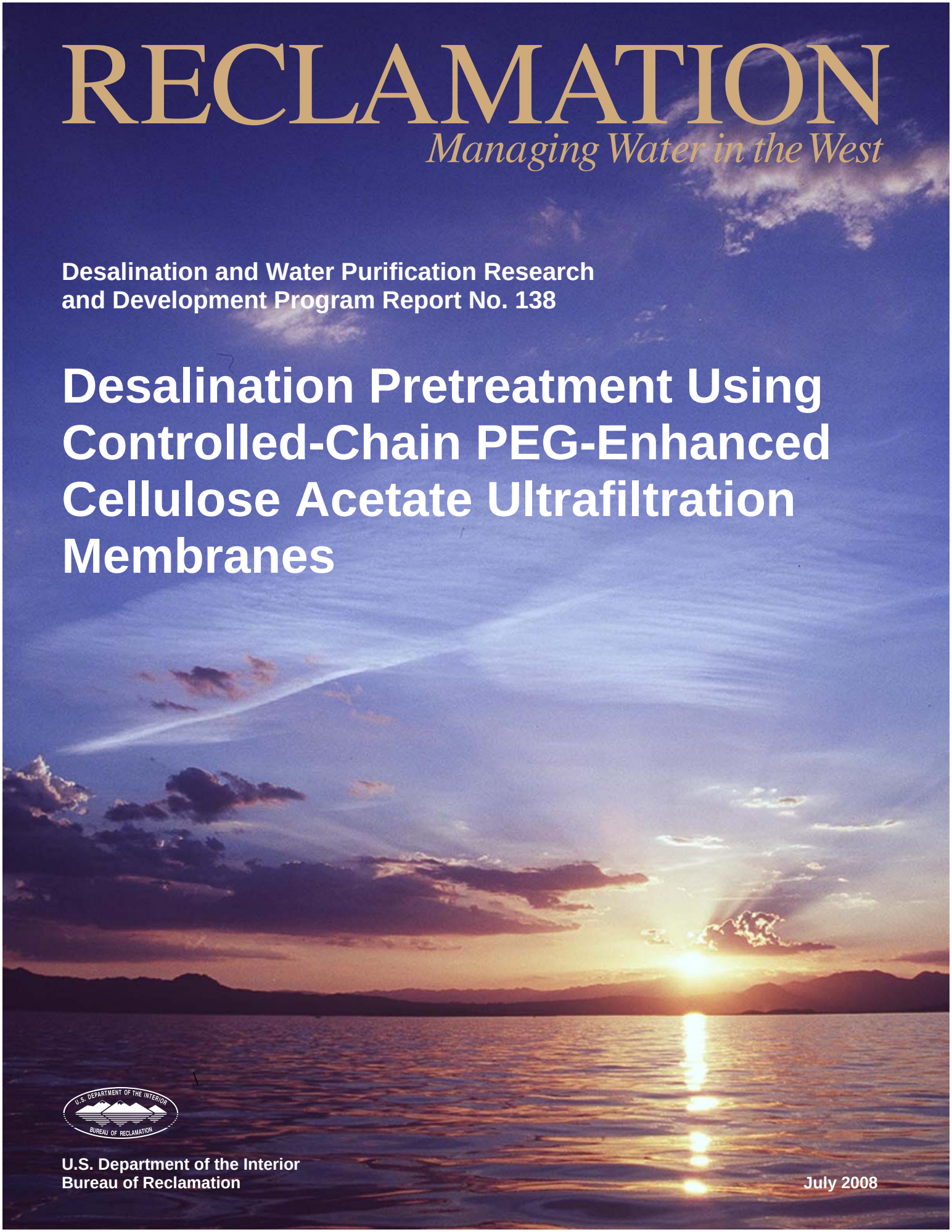

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Managing Water in the West

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Desalination Pretreatment Using Controlled-Chain PEG-Enhanced Cellulose Acetate Ultrafiltration Membranes

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In order to reduce hydrophobic interactions between natural organic matter (NOM) and the membrane surface, and thereby fouling due to NOM, hydrophilic poly(ethylene glycol) (PEG) monomer chains were attached to a commercially available membrane via in situ graft polymerization. Graft polymerization led to an increase in permeability when filtering synthetic seawater containing NOM.

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Desalination Pretreatment Using Controlled-Chain PEG-Enhanced Cellulose Acetate Ultrafiltration Membranes

Prepared for Reclamation Under Contract No. 05-FC-81-1149

by

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July 2008

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Abbreviations and Acronyms

ξ	zeta potential, millivolt
AFM	atomic force microscopy
ATR	attenuated total reflectance
CA	cellulose acetate
CTA	chain transfer agent
DI	deionized
FTIR	fourier transform infrared
g/L	grams per liter
IR	infrared
L/m^2-hr	liters per square meter per hour
mM	millimolars
nm	nanometer
NOM	natural organic matter
PEG	polyethylene glycol
SEM	scanning electron microscope
TOC	total organic carbon
UV	ultraviolet

1. Executive Summary

In order to reduce hydrophobic interactions between natural organic matter (NOM) and the membrane surface, and thereby fouling due to NOM, hydrophilic poly(ethylene glycol) (PEG) monomer chains were attached to a commercially available membrane via in situ graft polymerization. Free radical graft polymerization of the membrane was carried out using an oxidizing agent as initiator, PEG monomer, and a chain transfer agent as terminating agent. Graft polymerization was carried out by two different methods: bulk (i.e., immersing the membranes in the reactant solutions) and drop (i.e., adding reactants dropwise to the membrane surface). Two different feed solutions were used to characterize the modification. Dextran solution was used to compare the efficiency of each modification method. Synthetic seawater was then used to determine the influence of graft polymerization on flux decline, organic carbon rejection, and cake accumulation during filtration. The drop method of modification was found to be the optimal procedure, resulting in higher flux and rejection, along with improved fouling resistance. Graft polymerization led to an increase in permeability when filtering synthetic seawater containing NOM. Fourier transform infrared spectra demonstrated the occurrence of modification by showing carbonyl attachment and OH stretching. Atomic force microscopy images indicated lower cake accumulation patterns after modification.

2. Introduction

Although application of membranes in water purification has become one of the most significant and eco-friendly achievements of the 21st century, fouling has been a considerable barrier to its advancement. Filtration processes, such as ultrafiltration and microfiltration, play major roles in pretreatment and actual filtration of fresh waters, brackish and saline waters, and waste waters [1]. Filtration efficiency is influenced by several factors, such as surface charge (i.e., zeta, ζ, potential), hydrophilicity (polarity)/hydrophobicity, in addition to pore size [10, 11]. Commercially available cellulose acetate (CA) ultrafiltration membranes made from a blend of renewable cellulose diacetate and triacetate have relatively higher rate of permeation than polyacrylonitrile and polyethersulfone membranes [2], which can be explained by the presence of large negative ζ potential and hydrophilicitity [3]. Although credited with high water flux, CA membranes experience limitations such as rather narrow temperature and pH operational ranges [4], but the major problem associated with CA membranes is their high susceptibility to microbial attack.

Apart from these problems, fouling of the membrane, caused by the adsorption of organic matter onto the membrane surface, cannot be removed by crossflow filtration, backflushing, or backpulsing, and it leads to the continual flux decline. It is widely accepted that organic matter is considered a major promoter of abiotic fouling in filtration processes using membranes [6-8, 15]. Based on hydrophobic interactions between the membrane surface and natural organic matter (NOM) and/or microorganisms, it would be expected that use of hydrophilic membranes would decrease fouling. However, hydrophilic membranes experience lower fouling but suffer from limitations, such as susceptibility to surfactants and lack of mechanical strength, [6] and can be fouled by surfactants. Based on the above observations, an ideal membrane would be one with the low fouling properties of hydrophilic membranes along with the high chemical resistance of hydrophobic membranes.

Poly (ethylene glycol)-lipid (PEG-lipid) conjugates are widely used in the field of nanoparticulate drug delivery. They are used to provide a protective cloud of polymer around liposomes, thereby increasing longevity and stability of nanoparticle in the circulation by reducing disruptive interaction with different solutes such as plasma proteins [16, 17]. The success of PEG layers in nanoparticulate drug delivery is attributed to its hydrophilicity, which prevents the penetration of incompatible proteins to the liposome surface by disrupting their interactions. The high flexibility of PEG chains also plays a vital role in denying incoherent proteins to the surface. Hydrophilic polymers with rigid chains may not provide sufficient protective layer for liposomes, as noticed for liposome grafted Dextran [18, 19]. So the basic requirements for protective polymers are

hydrophilicity, flexibility, and solubility, which are characteristics of PEG [17]. Apart from these properties, PEG also possesses excellent characteristics, such as very low toxicity [20] and nonbiodegradability [21], which makes it an ideal choice for use in water purification industry. These distinguished properties of PEG have been explained by its chain's high mobility associated with conformational flexibility and water binding ability [18, 19, 22]. Another advantage of flexible polymers is that they easily form a dense conformational protective cloud as graft chains than many rigid polymers [17]. The success of using PEG as grafting polymer to CA ultrafiltration membrane depends on the ability to anchor the PEG chains to the membrane surface using appropriate modification processes.

Surface modification is considered a cost-effective technique to render the cultivating properties to the membrane while conserving its bulk characteristics [5]. One common surface modification method is graft polymerization of the membrane surface. Modification via graft polymerization has many advantages over other methods, such as its ease of use and controllable introduction of graft chains to the surface with the bulk properties unchanged [9]. Grafting of side chains can be performed in two ways: grafting-from and grafting-to methods. In the former method, the membrane surface consists of reactive radicals, while in the latter case, grafting chains carry the reactive radicals to initiate grafting [9]. Grafting can be achieved using different chemical techniques, such as chemical oxidation, plasma discharge method, and ultraviolet (UV) irradiation, and physical methods, such as radiation polymerization.

The work described here uses free radical chain polymerization via chemical oxidation due to its nondestructive nature, relatively low economic feasibility, and ease of covalent bonding, which leads to the potential for in situ modification [13]. The objective of the study was to modify CA membrane surfaces with grafted PEG chains via chemical oxidation and to evaluate the performance of modified membranes. Dextran solutions and simulated seawater were used as feed solutions to evaluate the modification of the membrane through graft polymerization.

3. Research Objectives

The objective of the present research is to analyze the influence of coupling of PEG monomer chains to commercially available CA ultrafiltration membrane surfaces through graft polymerization using appropriate initiating and terminating chemical reagents. The project is comprised of three parallel tasks: Graft polymerization (3.1), Characterization (3.2) and Evaluation (3.3).

3.1. Graft Polymerization

During graft polymerization, the following were investigated:

1. The formation of free radicals on the membrane surface through oxidation by persulfate.

2. The bonding of PEG monomer chains to the free radicals formed due to oxidation of the membrane.

3. The termination of the polymerization after appropriate time by using mercaptoethanol as chain transfer agent (CTA).

3.2. Characterization

Modification was characterized via:

1. Fourier transform infrared (FTIR) spectroscopic analysis of virgin membranes, as well as modified membranes, to determine the chemical and structural changes on the surface of the CA membrane.

2. Atomic force microscopy (AFM) of virgin and PEG grafted membranes to analyze the topography and roughness changes due to the grafting of polymer chains.

3.3. Evaluation

The evaluation of the modification was performed by:

1. Conducting filtration experiments with both virgin and modified membranes with different feed waters, such as a Dextran solution, a modeled seawater, and protein solutions.

2. Measuring water permeability and selectivity of total organic carbon (TOC) throughout the filtration process.

3. Determining the strength, stability, and longevity of virgin and modified membranes using characterization techniques.

4. Methods and Material

4.1. Membrane

A commercially available CA ultrafiltration membrane is used for the estimation of effectiveness of the graft polymerization as a tool for the modification. The presence of hydroxyl and hydroxymethyl groups in the CA backbone structure, as shown in figure 1, makes it vulnerable to graft polymerization by forming free radicals on the membrane surface [11].

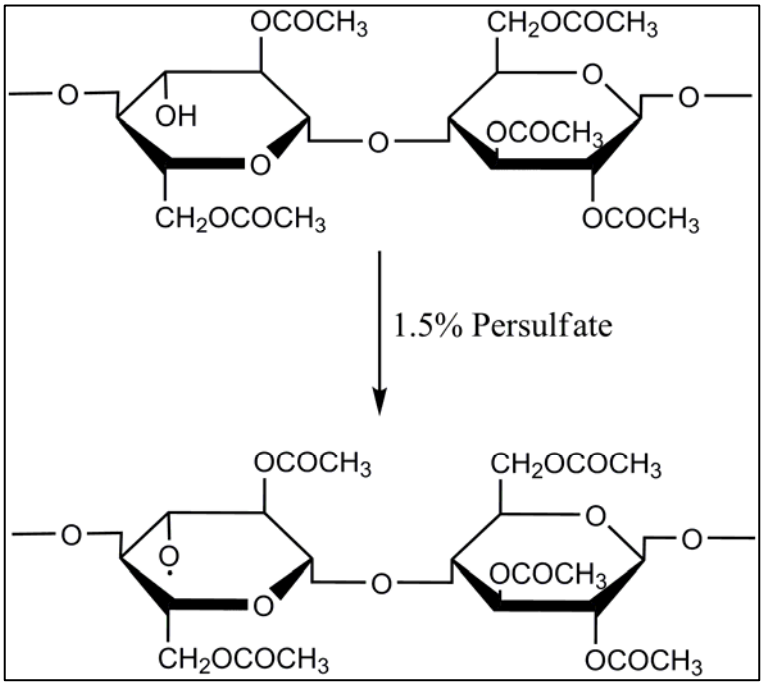


Figure 1. Free radical formation on CA by the action of persulfate.

4.2. Polymerization

Hydrophilic monomer chains of PEG are attached to the membrane surface through a free radical graft polymerization process. Monomer chain is initiated by forming free radicals on the CA membrane surface by oxidizing it with 1.5 percent persulfate solution [14,23-26]. Persulfate solution thus used produces free radicals on CA by abstracting hydrogen atom from the OH groups present in these molecules. These free radicals are used as anchors to attach PEG monomers to the membrane surface as shown in figure 2(a); 10 percent PEG solution is used for chain propagation from free radicals on the membrane. Sodium persulfate

was chosen as radical initiator so as to perform the graft polymerization in aqueous medium and its ability for hydrogen abstraction from the polymer surface. Ability of persulfate to produce free radicals on the membrane can be justified by FTIR analysis and sulfur mapping on the CA membrane reacted with persulfate. Cellulose acetate radicals formed due to oxidation can conjugate with persulfate radicals. Membrane samples were soaked in persulfate solution and then dried at room temperature to avoid possible decomposition of persulfate. The dried sample was then heated to 900 degrees Celsius (˚C) for 30 minutes. This process facilitates the reaction between membrane surface and persulfate [25]. Then, the sample was washed in deionized (DI) water several times to remove any unreacted persulfate solution. This sample was analyzed using FTIR and a scanning electron microscope (SEM) for identifying sulfur presence on the membrane. These analyses have shown strong sulfur signal, as shown in figures 2(b) and 2(c). Linear structure, terminal functional groups, and chosen low molecular weight of PEG result in minimal influence of crosslinking in the process of proposed graft polymerization. PEG of molecular weight 200 is used as the monomer solution. Low molecular weight of the monomer prevents the intensive formation of a thick hydrophilic layer, which deteriorates the mechanical properties and chemical resistance of the membrane surface. Lack of proper side chain termination mechanism also results in uncontrolled polymerization leading to bulky PEG layers on CA membrane surface. Thus, a CTA is used to terminate the polymerization by consuming the recurring end radical of PEG monomer chains. Mercaptoethanol was successfully used as a CTA many polymerization reactions. It is used here at a concentration of 0.5 percent for the membrane graft polymerization. Figure 2 shows the reactions involved in polymerization.

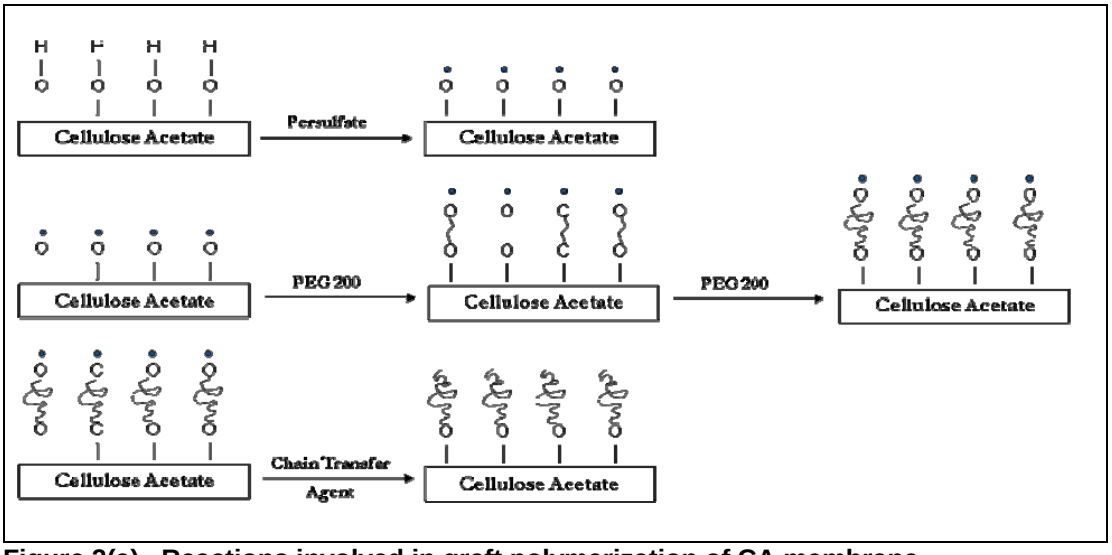


Figure 2(a). Reactions involved in graft polymerization of CA membrane.

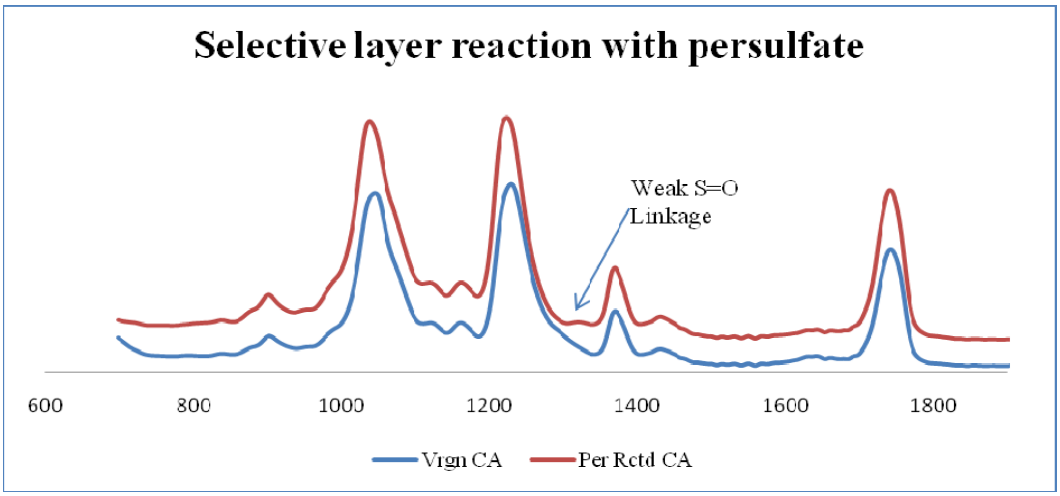


Figure 2(b). Infrared spectra of pure CA and CA reacted with oxidizing agent.

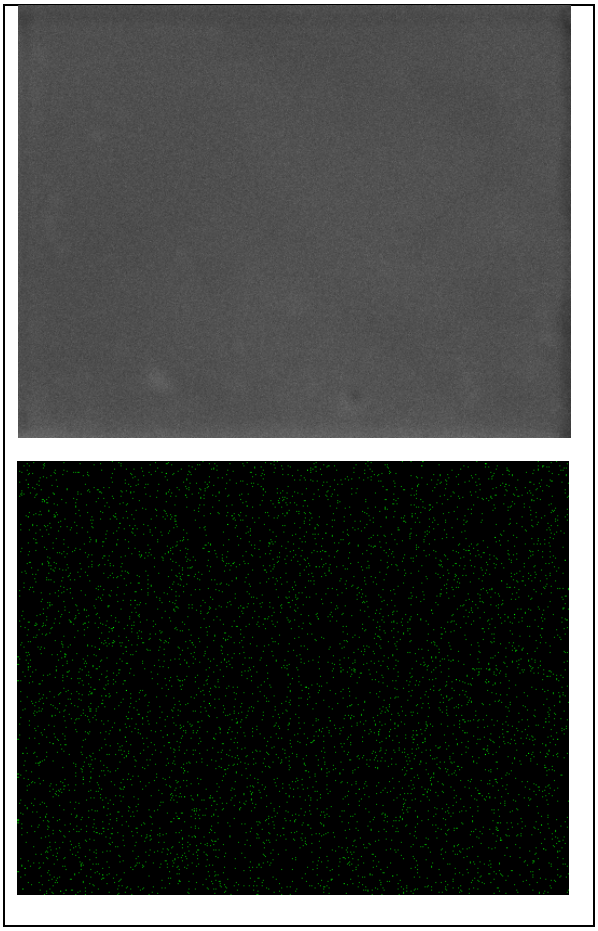


Figure 2(c). SEM and sulfur mapping images of membrane sample reacted with persulfate.

4.3. Methods

Graft polymerization of PEG on membrane selective layer is performed by two different methods compared here. In method one, called bulk method, CA membrane samples are completely immersed in liquid polymerization reagents associated with vigorous stirring. Membrane samples are initially immersed in the oxidizing agent for 10 minutes for free radical formation. Monomer chains are attached to these free radicals using a PEG monomer solution for 5 minutes. Later, these membrane samples are exposed to active 0.5 percent mercaptoethanol for 2.5 minutes for the termination of polymeric chain. Method two, called drop method, constitutes the same times of exposure as in the bulk method, but it differs from bulk method in the mode of exposure of chemical reagents to the selective layer of membrane samples. In this method, liquid reagents are added drop wise to the flatly held membrane samples on glass plate, as shown in figure 3, in the previously mentioned order. Although bulk method of modification leads to the successful polymerization, it allows for monomer chain formation inside the pores of the membranes, leading to pore blockage. This problem is rectified in drop method modification by restricting reagent flow into membrane pores by only involving the membrane selective layer in the polymerization reaction. Addition of chemical reagents drop wise onto the membrane surface layer eliminates the chance of those reagents reaching pores due to the vortex motion of reagents surrounding the membrane sample, as in the bulk method, and thereby greatly reduces the chances of pore blockage by preventing polymerization inside the pores.

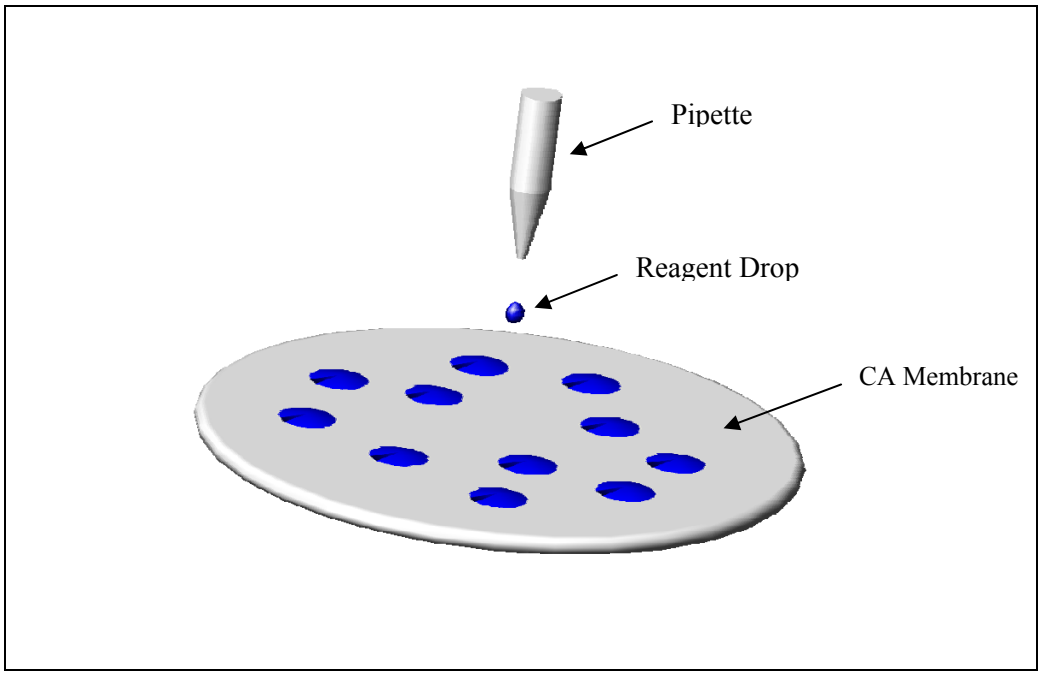


Figure 3. Schematic diagram of graft polymerization using drop method.

4.4. Fourier Transform Infrared Spectroscopy

Infrared spectroscopy is widely used to assess the chemical nature of a substance including chemical bonds, molecular orientations, molecular energy levels, and molecular interactions. Membranes, both virgin and modified, are analyzed using FTIR in attenuated total reflectance (ATR) mode. These FTIR measurements are performed using a Digilab UMA 600 FT-IT microscope with a Pike HATR adapter and an Excalibur FTS 400 spectrometer (Randolph, Massachusetts). Membrane samples are analyzed after each step of the polymerization; i.e., chain initiation with peroxide solution, chain propagation of graft polymerization with PEG solution, and chain termination using mercaptoethanol for both methods of modification.

4.5. Atomic Force Microscopy

Developments in the surface morphology of the membrane selective layer due to polymerization are analyzed by using AFM. Virgin and modified membranes are analyzed by AFM in tapping mode operation. AFM measurements are performed using a Nanoscope IIIa Scanning Probe Microscopy (Digital Instruments, Santa Barbara, California). Graft polymerization is evaluated by analyzing the membranes prior to, as well as after, numerous filtration operations.

4.6. Filtration Protocol

Filtration experiments using virgin and modified ultrafiltration membranes are conducted in 10-milliliter dead end amicon Bioseparations stirred ultrafiltration cells at pressure of 137.8 kilopascals, as shown in figure 4. Commercially available CA ultrafiltration membranes (molecular weight cutoff - 25 kiloDaltons; manufacturer's specifications can be found in Appendix A) were used for the modification. Prior to actual filtration, all membranes are soaked in DI water and precompacted with either DI water or 10 millimolars (mM) sodium chloride solution as per the feed solution properties. Precompaction is carried out until membranes attained steady flux values. Soaking in DI water causes the membrane to reach steady fluxes quickly during the precompaction [3].

Different kinds of feed solutions are used to determine the effectiveness of modification. One feed solution, constituted of dextran, is used to determine the influence of the modification on uncharged components. All membranes are precompacted with DI water prior to the filtration of 1 gram per liter of Dextran T 70 feed solution. Another feed solution is used to determine the influence of polymerization on the ability of membrane to perform in the presence of humic

substances and high saline conditions (i.e., simulate seawater). Modeled seawater contained 2 milligrams per liter each of Suwannee River humic and fulvic acids purchased from International Humic Substances Society, along with 0.1 mM Ca as a representative of naturally occurring divalent cations, 0.1 mM $NaHCO_3$ as a buffer system, 1M NaCl as background electrolyte, and 1 milligram per liter SiO_2. Prior to the actual filtration, membranes are precompacted with 0.1 mM NaCl; in this case, to facilitate the double layer compression of the membrane.

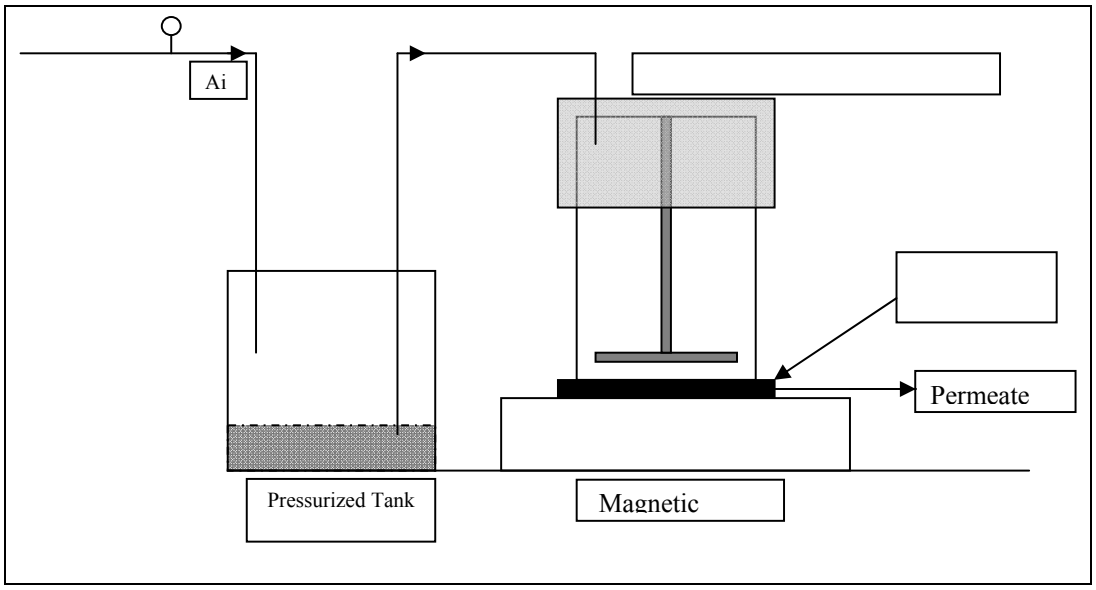


Figure 4. Experimental setup of dead end ultrafiltration of CA membrane.

Flux decline during the filtration process is determined by measuring the permeate flow rate every 15 minutes, and rejection of feed particles by membrane is measured by analyzing the permeate samples for TOC every 30 minutes. Samples of Dextran T 70 feed solution and its periodic permeate solutions are analyzed for TOC using a Tekmar-Dohrmann Phoenix 8000 UV-Persulfate TOC analyzer. In the case of modeled seawater, TOC analyses of the feed and permeate samples are performed by TOC-V_{CPN} combustion catalytic oxidation analyzer from schimadzu scientific instruments Inc.

5. Results

5.1. Dextran T70 Solution

Appendix B contains tables that list the values used to construct the figures referenced below.

The first set of filtration experiments was performed with 1g/l of Dextran solution as feed for a period of 6 hours at a pressure of 1.38 bar (20 pounds per square inch). In order to compare the bulk and drop methods with respect to flux decline and Dextran rejection, permeate flux data for membranes modified by both methods and for unmodified (i.e. virgin) membranes are shown in figure 5. During operation, initial fluxes for the virgin, bulk-modified, and drop-modified membranes averaged 71, 85, and 95 liters per square meter per hour (L/m^2-hr), respectively. While all the membranes experienced a decline in flux during the operation period, the drop-modified reached a steady flux that was higher than both the steady flux of virgin and bulk-modified membranes (figure 5). Both modification methods resulted in enhancements of flux due to grafting of hydrophilic monomer chains of PEG. Unmodified membranes achieved an average steady flux of 68.48 L/m^2-hr, while membranes modified by bulk and drop methods displayed average fluxes of 73.42 and 77.58 L/m^2-hr, respectively. Modification of the membrane resulted in a 10 percent increase in the permeability of Dextran solution, on average; with respect to flux decline, the drop method was more efficient.

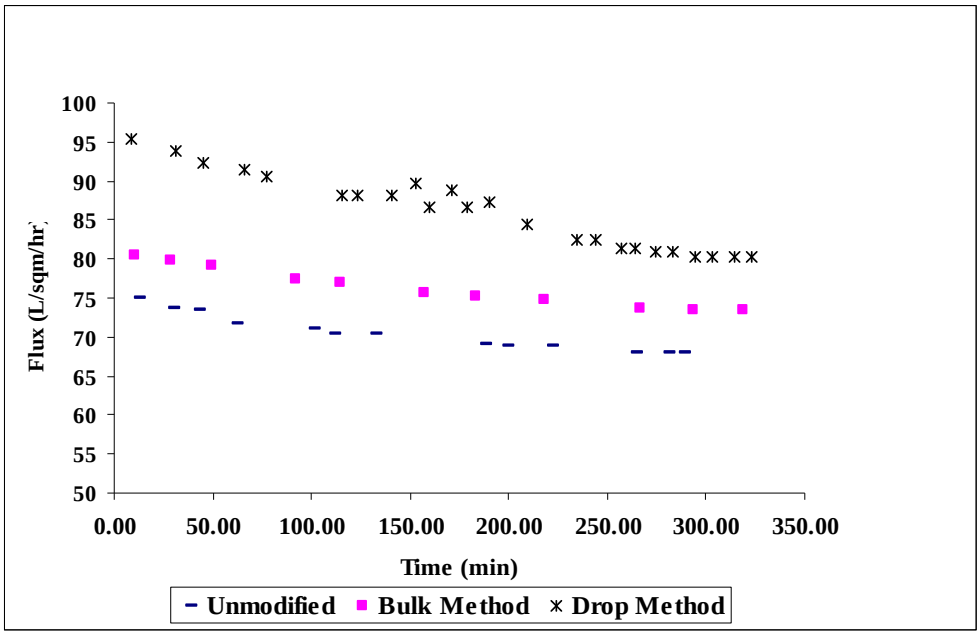


Figure 5. Comparison of flux between virgin and modified membranes – bulk and drop methods.

Dextran rejections for the virgin, drop, and bulk-modified membranes were low, consistent with ultrafiltration rejections, at the beginning of filtration (figure 6). As the membrane was operated, a cake layer accumulated on the membrane due to fouling, leading to an increase in the rejection. After 4 hours of filtration, both virgin and bulk-modified membranes had reached a steady state rejection of approximately 20 percent. The rejection of the drop-modified membrane was still increasing after 6 hours of operation, at which point the membrane rejected at a 25 percent rate.

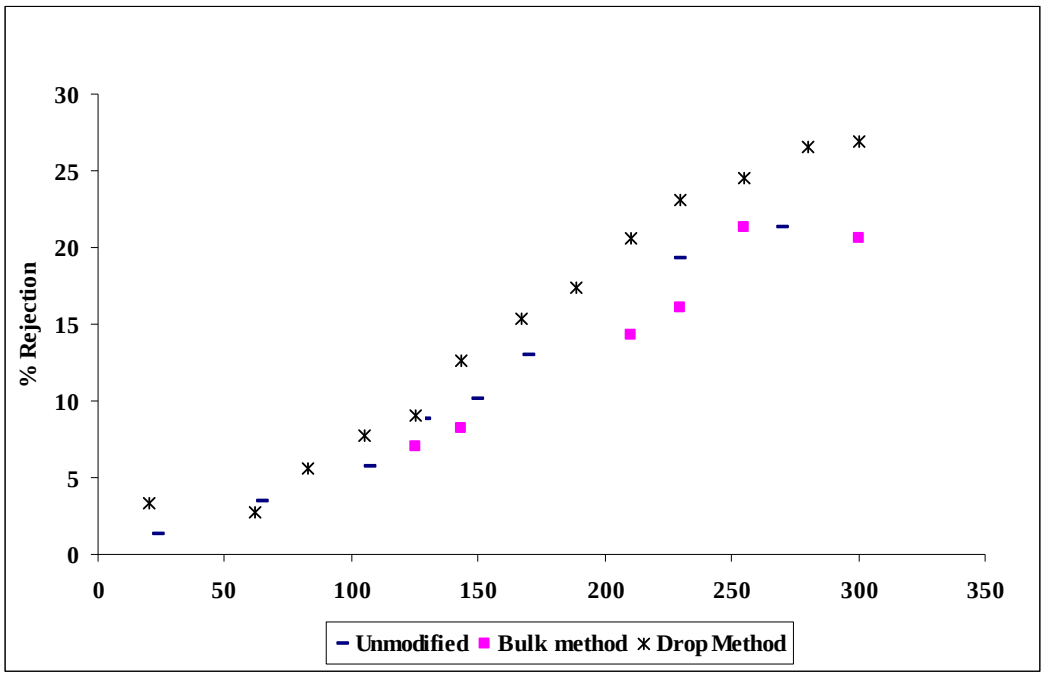


Figure 6. Comparison of TOC rejection between the virgin, bulk-modified, and drop-modified membranes.

Atomic force microscopy was used to estimate the cake accumulation on the surface of the membranes through measurements of roughness and peak counts, as shown in figure 7. There were no significant differences in patterns of cake accumulation between the fouled virgin (9.05 nanometer (nm), 156 peaks) and the fouled bulk-modified (9.09 nm, 150 peaks) membranes. The drop-modified membrane operation, however, displayed a lower fouled membrane roughness (8.33 nm) and peak count (105 peaks). This observation is hypothesized to be due to the better coverage of the membrane surface with PEG when the drop method was used. That is, with the bulk methods, some of the PEG chains were formed inside membrane pores, so the surface was not fully covered with PEG. Another evidence of this is the higher flux of the drop-modified membranes in comparison to the bulk-modified membranes (figure 5). Thus, flux decline, rejection

efficiency, and cake accumulation indicated that drop-modified membranes were more efficient and less susceptible to fouling.

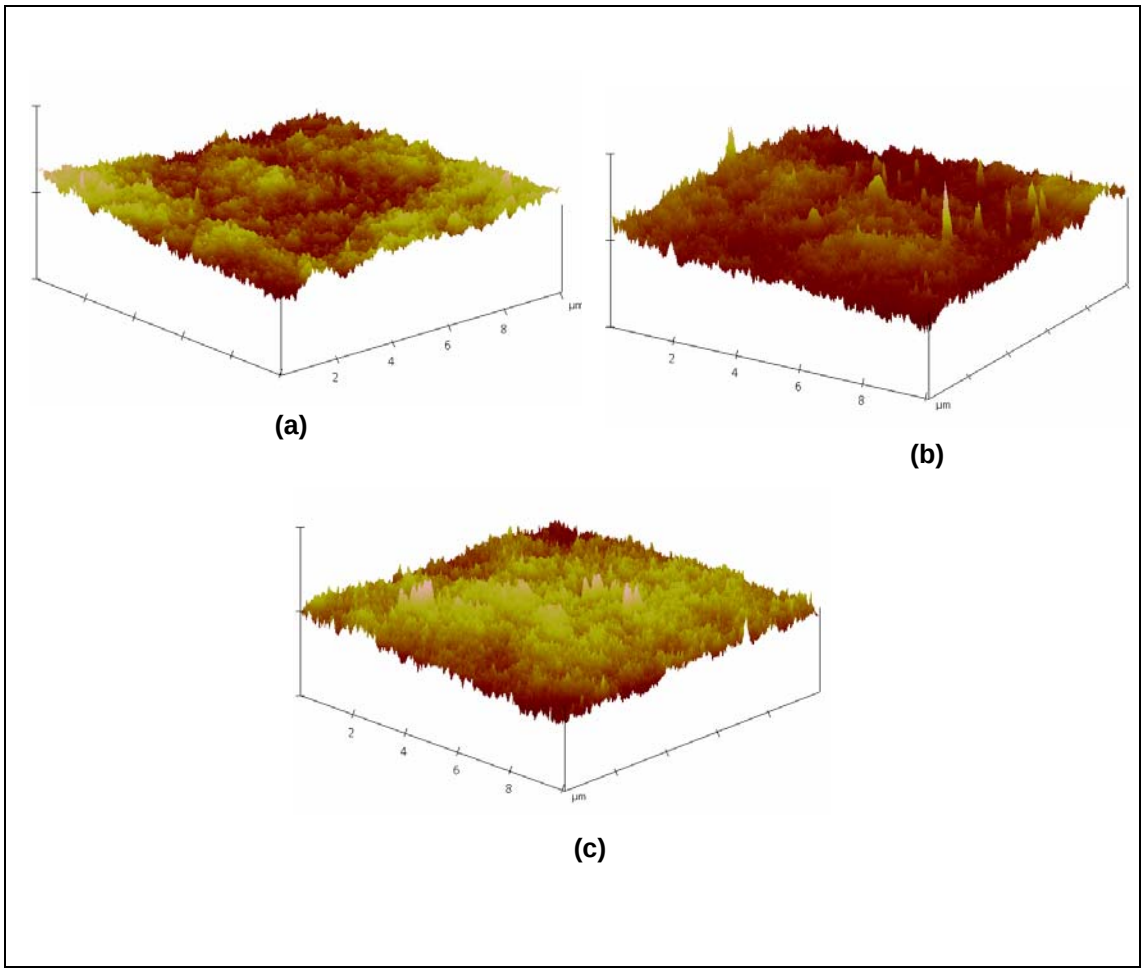


Figure 7. AFM images of: (a) virgin, (b) drop-modified, and (c) bulk-modified membranes, respectively.

Figure 8 shows the FTIR spectra of the chemical changes accompanying modification. A simple qualitative analysis of FTIR spectra showed an increase in 1738 cm^{-1} wavelength, related to the carbonyl groups and in the intensity of OH-stretching absorption at 3410 cm^{-1} of the treated samples. The former is hypothesized to be related to the occurrence of oxidation of CA membrane and the latter with grafting of PEG chains.

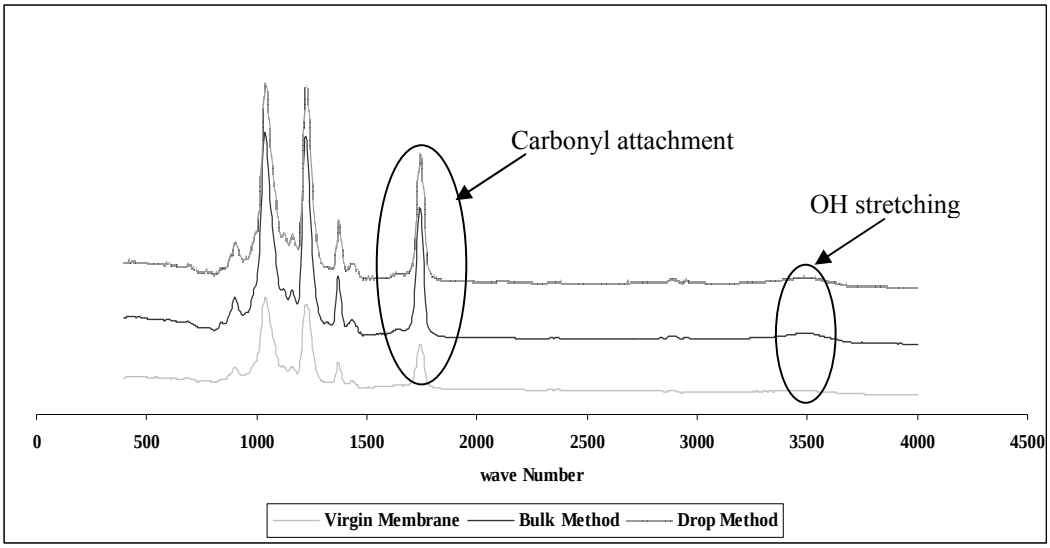


Figure 8. FTIR images of virgin and modified membranes.

5.2. Modeled Seawater

The second set of filtration experiments was performed with the synthetic seawater as the feed solution. Filtration experiments with different time intervals were performed using both virgin and modified membranes at a constant pressure of 1.38 bar (20 pounds per square inch). Experiments were run for 1 minute, 5 minutes, 15 minutes, 30 minutes, 1 hour, 2 hours, 4 hours, 6 hours, and 8 hours. These runs with different time periods were performed to determine the extent of fouling on the membrane leading to flux decline. Instantaneous fouling due to synthetic water was determined by the 1-minute run. Figures 9-11 show variations in flux for the virgin and modified membranes for the 1-minute, 15-minute, and 6-hour runs, respectively. Note that all runs were, at a minimum, duplicated. The permeability of unmodified and modified membranes at the beginning of precompaction averaged 117 and 140 L/m^2-hr, respectively. Flux decline during precompaction was comparable for both modified and unmodified membranes, as these values averaged 18 and 20 L/m^2-hr, respectively. Steady-state flux after precompaction was approximately 105 L/m^2-hr for unmodified membranes, while it averaged between 119 and 124 L/m^2-hr for modified membranes. Flux decline due to instantaneous fouling of the virgin membrane was nearly 100 percent greater than (see Appendix C) that of the modified membrane and it always stabilized at 15 percent higher fluxes than the virgin membrane, as shown in figures 9-11. The increase in the flux of the membrane was an indication of the enhancement of its surface hydrophilicity. This observation supported the performance and stability of the graft polymerization. To show the increase in flux due to modification alone (i.e., to show the increase in flux due to the addition of hydrophilic layer of PEG), several virgin membrane samples were precompacted and modified only after precompaction (figure 12).

This figure shows that modification led to an increase of 25 percent in the flux at the beginning of operation of the 6-hour run.

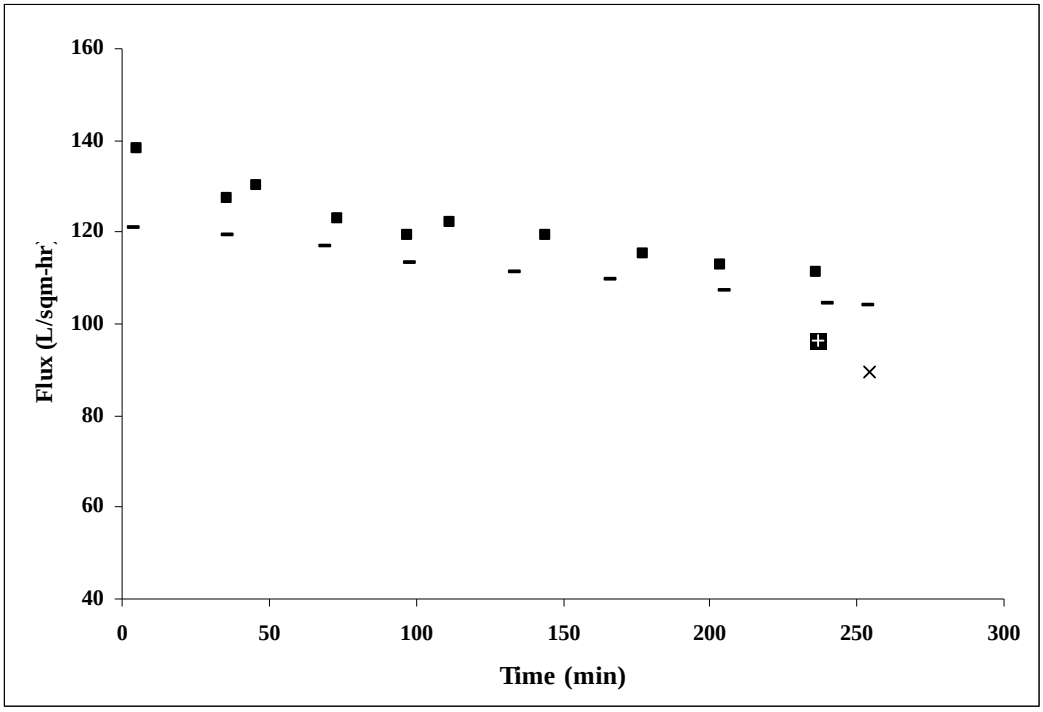


Figure 9. Variation of flux for the 1-minute run.

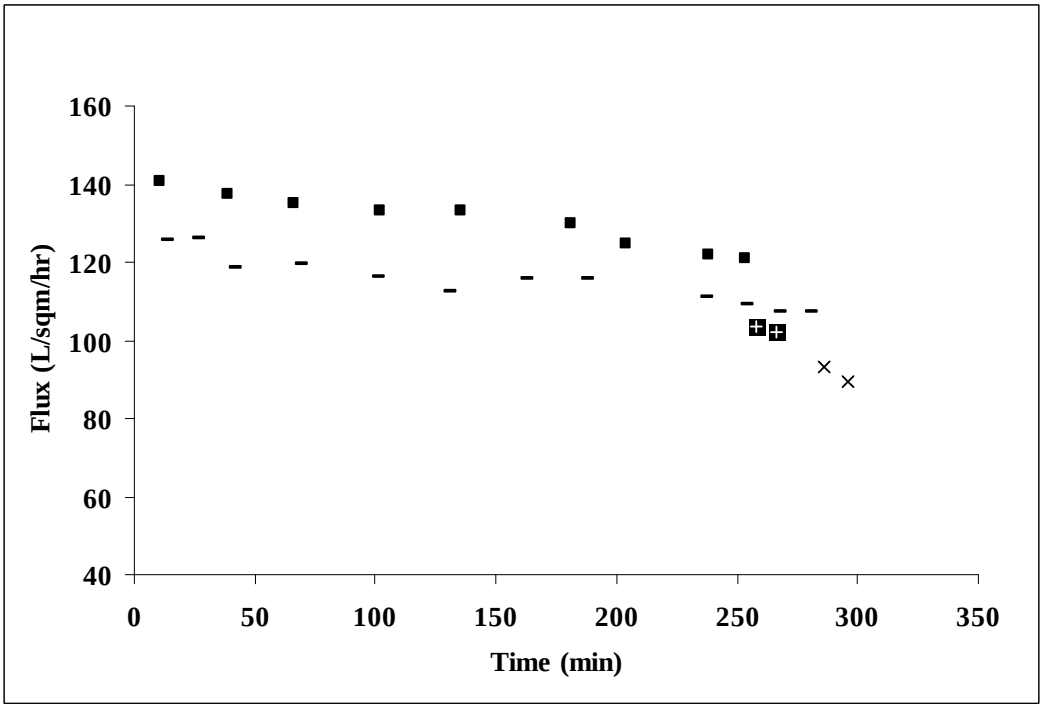


Figure 10. Variation of flux for the 15-minute run.

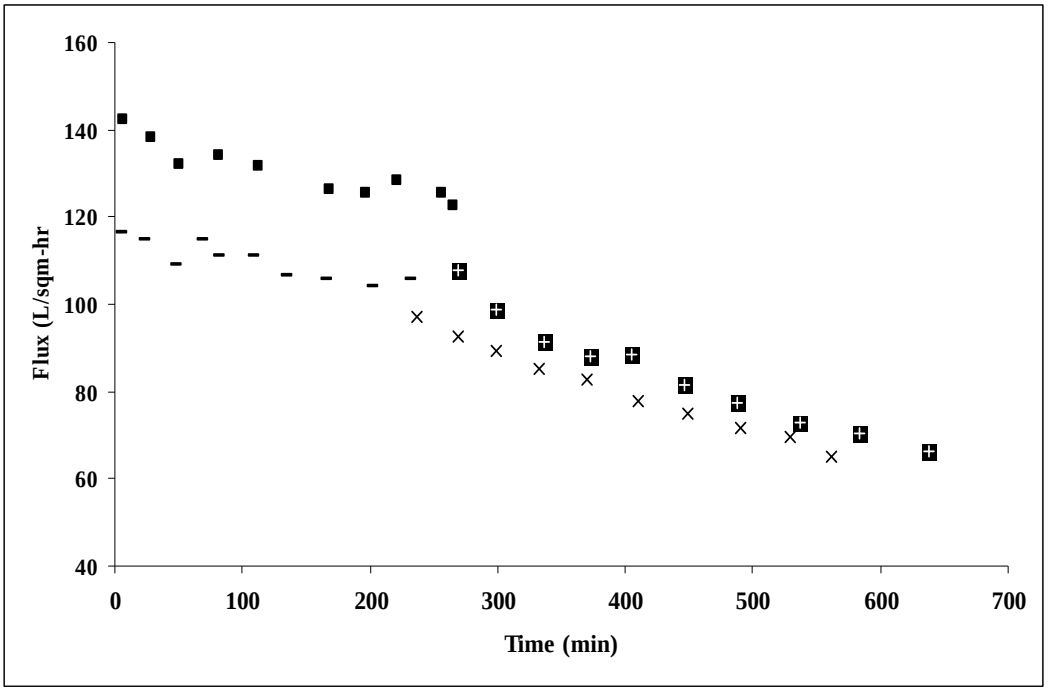


Figure 11. Variation of flux for the 6-hour run.

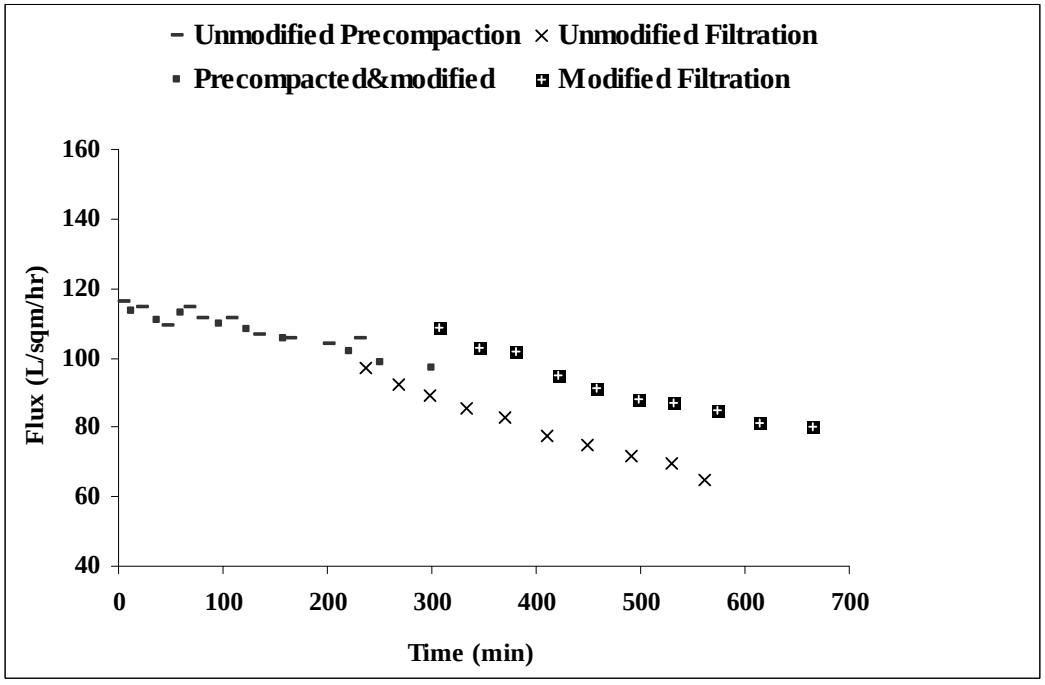


Figure 12. A 6-hour run showing the increase in the flux due to modification. Two virgin membranes were precompacted, after which one of them was modified.

Unmodified membranes displayed TOC rejections of 52.5 percent whereas polymerized membrane had TOC rejections of 45 percent. It is hypothesized that this small reduction in rejection after modification (figure 13) could have been due to the decrease in the negative charge of membrane due to graft polymerization.

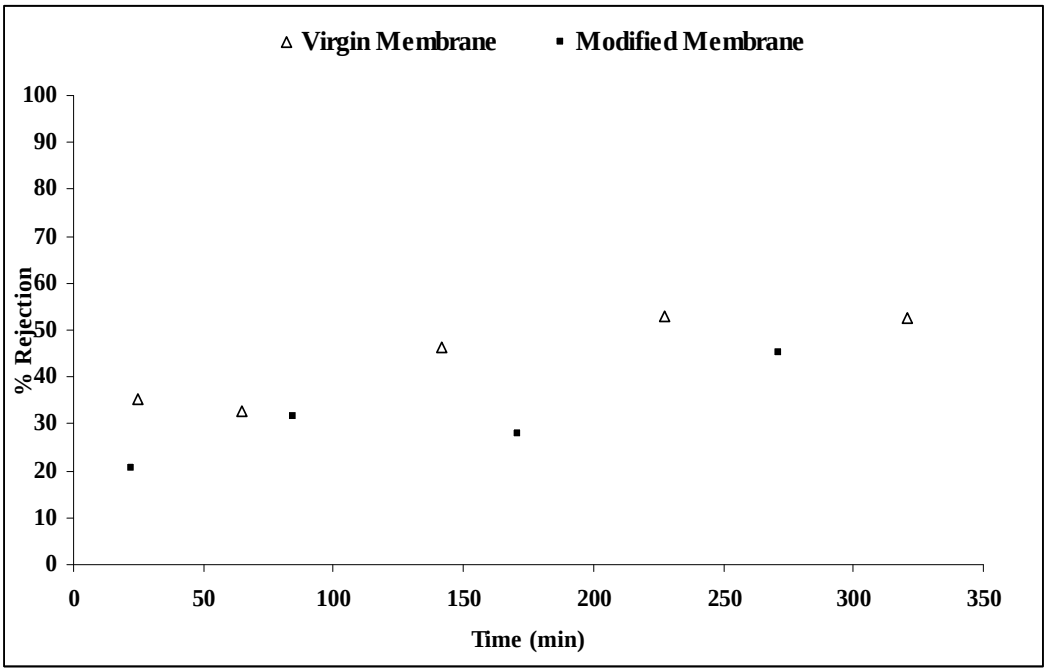


Figure 13. Percent TOC rejection of virgin and modified membranes.

AFM analysis of fouled samples of both modified and unmodified membranes indicated uniform deposition of material on modified membranes. For a given duration of filtration, unmodified membranes had higher roughness values (64.82 nm) than those of modified membranes (44.82 nm), as shown in figure 14 and table 1. Again, this shows the efficiency of the added PEG layer in decreasing cake accumulation on the membrane surface.

Table 1. Roughness and peak count values modified and virgin membranes

Method	Roughness (nm)	Peak Count
Virgin membrane	9.05	156
Bulk method	0.09	150
Drop method	8.33	105

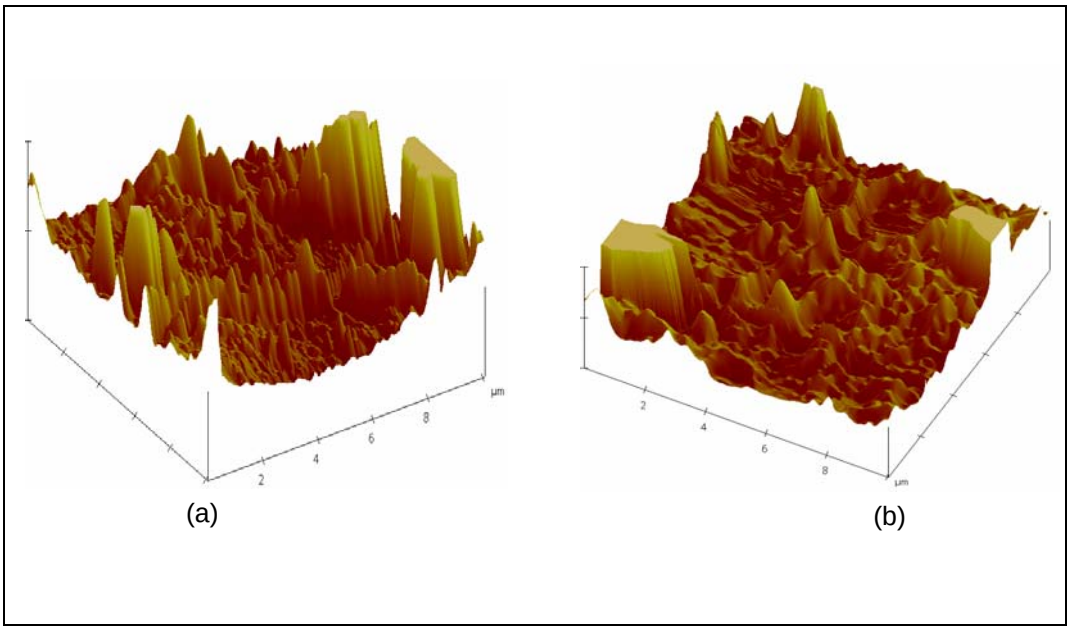


Figure 14. Three-dimensional AFM images of: (a) 9-hour fouled virgin membrane and (b) modified membrane.

5.3 Modification Occurrence

The progress of the graft polymerization during the modification of the CA membranes was observed using a UV-2401 PC UV-Vis Recording Spectrophotometer. Advance of the reaction was observed by recording the UV spectra of chemical reagents participating in the polymerization reaction at various times during the course of the reaction. As observed in figure 15, there was no observed change in the spectrum of persulfate at 210 nm during its reaction with the membrane selective layer since persulfate does not bind to the membrane. On the other hand, the absorbance of the peak formed by PEG showed time dependency (figure 16). This is hypothesized to be due to the uninterrupted grafting of PEG chains to the surface of membrane selective layer.

Figure 17 represents the UV absorption spectra recorded at various time intervals for the mercaptoethanol; that is, the CTA participating in the reaction. A slight change in the absorbance of the peak was recorded as it exposed to the membrane, which is hypothesized to be due to it being used in the reaction.

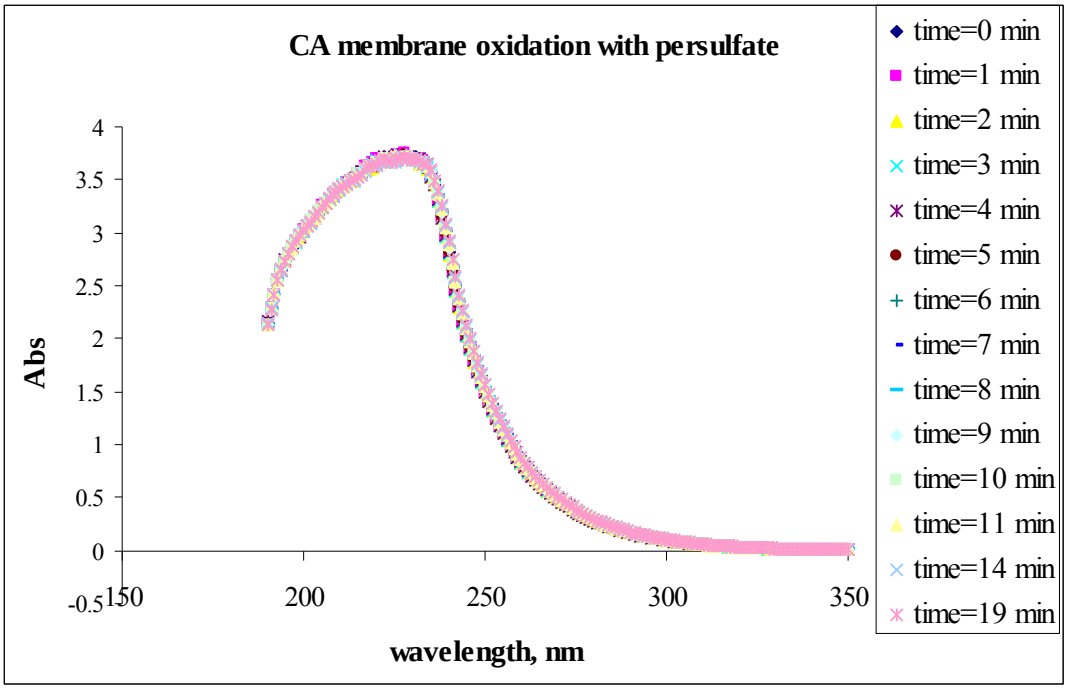


Figure 15. UV absorption spectra recorded during the oxidization of CA membrane by persulfate solution.

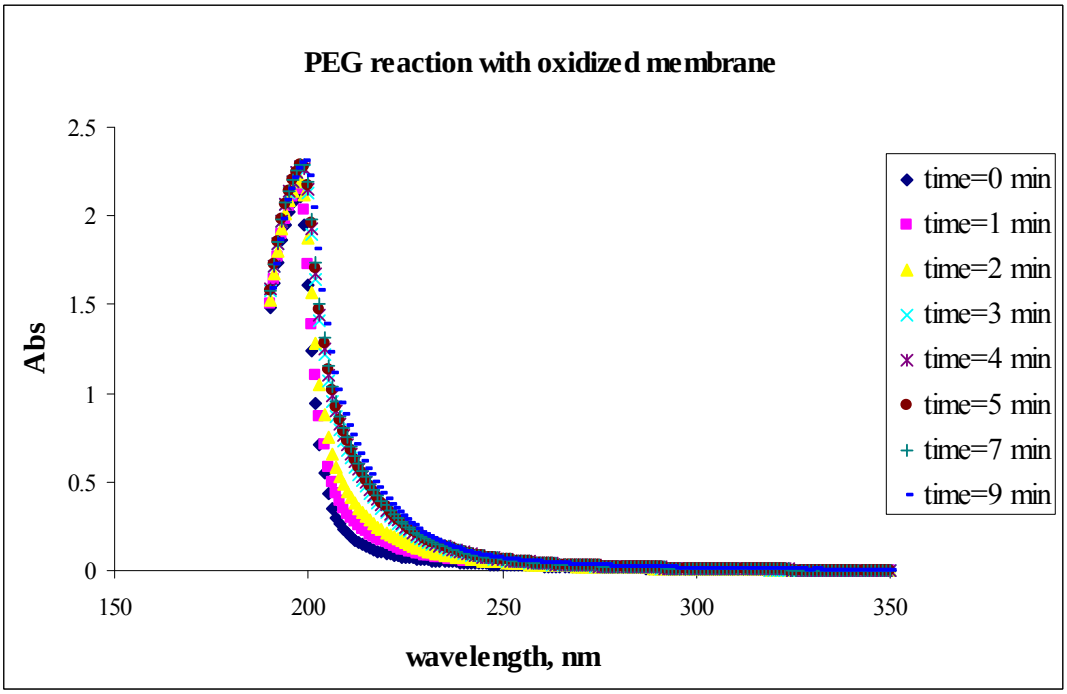


Figure 16. Time dependence growth of absorbance during addition of PEG to the oxidized membrane.

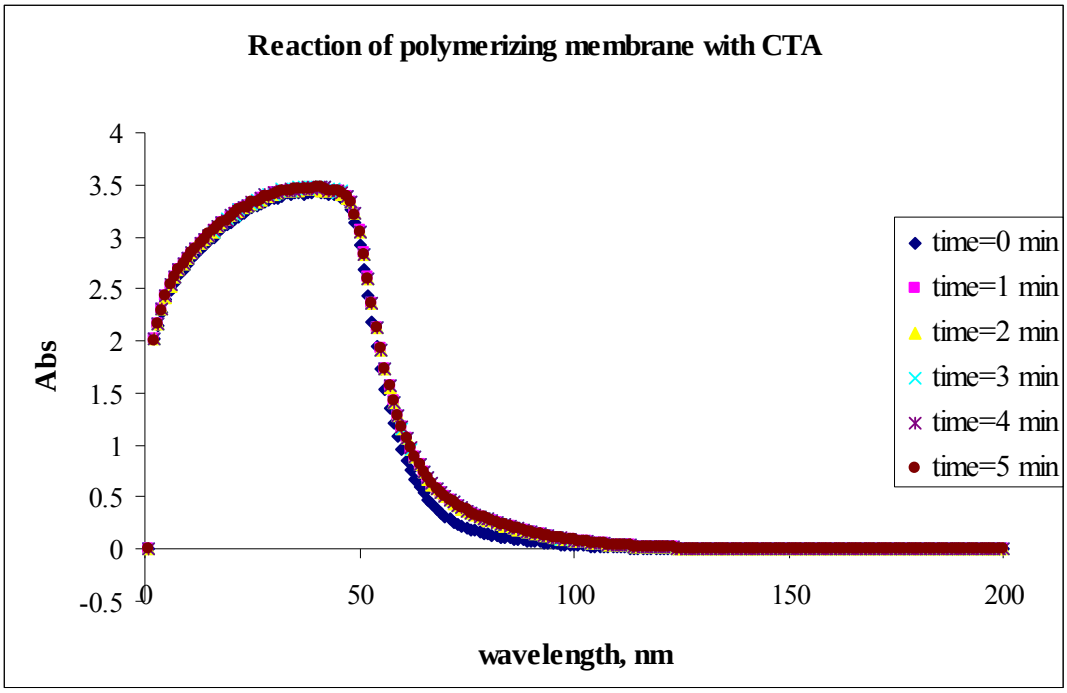


Figure 17. UV absorption spectra recorded during chain termination process.

6. Conclusions

- FTIR and AFM images indicated a successful modification of membrane via graft polymerization.
- The drop method of modification resulted in better flux and rejection properties to membrane.
- Higher fluxes, due to drop method of modification, could be due to the optimum occurrence of polymerization on the surface and through the pores of the membrane.
- Better flux and reduced instantaneous fouling of the membrane resulted due to modification in the case of modeled seawater.
- Reduced roughness of the modified membrane indicated finer fouling patterns after modification.
- Graft polymerization with persulfate/PEG/CTA increased the flux of the membrane, decreased the flux decline during operation, decreased cake accumulation, and had a marginal effect of organic matter rejection; thus, membrane operation was improved.

7. References

1. Teng, C.K., M.N.A. Hawalader, and A. Malek, An experiment with different pretreatment methods, Desalination 156 (2003) 51-58.

2. Shibata, T., Cellulose acetate in separation technology, Macromolecular Symposia 208 (2004) 353-369.

3. Xu, P., J.E. Drewes, T.-U. Kim, C. Bellona, and G. Amy, Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications (2006).

4. Cheryan, M., Ultrafiltration Handbook, Technomic, Pennsylvania (1986).

5. Nabe, A., E. Staude, and G. Belfort, Surface modification of polysulfone ultrafiltration membranes and fouling by BSA solutions, Journal of Memb. Sci., 133 (1997) 57-72.

6. Peng, W., and I. Escobar, Rejection efficiency of water quality parameters by reverse osmosis (RO) and nanofiltration (NF) membranes, Environmental Science and Technology, 37 (2003) 4435-4441.

7. Vrijenhoek, E.M., S. Hong, and M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, Journal of Membrane Science, 188 (2001) 115-128.

8. Zhu, X., and M. Elimelech, Colloidal fouling of reverse osmosis membranes: measurements and fouling mechanisms, Environmental Science and Technology, 31 (1997) 3654-3662.

9. Kato, K., E. Uchida, Y. Uyama, and Y. Ikada, Polymer surfaces with graft chains, Prog. Polym. Sci., 28 (2003) 209-259.

10. Randon, J., A. Larbot, C. Guizard, A. Julbe, and L. Cot, Influence of surface charge on ultrafiltration performance, Key Eng. Mater., 61 (1991) 155-160.

11. Brink, L.E.S., S.J.G. Elbers, T. Robbersten, and P. Both, The anti-fouling action of olymers preadsorbed on ultrafiltration and microfiltration membranes, Journal of Membrane Science, 74 (1993) 281-291.

12. Bonneyele, V., M.A. Sanz, J-P. Durand, L. Plasse, F. Gueguen, and P. Mazounie, Reverse osmosis on open intake seawater: Pre-treatment strategy, Desalination 167 (2004) 191-200.

13. Freger, V., J. Gilron, and S. Belfur, TFC polyamide membranes modified by grafting hydrophilic polymers: an FT-IR/AFM/TEM study, Journal of Membrane Science, 209 (2002) 283-292.

14. Morao, A., I.C. Escobar, M.T. Pessoa de Amorim, A. Lopes, and I.C. Goncalves, Postsynthesis modification of cellulose acetate ultrafiltration membrane for applications in water and wastewater treatment, Environmental Progress 24 (2005) 367-382.

15. Manttari, M., A. Pihlajamaki, and M. Nystrom, Comparison of nanofiltration and tight ultrafiltration membranes in the filtration of paper mill process water, Desalination 149 (2002) 131-136.

16. Song, L.Y., Q.F. Ahkong, Q. Rong, Z. Wang, S. Ansell, M.J. Hope, and B. Mui, Characterization of the inhibitory effect of PEG-lipid conjugates on the intracellular delivery of plasmid and antisense DNA mediated by cationic lipid liposomes, Biochimica et Biophysica Acta 1558 (2002) 1-13.

17. Torchilian, V.P., and V.S. Trubetskoy, Which polymers can make nanoparticulate drug carriers long-circulating?, Advanced Drug Delivery Reviews 16 (1995) 141-155.

18. Blume, G., and G. Ceve, Molecular mechanism of the lipid vescile longevity in vivo, Biochimica et Biophysica Acta 1146 (1993) 157-168.

19. Torchilian, V.P., V.G. Omelyanenko, I.M. Popisov, A.A. Bogdanov Jr., V.S. Trubetskoy, J.N. Herron, and C.A. Gentry, Poly (ethylene glycol) on the liposome surface: on the mechanism of polymer-coated liposome longevity, Biochimica et Biophysica Acta 1195 (1994) 11-20.

20. Pang, S.N.J., Final report on the safety assessment of polyethylene glycols (PEGs)-6, -8, -32, -75, -150, -14M, -20M., Journal of the American College of Toxicology 12 (1993) 429-456.

21. Zalipsky, S., Chemistry of polyethylene glycol conjugates with biologically active molecules, Advanced Drug Delivery Reviews 16 (1995) 157-182.

22. Needham, D., T.J. Melntosh, and D.D. Lasic, Repulsive interactions and mechanical stability of polymer-grafted lipid membranes, Biochimica et Biophysica Acta 1108 (1992) 40-48.

23. Burke, M., and C.H. Nicholls, Formation of free radicals in chemically modified wools by persulfate treatment, Textile Research Journal 38 (1968) 891-896.

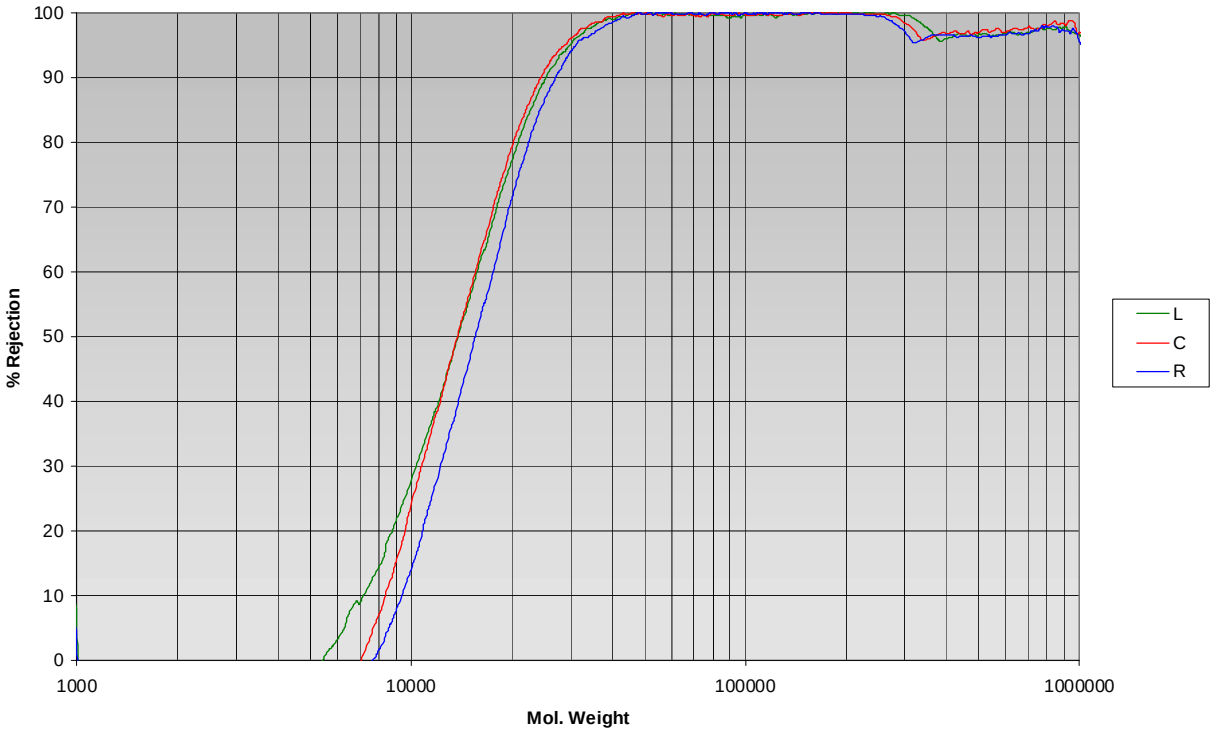
24. Minisci, F., O. Porta, F. Recupero, C. Punta, C. Gambarotti, B. Pruna, M. Pierini, and F. Fontana, A new, convenient, highly selective free radical hydroxy methylation of hetroaromatic bases by persulfate oxidation of ethylene glycol and glycerol, catalysed by $AgNo_3$, Synlett 5 (2004) 874-876.

25. Liu, S., and G. Sun, Radical graft functional modification of cellulose with allyl monomers: Chemistry and structural characterization, Carbohydrate Polymers 71 (2008) 614-625.

26. Dal-cin, M.M., M.D. Guiver, C.N. Striez, D.J. Carlsson, and A. Kumar. Surface-modified polysulfone membranes: Aqueous phase oxidation via persulfate radical, Journal of Applied Polymer Science 101 (2006) 1723-1730.

Appendix A

Molecular weight cut-off of cellulose acetate UF membrane:



Appendix B

Data Used to Construct Figures 5, 6, and 9-13:

Figure 5

Unmodified		Bulk Modified		Drop Modified	
Time	Flux	Time	Flux	Time	Flux
min	L/Sqm-hr	min	L/Sqm-hr	min	L/Sqm-hr
13	75.00313	10	80.5331	9	95.49578
30	73.73725	28.66	79.797	15	95.49578
43.08	73.42743	49.91	79.075	31	93.95553
62.58	71.62184	92.41	77.326	45	92.30138
101.33	71.03955	114.57	76.985	61.25	94.4634
112.33	70.46665	157.014	75.6525	77.5	90.54781
132.83	70.46665	183.674	75.32	96.75	91.97752
188.38	69.07402	218.424	74.68	115.9	88.26125
199.38	68.80208	266.918	73.73	122.9	88.26125
222.13	68.80208	293.918	73.42	140.9	88.26125
265.21	67.99894	318.418	73.42	160.15	86.51351
281.46	67.99894			171.48	88.70928
289.46	67.99894			189.81	87.37864
				197.81	80.16389
				216.31	80.53331
				227.81	84.01792
				234.81	82.43268
				257.14	81.28246
				263.64	81.28246
				282.99	80.90615
				293.99	80.16389
				314.39	80.16389
				322.89	80.16389

Figure 6

Unmodified		Bulk Modified		Drop Modified	
Time min	% Rejection	Time min	% Rejection	Time min	% Rejection
25	1.25	20	3.31	20	3.31
65	3.49	83	5.31	62	2.79
107	5.73	125	6.99	83	5.59
129	8.81	143	8.25	105	7.69
150	10.11	210	14.33	125	9.09
170	12.93	230	16.07	143	12.58
230	19.3	255	21.28	167	15.38
270	21.3	300	20.58	189	17.34
				210	20.62
				230	23.07
				280	26.57
				300	26.92

Figure 9

Unmodified			Modified	
Time Min	Flux L/(sqm-hr)		Time min	Flux L/(sqm-hr)
		Precompaction		
4	121.1102		5	138.2754
35.5	119.4624		35.5	127.2534
69	117.0732		46	130.0813
97.5	113.2966		73.5	122.804
133.5	111.1454		97	119.4624
166	109.7561		111.5	121.9512
204.5	107.0791		144	119.1921
240	104.5296		177.5	115.1539
253.5	103.9111		203.5	112.9323
			236	111.1454
		Filtration		
254.5	89.59681		237	96.48888

Figure 10

Unmodified			Modified	
Time	Flux		Time	Flux
min	L/(sqm-hr)		min	L/(sqm-hr)
		Precompaction		
14	125.4355		11	140.4878
26.5	126.338		38.5	137.19512
42	118.6552		66	135.08443
69.5	119.7339		102	133.03769
101	116.0417		135.5	133.03769
131	112.5704		181	130.0813
162.5	115.5327		204	124.54593
188	115.5327		238.5	121.95122
237.5	111.1454		253	121.11018
254	109.3007			
267.5	107.0791			
281	107.0791			
		Filtration		
286	93.40944		258	103.29986
296	89.59681		266.5	102.0987

Figure 11

Unmodified			Modified	
Time	Flux		Time	Flux
min	L/(sqm-hr)		min	L/(sqm-hr)
		Precompaction		
5	116.2979		7	142.3863
23.5	114.7776		28.5	138.2754
48	109.0744		51	132.0374
68	114.7776		81.5	134.0532
81.5	111.1454		113	131.5429
109	111.1454		168.5	126.338
134.5	106.4302		197	125.4355
165	105.789		221	128.1823
201.5	104.1165		256.5	125.4355
231	105.789		265	122.804
		Filtration		
237	97.02196		269	107.736
268.5	92.42619		299.5	98.65717
299	89.14201		336	91.46341
333	85.24745		372.5	88.24611
369.5	82.83479		404.5	88.6918
410	77.70343		447	81.67896

448.5	74.72756	487.5	77.36113
491	71.67745	537	72.76647
529.5	69.68641	583.5	70.2439
562	65.04065		

Figure 12

Unmodified			Modified	
Time Min	Flux L/(sqm-hr)		Time min	Flux L/(sqm-hr)
		Precompaction		
5	116.2979		12.5	113.24607
23.5	114.7776		37.5	110.95219
48	109.0744		59.75	112.72343
68	114.7776		95.75	109.59055
81.5	111.1454		122.25	108.36543
109	111.1454		157.75	105.75938
134.5	106.4302		193.25	114.40487
165	105.789		221.25	102.10314
201.5	104.1165		251	98.447894
231	105.789		280	107.0937
			299.25	96.879327
		Filtration		
237	97.02196		307.75	108.81558
268.5	92.42619		344.75	102.98484
299	89.14201		380.75	101.95135
333	85.24745		421.25	95.04002
369.5	82.83479		458.25	91.463415
410	77.70343		497.75	88.277717
448.5	74.72756		531	87.186608
491	71.67745		574	85.012468
529.5	69.68641		613.75	81.152201
562	65.04065		665	80.361261

Figure 13

Unmodified		Modified	
Time min	%Rejection	Time min	%Rejection
25	0.3520277	22	0.205325
64.5	0.328461	84.5	0.3172668
141.5	0.4622021	171	0.2777926
227.5	0.5281889	271	0.4510079
320.5	0.5258322		

Appendix C

From Figure 9,

Flux of stabilized virgin membrane during precompaction = 103 L/sqm-hr

Initial flux of virgin membrane during filtration = 89.6 L/sqm-hr

Initial flux of modified membrane during filtration = 96.4 L/sqm-hr

Flux loss due to inst. fouling (virgin) = (103-89.6)/103 = 0.13

Flux loss due to inst. fouling (modified) = (103-96.4)/103 = 0.06

Modification influence = (0.13-0.06)/0.06 = 116.7%