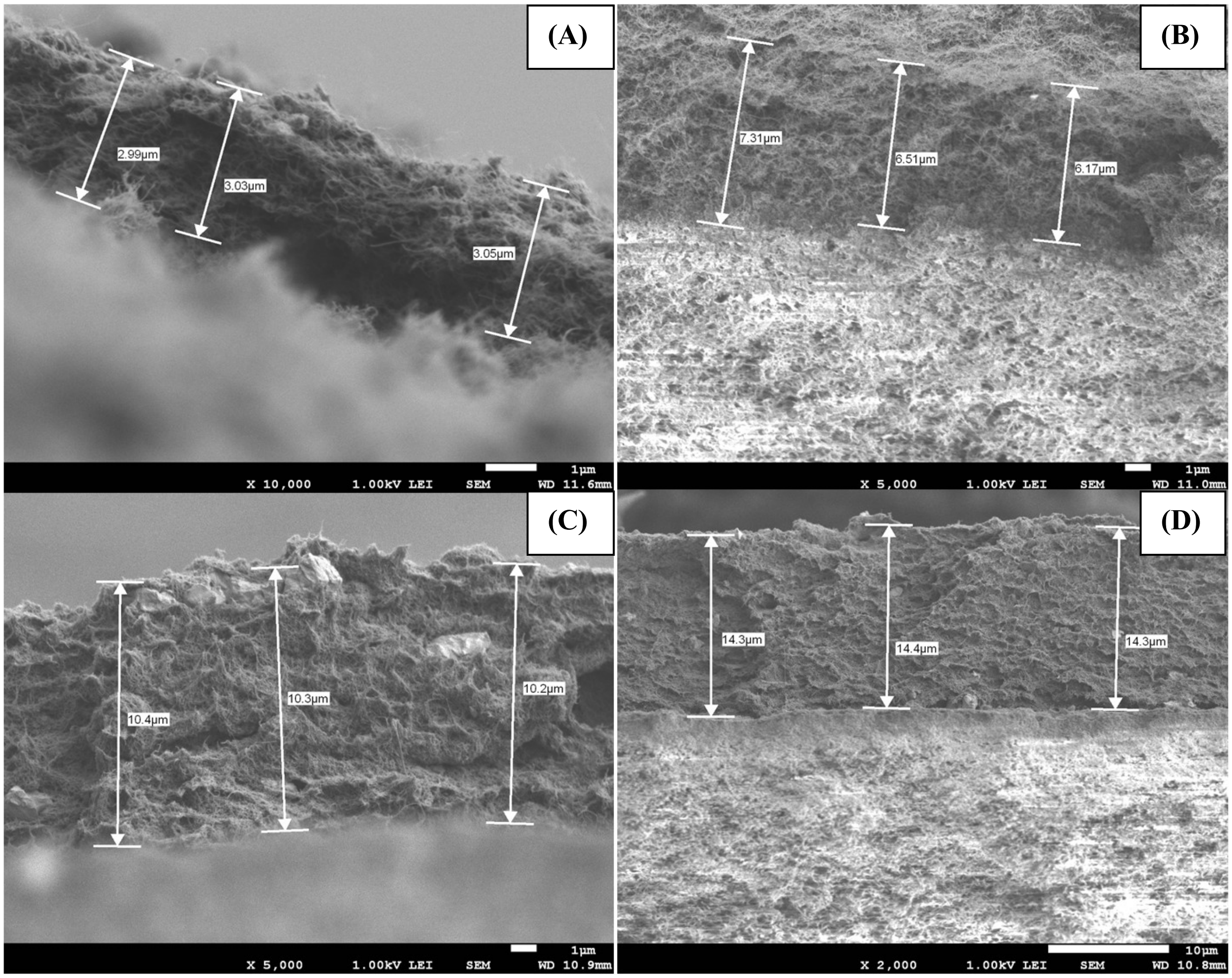

Figure 4.9: SEM images of the thickness profile for (A) 5 bilayer, (B) 10 bilayer, (C) 15 bilayer and (D) 20 bilayer polysulfone-CNT membrane developed by vacuum filtration assisted LBL assembly

The linearity of the curve in Figure 4.10 suggests that even though the orientation of the carbon nanotube is ensured, with increasing the number of bilayer the thickness of the MWNT LBL film increases consistently. Due to the low concentration of the MWNTs the aggregation of nanotube was also prevented. Another fact that explains the non-atomic layer distribution is that due to the vaccum filtration of the solution all MWNTs were forced to deposit on the membrane whereas for other LBL techniques (dip, spray and spin) usually the electrostatic force dominates the deposition. In this study, in addition to electrostatic interactions several other interactions such as hydrophobic interaction, vander walls attraction and the hydrogen bonding were dominant to hold the bilayers onto the base polysulfone membrane. There is no escape for the excess nanotubes that are not bound by the electrostatic interaction, rather depositing the total amount of nanotubes that leads to a thicker layer.

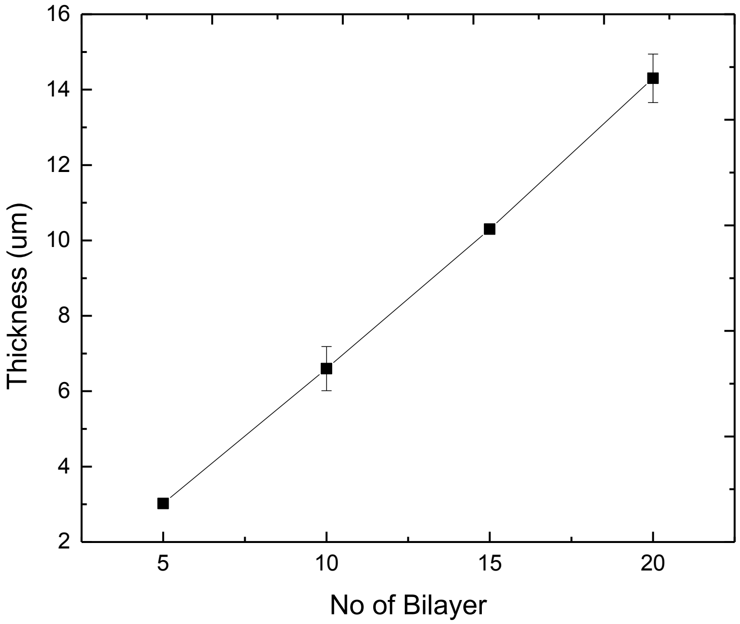

Figure 4.10: Thickness of the VF-LBL MWNT modified membrane with increasing number of bilayers

4.2.4 Electrical conductivity of the VF-LBL MWNT modified membranes

One of the main objectives of this research was to develop a conductive membrane for electrofiltration system. The electrical conductivity of the modified membranes with different bilayers was measured and presented in Figure 4.11. As shown in Figure 4.11, the conductivity of the membrane increases (i.e., resistivity decreases) with the increasing the number of bilayer. The total amounts of MWNTs in per unit cm^2 incorporated into 5, 10, 15 and 20 bilayer membranes were .26mg, .52 mg, .78 mg and 1.04 mg respectively. With the amount of MWNTs added the conductivity of the modified membrane surface was found as high as 4.1×10^3 s/m, which is in the same order of magnitude of graphite. Even with the lowest amount of MWNTs (used in the 5 bilayer membrane), it exhibits a very high conductivity of 3.8×10^3 s/m-almost the same as that of the 20 bilayer membrane. However, with increasing the number of bilayer the conductivity increases slightly. The increase in conductivity indicates improvement in MWNT network its electron transfer capacity. One particular advantage of the LBL modified conductive membrane is that it allows investigation of the effect of increasing MWNT concentration with controlled thickness of layers while other method such as crosslinking encounters difficulties in depositing MWNTs uniformly over the membrane surface[50].

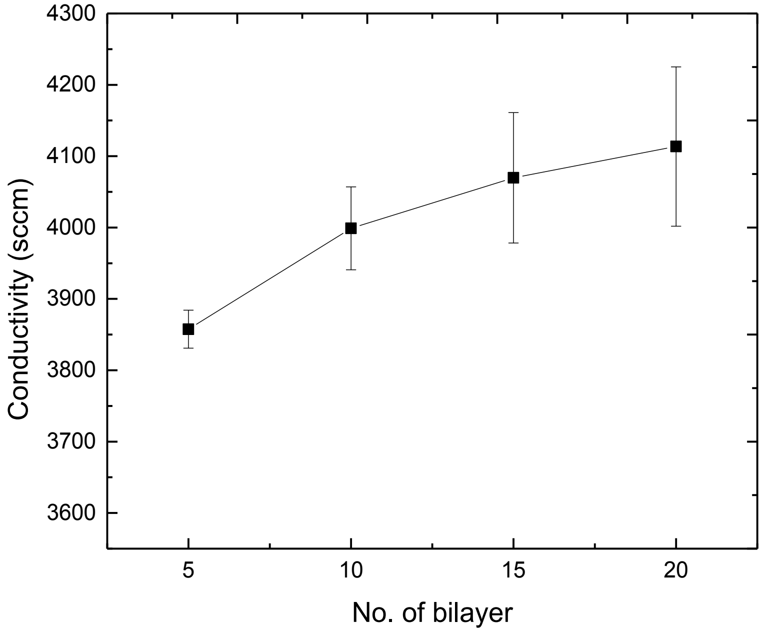

Figure 4.11: Electrical conductivity of the VF-LBL MWNT modified membrane as a function of number of MWNT bilayer

4.3 Performance of MWNT modified membranes

4.3.1 Water permeability and of the modified membranes

For any membrane filtration process, water permeability and selectivity (solute rejection) are the two most important parameters in determining the performance of the membrane. There is always a trade-off between permeability and selectivity in which as the selectivity increases, permeability decreases and vice versa. The pure water fluxes of the membranes with respect to different stages of modification are shown in Figure 4.12. The percentage (%) change in permeability is presented to demonstrate the effect of modification. The 60s plasma treated membrane was found to have a 5% increase in permeability compared to the pristine polysulfone membrane. With incorporation of MWNTs the permeability decreases except the 5 bilayer membrane. The permeability decreased 22% for 10 bilayer membrane and 30% and 37% for 15 and 20 bilayer membranes, respectively. In general, for pressure filtration processes, the membrane industry has a silent approval on permeability reduction less than 50% after modification if the membrane attributes unique properties. The flux reduction occurs due to the increase in membrane thickness that provides additional hydraulic resistance. Moreover, the intrinsic hydrophobicity of the carbon-based nanomaterials contributes to the flux reduction.

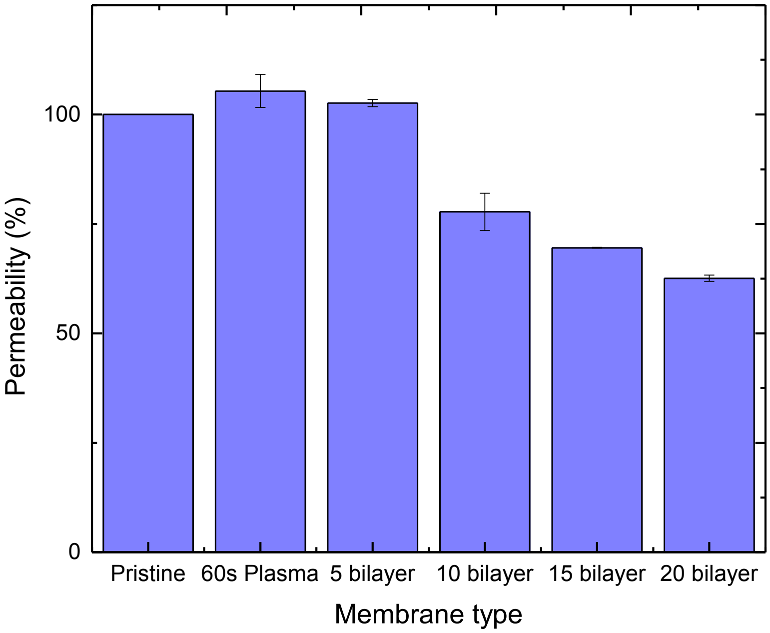

Figure 4.12: Pure water flux of the modified membranes with different number MWNT bilayers. Control means 60s plasma treated polysulfone membrane without CNT bilayer. Here the experiments were conducted with a constant transmembrane pressure of 30 psi at room temperature and all the results were calculated in terms of pristine polysulfone membrane

4.3.2 Solute rejection of the modified membranes

The selectivity of the membranes was determined by using a low molecular weight (20KD) polyethylene glycol (PEG) through a molecular weight cutoff (MWCO) experiments. As can be found in Figure 4.13, the pristine membrane achieved only 19% rejection of the PEG molecules of this specific molecular weight. The selectivity of the modified membranes exhibits a significant increase in selectivity; the 5 bilayer membrane showed 71% of PEG rejection. With increasing the number of bilayer, the solute rejection increased only slightly. The highest rejection was observed with 20 bilayer membrane (76%). The higher solute rejection of MWNT modified membrane may be attributed to the adsorption of the PEG on the surface of carbon nanotubes. The functional groups of carbon nanotubes offers more adsorption sites for the PEG and thus the concentration reduces on the permeate side. The results suggest that higher rejection can be achieved with this modified membrane- even 100% rejection would be possible for higher molecular weight compounds.

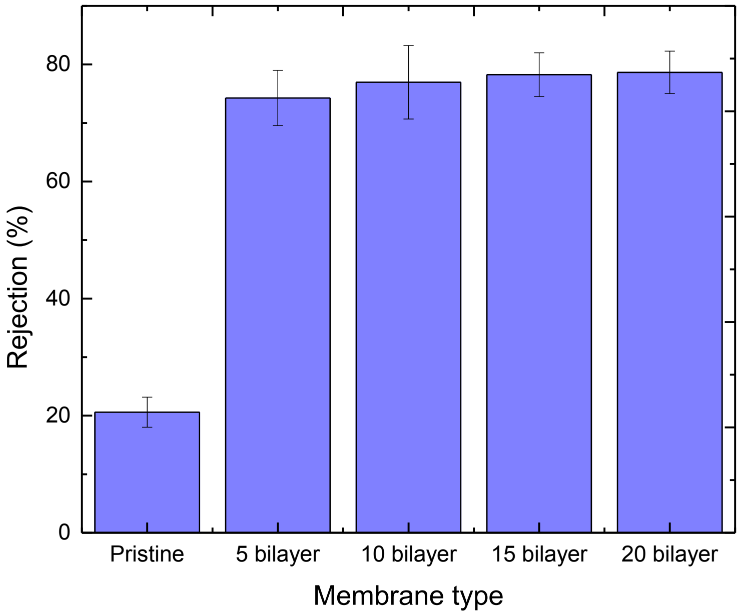

Figure 4.13: Comparison of selectivity (20KD PEG) of the pristine polysulfone membrane with the modified MWNT coated PSf membrane.

4.3.3 Removal of model organic compound by using MWNT conductive membrane in an electrofiltration system

The electrochemical filtration for organic matter degradation is defined by three primary steps: mass transfer, physical adsorption and the electron transfer mechanism [178]. The influent concentration of methyl orange is 14µM and the membrane was challenged with this concentration at a flow rate of 1.5 ml/min. The mass transfer of the influent and physical adsorption on the carbon nanotube surface is important for the oxidation of organic matter with the application of electrical potential (3V). For the different bilayer membrane the conductivity is different and thus the electron transfer rate is different. In this study the electrical potential was kept constant to visualize the effect of different bilayer membrane. The methyl orange degradation results are very promising and shown in figure 4.14. The pristine membrane shows 21% removal and the mechanism is only physical adsorption and sieving. Although the carbon nanotube concentration is very low for the 5 bilayer membranes but the organic matter removal becomes 98%. The membranes achieved 99% removal with the increase of bilayer. The results prove that the electron transfer at 3V was sufficient enough to achieve 98-99% removal. The electro-oxidation of methyl orange is explained by the direct oxidation as well as indirect oxidation depending on the anode potential[178]. The direct oxidation takes place when the physical adsorption of methyl orange on the CNT anode takes place and the rapid electron transfer accelerate oxidation as a function of anode potential.

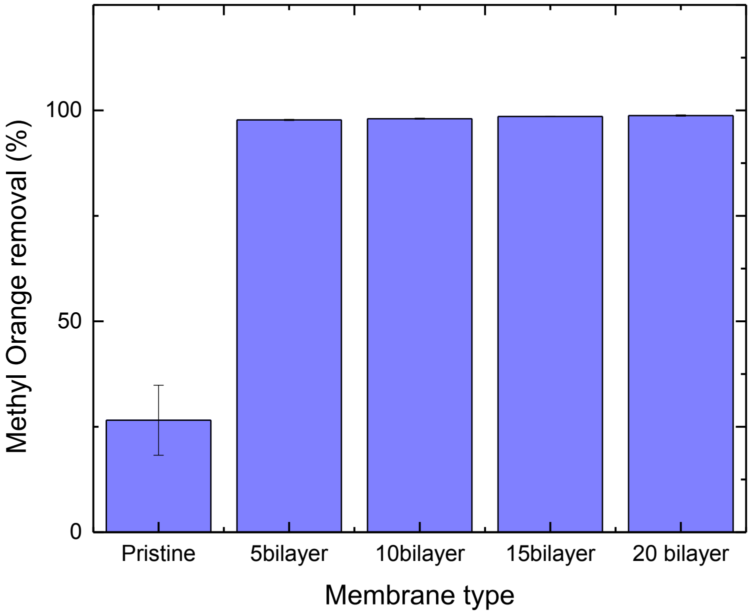

Figure 4.14: Removal of methyl orange through electrochemical filtration with hydrodynamic flow conditions

4.3.4 Inactivation of microorganisms (antimicrobial activity) of by using MWNT membrane in an electrofiltration cell

To examine the inactivation of microorganism with different applied potential the experiments has been done for one specific type of membrane. The 10 bilayer membrane has been used as control membrane as it shows consistent performance and the MWNT concentration is modest. The baseline loss of *E. coli* membrane integrity due to the MWNT toxicity was determined as 31.2%. The MWNT toxicity is due to its needle like structure that can rapture the cell membrane of microorganism and eventually inactivation and killing. The bacterial inactivation through electro-oxidation can also be explained as physical adsorption and oxidation of the microorganism cell membrane. As the anode potential increases to 1V, 2V and 3V the inactivation of *E. coli* also increases to 91.9%, 94.3% and 100%. These values indicate complete inactivation of the microorganism. Thus the results of this microbial inactivation are very significant and can reduce the biofouling tremendously which can be easily washed through tangential shearing during cross flow shearing.

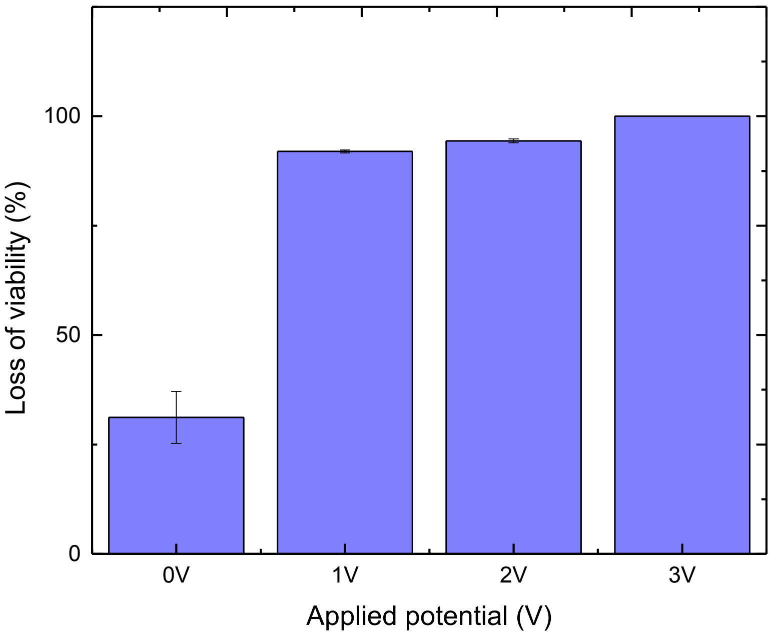

Figure 4.15: Electrochemical loss of *E. coli* viability versus applied potential

4.3.5 Stability of the MWNT LBL films under physical and chemical stresses

The stability of the LBL deposition was determined by physical (bath sonication) and chemical (low pH, high pH and salt concentration) stress test and the change in their contact angle was shown in figure 4.16. There is a slight increase in contact angle with the destructive physical test which can be caused by subsequent etching of the modified surface. There was no visible change in nanotube layer distortion though the physical stress is able to change the orientation of the top layer that leads to the higher hydrophobicity as well as increase in contact angle. There is no sharp decrease in contact angle for the chemical test and the chemical stress lowers the contact angle. At pH 2 the H^+ ions are able to decrease the charge density of the MWNT-COOH and the same effect is seem in pH 12 where OH^- ions can affect the charge density. For NaCl the contact angle became 82.9° from the control membrane having 102.9°. This effect can be explained by the dissociation of Na^+ and Cl^- ion that can combine with the MWNT-COOH and thus affecting the charge density of the charged MWNT-COOH layer. This result demonstrates insignificant changes under harsh chemicals and which is due to the charge distribution of the MWNT-COOH layer. Although the membrane shows slight increase and decrease but due to the higher value of hydrophobicity the results can be marked as stable and there is no possible mechanism of carbon nanotube dissociation on this stress tests.

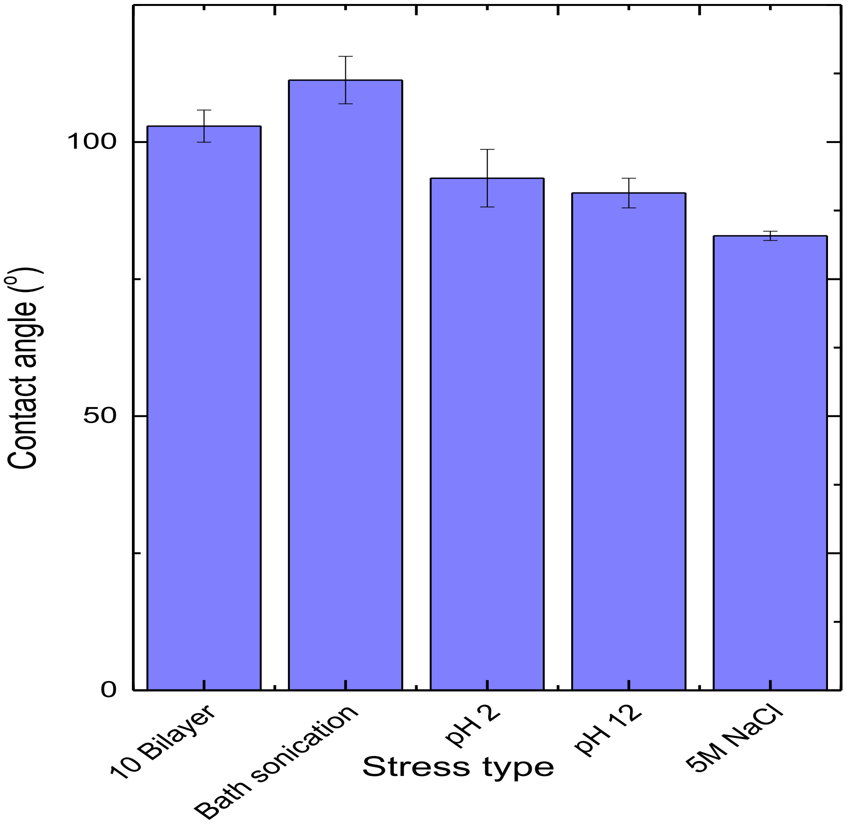

Figure 4.16: Contact angle after physical (Sonication) and chemical stress (pH 2, pH 12 and 5M NaCl)

5. CONCLUSIONS

By using the plasma treatment, polysulfone membrane was successfully functionalized with the oxygen containing functional groups and thus the wettability of the membrane was improved. Alongside with contact angle analyses that show improved wettability, several other analyses such as SEM, ATR-FTIR, XPS, EKA and permeability measurement confirmed the successful functionalization of polysulfone membrane. The contact angle analyses of plasma induced polysulfone membrane after EDC/NHS treatment has been found to be reduced and thus the membrane became more hydrophilic as well as stable amine reactive ester groups were created. After the membrane functionalization, the vacuum assisted layer by layer self assembly of MWNT-NH_2 and MWNT-COOH was used to generate desired number of MWNT bilayers. Characterization of the membrane surface showed highly hydrophobic membrane surface due to the inherent hydrophobicity of the carbon nanotubes. The thickness profile of different bilayer membrane presented linear behavior while the atomic layer deposition was difficult to ensure due to the high aspect ratio and orientation of the carbon nanotubes. The modified membrane surface exhibited excellent conductivity ($4.1\text{x } 10^3$ s/m), which is in the same order of magnitude of graphite. The conductivity showed slight increase with the increasing the number of bilayer as higher concentration of nanotube improves the electron transport network. The permeability trend of the modified membrane was slightly downward while the selectivity of the modified membrane has been improved significantly. The tradeoff between permeability and selectivity is well accepted fact for membrane industry as well as the membrane showed antifouling properties for long-term use. The developed membrane exhibits some unique properties to overcome the flux reduction (fouling) through high organic matter degradation and 100% bacterial inactivation aided with electrochemical filtration at very low electrical potential. The modified membrane was also found to be very stable against physical and chemical stresses. These results suggest the application of this modified conductive ultrafiltration membrane in a large scale water treatment plant will provide high quality product water (free of any pathogenic microorganisms).

6. RECOMMENDATIONS FOR FUTURE STUDIES

In this study plasma treatment has been used for the membrane functionalization as the plasma has the least impact on membrane bulk property, however there are many other methods such as physical adsorption by coating, graft polymerization etc. The effect of other type of surface modification technique is still to investigate for identifying the ultimate stability of the conductive layer. Moreover, additional characterization to determine the interaction between the membrane and nanomaterial as well as the each bilayer interaction can serve the optimization of the interaction forces. Due to the lab scale operation the effect of the permeability and rejection was only tested in a flow through dead end filtration setup. The influence of cross flow filtration system on longer term use and membrane stability under continuous flow mode need further study for scaling up this membrane application to commercial grade. The membrane was tested with controlled solution whereas in real life application the water may contain a variety of contaminants. Therefore further study should be performed to investigate the membrane performance by challenging with real source water rather than known concentration of contaminants.

BIBLOGRAPHY

[1] P. Gerland, A.E. Raftery, H. Ševčíková, N. Li, D. Gu, T. Spoorenberg, L. Alkema, B.K. Fosdick, J. Chunn, N. Lalic, G. Bay, T. Buettner, G.K. Heilig, J. Wilmoth, World population stabilization unlikely this century, Science, (2014).

[2] W.H. Organization, " Progress on Drinking-Water and Sanitation–2012 Update" launched on 6 March 2012, (2012).

[3] I.P.o.C.C. (IPCC), Climate Change 2014: Impacts, Adaptation, and Vulnerability, (2014).

[4] M.E. McClain, Balancing water resources development and environmental sustainability in Africa: a review of recent research findings and applications, Ambio, 42 (2013) 549-565.

[5] R.W. Baker, Membrane Technology and Applications, 2 ed., John Wiley & Sons, Ltd., 2004.

[6] K. Sunada, T. Watanabe, K. Hashimoto, Studies on photokilling of bacteria on TiO_2 thin film, Journal of Photochemistry and Photobiology A: Chemistry, 156 (2003) 227-233.

[7] T. Xu, C.S. Xie, Tetrapod-like nano-particle ZnO/acrylic resin composite and its multi-function property, Progress in Organic Coatings, 46 (2003) 297-301.

[8] Q. Li, S. Mahendra, D.Y. Lyon, L. Brunet, M.V. Liga, D. Li, P.J.J. Alvarez, Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications, Water Research, 42 (2008) 4591-4602.

[9] C. Dong, G. He, H. Li, R. Zhao, Y. Han, Y. Deng, Antifouling enhancement of poly(vinylidene fluoride) microfiltration membrane by adding Mg(OH)(2) nanoparticles, Journal of Membrane Science, 387 (2012) 40-47.

[10] A.S. Brady-Estevez, S. Kang, M. Elimelech, A single-walled-carbon-nanotube filter for removal of viral and bacterial pathogens, Small, 4 (2008) 481-484.

[11] A.S. Brady-Estevez, M.H. Schnoor, C.D. Vecitis, N.B. Saleh, M. Ehmelech, Multiwalled Carbon Nanotube Filter: Improving Viral Removal at Low Pressure, Langmuir, 26 (2010) 14975-14982.

[12] A.S. Brady-Estevez, M.H. Schnoor, S. Kang, M. Elimelech, SWNT-MWNT Hybrid Filter Attains High Viral Removal and Bacterial Inactivation, Langmuir, 26 (2010) 19153-19158.

[13] L. Yan, S. Hong, M.L. Li, Y.S. Li, Application of the Al2O3-PVDF nanocomposite tubular ultrafiltration (UF) membrane for oily wastewater treatment and its antifouling research, Separation and Purification Technology, 66 (2009) 347-352.

[14] S. Byun, S.H. Davies, A.L. Alpatova, L.M. Corneal, M.J. Baumann, V.V. Tarabara, S.J. Masten, Mn oxide coated catalytic membranes for a hybrid ozonation-membrane filtration: Comparison of Ti, Fe and Mn oxide coated membranes for water quality, Water Research, 45 (2011) 163-170.

[15] C.D. Vecitis, M.H. Schnoor, M.S. Rahaman, J.D. Schiffman, M. Elimelech, Electrochemical Multiwalled Carbon Nanotube Filter for Viral and Bacterial Removal and Inactivation, Environmental Science & Technology, 45 (2011) 3672-3679.

[16] M.S. Rahaman, C.D. Vecitis, M. Elimelech, Electrochemical Carbon-Nanotube Filter Performance toward Virus Removal and Inactivation in the Presence of Natural Organic Matter, Environmental Science & Technology, 46 (2012) 1556-1564.

[17] G. Gao, Q. Zhang, C.D. Vecitis, CNT–PVDF composite flow-through electrode for single-pass sequential reduction–oxidation, Journal of Materials Chemistry A, 2 (2014) 6185-6190.

[18] B.S. Karnik, S.H. Davies, M.J. Baumann, S.J. Masten, Fabrication of catalytic membranes for the treatment of drinking water using combined ozonation and ultrafiltration, Environmental Science & Technology, 39 (2005) 7656-7661.

[19] L.M. Corneal, M.J. Baumann, S.J. Masten, S.H.R. Davies, V.V. Tarabara, S. Byun, Mn oxide coated catalytic membranes for hybrid ozonation-membrane filtration: Membrane microstructural characterization, Journal of Membrane Science, 369 (2011) 182-187.

[20] B.S. Karnik, M.J. Baumann, S.J. Masten, S.H. Davies, AFM and SEM characterization of iron oxide coated ceramic membranes, Journal of Materials Science, 41 (2006) 6861-6870.

[21] M.M. Pendergast, E.M.V. Hoek, A review of water treatment membrane nanotechnologies, Energy & Environmental Science, 4 (2011) 1946-1971.

[22] S. Pourjafar, A. Rahimpour, M. Jahanshahi, Synthesis and characterization of PVA/PES thin film composite nanofiltration membrane modified with TiO2 nanoparticles for better performance and surface properties, Journal of Industrial and Engineering Chemistry, 18 (2012) 1398-1405.

[23] M.A. Smith, D.A. Ladner, Functionalized nanoparticles as removable membrane coatings, Abstracts of Papers of the American Chemical Society, 242 (2011).

[24] N.A. Kotov, Layer-by-layer self-assembly: The contribution of hydrophobic interactions, Nanostructured Materials, 12 (1999) 789-796.

[25] Y. Fu, S. Bai, S. Cui, D. Qiu, Z. Wang, X. Zhang, Hydrogen-Bonding-Directed Layer-by-Layer Multilayer Assembly: Reconformation Yielding Microporous Films, Macromolecules, 35 (2002) 9451-9458.
[26] B.-S. Kim, S.W. Park, P.T. Hammond, Hydrogen-Bonding Layer-by-Layer-Assembled Biodegradable Polymeric Micelles as Drug Delivery Vehicles from Surfaces, ACS Nano, 2 (2008) 386-392.
[27] S.A. Sukhishvili, Responsive polymer films and capsules via layer-by-layer assembly, Current Opinion in Colloid & Interface Science, 10 (2005) 37-44.
[28] J. Shen, Y. Hu, C. Qin, M. Ye, Layer-by-Layer Self-Assembly of Multiwalled Carbon Nanotube Polyelectrolytes Prepared by in Situ Radical Polymerization, Langmuir, 24 (2008) 3993-3997.
[29] R.C. Millward, C.E. Madden, I. Sutherland, R.J. Mortimer, S. Fletcher, F. Marken, Directed assembly of multilayers - the case of Prussian Blue, Chem. Commun., (2001) 1994-1995.
[30] K.J. McKenzie, F. Marken, M. Hyde, R.G. Compton, Nanoporous iron oxide membranes: layer-by-layer deposition and electrochemical characterisation of processes within nanopores, New J. Chem., 26 (2002) 625-629.
[31] Y. Lvov, B. Munge, O. Giraldo, I. Ichinose, S.L. Suib, J.F. Rusling, Films of manganese oxide nanoparticles with polycations or myoglobin from alternate-layer adsorption, Langmuir, 16 (2000) 8850-8857.
[32] L. Espinal, S.L. Suib, J.F. Rusling, Electrochemical catalysis of styrene epoxidation with films of MnO(2) nanoparticles and H(2)O(2), Journal of the American Chemical Society, 126 (2004) 7676-7682.
[33] J. Kim, A. Sotto, J. Chang, D. Nam, A. Boromand, B. Van der Bruggen, Embedding TiO2 nanoparticles versus surface coating by layer-by-layer deposition on nanoporous polymeric films, Microporous Mesoporous Mat., 173 (2013) 121-128.
[34] L. Liu, M. Son, H. Park, E. Celik, C. Bhattacharjee, H. Choi, Efficacy of CNT-bound polyelectrolyte membrane by spray-assisted layer-by-layer (LbL) technique on water purification, RSC Advances, 4 (2014) 32858-32865.
[35] X. Liu, S.R. Qi, Y. Li, L. Yang, B. Cao, C.Y.Y. Tang, Synthesis and characterization of novel antibacterial silver nanocomposite nanofiltration and forward osmosis membranes based on layer-by-layer assembly, Water Research, 47 (2013) 3081-3092.

[36] A. Wolz, S. Zils, M. Michel, C. Roth, Structured multilayered electrodes of proton/electron conducting polymer for polymer electrolyte membrane fuel cells assembled by spray coating, Journal of power sources, 195 (2010) 8162-8167.

[37] D.S. Liu, J.N. Ashcraft, M.M. Mannarino, M.N. Silberstein, A.A. Argun, G.C. Rutledge, M.C. Boyce, P.T. Hammond, Spray Layer-by-Layer Electrospun Composite Proton Exchange Membranes, Advanced Functional Materials, 23 (2013) 3087-3095.

[38] X. Zhao, B.T. Chu, B. Ballesteros, W. Wang, C. Johnston, J.M. Sykes, P.S. Grant, Spray deposition of steam treated and functionalized single-walled and multi-walled carbon nanotube films for supercapacitors, Nanotechnology, 20 (2009) 065605.

[39] F. Jiang, Y.K. Leong, M. Saunders, M. Martyniuk, L. Faraone, A. Keating, J.M. Dell, Uniform Dispersion of Lanthanum Hexaboride Nanoparticles in a Silica Thin Film: Synthesis and Optical Properties, Acs Applied Materials & Interfaces, 4 (2012) 5833-5838.

[40] R. Mahajan, R. Burns, M. Schaeffer, W.J. Koros, Challenges in forming successful mixed matrix membranes with rigid polymeric materials, Journal of Applied Polymer Science, 86 (2002) 881-890.

[41] J.-F. Li, Z.-L. Xu, H. Yang, L.-Y. Yu, M. Liu, Effect of TiO2 nanoparticles on the surface morphology and performance of microporous PES membrane, Applied Surface Science, 255 (2009) 4725-4732.

[42] E. Łukowska, Plasma techniques in polymeric treatment for membrane applications: a review, Biocybernetics and Biomedical Engineering, 30 (2010) 57-72.

[43] J. Maria Arsuaga, A. Sotto, G. del Rosario, A. Martinez, S. Molina, S.B. Teli, J. de Abajo, Influence of the type, size, and distribution of metal oxide particles on the properties of nanocomposite ultrafiltration membranes, Journal of Membrane Science, 428 (2013) 131-141.

[44] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li, The influence of nano-sized TiO2 fillers on the morphologies and properties of PSFUF membrane, Journal of Membrane Science, 288 (2007) 231-238.

[45] S. Ciston, R.M. Lueptow, K.A. Gray, Controlling biofilm growth using reactive ceramic ultrafiltration membranes, Journal of Membrane Science, 342 (2009) 263-268.

[46] S. Ciston, R.M. Lueptow, K.A. Gray, Bacterial attachment on reactive ceramic ultrafiltration membranes, Journal of Membrane Science, 320 (2008) 101-107.

[47] M.R. Wiesner, J.-Y. Bottero, Environmental nanotechnology, Applications and Impacts of Nanomaterials, (2007).

[48] X. Cao, J. Ma, X. Shi, Z. Ren, Effect of TiO2 nanoparticle size on the performance of PVDF membrane, Applied Surface Science, 253 (2006) 2003-2010.

[49] T.W. Ebbesen, H.J. Lezec, H. Hiura, J.W. Bennett, H.F. Ghaemi, T. Thio, Electrical conductivity of individual carbon nanotubes, Nature, 382 (1996) 54-56.

[50] C.F. de Lannoy, D. Jassby, D.D. Davis, M.R. Wiesner, A highly electrically conductive polymer-multiwalled carbon nanotube nanocomposite membrane, Journal of Membrane Science, 415 (2012) 718-724.

[51] C.-F. de Lannoy, D. Jassby, K. Gloe, A.D. Gordon, M.R. Wiesner, Aquatic Biofouling Prevention by Electrically Charged Nanocomposite Polymer Thin Film Membranes, Environmental Science & Technology, 47 (2013) 2760-2768.

[52] Y.-P. Sun, K. Fu, Y. Lin, W. Huang, Functionalized carbon nanotubes: properties and applications, Accounts of Chemical Research, 35 (2002) 1096-1104.

[53] M. Hu, B. Mi, Enabling Graphene Oxide Nanosheets as Water Separation Membranes, Environmental Science & Technology, 47 (2013) 3715-3723.

[54] F. Ma, N. Yuan, J. Ding, The conductive network made up by the reduced graphene nanosheet/polyaniline/polyvinyl chloride, Journal of Applied Polymer Science, 128 (2013) 3870-3875.

[55] K.A. DeFriend, M.R. Wiesner, A.R. Barron, Alumina and aluminate ultrafiltration membranes derived from alumina nanoparticles, Journal of Membrane Science, 224 (2003) 11-28.

[56] M.M. Cortalezzi, J. Rose, A.R. Barron, M.R. Wiesner, Characteristics of ultrafiltration ceramic membranes derived from alumoxane nanoparticles, Journal of Membrane Science, 205 (2002) 33-43.

[57] S.L. Yu, W.X. Shi, Y. Lu, J.X. Yang, Characterization and anti-fouling performance of nano-Al2O3/PVDF membrane for Songhua River raw water filtration, Water Science and Technology, 64 (2011) 1892-1897.

[58] L. Yan, Y.S. Li, C.B. Xiang, S. Xianda, Effect of nano-sized Al2O3-particle addition on PVDF ultratiltration membrane performance, Journal of Membrane Science, 276 (2006) 162-167.

[59] L. Yan, Y.S. Li, C.B. Xiang, Preparation of poly(vinylidene fluoride)(pvdf) ultrafiltration membrane modified by nano-sized alumina (Al2O3) and its antifouling research, Polymer, 46 (2005) 7701-7706.

[60] Q. Yang, H.H. Himstedt, M. Ulbricht, X. Qian, S.R. Wickramasinghe, Designing magnetic field responsive nanofiltration membranes, Journal of Membrane Science, 430 (2013) 70-78.

[61] I. Raciny, K.R. Zodrow, D. Li, Q. Li, P.J.J. Alvarez, Addition of a magnetite layer onto a polysulfone water treatment membrane to enhance virus removal, Water Science and Technology, 63 (2011) 2346-2352.

[62] S. Balta, A. Sotto, P. Luis, L. Benea, B. Van der Bruggen, J. Kim, A new outlook on membrane enhancement with nanoparticles: The alternative of ZnO, Journal of Membrane Science, 389 (2012) 155-161.

[63] C.P. Leo, W.P.C. Lee, A.L. Ahmad, A.W. Mohammad, Polysulfone membranes blended with ZnO nanoparticles for reducing fouling by oleic acid, Separation and Purification Technology, 89 (2012) 51-56.

[64] S. Liang, K. Xiao, Y. Mo, X. Huang, A novel ZnO nanoparticle blended polyvinylidene fluoride membrane for anti-irreversible fouling, Journal of Membrane Science, 394 (2012) 184-192.

[65] J.-H. Li, X.-S. Shao, Q. Zhou, M.-Z. Li, Q.-Q. Zhang, The double effects of silver nanoparticles on the PVDF membrane: Surface hydrophilicity and antifouling performance, Applied Surface Science, 265 (2013) 663-670.

[66] A. Mollahosseini, A. Rahimpour, M. Jahamshahi, M. Peyravi, M. Khavarpour, The effect of silver nanoparticle size on performance and antibacteriality of polysulfone ultrafiltration membrane, Desalination, 306 (2012) 41-50.

[67] H. Basri, A.F. Ismail, M. Aziz, K. Nagai, T. Matsuura, M.S. Abdullah, B.C. Ng, Silver-filled polyethersulfone membranes for antibacterial applications - Effect of PVP and TAP addition on silver dispersion, Desalination, 261 (2010) 264-271.

[68] J.C. Mierzwa, V. Arieta, M. Verlage, J. Carvalho, C.D. Vecitis, Effect of clay nanoparticles on the structure and performance of polyethersulfone ultrafiltration membranes, Desalination, 314 (2013) 147-158.

[69] R. Saranya, G. Arthanareeswaran, S. Sakthivelu, P. Manohar, Preparation and Performance Evaluation of Nanokaolinite-Particle-Based Polyacrylonitrile Mixed-Matrix Membranes, Industrial & Engineering Chemistry Research, 51 (2012) 4942-4951.
[70] C.P. Leo, N.H.A. Kamil, M.U.M. Junaidi, S.N.M. Kamal, A.L. Ahmad, The potential of SAPO-44 zeolite filler in fouling mitigation of polysulfone ultrafiltration membrane, Separation and Purification Technology, 103 (2013) 84-91.
[71] T.-S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, Progress in Polymer Science, 32 (2007) 483-507.
[72] P.S. Goh, A.F. Ismail, S.M. Sanip, B.C. Ng, M. Aziz, Recent advances of inorganic fillers in mixed matrix membrane for gas separation, Separation and Purification Technology, 81 (2011) 243-264.
[73] G.J. Dahe, R.S. Teotia, J.R. Bellare, The role of zeolite nanoparticles additive on morphology, mechanical properties and performance of polysulfone hollow fiber membranes, Chemical Engineering Journal, 197 (2012) 398-406.
[74] R. Han, S. Zhang, C. Liu, Y. Wang, X. Jian, Effect of NaA zeolite particle addition on poly(phthalazinone ether sulfone ketone) composite ultrafiltration (UF) membrane performance, Journal of Membrane Science, 345 (2009) 5-12.
[75] H.H. Himstedt, K.M. Marshall, S.R. Wickramasinghe, pH-responsive nanofiltration membranes by surface modification, Journal of Membrane Science, 366 (2011) 373-381.
[76] V. Vatanpour, S.S. Madaeni, R. Moradian, S. Zinadini, B. Astinchap, Novel antibifouling nanofiltration polyethersulfone membrane fabricated from embedding TiO2 coated multiwalled carbon nanotubes, Separation and Purification Technology, 90 (2012) 69-82.
[77] V. Vatanpour, S.S. Madaeni, R. Moradian, S. Zinadini, B. Astinchap, Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite, Journal of Membrane Science, 375 (2011) 284-294.
[78] A. Razmjou, J. Mansouri, V. Chen, The effects of mechanical and chemical modification of TiO2 nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes, Journal of Membrane Science, 378 (2011) 73-84.

[79] P. Daraei, S.S. Madaeni, N. Ghaemi, E. Salehi, M.A. Khadivi, R. Moradian, B. Astinchap, Novel polyethersulfone nanocomposite membrane prepared by PANI/Fe3O4 nanoparticles with enhanced performance for Cu(II) removal from water, Journal of Membrane Science, 415 (2012) 250-259.

[80] S.J. Oh, N. Kim, Y.T. Lee, Preparation and characterization of PVDF/TiO2 organic-inorganic composite membranes for fouling resistance improvement, Journal of Membrane Science, 345 (2009) 13-20.

[81] J.H. Kim, K.H. Lee, Effect of PEG additive on membrane formation by phase inversion, Journal of Membrane Science, 138 (1998) 153-163.

[82] C.M. Zimmerman, A. Singh, W.J. Koros, Tailoring mixed matrix composite membranes for gas separations, Journal of Membrane Science, 137 (1997) 145-154.

[83] R. Abedini, S.M. Mousavi, R. Aminzadeh, A novel cellulose acetate (CA) membrane using TiO2 nanoparticles: Preparation, characterization and permeation study, Desalination, 277 (2011) 40-45.

[84] A. Sotto, A. Boromand, S. Balta, J. Kim, B. Van der Bruggen, Doping of polyethersulfone nanofiltration membranes: antifouling effect observed at ultralow concentrations of TiO2 nanoparticles, Journal of Materials Chemistry, 21 (2011) 10311-10320.

[85] H. Wu, B. Tang, P. Wu, Novel ultrafiltration membranes prepared from a multi-walled carbon nanotubes/polymer composite, Journal of Membrane Science, 362 (2010) 374-383.

[86] A. Rahimpour, M. Jahanshahi, B. Rajaeian, M. Rahimnejad, TiO2 entrapped nano-composite PVDF/SPES membranes: Preparation, characterization, antifouling and antibacterial properties, Desalination, 278 (2011) 343-353.

[87] K. Zodrow, L. Brunet, S. Mahendra, D. Li, A. Zhang, Q. Li, P.J.J. Alvarez, Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal, Water Research, 43 (2009) 715-723.

[88] M.Z. Rong, M.Q. Zhang, W.H. Ruan, Surface modification of nanoscale fillers for improving properties of polymer nanocomposites: a review, Mater. Sci. Technol., 22 (2006) 787-796.

[89] J.W. Kim, H.S. Choi, Surface crosslinking of high-density polyethylene beads in a modified plasma reactor, Journal of Applied Polymer Science, 83 (2002) 2921-2929.

[90] R. Landgraf, M.K. Kaiser, J. Posseckardt, B. Adolphi, W.J. Fischer, Functionalization of Polymer Sensor Surfaces by Oxygen Plasma Treatment, Procedia Chemistry, 1 (2009) 1015-1018.

[91] P. Favia, R. d'Agostino, F. Palumbo, Grafting of chemical groups onto polymers by means of RF plasma treatments: a technology for biomedical applications, Le Journal de Physique IV, 7 (1997) C4-199-C194-208.

[92] I. Gancarz, G. Poźniak, M. Bryjak, A. Frankiewicz, Modification of polysulfone membranes. 2. Plasma grafting and plasma polymerization of acrylic acid, Acta polymerica, 50 (1999) 317-326.

[93] V. Chirila, G. Marginean, W. Brandl, Effect of the oxygen plasma treatment parameters on the carbon nanotubes surface properties, Surface and Coatings Technology, 200 (2005) 548-551.

[94] M. Bryjak, I. Gancarz, Membrane Prepared via Plasma Modification, in: Membranes for Membrane Reactors, John Wiley & Sons, Ltd, 2011, pp. 549-568.

[95] M. Nyström, P. Järvinen, Modification of polysulfone ultrafiltration membranes with UV irradiation and hydrophilicity increasing agents, Journal of membrane science, 60 (1987) 275-296.

[96] K. Kim, K. Lee, K. Cho, C. Park, Surface modification of polysulfone ultrafiltration membrane by oxygen plasma treatment, Journal of Membrane Science, 199 (2002) 135-145.

[97] I. Gancarz, G. Poźniak, M. Bryjak, Modification of polysulfone membranes 1. CO2 plasma treatment, European Polymer Journal, 35 (1999) 1419-1428.

[98] M.L. Steen, A.C. Jordan, E.R. Fisher, Hydrophilic modification of polymeric membranes by low temperature H< sub> 2</sub> O plasma treatment, Journal of membrane science, 204 (2002) 341-357.

[99] D.S. Wavhal, E.R. Fisher, Hydrophilic modification of polyethersulfone membranes by low temperature plasma-induced graft polymerization, Journal of Membrane Science, 209 (2002) 255-269.

[100] S. Liang, Y. Kang, A. Tiraferri, E.P. Giannelis, X. Huang, M. Elimelech, Highly Hydrophilic Polyvinylidene Fluoride (PVDF) Ultrafiltration Membranes via Postfabrication Grafting of Surface-Tailored Silica Nanoparticles, ACS Applied Materials & Interfaces, 5 (2013) 6694-6703.

[101] M.R. Sanchis, V. Blanes, M. Blanes, D. Garcia, R. Balart, Surface modification of low density polyethylene (LDPE) film by low pressure O2 plasma treatment, European Polymer Journal, 42 (2006) 1558-1568.

[102] R. Foerch, G. Kill, M.J. Walzak, Plasma surface modification of polyethylene: short-term vs. long-term plasma treatment, Journal of Adhesion Science and Technology, 7 (1993) 1077-1089.

[103] R.K. Iler, Multilayers of colloidal particles, Journal of Colloid and Interface Science, 21 (1966) 569-594.

[104] G.B. Sukhorukov, E. Donath, H. Lichtenfeld, E. Knippel, M. Knippel, A. Budde, H. Möhwald, Layer-by-layer self assembly of polyelectrolytes on colloidal particles, Colloids and Surfaces A: physicochemical and engineering aspects, 137 (1998) 253-266.

[105] M.A.C. Stuart, W.T.S. Huck, J. Genzer, M. Muller, C. Ober, M. Stamm, G.B. Sukhorukov, I. Szleifer, V.V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, Emerging applications of stimuli-responsive polymer materials, Nat Mater, 9 (2010) 101-113.

[106] P.M. Nguyen, N.S. Zacharia, E. Verploegen, P.T. Hammond, Extended release antibacterial layer-by-layer films incorporating linear-dendritic block copolymer micelles, Chemistry of Materials, 19 (2007) 5524-5530.

[107] M.J. Serpe, C.D. Jones, L.A. Lyon, Layer-by-layer deposition of thermoresponsive microgel thin films, Langmuir, 19 (2003) 8759-8764.

[108] H. Ai, M. Fang, S.A. Jones, Y.M. Lvov, Electrostatic layer-by-layer nanoassembly on biological microtemplates: platelets, Biomacromolecules, 3 (2002) 560-564.

[109] P. Podsiadlo, S.-Y. Choi, B. Shim, J. Lee, M. Cuddihy, N.A. Kotov, Molecularly engineered nanocomposites: layer-by-layer assembly of cellulose nanocrystals, Biomacromolecules, 6 (2005) 2914-2918.

[110] H. Krass, G. Papastavrou, D.G. Kurth, Layer-by-layer self-assembly of a polyelectrolyte bearing metal ion coordination and electrostatic functionality, Chemistry of materials, 15 (2003) 196-203.

[111] W.B. Stockton, M.F. Rubner, Molecular-Level Processing of Conjugated Polymers. 4. Layer-by-Layer Manipulation of Polyaniline via Hydrogen-Bonding Interactions, Macromolecules, 30 (1997) 2717-2725.

[112] F. Wang, N. Ma, Q. Chen, W. Wang, L. Wang, Halogen bonding as a new driving force for layer-by-layer assembly, Langmuir, 23 (2007) 9540-9542.

[113] Y. Shimazaki, M. Mitsuishi, S. Ito, M. Yamamoto, Preparation and characterization of the layer-by-layer deposited ultrathin film based on the charge-transfer interaction in organic solvents, Langmuir, 14 (1998) 2768-2773.

[114] Y. Lvov, K. Ariga, I. Ichinose, T. Kunitake, Layer-by-layer architectures of concanavalin A by means of electrostatic and biospecific interactions, Journal of the Chemical Society, Chemical Communications, (1995) 2313-2314.

[115] O. Crespo-Biel, B. Dordi, D.N. Reinhoudt, J. Huskens, Supramolecular layer-by-layer assembly: alternating adsorptions of guest-and host-functionalized molecules and particles using multivalent supramolecular interactions, Journal of the American Chemical Society, 127 (2005) 7594-7600.

[116] Y. Ogawa, Y. Arikawa, T. Kida, M. Akashi, Fabrication of Novel Layer-by-Layer Assembly Films Composed of Poly (lactic acid) and Polylysine through Cation− Dipole Interactions, Langmuir, 24 (2008) 8606-8609.

[117] Y. Li, X. Wang, J. Sun, Layer-by-layer assembly for rapid fabrication of thick polymeric films, Chemical Society Reviews, 41 (2012) 5998-6009.

[118] X. Peng, J. Jin, E.M. Ericsson, I. Ichinose, General Method for Ultrathin Free-Standing Films of Nanofibrous Composite Materials, Journal of the American Chemical Society, 129 (2007) 8625-8633.

[119] Q. Chen, P. Liu, F. Nan, L. Zhou, J. Zhang, Tuning the Iridescence of Chiral Nematic Cellulose Nanocrystal Films with a Vacuum-Assisted Self-Assembly Technique, Biomacromolecules, 15 (2014) 4343-4350.

[120] Q. Chen, P. Liu, C. Sheng, L. Zhou, Y. Duan, J. Zhang, Tunable self-assembly structure of graphene oxide/cellulose nanocrystal hybrid films fabricated by vacuum filtration technique, RSC Advances, 4 (2014) 39301-39304.

[121] O.C. Compton, K.W. Putz, L.C. Brinson, S.T. Nguyen, Composite graphene oxide-polymer laminate and method, in, Google Patents, 2014.

[122] J. Liu, I.A. Aksay, D. Choi, R. Kou, Z. Nie, D. Wang, Z. Yang, Self assembled multi-layer nanocomposite of graphene and metal oxide materials, in, Google Patents, 2013.

[123] M.N. Hyder, R. Kavian, Z. Sultana, K. Saetia, P.-Y. Chen, S.W. Lee, Y. Shao-Horn, P.T. Hammond, Vacuum-Assisted Layer-by-Layer Nanocomposites for Self-Standing 3D Mesoporous Electrodes, Chemistry of Materials, 26 (2014) 5310-5318.

[124] A. Tiraferri, Y. Kang, E.P. Giannelis, M. Elimelech, Highly Hydrophilic Thin-Film Composite Forward Osmosis Membranes Functionalized with Surface-Tailored Nanoparticles, Acs Applied Materials & Interfaces, 4 (2012) 5044-5053.

[125] R. Malaisamy, D. Berry, D. Holder, L. Raskin, L. Lepak, K.L. Jones, Development of reactive thin film polymer brush membranes to prevent biofouling, Journal of Membrane Science, 350 (2010) 361-370.

[126] A. Tiraferri, C.D. Vecitis, M. Elimelech, Covalent Binding of Single-Walled Carbon Nanotubes to Polyamide Membranes for Antimicrobial Surface Properties, Acs Applied Materials & Interfaces, 3 (2011) 2869-2877.

[127] H. Therien-Aubin, L. Chen, C.K. Ober, Fouling-resistant polymer brush coatings, Polymer, 52 (2011) 5419-5425.

[128] L. Chaves Simoes, M. Simoes, Biofilms in drinking water: problems and solutions, RSC Advances, 3 (2013) 2520-2533.

[129] M.S. Mauter, Y. Wang, K.C. Okemgbo, C.O. Osuji, E.P. Giannelis, M. Elimelech, Antifouling Ultrafiltration Membranes via Post-Fabrication Grafting of Biocidal Nanomaterials, Acs Applied Materials & Interfaces, 3 (2011) 2861-2868.

[130] L.Y. Ng, A.W. Mohammad, C.P. Leo, N. Hilal, Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review, Desalination, 308 (2013) 15-33.

[131] S. Kang, M. Pinault, L.D. Pfefferle, M. Elimelech, Single-Walled Carbon Nanotubes Exhibit Strong Antimicrobial Activity, Langmuir, 23 (2007) 8670-8673.

[132] F. Zhao, F. Qiu, X. Zhang, S. Yu, H.-S. Kim, H.-D. Park, S. Takizawa, P. Wang, Preparation of single-walled carbon nanotubes/polyvinylchloride membrane and its antibacterial property, Water Science & Technology, 66 (2012) 2275-2283.

[133] S. Kang, M. Herzberg, D.F. Rodrigues, M. Elimelech, Antibacterial Effects of Carbon Nanotubes: Size Does Matter!, Langmuir, 24 (2008) 6409-6413.

[134] W. Hu, C. Peng, W. Luo, M. Lv, X. Li, D. Li, Q. Huang, C. Fan, Graphene-Based Antibacterial Paper, ACS Nano, 4 (2010) 4317-4323.

[135] J. Lee, H.-R. Chae, Y.J. Won, K. Lee, C.-H. Lee, H.H. Lee, I.-C. Kim, J.-m. Lee, Graphene oxide nanoplatelets composite membrane with hydrophilic and antifouling properties for wastewater treatment, Journal of Membrane Science, 448 (2013) 223-230.

[136] J. Zhang, Z. Xu, M. Shan, B. Zhou, Y. Li, B. Li, J. Niu, X. Qian, Synergetic effects of oxidized carbon nanotubes and graphene oxide on fouling control and anti-fouling mechanism of polyvinylidene fluoride ultrafiltration membranes, Journal of Membrane Science, 448 (2013) 81-92.

[137] L. Qi, Z. Xu, X. Jiang, C. Hu, X. Zou, Preparation and antibacterial activity of chitosan nanoparticles, Carbohydrate Research, 339 (2004) 2693-2700.

[138] J. Castillo-León, R. Rodriguez-Trujillo, S. Gauthier, A.C.Ø. Jensen, W.E. Svendsen, Micro-“factory” for self-assembled peptide nanostructures, Microelectronic Engineering, 88 (2011) 1685-1688.

[139] E. Gazit, Self-assembled peptide nanostructures: the design of molecular building blocks and their technological utilization, Chemical Society Reviews, 36 (2007) 1263-1269.

[140] Y. Feng, W. Xia, Preparation, characterization and antibacterial activity of water-soluble O-fumaryl-chitosan, Carbohydrate Polymers, 83 (2011) 1169-1173.

[141] A. Cooper, R. Oldinski, H. Ma, J.D. Bryers, M. Zhang, Chitosan-based nanofibrous membranes for antibacterial filter applications, Carbohydrate Polymers, 92 (2013) 254-259.

[142] C. Lee, J.Y. Kim, W.I. Lee, K.L. Nelson, J. Yoon, D.L. Sedlak, Bactericidal effect of zero-valent iron nanoparticles on Escherichia coli, Environmental science & technology, 42 (2008) 4927-4933.

[143] S.A. Mahdy, Q.J. Raheed, P. Kalaichelvan, Antimicrobial Activity of Zero-Valent Iron Nanoparticles, International Journal of Modern Engineering Research, 2 (2012) 578-581.

[144] C.X. Liu, D.R. Zhang, Y. He, X.S. Zhao, R.B. Bai, Modification of membrane surface for anti-biofouling performance: Effect of anti-adhesion and anti-bacteria approaches, Journal of Membrane Science, 346 (2010) 121-130.

[145] E. Erdim, E. Soyer, S. Tasiyici, I. Koyuncu, Hybrid photocatalysis/submerged microfiltration membrane system for drinking water treatment, Desalination and Water Treatment, 9 (2009) 165-174.

[146] H.W. Bai, L. Liu, Z.Y. Liu, D.D. Sun, Hierarchical 3D dendritic TiO2 nanospheres building with ultralong 1D nanoribbon/wires for high performance concurrent photocatalytic membrane water purification, Water Research, 47 (2013) 4126-4138.
[147] C. Pulgarin, J. Kiwi, V. Nadtochenko, Mechanism of photocatalytic bacterial inactivation on TiO2 films involving cell-wall damage and lysis, Applied Catalysis B-Environmental, 128 (2012) 179-183.
[148] R.A. Damodar, S.-J. You, H.-H. Chou, Study the self cleaning, antibacterial and photocatalytic properties of TiO2 entrapped PVDF membranes, Journal of Hazardous Materials, 172 (2009) 1321-1328.
[149] Y. Kikuchi, K. Sunada, T. Iyoda, K. Hashimoto, A. Fujishima, Photocatalytic bactericidal effect of TiO2 thin films: Dynamic view of the active oxygen species responsible for the effect, Journal of Photochemistry and Photobiology A: Chemistry, 106 (1997) 51-56.
[150] A. Zielinska, E. Kowalska, J.W. Sobczak, I. Lacka, M. Gazda, B. Ohtani, J. Hupka, A. Zaleska, Silver-doped TiO2 prepared by microemulsion method: Surface properties, bio- and photoactivity, Separation and Purification Technology, 72 (2010) 309-318.
[151] A. Rahimpour, M. Jahanshahi, A. Mollahosseini, B. Rajaeian, Structural and performance properties of UV-assisted TiO2 deposited nano-composite PVDF/SPES membranes, Desalination, 285 (2012) 31-38.
[152] X. Huang, M. Leal, Q. Li, Degradation of natural organic matter by TiO2 photocatalytic oxidation and its effect on fouling of low-pressure membranes, Water Research, 42 (2008) 1142-1150.
[153] V. Likodimos, D.D. Dionysiou, P. Falaras, CLEAN WATER: water detoxification using innovative photocatalysts, Reviews in Environmental Science and Bio-Technology, 9 (2010) 87-94.
[154] K. Dai, Z. Chen, L.H. Lu, G.P. Zhu, Z.L. Liu, Q.Z. Liu, Superhydrophilic zinc oxide film prepared by controlling ZnO microrods growth and its attractive recyclable photocatalytic performance, Thin Solid Films, 539 (2013) 23-28.
[155] Y. Mansourpanah, S.S. Madaeni, A. Rahimpour, A. Farhadian, A.H. Taheri, Formation of appropriate sites on nanofiltration membrane surface for binding TiO2 photo-catalyst: Performance, characterization and fouling-resistant capability, Journal of Membrane Science, 330 (2009) 297-306.

[156] J. Sawai, S. Shoji, H. Igarashi, A. Hashimoto, T. Kokugan, M. Shimizu, H. Kojima, Hydrogen peroxide as an antibacterial factor in zinc oxide powder slurry, Journal of Fermentation and Bioengineering, 86 (1998) 521-522.

[157] R. Brayner, R. Ferrari-Iliou, N. Brivois, S. Djediat, M.F. Benedetti, F. Fiévet, Toxicological Impact Studies Based on Escherichia coli Bacteria in Ultrafine ZnO Nanoparticles Colloidal Medium, Nano Letters, 6 (2006) 866-870.

[158] H. Bai, Z. liu, D.D. Sun, Hierarchical ZnO nanostructured membrane for multifunctional environmental applications, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 410 (2012) 11-17.

[159] S.R. Chae, E.M. Hotze, A.R. Badireddy, S. Lin, J.O. Kim, M.R. Wiesner, Environmental implications and applications of carbon nanomaterials in water treatment, Water Science and Technology, 67 (2013) 2582-2586.

[160] P. Lei, F. Wang, X.W. Gao, Y.F. Ding, S.M. Zhang, J.C. Zhao, S.R. Liu, M.S. Yang, Immobilization of TiO2 nanoparticles in polymeric substrates by chemical bonding for multi-cycle photodegradation of organic pollutants, Journal of Hazardous Materials, 227 (2012) 185-194.

[161] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: A review, Water Research, 44 (2010) 2997-3027.

[162] D. Wandera, S.R. Wickramasinghe, S.M. Husson, Stimuli-responsive membranes, Journal of Membrane Science, 357 (2010) 6-35.

[163] Z. Liu, F. Luo, X.-J. Ju, R. Xie, Y.-M. Sun, W. Wang, L.-Y. Chu, Gating Membranes for Water Treatment: Detection and Removal of Trace Pb2+ Ions Based on Molecular Recognition and Polymer Phase Transition, J. Mater. Chem. A, (2013).

[164] A. Shvedova, V. Castranova, E. Kisin, D. Schwegler-Berry, A. Murray, V. Gandelsman, A. Maynard, P. Baron, Exposure to carbon nanotube material: assessment of nanotube cytotoxicity using human keratinocyte cells, Journal of Toxicology and Environmental Health Part A, 66 (2003) 1909-1926.

[165] A.R. Murray, E. Kisin, S.S. Leonard, S.H. Young, C. Kommineni, V.E. Kagan, V. Castranova, A.A. Shvedova, Oxidative stress and inflammatory response in dermal toxicity of single-walled carbon nanotubes, Toxicology, 257 (2009) 161-171.

[166] P. Wu, S.-S. Yuan, C.-C. Ho, W.-Y. Hsieh, Q.-S. Hong, S.-L. Yu, W. Chen, H.-Y. Chen, C.-D. Wang, K.-C. Li, P.-C. Yang, H.-W. Chen, Focal Amplification of HOXD-Harboring Chromosome Region Is Implicated in Multiple-Walled Carbon Nanotubes-Induced Carcinogenicity, Nano Letters, 13 (2013) 4632-4641.

[167] A. Magrez, S. Kasas, V. Salicio, N. Pasquier, J.W. Seo, M. Celio, S. Catsicas, B. Schwaller, L. Forró, Cellular Toxicity of Carbon-Based Nanomaterials, Nano Letters, 6 (2006) 1121-1125.

[168] K.-H. Liao, Y.-S. Lin, C.W. Macosko, C.L. Haynes, Cytotoxicity of Graphene Oxide and Graphene in Human Erythrocytes and Skin Fibroblasts, ACS Applied Materials & Interfaces, 3 (2011) 2607-2615.

[169] G. Hartung, G. Mansoori, In vivo General Trends, Filtration and Toxicity of Nanoparticles. J Nanomater Mol Nanotechnol 2: 3, of, 21 (2013) 17-22.

[170] F. Ahmed, C.M. Santos, J. Mangadlao, R. Advincula, D.F. Rodrigues, Antimicrobial PVK:SWNT nanocomposite coated membrane for water purification: Performance and toxicity testing, Water Research, 47 (2013) 3966-3975.

[171] M.Z. Rong, M.Q. Zhang, Y.X. Zheng, H.M. Zeng, R. Walter, K. Friedrich, Structure-property relationships of irradiation grafted nano-inorganic particle filled polypropylene composites, Polymer, 42 (2001) 167-183.

[172] Y. Lin, M.J. Meziani, Y.-P. Sun, Functionalized carbon nanotubes for polymeric nanocomposites, Journal of Materials Chemistry, 17 (2007) 1143-1148.

[173] L. Brunet, D.Y. Lyon, K. Zodrow, J.C. Rouch, B. Caussat, P. Serp, J.C. Remigy, M.R. Wiesner, P.J.J. Alvarez, Properties of membranes containing semi-dispersed carbon nanotubes, Environmental Engineering Science, 25 (2008) 565-575.

[174] M. Ben-Sasson, K.R. Zodrow, Q. Genggeng, Y. Kang, E.P. Giannelis, M. Elimelech, Surface functionalization of thin-film composite membranes with copper nanoparticles for antimicrobial surface properties, Environ Sci Technol, 48 (2014) 384-393.

[175] S. Modarresi, M. Soltanieh, S.A. Mousavi, I. Shabani, Effect of low-frequency oxygen plasma on polysulfone membranes for CO2/CH4 Separation, Journal of Applied Polymer Science, 124 (2012) E199-E204.

[176] F. Perreault, M.E. Tousley, M. Elimelech, Thin-Film Composite Polyamide Membranes Functionalized with Biocidal Graphene Oxide Nanosheets, Environmental Science & Technology Letters, 1 (2013) 71-76.

[177] A. Mehta, A.L. Zydney, Permeability and selectivity analysis for ultrafiltration membranes, Journal of Membrane Science, 249 (2005) 245-249.

[178] H. Liu, C.D. Vecitis, Reactive Transport Mechanism for Organic Oxidation during Electrochemical Filtration: Mass-Transfer, Physical Adsorption, and Electron-Transfer, Journal of Physical Chemistry C, 116 (2012) 374-383.

[179] A.A. Fridman, Plasma Chemistry, Cambridge University Press, (1998) p 978.

[180] F.N. Muya, L. Phelane, P.G. Baker, E.I. Iwuoha, Synthesis and Characterization of Polysulfone Hydrogels, Journal of Surface Engineered Materials and Advanced Technology, 2014 (2014).

[181] K.M. Persson, V. Gekas, G. Trägårdh, Study of membrane compaction and its influence on ultrafiltration water permeability, Journal of Membrane Science, 100 (1995) 155-162.

[182] I.H. Huisman, P. Prádanos, A. Hernández, The effect of protein–protein and protein–membrane interactions on membrane fouling in ultrafiltration, Journal of Membrane Science, 179 (2000) 79-90.