Ceramic Membrane combined with Powdered Activated Carbon (PAC) or Coagulation for Treatment of Impaired Quality Waters

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ABSTRACT

Ceramic Membrane combined with Powdered Activated Carbon (PAC) or Coagulation for Treatment of Impaired Quality Waters

Juma Zubeir Hamad

Ceramic membranes (CM) are robust membranes attributed with high production, long life span and stability against critical conditions. While capital costs are high, these are partially offset by lower operation and maintenance costs compared to polymeric membranes. Like any other low-pressure membrane (LPM), CM faces problems of fouling, low removal of organic matter and poor removal of trace organic compounds (TOrCs). Current pretreatment approaches that are mainly based on coagulation and adsorption can remove some organic matter but with a low removal of the biopolymers component which is responsible for fouling. Powdered activated carbon (PAC) accompanied with a LPM maintains good removal of TOrCs. However, enhanced removal of TOrCs to higher level is required. Submicron powdered activated carbon (SPAC), obtained after crushing commercial activated carbon into very fine particle, and novel activated carbon (KCU 6) which is characterized with larger pores and high surface area were employed. A pre-coating approach, which provides intimated contact between PAC and contaminants, was adopted for wastewater and (high DOC) surface water treatment. For seawater, in-line coagulation with iron III chloride was adopted. Both SPAC and KCU 6 showed good removal of biopolymers at a dose of 30 mg/L with > 85 % and 90 %, respectively. A dose of 40 mg/L of SPAC and 30 mg/L KCU 6 pre-coats were successful used in controlling membrane fouling. SPAC is suggested to remove biopolymers by physical means and adsorption while KCU 6 removed biopolymers through adsorption. Both KCU 6 and SPAC attained high removal of TOrCs whereas KCU 6 showed outstanding performance. Out of 29 TOrCs investigated, KCU 6 showed > 87 % TOrCs rejection for 28 compounds. In seawater pretreatment, transparent exopolymer particles (TEP) were found to be an important foulant. TEP promoted both reversible and irreversible fouling. TEP are highly electronegative while alumina CM is positively charged which support strong TEP–alumina binding. The influence of TEP fouling was minimized with a low dose of 0.5 – 1 mg/l Fe coagulant. Bacteria were almost completely removed; Silt Density Index (SDI) value was maintained to 2 % per minute and a constant permeate turbidity of 0.05 NTU was achieved.

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
AF	Air Flushing
AOP	Advanced Oxidation Processes
BAC	Biological Activated carbon
BET	Brumauer-Emmett-Teller
BW	Backwashing
CAS	Conventional Activated Sludge
CEB	Chemical Enhanced Backwashing
COD	Chemical Oxygen Demand
CIP	Cleaning in place
DOC	Dissolved Organic carbon
EDCs	Endocrine disrupting compounds
EDX	Energy Dispersive X-ray spectroscopy
EfOM	Effluent Organic Matter
EPS	Exopolymer particle substance
FEEM	Fluorescence Excitation Emission Matrix
FF	Forward Flushing
GAC	Granular activated carbon
HPC	Hierarchical Porous Carbon
HS	Humic substance
IEP	Isoelectric point
KCU	Kaust-Cornell University
LC-OCD	Liquid Chromatography with Organic Carbon Detector
LPM	Low pressure membrane
MBR	Membrane bioreactor
MF	Microfiltration
NF	Nanofiltration
NOM	Normal organic matter
NPAC	Normal powdered activated carbon
OMPs	Organic micro-pollutants
PAC	Powdered activated carbon
PhACs	Pharmaceutical active compounds
RO	Reverse Osmosis
SDI	Silt Density Index
SEM	Scanning Electron Microscopy
SOCs	Synthetic Organic Compounds
SPAC	Submicron powdered activated carbon
SWRO	Seawater reverse osmosis
TEP	Transparent Exopolymer Particle
TMP	Trans-membrane pressure
TOC	Total Organic Carbon
TOrCs	Trace organic compounds

LIST OF SYMBOLS

μ	water viscosity
d_{50}	average diameter of particles
d_{10}	effective particle sizes
C_e	equilibrium concentration of remaining organic matters contained in the permeate water after filtration
C_s	equilibrium concentration of remaining organic matters contained in the permeate water after filtration
K_F	concentration of adsorbed organic matters
K_L	Saturation coefficient of Langmuir isotherm
$1/n$	Freundlich empirical coefficient
q_m	Maximum adsorption capacity
R^2	Correlation coefficient
R_T	Total hydraulic membrane resistance
Ra	Roughness

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EXECUTIVE SUMMARY

Low-pressure membranes (microfiltration (MF) and ultrafiltration (UF)) hold a dominant position in the market to replace most conventional treatment systems for drinking water. They are also accepted as a pre-treatment option prior to reverse osmosis (RO) membranes used for desalination. Moreover, low-pressure membranes are used in wastewater treatment and reuse. The introduction of ceramic membranes (which are inorganic membranes) in the drinking water industry appears to have a bright future in the market to compete with polymeric membranes.

Ceramic membranes are promoted in drinking water treatment due to their unique potential advantages. High flux during filtration and backwashing, resistance to high temperature and pressure, low-pressure operation and chemical stability make them attractive in water treatment. Ceramic membranes are robust against high pressure and extreme pH (1-14). They can sustain aggressive chemical cleaning and high backwashing fluxes that provide more effective hydraulic and chemical cleaning compared to polymeric membranes. However, the capital cost of ceramic membranes is still high compared to polymeric membranes. High investment costs of ceramic membranes can be neutralized based on the above-mentioned merits. Also optimized pre-treatment may make a significant contribution to maintaining remarkable performance of ceramic membranes.

Ceramic membranes like any other membranes are affected by fouling which increases operation and maintenance costs. Most of the membrane fouling is attributed to natural organic matter (NOM) or effluent organic matter (EfOM) components that block membrane pores. Also particulates retained on the membrane surface cause cake layer

fouling. Pre-treatment practices are normally employed in order to control or reduce fouling. Despite fouling, other problems associated with low-pressure membranes are low ability to remove NOM or EfOM as well as inability to remove micro-pollutants and viruses. Therefore, to achieve more efficient use, ceramic membranes need pre-treatment like coagulation or adsorption.

Pre-treatment using powdered activated carbon and coagulation with Iron III chloride were employed in this research. Surface water (from Delft canal water with a high DOC), seawater (from the Red Sea) and secondary wastewater effluent (from the Jeddah Wastewater Treatments) were used as feed waters. The research employed a ceramic membrane pilot plant operated at constant flux mode and a bench scale set up of Amicon unstirred cells operated at constant pressure mode. Polymeric membranes were also used in some cases to compare the performances between polymeric and ceramic membranes.

The study focused on mitigating three problems associated with low-pressure membranes applications. These problems are fouling, low removal of organic matter and poor removal of trace organic compounds. Submicron powdered activated carbon (SPAC), obtained by crushed commercial PAC (SASuper) from NORIT, and novel PACs – HPCs or KCUs, prepared by collaborative project between KAUST and Cornell University, were used as pre-coat materials onto ceramic membranes. The pre-coat approach was adopted for treatment of (high DOC) surface water and wastewater effluent. In-line coagulation using iron III chloride was adopted for seawater pre-treatment filtration. With seawater, the main focus was to provide a better quality feed for reverse osmosis (RO) membranes using ceramic membranes without compromising high production at low operation and maintenance cost.

The effective size of the produced SPAC was 0.3 µm. SPAC was mixed with Milli Q water to form a slurry solution with a concentration of 7.5 g/L. The pre-coat layers were introduced by dosing SPAC solution at a rate of 6.7 L/h for 30 seconds. Filtration was done at an average flux of 160 L/m^2h. Filtration cycles of 1 up to 4 hours were adopted. NOM and EfOM were characterized by using Fluorescence Excitation Emission Matrix spectrofluorometer (FEEM), Liquid Chromatography with Organic Carbon Detection (LC-OCD) and Transparent Exo-polymer Particles (TEP) qualitative measurements. The fouling trends were analyzed by assessing trans-membrane pressure increase under constant flux mode operation.

From canal water results, it was observed that ceramic MF membranes, in one hour cycles pre-coated with an equivalent dose of 40 mg/L of SPAC, was able to control successfully both reversible and irreversible fouling from surface water with an average DOC of 5.5 mg/L. With 20, 13.5 and 10 mg/L SPAC doses, irreversible fouling was reduced to 42 %, 29 % and 7 %, respectively. The characterization of NOM using LC-OCD revealed interesting results that showed high removal of biopolymers (> 85 %) with a SPAC pre-coat at a dose of 30 mg/L. This suggests that most of biopolymers were removed by physical means (straining). FEEM measurements showed a significant reduction of fluorescence of proteins-like (93 %) and humic-like (82 %) organic matter components. TEP measurement showed significant rejection/retention of acidic polysaccharides (70 %) after one hour of filtration.

In wastewater effluent results using the bench scale unit, it was observed that a biopolymers removal of 80 % was attained with a ceramic MF membrane (AAO100) pre-coated with 30 mg/L of SPAC. When a 0.45 µm filter was pre-coated with the same dose of SPAC, 72 % removal of biopolymers was achieved compared to 62 % removal achieved with adsorption. The additional amount of biopolymers (8 %) removed is suggested to be removed by the ceramic membrane; through adsorption, a maximum of 62 % of biopolymers could be removed. In the short period of contact time, maximum removal of biopolymers with SPAC through adsorption alone is not possible. However, the finer particles provide more external surface area and increase the contact between adsorbent and adsorbate that could contribute to an increased rate of kinetics and boost the removal level of biopolymers in a short contact time.

In a second phase of the study, five different PACs were employed to evaluate the removal of EfOM components from wastewater effluent. Ultimately, the best PAC was chosen based on performance in terms of fouling and biopolymers removal. Novel PACs – KCUs (KCU 6, KCU 8 and KCU 12) were partially generated by our collaborators while the rest that are wood based PAC (SA Super, G 60) were commercially available from Norit. The pre-coating layer was created by filtering on the membrane the required dose of PAC in the form of a solution prepared with Milli Q water. Feed water was then filtered through the pre-coated membrane.

Raw feed water (wastewater effluent) from the Jeddah treatment plant was pre-filtered with a 0.45 um filter to remove particulate and some colloidal matter. A ceramic (AA0100) membrane (Anodisc 25, 0.1 µm, 25 mm, 50 circles, Whatman) was used to conduct experiments. The nominal pore size, thickness and diameter are 0.1 µm, 60 µm and 25 mm, respectively. This membrane was hydrophilic, based on data obtained from contact angle measurement (average of 10.68°). To study the influence of pre-coat alone, 0.45 µm filters were used. NOM components pass through a 0.45 um so the pre-coated filter represents the pre-coat removal without the ceramic membrane. Hence the filter here acted as a support layer for pre-coating and the results obtained were expressed as performance of pre-coating layer. Moreover, this study also revealed that PAC did not contribute to any fouling experienced by the membrane filtration process although it has a small effect on initial flux.

KCU 6 was found to be the most effective carbon in removing biopolymers (> 90%) and humic substances (57 %) and suppressing significantly the increases of membrane resistance at a dose of 30 mg/l. The AAO100 ceramic membrane alone removed a significant portion of biopolymers (≈ 50 %) but caused an exponential increase of membrane resistance due to pore blocking (fouling). Removal of biopolymers with adsorption experiments using crushed powder of AAO100 ceramic membrane was insignificant. This suggests that size exclusion from membrane pores was the main mechanisms for removal when the membrane alone was used. Comparison of EfOM removal results between AA0100 and 0.45 µm pre-coats showed similar results, which supported the notion that the major removal mechanism of EfOM is through adsorption. Among the different fractions of EfOM, biopolymer removal was found to correlate the most with the enhanced membrane performance.

These results correlate well with BET analysis of PACs, which showed that the KCU 6 exhibits a wider distribution of large pore sizes (maximum 33 nm) and high BET surface area (1,280 m^2/g) compared to other PACs. This provides good properties for biopolymers removal. In addition, an adsorption experiment showed that KCU 6 performed better in terms of adsorption of high molecular weight NOM. High removal of biopolymers was also observed with both KCU 6 and SPAC. The differences in increase of the membrane resistances between the two PACs (KCU 6 and SPAC) and comparison of the adsorption results affirm that the KCU 6 removal mechanism is adsorption while SPAC is suggested to exhibit both adsorption and physical removal (straining) mechanisms.

In addition, the potential of SPAC and KCU 6 for trace organic compounds (TOrCs) removal with pre-coat approach was critically examined. Pilot experiments with a ceramic MF membrane showed 95 %, 85 % and 43 % removal of atrazine from canal water when 20 and 10 mg/L of SPAC pre-coats and 10 mg/L of NPAC pre-coats were used, respectively. These findings suggest that the use of SPAC pre-coats have the capability to reduce the micro-pollutants to significant levels depending on feed water quality and SPAC pre-coat dose used.

A detailed study involving 29 TOrCs revealed that the novel PAC (KCU 6) at a dose of 30 mg/l, attained a high removal of TOrCs (> 90 %) for most of the TOrCs analyzed with the exception of acesulfame (27 % removal) and TCPP (88 % removal). Acesulfame is highly hydrophilic compared to other trace organic compounds analyzed and this might be the reason for poor removal. Good removal was also observed with 30 mg/L SPAC pre-coats as well. Out of 29 TOrCs model compounds, 23 compounds achieved > 90 % removal. Compounds that showed removal below 90 % are ibuprofen (82 %), sucralose (79 %), acesulfame (27 %), primidone (74 %), sulfumethoxazole (75 %) and TCPP (84 %). Most of these compounds are hydrophilic.

It was found that molecular mass, charge and hydrophobicity of the TOrCs were not the key factors determining the fate of TOrCs removal in the PAC pre-coating approach. The presence of NOM and the amount of pre-coat dose used were the key factors that influence the removal of TOrCs. The hybrid system of ceramic membrane and KCU 6 pre-coat achieved high level of TOrCs removal, comparable to what could be achieved with expensive systems such as an MBR followed by RO or oxidation (ozone) with NF or RO.

The last part of the research was focused on application of ceramic membranes for seawater pre-treatment and optimization of coagulation pre-treatment combined with ceramic micro-filtration/ultrafiltration as pre-treatment for seawater desalination. The combination of chemical coagulation and micro- filtration (MF)/ultra-filtration (UF) is considered to be an effective pre-treatment for seawater prior to reverse osmosis (RO).

The focus of this part of research was first to investigate the application of ceramic membranes for seawater pretreatment. The filtrate water qualities in terms of turbidity, Silt Density Index (SDI) and bacteria removal were analyzed. The foulants associated with seawater were also critically analyzed. In addition, this part of research aimed to optimize the coagulation pre-treatment using Fe (III) chloride prior to MF/UF ceramic membranes with a focus on fouling and natural organic matters (NOM) elimination. Optimization aimed on providing better feed water to seawater reverse osmosis (SWRO) with minimum NOM loading and low fouling precursors. NOM removal and fouling reduction for both ceramic and RO membranes was the main target for this part of research.

Assessment of flux recovery and membrane permeability after membrane cleaning (either hydraulically or chemically) was also studied. The influence of transparent exopolymer particles (TEP) on the fouling of ceramic membranes in seawater applications was investigated. Anopore ceramic membranes (AAO100 and AAO20) with a pore size of 100 nm and 20 nm, respectively, were used with a constant pressure bench scale set-up. In some cases polymeric membranes (MF PVDF and UF MCE), were used for the comparison purposes. Also, the pilot plant with monolith ceramic MF membrane was used. Red Sea water collected from Thuwal Saudi Arabia was used as feed water. Milli Q water was used for hydraulic backwashing (BW) instead of permeate to prevent cross contamination. Sodium hypochlorite was employed for chemical enhanced backwashing (CEB) and chemical cleaning (CIP) of ceramic membranes.

Samples of feed and permeates waters were analyzed with a UV spectrophotometer, LC-OCD Model 8 Chromatograph for organics in water, and FEEM. Also, silt density index of the seawater permeate measured based on a 500 mL sample collected after 15 minutes (SDI_{15}) was adopted. The fouling of the membrane was assessed by flux decline and the fouled membranes were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX) and Epifluorescence.

The results showed that ceramic membrane filtration reduced the SDI_{15} of seawater from 6.1 units to 2.1 units, which conform to the requirement of $SDI_{15} < 3$ needed for SWRO feed. The SDI_{15} value was further improved to 1.9 units when in-line coagulation was applied at a dose of 1 mg/L Fe. Almost completely removal of bacteria was achieved with and without coagulation while turbidity of the permeate water was stabilized at 0.05 NTU regardless of feed variations. The ceramic membrane alone used without coagulation, showed low recovery after backwashing and significant increase of trans-membrane pressure (TMP) during operation.

This increase of TMP could be related to the presence of sticky polysaccharide-like material called transparent exopolymers particles (TEP) that are known to be abundant in seawater and contribute to organic fouling and eventually biofouling. TEP showed resistance and stickiness behavior on the ceramic membrane surfaces even after aggressive backwashing. This may be responsible for the low flux recovery observed after backwashing.

The optimum dose of coagulant was found to be 3 mg/l Fe^{3+} and 4 mg/l Fe^{3+} for the AAO20 UF ceramic membrane and the AAO100 MF ceramic membrane, respectively, in terms of high molecular weight NOM (biopolymers and humic substances) removal. The removal of high molecular weight components of NOM increased as the pH decreased. The ceramic MF/UF membranes achieved high removal of biopolymers (≥ 60 %) and humics (> 50 %) when a coagulant of 3 - 4 mg/l of Fe^{3+} was applied at levels of pH 4 and 5. In terms of flux improvement a dose of 1 mg/l Fe^{3+} was sufficient based on bench-scale experiment. This was later confirmed at the pilot scale operated at a much lower dose of 0.5 mg/L Fe^{3+}. Therefore coagulation is recommended for smooth operation of CM filtration and for provision of low-fouling feed water prior to SWRO membranes.

Comparison between ceramic membranes and polymeric membranes showed that both UF membranes (AAO20 - ceramic & MCE - polymeric) achieved about 20 – 30 % removal of biopolymers without coagulation. No significant removal was attained with humic substances without a coagulant. With a coagulant, 50 – 60 % removal of biopolymers was achieved and humic substances removal was increased to 40 – 50 % removal. Flux decline was improved with the use of a coagulant resulting in longer filtration cycles. Proteins showed more influence on flux decline than humic substances.

The results showed that ceramic membranes backwashed with Milli Q attained a 10 -15 % flux recovery. The use of CEB (sodium hypochlorite 3000 ppm) improved flux recovery to 80 % and almost 100 % after CIP. The low recovery after backwashing was attributed to the presence of TEP retained on the membranes that are hypothesized to be more sticky and difficult to be removed by hydraulic backwashing. TEP showed resistance against hydraulic backwashing resulting into low flux recovery. The use of sodium hypochlorite for CEB played an important role in breaking up the structure of TEP (which exhibited a behavior of attaching other foulants) and hence improved the flux recovery.

SEM, EDX and Epifluorescence images showed the presence of microorganisms, particulates and TEP believed to be the key contributors to flux decline. FEEM confirmed the presence of protein- like and marine humic-like organic matter in Red Sea water. In conclusion, coagulation at favorable pH conditions can enhance removal of difficult components of NOM (TEP, biopolymers and humic substances) known as a main source of fouling of membranes, while improving flux decline and lowering the frequency of membrane cleaning.

Summary of key results

Ceramic membrane combined with PAC pre-coat for surface water and wastewater treatment.

		High DOC Surface water	**Wastewater effluent**
Ceramic MF + SPAC pre-coat	Removal of NOM	30 mg/L of SPAC removed 80 % of biopolymers mainly by physical (straining) mechanism	30 mg/L of SPAC removed 80 % of biopolymers which also suggests physical removal as a dominant mechanism
	Fouling Reduction	40 mg/L of SPAC controlled the membrane fouling	30 mg/L of SPAC significantly reduced

			membrane fouling
	TOrCs removal	20 mg/L SPAC removed 95 % of atrazine while 20 mg/L NPAC removed only 50 % of atrazine (used as a model micro-pollutant)	30 mg/L SPAC removed > 90 % of 23 compounds out of 29 TOrCs model compounds
Ceramic MF + KCU 6 pre-coat	Removal of NOM		30 mg/L of KCU 6 removed 90 % of biopolymers mainly by an adsorption mechanism
	Fouling Reduction		30 mg/L of KCU 6 controlled the membrane fouling
	TOrCs removal		30 mg/L KCU 6 removed > 90 % of 27 compounds out of 29 TOrCs model compounds

Ceramic membrane for seawater pre-treatment

	Ceramic MF membrane	**Ceramic UF membrane**
Optimum dose for NOM removal	4 mg/L Fe	3 mg/L Fe
Optimum dose for flux maintenance	0.5 – 1 mg/L Fe	1 mg/L Fe
Turbidity improvement	Consistent turbidity of 0.05 NTU for permeate was achieved with and without in-line coagulation despite fluctuations in feed water qualities.	
SDI improvement	SDI value improved from 6.1 to 2.1 % per minute after membrane filtration and further improved to 1.9 % per minute with the use of in-line coagulation	
Bacteria removal	Almost complete removal of bacteria was achieved w/o coagulation	
TEP control	• TEP sticking on the membrane surface were successful removed by chemical cleaning with 3000 ppm of NaOCl • Coagulation decreased sticking effect of TEP and hence reduced significantly membrane fouling	TEP removed with CIP process (3 000 ppm NaOCl) and controlled with coagulation

CHAPTER 1

1.0 Introduction

1.1: Background

The application of low pressure membranes (microfiltration-MF/ultrafiltration-UF) in drinking water treatment started in the early 1980’s while for seawater pre-treatment it started in the end of the last century (Vial and Doussau, 2003). Low pressure membranes are replacing conventional treatment methods for various reasons among them are high demand of chemicals, high production of sludge and a bigger footprint compared to UF/MF membrane systems (Teng et al., 2003). MF/UF systems provide stable water quality with simple design and operation (Busch et al., 2009). Moreover, MF/UF have become cost competitive to conventional pre-treatment methods (Remize et al., 2009).

Low-pressure ceramic membranes are promoted in drinking water treatment due to their unique potential advantages. High flux during filtration and backwashing, resistance to high temperature and pressure, low pressure operation and chemical stability make them attractive in water treatment (Heijman et al., 2008). Hence, proper pre-treatment is required to address the problem of fouling.

Fouling and low ability to remove natural organic matter (NOM) are some of the drawbacks of MF/UF membranes. The problems with NOM are not only limited to fouling but NOM can also cause bacterial re-growth in distribution systems since bacteria use (a small part of) NOM as a substrate (Lin et al., 1999). These associated problems of NOM justify the need to find the appropriate treatment/pre-treatments mechanisms to limit the amount of NOM in distribution systems as well as before membrane filtration.

Apart from NOM, organic micro-pollutants and viruses constitutes a group of undesirable components in drinking water that are difficult to be removed by MF/UF membrane alone without pre-treatment. Synthetic organic chemicals (SOCs) and viruses cannot be removed without pre-treatment like coagulation (Mozia et al., 2004, Suzuki et al., 1998). Pore sizes of MF ceramic membranes are typical 0.1 μm while the sizes of viruses range between 0.005 - 0.1 μm. This makes the task of virus removal with ceramic MF membrane alone to be almost impossible so other supplementary pre-treatments are needed. The hybrid membrane system using coagulation showed positive results in terms of virus removal (Oh et al., 2006) and this might be an option for wastewater effluent treatment as well.

Despite the constraint of cost, ceramic membranes may offer a sustainable option for treatment of wastewater and surface water as well as a pre-treatment alternative for seawater when the membrane is combined with coagulation or adsorbents. Therefore pre-treatments with submicron powdered activated carbon, novel powdered activated carbons and in-line coagulation prior to MF or UF Ceramic membranes filtration may offer an alternative choice to polymeric membranes in water treatment. The need to come up with a new generation of PAC is justified by the fact that until now the commercially available activated carbons have not succeeded in eliminating significantly biopolymers which are regarded to be responsible for MF/UF membrane fouling. A recent study conducted by (Johir et al., 2013) showed that granular activated carbon (2000 mg/L) added to a submerged membrane bioreactor achieved only 20 % biopolymers removal in wastewater. Therefore further development to search for potential activated carbons that are capable to adsorb biopolymers is a matter of priority.

1.2 Ceramic membranes

The use of ceramic membranes for drinking water has been common in Japan for over decade now and has started to penetrate into Europe and the USA in the past few years. There is also interest to use ceramic membrane for treatment of produced water, which is difficult kind of water that requires robust membranes.

1.3 Structure, shapes and materials of ceramic membranes

1.3.1 Structure and shapes

Ceramic modules are available in hexagonal and round shape (Figure 1.1). A multi-channel construction provides a large membrane packing density compared to a tubular element (Figure 1.1). Ceramic membranes have three layers, a macro-porous layer which is an outside layer that acts as a supporting layer, a meso-porous layer which is intermediate layer acting as a buffer between outside layer and inside layer and a micro-porous top layer which is inside layer of the membrane used as a separation layer.

Figure 1.1: Ceramic membranes multi-channels, tubular, hexagonal and round shapes
Source: http://www.lenntech.com/ceramic-membranes.htm

1.3.2 Ceramic membranes materials

The ground materials for ceramic membranes are metal oxides of Aluminium (α-Al_2O_3 and γ-Al_2O_3), Silicon (Si), Titanium (Ti) or Zirconium (Zi) and also carbides of Silicon (Doeke et al., 2007). Oxides of Ti and Si are more stable than Al or Si oxides. However, the membrane can be composed by a mixture of above mentioned metallic oxides like ZrO_2-SiO_2 (Lenntech, 2006).

1.4 Ceramic membranes fabrications

Ceramic membranes are manufactured by the process called the sol-gel process. The colloidal solution (sol) is converted to gelatinous substance (gel). The formation of gel basically depends on a hydrolysis condensation process to form an absolute network of hydrous metallic oxide. The hydrolysis process needs to be orderly to evade precipitation of metallic oxide (Kuzmanovic, 2004).

A real metallic oxide pattern is molded by chemical ties (bonds) in the mixed solution after controlling and adjustment of thermal disintegration and sol-gel transition (Agoudjil et al., 2005). The sol-gel process is done under high temperature and the production of varieties of metallic oxides is dependent on various ranges of temperature.

1.5 Pretreatment with activated carbon

MF or UF membrane is an alternative to replace conventional treatment. However, low-pressure membranes alone have low efficiencies in removal of NOM, color and trace organic compounds (TOrCs). To enhance the ability of eliminating these contaminants, the use of activated carbons was considered to assist removal of TOrCs through adsorption mechanisms (Tomaszewska and Mozia, 2002).

Activated carbons have a large surface area, high grade of surface activities and strong affinity towards dissolved organic adsorption (Jia et al., 2005). These merits make activated carbon to have the potential of enhancing membrane filtration above the critical flux operation (Satyawali and Balakrishnan, 2009). In water treatment, activated carbon has been found to be useful in removing dissolved organic impurities, odor, taste and color through adsorption. The ability of activated carbon to remove NOM is strongly depends on the dose applied and contact time (Delgado et al., 2012). To reduce the contact time between contaminant and activated carbon, fine particles of activated carbon (SPAC) have been used. SPAC was found to be capable of removing geosmin at a shorter contact time and lower dose than NPAC (Matsui et al., 2007).

However, the efficiency of activated carbon depends on the physical and chemical properties of the substances to be adsorbed and size of pores of the activated carbon. The pores sizes in activated carbon typically range from 0.5 nm to 500 nm. Pores having a diameter of more than 50 nm are classified as macropores and pores that are less than 2 nm are termed as micropores and, in between the two ranges, are called mesopores (Metcalf and Eddy, 2006, Chen, 2005). A good adsorbent must have combinations of all pore ranges from macro to micropores. Powdered activated carbon (PAC) with a fairly large portion of micro and meso-pores were observed to be more prone to pore obstruction (Chen, 2005).

Also a good adsorbent must have a high surface area and large pore network that will allow high molecular weight adsorbates to be adsorbed (Schippers et al., 2007a). The surface areas of different activated carbons typically range from 500 - 1,500 m^2/g. The bulk density of granular activated carbon (GAC) ranges between 0.22 – 0.5 kg/L while PAC ranges between 0.34 – 0.74 kg/L (Armenate, 2007).

1.6 Pretreatment with coagulation

The use of coagulation has gain importance in membrane technology as a pre-treatment method that reduces membrane fouling. With coagulation, suspended and colloidal matter is destabilized. NOM removal during coagulation could be either by formation of insoluble complexes with hydrolysis species or adsorption onto a hydroxide precipitate (Schippers et al., 2007b). The process of coagulation depends on the type and quantity of coagulant used, temperature, pH, flocculation speed (G value), and residence time.

Previous studies on the behavior of flocs in monolithic ceramic membrane filtration with pre coagulation revealed that flocs formed are disintegrated with pumping and re – aggregated with increasing contact and reaction time on the way to the membrane (Yonekawa et al., 2004). It was reported that the amounts of flocs at the upper part were greater than in a lower part of monolith ceramic membrane. This is because the disaggregated flocs were already charged neutralized and within a given time floc recovery took place.

This phenomenon of flocs recovery after breakage also eliminates the importance of flocculation the process and sedimentation prior to membrane filtration. Elimination of the flocculation and sedimentation pre-treatments step, has been successful done in many plants in Japan so the cost for flocculation and sedimentation processes is saved (Yonekawa et al., 2004). Two types of microfiltration coagulation hybrid systems are in practice. In-line coagulation followed by microfiltration and submerged membrane coagulation hybrid. A submerged membrane coagulation hybrid system effectively removed high molecular weight NOM (> 900 Da) and improved membrane filterability of seawater (Jeong et al., 2013b).

1.7 Removal of natural organic matter (NOM), trace organic compounds (TOrCs), bacteria and viruses with MF/UF membranes

1.7.1 NOM removal

NOM is not considered to be harmful, but the problems associated with NOM require limitation of the amount of NOM in distribution systems. Bacterial re-growth in distribution systems and formation of disinfection by-products when combined with chlorine are among those problems. Trace compounds such as pesticides can also be found in the NOM composition. In addition, NOM is a major cause of fouling in membrane (Meyn et al., 2007).

To significantly eliminate NOM, high doses of activated carbon are needed. A hybrid system composed of a submerged membrane adsorption bioreactor used 5,000 mg/l of PAC (introduced into membrane bioreactor at the beginning of the experiment) to achieve 96 % removal of DOC (Guo et al., 2008).

Ceramic membranes have the ability to eliminate, entirely suspended particles and bacteria but failed to significantly reduce NOM, disinfection by-products, taste and odour composites (Matsui et al., 2007). Concentration of NOM, flux, concentration of adsorbent and presence of other adsorbates affect removal of NOM. Powdered activated carbon (PAC) is still useful in reduction of NOM. The PAC cake layer prevents humic acid (HA) from plugging (fouling) the membrane (Tomaszewska and Mozia, 2002)

Previous research performed by (Matsui et al., 2005), involving ceramic MF membrane in combination with submicron powdered activated carbon (SPAC) and normal activated carbon (NPAC), found that the SPAC (0.8 µm) removed more NOM than the as-received PAC (33 µm). Also, NPAC reduced the NOM concentration by 10 % after 120 minutes of contact time, whereas the SPAC decreased NOM by 20 % in only 1 minute and by more than 25 % in 10 minutes. The system was operated at a constant filtration rate of 1.5 m/d and PAC dose was ranged between 5 - 20 mg/l. It was concluded that the advantage of SPAC was in achieving the same level of NOM removal as NPAC at a low dose which is 4 times less compared to NPAC (Matsui et al., 2005). PAC-NOM molecule interaction during the adsorption process was found to produce PAC cake fouling in PAC hybrid systems (Zhao et al., 2005a). In ceramic membranes, this kind of fouling may be easily removed with high backwashing flux.

1.7.2 Trace Organic Compounds (TOrCs)/Organic Micro-pollutants (OMPs) removal

Organic micro-pollutants (OMPs) are dissolved compounds that are potentially persistent in the environment and have negative effects on human health and the environment even at a low concentration (Sobecka et al., 2005a). The existence of OMPs in water bodies has gained importance due to the associated risk in health related issues (Verliafde et al., 2007). These compounds exist over a wide range as a consequence of various processes including wastewater treatment, agricultural activities, industrial activities and formation of disinfection by-products (DBPs).

Insufficient OMPs rejection in treatment of waste water discharge from industries and households has been reported to cause migration of the contaminants to drinking water sources (Cirja et al., 2008). OMPs can be also found in leachate at very low concentrations but in a wide range of occurence (Yiping et al., 2008).

These pollutants have been described as pharmaceuticals, detergents, surfactants, pesticides, polycyclic aromatic hydrocarbons, esters, chlorinated organics, glycols, aliphatic/aromatic amines, alcohols, and phenols (Sobecka et al., 2005a). The pollution is not caused by production processes alone but rather dominated by the uses of the products. In the daily life that we live, emerging contaminants can be found mainly in commercial products that are used in large quantities. Some are persistent and some are biodegradable (Kunst and Kosutic, 2008).

Besides the amount of organic micro-pollutants produced from the industrial and agricultural sector, more OMPs can be produced as products of disinfection during water treatment. An example is NDMA (Nitrosodimethylamine) which is a carcinogenic by-products produced as a result of ozonation and also chlorination treatment trains (Schafer et al., 2010). Moreover, during heavy rain periods floods may carry organic micro-pollutants wastes from sewer and final contribute to increases in micro-pollutants in surface waters and ground water (Krein and Bierl, 1999).

Production of potable water requires the removal of both trace organic compounds (TOrCs) and NOM (Humbert et al., 2008). NOM presence in water increases coagulant doses, causes bacteria re-growth, generates harmful disinfection by-products and above all reduces significantly the efficiency of activated carbon by competing with organic micro-pollutants for adsorption sites (Humbert et al., 2008). As more OMPs continue to emerge as a consequences of development, the application of conventional treatment methods is critical challenged for failing to combat these emerging OMPs and thus there is a need to improve or replace these conventional systems (Liao and Randtke, 1986).

Advanced treatment processes like membrane filtration, adsorption with activated carbon and oxidative treatment are considered whenever the problem of OMPs is addressed (Kunst and Kosutic, 2008). Removal of micro-pollutants is recommended to be done not only in drinking water but also in wastewater to avoid the release of contaminants into receiving water like rivers (Bolong et al., 2009a). Current removal techniques, which are mostly used to deal with the problem of OMPs, are bank filtration, advanced oxidation processes, adsorption with activated carbon, membrane filtration, innovative ion exchange resins and membrane bioreactors (MBR). Advanced processes showed satisfactory results in terms of TOrCs removal (Chang et al., 2009) although the main challenge is production of byproducts (Auriol et al., 2006).

The research done by (Orlandini, 1999) indicates that atrazine removal was significantly improved with granular activated carbon (GAC) filters (adsorption columns) that treated ozonated water compared with non-ozonated. Reduced competitive adsorption and reduced pre-loading of ozonated NOM were considered as the reasons for such improvement. Another study done by (Heijman and Hopman, 1999) described that the GAC performance in elimination of pesticides is influenced by existence of NOM as co-competitor of adsorption site. The amount of NOM in surface waters is considered to be about 1000 times more than pesticides and this makes prediction of pesticides removal to be rather difficult.

GAC has been frequently applied effectively in removing synthetic organic chemicals (SOCs) from surface and ground waters (Jarvie et al., 2005). Two factors are important for activated carbon, the rate of adsorption (kinetics) and the capacity of the adsorbent. According to Jarvie et. al (2005) the dissolved organic carbon (DOC) which present in ground and surface waters can significantly reduce both adsorption capacity and kinetics for SOCs by GAC. Moreover, selection of effective activated carbons for treatment objectives remains as a challenge since the combined effects of physical and chemical adsorbent characteristics on the adsorption of trace organic compounds in the presence of natural organic matter (NOM) are not well understood (Quinlivan et al., 2004).

1.7.3 Bacteria removal

The size of bacteria in general ranges between 0.5 – 5 µm. MF and UF membranes can easily remove the bacteria without pre-treatment (Kim et al., 2005a). Therefore, ceramic membrane with pore sizes of 0.1 µm can completely remove bacteria without pre-treatment. Moreover, the formation of a cake layer may make the task of bacteria removal to be much easier.

1.7.4 Viruses removal

The pore size of MF ceramic membranes is typical 0.1 µm while the sizes of viruses range between 0.005 - 0.1 µm, which indicates that virus removal with a ceramic MF membrane alone is almost impossible. To enhance virus removal, ceramic membrane should be coupled with other pretreatments techniques like coagulation. The hybrid membrane system using coagulation or adsorption processes showed positive results in terms of virus removal (Oh et al., 2006).

Addition of PAC and formation of cake layer in ceramic MF enhanced the removal of viruses to below the limit of detection after operating for 9 weeks (Oh et al., 2006). Suitable dosing of coagulant in in-line coagulation prior to ceramic membranes may represent the appropriate solution regarding viruses' removal. In research done by (Heijman, 2007) it was found that virus removal was less effective at an iron dose of 2 mg/l – Fe/L but with 4 mg-Fe/L dose the removal varied from log removal of 4.7 to 6.2 increasing with the increase of time after backwashing as shown by Figure 1.2 below.

Addition of PAC and formation of a cake layer in ceramic MF enhanced the removal of viruses after prolonged period of two months (Kim et al., 2006).

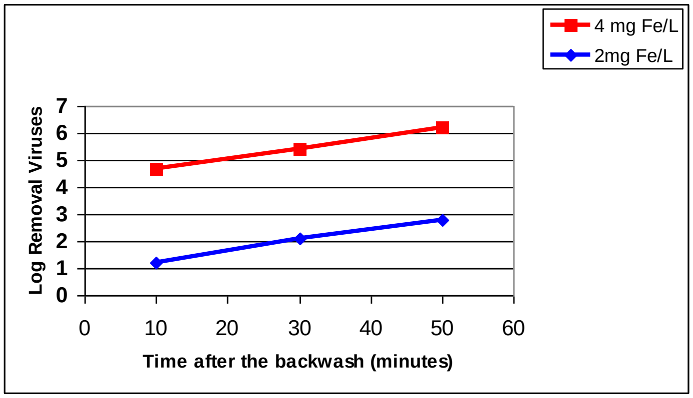

Figure1.2: Log removal of MS2-phages as a function of backwash time
Source: (Heijman et al., 2007).

1.8 Natural Organic matter (NOM) fouling

Fouling caused by natural organic matter (NOM) or effluent organic matter (EfOM) is a common problem for MF/UF membranes. Membrane fouling is categorized by reversible (back-washable) and irreversible (non-back-washable) fouling. Back-washable fouling can be eliminated by hydraulic backwashing and air/water flushing while non-back-washable fouling requires chemical cleaning (Jiang et al., 2003). Pre-treatment with coagulation or adsorption are approaches used to deal with fouling. These pre-treatment options play a major role in reducing the NOM concentration which contributes most to membrane fouling (Jermann et al., 2007).

To understand potential NOM foulants, the feed water and permeates need to be characterized with advanced techniques of NOM characterization. Liquid chromatography equipped with organic carbon detection (LC-OCD), which separates the NOM components in column based on difference in weight and retention time, has been recently used (Batsch et al., 2005, Huber et al., 2011, Kennedy et al., 2005). Table 1.1 below described the fractions of NOM according to their molecular weight cutoff.

Table 1.1: Fractions of NOM

Fraction classifications	**Definition**
Humics substances (HS)	A group of humic acid (HA) and fulvic acids (FA) with MW ranging between 1 – 20, KDa
Building Blocks (BB)	Products of oxidation and weathering processes of HS (0.3 – 0.5 KDa)
Low molecular Weight organic Acids (LMWOA)	Aliphatic LMWOA (< 0.35 KDa)
Low Molecular weight Neutrals (LMWN)	Derived from aldehydes, alcohols and ketones (< 0.35 KDa)
Biopolymers	Related to proteins/peptides and polysaccharides, derived from group of algae and also bacteria (> 20 KDa)

100 KDa ≈ 10 nm

Source (Kennedy et al., 2007)

Fluorescence Excitation Emission Matrix (FEEM) is another rapid and easy method to characterize NOM in terms of humic substance and proteins. This method has attracted many researchers in the field of water (Carstea et al., 2010, Henderson et al., 2009, Hambly et al., 2010, Baker et al., 2004, Peiris et al., 2010, Hudson et al., 2008, Gone et al., 2009). Another distinguishing method is TEP measurement. This method was original developed by Passow and Alldredge (Passow and Alldredge, 1995). TEP are acidic transparent polysaccharides which are flexible in structure (gel like) and sticky (Villacorte et al., 2010). Fouling due to NOM originating from TEP is expected from seawater due to the abundance of TEP occurring in marine water.

1.9 Research goals and objectives

1.9.1 Research questions

- Is the pre-coat approach a reliable pre-treatment option for ceramic membranes operation?

- What is the effectiveness of SPAC/PAC pre-coats in control of fouling and removal of contaminants (NOM/EfOM and trace organic compounds)?
- Is a novel PAC characterized with a network of large pores effective for fouling reduction and removal of high molecular weight organic matter as well as trace organic compounds?
- Can Iron III chloride (used as a coagulant) enable improved filterability of ceramic membrane, and help to reduce marine organic components in seawater permeate?
- What are the optimised doses and pH of coagulant needed for seawater pre-treatments?
- What is the role of organic matter components in fouling of ceramic membranes?
- Does a ceramic membrane combined with coagulation provide better-feed water for RO?

1.9.2 Hypotheses

- SPAC pre-coated on MF membrane will provide a better removal of NOM and trace organic compounds than NPAC
- The pre-coat approach may offer comparable or better removal efficiency of organic matter compared to the common method of PAC dosing
- Novel PAC, with pores 3 – 50 nm, may provide good adsorption of biopolymers and trace organic compounds (TOrCs) and reduce fouling significantly

- Changes of pH and dose in the coagulation process will affect, positively or negatively, the removal of the high molecular weight fraction of NOM in seawater filtration.
- Resistances due to PAC pre-coats and coagulant on the membrane surface are negligible.
- Fouling can be reduced significantly with application of PAC pre-coats of SPAC and novel PAC
- Coagulation with iron III chloride can improve filterability of seawater in ceramic membrane and help to remove high molecular weight marine organic matter.
- Transparent exopolymers particles (TEP) and biopolymers significantly influence fouling of ceramic membranes.

1.9.3 Research goals

- To determine the influence of pretreatments (SPAC, novel PAC and Iron III chloride) on flux/pressure, membrane fouling and contaminants removal (NOM and TOrCs)
- To determine effective pretreatments methods for ceramic membranes which minimize the use of chemical cleaning without compromising the high flux.
- To study the application of ceramic membranes for seawater reverse osmosis (SWRO) pre-treatment.
- To optimize the coagulation pre-treatment prior to ceramic membrane of seawater by using Iron III chloride based on filterability and removal of high molecular weight NOM.

1.9.4 Research objectives

- To remove NOM/EfOM and trace organic compounds using hybrid systems of ceramic membranes
- To characterize the composition of the organic matter foulants responsible for reversible and irreversible fouling by using LC-OCD, FEEM and TEP analyses.
- To optimize the in-line coagulation process based on coagulant dose and pH of feed water.
- To reduce and control fouling and improve membrane filterability of ceramic MF membranes.
- To develop efficient use of ceramic membranes for RO pre-treatment.
- To characterize membranes (ceramic) and pre-coating materials (activated carbons).

1.10 Structure of the Thesis

Chapter 1 is an introductory part, which introduces the goal and objectives of this study. Hypotheses and research questions formulated in this chapter guide the rest of the research.

Chapter 2 is based on characterization of materials used in this research. PACs were characterized in terms of particle sizes distribution, elemental compositions, BET surface area and pore diameter distributions as well as adsorption capabilities of different NOM components. Ceramic membranes were characterized in terms of surface charge (zeta potential), pore sizes and pore distributions, surface roughness (morphology), pure water permeability (PWP) and hydrophobicity. In some cases, these characteristics were compared with polymeric membranes.

Chapter 3 describes the benefit of using submicron-powdered activated carbon (SPAC) as pre-coat to treat high-DOC surface water. The study focused on NOM removal, in particular high molecular weight NOM, and fouling control and reduction.

Chapter 4 is based on the performance of novel PACs generated from sugar-based materials. Novel hierarchical porous carbons (HPCs) or commonly known as KCUs produced by KAUST and Cornell University from a collaborative project were used. The performance of these novel PACs (used as a pre-coat) was compared with commercial PACs in terms of NOM removal and fouling reduction. All PACs were pre-coated on ceramic membranes prior to wastewater effluent filtration.

Chapter 5 is focused on trace organic compounds (TOrCs) removal. The best performing novel PAC (KCU 6 or HPC 4-2) in terms of NOM and fouling reduction, and SPAC were challenged by TOrCs removal. A pre-coat approach was adopted using ceramic membranes, and wastewater effluent and canal water were used as feed waters.

Chapter 6 is based on application of ceramic membranes for pre-treatments of seawater reverse osmosis (SWRO). The study was focused on how ceramic membranes can improve SDI, turbidity and remove bacteria prior to SWRO. The role of coagulation in improving the membrane filterability was discussed. Flux recovery after backwashing (BW), chemical enhanced backwashing (CEB) and chemical cleaning was assessed. The influence of TEP on ceramic membranes fouling was also studied.

Chapter 7 is based mainly on optimization of the coagulation process for seawater filtration with ceramic membranes. The optimization focused on removal of high molecular weight NOM and filterability. In this chapter, optimum coagulant doses for

NOM removal and membrane filterability were determined. Then the optimum pH of feed water (seawater) based on NOM removal was determined. This chapter also assesses the influence of high molecular weight NOM on ceramic membrane fouling using synthetic seawater.

Chapter 8 contains the main conclusions of this study and also recommendations for future studies.

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CHAPTER 2

2.0 Characterization of Pre-coats Materials and Ceramic Membranes

2.1 Introduction

Interaction between membrane properties, feed water qualities and pre-treatment materials may positively or negatively affect the filterability process of membranes. Therefore the properties of the membranes and pre-coat materials should be studied. In this chapter, low pressures membranes used in this research and powdered activated carbons (PACs) used as pre-coat materials were characterized. Characterizations of PACs were focused on elemental analysis, particle sizes distribution, BET surface area, pore size distribution and adsorption capacities/isotherms. Membranes characterizations were focused on pure water permeability (PWP), hydrophilic properties (contact angle), surface and structure of membrane pores; membrane pore sizes distribution and surface charges of membranes.

Flat sheet Anopore ceramic membranes, AAO100 and AAO20, which are microfiltration and ultrafiltration membranes, respectively, made of alumina as well as a monolith ceramic membrane from METAWATER were characterized. These membranes were compared with polymeric microfiltration and ultrafiltration membranes (MF PVDF and mixed cellulose ester (MCE) membrane, respectively). Commercial PACs from NORIT, which are wood based (SASuper and G60), and novel PACs (KCU 6, KCU 8 and KCU 12), which are sugar-based materials used as pre-coat materials were also characterized. KCUs are hierarchical porous carbons (HPCs) with a large network of mesopores and large surface area. They are synthesized by 20 g of a 15-wt% suspension of 4, 8 or 12 nm colloidal silica mixed well in a centrifuge with 1.5 g of glucose D. The centrifuge tube is then plunged into liquid nitrogen and the frozen sample is allowed to freeze until it becomes completely dry. The dry composite is then carbonized at 1000 ºC at a ramp rate of 3 ºC/min for 2h in the presence of nitrogen. The composite is then stirred in a 3M NaOH solution at 80 ºC for over 12 hours to remove silica portion. This is followed by washing the sample with Milli Q water up to neutral pH and dried at 130 ºC for at least 12 hours before use. Based on size of silica used, these hierarchical porous carbons (HPCs) were named as HPC 4-2, HPC 8-2 and HPC 12 -2 where 2 is represents the ratio of silica to carbon by weight and 4, 6, and 8 represents the size of silica. However, in this research HPC 4-2, HPC 8-2 and HPC 12-2 were named as KCU 6, KCU 8 and KCU 12, respectively. KCU is stands for KAUST Cornell University.

2.2 Elemental analysis of PACs

The composition of selected activated carbons was analyzed with CHNS/O Flash 2000. The instrument works between 100 – 1100 ^{o}C. It is equipped with a reactor and uses helium for combustion that convert the samples into gases of nitrogen, carbon dioxide, steam, sulphur dioxide and carbon monoxide. From the reactor the gases are separated with a column and pass through the detector for analysis. The following composition of PACs was obtained as expressed in Table 2.1.

Table 2.1: Elemental composition of commercial and new generations PACs

	% Hydrogen	% Carbon	% Nitrogen	% Oxygen
SASuper	0.45	85.57	< 0.07	1.67
G60	1.62	76.84	0	4.01
KCU 8	0.11	86.53	0	2.9

SASuper and novel PACs (KCUs) exhibited similar elementary composition in which carbon content was above 85 % (Table 2.1). The PACs have low level of oxygen content that favors adsorption capabilities. Low oxygen content activated carbons have exhibited good adsorption capacities (Lillo-Ródenas et al., 2005).

2.3 Particle size distribution of PACs

The particles sizes of selected PACs were analyzed using a Master sizer (Laser Particle Analyzer) from Malvern. The instrument is equipped with a continuous stirrer to keep the particles stabilized in aqueous solution. The particles were measured by a laser diffraction technique. The maximum particle size that could be measured with the Malvern Mastersizer is 550 µm and the detection limit is 0.05 um (Jia et al., 2005). The particle size distribution results are summarize in Figure 2.1 below and Table 2.2

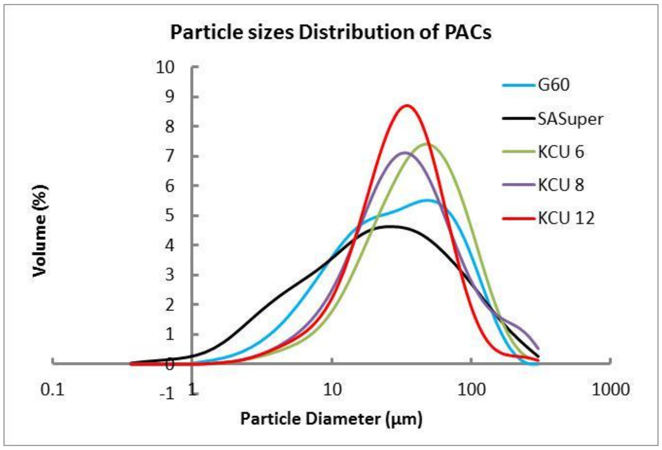


Figure 2.1: Particle size distribution of PACs.

Table 2.2: Effective and average particles distribution of PACs.

	Average Particle sizes (um) - d50	Effective particle size (um) - d10	D90 (um)
SASuper	20.63	3.49	93.02
G60	26.95	6.31	87.68
KCU 6	38.28	11.73	98.8
KCU 8	30.83	9.59	100.44
KCU 12	29.24	10.29	68.28

Commercial PACs have smaller average particles than new hierarchy PACs (KCUs) as shown in Table 2.2. However KCU 12 exhibited a narrow particle distribution (Figure

2.1). SASuper was observed to have smaller effective particle sizes compared with other PACs. A smaller the particle sizes means more external surface area that can increase the kinetics of adsorption.

When PAC is further ground into very fine particles then submicron-powdered activated carbon (SPAC) is produced. SPAC was derived from SA Super after 15 hours of grinding. The particles size distribution of SPAC is shown below:

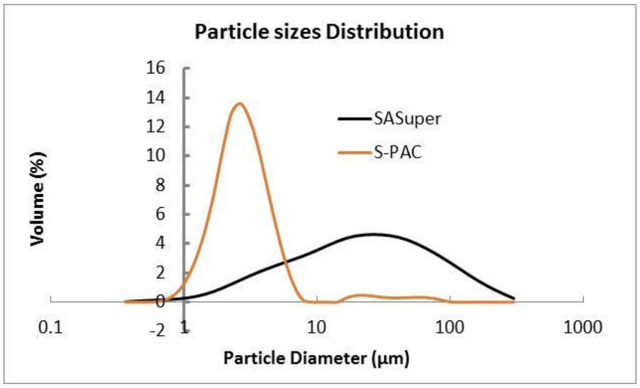


Figure 2.2: Particle sizes distribution of SASuper and SPAC.

Table 2.3: Average particle sizes of SASuper and SPAC.

	Average Particle sizes (µm) – d_{50}	Effective particle size (µm) – d_{10}	d_{90} (µm)
SASuper	20.63	3.49	93.02
S-PAC	2.5	1.41	4.62

After 15 hours of grinding, the particle sizes of SASuper were reduced from an average particle size of 20.6 um to 2.5 µm (Table 2.3) and the narrow distribution ranged from 1.41 to 4.62 µm. A pre-coat layer comprised of SPAC would be very compact and may influence the initial flux. The average bed pore diameter made with SPAC pre-coat is estimated to be 0.4 µm. This value was derived from the following equation:

D = 0.15 d where d is the diameter of the particle.

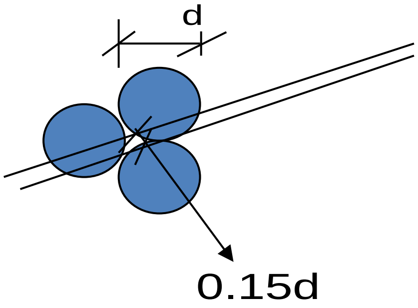


Figure 2.3: Pore space between three particles

If the pore bed diameter of SPAC is made with the effective particles size, then the bed pore diameter will be 0.21 µm. The pore space made with both average and effective particle sizes of SPAC provide a chance of biopolymers removal by physical means. The sizes of biopolymers are assumed to be between 3 – 50 nm as described in Chapter 4.

The pore bed diameter of the pre-coat layer made up of SASuper is 3.1 µm when average particle sizes come in contact with each other horizontally. This is decreased to 0.5 µm when the pore space is made with effective particles sizes of SPAC, which would provide little chance of biopolymers removal, by physical means.

2.4 BET (pore size, surface area)

The pore size of activated carbon determines the fate of NOM components adsorption. Pores are classified into three groups. Micropores have pore sizes below 2 nm, mesopores range from 2 to 50 nm and macropores have pores greater than 50 nm. Micropores are good for trace organic compounds removal but not for NOM removal. Most of the commercial PACs showed good performance in terms of traces organic compounds and low molecular weight NOM, especially when the pores fall in mesopore ranges. Another parameter that determines the performance of PACs is surface area. The capacity of PAC is measured by internal surface area. Higher surface area of PAC means more adsorption of contaminants and more time for PAC to become saturated due to high capacity. Pore sizes and internal surface area of PAC can be characterized by physiosorption techniques. Internal surface area is measured with the BET model that is based on the Langmuir model after modification to allow multilayer composition. The BET surface area and pores of selected PACS were measured with an ASAP 2020 - Physisorption Analyzer. The results are shown below in Figure 2.3 and Table 2.4.

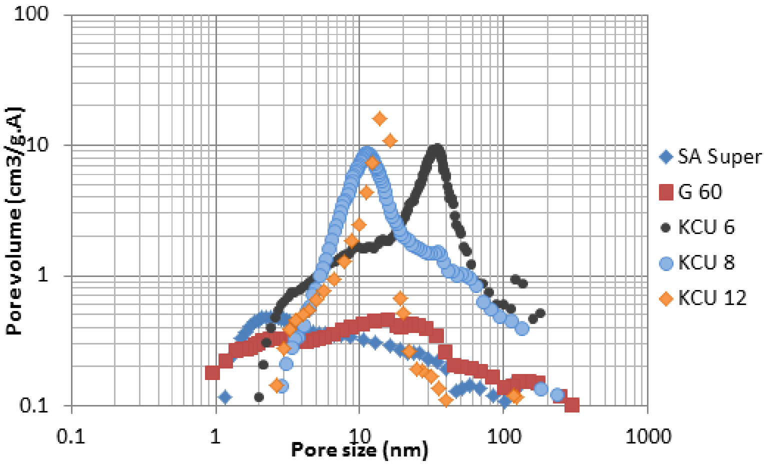


Figure 2.4: Pore sizes distribution of PACs

Table 2.4: BET surface area and pore characteristics of PACs

Type of PAC	Total BET Surface Area (m^2/g)	Total pore volume (cm^3/g)	Mesopores surface area (m^2/g)	Mesopores volume (cm^3/g)	Maximum pore diameter (nm)
SASuper	903	0.8	347	0.53	2.28
G60	909	0.86	310	0.51	2.83, 13.34
KCU 6	1280	3.96	747	3.83	33
KCU 8	1265	3.58	734	3.44	11.2
KCU 12	1121	2.7	670	2.7	13.6

Novel PACs (KCUs) showed higher BET surface area compared to commercial PACs (Table 2.4), implying higher capacities for adsorption. KCU 6 and KCU 8 have a good range of mesopores (Figure 2.3) and higher total pore volumes (Table 2.4), making them to qualify as a good candidates for contaminants removal. However KCU 6 has an added advantage of having much bigger pores with maximum size of 33 nm (Table 2.4). This differentiates KCU 6 with other PACs as a candidate for removal of high molecular weight NOM, especially biopolymers.

2.5: Adsorption Isotherms (Novel PACs and Commercial PACs)

2.51 Adsorption

Adsorption is the process that removes contaminants from liquid phase by accumulation at the interface between liquid phase and a separate (solid) phase. The adsorbing solid is referred to as adsorbent and the substance to be adsorbed from liquid or gas phase as an adsorbate (Qasim et al., 2004). Adsorption differs from absorption, which is process whereby the molecules or atoms of one phase penetrate nearly uniformly with those of another phase to form a homogeneous solution. The combination of the two processes, adsorption and absorption, is termed as sorption (Watts, 1997).

The adsorbate can be either physically adsorbed (physical adsorption), influenced by physical attraction with van der Waal forces, or chemically adsorbed (chemisorption) that involves transfer of electrons and formation of chemical bonds between adsorbent and adsorbate. Physical adsorption is more rapid and the most common mechanism in water treatment and is reversible while chemisorption is an irreversible process (Crittenden et al., 2005).

The process of adsorption is influenced by two characteristics for the given solvent-solute system. These characteristics are i) the hydrophobic character of the solute relative to the particular solvent and ii) the affinity of the solute for the solid. In many cases in water and wastewater treatment schemes, the combination of these two characteristics takes place. The common adsorbents used in water treatments are activated carbon, activated alumina, silica gel, manganese dioxide, iron oxide and zeolites.

In general, the extent of adsorption is influenced by the following factors: specific surface area or BET surface area (a larger the area means more capacity), pore size distribution (mesopores are good for high molecular weight compounds removal while micropores for trace organic compounds) and surface chemistry (acidic compounds differ with basic compounds in some cases). Other factors are solubility (low solubility adsorbate and nonpolar solvents – stronger adsorption), molecular size of adsorbate, pH (affects ionized species), inorganic salts (enhance adsorption of ionized species), temperature (adsorption decreases as temperature increases) and substituent groups (Cloirec and Faur, 2006).

2.5.2 Isotherms (Frendlich and Langmuir)

Adsorption is usually described by isotherms, that is, the amount of adsorbate on the adsorbent as a function of concentration at constant temperature (Qasim et al., 2004). The following equation is described the adsorption isotherms at equilibrium.

$$q = f(C) \longrightarrow \quad q = x/m$$

Where x is mass of adsorbate adsorbed and m is concentration of adsorbent

The equilibrium isotherm equation can be expressed as;

$$q = x/m = (C_o - C)V/m \qquad \text{(Roy, 1995)}$$

Where: q = solid phase conc. (e.g., µg/g), C = equilibrium of water-phase conc. (e.g., µg/g), m = activated carbon concentration (kg), V = volume (m^3) and x = mass adsorbed (kg or g)

The equilibrium tests are batch tests that take more than 10 days for GAC and about 1 day for PAC.

There are three common equations that are used to express isotherms are the Freundlich, Langmuir and BET isotherm equations.

Freundlich isotherm

The Freundlich equation is an empirical formula that is most widely used for adsorption in aqueous systems.

$q = K_F C_e^{1/n}$ (Cloirec and Faur, 2006)

Where: Cs = amount of solute adsorbed per unit weight of adsorbent = x/m (g/g)

C_e = equilibrium concentration of the solute in mg/L, K_F = adsorption capacity ((mg/g)/(1/µg) and 1/n = adsorption intensity (constant)

The equation can be linearized and becomes

Log Cs = log K_F + 1/n Log C_e and when a graph of Log Cs against Log Ce is plotted. Then, slope = 1/n (adsorption intensity) and log Cs intercept = K_F (adsorption capacity)

When $1/n < 1$ then it is favorable adsorption but when $1/n > 1$ then it is unfavorable adsorption (Cloirec and Faur, 2006).

Langmuir Isotherm

The Langmuir equation is valid for a single layer adsorption. The assumptions made are:-

- Maximum adsorption corresponds to saturated monolayer of the solute on the adsorbent surface
- The adsorption energy is same at all the sites
- There is no transmigration of adsorbate on the plane of the surface.

$$q = \frac{bq_m C_e}{1 + bC_e} \qquad \text{(Crittenden et al., 2005)}$$

Where q_m = maximum adsorption capacity

b = Langmuir isotherm constant

Upon Linearization:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{bq_m}\frac{1}{C_e}$$

When plotting 1/q vs. 1/Ce, then slope = $1/bq_m$ and intercept = $1/q_m$

The Langmuir model is based on monolayer coverage while the Freundlich model is applicable for heterogeneous surfaces (Ng et al., 2002). If the coefficient of 1/n > 1 then the variation in adsorbed adsorbent is greater than the variation in solute concentration (Ng et al., 2002).

2.5.3 Adsorption Experiments

To understand the capacity and kinetics of activated carbon, adsorption experiments are normally carried out. For determination of kinetics, feed samples with a known initial concentration of adsorbate are allowed to be adsorbed by an added adsorbent like activated carbon over different time intervals. The same dose of adsorbent is used for all samples and the saturation point is determined. The saturation point is the equilibrium time when there is no more adsorption taking place. At equilibrium, the adsorbent is saturated with no more adsorption. Actual adsorption experiments are thus based on equilibrium time.

The capacity of activated carbon can be measured in two ways. The first method is to keep a constant volume of feed and add different adsorbent doses to each beaker. The second method involves adding same the adsorbent dose to each beaker but changing the volumes of the feed. In this chapter, the first method was adopted.

2.5.4 DOC components Isotherms based on LC-OCD and FEEM measurements

Wastewater effluent rom Jeddah, containing effluent organic matter (EfOM), was employed for these adsorption experiments. The wastewater effluent was filtered through 0.45 µm filters to remove suspended particles. Clean 200 mL bottles were used for 100 mL samples. A minimum of 5 samples was used for each PAC adsorption experiment. PAC was measured using an analytical balance with an accuracy of 99.99 %. Different weights of PAC were measured from 60, 30, 15, 7.5 and 3 mg and added to the feed samples of 100 mL. These corresponded to 600, 300, 150, 75 and 30 mg/L concentrations. Additional samples were prepared for KCU 8 at final concentrations of 120 and 60 mg/L. After addition of different PACs into feed water samples, the samples were allowed to achieve equilibrium concentrations with the aid of a shaker table for 24 hours. This time was assumed based on kinetics experiments using UV_{254} absorbance measurements that showed exhaustion of commercial PAC after 2 hours. UV_{254} absorbance measurements are specific to aromatic compounds, an appropriate assumption for humic substances but not necessarily for biopolymers. A reference sample (without addition of PAC) was also added. After 24 hours, the samples were filtered through 0.45

µm filters to remove residual PACs. LC-OCD was then used to analyze the removal of EfOM components. The characteristics of the feed water used for adsorption experiments are shown below:

Table 2.5: Characteristics of feed water used for adsorption experiments (based on LC-OCD).

	DOC (mg/L)	Biopolymers (mg/L)	Humic substances (mg/L)	Building Blocks (mg/L)	Neutrals (mg/L)	UV_{254} (1/cm)	$SUVA_{254}$ (L/mg-m)
Wastewater Effluent	4.92	0.29	1.8	0.87	1.82	0.136	2.76

The amount of low molecular weight acid (L.M.W Acids) in wastewater effluents was < 0.01 mg/L which is not significant and hence it was neglected.

2.5.4.1 Biopolymers Isotherms

Biopolymers are high molecular weight components of NOM with a molecular weight of > 20,000 Da. They contribute < 15 % of the NOM components in wastewater effluents but their contribution to the membrane fouling is significant. Commercial PACs have failed to remove biopolymers to the adequate level. This raised the need to develop new PACs that can deal with the challenge of biopolymers removal through adsorption. The adsorption capacity of commercial and novel PACs in terms of biopolymers removal was assessed, and Langmuir model and Freundlich models were used to assess the performance of these PACs. The results are documented in Table 2.6 and Figure 2.5 below. The detection limit of LC-OCD is < 1 ppb (http://www.doc-labor.de/Specs.html).

Table 2.6: Biopolymers removal assessment

		Biopolymers Conc. (Co) (mg/L)				
Wastewater 1		0.2901				
Wastewater 2		0.3040				
Type of PAC	**m (mg/L)**	**Ce (mg/L)**	**x (mg/L)**	**Cs (mg/g)**	**Log Ce**	**Log Cs**
SA Super	600	0.0010	0.2891	0.4809	-2.9992	-0.3179
	300	0.0032	0.2869	0.9501	-2.4940	-0.0222
	150	0.0509	0.2392	1.5434	-1.2933	0.1885
	75	0.1249	0.1652	2.1441	-0.9033	0.3312
	30	0.2574	0.0327	0.9383	-0.5893	-0.0277
G60	600	0.0065	0.2836	0.4727	-2.1852	-0.3254
	300	0.0284	0.2617	0.8720	-1.5465	-0.0595
	150	0.0844	0.2058	1.3621	-1.0739	0.1342
	75	0.1706	0.1195	1.5320	-0.7679	0.1853
	30	0.2814	0.0087	0.2561	-0.5507	-0.5916
KCU 6	600	0.0043	0.2858	0.4796	-2.3642	-0.3191
	300	0.0086	0.2816	0.9177	-2.0667	-0.0373
	150	0.0119	0.2782	1.8064	-1.9251	0.2568
	75	0.0279	0.2622	3.4139	-1.5538	0.5333
	30	0.0893	0.2008	6.7058	-1.0492	0.8265
KCU 8	600	0.0038	0.2863	0.4779	-2.4184	-0.3206
	300	0.0029	0.2872	0.9754	-2.5350	-0.0108
	150	0.0126	0.2776	1.7889	-1.9006	0.2526
	120	0.0035	0.3005	2.4871	-2.4592	0.3957
	75	0.0178	0.2724	3.5814	-1.7505	0.5541
	60	0.0410	0.2630	4.3490	-1.3869	0.6384
	30	0.1171	0.1731	5.2205	-0.9316	0.7177
KCU 12	600	0.0038	0.2863	0.4740	-2.4149	-0.3242
	300	0.0177	0.2725	0.8900	-1.7531	-0.0506
	150	0.0309	0.2593	1.6809	-1.5107	0.2255
	75	0.0665	0.2236	2.8910	-1.1771	0.4610
	30	0.1803	0.1098	3.4868	-0.7440	0.5424

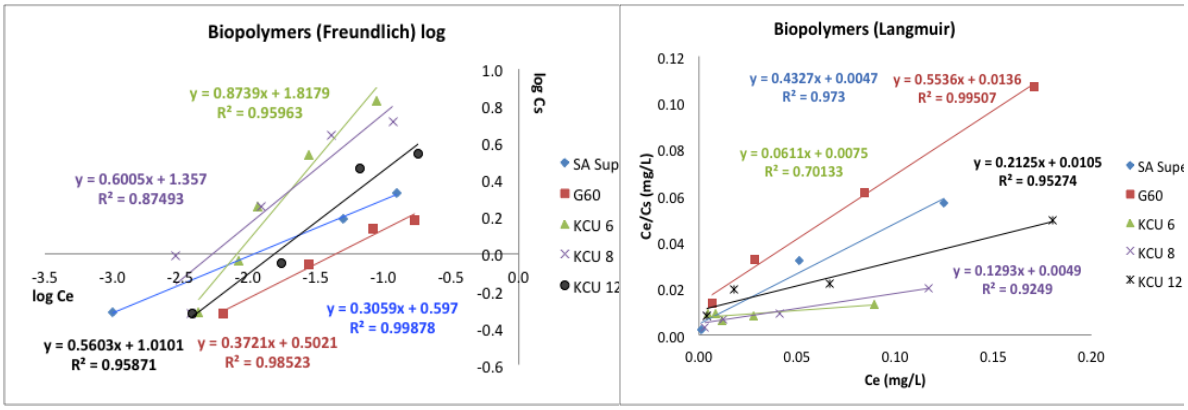
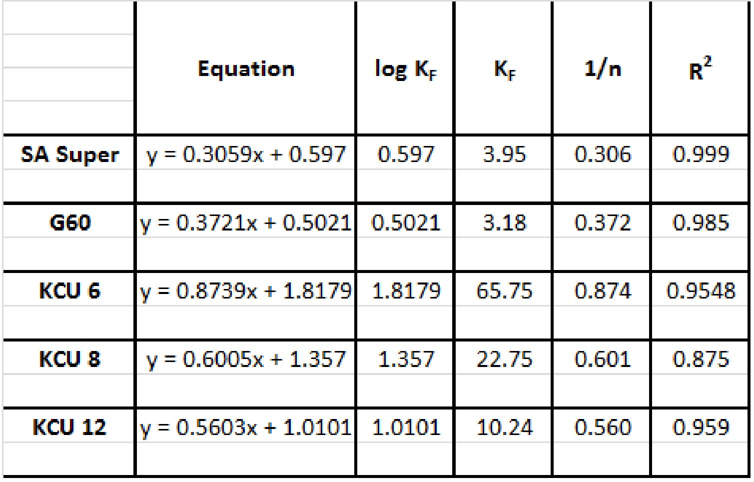


Figure 2. 5: Freundlich (left) and Langmuir (right) Isotherms for biopolymers.

The Freundlich model showed the best fit and a good correlation compared to Langmuir. The Freundlich model is considered to be more useful over a wide range of concentrations while the Langmuir model is best fit for low concentrations of adsorbates (Mourao et al., 2006). From Freundlich isotherms equations, the capacities and intensities constant values were calculated. The results are shown in Table 2.7 below:

Table 2.7: Freundlich Isotherm Constants - Biopolymers



	Equation	log K_F	K_F	1/n	R^2
SA Super	y = 0.3059x + 0.597	0.597	3.95	0.306	0.999
G60	y = 0.3721x + 0.5021	0.5021	3.18	0.372	0.985
KCU 6	y = 0.8739x + 1.8179	1.8179	65.75	0.874	0.9548
KCU 8	y = 0.6005x + 1.357	1.357	22.75	0.601	0.875
KCU 12	y = 0.5603x + 1.0101	1.0101	10.24	0.560	0.959

KCU 6 performed better than the other PACs showing a high capacity value (K_F = 65.75) and much better intensity (1/n = 0.874) as presented in Table 2.6. This complies with the findings explained in part 2.3 of this chapter which highlight KCU 6 due to its high BET surface area but most importantly, the sizes of its pores (bigger pores). Other novel PACs (KCUs) showed better performance than commercial PAC with regard to biopolymers removal. No significant differences were observed between two commercial PACs. To conclude, KCU 6 continues to show the merits of the best PAC candidate for pre-coating on ceramic membranes.

2.5.4.2 Humic substances Isotherms

In wastewater, humic substances contribute 30 – 40 % of the NOM components. The size of humic substances in terms of molecular weight is 1000 – 20,000 Da. Microfiltration membranes are not able to remove humic substances without pretreatment such as coagulation or activated carbon. However, very high removal of humics is not easy even at a high dose as shown in Table 2.8. The Freundlich model fit better (good correlations) than the Langmuir model (Figures 2.6). With regard to humic substances adsorption, all PACs (commercial and novel) showed similar adsorption capacities (Table 2.9).

Table 2.8: Humic substance removal assessment

		H.S Conc. (Co) (mg/L)				
Wastewater 1		1.797				
Wastewater 2		1.991				
Type of PAC	**m (mg/L)**	**Ce (mg/L)**	**x (mg/L)**	**Cs (mg/g)**	**Log Ce**	**Log Cs**
SA Super	600	0.2155	1.5815	2.6307	-0.6665	0.4201
	300	0.3501	1.4469	4.7909	-0.4558	0.6804
	150	0.5083	1.2887	8.3141	-0.2939	0.9198
	75	0.6985	1.0985	14.2573	-0.1559	1.1540
	30	1.2077	0.5893	16.9090	0.0820	1.2281
G60	600	0.1630	1.6340	2.7233	-0.7878	0.4351
	300	0.2371	1.5599	5.1973	-0.6250	0.7158
	150	0.3877	1.4093	9.3288	-0.4115	0.9698
	75	0.6285	1.1685	14.9809	-0.2017	1.1755
	30	1.1500	0.6470	18.9465	0.0607	1.2775
KCU 6	600	0.3847	1.4123	2.3701	-0.4149	0.3748
	300	0.5162	1.2808	4.1747	-0.2872	0.6206
	150	0.6401	1.1569	7.5108	-0.1938	0.8757
	75	0.7890	1.0079	13.1242	-0.1029	1.1181
	30	1.0522	0.7448	24.8676	0.0221	1.3956
KCU 8	600	0.3329	1.4641	2.4439	-0.4777	0.3881
	300	0.5117	1.2853	4.3649	-0.2910	0.6400
	150	0.6268	1.1702	7.5425	-0.2029	0.8775
	120	0.7160	1.2750	10.5518	-0.1451	1.0233
	75	0.8203	0.9767	12.8427	-0.0860	1.1087
	60	0.8617	1.1293	18.6764	-0.0646	1.2713
	30	1.1489	0.6481	19.5515	0.0603	1.2912
KCU 12	600	0.4713	1.3257	2.1948	-0.3267	0.3414
	300	0.5708	1.2262	4.0052	-0.2435	0.6026
	150	0.7434	1.0536	6.8305	-0.1288	0.8345
	75	0.8762	0.9208	11.9039	-0.0574	1.0757
	30	1.1381	0.6589	20.9176	0.0562	1.3205

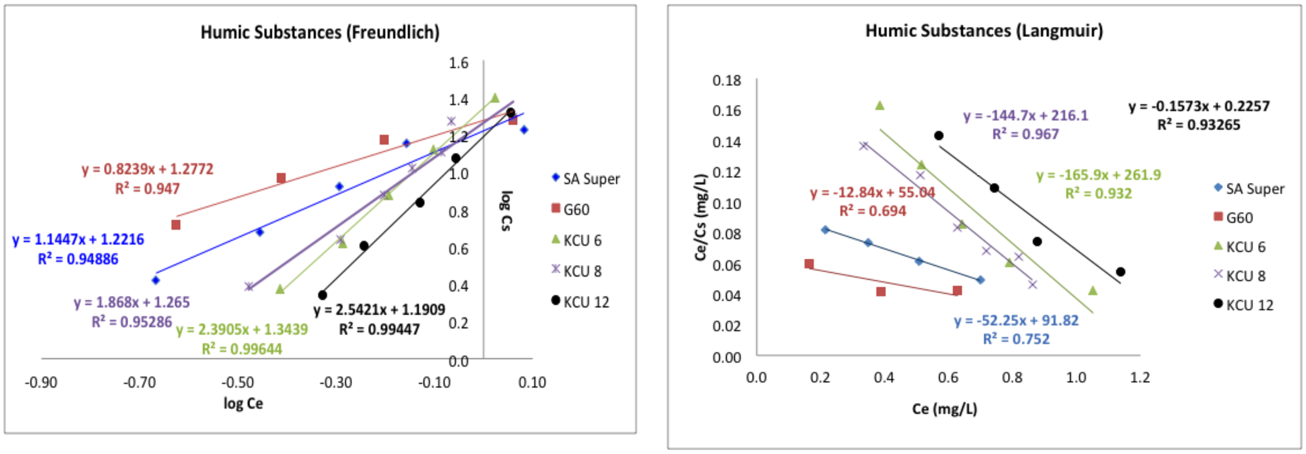


Figure 2. 6: Freundlich (left) and Langmuir (right) Isotherms for Humic Substances.

Table 2.9: Freundlich Isotherm Constants – Humic substances

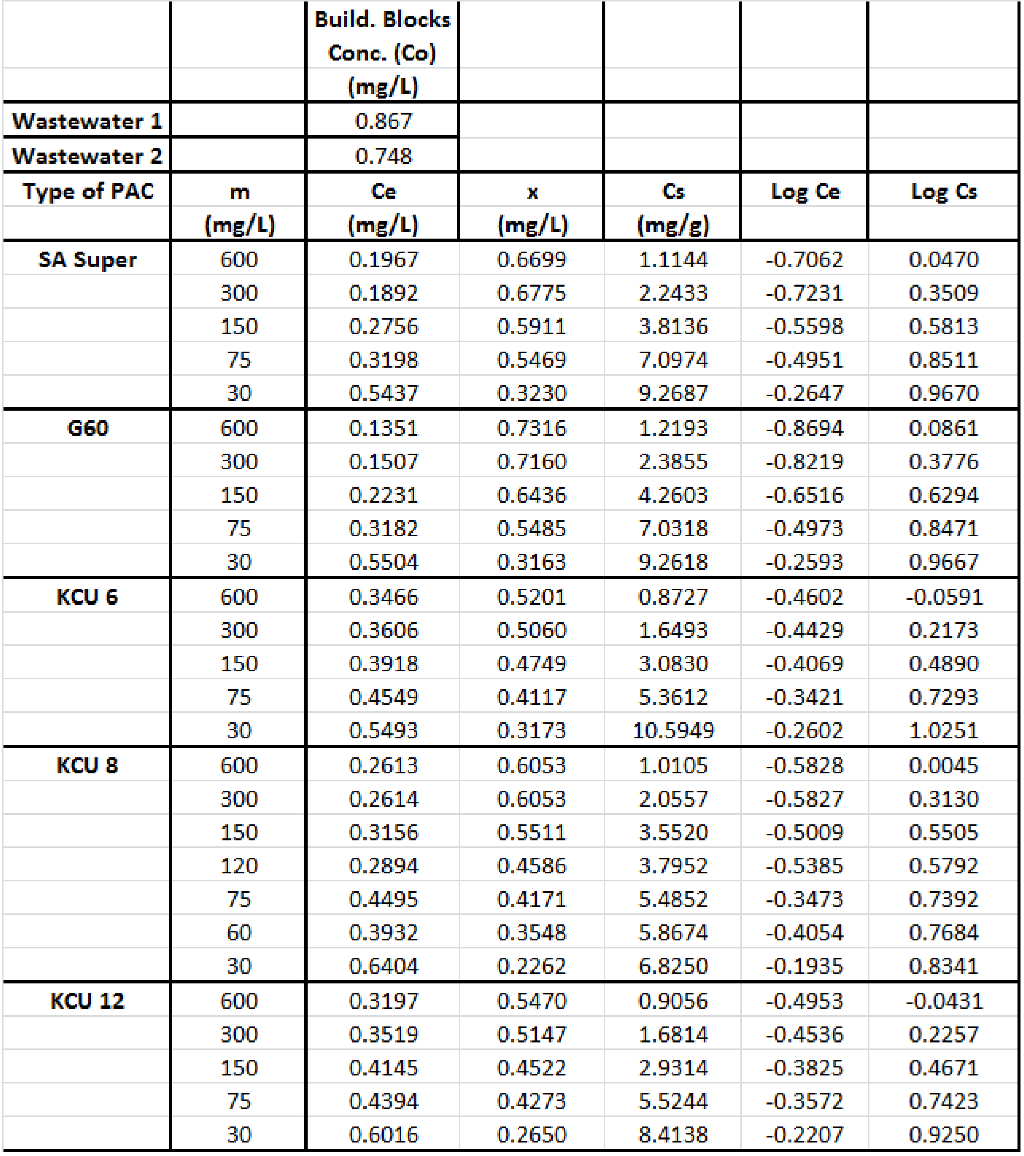
	Equation	log K_F	K_F	1/n	R^2
SA Super	y = 1.1447x + 1.2216	1.2216	16.66	1.1417	0.95
G60	y = 0.8239x + 1.2772	1.2772	18.93	0.8239	0.947
KCU 6	y = 2.3905x + 1.3439	1.3439	22.07	2.3905	0.996
KCU 8	y = 1.868x + 1.265	1.265	18.41	1.868	0.953
KCU 12	y = 2.5421x + 1.1909	1.1909	15.52	2.5421	0.995

2.5.4.3 Building blocks Isotherms

Building blocks (BB) are the product of further degradation of humic substances (HS). Their molecular weight is 300 – 500 Da so they are also difficult to remove by low-pressure membranes alone without pretreatment. The BB contribution to low pressure membranes fouling is considered to be low and not significant because of their molecular weight sizes compared to membrane pores. However in wastewater reclamation using RO membranes, building blocks may significantly contribute to fouling.

The results of building blocks removal analyzed by LC-OCD are expressed in Table 2.10. The Freundlich model showed good correlations compared to the Langmuir model (Figures 2.7). Therefore it was adopted for detailed analysis of the PAC capacities. It was observed that KCU 6 had a high K_F value compared to other PACs (Table 2.11). This means that KCU 6 has a high adsorption capacity for building blocks.

Table 2.10: Building blocks removal assessment



		Build. Blocks Conc. (Co) (mg/L)				
Wastewater 1		0.867				
Wastewater 2		0.748				
Type of PAC	**m (mg/L)**	**Ce (mg/L)**	**x (mg/L)**	**Cs (mg/g)**	**Log Ce**	**Log Cs**
SA Super	600	0.1967	0.6699	1.1144	-0.7062	0.0470
	300	0.1892	0.6775	2.2433	-0.7231	0.3509
	150	0.2756	0.5911	3.8136	-0.5598	0.5813
	75	0.3198	0.5469	7.0974	-0.4951	0.8511
	30	0.5437	0.3230	9.2687	-0.2647	0.9670
G60	600	0.1351	0.7316	1.2193	-0.8694	0.0861
	300	0.1507	0.7160	2.3855	-0.8219	0.3776
	150	0.2231	0.6436	4.2603	-0.6516	0.6294
	75	0.3182	0.5485	7.0318	-0.4973	0.8471
	30	0.5504	0.3163	9.2618	-0.2593	0.9667
KCU 6	600	0.3466	0.5201	0.8727	-0.4602	-0.0591
	300	0.3606	0.5060	1.6493	-0.4429	0.2173
	150	0.3918	0.4749	3.0830	-0.4069	0.4890
	75	0.4549	0.4117	5.3612	-0.3421	0.7293
	30	0.5493	0.3173	10.5949	-0.2602	1.0251
KCU 8	600	0.2613	0.6053	1.0105	-0.5828	0.0045
	300	0.2614	0.6053	2.0557	-0.5827	0.3130
	150	0.3156	0.5511	3.5520	-0.5009	0.5505
	120	0.2894	0.4586	3.7952	-0.5385	0.5792
	75	0.4495	0.4171	5.4852	-0.3473	0.7392
	60	0.3932	0.3548	5.8674	-0.4054	0.7684
	30	0.6404	0.2262	6.8250	-0.1935	0.8341
KCU 12	600	0.3197	0.5470	0.9056	-0.4953	-0.0431
	300	0.3519	0.5147	1.6814	-0.4536	0.2257
	150	0.4145	0.4522	2.9314	-0.3825	0.4671
	75	0.4394	0.4273	5.5244	-0.3572	0.7423
	30	0.6016	0.2650	8.4138	-0.2207	0.9250

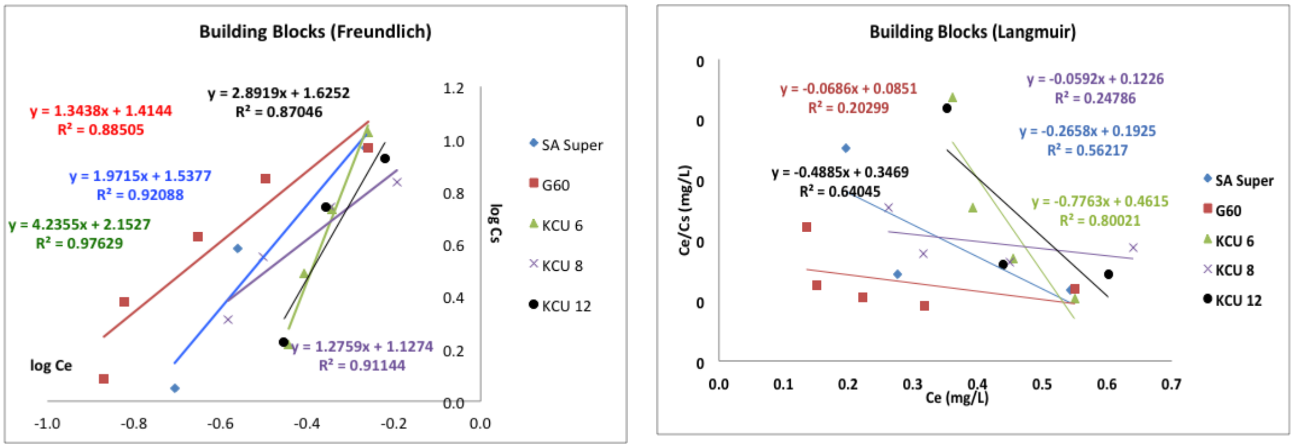


Figure 2. 7: Freundlich (left) and Langmuir (right) Isotherms for Building Blocks

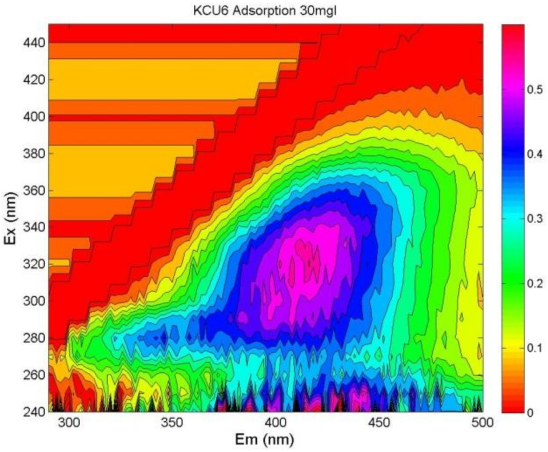
Table 2.11: Freundlich Isotherm Constants – Building blocks

	Equation	log K_F	K_F	1/n	R^2
SA Super	y = 1.9715x + 1.5377	1.5377	34.49	1.97	0.921
G60	y = 1.3438x + 1.4144	1.4144	25.97	1.34	0.885
KCU 6	y = 4.2355x + 2.1527	2.1527	142.13	4.24	0.976
KCU 8	y = 1.2759x + 1.1274	1.1274	13.41	1.28	0.911
KCU 12	y = 2.8919x + 1.6252	1.6252	42.19	2.89	0.87

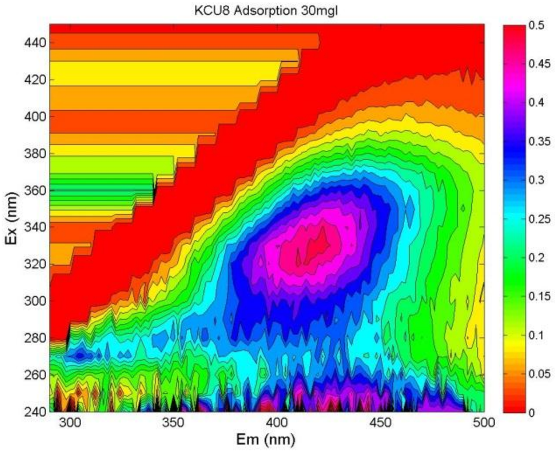
2.5.5 Florescence Excitation Emission Matrix (FEEM) of Wastewater Effluent before and after adsorption.

To complement the previous results obtained from LC-OCD measurements, another sample measurement technique was employed. Florescence excitation emission matrix (FEEM) was applied to characterize the NOM components based on humic-like organic matter and protein-like organic matter. A Fluoromax-4 Spectrofluorophotometer manufactured by Horiba Jobin Yvon was employed to explore more information on removal of protein-like and humic-like components of NOM. FEEM in terms of humic substances and proteins was found to exhibit three peaks. These peaks are described as humic-like, fulvic-like and protein-like organic matter. Peaks with excitation/emission ranges of 237-260/400-500 nm and 300-370/400-500 nm correspond to humic- and fulvic-like components, respectively (Henderson et al., 2009). The protein-like peak lies in excitation/emission range of 225-275/309-340 nm as described by (Hambly et al., 2010). FEEM at low doses (30 mg/L) were developed to demonstrate the performances of four PACs (Figure 2.8).

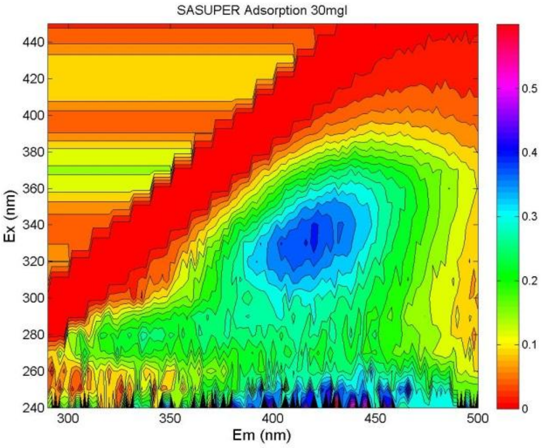
2.5.5.1 FEEM of samples at a low dose of 30 mg/L PAC adsorption



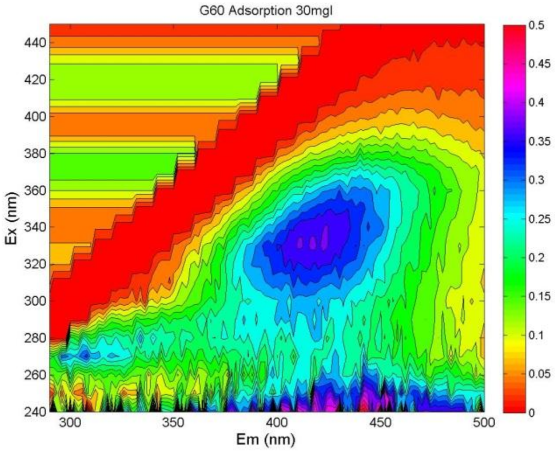
(a)



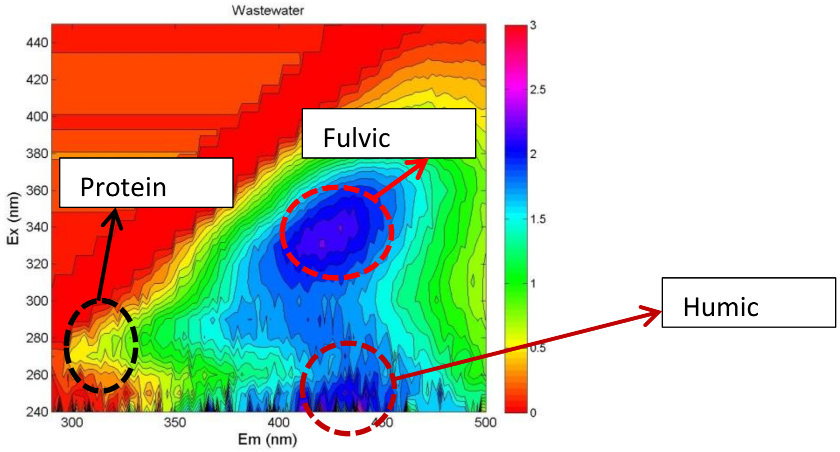
(b)



(c):



(d)



(e)

Figure 2. 8: FEEM of (a) wastewater after KCU 6 adsorption (b) KCU 8 adsorption (c) SASuper adsorption (d) G60 adsorption all at a dose of 30 mg/L and (e) wastewater feed.

The data derived from peaks of humic-like, fulvic-like, and protein-like components of selected samples (Figure 2.8) before and after adsorption are presented in Table 2.12 below:

Table 2.12: FEEM results of wastewater after PAC adsorption at 30 mg/L

	PEAK 1 (Fulvic like)			**PEAK 2 (Humic like)**			**PEAK 3 (Protein like)**		
PAC dose = 30 mg/L	**Ex./Em**	**Intensity**	**% Removal**	**Ex./Em**	**Intensity**	**% Removal**	**Ex/Em**	**Intensity**	**% Removal**
WW	340/430	2.285		240/442	2.921		280/320	0.765	
KCU 6	320/416	0.507	78 %	246/420	0.648	78%	280/322	0.3	61 %
KCU 8	330/420	0.502	78%	240/420	0.521	82%	270/304	0.367	52 %
SASUper	340/420	0.408	82%	240/430	0.734	75%	270/308	0.29	62 %
G60	330/422	0.39	83%	240/442	0.524	82%	270/308	0.341	55%

Humic substances peak removals (humic- and fulvic-like) showed similar levels of removal for all PACs (Table 2.12), which agree with results presented for LC-OCD in terms of humic substances removal. Protein-like peaks removals by SASuper and KCU 6 were the same (61 – 62 %) while KCU 8 and G60 showed similar values (52 – 55 %). In general no significant differences in terms of removal of proteins (which is part of the biopolymers) were observed in removal of proteins. This leads to the conclusion that other species of biopolymers (not proteins) are well removed by KCU 6 compared with other PACs, based on the difference observed in LC-OCD results.

2.6 Zeta Potential of Ceramic membranes and Polymeric membranes (PVDF and MCE)

Negative particles form a layer in which positive ions are strongly bound. This layer is called the Stern layer. Beyond the Stern layer, an electrical double layer is formed whereby both ions (positive and negative) are freely floated (Figure 2.9). The potential measured in the electrical double layer is termed as the zeta potential.

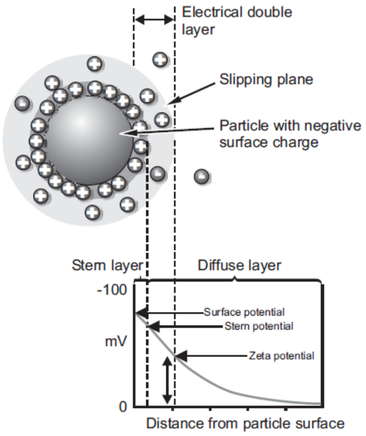


Figure 2.9: Zeta potential
Source: http://www.nbtc.cornell.edu/facilities/downloads/Zetasizer%20chapter%2016.pdf

Zeta potential is highly dependent on changes of pH of the electrolyte. For amphoteric particles, at low pH, they become positively charge and at a high pH they change to a negative charge. When the charge is 0 at certain pH, then this point is called the isoelectric point (IEP) or point of zero charge (ZPC). The surface charge of the membranes used in this research was measured by the electrokinetic method using an

Anton Paar Surpass instrument. Sodium chloride and potassium chloride at concentrations of 10 mM were used as electrolyte. The pH range of 2 – 10 was used. The adjustable gap was used and the gap was set at approximately 100 um for good reproducible data with a correlation of > 99 %. The measurements started from low pH to high pH that was adjusted with automatic addition of a few drops of 0.1 M of KOH or NaOH to the electrolyte. The results obtained are expressed in Figure 2.10 below:

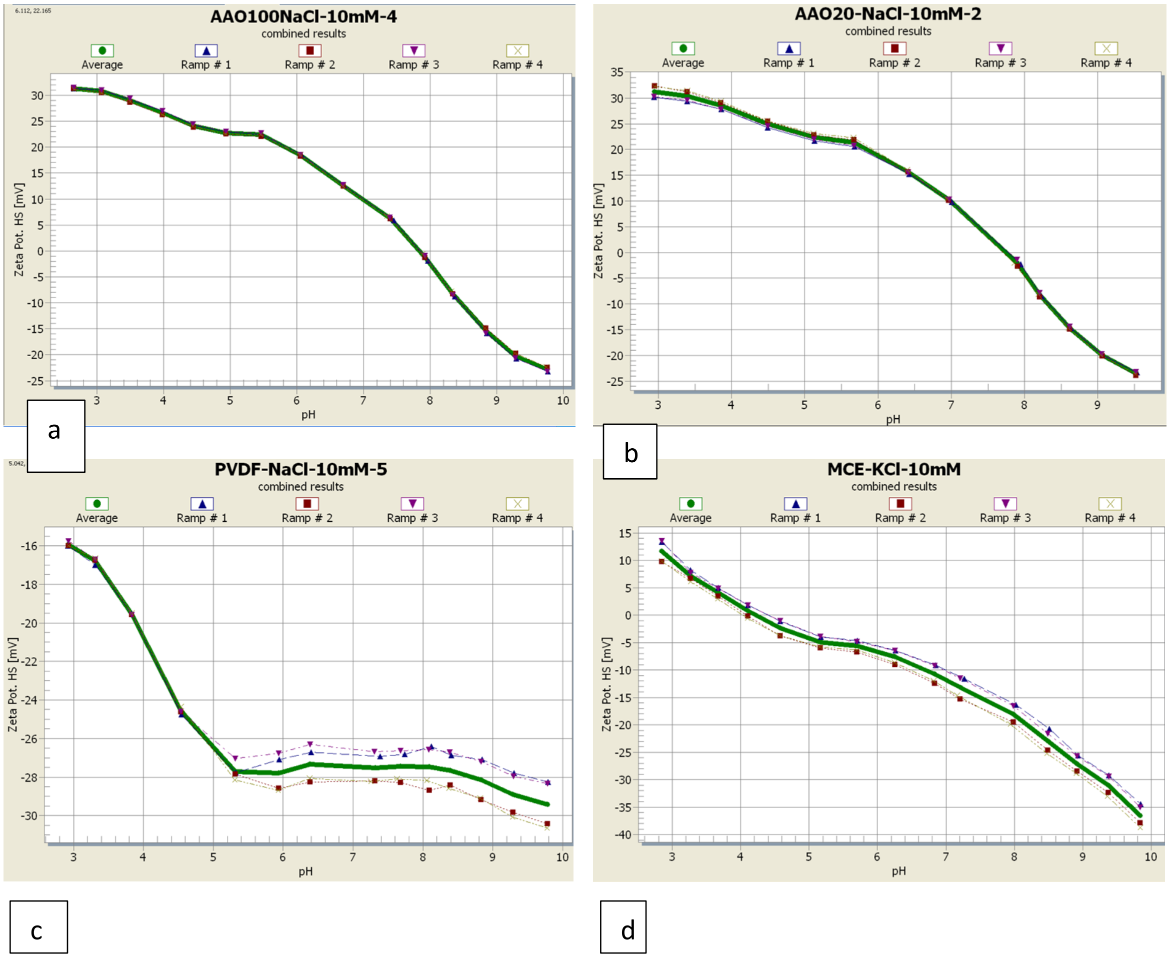


Figure 2.10: Zeta potential of (a) AAO100 ceramic membrane (b) AAO20 ceramic membrane (c) MF PVDF membrane measured with 10 mM of NaCl electrolyte and (d) Zeta potential of MCE UF membrane measured with 10 mM of KCl electrolyte.

Good correlation (> 99 %) was achieved for all measured samples in which all points were measured 4 times. The Anopore MF membrane showed the isoelectric point at pH of 7.85 (Figure 2.10 a) while Anopore UF membrane showed isoelectric point at pH of 7.75 (Figure 2.10 b). In contrast, the PVDF membrane showed a highly negatively charge without reaching the IEP point (Figure 2.10 c) when 10 mM of NaCl salt was used as an electrolyte while the MCE membrane showed an IEP value of 4 with 10 mM of KCl applied as an electrolyte (Figure 2.10 d).

Based on the zeta potential analysis, ceramic membranes made of alumina are positively charged and polymeric membranes applied in this research were negatively charged. The isoelectric point of Anopore ceramic membranes (whether MF or UF) were found to be typical 8. This agrees with other findings that found the IEP value of α-alumina membrane was > 8 when measured with streaming potential and 8.5 with electro-viscous potential (Huisman et al., 1998) based on 1 mM salt concentration. Another study found that the isoelectric point of an alumina ceramic membrane using 10 mM of sodium chloride electrolyte was observed at pH 6 measured with the electro-osmotic method (Zhao et al., 2005).

The isoelectric point of a ceramic membrane made of alumina was reported to have a point of zero charge at pH of around 8.1-8.3 in a solution of sodium chloride (Mullet et al., 1997). Membrane charge is regarded as important since it is believed to influence the fouling behavior of a membrane (Kim et al., 1997). Therefore, interaction between the membrane surface charge and foulants can be studied and interpreted if the zeta potential of the membrane is known.

2.7 Scanning Electron Microscopy (SEM) Images of Ceramic membranes and Polymeric membranes

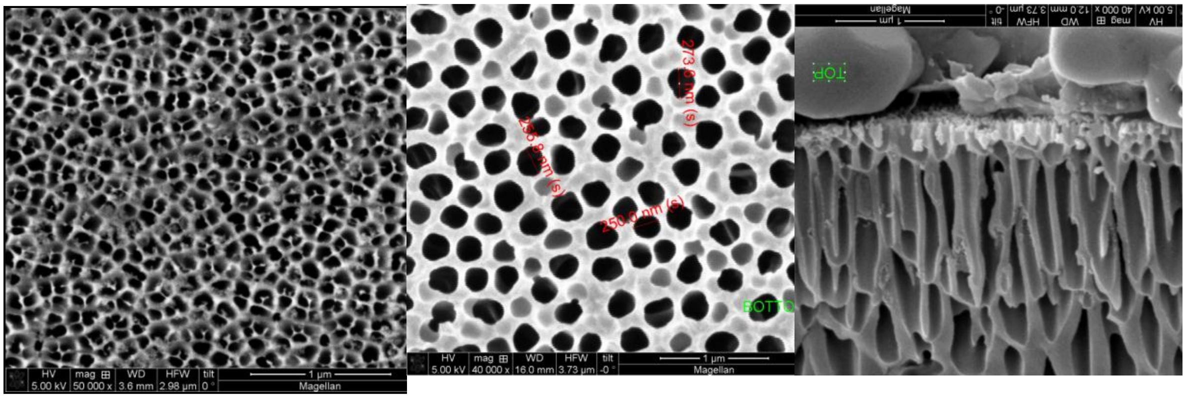
The flat sheet membranes were characterized using Scanning Electron Microscopy (SEM) using a QUANTA 3D FEG and NOVA NANO from FEI Company. Samples were coated with gold ≈ 5 mm K575X from Quorum Tech.

2.7.1 SEM Images of Anopore Ceramic membranes (AAO100, AAO20 and Metawater Ceramic MF Membrane)

2.7.1.1 Anopore Ceramic Membranes (AAO100 and AAO20)

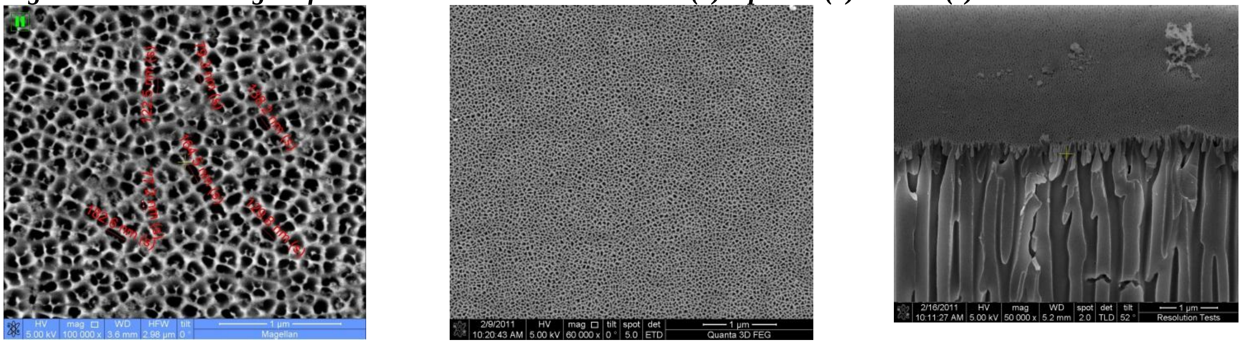
Fabrication of Anopore ceramic membrane is done by electrolysis method compared to METAWATER membrane that made of sintering process. When Aluminium is anodized in neutral electrolyte like Aluminium phosphate, a thin uniform oxide layer is formed (about 1.2 nm). When acidic solution like oxalic acid is used instead, a thick porous oxide layer is formed which etched partially due to solvent power of the acid solution. The growth continues with etching of oxide forming different pore diameter at bottom and top depending on the acidic electrolyte used.

The top view and cross-sectional images of Anopore ceramic membranes were investigated with Scanning Electron Microscopy (SEM) as shown in the Figures 2.11 and 2.12 below. The AAO100 is a microfiltration (MF) membrane with typical pore size of 0.1 µm and the AAO20 is an ultrafiltration (UF) membrane with typical pore size of 0.02 µm.



(a) (b) (c)

Figure 2.11: SEM images of AAO100 ceramic MF membrane (a) top view (b) bottom (c) cross-sectional



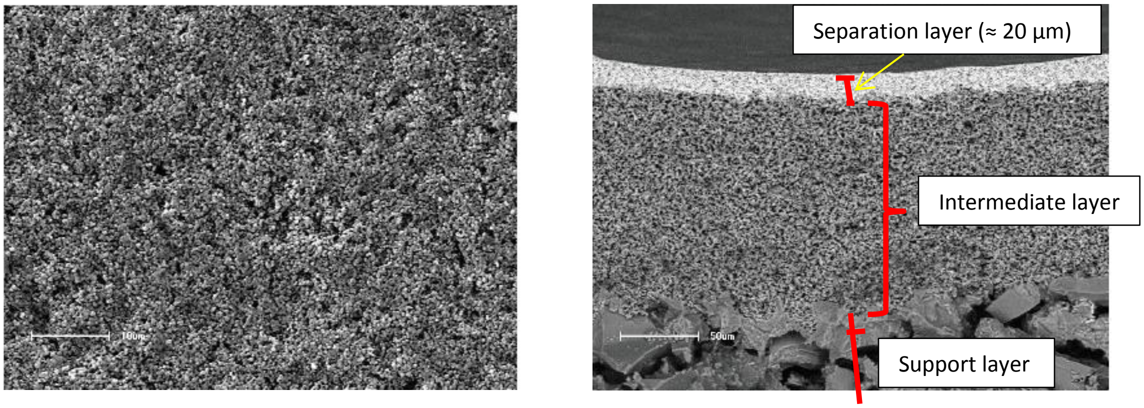
(d) (e) (f)

Figure 2.12: SEM images of AAO20 ceramic UF membrane (d) top view (e) bottom (f) cross-sectional

The pores of the AAO100 membrane are homogeneous with smaller pores at the top (Figure 2.11) and two times bigger pores at the bottom (Figure 2.11). The difference in pore sizes between the top and bottom makes the pores of AAO100 have a flattened tubular shape (Figure 2.11). The pores of AAO100 are typically 100 nm on average according to manufacturer. However, these pores actually vary between 77 – 183 nm (Figure 2.11) with uniform structure. This kind of structure helps the membranes to have high porosity since it believed that membranes with low porosity at the support layer are more prone to fouling (Jones and O'Melia, 2000). The Anopore UF ceramic membrane has a conical shape (typical 20 nm at top and 200 nm at the bottom of membrane) as shown in Figure 2.12. This contributes to Anopore ceramic membranes having a high permeability compared to polymeric membranes. Also, this structure supports effective backwashing.

2.7.1.2 METAWATER Ceramic MF Membrane

The Metawater ceramic MF membrane, unlike the Anopore membranes, has non-uniform pores (Figure 2.13 a). Different method was used to prepare Metawater ceramic membranes compared to Anopore ceramic membranes that are fabricated by anodic oxidation. Metawater ceramic membranes are prepared by sol-gel method in which the dried gel of alumina is sintered at high temperature between 400 – 900 °C. The white band appearing in the cross-sectional SEM image of the alumina membrane is the separation layer (Figure 2.13 b). The thickness of the separation layer is approximately 20 µm. The bottom layer, which is more porous, is the support layer. The two layers are connected with an intermediate layer, which acts as a buffer between separation layer and support layer (Figure 2.13 b). The intermediate layer is much thicker than the other two layers.



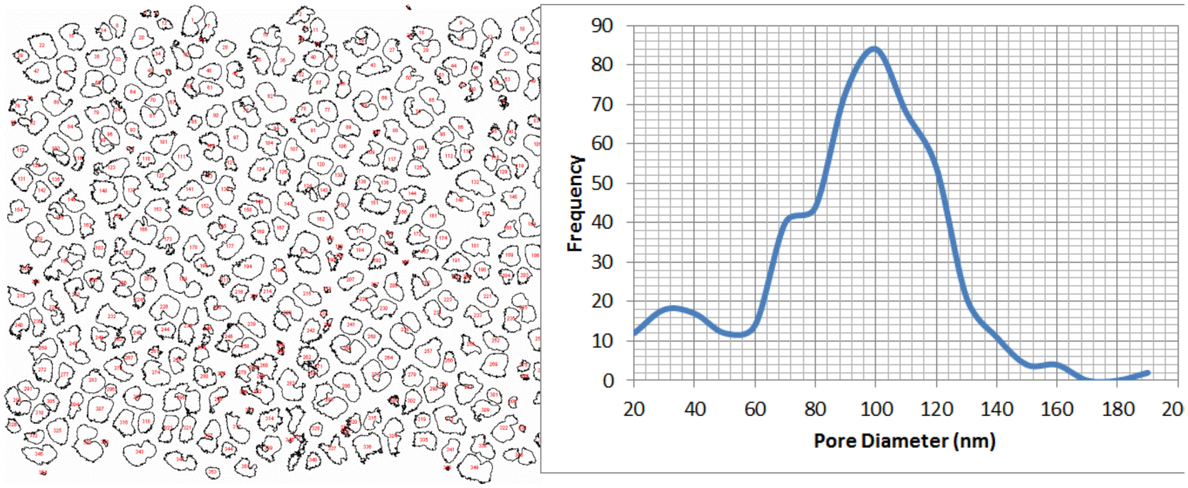
(a) **(b)**

Figure 2.13: SEM images of Metawater Ceramic MF membrane (a) Top view (b) cross-sectional
Source: (Meyn, 2011)

The separation layer was made thin in order to maintain a high flux and lower the trans-membrane pressure (TMP). TMP is direct proportional to the thickness of the separation layer. The strength of ceramic membrane is based on this layer (separation layer), which made of inorganic materials. While separation layers of polymeric membranes are vulnerable to high backwashing flux and chemical cleaning that ultimately wear out this layer, ceramic membranes remained durable. Intermediate and support layer structure support high flux operation and effective backwashing.

2.7.2 Pore size distribution of AAO100 and AAO20

The pore size distribution was calculated by Image J software based on the top view image of a membrane. The AAO membranes have uniform pores that can be easily estimated by the software. Pores are assumed to be circular in shape (Figure 2.14 a) and the diameter of each pore was calculated and the pore distribution curves were plotted (Figure 2.14 b).

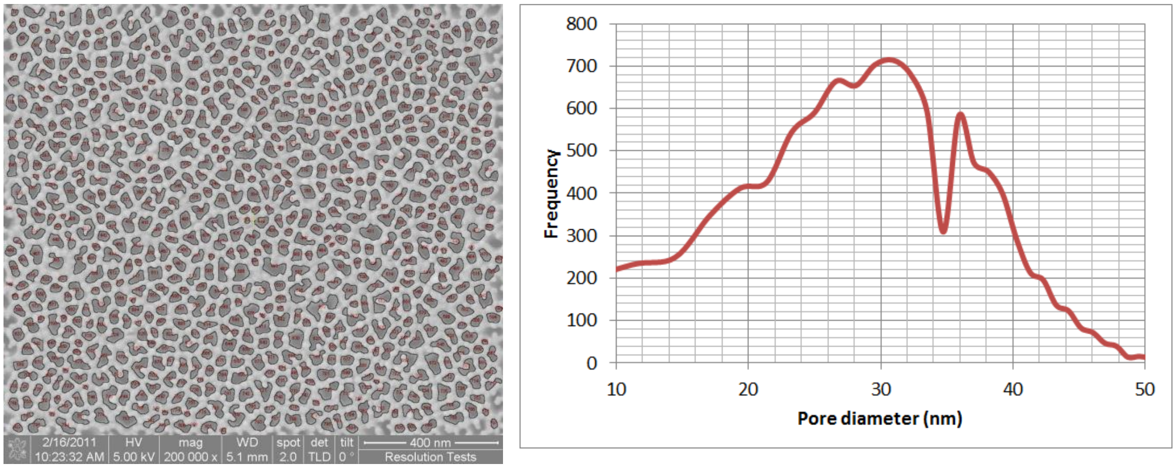


(a): SEM Image of AAO100 modified

(b): Pore size distribution of AAO100 membrane

Figure 2.14: (a) SEM image of AAO100 modified with Image J software (b) Pore size distribution of AAO100 membrane

The average pore size of the Anopore MF ceramic membrane is 100 nm (Figure 2.14 b). This corresponds precisely to the value given by manufacture for the pore size of AAO100, which is 0.1 µm.



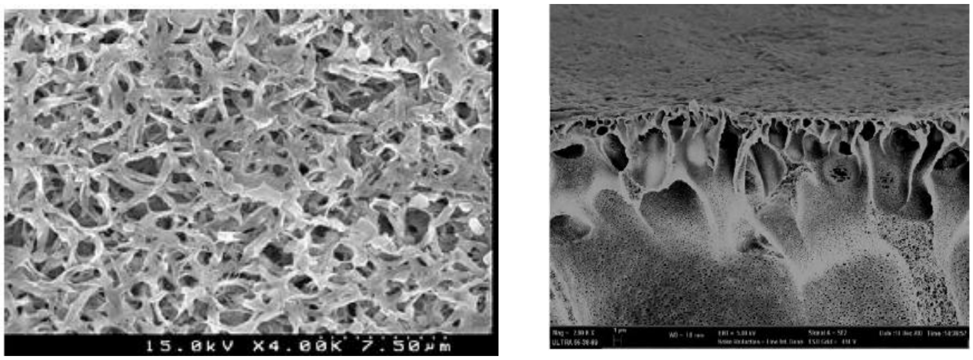
(a) **(b)**

Figure 2.15: (a) SEM image of AAO20 modified with Image J software (b) Pore size distribution of AAO20 membrane

The average pore size of the AAO20 UF membrane (Figure 2.15 a), derived from the pore distribution curve (Figure 2.15 b), is 30 nm. The value specified by the manufacture is 20 nm, which is 10 nm less, compared to the calculated value. Hence, it may be concluded that the Image J software can more precisely estimate the pores that are in microfiltration range rather than ultrafiltration range, which is constrained by smaller, pore sizes.

2.7.3 SEM Images of polymeric membranes (PVDF and MCE)

PVDF is prepared by isothermal immersion precipitation using ethanol and water solvents. PVDF membranes are preferable in polymeric membrane technology since they can tolerate chloride and acid during chemical cleaning (Muthukumaran et al., 2011). The pores of PVDF and MCE have irregular shapes (Figure 2.30 – 2.33). This kind of structure may influence membrane fouling occurrence and effectiveness of backwashing.

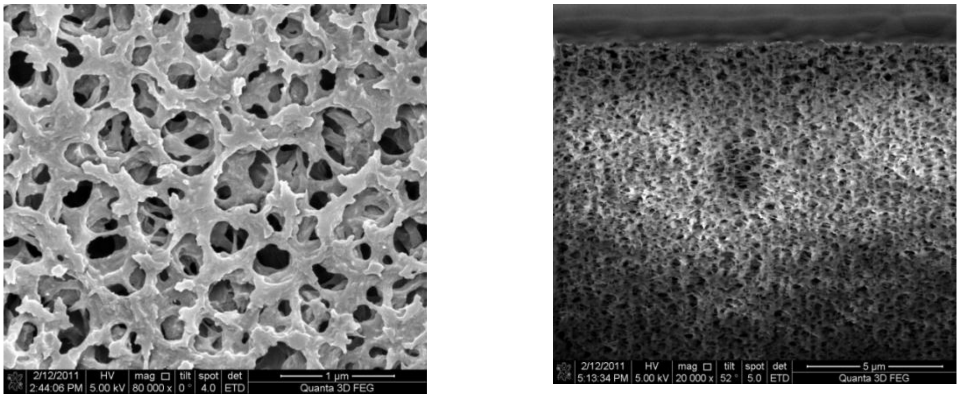


a: MF PVDF (top view)

Source (Morehouse et al., 2006)

b: MF PVDF (cross-sectional)

Source: (Yang et al., 2010)



c: MCE membrane (Top view)

d: MCE – cross-sectional

Figure 2.16: SEM images of MF PVDF (a) Top view (b) Cross-sectional and SEM images of MCE membrane (c) Top view (d) Cross-sectional

2.8 Membrane surface characteristics measured with Atomic Force Microscopy (AFM): AAO100 membrane compared with MF PVDF membranes.

AFM is a technique used to characterize the morphology/topography of the membrane surface (Morehouse et al., 2006). The AFM device has a sharp tip (probe) that works in contact mode or tapping mode over the sample surface to measure the roughness of the surface (Figure 2.17). The probe is supported with a cantilever and a laser beam from a laser diode is reflected to the probe and detected by a photo-detector (Hilal and Johnson, 2010).

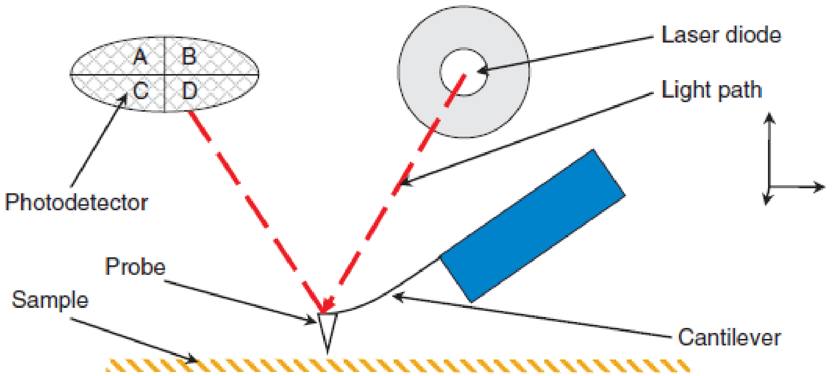


Figure 2.17: Basic set-up of AFM (Hilal and Johnson, 2010)

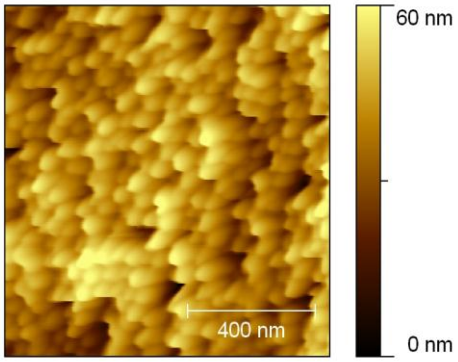
The roughness of the surface can be measured with Root mean Square (RMS) or roughness (Ra) equations. The unit used in micrometer (µm) or nanometer (nm).

$$RMS = \sqrt{\sum_{i=1}^{N}(Zi - Zcp)^2/N}$$

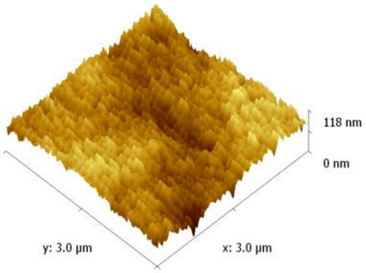
$$R_a = \frac{\sum_{i=1}^{N}|Z_i - Z_{cp}|}{N}$$

Where Zi = surface height and Zcp = Average of N height measurements

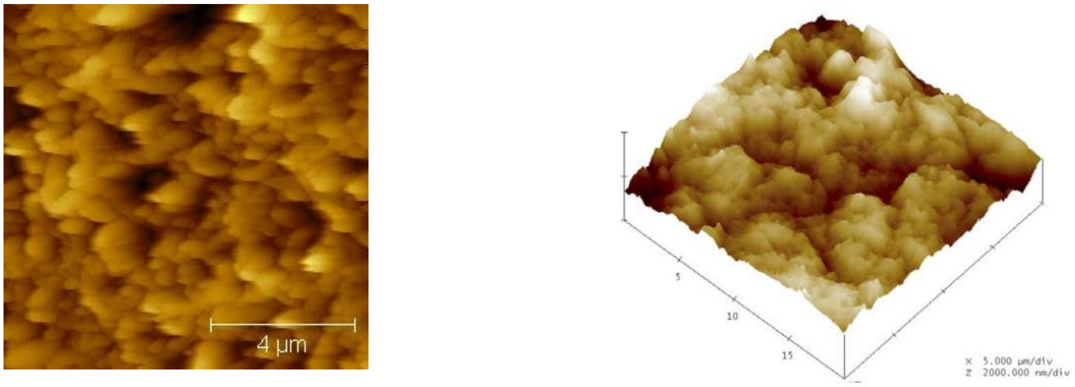
Source: (Morehouse et al., 2006)



(a): AAO new membrane Roughness (Ra) = 7.14 nm



(b): AAO Initial membrane roughness (Ra) = 11.8 nm



(c): AFM of MF PVDF (Ra = 72 nm)

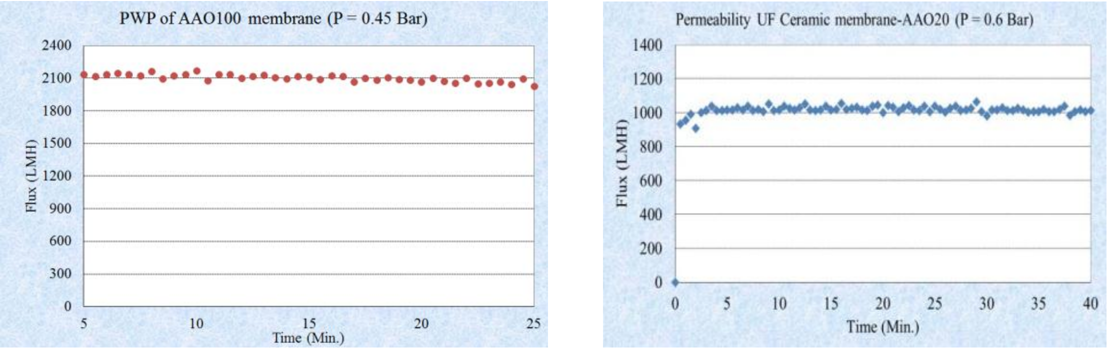
(d): Initial MF PVDF membrane (RMS) = 190±40.
Source: (Pontié et al., 2007)

Figure 2.18: AFM images of AAO membrane (a) and (b) and MF PVDF membrane (c) and (d)

The Anopore MF ceramic membranes showed a much smoother surface compared to the MF PVDF membrane (Figure 2.18). This indicates that the ceramic MF membrane has low risk of cake layer fouling compared to the polymeric membrane.

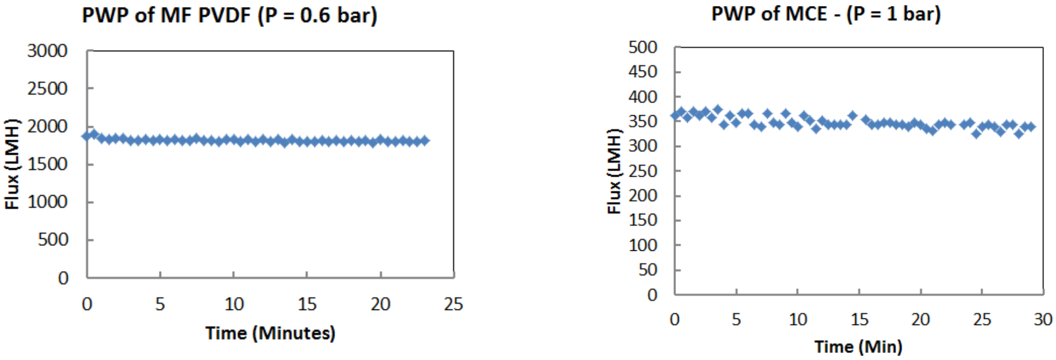
2.9 Pure water Permeability (PWP) of Membranes (Ceramic vs. Polymeric)

Ceramic membranes (AAO100 and AAO20) have high permeability compared to polymeric membranes used for the bench scale experiments. The permeability of the MF ceramic membrane (AAO100) is 4,600 LMH/bar (Figure 2.19 a) compared to the MF PVDF membrane which was 3,000 LMH/bar (Figure 2.19 c). Both membranes have typical pore sizes of 0.1 um. The ceramic UF membrane (AAO20) showed a high permeability of 1,750 LMH/bar (Figure 2.19 b) while the Mixed Cellulose Esther membrane (MCE) has a low permeability of 350 LMH/bar (Figure 2.19 d). The typical pore sizes of AAO20 and MCE are 20 nm and 25 nm respectively. Pore structures of the Anopore ceramic membranes, which are uniform, might be the reason behind the high permeability of these membranes.



(a): PWP of Anopore Ceramic MF (AAO100) = 4600 LMH/bar

(b): PWP of Anopore Ceramic UF (AAO20) = 1750 LMH/bar



(c): PWP of MF PVDF membrane = 3000 LMH/bar

(d): PWP of MCE UF membrane = 350 LMH/bar

Figure 2.19: Permeability of (a) AAO100, (b) AAO20, (c) MF PVDF and (d) MCE Membranes

The permeability of the alumina ceramic membrane from METAWATER Co. Ltd of Japan was 1,065 LMH/bar as shown in Figure 2.20 below. This membrane was used for pilot experiments.

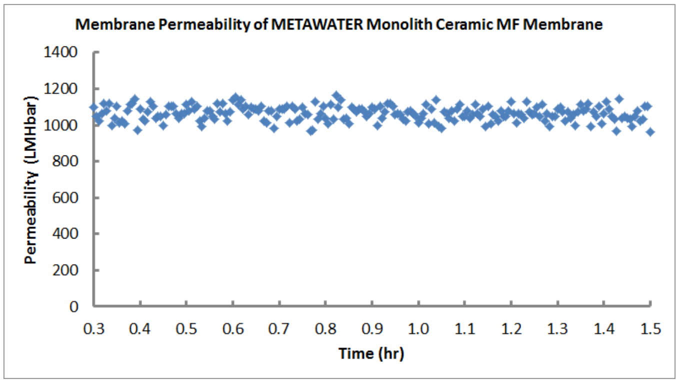


Figure 2.20: PWP of Metawater Ceramic MF membrane

The microfiltration flat sheet membranes have a high permeability compared with the monolith ceramic MF membrane, which is probably because they have a thin, supporting layer. But for Anopore ceramic membranes, the structure of pores is more uniform which is surely an added advantage. In general, ceramic microfiltration (both flat sheet and monolith) have high permeability which good for high production.

2.10 Contact Angles of AAO100 (virgin vs. fouled)

The hydrophobicity of the membrane surface is measured by contact angle. An optical Tensiometer (Goniometer) CAM 200 from KSV was used to measure the contact angle of the Anopore ceramic MF membrane. The instrument is mounted with a recording camera that recorded the drop formed for few seconds. From this record, the drop is then analyzed with the software to determine the contact angle. The virgin ceramic AAO100 membrane found to have a contact angle of 18.2^0 (Table 2.13). Hence, the AAO100 is categorized as a hydrophilic membrane. When the membrane was fouled with wastewater effluent, the contact angle increased to 53.6^0, which still exhibited hydrophilic behavior.

Table 2.13: Contact measurement of AAO100 membrane (virgin vs. fouled)

Initial AAO100 membrane	**Fouled AAO100 Membrane**
$18.2^0 \pm 0.2$	53.6^0

Therefore ceramic membranes are categorized as hydrophilic membranes. Hydrophilic membranes exhibited antifouling behavior against NOM and effective backwash ability (Shibutani et al., 2011). The contact angle of the MF PVDF virgin membrane, which is polymeric membrane with a typical same pore size similar to the AAO100 membrane, is 79^0 (hydrophilic). However the contact angle was reduced to 52^0 when the membrane was fouled, and changed to 77^0 after chemical cleaning (Pontié et al., 2007). The changes observed to take place when the membrane fouled indicates that fouling influence the hydrophilic behavior of the membrane. It also indicates that most of these foulants are hydrophilic.

2.11 Conclusions

- The effective particles sizes of SPAC is 1.4 µm and the maximum pore sizes of the ceramic MF membrane is 0.19 µm which indicates that SPAC, as a pre-coat, will not go through the membranes pores and 100 % pre-coating can be achieved.
- The ceramic membranes made of alumina have a positively charged surface while polymeric membranes used in this research (PVDF MF membrane and MCE) are negatively charged.
- Ceramic membranes made up of alumina are hydrophilic and exhibited high permeability compared to polymeric membranes.
- A novel PAC (KCU 6) has a large BET surface area and a wide distribution of pores with much bigger pores compared to other PACs, and hence showed good sorption capabilities especial for adsorption of biopolymers.
- AFM images showed that the Anopore MF ceramic membrane has a smooth surface compared to PVDF MF membrane, and hence is expected to be less prone to cake layer fouling.
- SEM images showed that the ceramic Anopore membranes have uniform and homogeneous pores compared to polymeric membranes, suggesting that high permeability can be achieved with ceramic Anopore membranes. However, the Metawater ceramic membrane exhibited non-uniform pores, which reflects the difference method, used during fabrication.

- Elemental analysis of different PACs showed similarity in composition between novel PACs (KCUs) and SASuper.

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CHAPTER 3

3.0 Ceramic membranes combined with submicron powdered activated carbon (SPAC) for treatment of surface water: *NOM removal and fouling control*

Chapter 3 is based on:

"**Submicron powdered activated carbon used as a pre-coat in ceramic micro-filtration**." Desalination and Water Treatment **9**(2009): 86-91.

S.G.J. Heijman, J.Z. Hamad, M. Kennedy, J.C. Schippers, G.L. Amy

Ceramic microfiltration with a sub-micron powdered activated carbon pre-coat for water treatment

S.G.J. Heijman*, B. Hofs, J.Z. Hamad, M. Kennedy, G. Amy

IWA Regional Conference and Exhibition on Membrane Technology & Water Reuse 18-22 October 2010 Istanbul-Turkey

Fouling Control in Ceramic MF membrane using Sub-micron Powdered Activated Carbon Pre-coat.

(**J. Z. Hamad, M. D. Kennedy, B. Hofs, S.G.J. Heijman, G. L. Amy, J.C Schippers – IWA (Conference Proceedings -Aachen Germany 4-7 Oct. 2011)**

3.1 Introduction

Rivers and lakes are the most common surface water bodies that have been used for drinking water sources for many years. Conventional treatment has been widely used but the increase of environmental pollution and the need to meet national and global water standards has forced water utilities to look for more stringent barriers. This has resulted in innovation and application of low pressure membranes for surface water treatments to replace conventional treatment (Galjaard et al., 2001). These barriers have been further cemented by hybrid systems that combined low-pressure membranes with other pretreatment techniques like, for example, coagulation to ensure stable operation and an acceptable final product.

The role of hybrid systems involving microfiltration/ultrafiltration (MF/UF) membranes in water treatment is to remove particulate, colloidal and dissolved organic matter in order to maintain good water quality with good taste, color and odor (Lipp et al., 2005). Colloidal and dissolved organic matter are responsible for membrane fouling whereby the colloidal portion is noted to cause severe fouling (Sundaramoorthy et al., 2005). Fouling of a membrane can take place through adsorption of contaminants on a membrane surface or pore blocking, cake deposition and gel formation (Bacchin et al., 2006). In general, these foulants are not desirable and their removal before reaching membrane is highly recommended.

Other undesirable constituents like micro-pollutants, bacteria and viruses are potentially removed by hybrid systems (Fiksdal and Leiknes, 2006). Cake layer fouling is controlled by hydraulic backwashing. Ceramic membranes are superior membranes that can withstand high backwashing flux compared to polymeric membranes (Palacio et al., 2009). Other foulants need chemical enhanced backwashing or chemical cleaning to be removed and restore membrane permeability. The use of 3000 mg/l of chlorine (Cl_2) to soak ceramic membrane for 24 hours was found to restore membrane permeability (Lehman and Liu, 2009). To enhance smooth operation, ceramic membranes need to be combined with common pretreatments.

The common pre-treatment techniques that are used in water industry are coagulation, adsorption and oxidation (Huang et al., 2009). Among oxidation processes is the use of ozone, which can also be applied in disinfection. Ozone pre-treatment of secondary waste water effluent was effective in degrading colloidal NOM which is regarded as responsible for most of the fouling occurrence (Lehman and Liu, 2009). A combination of polyaluminium chloride (1 mg/l) and ozonation (4 mg/l) followed by ceramic membrane filtration at a constant flux of 170 LMH stabilized filtration performance (Lehman and Liu, 2009). Also it has been reported that coagulation pre-treatment is a successful and inexpensive method for fouling reduction (Huang et al., 2009). Robust compact flocs are needed in conventional pre-treatment but only pin flocs are required for membrane filtration (Pearce, 2010).

There is an increased interest in the use of activated carbon for eliminating organic compounds as well as some of inorganic compounds (Cloirec and Faur, 2006). Activated carbon is widely used for treatment of trace organic compounds (Li et al., 2002) through adsorption. Introduction of PAC inside a microfiltration membrane bioreactor improved filterability and lowered the impact of effluent organic matter on fouling (Mohiuddin et al., 2007). Trace organic compounds compete with NOM for adsorption sites. Adsorption competition is not limited to NOM and trace organic compounds (TOrCs) only, but also between NOM and metal ions. Competition between NOM and metal ions for adsorption site is mainly pH dependent (Faur-Brasquet et al., 2002). The adsorption kinetics is highly dependent on the particle sizes of activated carbon. Activated carbon with particle sizes larger more than 1 mm is termed as granular activated carbon (GAC) and can be packed in columns for adsorptive filtration, and GAC can be regenerated (Armenate, 2007). When GAC is ground into powder it is called powdered activated carbon (PAC). The typical sizes of PAC ranges between 5 µm to 50 µm and can be used by direct addition to the feed water and removed after the use ((Armenate, 2007) and (Schippers et al., 2007)). The finer activated carbon with less than 5 um particle size is termed as Submicron Powdered Activated carbon, abbreviated as SPAC. Figure 3.1 presents the distribution of particle sizes of normal PAC (NPAC) vs. SPAC from the study of Matsui et al. (2007); their effective sizes of NPAC and SPAC are 2 µm and 0.3 µm respectively.

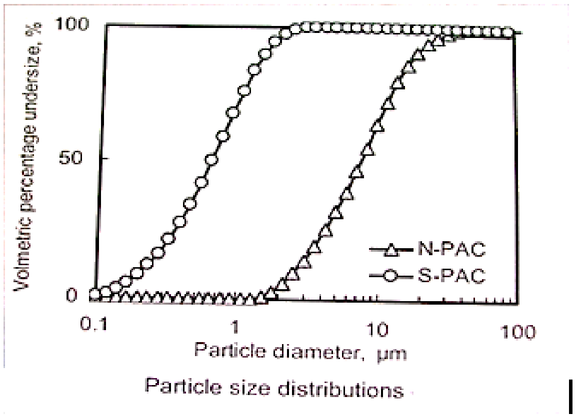


Figure 3.1: Particle size distributions of SPAC and NPAC
Source: (Matsui et al., 2007)

The use of SPAC is a promising pre-treatment approach that could reduce fouling. When NPAC is ground to finer particles to produce SPAC, the amount of dose could be reduced to 25 % compared to NPAC. This low SPAC dose can maintain the same good removal efficiency of NOM as NPAC (Matsui et al., 2005). The cake layer formed by the SPAC associated with other foulants, either adsorbed or attached, to the SPAC is very thin, porous and has negligible impact on membrane resistance (Hamad, 2008). It was also observed that the cake layer formed by PAC inhibits the humic acid (HA) from blocking the membrane pores (Tomaszewska and Mozia, 2002). The interaction between powdered activated carbon (PAC) and NOM molecules through adsorption was found to cause PAC cake fouling (Zhao et al., 2005). The rate of NOM adsorption is dependent on the sizes of PAC particles.

It was stated that changes of particles size do not influence the porous structure of activated carbon so the total surface area of the activated carbon remained constant (Armenate, 2007). This implies that adsorption capabilities of different particle sizes from the same activated carbon remained almost the same, and the only difference will be in terms of the kinetics; smaller particles will reach equilibrium faster than larger particles. This has been documented by Schippers who mentioned that one day is needed for PAC to achieve equilibrium while granular activated carbon (GAC) requires some days (Schippers et al., 2007).

However, constricted pore distribution permits adsorption of trace organic compounds alone (Newcombe et al., 1997). It was claimed that pore sizes below 0.8 nm increases competition and above that to 2 nm reduces competition between NOM and trace organic compounds (Pelekani and Snoeyink, 2000). Shielding phenomena caused by large molecular weight NOM affects the adsorption of micro-pollutants (Pelekani and Snoeyink, 2000).

In this chapter, commercial powdered activated carbon was grounded to very fine particles, SPAC, and used as pre-coat. SPAC was first used by the Matsui group that recognized SPAC to have a potential ability to remove NOM at a low dose compared to NPAC. There are two ways of PAC dosing. A common method is a step input whereby PAC is dosed to the reactor at a constant rate, and a novel method known as pulse input in which dosing is performed at the beginning of the filtration cycle (Gao et al., 2011). In this study the later method was adopted and termed as pre-coating. SPAC was used as pre-coat and was dosed at the beginning of the filtration cycle. NOM characterization was carried out to determine the components that have greatest influence on fouling. The increase of membrane resistance was assessed and the benefits of SPAC were clearly shown. Surface water, from canal water, was used for most of the experiments while wastewater effluent from Jeddah was used to validate the results obtained from canal water in a bench scale setup.

3.2 Goal and Objectives

3.2.1 Goal

- To determine the role of submicron powdered activated carbon (SPAC) pre-coats in controlling membrane fouling and NOM components removal.

3.2.2 Objectives

- Removal of NOM and its components using ceramic membranes pre-coated with SPAC
- To characterize the composition of the NOM foulants responsible for reversible and irreversible fouling by using LC-OCD, FEEM and TEP analysis.
- Fouling control/reduction and improve ceramic MF membrane filterability.

3.3 Materials and Method

3.3.1 Water sources

Feed water was obtained from Delft Canal water (Netherlands) and wastewater effluent from Jeddah (Saudi Arabia).

3.3.1.1 Delft Canal water and Wastewater effluents

The characteristics of Delft canal water and wastewater effluents are tabulated below (Table 3.1):

Table 3.1: Characteristics of Feed waters

	TURBIDITY (NTU)	**DOC (mg/l)**	**UV254 (cm-1)**	**SUVA**	**pH**	**Ca (mg/L)**
Canal water	0.5 - 3	12 - 18	0.5 - 0.6	3.3 – 4.2	7.6	90 - 120
Wastewater Effluents	0.25	4.6	0.11	2.39	7.5	80

3.3.2 Submicron powdered activated carbon (SPAC)

NPAC supplied by NORIT Company with an effective size of 2 µm was ground in a ball mill for 15 hours to produce SPAC. The effective size of the produced SPAC was measured by a Beckman Coulter LS230 Laser diffraction device with wet module was 0.3 µm. This was later confirmed by Malvern Mastesizer that showed an average particle size of about 3 um (Figure 3.2 and Table 3.2). SPAC was then mixed with Milli Q water to a concentration of 7.5 g/L. To keep the solution homogeneous, a stirrer was used. The size distribution of NPAC ranges from 5 um to 50 um, while SPAC is smaller than 5 um.

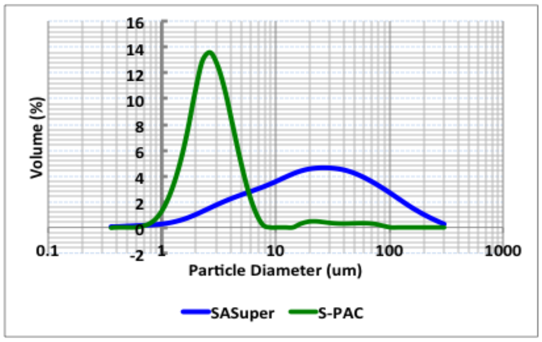


Figure 3.2: Particle size distribution measured with Master-sizer.

Table 2.2: Average and effective particle sizes measured with Master-sizer

	Average Particle sizes (um) - d50	Effective particle size (um) - d10	d90 (um)
SASuper	20.63	3.49	93.02
SPAC	2.5	1.41	4.62

3.3.3 Membrane characteristics

The ceramic MF membrane used to conduct pilot scale experiments was supplied by METAWATER Co., Ltd from Japan. The specification of the membrane is presented in Table 3.3. Flat-sheets Anopore MF ceramic membranes (AAO100) and a polymeric membrane made of PVDF, both with pore sizes of 100 nm, were used in a bench scale set-up. Also 0.45 um filters were used to pre-filtered the wastewater effluents as well as to determine the removal efficiency of pre-coats layers after these filters were pre-coated with SPAC prior to wastewater filtration.

Table 2.3: Specification of monolith ceramic membrane (METAWATER)

Description	**Parameter**
Membrane Diameter	30 mm
Module length	1 m
Channels diameter	2.5 mm
Number of channels	55
Surface area	0.4 m^2
Membrane pore size	100 nm
Operating Pressure	0.05 – 1 bar
Backwashing Pressure	5 bars
Mode of Filtration	Dead end

3.3.4 Experimental set-up

3.3.4.1 Ceramic MF Pilot plant

The layout of the ceramic pilot is shown below (Figure 3.3). The pilot plant was designed by KWR Watercycle Research Institute from Netherlands.

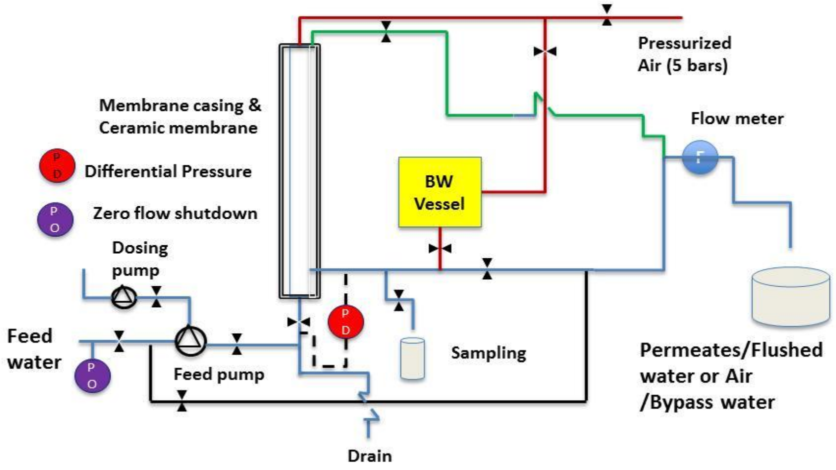


Figure 3.3: Ceramic MF Pilot plant

The pilot has both manual and automatic operational modes. It consists of four main operations: Filtration (F), Backwashing (BW), Air Scoring or Flushing (AF) and Forward Flush (FF). Chemica enhanced backwashing (CEB) and chemical cleaning (CIP) were performed manually. Sodium hydroxide with a concentration of 0.1 N was used for CEB while 3 % citric acid followed by 3000 mg/L sodium hypochlorite was used for CIP. The membrane was soaked in Citric acid for 6 hours and flushed with Milli Q for 1 minute. The procedure was repeated with Sodium hypochlorite.

3.3.4.2 Amicon (un) stirred cell

An Amicon stirred cell, without stirring, was employed to conduct the experiments. The feed water was put in a pressure vessel, which was connected to nitrogen gas that could be adjusted to the required pressure. The pressurized feed water was passed through the membrane placed in the stirred cell. The permeate water was collected in a beaker placed on a digital balance that measured the weight of the permeate water. The balance was connected to a computer and with the help of software; the data from the balance were recorded in a computer at fixed time intervals. The layout of the set-up is shown in Figure 3.4.

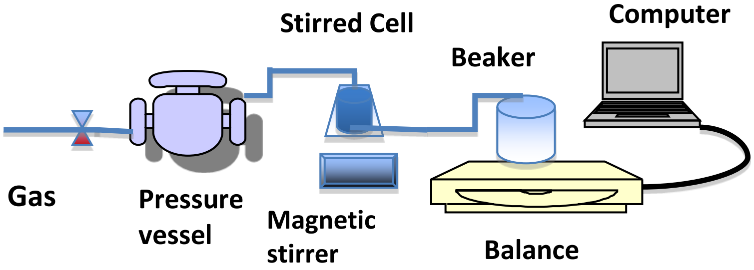


Figure 3.4: Layout of Amicon (un) stirred cell set-up

3.3.5 Fouling experiments

The pre-coat layers were introduced by dosing the SPAC solution at a rate of 6.7 L/h for 30 seconds. This was equivalent to introduction of 40 layers of SPAC over ceramic membrane channels based on the effective size of SPAC particles. The feed flux of raw water was set to 250 LMH during the dosing period (30 seconds) to enhance better distribution of PAC on membrane channels. The filtration cycles of 1, 2, 3 and 4 hours corresponded to equivalent doses of 40, 20, 13.5 and 10 mg/L, respectively. Filtration was performed at a typical constant flux of 160 LMH. To reduce feed water amount, some membrane channels were blocked. This reduced the membrane area from 0.4 m^2 to 0.065 m^2, which in turn reduced the use of the feed water from 64 liters to 10.5 liters in a one-hour filtration cycle. This also reduced the amount of SPAC usage and increased flexibility to do fouling experiments. Filtration cycles of 1 up to 4 hours were adopted. The trend of fouling was analyzed by using trans-membrane pressure (TMP) increase at constant flux. The results were compared with blank (with no dose of PAC) experiments to determine the increase of irreversible fouling as a function of slope increase. All experiments were performed at a room temperature of 20 ^{0}C and samples for DOC, UV, FEEM, TEP and LC-OCD were collected.

Fouling trend was analyzed by monitoring TMP increase at constant or average fluxes. The total membrane resistance (R_T) in m^{-1} was calculated by the following equation (1):

$$R_T = \frac{\text{TMP}}{\mu \times J} \tag{1}$$

Where TMP is the trans-membrane pressure difference across the membrane (N/m^2), J is the flux (m^3/m^{2}h) while μ is the viscosity of the solution, which can be obtained by equation (2):

$$\mu = \frac{0.497}{(T + 42.5)^{1.5}} \tag{2}$$

Where: T is the temperature of the feed water at a room temperature (20°C).

3. 3.6 NOM Characterizations: DOC, UV, LC-OCD, FEEM and TEP

Measurements of the dissolved organic carbon (DOC) were performed by using Total Organic Carbon analyzer (TOC-V$_{\text{CPH}}$ Shimadzu) while UV absorbance was measured by using a UV-Vis Spectrophotometer (UV-2550 Shimadzu), Liquid chromatography with on-line organic carbon detection (LC-OCD) was used to classify the NOM components according to their molecular weight based on retention time in a chromatography column. NOM characterization with LC-OCD is quite useful for identification of organic foulants. The LC-OCD technique use a column to separate NOM components based on their molecular weight. The larger components of NOM are separated first and detected with an organic carbon detector (OCD). Therefore, based on elution time, NOM components can be separated according to their molecular weight. The typical NOM components are biopolymers (> 20,000 Da), humic substances (1,000-20,000 Da), building blocks (300-500 Da) low molecular weight acids (< 350 Da) and neutrals (< 350 Da).

Furthermore, NOM was also characterized by using Fluorescence Excitation Emission Matrix spectrofluorometer (FEEM). Each sample was diluted using Milli Q to reduce the DOC level to 1 mg/L. To eliminate Raman peaks, the FEEM result of the blank (Milli Q) was subtracted from sample. MATLAB 7.5 software was used for data processing. Contour plots composed of 3D parameters (Emission, Excitation and Intensity) were used to classify the regions of humic-like and protein-like organic matter. Therefore, the differences of intensities between feed water and permeates provide insight into rejections of proteins and humic substances.

Another method used to quantify the natural organic matter is transparent exopolymeric particles (TEP) measurement. The method for measuring TEP was first developed by Passow and Alldredge (Passow and Alldredge, 1995) and was based on measurement of particulate TEP retained on filters > 0.4 µm (polycarbonate). TEP measurements were employed for measuring the acidic polysaccharides removed by SPAC pre-coats. The water samples were filtered through 0.4 µm polycarbonate flat sheet filters as mentioned above. The filters (membranes) were then stained with Alcian blue (specific dye to stain TEP). The more the Alcian blue adsorbed implies more TEP. The polycarbonate filters were dissolved in sulfuric acid to extract the TEP. The absorbance of dissolved solution of Alcian blue is measured at a wavelength of 787 nm whereas TEP amount is quantified as absorbance per volume of sample filtered.

3.4 Results and Discussions

3.4.1 DOC, UV254 Removal and NOM characterizations: MF PVDF membrane pre-coated with SPAC for Canal water treatment – Bench scale

A MF PVDF membrane with a pore size of 0.1 µm, similar to the ceramic MF membrane, was selected for the bench scale experiments to explore the efficiency of SPAC over NPAC pre-coats in terms of NOM components removal. The clean ceramic membrane operates at 150 LMH flux with a pressure of lower than 0.2 bars. Therefore, based on these conditions, the flux and operating pressure of the PVDF membrane was also controlled to maintain similar operating conditions. The samples collected from both PAC pretreatments were analyzed to determine the fate of NOM constituents by adsorption as a function of filtration time. The samples were collected after every 15 minutes during 1 hour of filtration. All of the samples were analyzed in Het Laboratory (Harlem, Netherlands) and the summary of the results is documented below (Table 3.4 and Figure 3.5 – 3.6).

Table 2.4: NOM Fractions of canal water permeates filtered through MF PVDF membrane pre-coated with SPAC/ NPAC (30 mg/L) @ 150 LMH Flux

Sample	Biopolymers (mg/L)	Humic Substances (mg/L)	Building Blocks (mg/L)	Neutrals (mg/L)	Acids (mg/L)	DOC (mg/L)	UV254 (cm-1)	SUVA (L/mg.cm)
S0	0.081	1.543	0.215	0.345	0	2.184	0.062	2.82
S15	0.082	4.71	0.806	0.519	0.008	6.125	0.195	3.18
S30	0.135	6.344	1.099	0.876	0.018	8.472	0.269	3.17
S45	0.182	8.142	1.521	0.989	0	10.834	0.376	3.47
S60	0.483	9.255	2.031	1.502	0.06	13.331	0.464	3.48
Feed	1.299	10.299	2.195	1.639	0	15.432	0.562	3.64
N0	0.329	2.071	0.25	0.211	0.007	2.868	0.085	2.97
N15	0.904	7.442	1.102	0.813	0.098	10.359	0.343	3.31
N30	1.028	8.501	1.617	1.006	0.159	12.311	0.416	3.38
N45	1.071	9.122	1.9	0.989	0	13.082	0.440	3.36
N60	1.137	9.649	2.231	1.305	0	14.322	0.496	3.46

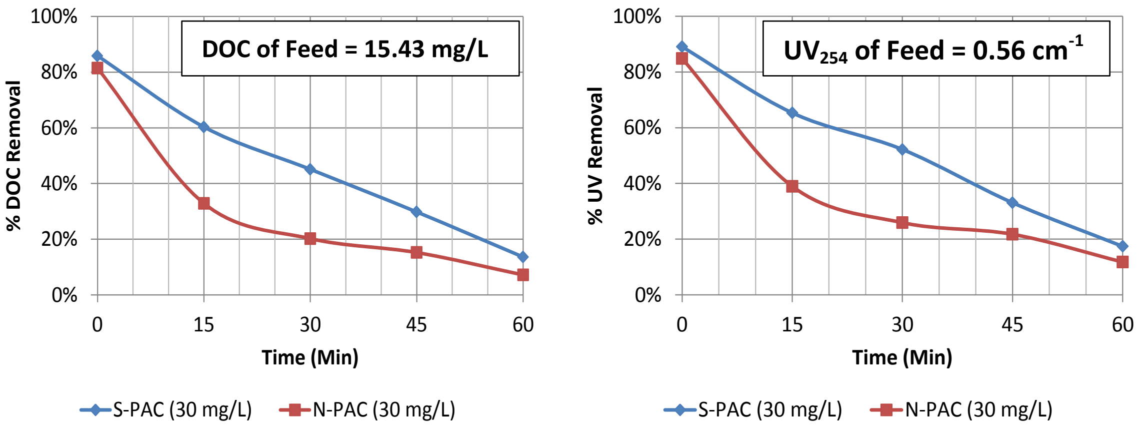


Figure 3.5: Percentage Removal of DOC and UV254 with SPAC/NPAC (30 mg/L) combined with MF PVDF membrane

The average DOC and UV254 removal for SPAC (30 mg/L) is 46 % and 51 %, respectively, while for the NPAC (30 mg/L) it is 28 % and 33 %, respectively (Figure 3.5). The results agree with another study that found 10 – 30 % of DOC was removed by 20 mg/l of PAC through an adsorption mechanism (Newcombe et al., 2002).

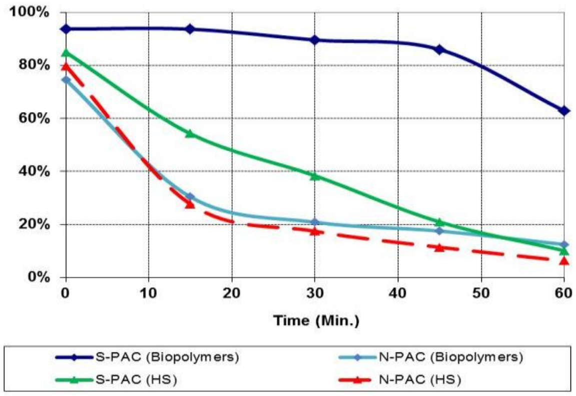


Figure 3.6: Biopolymers and HS Components - Canal permeates filtered through pre-coated (SPAC/NPAC) membrane (MF PVDF).

Figure 3.6 showed > 85 % biopolymers removal with SPAC (30 mg/l) pre-coats after 1 hour of filtration while only 20 % removal of biopolymers achieved by NPAC (30 mg/l). S-PAC managed to remove 40 % of the humic substances while NPAC removed only 25 % after one hour. Humic substances, constituting two-thirds of the NOM fractions of canal water, showed poor removal especially with NPAC (Table 3.4). SPAC has fine particles that are believed to facilitate physical removal of biopolymers. The detailed analysis of physical removal of biopolymers is discussed in section 3.4.2. However, in bench scale test, in the presence of high concentration of biopolymers, straining of biopolymers in a SPAC pre-coat layer can cause a high increases of cake resistance developed by NOM-PAC interaction with high DOC feed water (Figure 3.7). Humic substances can be removed by micropores (< 2 nm) and mesopores but the shielding mechanisms of a NOM-PAC cake layer and biopolymers are hypothesized to make humic substance removal lessen as the filtration continues.

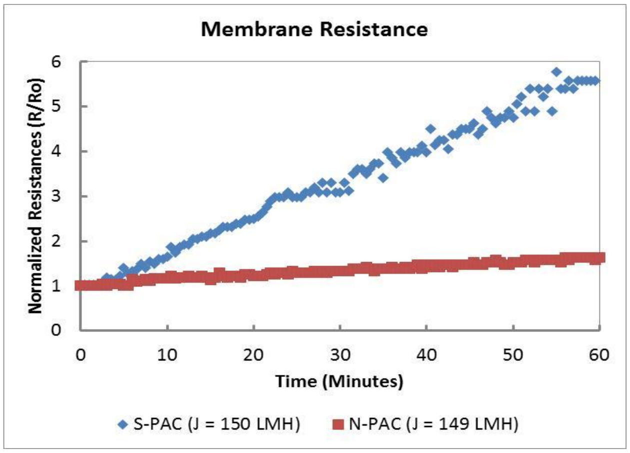


Figure 3.7: Membrane Resistance increases with SPAC or NPAC pre-coats at 30 mg/L - Canal permeates filtered through pre-coated (SPAC/NPAC) membrane (MF PVDF).

3.4.2 DOC and NOM components removal: AAO100 ceramic MF membrane pre-coated with SPAC for treatment of wastewater effluent – Bench scale

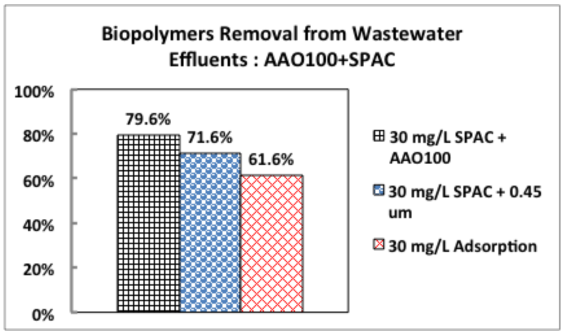
A detailed analysis was carried out to verify the ability of the SPAC pre-coat layer to remove biopolymers by physical means (e.g., straining). Wastewater effluent pre-filtered with 0.45 um filters was used as feed water. The Anopore ceramics MF membrane (0.1 um), made of alumina, and 0.45 um filters were used. These filters were pre-coated with different doses (30, 20 and 15 mg/l) of SPAC. Wastewater effluents were filtered through pre-coated membranes and the permeate waters were collected. With the help of LC-

OCD, both feed and permeate waters were characterized to determine the removal levels of NOM components. The purpose of using 0.45 um filters is to determine the amount of NOM components removed by the pre-coat alone since most of the DOC components will pass through the 0.45 um filters. The maximum removal of NOM components was determined by adsorption experiments at the same doses used in pre-coating experiments. Adsorption experiments were carried out for 24 hours and the results were compared with pre-coating results. The results are presented in Table 3.5 below.

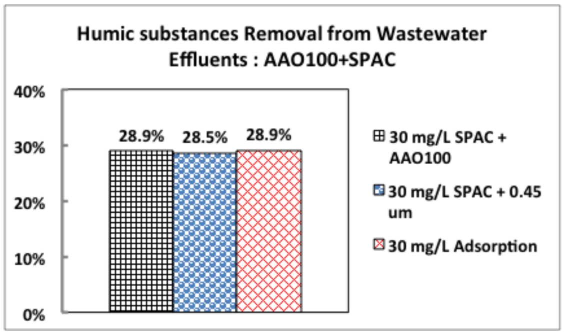
Table 2.5: NOM characterization of SPAC pre-coats permeates and feed

Samples	DOC (mg/L)	Biop. (mg/L)	Humic Subst. (mg/L)	Build. Blocks (mg/L)	Neutrals (mg/L)	LMW Acids (mg/L)
SPAC-15mg/L+AAO100	3.636	0.098	1.816	0.633	1.088	0.007
SPAC-15mg/L+0.45um	3.807	0.127	1.857	0.694	1.129	0.006
SPAC-15mg/L Adsorption	3.486	0.139	1.734	0.606	1	0.004
SPAC-20mg/L+AAO100	3.548	0.06	1.628	0.77	1.09	0.005
SPAC-20mg/L+0.45um	3.287	0.08	1.659	0.576	0.949	0
SPAC-20mg/L Adsorption	3.187	0.115	1.634	0.537	0.804	0.008
SPAC-30mg/L+AAO100	3.327	0.051	1.521	0.751	1.002	0.003
SPAC-30mg/L+0.45um	3.066	0.071	1.529	0.571	0.883	0.003
SPAC-30mg/L Adsorption	2.968	0.096	1.52	0.485	0.87	0.004
Feed	4.625	0.25	2.139	0.913	1.284	0.009

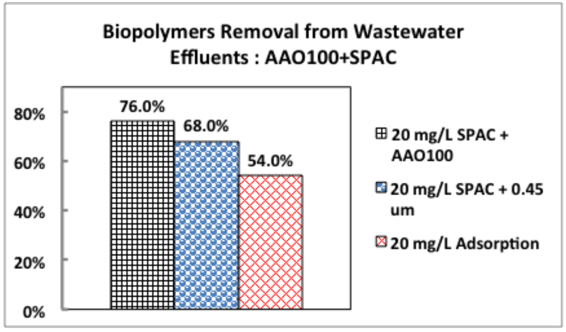
Biopolymers removal with AAO100 pre-coat at a dose of 30 mg/l was 80 % and 72 % with 0.45 µm while adsorption achieved 62 % (Figure 3.8). These results verify that the pre-coat layer rather than membrane removes most of the biopolymers since 72 % removal was achieved with 0.45 µm filters. The increase of removal to 80 % with the pre-coated ceramic membrane indicates that the additional amount of biopolymers (8 %) was removed by the ceramic membrane. Adsorption experiments with 30 mg/l of SPAC showed that adsorption is also a possible removal mechanism that might be involved in biopolymers removal. Through adsorption, a maximum of 62 % of biopolymers could be removed (Figure 3.8 a). Given an adequate time for adsorption, other commercial PACs, SASuper and G60, showed 67 % and 68 % biopolymers removal, respectively, in a 24-hour experiment. For a short period of contact time, maximum removal of biopolymers with SPAC through adsorption alone is not possible. However, the finer particles provide more external surface area and increase the contact between adsorbent and adsorbate, which could be a factor for an increase of the kinetics of adsorption, increasing the removal level of biopolymers in a short contact time. It is interesting to note that the amount of humic substances removed with 30 mg/l of SPAC was 29 % regardless of the pre-coating or adsorption (Figure 3.8 d). When the doses decreased, the level of removals also declined for both biopolymers and humic substances (Figure 3.8 a – 3.8 f).



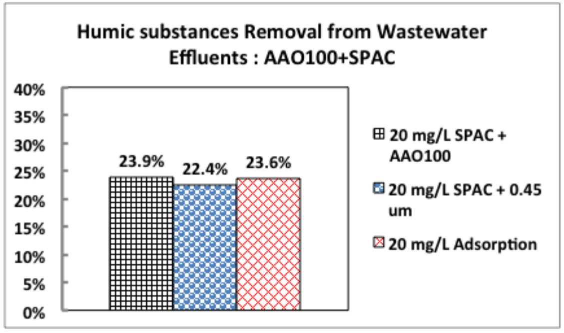
(a): Biopolymers removal with 30 mg/l SPAC



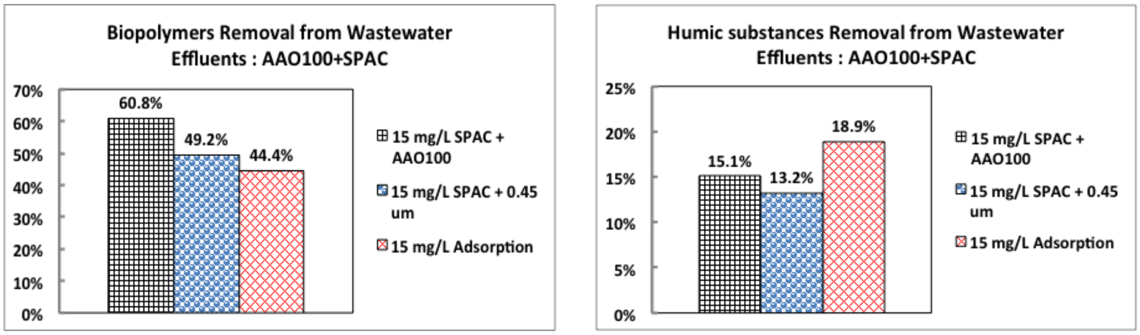
(d): Humic substances removal with 30 mg/l SPAC



(b): Biopolymers removal with 20 mg/l SPAC



(e): Humic substances removal with 20 mg/l SPAC



(c): Biopolymers removal with 15 mg/l SPAC

(f): Humic substances removal with 15 mg/l SPAC

Figure 3.8: Biopolymers removals with SPAC at a dose of (a) 30 mg/L, (b) 20 mg/L, (c) 15 mg/L and Humic substances removals with SPAC at a dose of (d) 30 mg/L, (e) 20 mg/L and (f) 15 mg/L.

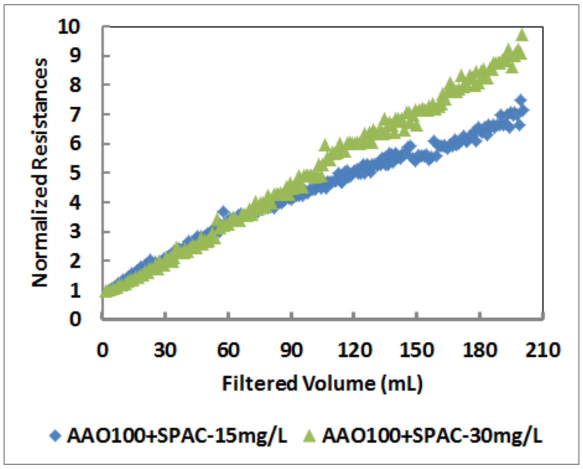


Figure 3.9: Increases of membrane resistance with different applied SPAC doses pre-coated on AAO100 membrane

In Figure 3.9, SPAC at a dose of 30 mg/l exhibited a higher increase of the membrane resistance compared to a low dose of 15 mg/l. It is expected that the one that gives a high increase of membrane resistance should exhibit low removal of biopolymers if adsorption is the only removal mechanism. However, a 30 mg/l SPAC pre-coat showed a higher increase of membrane resistance as well as high removal of biopolymers, which suggests that physical removal, is also taking place, increasing the removal rate of biopolymers. Biopolymers, due to their larger sizes, can be trapped between the porous spaces (interstices) between the fine SPAC particles. Thus, it can be concluded that mechanisms, adsorption and physical removal, are taking place. The fine particles have the advantage of speeding the kinetics of adsorption due to an increased external surface area that favors more contact between adsorbate and adsorbent. When adsorption is exhausted, then physical removal becomes a dominant mechanism and in this way the breakthrough will be observed. Also, if the applied pressure is increased then there is a chance of biopolymers passing through the pre-coat layer and the membrane barrier due to cake compression since biopolymers are flexible in nature.

3.4.3 DOC and UV254 removal: Ceramic MF combined with SPAC for Canal water treatment – Pilot scale

The DOC removal as well as UV_{254} removal from canal water using SPAC (30 mg/L) pre-coated on a ceramic MF membrane was determined. The influence of the SPAC pre-coat with respect to filtration time was critically analyzed by taking samples at different intervals of time. A pre-coat dose of 30 mg/l of SPAC was used. To facilitate even distribution of SPAC in membrane channels, a high flux of 250 LMH was applied during pre-coating. The DOC and UV_{254} results are expressed in Figure 3.10 below.

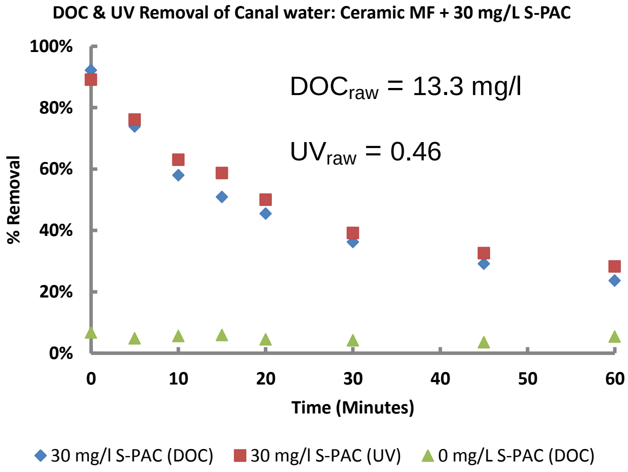


Figure 3.10: DOC & UV254 Removal for canal water with Ceramic membrane pre-coated with SPAC (30 mg/l) @ 150L/m^2.h Flux

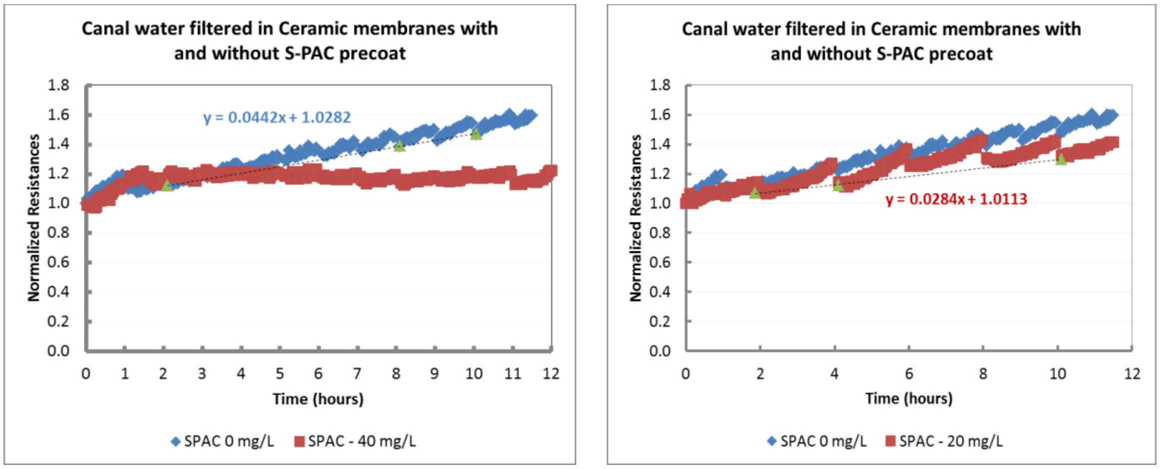
Table 2.6: DOC & UV$_{254}$ Removal for canal water with ceramic membrane pre-coated with SPAC (30 mg/l) @ 150 L/m^2.h Flux

	Ceramic membrane+30 mg/l SPAC				**Without SPAC**	
Time (Min.)	**DOC (mg/l)**	**% DOC Removal**	**UV (cm^{-1})**	**% UV Removal**	**DOC (mg/L)**	**% DOC Removal**
0	1.04	92.2%	0.05	89.1%	12.38	6.8%
5	3.47	73.9%	0.11	76.1%	12.64	4.8%
10	5.58	58.0%	0.17	63.0%	12.54	5.6%
15	6.52	50.9%	0.19	58.7%	122.49	5.9%
20	7.24	45.5%	0.23	50.0%	12.68	4.5%
30	8.47	36.2%	0.28	39.1%	12.72	4.2%
45	9.41	29.1%	0.31	32.6%	12.81	3.5%
60	10.14	23.6%	0.33	28.3%	12.56	5.4%
Raw Canal	13.28		0.46			

Average DOC and UV$_{254}$ removals for Canal water using 30 mg/l of SPAC combined with the ceramic MF membrane were 40 % (Figure 3.10 and Table 3.6). The DOC removal with the ceramic membrane alone was < 10 % indicating that membrane alone is not capable of removing NOM without pre-treatment. In Figure 3.10 above, DOC removal declined with the time, suggesting that SPAC becomes exhausted by NOM loading. Normally, DOC removal depends on the feed water quality (raw water) as well as pre-treatment dose. This can be explained by the results observed in the research conducted by (Myers et al., 2007) that aimed to reduce DOC feed water to the level of 4 mg/l from 7-14 mg/l using ceramic membrane combined with Iron III chloride and powdered activated carbon ($FeCl_3$ and PAC). It was found that 100 mg/l coagulant doses managed to remove 52.6 % of DOC and addition of 80 mg/l of PAC increased the DOC removal to 66.8 %. However, to reduce the DOC level to < 1 mg/L, a very high dose of PAC (4,000 mg/l) would be needed.

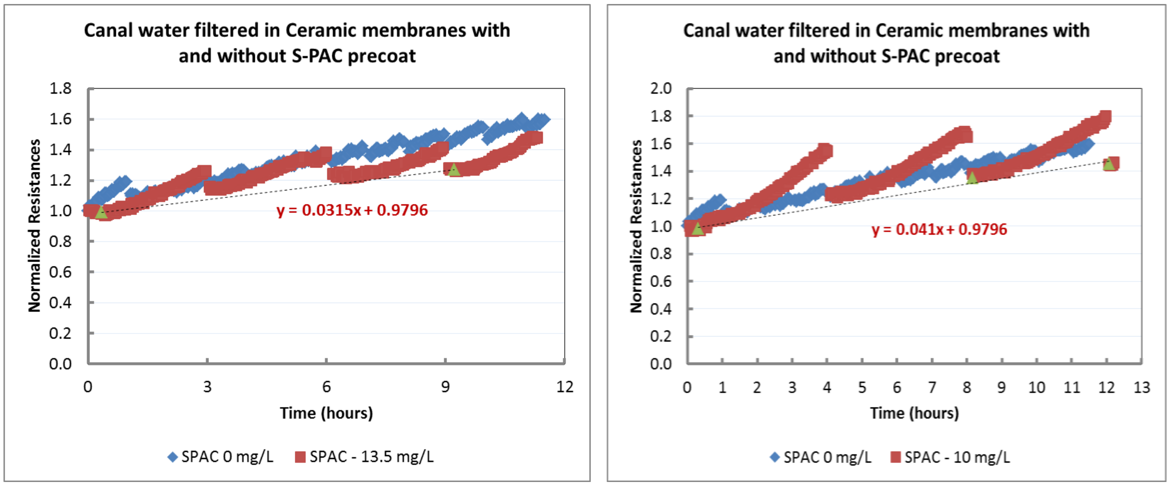
3.4.4 Fouling control for Ceramic MF membrane with SPAC – Pilot scale

The level of fouling was determined through a 12-hour experiment conducted with and without pre-coat layers of SPAC. Equivalent doses of 40, 20, 13.5 and 10 mg/L of SPAC pre-coats were used and the results were compared with a control experiment (without SPAC). The average constant flux of 160 LMH was used and filtration cycles of 1, 2, 3 and hours were adopted for four different experiments. New filtration cycle started after aggressive backwashing (BW) at very high flux (10 times the operating flux) for about 15 seconds. This was followed by air flushing (AF) for about 10 seconds and forward flushing (FF) for 30-45 seconds. Then a new pre-coat layer was introduced as explained in the methodology. After 12 hours of operation, the membrane was cleaned with chemicals (citric acid 1 % followed by sodium hypochlorite 3000 ppm). The results documenting the trend of fouling are shown in Figure 3.11.



(a) Backwashing interval – one hour

(b) Backwashing interval – two hours



(c) Backwashing interval – three hours (d) Backwashing interval – four hours

Figure 3.11: Resistances increase for ceramic membrane pre-coated with (a) 40 mg/L SPAC (in 1-hour cycles), (b) 20 mg/L SPAC (in 2 hours cycles), (c) 13.5 mg/L SPAC (in 3 hours cycles) and (d) 10 mg/L in four hours cycles.

The first cycle of filtration in Figure 3.11 (a) showed different characteristics with the use of SPAC. The membrane resistance increased up to 20 % at the end of filtration and was not recovered in the second cycle. However, from the second cycle and the rest of the filtration cycles, a negligible increase of membrane resistance was observed. A modest increase of resistance in the first cycle might be caused by residual foulants due to inadequate cleaning of the membrane before use. This trend was not observed in other set of experiments as elaborated with Figures 3.11 (b) – 3.11 (d). These new experiments started after carrying out the CIP process.

The slope of irreversible fouling increased to 0.0442 hr^{-1} in the control experiment (Figure 3.11 a). When 40 mg/L SPAC pre-coat was used, no significant increase in membrane resistance was noticed after the first cycle, the slope was almost zero as shown in Figure 3.11 (a). This clearly indicates that 40 mg/L of SPAC pre-coats, renewed after every 1 hour after backwashing, can control both reversible and irreversible fouling. Therefore the use of SPAC pre-coat can significantly reduce the frequency of chemical cleaning of the membrane.

Other pre-coat doses applied (20, 13.5 and 10 mg/L) improved the membrane filterability and reduced the fouling potential with lower performance as the dose decreased. The gradient of the irreversible fouling of ceramic membrane pre-coated with 20 mg/l of SPAC was 0.0284/hour, which is equal to a 46 % reduction of irreversible fouling (Figure 3.11 b). The SPAC pre-coats of 13.5 mg/L and 10 mg/L resulted in gradient increases of 0.0315/hour (Figure 3.11 c) and 0.041/hour (Figure 3.11 d), which are equivalent to 29 and 7 % of irreversible fouling reduction, respectively. This indicates that the amount of SPAC doses and duration of filtration cycle play a significant role in fouling reduction and control. The approach of SPAC pre-coats applied to the MF ceramic membrane can decrease frequent uses of chemicals, and prolong the life span of the membranes (Hugaboom et al., 2009).

3.4.5 NOM characterization with LC-OCD: Pilot experiments

Cumulative samples of permeate were taken at 10 min., 1, 2, 3 and 4 hours to characterize the NOM fraction removed by 10 mg/L of SPAC in combination with ceramic membrane filtration during the 4-hour-filtration-cycle of the fouling experiment. Table 3.7 summarizes the results in which, the concentration of LMW acids in a feed was neglected since it was < 2 µg/l.

Table 3.7: Fraction of DOC for feed and permeates of surface water filtered by MF Ceramic membrane pre-coated with 10 mg/L SPAC

Time (Hours)	**Equivalent dose of SPAC (mg/L)**	**Biopolymers (µg/l)**	**H.S (µg/l)**	**B.B (µg/l)**	**Neutral (µg/l)**	**DOC (mg/l)**
0.17	200	8	830	62	146	1.17
1	40	49	1830	220	182	2.43
2	20	99	2510	538	308	3.56

3	13.5	102	2840	547	378	3.94
4	10	109	3030	546	403	4.15
Raw		**119**	**3970**	**734**	**593**	**5.56**

The feed water organic matter composition is mostly dominated by humic substances (72 %) as shown in Table 3.7. The biopolymers fraction was low (2.2 %) especially during the winter period when these experiments were carried out. Hence it was expected that there would be a lower tendency of fouling on the microfiltration membranes compared to the summer period. Nevertheless, the treatment of water is not confined to a specific period, thus these results are still representative as they are characteristic of the low NOM loading season. Figure 3.12 below shows the percentage of NOM fraction removals as a function of filtration time.

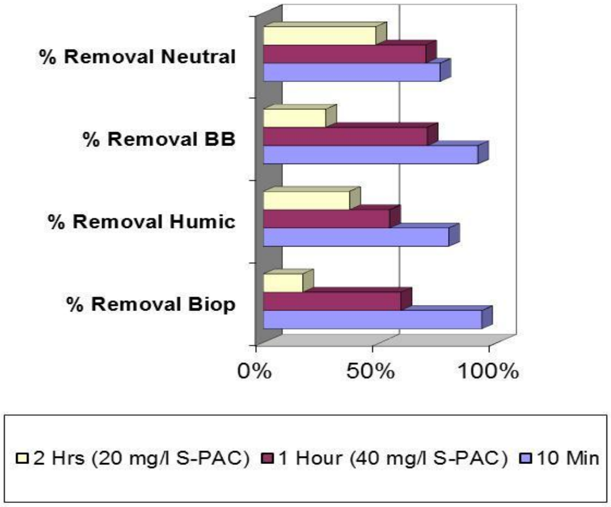
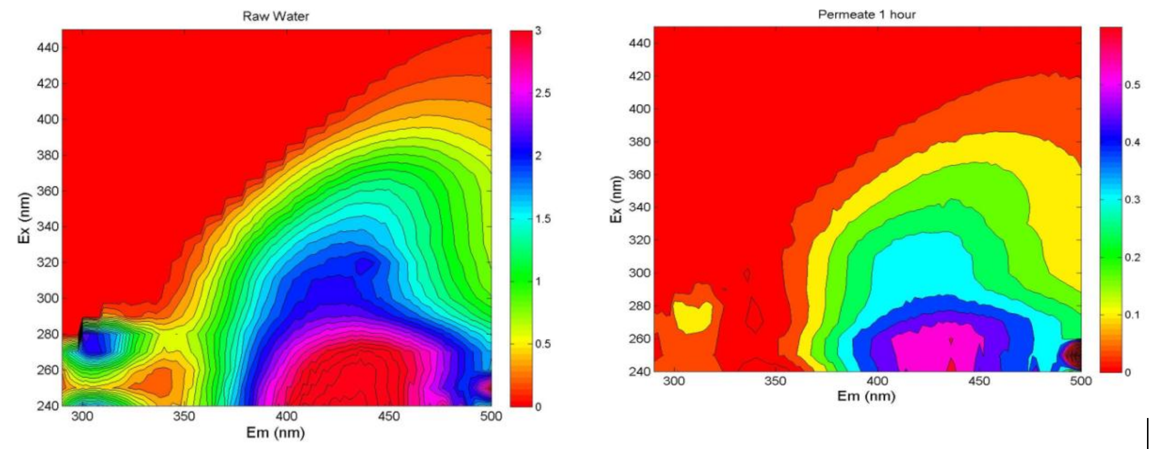


Figure 3.12: Fractions of DOC of canal water removed by 40 and 20 mg/l SPAC pre-coated onto MF Ceramic membrane @ 160 l/m^2.h Flux.

The results from Figure 3.12 show that low molecular weight NOM (building blocks and neutrals) were well removed to nearly 70 % for both after one hour. High molecular weights NOM (biopolymers and humic substances), which are considered to be responsible for irreversible fouling, are significantly removed after the first hour of filtration (approximately 60 % of biopolymers and 53 % of humic substances). The removal is significant after the first hour of filtration especially for biopolymers (> 20,000 Da), but subsequently poor removal was observed probably due to exhaustion of the pre-coat layer. This implies that backwashing and introducing new pre-coat layers after one-hour filtration cycle is feasible for controlling the fouling. Other low molecular weight NOM components were also well removed during the first hour of filtration and fairly well removed thereafter although they have negligible influence in terms of fouling. The mechanisms of biopolymers removal could be related to the previous work (Heijman et al., 2008) which described how biopolymers were physically removed by straining through SPAC particles.

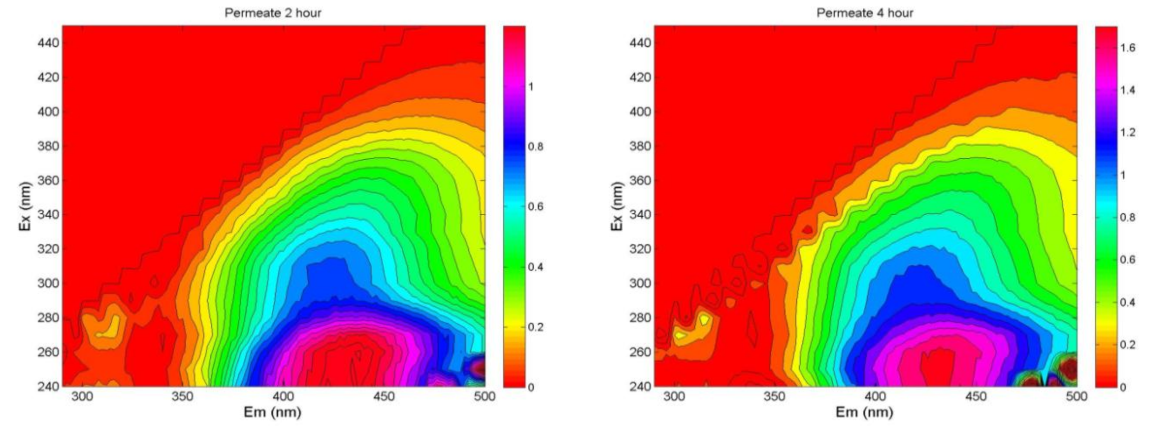
3.4.6 NOM characterizations with FEEM

Proteins (which are a part of the biopolymers) and humic/fulvic substances were characterized by Fluorescence Excitation Emission Spectroscopy (FEEM). The samples of permeates were collected after 1 hour, 2 hours and 4 hours. Permeates and feed water were analyzed with FEEM to determine the removal of protein-like and humic-like organic matter by ceramic membrane filtration pre-coated with 10 mg/L of SPAC in 4 hours filtrations cycles. The results are shown in Figure 3.13 below with the results summarized in Table 3.8.



*(a): **F**EEM spectra for Feed water*

*(b): **F**EEM spectra for Permeate after 1 hour – 40 mg/L SPAC*



*(c): **F**EEM spectra for Permeate after 2 hours – 20 mg/L SPAC*

*(d): **F**EEM spectra for Permeate after 4 hours – 10 mg/L SPAC*

Figure 3.13: FEEM spectra for (a) Feed water (b) Permeate after 1 hour – 40 mg/L SPAC (c) Permeate after 2 hours – 20 mg/L SPAC and (d) Permeate after 4 hours – 10 mg/L SPAC

Table 2.8: FEEM fractions of NOM removals using 10 mg/L of S-PAC pre-coated onto MF ceramic membrane @ 160 L/m^2.h Flux.

Sample	*Excitation/Emission (Ex/Em)*	*Intensity*	*Comments*
Canal water - Feed (DOC = 5.6 mg/l)	Humic peak: 240/434 Protein peak: 280/304	3.5 2.2	Humic-like Protein-like
Permeate after 1 hour – 40 mg/L SPAC (DOC = 2.4 mg/l)	Humic peak: 240/434 Protein peak: 280/304	0.62 0.15	82 % Rejection of fluorescence for Humic-like 93 % Rejection of fluorescence for Protein-like
Permeate after 2 hours – 20 mg/L SPAC	Humic peak: 260/438 Protein peak: 270/314	1.32 0.17	62 % Rejection fluorescence for Humic-like

(DOC = 3.6 mg/l)			92 % Rejection fluorescence for Protein-like
Permeate after 4 hours – 10 mg/L SPAC (DOC = 4.2 mg/l)	Humic peak: 260/432 Protein peak: 270/302	1.73 0.36	51 % Rejection fluorescence for Humic-like 83 % Rejection fluorescence for Protein-like

The results from Figure 3.13 (a – d) and Table 3.8 show the humic-like peaks at the excitation/emission ranges of 240-260 nm/432-438 nm which corresponds to the humic like peak described by Henderson group (Henderson et al., 2009). Protein peaks are found at excitation emission ranges of 270-280 nm/302-314 nm (Table 3.8), which corresponds to the protein like peaks ranges of 225-275 nm/309-340 nm mentioned by Hambly and co-workers (Hambly et al., 2010). Significant rejection of proteins and humic substances was attained after the first hour with equivalent dose of 40 mg/L SPAC (Table 3.8). These were equivalent to 93 % proteins and 82 % humic substance reduction of fluorescence.

Humic substances rejection declined afterwards to 62 % and 51 % after 2 hours and 4 hours, respectively. Alternatively, proteins rejection was maintained at 92 % with 20 mg/L SPAC at end of 2 hours filtration and declined to 82 % at the end of the fourth hour, which is equivalent to 10 mg/L SPAC. FEEM results support the LC-OCD results obtained earlier that showed significant removal of biopolymers and humic substances at 30 – 40 mg/L SPAC doses. This is also suggests that rejection of biopolymers plays a major role in controlling irreversible fouling.

3.4.7 Characterizations of TEP (Feed vs. Permeates) – Pilot scale

Transparent Exopolymer Particles (TEP) is a form of acidic polysaccharides that belongs to the group of biopolymers, which is known to be a source of biofouling (Kennedy, M. D., J. Kamanyi, et al. 2008). To eliminate the source of biofouling is becoming an important issue in low-pressure membranes especially when these membranes bear the role of pre-treatment option prior to RO membrane or NF membranes.

TEP was measured for samples of feed water and permeates collected after 1, 2 and 4 hours. The summary of the results is shown below (Table 3.9):

Table 2.9: TEP levels and removals after 1, 2 and 4 hours of surface water filtration onto MF Ceramic membrane pre-coated with 10 mg/L of S-PAC.

Sample	**TEP (absorbance/cm/L) > 0.4 µm**	**TEP Removal**
Feed water (DOC = 5.6 mg/l)	0.7	
Hour 1 Permeate (DOC = 2.4 mg/l)	0.2	70 %
Hour 2 Permeate (DOC = 3.6 mg/l)	0.5	30 %
Hour 4 Permeate (DOC = 4.15 mg/l)	0.6	15 %

The results in Table 3.9 show that significant reduction of the fouling in terms of TEP achieved 70 % after the first 1 hour of filtration with equivalent dose of 40 mg/L of SPAC. The rejection declined to 30 % in the second hour (20 mg/L SPAC) and dropped to 15 % after 4 hours (10 mg/L SPAC). TEP measurements, like FEEM measurements, showed a substantial reduction of TEP or acidic polysaccharides, which are a component of biopolymers. Furthermore, the TEP reduction seems to be the similar to the observed fouling reduction. This suggests that TEP is indeed an important foulant, and that the irreversible TMP increase is also contributed by TEP. These results suggest that application of SPAC combined with ceramic membrane filtration could contribute to the controlling of fouling in RO/NF membranes.

3.5 Conclusions

Bench scale results

The removals of DOC and UV_{254} were found to be 46 % and 51 %, respectively, from canal water of average DOC 15 mg/L using 30 mg/L of SPAC with a PVDF MF membrane. The characterization of NOM using LC-OCD revealed interesting results that showed high removal of biopolymers (> 85 %) with SPAC, which is suggested to be done mostly by physical means (straining). Due to biopolymers straining on the cake layer of SPAC pre-coat, the increase of total membrane resistance was 3.5 times higher than NPAC pre-coat.

The study done with the Anopore ceramic membrane (AAO100) and 0.45 um filter pre-coated with 30 mg/l SPAC, and compared with adsorption experiment at the same dose, revealed that most of the biopolymers were removed by the pre-coating layer. The maximum biopolymers that can be removed by SPAC adsorption is 62 % but when SPAC is pre-coated onto the AAO100 membrane, removal was increased to 80 % which means that additional removal (minimum of 18 %) is likely due to physical means by either SPAC or the membrane. If we consider that adsorption was fully utilized by the pre-coat (which is not true in just a short contact time with pre-coat), then still the pre-coated 0.45 µm filter achieved 72 %, which corresponds to 10 % additional removal compared to adsorption. But also it has been shown that increased SPAC dose increases cake resistances during filtration as more biopolymers are trapped and ultimately lead to TMP increases. So it can be concluded that physical removal is contributing in removal of biopolymers as well as adsorption.

Pilot scale results

It was also observed that a ceramic MF membrane – in one hours cycles - pre-coated with an equivalent dose of 40 mg/L of SPAC has the potential to control both reversible and irreversible fouling for a surface water with an average DOC of 5 mg/L. Irreversible fouling was reduced to 42 %, 29 % and 7 % with 20, 13.5 and 10 mg/L equivalent doses of SPAC pre-coats, respectively. Both biopolymers and humic substances were removed to an average of about 60 %. FEEM and TEP measurements showed a significant reduction of fluorescence of proteins and removal of acidic polysaccharides to about 92 % and 70 %, respectively, in one-hour cycles of filtration. These findings suggest that the use of SPAC combined with ceramic MF membranes may be considered as an effective pre-treatment for RO or NF membranes in controlling (bio) fouling. Also, the use of SPAC pre-coats has the capability to control or reduce the fouling of MF ceramic membranes depending on feed water quality and SPAC pre-coat dose used.

3.6 References

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CHAPTER 4

4.0 Ceramic MF membranes combined with powdered activated carbons (PACs) for treatment of secondary wastewater effluents: *Effluent organic matters (EfOM) removal and fouling control*

Chapter 4 is based on

Hierarchical Porous Carbons with ultra-large mesopores for organic fouling abatement of low pressure membranes

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4.1 Introduction

Application of commercial powdered activated carbon (PAC) and granular activated carbon (GAC) has been successful in terms of removal of trace organic compounds and improvement of taste and odor of drinking water. However there is less achievement in removal of problematical fractions of natural organic matter (natural organic matter (NOM) and effluent organic matter (EfOM). Failure to remove NOM/EfOM has a huge impact on membrane fouling and later development of disinfection by-products in systems that use chlorine for disinfection.

Despite these deficiencies, both conventional and advanced treatment systems have adopted the use of activated carbon as a polishing step. In advanced treatment systems, PAC has been commonly used with low-pressure membranes (microfiltration (MF) or ultrafiltration (UF)). Most MF and UF membranes are fabricated with organic materials (polymers). However, these polymer-based membranes are not robust enough to overcome the effects of aggressive cleaning.

Most of the research on application of MF/UF membranes to treat wastewater have been based on polymeric membranes (Muthukumaran et al., 2011). The performance of these membranes are subject to the conditions of feed water, type of membrane and operating protocol (Lehman and Liu, 2009). MF/UF membranes are effective in removing turbidity and pathogens but not effective in removing dissloved substances such as precursors of disinfection by-products (DBPs) or organic micro pollutants (Huang et al., 2009). Also, fouling due to organic matter is a problem for both potable water and wastewater treatment (Fabris et al., 2007a).

Fouling of a membrane is evitable for MF/UF membranes in wastewater treatment (Lehman and Liu, 2009) although though adequate pre-treatment, fouling can be reduced significantly (Huang et al., 2010). To deal with fouling problem, aggressive backwashing and chemical cleaning are needed and it is at this point where ceramic membranes become a vital option (Palacio et al., 2009). Over the last decade, ceramic membranes, made up of inorganic materials of a more robust structure, have been introduced in water treatment applications (Lehman and Liu, 2009, Sondhi et al., 2003). Similar to polymeric membranes, fouling and low ability to remove natural organic matter (NOM) or effluent organic matter (EfOM) from wastewater is a major constraint for effective performance of ceramic MF (or UF) membranes.

In the previous chapter, a submicron powdered activated carbon (SPAC) pre-coat was found to be effective in terms of biopolymers removal and fouling reduction. Any PAC can be converted to SPAC, but the best SPAC will be determined based on capacity and kinetics. A PAC with a good mesoporous range is hypothesized to produce good SPAC as well, since it may be capable of removing biopolymers to a large extent through adsorption, ultimately leading to fouling reduction. This justifies the need to search, develop or produce a better PAC with a wider range of mesopores for enhancement of biopolymers adsorption. Therefore in this chapter, performance of commercial PACs from NORIT and novel PACs were critically examined and a proposal for the best PAC to be used as pre-coat was made. The study has been confined to the pre-coating approach that provides full contact to adsorbate over negligible contact time.

4.2 Background

4.2.1 Effluent organic matter (EfOM) and adsorption competition

EfOM contains degradation and soluble microbial products (SMP) derived from bacteria during wastewater treatment. It also contains NOM moieties, such as humic substances (Krasner et al., 2009, Her et al., 2003). Simply, EfOM is defined as a mixture of NOM, SMPs, and micro-pollutants (Henderson et al., 2011), and nutrients like dissolved organic nitrogen (DON)(Chen et al., 2009). NOM and EfOM differ in terms of origin whereby NOM is derived from aromatic substances and EfOM from biological treatment processes of wastewater facilitated by bacteria.

SMP obtained from EfOM is a substrate metabolite which contains macromolecules and cellular moieties (protein and polysaccharides) (Krasner et al., 2009). EfOM has shown to be a precursor to DBPs formation in finished drinking water due to numerous biogeochemical mechanisms, e.g. photolysis, hydrolysis, biodegradation, adsorption and also volatilization (Krasner et al., 2009, Chen et al., 2009). This product of biological treatment has also been found to be an important foulant in membrane systems (Laabs et al., 2006).

The fouled membrane accumulates macromolecules that block membrane pores and eventually forms a cake layer on the membrane surface. These accumulations of macromolecules are capable of adsorbing trace organic compounds to some extent. Caffeine and paracetamol were found to be adsorbed into alginate at levels of 58 % and 25 %, respectively (Hajibabania et al., 2011). Also it was found that trace organic compounds were adsorbed onto sludge/biosolids (Hyland et al., 2012). Hence in the absence of activated carbon, some trace organic compounds can be adsorbed into the matrix of NOM. But in its presence, trace organic compounds tend to compete with NOM in adsorption. Mesoporous activated carbon may decreases this competition by offering more porous adsorption sites for both NOM and micropollutants (Pelekani and Snoeyink, 2000).

4.2.2 Pretreatment options to control organic fouling

Many studies had attempted to overcome fouling propensity, which affect filterability of membranes. There have been proposed various pre-treatment steps prior to low pressure (MF) membranes (both polymeric and ceramic membranes), e.g., by modifying system design with addition of coagulation/flocculation, granular activated carbon (GAC), powdered activated carbon (PAC), magnetic ion exchange (MIEX$^{®}$), pre-ozonation step and also membranes surface modification when coated by several proposed materials, such as PAC and metal-oxides (Chen et al., 2011, Konieczny et al., 2009, Harman et al., 2010, Thiruvenkatachari et al., 2006, Fabris et al., 2007b, Konieczny et al., 2006). In general, activated carbon plays a central role in controlling organic contaminants.

4.2.3 Preparations of activated carbon

Activated carbon preparation is based on two ways of activation, physical activation and chemical activation. Commercial activated carbons are normally activated with steam or carbon dioxide (Deryło-Marczewska et al., 2004). In physical activation, the raw material (like wood) is heated in increments of temperature with a gradual increase at a rate of 8 ^{0}C /minute until reaching 750 ^{0}C. This is followed by heating with carbon dioxide and providing enough time to burn off, and then allowed to cool at a room temperature.

Chemical activation differs from physical activation in the initial steps. In chemical activation the raw material is washed for 24 hours with sulphuric acid followed by Milli Q water that removes any acid remaining. When it is completely dry, phosphoric acid is added and heated to remove the acid then physical activation steps are followed with final activation temperature set to 450 ^{0}C instead of 750 ^{0}C (Mourao et al., 2006). Activation temperature determines the surface nature of activated carbon. If the activation temperature is below 800 ^{0}C then an acidic surface is formed and when it is above 900 ^{0}C it changes into a basic nature (Park and kim, 2001). Activated carbon prepared by chemical activation with hydroxide was found to have a high adsorption capacity (Lillo-Ródenas et al., 2005).

4.2.4 Pore size distribution and adsorption of organic matter

The sizes of pores of activated carbons have major impact on adsorption (Deryło-Marczewska et al., 2004). Severe pore blockage by NOM was observed in micro-pores and minimum blockage effect was observed in macro-porous (Zhang et al., 2011). Pore blockage is minimized if the PAC has a wider pore distribution while large molecular weight NOM affects adsorption of trace organic compounds (Newcombe et al., 2002b, Qi et al., 2007). Moreover, access to the pores entrance for low molecular weight NOM is limited by large NOM (Newcombe et al., 2002a).

The wide ranges of sizes of NOM make its components to act differently in terms of adsorption that relies on pore sizes of activated carbon. Adsorption of low molecular weight NOM was higher than high molecular weight NOM (Newcombe et al., 2002a, Filloux et al., 2012). High molecular weights NOM (biopolymers) are estimated to have sizes that are > 3 nm. Most of the available commercial activated carbons have pores that are below to 3 nm (Li et al., 2002, Pelekani and Snoeyink, 2000, Newcombe et al., 2002a, Lu and Sorial, 2004). Therefore micro-pores have limited ability in NOM removal, in particular high molecular weight NOM.

A narrow pore size works with micro-pollutants removal although NOM screening may provide pore blockage and minimize adsorption of low molecular weight NOM as well as micro-pollutants. A bituminous based activated carbon, F400, showed better adsorptive capacity compared to ACC-10 and ACC-15 activated carbons that have narrow pore distribution than F400 (Lu and Sorial, 2004). Nevertheless, in a common pre-treatment method, enough contact time is required for PAC to adsorb undesirable organic materials and a proper dose should be determined based on feed water quality.

A PAC dose of 100 mg/l combined with a low pressure membrane removed only 19 % of biopolymers in wastewater effluent, leading to poor filterability (Filloux et al., 2012). Biopolymers have a significant role in the fouling of low pressure membranes compared to other EfOM components (Filloux et al., 2012) although low molecular weight EfOM dominates the composition of NOM (Kim and Dempsey, 2012).

But still the big question is to find out the best PAC that will be effective in removal of high molecular weight NOM, trace organic compounds and fouling reduction. Gao and co-authors expressed the need to develop new PAC (Gao et al., 2011). This new PAC should have the potential to remove high molecular weight NOM and trace organic compounds and improve filterability of membranes.

BET surface area of powdered activated carbon alone is not sufficient to explain the adsorption process without characterization of pore size distribution (Cloirec and Faur, 2006). From this fact, the hypothesis that will help to determine the best performing PAC was formulated. Based on estimation of the biopolymers sizes it was hypothesized that

PAC with pore sizes between 3 nm to 50 nm would be effective for biopolymers removal and fouling control.

4.3 Goals and objectives

This research work focused on investigation of a better PAC to be used as a pre-coat for enhancing removal of high molecular weight EfOM from wastewater effluent through adsorption. Also it was aimed at improving filterability of ceramic microfiltration membranes. Bench scale experiments using secondary wastewater effluent from Jeddah were conducted. Powdered activated carbon (PAC) was introduced to provide a thin adsorptive layer on the membrane surface. This coating layer can be removed by backwashing and introduced again at the beginning of a new filtration cycle. The summary of the objectives of this research were as follows:

1. To estimate, by a mathematical model, the particle diameters (sizes in nanometers) of biopolymers.
2. To assess the performance of different PACs (novel PACs compared to commercial PACs) on fouling reduction/control with a pre-coated ceramic MF membrane.
3. To assess EfOM components removal achieved by a pre-coated ceramic membrane and compared to adsorption.

4.4 Materials and Methods

4.4.1 Materials

4.4.1.1 Feed water

The feed water for this study was wastewater effluent collected from Wastewater Treatment Plant (WWTP) in Jeddah, Saudi Arabia. Raw feed water was pre-filtered with 0.45 um filters (Millipore, nylon membrane 0.45 µm HNWP) to remove particulate and some colloidal matter. All filters were initially immersed in MilliQ water for conditioning. The pre-filtered feed raw water was subsequently stored in 4°C in a cold room to avoid degradation. The average quality of feed water measurements is illustrated in Table 4.1.

Table 4.1: Feed water quality

Parameter	DOC (mg/L)	UV254 (cm-1)	SUVA (L/mg-m)	pH	Conductivity (uS/cm)	Turbidity (NTU)	Ca^{2+} (mg/L)
Value	4.68±0.5	0.11±0.01	2.38±0.2	7.2 - 7.8	2.98-3.21	0.24-0.27	80

4.4.1.2 Membranes

A ceramic MF (AA0100) membrane (Anodisc 25, 0.1 µm, 25 mm, 50 circles, Whatman) was used to conduct the experiments. The nominal pore size, thickness and diameter were 0.1 µm, 60 µm and 25 mm, respectively. This membrane was hydrophilic, based on data obtained from contact angle measurements (average of 10.7°).

4.4.1.3 Powdered activated carbon

The five different employed PACs in this study were partly generated through a joint project between King Abdullah University of Science and Technology (KAUST) and Cornell University in collaborative work (KCU 6, KCU 8, KCU 12) while the rest were commercially available from Norit (SA Super, Darco G-60). SA Super PAC was made from vegetable raw materials by steam activation (Szlachta and Adamski, 2007) while G60 was produced from wood based materials with the same method of activation as SASuper. The characteristics of the five PACs are tabulated below (Tables 4.2 and 4.3) as adapted from Chapter 2.

Table 4.2: Average particles sizes of commercial PACs and new generation (novel) PACs

	Average Particle sizes (um) - d50	**Effective particle size (um) - d10**	**D90 (um)**
SASuper	20.63	3.49	93.02
G60	26.95	6.31	87.68
KCU 6	38.28	11.73	98.8
KCU 8	30.83	9.59	100.44
KCU 12	29.24	10.29	68.28

Table 4.3: BET surface area and pore sizes of commercial PACs and new generation (novel) PACs

Type of PAC	BET surface Area (m^2/g)	Pore Volume (cm^3/g)	Mesopores surface area (m^2/g)	Mesopores volume (cm^3/g)	Max. pore diameter (nm)
SASuper	903	0.8	347	0.53	2.28
G 60	909	0.86	310	0.51	2.83, 13.34
KCU 6	1280	3.96	747	3.83	33
KCU 8	1265	3.58	734	3.44	11.2
KCU 12	1121	2.7	670	2.7	13.6

4.4.2 Sample analysis

The analysis of permeates and feed waters in this study included ultraviolet absorbance at a wavelength of 254 nm (UV_{254}) and NOM characterizations. Water samples were analyzed by DR 5000^{TM} UV-Vis Spectrophotometer (HACH) to determine UV_{254} adsorption. Liquid chromatography–organic carbon detection (LC-OCD) was employed for analyzing EfOM compositions of feed and permeates water samples. More characterization of EfOM was done by a Fluorescence spectrometer (Fluoromax–4 from Horiba) which measured fluorescence excitation emission matrix (FEEM) spectra in order to define humic-like and protein-like organic matter. The data obtained were processed by MATLAB software to determine the intensity peak of each sample. Three peaks identified from FEEM spectra were decided based on adopted ranges of excitation-emission as shown in a Table 4.4 below.

Table 4.4: Typical FEEM Peak ranges

NOM Components	*Excitation (Ex.)*	*Emission (Em.)*
Humic-like Primary Peak	330 - 350	420 - 480
Humic-like secondary Peak	250 - 260	380 - 480
Protein-like Peak	270 - 280	300 - 350

Source: (Salinas, 2011)

4.4.3 Experimental set up

The experiments were performed at the bench scale under average flux. The set-up is illustrated in Figure 4.1 where a modified Amicon unstirred cell was employed. Based on (Amy, 2008), this type of cell represents an operational condition of dead-end filtration mode. The Amicon cell is composed of cap and cell house, cylinder and membrane holder, O-rings made of rubber, filtrate outlet, pressure inlet and retaining stand for the cell house (Zeng et al., 2009). Nitrogen gas was utilized to pressurize feed water from the pressure vessel to the membrane cell. A 500 mL clean beaker was used to collect the filtered permeate water while an automatic balance recorded the weight of collected permeate water at intervals of one minute at room temperature. An average constant flux was maintained by a manual adjustment of pressure. The setup for the bench scale experiment is shown in Figure 4.1 below:

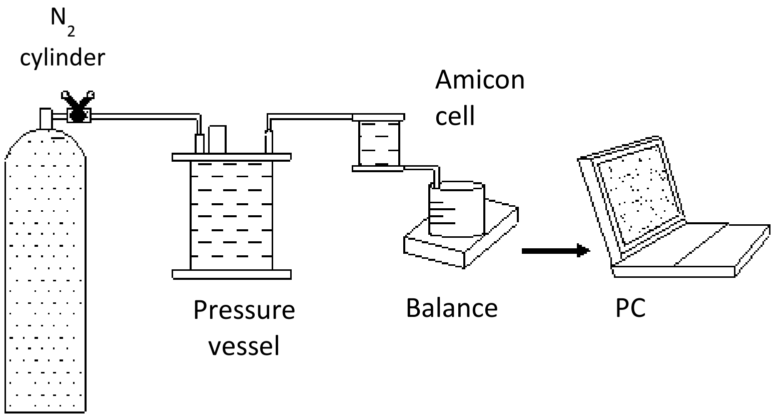


Figure 4.1: Amicon (un) stirred cell- Bench scale setup

4.4.4 PAC pre-coating on the membrane surface

Required dose of PAC was measured in a balance and mixed with pure MilliQ water to form a PAC solution. PAC solution was then filtered through a AAO100 membrane placed in the Amicon cell to form a coating layer ready for feed filtration. This method was implemented for both AA0100 and 0.45 µm membranes.

To study the contribution of pre-coating layer alone, 0.45 um filters were used. NOM components are expected to pass through a 0.45 um filter so the pre-coated filter may be used to represent the pre-coat removal without a membrane. The filter acts as a support layer for pre-coating and the results obtained was expressed as performance of the pre-coating layer.

4.4.5 Data analysis

The total membrane resistance (R_T) in m^{-1} was determined by following equation (1):

$$R_{\mathrm{T}} = \frac{\mathrm{TMP}}{\mu \times J} \tag{1}$$

Where TMP is the trans-membrane pressure difference across the membrane (N/m^2),

J is the flux (m^3/m^{2}h) while µ is the viscosity of the solution, which could be obtained by equation (2):

$$\mu = \frac{0.497}{(T + 42.5)^{1.5}} \tag{2}$$

Where T is stands for temperature of the feed water, in this case room temperature (20°C).

4.5 Results and Discussions

4.5.1 Estimated sizes of biopolymers in terms of nanometers (nm)

A number of studies have identified biopolymers to play a significant role in fouling of low pressure membranes (Amy, 2008), (Filloux et al., 2012). The deficiency of most of the commercial PACs is related to their failure in removal of high molecular weight NOM. Most of these PACs contain pores that are smaller compared to the size of biopolymers (Newcombe et al., 2002a, Pelekani and Snoeyink, 2000). But the actual sizes of biopolymers in terms diameter are still unknown. However, what is known from the literature is that biopolymers have a wide range of sizes and not a fixed size. This makes things more difficult in search of a suitable PAC capable of adsorbing biopolymers. Nevertheless, the size of biopolymers in terms of molecular weight is well documented (Huber et al., 2011). This serves as a good base to estimate the sizes of biopolymers and come up with a suitable PAC proposal in terms of pore sizes that will ultimately be effective in terms of biopolymers removal as well as in fouling reduction.

Biopolymer sizes are classified in terms of molecular weight measured in Daltons (Da). The molecular weight of biopolymers as defined as > 20,000 Da or 20 kilo Daltons - kDa (Huber et al., 2011). Table 4.5 below defines the relationship between molecular weight presented in terms of kDa and diameter sizes in terms of nanometers (nm).

Table 4.5: Relationship between kilo Daltons (kDa) and nanometers (nm)

KDa	Nanometre (nm)
1000	100
500	20
100	10
50	4
10	2.5
5	1.5

http://www.etseq.urv.es/doctorat/index/running/2003_2005/courses_w/memb_sep/Memb07.pdf

If the values are converted to log scale and a plot of log nm against log kDa is plotted, then the equation obtained can be used to estimate the sizes of biopolymers.

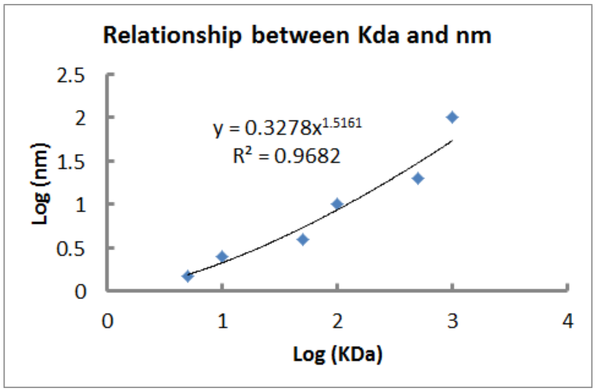


Figure 4.2: Relationship between kilo Daltons (kDa) and nanometers (nm)

The equation governing the relationship between sizes in nanometer (nm) and MW (kDa) is described below with a correlation of 97 %.

$y = 0.3278x^{1.5161}$
$R^2 = 0.9682$

The sizes of biopolymers range between 20 kDa – 1000 kDa. By applying the above equation to convert the values into nanometers, then the sizes of biopolymers will range between 3.1 – 54 nm. This enables one to formulate a hypothesis that any PAC possessing pores (mesoporous) between 3 - 50 nm will provide good removal of biopolymers. KCU 6 correlates well with this hypothesis. The BET measurements showed that KCU 6 possesses a maximum pore diameter of 33 nm and wide distribution range of mesoporous pores that are likely good for biopolymers removal. In seawater the size of biopolymers is estimated to be from 10 – 50 KDa which is equivalent to 2.5 – 4 nm (Jeong et al., 2013). Therefore KCU 8, KCU 6 and even G60 could be also useful for removal of biopolymers from seawater sources.

4.5.2 EfOM components removal with membrane (AAO100) alone: adsorption vs. size exclusion

Organic matter is a major contributor to membrane fouling (Pontie et al., 2006). A microfiltration membrane can remove some portion of organic matter (mainly high molecular weight organic matter) by size exclusion or adsorption. The removal of high molecular weight NOM by the membrane alone was assessed using pre-filtered (with 0.45 µm filters) wastewater effluent. The pre-filtered feed water was then filtered with the AAO100 and 0.45 µm membranes and the permeate waters were collected and analyzed by LC-OCD. The results are expressed in Table 4.6 and Figure 4.3 below.

Table 4.6: EfOM components before and after wastewater effluent filtration with membranes

	DOC (mg/l)	**Biopolymers (mg/l)**	**Humics Substance (mg/l)**
AAO100 Permeate	4.711	0.13	2.135
0.45um Permeate	4.772	0.233	2.153
Feed	4.717	0.239	2.237

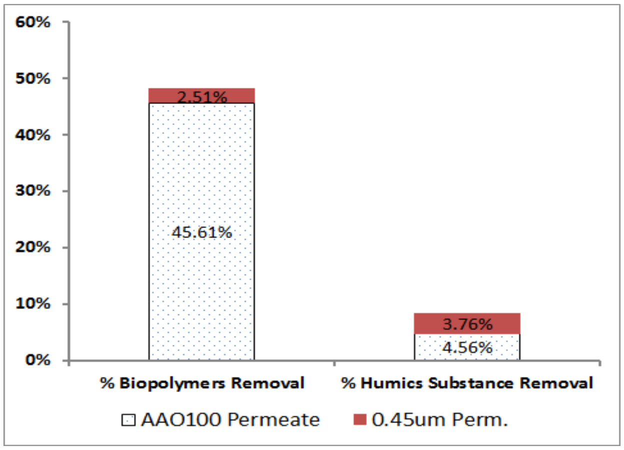


Figure 4.3: Biopolymers and humic substances removal with AAO100 and 0.45 um membranes filtration

The ceramic MF membrane alone showed good removal of biopolymers (> 45 %) but low removal of humic substances (< 5 %) as shown in Figure 4.3. A UF membrane that has tighter pores than the MF membrane retained 68 % of biopolymers from a surface water treatment plant (Siembida-Lösch et al., 2012). The removal of biopolymers and humic substances with 0.45 µm filters was below 4 % (Figure 4.3), which justifies the application of these filters to represent the removal of NOM components by the pre-coat layer alone.

To differentiate between adsorption and size exclusion mechanisms, adsorption experiments were carried out. Assessment of adsorption synergy of ceramic membrane was performed to investigate the adsorption capabilities of the AAO100 membrane. This includes the study of BET surface area of the ceramic powder to understand the potential ability of pore adsorption. The adsorption experiments were then carried out. Feed water in 200 mL clean bottles was mixed with different concentrations of ceramic powder (60, 90, 120, 150 and 200 mg/L) and shaken (mixed) for 24 hours. These samples were then pre-filtered with 0.45 µm filters to separate the particles and permeate. Using LC-OCD, the removals of biopolymers and humic substances were determined as expressed in Table 4.7 and Figure 4.4 below.

Table 4.7: EfOM components adsorption of wastewater by ceramic powder

Ceramic Powder Conc.	DOC (mg/l)	Biopolymers (mg/l)	Humics Substance (mg/l)
200 mg/l	4.622	0.138	1.573
150 mg/l	4.549	0.143	1.603
120 mg/l	4.623	0.135	1.633
90 mg/l	4.44	0.132	1.582
60 mg/l	4.231	0.139	1.614
Wastewater	4.295	0.151	1.675

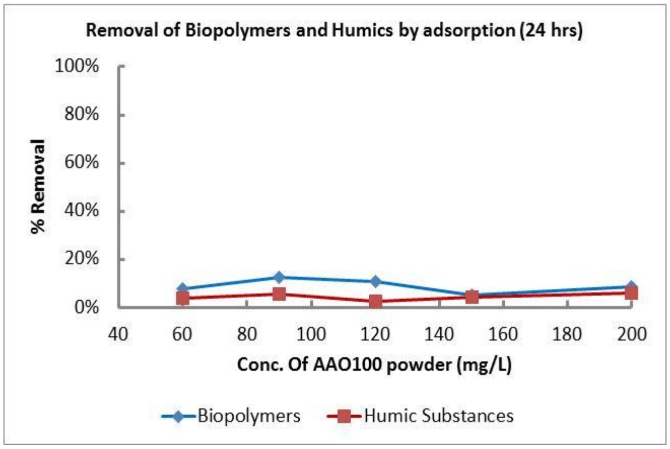


Figure 4.4: Adsorption of high molecular weight organic matter by different doses of powdered ceramic membranes

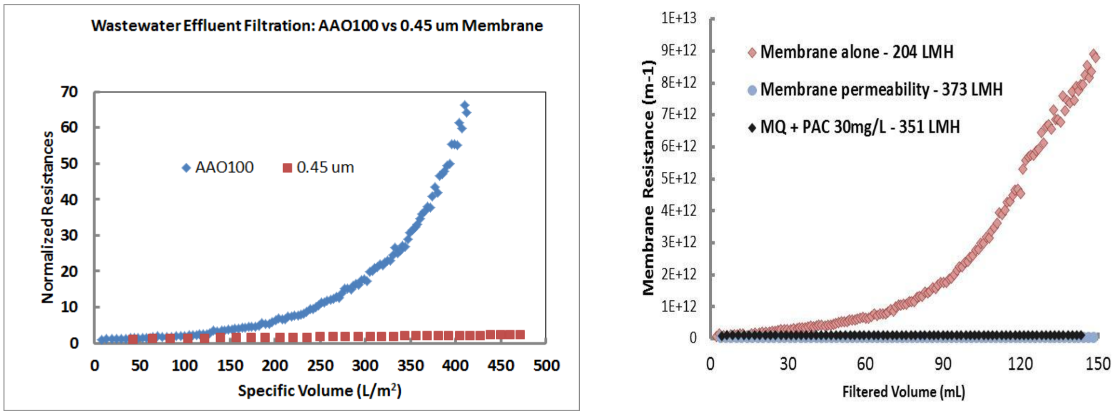
The total BET surface area of the ceramic membrane powder measured by the ASAP 2020 instrument was 1.06 m^2/g while pore volume was 0.002 cm^3/g and average pore size was 8 nm. These parameters imply that the ceramic membrane made up of alumina has low sorption capacity and may have negligible contribution to biopolymers adsorption compared to PAC. Adsorption experiments using powdered ceramic membranes showed poor removal of high molecular weight NOM (Table 4.7 and Figure 4.4) which strongly supports the BET results. Only a small amount of biopolymers could be removed by adsorption. This suggests that size exclusion is the main mechanisms for biopolymers removal by AAO100. Therefore, since the ceramic MF membrane alone showed significant removal of biopolymers (≈ 50 %), this suggests that pore blockage is the main fouling mechanism.

4.5.3 Performance of PAC pre-coated on ceramic MF membranes

4.5.3.1 Performance of ceramic membrane without pre-coat and influence of pre-coat layer on membrane resistances

The performance of ceramic membranes without pre-coat (membrane alone) in terms of increase of membrane resistances was investigated. The results were then compared with resistances obtained when feed water was filtered with 0.45 µm filters without PAC. The total filtered volume was 150 mL for both cases. The system was operated at an average constant flux in the case of the AAO100 membrane and constant pressure for 0.45 µm filter. The comparison between two membranes in terms of membrane increases is expressed by the results in Figure 4.5.

The influence of PAC resistances was also determined by pre-coating the AAO100 membrane, followed by filtration with Milli Q water. The obtained results were then compared with the permeability of the AAO100 membrane and feed water filtration with AAO100 alone at a filtered volume of 150 mL. The results are presented in Figure 4.6 below. The total resistances were calculated based on equation 1:



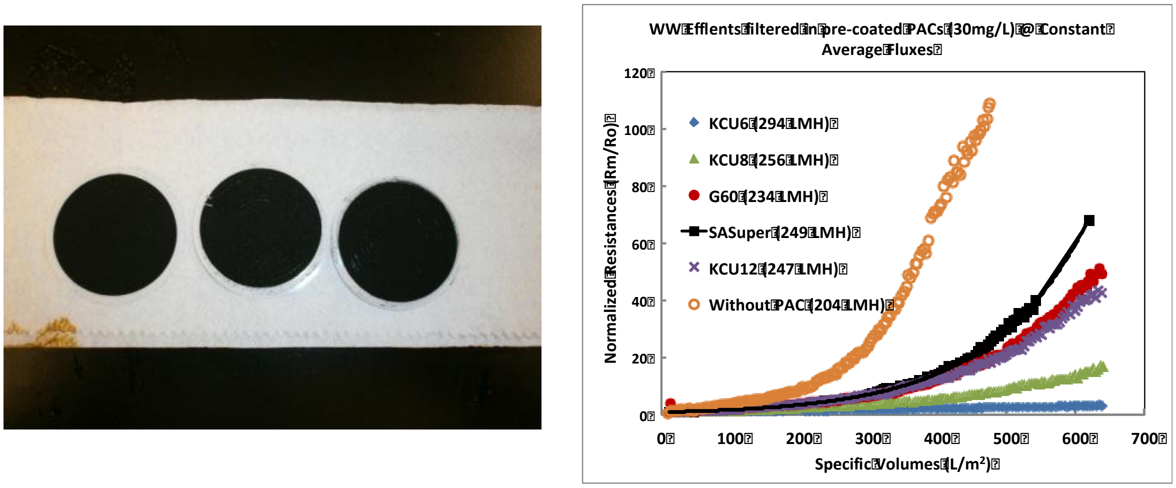
(a) **(b)**

Figure 4.5: Comparison of membrane resistances (a) between AAO100 and 0.45µm membranes without pre-coat and (b) influence of PAC layer on membrane resistances

Figure 4.5 (a) reveals a comparison between the 0.45 µm and AAO100 membranes, showing that the increase of membrane resistance of 0.45 µm filters is negligible, compared with the increase of membrane resistance of the AAO100 membrane. This indicates that EfOM components are not retained by 0.45 µm while AAO100 retains EfOM that ultimately leads to the increase of membrane resistance. The PAC pre-coat has negligible influence on increase of membrane resistances although it may have slight effect on initial flux due to increased thickness caused by combination of pre-coat layer and membrane (Figure 4.5 b).

4.5.3.2 Performance of ceramic MF membrane pre-coated with different PACs

The pre-coating of PAC was performed by filtering a clean solution of activated carbon on the ceramic membrane to form a thin pre-coat layer on the membrane surface (Figure 4.6 a). For the AAO100 membrane, 6 mg of PAC mixed with Milli Q water was filtered. After membrane pre-coating, 200 mL of feed water was filtered through the pre-coated membrane (AAO100), corresponding to 30 mg/L of equivalent PAC dose. The constant flux operation was precisely maintained manually by adjusting the pressure throughout the experiments. The total membrane resistance of pre-coated AAO100 was determined based on the membrane resistance equation described in section 4.3.5. The performance of novel PACs (KCUs) and commercial PACs pre-coats in terms of membrane resistance increases are presented in Figure 4.6 (b) below:



(a) **(b)**

Figure 4.6: Pre-coated AAO100 membranes (a) and Total membrane resistances increases of PACs pre-coated membranes (b).

Application of PAC to pre-coat the membrane surface helps to improve membrane performance by suppressing total membrane resistance, which is a function of operational trans-membrane pressure (TMP) and flux (Figure 4.6 b). The total membrane resistance exponentially increased when filtration was done with the membrane alone due to membrane pore fouling. By applying PAC, total membrane resistance was suppressed significantly with different performance levels. The sequence of PAC performance in mitigating total membrane resistance followed the following series KCU 6>KCU 8>KCU12>G60 >SASuper.

The results showed that KCU6 and KCU8 achieved excellence performance by suppressing the increase of membrane resistance to a lower level. KCU 6 showed superior performance that suggests it has good adsorption capabilities of high molecular weight NOM. The KCU 6 pre-coat performance is attributed to its unique characteristics that are supported by a large surface area and a wide range of pore size distribution that includes large pore diameters (refer to Table 4.3 results). These characteristics are assumed to facilitate adsorption of high molecular weight NOM components. The currently available commercial PACs are not effective in dealing with the problem of NOM fouling, especially that caused by high molecular weight NOM, so development of new PACs was suggested (Gao et al., 2011). KCU 6 proved to be reliable candidate since it was effective in mitigating fouling when applied as a pre-coat prior to membrane filtration.

4.5.4 EfOM Removal Analysis

NOM components can be characterized by using available advanced techniques like LC-OCD or FEEM (Henderson et al., 2011). EfOM components are membrane foulants, which can be trapped inside the pores of the membrane and/or deposited on the membrane surface, which further forms a cake layer that suppresses operating flux or elevates trans-membrane pressure (TMP). The enhanced performance of the AA0100 membrane filterability was improved after pre-coating the membrane with PAC as discussed in section 4.4.3.2. Further study was conducted and included coating of 0.45 µm membrane filters. The procedure for coating both membranes (AAO100 and 0.45 µm) and filtration processes are explained below.

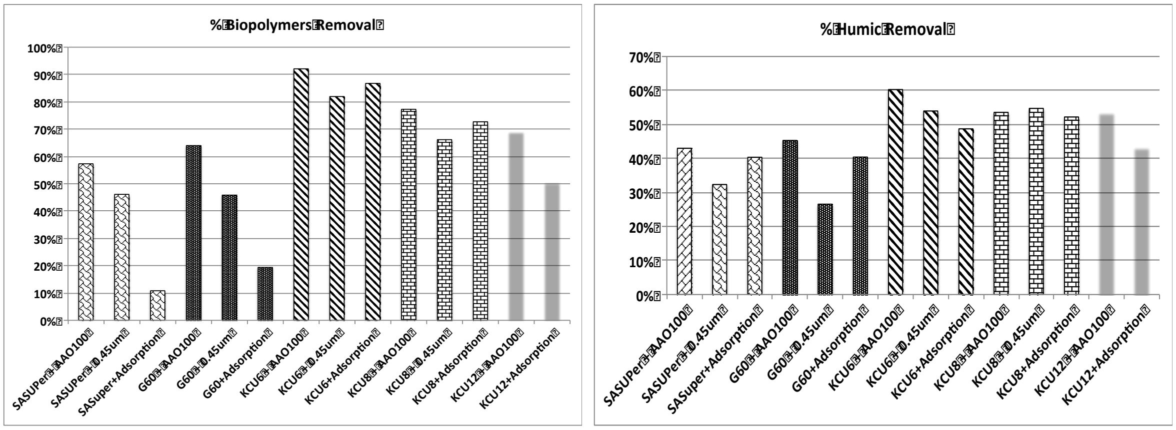
Average weights of 6 mg and 4.5 mg of PACs mixed with Milli Q water were filtered on AAO100 membranes and 0.45 µm filters, respectively, to form pre-coat layers. A total of 200 and 150 mL of feed water was then filtered through the pre-coated membrane (AAO100) and 0.45 µm filters, respectively, corresponding to an equivalent dose of 30 mg/L of PAC. Water permeates and feed water samples were analyzed with LC-OCD and FEEM to determine the removal efficiencies by these PACs. The results were compared with adsorption experiments performed by introducing 3 mg of PACs into 100 mL of feed water placed in 200 mL closed bottles and shaken (mixed) for 24 hours. The samples were then filtered with 0.45 µm filters to separate the PACs particles from the water.

The performance of the pre-coat layer alone was assessed with the results obtained from pre-coat of 0.45 µm filters. It can be argued that a 0.45 µm pore size is too big to retain organic fractions as shown by previous results presented in Figure 4.5. Also, it has been reported that fouling is a phenomenon associated with deposition of NOM fractions that have a similar size to the membrane pore (Kim et al., 2005).

It was observed that organic components removal was significantly increased when the membrane was pre-coated with PAC as compared to removal achieved by the membrane alone, in particular with novel PACs. The detailed results of removal of EfOM constituents by pre-coated PAC on AA0100 and 0.45 µm membranes, and adsorption are shown in Table 4.8, Figure 4.7 a and Figure 4.7 b. The concentrations of low molecular weight (LMW) acids were too low in feed water and permeate and hence it was not considered in the analysis.

Table 4.8: EfOM components removal with PACs pre-coats at 30 mg/L doses

	DOC (mg/L)	Biopolymers (mg/L)	Humic Substances (mg/L)	Building Blocks (mg/L)	Neutrals (mg/L)	UV254 (cm^{-1})	SUVA (L/mg-cm)
SASUPer + AAO100	2.69	0.13	1.34	0.52	0.68	0.06	2.01
SASUPer + 0.45um	3.38	0.170	1.59	0.64	0.98	0.08	2.24
SASuper+Adsorption	3.55	0.194	1.27	0.59	1.49	0.05	1.26
G60 + AAO100	2.57	0.114	1.29	0.45	0.72	0.06	2.31
G60 + 0.45um	3.50	0.171	1.73	0.62	0.98	0.08	2.43
G60+Adsorption	2.91	0.176	1.27	0.49	0.98	0.04	1.43
KCU6 + AAO100	1.90	0.025	0.94	0.41	0.53	0.03	1.60
KCU6 + 0.45um	2.30	0.057	1.09	0.49	0.67	0.04	1.70
KCU6+Adsorption	2.76	0.029	1.09	0.55	1.09	0.04	1.41
KCU8 + AAO100	2.35	0.072	1.10	0.48	0.69	0.04	1.65
KCU8 + 0.45um	2.26	0.107	1.07	0.46	0.62	0.04	1.75
KCU8+Adsorption	2.80	0.060	1.02	0.50	1.22	0.04	1.26
KCU12 + AAO100	2.32	0.098	1.10	0.48	0.65	0.04	1.72
KCU12+Adsorption	3.13	0.108	1.15	0.58	1.28	0.05	1.39
Feed for Pre-coating	5.663	0.316	2.353	0.965	1.92	0.116	
Feed for adsorption	4.532	0.218	2.125	0.793	1.322	0.121	



(a) **(b)**

Figure 4.7: Removal of (a) Biopolymers and (b) Humic substances from wastewater effluents with PACs pre-coated onto AAO100 membranes

Figure 4.7 (a) shows that the KCU 6 pre-coat combined with the ceramic MF membrane adsorbed most of the biopolymers from wastewater effluents to about 93 %. The use of 0.45 µm filters showed 85 % removal, which proves that almost all biopolymers were removed by the pre-coat layer rather than AAO100 ceramic membrane. Furthermore, this suggests that adsorption is the major removal mechanism of biopolymers. Besides, the results were much better than adsorption process could achieve (78 %) which supports the pre-coating approach. Also this correlate with earlier discussed results that showed significant reduction of membrane resistance increase achieved by KCU 6, which corresponds to the high removal of biopolymers shown by KCU 6 pre-coats. Other PACs showed less removal of biopolymers compared to KCU 6 (KCU 8 removed 78%, 69 % by KCU 12, 64 % by G60, and 58 % by SASuper).

Both KCU 6 and KCU 8 showed a difference of about 10 % when KCUs were pre-coated with AAO100 and 0.45 µm membranes. This indicates that the pre-coat layer removed most of the biopolymers and the AAO100 membrane removed only about 10 % of biopolymers. The difference between the two membranes was about 20 % in case of G60, which suggests that one third of the biopolymers were removed by AAO100 alone. The extents of biopolymers removal by PACs pre-coat have a direct relationship with the levels of membranes resistances developed. High removals of biopolymers reflect low increases of membrane resistances.

Figure 4.7 (b) illustrates humic substances (HS) removal by pre-coated AA0100 and 0.45 µm membranes, later compared with adsorption experiments at a dose of 30 mg/L of PACs. Data showed that KCU 6 removed about 60 % of HS while KCU 8, KCU 12, G 60 and SA Super removed 55 %, 53 %, 46 % and 43 %, respectively. These were not very significant changes, but again KCU 6 performed slightly well in terms of HS removal. It has been demonstrated before that 0.45 µm filters and AAO100 membranes have negligible removal of humic substances as described in section 4.4.3.1. Therefore, this proves that adsorption of contaminants by PAC pre-coats is the major removal mechanism of HS. Figure 4.8 simplifies the results discussed above which confirms KCU 6 capabilities in terms of high removal of high molecular weight NOM.

This superior performance of KCU6 in biopolymers removal is a breakthrough in PAC pretreatment technology since it has been reported in recent studies that PAC removed only 19 % of biopolymers that led to insignificant improvement of membrane filterability (Filloux et al., 2012). But also the pre-coat approach improved the removal of high molecular weight NOM compared to common addition method of PAC, represented here by adsorption experiments.

In general, it can be concluded that KCU 6 attained the highest performance in adsorbing high MW organic matter. Also, biopolymers are related to the increase of membrane resistance and play a role in both reversible and irreversible fouling (Henderson et al., 2011). Also high removal of biopolymers with KCU 6 pre-coats correlated well with the increase of membrane resistances as shown previously.

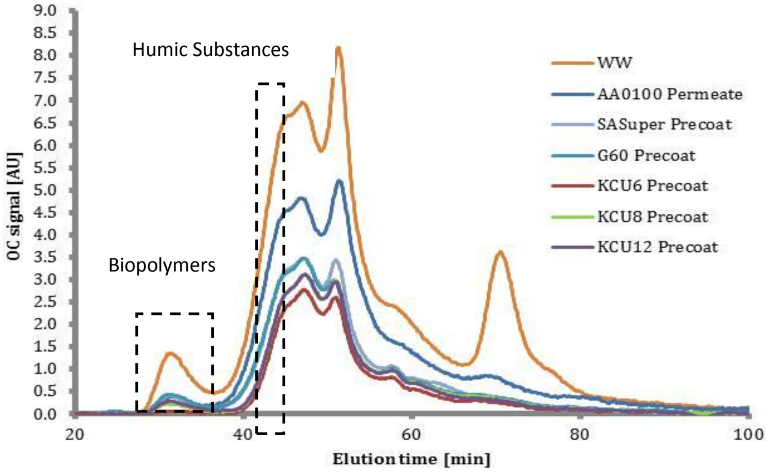


Figure 4.8: LC-OCD Chromatograms of AA0100 pre-coats

To reinforce the results obtained from LC-OCD, further analysis of samples were done by using Fluorescence Excitation Emission Matrix (FEEM). FEEM provides insight into removal of protein-like and humic-like organic matter through the differences in the peaks of samples before and after filtrations. The FEEM images of samples and their corresponding peaks are shown in Figure 4.9 below:

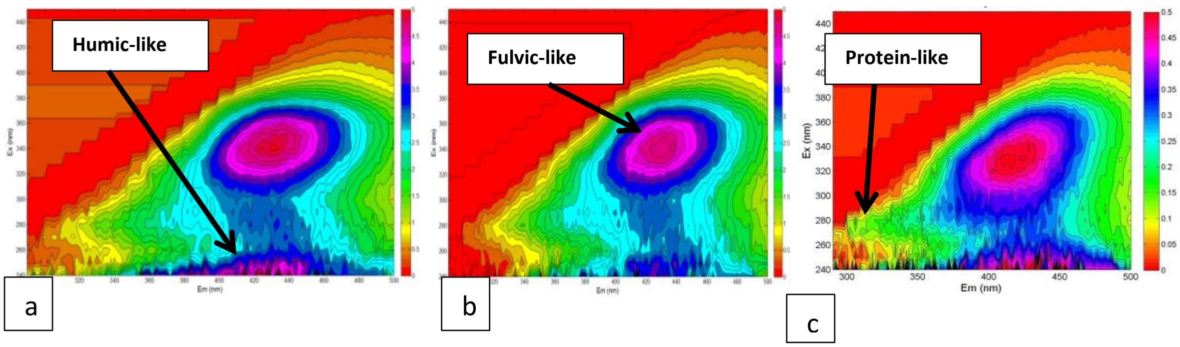


Figure 4.9: FEEM spectra of (a) Feed water, (b) AAO100 Permeate and (c) Permeate of KCU 6 at 30 mg/L pre-coat dose

The fluorescence Excitation Emission Matrix (FEEM) data analysis of feed and permeate waters samples are presented in Table 4.9 which shows three peaks from the MatLab plots (shown in **Error! Reference source not found.**9). Peak (1) represents a humic-like rimary peak (fulvic-acid peak), Peak (2) is corresponds to humic-like secondary peak (humic-acid) and Peak (3) is represents protein-like peak as described previous in Table 4.4.

Table 4.9: FEEM Peak intensities analysis of various PAC types and experiment methods

Sample	**Ex/Em (1)**	**Peak 1 (% Reduction)**	**Ex./Em (2)**	**Peak 2 (% Reduction)**	**Ex/Em (3)**	**Peak 3 (% Reduction)**
Feed water	340/430	-	240/424	-	270/316	-
AA0100 permeate	340/430	0%	240/424	0%	280/326	46.2%
0.45µm permeate	340/430	0%	240/424	0%	280/312	0%
SA Super AA0100	330/418	68.8%	240/422	72.2%	280/332	70.7%

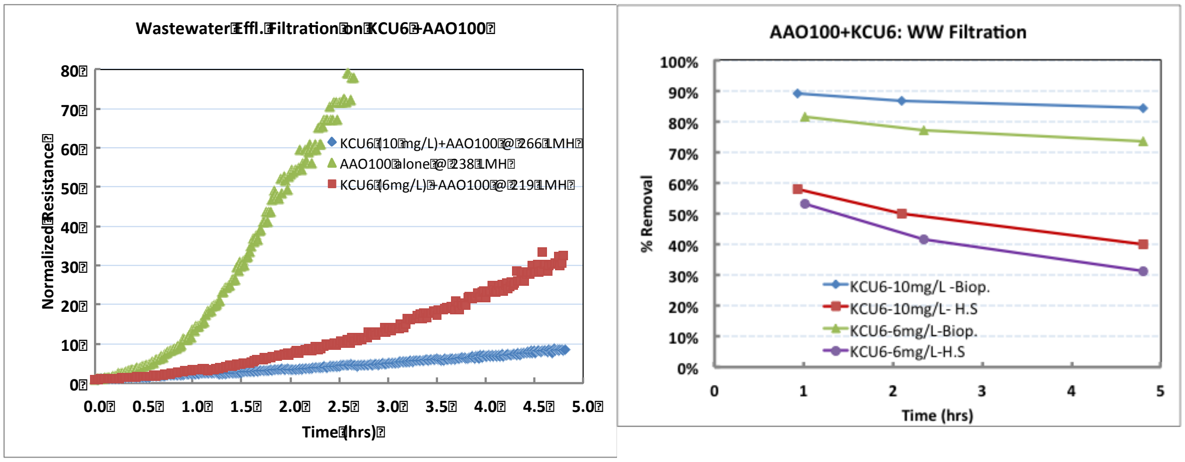
SA Super 0.45μm	330/418	64.1%	240/424	59.1%	280/336	48.6%
G 60 AA0100	340/430	62.5%	240/426	58.9%	280/322	66.2%
G 60 0.45μm	340/426	56.6%	240/424	52.2%	280/324	61.7%
KCU 6 AA0100	330/416	85.7%	240/424	81.4%	330/280	81.6%
KCU 6 0.45μm	330/424	81.7%	240/424	75.0%	314/280	80.2%
KCU 8 AA0100	330/414	81.3%	240/424	80.9%	280/334	75.1%
KCU 8 0.45μm	330/414	80.9%	240/426	70.5%	280/334	74.5%
KCU 12 AA0100	330/416	80.3%	240/424	61.8%	280/324	52.0%
KCU 12 0.45μm	330/416/	72.7%	240/414	54.0%	280/332	61.4%

The results in Table 4.9 show that the AA0100 pre-coat method was effective in reducing peak intensities in all peaks (1), (2) and (3) which corresponds to humic substances and proteins removal. The peak of fulvic-like fluorescence reduction by the PAC pre-coating was about 60 – 85 %. PAC pre-coated on the AA0100 membrane achieved about 50 - 80 % reduction of the peak of protein-like substances. Reduction of 60 – 80 % of the peak of secondary humic-like fluorescence was achieved. However, the membrane alone was able to remove proteins like peak to 46 %, which is a part of biopolymers. This finding confirms previous results that the AA0100 membrane could remove portions of biopolymers substances from the feed water.

The PAC pre-coats appear to yield similar performance for AA0100 membranes and 0.45 μm filters. The reduction of peak (1) was about 56 – 81 % while 48 - 80% removal of peak (3) and 52 - 75% of peak (2) was achieved. This data might also prove that the PAC layer coated on the membrane surface was able to adsorb humic-like and protein-like substances from the feed waters. In general, PAC pre-coating shows significant enhancement of targeted organic matter removal efficiency as compared to the membrane alone. In addition, the pre-coat method with extremely short contact time shows remarkable performance in EfOM constituent removal. In particular, KCU 6 successfully achieved the highest removal performance of other PACs used (> 80 % for all peaks).

4.5.6 Performance of KCU 6 at a low dose

The removal efficiency of KCU6 was assessed in depth to determine the lowest dose that can be applied. AAO100 membranes were pre-coated with equivalent doses of 10 mg/L and 6 mg/L respectively. Filtration using wastewater effluent from Jeddah was performed and operating pressure was careful adjusted to maintain average fluxes operations. The results are shown in the Figures 4.10 (a) and (b) below.



(a) (b)

Figure 4.10: Comparison of (a) total membrane resistances and (b) removal of biopolymers and humic substances at pre-coat doses of 6 and 10 mg/L of KCU 6.

Membrane resistances increased from 10 times to 30 times when the pre-coated dose of KCU 6 was reduced from 10 mg/L to 6 mg/L (Figure 4.10 a). These results imply that a dose of 10 mg/l of KCU 6 still offers a low increase of membrane resistance and may be considered as a low pre-coat dose for smooth operation of wastewater effluent filtration. Figure 4.10 (b) above showed that biopolymers removal decreased from 84 % to 73 % when the pre-coat dose was reduced from 10 mg/L to 6 mg/L. Humic substances removal also decreased from 40 % to 30 % following reduction of the pre-coat dose. In general KCU 6 can maintain high removal of biopolymers at a low dose of 10 mg/l. The high removal of biopolymers achieved correlated well with the low increase of membrane resistance, which indicates that the pre-coat layer eliminated most of biopolymers before reaching the membrane and hence fouling was significantly reduced. However a high dose of KCU 6 is required to achieve 100 % removal. This dose could be above 600 mg/l since adsorption and pre-coating layers of KCU 6 showed 99 % of biopolymers removal with adsorption dose of 600 mg/l and 97 % removal of biopolymers with a dose of 300 mg/l pre-coat (Table 4.10)

Table 4.10: Biopolymers removal with pre-coating and adsorption at different KCU 6 doses

Dose (mg/L)- Adsorption	% Biopolymers removal	Dose (mg/L)- Pre-coat+AAO100	% Biopolymers removal
600	99	300	97
300	97	150	96
150	96	100	96
75	91	60	94
30	70	40	93
		30	88

However, the increase of pre-coat dose of KCU 6 from 40 mg/l to 300 mg/l elevated the biopolymers removal to just 4 % extra, indicating that a low dose of 30 or 40 mg/l of KCU 6 is sufficient for pre-coating and still attaining high removal of biopolymers (Table 4.9).

4.5.6 Comparison between SPAC and KCU 6 with respect to removal mechanisms

A comparative study to understand the removal mechanisms of high molecular weight NOM with pre-coats of KCU 6 and SPAC was carried out. A dose of 30 mg/l of pre-coat was adopted to be pre-coated on the AAO100 membrane prior to wastewater effluent filtration. To observe the difference, normal PAC (SASuper) was also used and filtration without pre-coat was performed as a reference experiment. The average flux was maintained by adjusting the pressure and the increase of trans-membrane pressure was monitored. Samples of permeate waters at 25 milliliter volume were collected periodically in the first 100 mL of filtrate and at a volume of 50 mL after first 100 ml collection. Samples were analyzed with LC-OCD and the UV$_{254}$ was measured by using UV spectrophotometer. The summary of the data is presented in Table 4.11 below. The concentration of LMW acids in wastewater was too low so it was neglected.

Table 4.11: DOC components characterized with LC-OCD and UV spectrophotometer.

	DOC (mg/L)	**Biop. (mg/L)**	**Humic Subst. (mg/L)**	**Build. Blocks (mg/L)**	**Neutrals (mg/L)**	**UV254 (cm-1)**	**Vol. (mL)**	**SUVA (L-mg-cm)**	**Specific volume (L/m2)**
SPAC-25	1.731	0.003	0.459	0.316	0.847	0.011	25	0.64	79.6
SPAC-50	1.55	0.018	0.694	0.35	0.474	0.02	50	1.29	159.2
SPAC-75	2.41	0.022	0.845	0.556	0.884	0.028	75	1.16	238.7
SPAC-100	2.862	0.037	1.02	0.694	0.997	0.036	100	1.26	318.3
SPAC-150	2.955	0.034	1.257	0.656	0.946	0.049	150	1.66	477.5
SPAC-200	3.375	0.05	1.48	0.696	1.082	0.065	200	1.93	636.6
KCU6-25	0.767	0.003	0.281	0.148	0.335	0.005	25	0.65	79.6
KCU6-50	1.455	0.017	0.403	0.312	0.722	0.009	50	0.62	159.2
KCU6-75	1.2	0.019	0.574	0.295	0.301	0.012	75	1.00	238.7
KCU6-100	1.311	0.012	0.522	0.237	0.489	0.014	100	1.07	318.3
KCU6-150	1.327	0.01	0.592	0.329	0.396	0.017	150	1.28	477.5
KCU6-200	1.484	0.019	0.666	0.392	0.407	0.02	200	1.35	636.6
SASuper-25	0.686	0.024	0.317	0.135	0.2	0.009	25	1.31	79.6
SASuper-50	1.244	0.045	0.548	0.238	0.402	0.017	50	1.37	159.2
SASuper-75	1.419	0.051	0.669	0.316	0.369	0.023	75	1.62	238.7
SASuper-100	1.634	0.051	0.78	0.376	0.4	0.027	100	1.65	318.3
SASuper-150	2.067	0.077	0.942	0.468	0.548	0.036	150	1.74	477.5
SASuper-200	2.448	0.091	1.109	0.551	0.659	0.047	200	1.92	636.6
AAO100-25	3.728	0.116	1.44	0.808	1.316	0.099	25	2.66	79.6
AAO100-50	3.737	0.122	1.521	0.798	1.269	0.102	50	2.73	159.2
AAO100-75	3.704	0.105	1.544	0.773	1.262	0.101	75	2.73	238.7
AAO100-100	3.703	0.108	1.516	0.784	1.257	0.101	100	2.73	318.3
AAO100-150	3.712	0.102	1.537	0.794	1.252	0.1	150	2.69	477.5
AAO100-200	3.693	0.086	1.527	0.8	1.231	0.101	200	2.73	636.6
Feed WW	3.831	0.174	1.643	0.753	1.231	0.109		2.83	

4.5.6.1 DOC Removal

The reference experiment showed that the DOC removal was below 5 %, which means that the membrane alone is not capable of removing EfOM, notable low molecular weight EfOM. KCU 6 at a pre-coat dose of 30 mg/l showed superior quality by maintaining 60 % removal of DOC, which is quite good when compared with commercial PACs. SASuper and SPAC showed lower removal of DOC (below 50 % and 40 %, respectively), which was inversely proportion to the specific filtered volume (Figure 4.11). Experience showed that to enhance the DOC removal to a higher level requires a multi-barrier system (involves more than one pre-treatment) combined with much tighter membranes than microfiltration. A recent study on TOC removal by a UF system associated with coagulation and PAC pre-treatments at a dose of 120 mg/l and 40 mg/l, respectively, achieved 73 % DOC removal (Legge, 2012). Therefore a single pretreatment system of KCU 6 pre-coat and ceramic MF membrane appears to compete well with multi-barrier systems that are costly and expensive to operate.

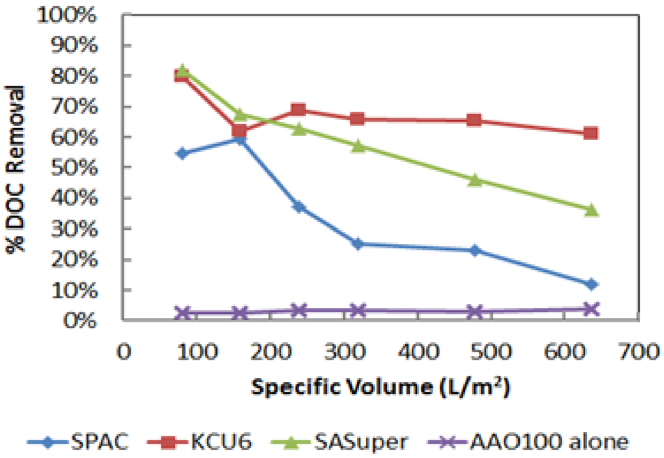
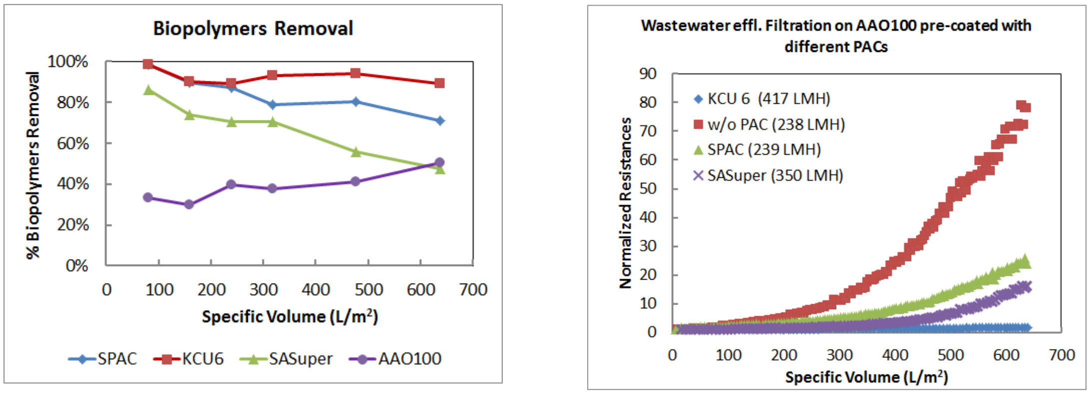


Figure 4.11: DOC removal with 30 mg/l of PACs pre-coated on AAO100

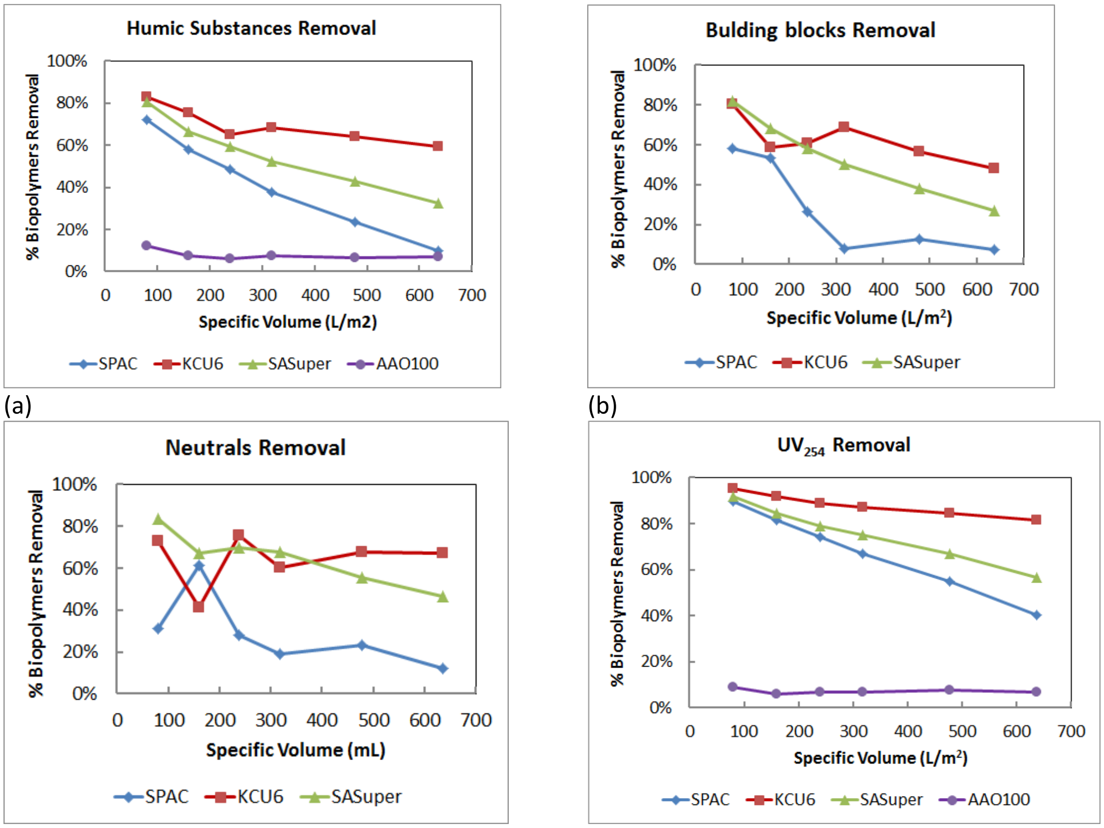
4.5.6.2 NOM components removal

KCU 6 at a dose of 30 mg/l maintained high removal of biopolymers > 90 % followed by SPAC (> 80 %) while SASuper removed biopolymers to about 60 % (Figure 4.20). Biopolymers are the most important components of NOM that influence fouling in low-pressure membranes if it is not well treated. Significant removal achieved with PAC pre-coating layers means less fouling of the membranes. With the membrane alone, biopolymers retention was about 45 % on average, having a significant impact on membrane fouling (Figure 4.12 (a) and 4.12 (b)). Other NOM components (humic substances, building blocks and neutrals) were barely removed by the membrane alone due to their smaller sizes compared to membrane pores (Figure 4.13 (a), (b) and (c)). Also UV absorbance was not significantly reduced by the membrane alone (Figure 4.13 d).



(a) (b)

Figure 4.12: AAO100 membrane pre-coated with SPAC, SASuper, and KCU 6 at a dose of 30 mg/L and membrane alone (a) Biopolymers removal and (b) Increase of membrane resistances



(a) (b) (c) (d)

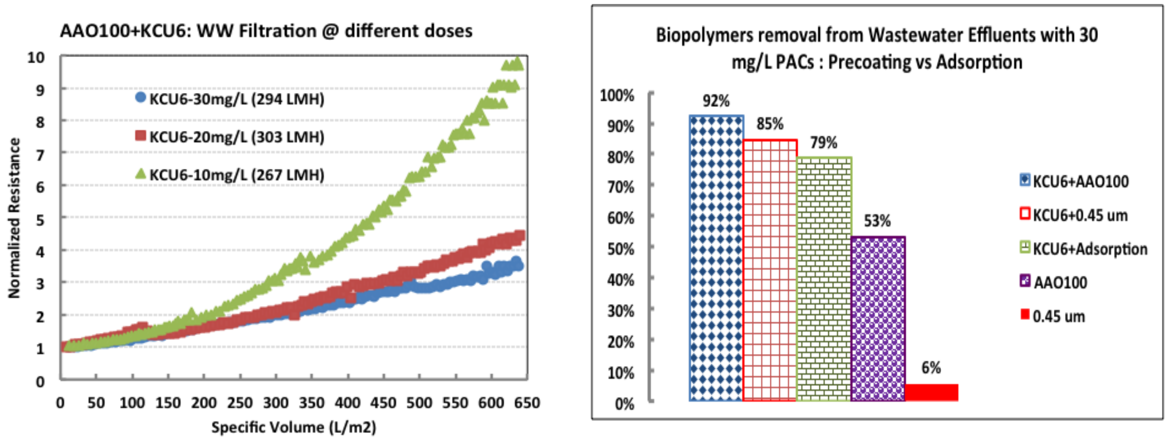
Figure 4.13: AAO100 membrane pre-coated with SPAC, SASuper, and KCU 6 at a dose of 30 mg/L and membrane alone (a) Humic substances removal, (b) Building block removal, (c) Neutrals removal and (d) UV254 removal

High average flux operation was observed for KCU 6 (417 LMH) while an average flux of 239 LMH was observed with SPAC pre-coats and an average flux of 238 LMH with the membrane alone at an initial pressure of 0.1 bars in all cases. This indicated that the SPAC pre-coat has negligible resistance but KCU 6 promoted the increase filterability to high flux operation. It can be argued that physical removal of biopolymers is taking place by the cake layer of the SPAC pre-coat due to a tight coat layer of average size of 3 µm. Physical removal of biopolymers influenced the increase of a total membrane resistance without fouling the membrane.

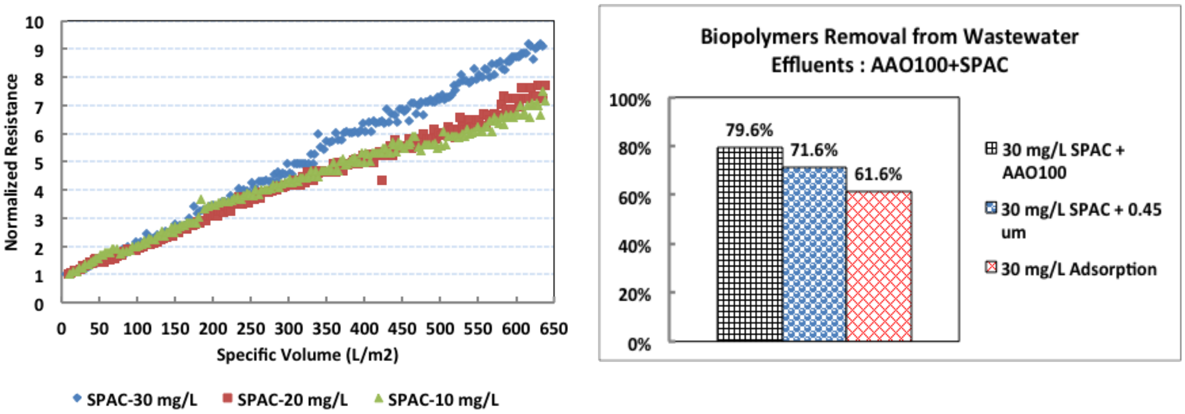
In the case of KCU 6, the main removal mechanism of biopolymers was adsorption, which was influenced by the unique characteristic of KCU 6, which has larger pores up to

33 nm. This wide range distribution of larger pores promoted biopolymers adsorption to a large extent by the pre-coat layer of KCU 6, resulting in promotion of high flux operation with a low increase of total membrane resistance (Figure 4.12 b). In both cases, where the KCU 6 pre-coat favored adsorption of biopolymers and the SPAC pre-coat favored more physical removal of biopolymers, the ceramic membrane was well protected because of the functional pre-coat barriers.

Novel PAC (KCU 6) and commercial PAC (SASuper) retained about 60 % of low molecular weight neutrals. SPAC retained an average of 20 % of neutrals, which however decreased with filtration time. Low removal of neutrals by SPAC might be caused by a shielding effect of high molecular weight EfOM that covers the SPAC cake layer, influencing by physical removal of biopolymers. This consolidated cake layer decreases the access to adsorption of low molecular weight EfOM. Removal of low molecular weight EfOM is also considered to be important in wastewater reclamation. Recent research claimed that RO membrane were mostly fouled by low molecular weight NOM (Bartels, 2012).



(a) (b)



(c) (d)

Figure 4.14: (a) Increases of membranes resistance of AAO100 membrane pre-coated with 30, 20 and 10 mg/L KCU 6, (b) Biopolymers removal with KCU 6 at 30 mg/l, (c) Increases of membranes resistance of AAO100 membrane pre-coated with 30, 20 and 10 mg/L SPAC @ 200 LMH and (d) Biopolymers removal with SPAC at 30 mg/L.

The difference between KCU 6 and SPAC in terms of biopolymers removal, in relation to increase of membrane resistance, is demonstrated in Figures 4.14 (a), (b), (c) and (d). KCU 6 showed an increase of the total membrane resistance when pre-coat dose was reduced from 30 mg/l to 10 mg/l (Figure 4.14 (a)). In the case of SPAC, the situation was vice versa, where when the dose was reduced; the increase of membrane resistance was also reduced (Figure 4.14 (c)). This means that with a high dose, more biopolymers are physical eliminated which leads to an increase of the cake resistance that eventually contributes to the total increase of membrane resistance.

4.6 Conclusions and Recommendations

4.6.1 Conclusions

This bench scale studies investigated five different types of PAC as the material to coat the AA0100 ceramic microfiltration membrane as well as a 0.45 µm polymeric membranes. Also the best-performing novel PAC was compared with submicron powdered activated carbon (SPAC). The following conclusions can be drawn

- ❑ KCU 6 was found to be the most effective carbon in removing biopolymers (> 90%) and humic substances (≈ 60 %) while suppressing increases of membrane resistance to 98% at a dose of 30 mg/l.
- ❑ The AAO100 ceramic membrane alone removed a significant portion of biopolymers (≈ 50%) but caused an exponential increase of membrane resistance due to pore blocking (fouling).
- ❑ Comparison of EfOM removal results of AA0100 and 0.45 µm pre-coats supported the premise that the major removal mechanism of EfOM is adsorption.
- ❑ Removal of biopolymers in adsorption experiments using AAO100 ceramic powder was insignificant and BET surface area of ceramic MF powder was low. This suggests that size exclusion was the main mechanism for biopolymers removal when the membrane was used alone.
- ❑ Among the different fractions of EfOM removed, the biopolymer fraction was well correlated with the improved membrane performance. High removal of biopolymers related to low increase of membrane resistance.
- ❑ Moreover, this study also revealed that PAC did not contribute to any significant fouling.
- ❑ These results correlate well with the previous results on BET analysis of PACs which showed that KCU6 exhibits a wider distribution of large pore sizes (max. 33 nm) and high BET surface area (1280 m^2/g) compared to other PACs, attributes for good biopolymers removal. Also, adsorption experiments showed that KCU 6 performed better in removal of high molecular weight NOM.

- ☐ High removal of biopolymers was observed with both KCU 6 and SPAC. Studies of resistance increases between the two PACs affirmed that the KCU 6 removal mechanism was based on adsorption while the SPAC exhibits both adsorption and physical removal mechanisms.

4.6.2 Recommendations

It is recommended to scale up this study from bench scale to pilot scale. Further grounding of KCU 6 into fine particles, which would aim to combine physical and adsorption mechanisms, is also recommended for future experiments.

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CHAPTER 5

5.0 Trace Organic Componds (TOrCs) Removal with Ceramic MF membranes combined with submicron powdered activated carbon (SPAC) or novel PAC

Chapter 5 based on

Ceramic Microfiltration Membrane combined with submicron-powdered carbon (SPAC) for removal of trace organic compounds (TOrCs) from wastewater effluents

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To be submitted to relevant journal

Novel powdered activated carbon PAC pre-coated on ceramic microfiltration membrane for removal of trace organic compounds (TOrCs) from wastewater effluents

J. Z. Hamad*, M. Alidina*, Rubal Dua, Peng Wang, G. L. Amy* and M. D. Kennedy

Paper expected to be published later.

5.1 Introduction

Production of potable water for domestic and other uses is posing a major challenge due to increasing demand associated with population growth (Pisarenko et al., 2012). Limited fresh water sources available are vulnerable to climate change, thus taking the problem to another dimension. In order to meet future water demands, supplementary water sources like wastewater effluent are currently being considered for water reuse. Wastewater effluents are rich in nutrients and trace organic compounds. Trace organic compounds (TOrCs) composed of pharmaceutically active compounds (PhACs), endocrine disrupting compounds (EDCs) and personal care products (PCPs) are found in wastewater (Hyland et al., 2012). Also intrusion of TOrCs in surface water may take place during wastewater effluent discharge into sources that are dedicated for drinking water (Grünheid et al., 2005).

TOrCs are known to cause negative health impacts so proper treatment of wastewater is required (Hajibabania et al., 2011, Gerrity et al., 2012). Activated carbon has been widely used in the form of granular activated carbon (GAC) or powdered activated carbon (PAC) to remove or reduce the TOrCs to accepted regulation standards (Qi et al., 2007). A combination of PAC and ultrafiltration membranes was found to be effective in the removal of trace organic compounds (Campos et al., 1998a). TOrCs can be removed through the adsorption process which is determined by PAC pores.

The pore diameters of activated carbon are typically range from 0.5 nm to 500 nm. Pores greater than 50 nm are classified as macropores and pores less than 2 nm are termed as micropore and anything that is between these two ranges are called mesopores (Metcalf and Eddy, 2006, Chen, 2005). A good adsorbent must have a combination of all pore ranges from macro to micropores. Powdered activated carbon (PAC) with a relatively large fraction of micropores and mesopores was observed to be more resistant against pore blockage effects (Chen, 2005) and hence are good for adsorption.

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase. The adsorbing solid is referred to as adsorbent and the substance to be adsorbed from liquid or gas phase as an adsorbate (Qasim et al., 2004). The process of adsorption is influenced by two characteristic properties for the given solvent-solute system. These characteristics are i) the hydrophobic character of the solute relative to the particular solvent and ii) the affinity of the solute for the solid. These two characteristics will affect the removal mechanisms of TOrCs.

The filtration of wastewater containing natural organic matter (NOM) and TOrCs through GAC filters is subjected to two main constraints: preloading and competitive adsorption. NOM moves faster through the GAC column and hence pre-adsorption of the NOM takes place in the lower part of the filter bed. This type of adsorption is termed as NOM preloading (Orlandini, 1999). Competitive adsorption is a process in which two or more adsorbates compete for the available adsorption sites. Competitive adsorption between NOM and synthetic organic compounds (SOCs) may reduce the activated carbon adsorption capacity for SOCs (Upadhyaya, 1995). Another study found that the presence of NOM significantly reduced the adsorption of synthetic organic chemicals (Zhang et al., 2011). The presence of NOM in surface water is more than 100 times higher in concentration compared to SOCs (Orlandini, 1999). It has been also observed that low molecular weight NOM highly compete with 2-methylisoborneol (MIB) (Newcombe et al., 2002b). Therefore under competition adsorption, TOrCs are likely to be affected to a greater degree than NOM; NOM adsorption rates are much slower than SOCs adsorption rates.

In this research, powdered activated carbon used as a pre-coat on ceramic membrane was employed. Commercially available carbon ground to fine particles (submicron powdered activated carbon - SPAC) with average particle size of 3 µm and a novel PAC (KCU 6) that initially showed potential ability to remove biopolymers was employed. The average particle size of KCU 6 was 38 µm. In the first part of the study, surface water derived from Delft canal water of Netherlands was used. Canal water was spiked with 2 µg/l of atrazine prior to filtration on pre-coated ceramic membrane. The performance of SPAC pre-coat was compared with normal PAC (N-PAC) in both bench and pilot scale experiments. Performances of SPAC and NPAC with applied doses of (40 and 20 mg/L) of SPAC and 20 mg/l NPAC were assessed.

In the second phase of the study, detailed analysis of TOrCs removal was performed using wastewater effluents spiked with 29 different trace organic compounds. SPAC and KCU6 were compared with and without NOM competition in a bench scale experiments. Milli Q water was spiked with TOrCs was used to determine the removal of TOrCs without competition of NOM. Pre-coat doses of 10 mg/L were used in both competitive and uncompetitive modes while a dose of 30 mg/l was used in competitive mode only.

5.2 Background: Removal of TOrCs

As the world is making progress in development, the trend of water quality is also deteriorating due to increasing number of emerging organic micropollutants from industries, agriculture, domestic products and wastewater. Treatment plants for wastewater and drinking water are forced to introduce robust barriers to overcome the problem of organic micropollutants. The main concern is the adverse effects on health and the environment caused by these contaminants. TOrCs are exchanged between water bodies by means of pharmaceutical pathways (Figure 5.1). Wastewater is also susceptible to the presence of organic micropollutants and hence both drinking water and waste water plants strive for more robust barriers against micropollutants.

Conventional treatment processes have proven to be not effective in the removal of organic micropollutants. Therefore advanced treatment processes like membrane filtration, adsorption with activated carbon and oxidative treatment should be considered (Kunst and Kosutic, 2008). Treatment of TOrCs is recommended in wastewater to avoid the release of contaminants in receiving waters (e.g. rivers) dedicated for drinking water production (Bolong et al., 2009b). Current available technologies for TOrCs treatments include bank filtration, advanced oxidation processes, activated carbon adsorption, membrane filtration, ion exchange and membrane bioreactors (MBR).

Nanofiltration and reverse osmosis membranes have the potential ability to remove organic micropollutants. However, high-pressure membranes are still expensive processes due to high-energy consumption incurred during operation. Another option is membrane bioreactors that have common use in wastewater treatment. Hybrid systems are known to be very useful in dealing with micropollutants. Advanced oxidation processes and ion exchange play an important role in removal of the organic micropollutants and therefore depending on the targeted contaminants these processes have proven to be robust against most of the organic micropollutants. Activated carbon in various forms (granular and powder) has proven to be very helpful in removal of most of the micropollutants. Bank filtration used as a natural filtration method is known to perform effectively in terms of organic micropollutants removal. It can be used prior to activated carbon to reduce the NOM loading. Both bank filtration and activated carbon are considered as affordable technologies for TOrCs removal.

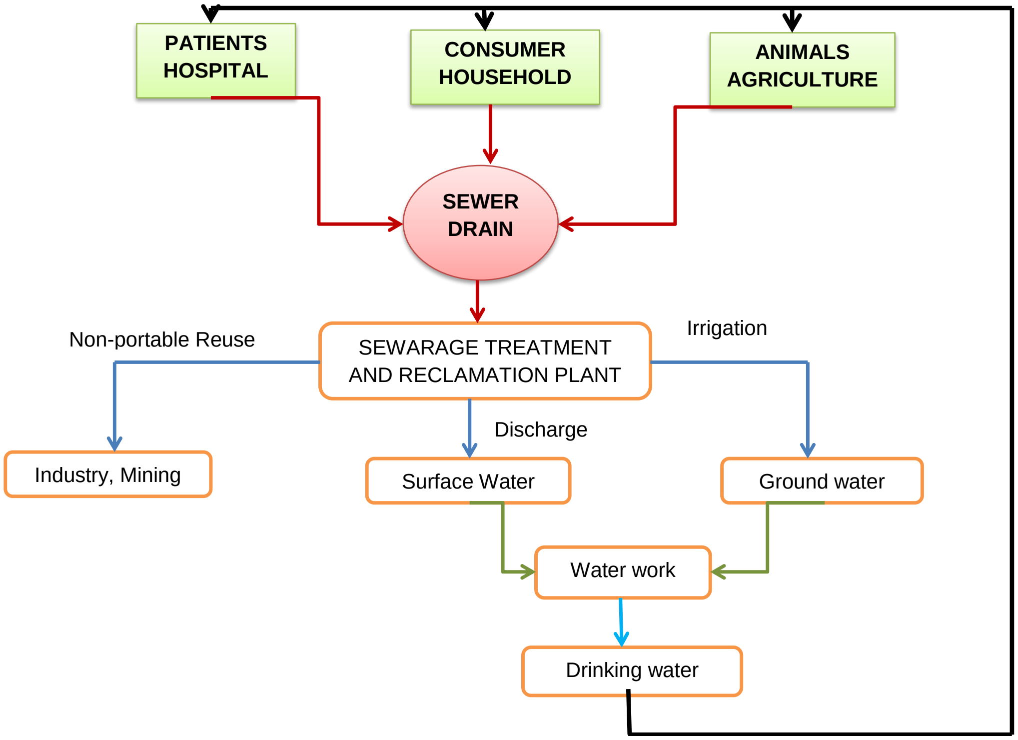


Figure 5.1: Pharmaceuticals pathway in water reuse
(**Source**: W. A. Nugroho et. al. 2010)

5.2.1 Removal of TOrCs by Bank filtration and Soil treatment

Bank filtration is a natural filtration method that purifies water by passing through the banks of a river or lake. Water from a river or lake is then extracted by wells located some distance away from the water body. Many organic micropollutants present in Rhine River water are successful eliminated during River bank Filtration (RBF) whereby the main mechanism for removal is microbial biodegradation (Sacher and Brauch, 2002). Biodegradation of organic constituents is facilitated by the presence of microorganisms.

Formation of a biofilm and attachment of constituents allow retention of biomass (RITTMANN, 1985).

Bank filtration is an efficient approach for the reduction of most organic micropollutants. However, removal of pesticides in bank filtration depends on properties of the contaminant in particular. For example atrazine removal with river bank filtration from Rhine River was found to be only 10 % compared with 100 % removal of lindane (Schmidt et al., 2003). Another study done by (Heberer et al., 2001) revealed that several compounds like carbamazepine, clofibricacid, primidone, propyphenazone, bentazone, o-p' DDA, TCIPP and TCEP were persistent during river bank filtration. Therefore, bank filtration does not guarantee the complete removal of all potential organic micropollutants present in the water but remarkable removal can be achieved for most organic micropollutants.

Natural systems like soil filtration under aerobic conditions improved TOrCs removal and the presence of NOM facilitates degradation of some of these TOrCs (Rauch-Williams et al., 2010). Soil treatment alone achieved > 80 % removal of acetaminophen, atenolol and caffeine (Teerlink et al., 2012). But primidone, TCEP, atrazine and carbamazepine were poorly removed to < 20 %. Moderate removal between 20 – 80 % was observed for DEET, oxybenzone, sulfamethoxazole, TCPP and trimethoprim.

5.2.2 Removal of TOrCs by Adsorption with Activated carbon

Two forms of activated carbon are available, Granular Activated Carbon (GAC) and Powdered Activated Carbon (PAC). The particle diameter < 0.15 mm is classified as PAC and above that is classified as GAC (Karanfil., 2006). GAC is normally used in a packed filtration column and PAC is used in the form of slurry. PAC is further classified into two forms Normal Powdered Activated Carbon (NPAC) and Submicron Activated Carbon (SPAC) that have very fine particles.

Activated carbon has been widely used in drinking water for removal of synthetic organic compounds, reduction of natural organic matter (NOM) and improving the taste and odour of drinking water (Karanfil., 2006). It is the cheapest adsorbent applied in drinking water treatment so far (Rossner and Knappe, 2008). The mechanism used for removal is adsorption whereby micropollutants are adsorbed onto the solid phase of activated carbon. However, adsorption of synthetic organic chemicals (SOCs) faces competition in the presence of NOM (Karanfil., 2006). High molecular weight NOM causes pore blocking in membranes while low molecular weight NOM competes with trace organic compound during adsorption (Heberer et al., 2001).

The study done by (Heijman and Hopman, 1999) described that the performance of GAC in the removal of micropollutants depends on the properties of natural organic matter (NOM) and not only on the properties of the micropollutants. The combination of activated carbon with conventional treatment achieved 90 % removal of 44 studied pesticides (Ormand et al., 2008). Therefore GAC play a major role in removal of most of the organic micropollutants in water.

In order to increase the kinetics and reduce the contact time, powdered activated carbon (PAC) is applied in treatment of water to remove micro pollutants like pesticides. SPAC and NPAC are usually used in the form of slurry. The big disadvantage however is that PAC cannot be regenerated like GAC. However the performance of PAC in removal of organic micropollutants like pesticides is very significant. The most common model pesticide is atrazine, which has a maximum contaminant level of 3µg/l according to

USEPA. It is known to be a persistent organic micropollutant (Lua et al., 2009, Plakas and Karabelas, 2009).

Past research on pesticides removal by NPAC prior to low pressure membrane filtration found that 5 mg/l of NPAC was able to reduce atrazine from 10 µg/L to 3 µg/L, which is 70 % removal (Crozes and Seacord, 2001). The research done by (Hamad et al., 2008) found that a highly concentrated DOC (18 mg/l) surface water spiked with high dose of atrazine (100 µg/l), achieved an average removal of 90 % of atrazine using 30 mg/l SPAC pre-coated on MF PVDF membrane. The contact time was less than 1 second. Therefore, with the pre-coat approach, the contact time was reduced significantly and efficient removal of micropollutants was maintained.

5.2.3 Biological Activated Carbon (BAC) Filtration

Biological treatment of drinking water has gained popularity for the removal of a variety of compounds due to its low cost and reduced health and taste impacts (Rogalla et al., 1990). Biological Activated Carbon (BAC) is created when a GAC column is used to filter raw water for a long period (more than 3 months) and forms a biological layer (film) in which microbes consume biodegradable dissolved organic carbon (BDOC) as food. These microbes are attached to the surface and in large pores so they block the pathway of micro pollutants and enhance their removal biologically. The use of ozone can improve biodegradation by transforming DOC to BDOC.

The combination of ozonation and BAC filtration was found to be very effective in removal of phenol (10 mg/l) that was used as a model for organic micropollutants. The extent of removal reached 99 % when an ozone dose of 0.9 mg O_3/mg TOC was applied at a contact time of 5 minutes (Sobecka et al., 2005b). The research done by (Orlandini,

1999) indicates that atrazine removal was significantly improved with GAC filters (adsorption columns) that received ozonated water compared with non-ozonated. It was stated that the reduced competitive adsorption and pre-loading of ozonated NOM were the reasons for such improvement. Nugroho (Nugroho et al., 2010) investigated the use of ozone prior to BAC. This hybrid system was found to be able to eliminate 14 selected pharmaceutical compounds below the detection limits. The study also confirms that an increase of Empty Bed Contact time (EBCT) increased the contaminants removal.

However, when GAC changed to BAC, the removal of trihalomethane (THMs) deteriorated and became poorly removed while other disinfection by-products like haloacetic acids (HAA_5) were well removed. Kim and Kang (Kim and Kang, 2008) found that the removal efficiency of HAA_5 increased to more than 99 % after six months of granular activated carbon filter-adsorber (GAC FA) operation and commented that biodegradation was the main mechanism for such achievement. In contrast, the removal of THMs decline to less than 10 %.

5.2.4 Removal of TOrCs by Membranes

Membranes are classified into two main types, low-pressure membranes (microfiltration (MF) and ultrafiltration (UF)) and high-pressure membranes (nanofiltration (NF) and reverse osmosis (RO)). Low pressure membranes have bigger pore sizes than high pressure membranes and therefore they cannot remove the organic micropollutants without pretreatments (Seo et al., 1997). The use of activated carbon and membrane technology has proven to be effective in the removal of micropollutant (Bolong et al., 2009b). Hybrid systems of MF and UF are also employed to enhance organic micro pollutants removal. Jia and co-workers (Jia et al., 2009) studied the performance of a hybrid system of PAC in a submerged microfiltration membrane in two dosing modes, continuous PAC dosing and mixing batch reactor. This study led to a model that describes the performance of two operational modes in terms of removal of trace organic compounds. However, studies showed that high-pressure membranes (NF/RO) and membrane bioreactors (MBR) are the most effective methods to eliminate trace organic compounds.

5.2.4.1 Removal of TOrCs by Reverse osmosis (RO)/Nanofiltration (NF)

Membrane processes like reverse osmosis (RO) and nanofiltration (NF) are considered as a viable options for the removal of low molecular weight organic compounds like pesticides (Plakas and Karabelas, 2009). Feed water is forced through a membrane by high pressure exerted on the feed water membrane side. Some water is passed (permeate) and some is retained (concentrate). Removal is due to a size exclusion mechanism (physical removal) as the pore size of nano-filtration is approximately 0.5 – 2 nm while the RO membrane has pore sizes ranging between 0.2–1 nm (Kunst and Kosutic, 2008).

Polar micropollutants are more difficult to be removed from water but these contaminants can be successful removed by NF and RO (Arne Verliafde et al., 2007). Rejection of organic micropollutants by NF membranes depends on both solute and membrane properties like size, polarity and charge for solute properties and pore size, charge and hydrophobicity in the case of membrane properties (Bellona and Drewes, 2005). Nanofiltration can reject more than 90 % of organic micropollutants, mainly larger size micro pollutants but also smaller hydrophilic or charged organic compounds (Arne Verliafde et al., 2007). Plakas and Karabelas (2009) reported that tannic acid (TA) exhibits the greatest effect on triazine (Atrazine and Prometryn) retention among four humic substances (Humic acid HA, Fulvic acid FA, NOM, TA) used. The dose applied for humic substances was 10 mg/l for all cases. Almost complete removal of the triazine (95 - 100 %) for all three applied membranes (NF90, NF270 and XLE) was attained. The study also found that removal of triazine improved in the presence of calcium which tends to enhance the interaction between humic substances (HS) and triazine.

Other organic contaminants like polycyclic aromatic hydrocarbons (PAHs) are highly removed by NF membranes. More polar, less volatile and less hydrophobic compounds show less retention. The mechanism of retention of micro pollutants by NF membrane is due to both hydrophobic adsorption and size exclusion (Y. Yoon et al., 2006). However, the big challenge on the use of NF and RO membrane is on how to dispose of the concentrate. It is advised to determine disposal options before operation since unregulated discharge of the concentrate may impair the quality of surface water or ground water (M.M. Nederlof et al., 2005).

5.2.4.2 Removal of TOrCs by Membrane bioreactor (MBR)

Membrane bioreactors (MBR) have become an option to gradually replace the conventional activated sludge (CAS) process. MBR uses a membrane, either submerged or externally mounted to a suspended growth bioreactor, to separate biomass and particles from purified water. The main advantages of an MBR are smaller footprint and superior effluent quality (H. De Wever et al., 2007). MBR technology is considered the most promising development in microbiological wastewater treatment.

MBR treatment appears to enhance removal of micro pollutants with intermediate biodegradability, is less sensitive to operational variables, and shows higher robustness than conventional systems. Although, according to De Weveret and co-workers (2007), some micro pollutants are still persistent to MBR treatment. On the other hand, several studies clearly outlined the strong potential of MBR technology in reducing ecological risks associated with PhACs, as well as other polar micropollutants.

Recent research done by Yiping and co-workers revealed that anaerobic MBR technology was very effective in removal of organochlorines pesticides (94 %) but less effective for polyaromatic hydrocarbons PAHs removal (59 %) (Xu Yiping et al., 2008). The MBR system was found to be effective in removal of highly hydrophobic trace organic compounds to > 85 % while hydrophilic compounds were poorly removed to about < 20 % (Tadkaew et al., 2011). Further improvement of the process will increase its cost-effectiveness and thus MBR technology is expected to take a leading role in treatment of wastewater.

5.2.5 Removal of TOrCs by Advanced oxidation processes

Advanced oxidation processes (AOP) are being used to replace the conventional disinfection treatment. Various combinations of UV, Ozone and Hydrogen peroxide are used as AOP. But that is not the only advantage of AOP since they can also be applied for removal of micropollutants. The major concern when a combination of ozone and hydrogen peroxide or UV is used is the formation of bromate which is regarded as carcinogenic disinfection by-product (K. Li et al., 2008). Despite production of disinfection byproducts ozone is very reliable for the removal of organic micropollutants. For example, phenol (10 mg/dm^3) was removed to 99 % when a small dose of ozone (1.9 O_3/mg TOC) was applied with 5 minutes of contact time (Sobecka et al., 2005b).

Other research has shown that optimisation of H_2O_2/O_3 has a positive impact on reducing humic and fulvic acids that are responsible for the formation of trihalomethanes after ozonation or chlorination processes. A dose of 0.04 H_2O_2/O_3 used for 20 min reduced the COD and TOC to 50 % and 78 %, respectively (Alsheyab and Munoz, 2006). The presence of NOM has a negative impact on advanced oxidation processes as it also interferes with UV light absorption (Alsheyab and Munoz, 2006). Ormandet and co-workers (2008) studied the removal of 44 pesticides and observed that 70 % removal of pesticides could be achieved by ozone oxidation. However, the use of ozone is regarded beneficial if the precursors (bromide and NOM) that are responsible for formation of disinfection by-products are removed or significantly reduced prior to ozonation.

5.2.6 Removal of TOrCs by Ion exchange

Ion exchange can play an important role in the removal of organic micro pollutants from drinking water. Biological treatment with activated carbon combined with ion exchange results in significant removal of trichloroethylene and trichloroethane to 82 % removal (Rogalla et al., 1990). Humbert and co-workers (H. Humbert et al., 2008) studied the removal of pesticides using different removal media from raw water (DOC = 6 mg/l) spiked with 1 µg/l of model pesticides (atrazine) and found that the carbonaceous resin AMBERSORB (8 mL/L dose) was very efficient in removal of atrazine by 84 % compared with 20 mg/L of PAC (powdered activated carbon) after 30 minutes of contact time for both experiments.

Another study by Rossner and Knappe (2008) found that silicate zeolite and carbonaceous resin have a higher uptake of MTBE (methyl tertiary butyl ether) than GAC. Some ionic resins showed poor removal of organic micropollutants. MIEX and DOWEX 11 resins showed poorer removal of atrazine and isoproton than PAC at 30 minutes of contact time (H. Humbert et al., 2008). The efficiency of resins (ion exchange) in removal of micro pollutants depends on the property of the resins but most the important issue is the physical and chemical characteristics of the targeted contaminants.

5.2.7 Removal of TOrCs by Hybrids systems

The use of hybrid systems composed of two or more techniques appears to be useful for removing persistent organic contaminants or highly polluted water. The Reungoat group (J. Reungoat et al., 2010) studied the removal of micro pollutants in a full scale reclamation plant using ozonation and activated carbon and other combined conventional treatment methods as shown by the process train in Figure 5.2. The study investigated the removal of 54 micropollutants that were removed gradually in each treatment stage but the overall treatment found that, out of 54 micropollutants, 50 compounds were removed to about 90 % on average.

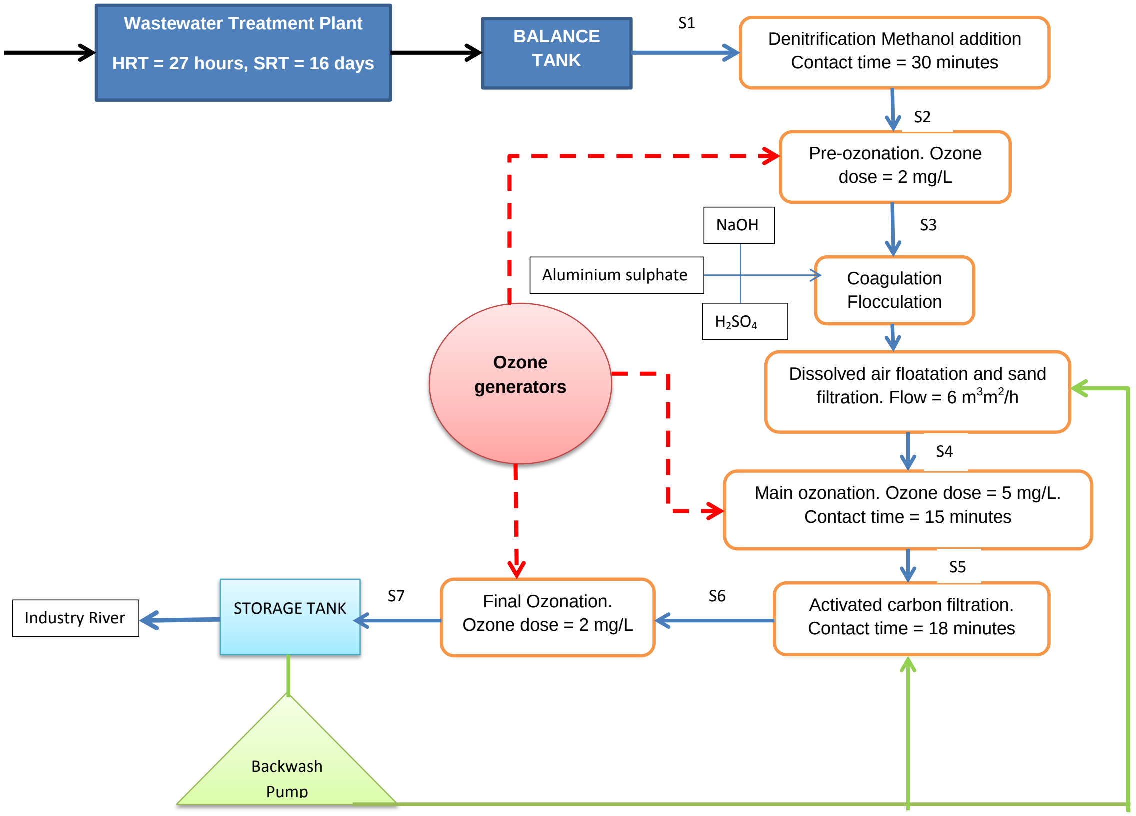


Figure 5.2: Reclamation plant

MBR systems followed by nanofiltration (NF) showed > 80 % removal of TOrCs when an MBR was combined with NF 270, while MBR followed by NF 90 improved the removal to > 85 % (Alturki et al., 2010). Also an MBR combined with PAC could be an interesting combinations for removal of TOrCs (Auriol et al., 2006).

5.3 Objectives

Submicron powdered activated carbon (SPAC) and novel PAC (KCU 6), have proven to have a unique ability to remove biopolymers mainly due to physical removal (SPAC) and adsorption (KCU 6). This raises the need to challenge both PACs on trace organic compounds removal. Therefore the objective of this chapter is to determine the performance of SPAC and KCU 6 pre-coated on ceramic MF membranes for removal of trace organic compounds in the presence of NOM competition.

5.4 Materials and Methods

5.4.1 Feed water

Canal water from Delft (Netherlands) and Jeddah wastewater effluents were used. The characteristics of these waters are shown below in Table 5.1.

Table 5.1: Characteristics of Feed waters used for TOrCs Experiments

	Wastewater Effluent	**Canal water**
DOC (mg/l)	4.5	13
UV_{254} (cm^{-1})	0.11	0.45
SUVA (L/mg-m)	2.4	3.46
pH	7.6	7.5
Conductivity	≈ 200	≈ 300
Ca^{2+} (mg/l)	80	90 - 120

5.4.2 Pre-coats materials

The particle sizes of submicron powdered activated carbon (SPAC) and novel PAC (KCU 6) used as a pre-coat material is described in Table 5.2.

Table 5.2: Particle sizes of KCU 6 and SPAC as measured by Master-sizer

	Average Particle sizes (um) – d_{50}	**Effective particle size (um) – d_{10}**	**d_{90} (um)**
S-PAC	2.5	1.4	4.6
KCU 6	38.3	11.7	98.8

The parent material of SPAC is SASuper. SPAC was prepared in slurry form so it was not easy to measure the BET surface area in such form. Therefore the parent material SASuper was used instead to estimate surface area.

Table 5.3: BET surface areas of KCU 6 and SPAC/SASuper

Type of PAC	Total BET surface area (m^2/g)	Total pore volume (cm^3/g)	Mesopores surface area (m^2/g)	Mesopores volume (cm^3/g)	Maximum pore diameter
SASuper/SPAC	903	0.8	347	0.53	2.28
KCU 6	1280	3.96	747	3.83	33

5.4.3 Membranes

A monolith ceramic micro-filtration membrane from METAWATER Co. Ltd of Japan was used in pilot scale experiments and Anopore microfiltration membranes from Whatman Company were used in bench scale experiments. Also PVDF membranes pre-coated with SPAC were used in bench scale experiments of canal water.

5.4.4 Selected TOrCs and their relative hydrophobicity values

Trace organic compounds are commonly present at a low concentration level. Hydrophobicity of trace organic compounds is measured by the hydrophobicity coefficient expressed as relative hydrophobicity (Log D) (Alexander et al., 2012, Alturki et al., 2010). TOrCs with Log D value of < 1 are regarded as hydrophilic and > 3 are termed as hydrophobic. If the value is between 1 – 3 then it is defined as intermediate hydrophobic (Hajibabania et al., 2011). The relative hydrophobicity of acidic and basic TOrCs is governed by the following equations:

$$\text{Log D} = Log\ kow + Log\left(\frac{1}{1+10^{pH-pKa}}\right) \qquad \text{Acidic - compound.}$$

$$\text{Log D} = Log\ kow + Log(\frac{1}{1+10^{pKa-pH}})$$ Basic -compound.

Where Log Kow is octanol-water coefficient, pKa is acid dissociation constant.

(Hyland et al., 2012)

A total of 29 organic micro-pollutants were selected in this study. The characteristics of these compounds are shown in Tables 5.4 and 5.5 below. The values of pKa and Log Kow were collected from the literature. Their relative hydrophobicity values (Log D) were calculated by the above-mentioned equations at pH of 7.5, which was approximately the pH of wastewater effluent used in this experiment.

Table 5.4: Characteristics of trace organic compounds analyzed in ESI positive mode with LC-MS/MS

	Name of TOrC	Formula	Molecular mass (g/mole)	pKa	Log Kow	Log D (@ pH 7.5)
1	**Acetaminophen**	$C_8H_9NO_2$	151.2	1.72 (i)	0.47 (i)	0.47
2	**Amitriptyline**	$C_{20}H_{23}N$	277.4	9.4 (a)	4.92 (a)	3.01
3	**Atenenol**	$C_{14}H_{22}N_2O_3$	266.3	9.6 (b)	0.16 (b)	-1.94
4	**Atrazine**	$C_8H_{14}ClN_3$	215.7	1.70 (b)	2.61 (b)	2.61
5	**Caffeine**	$C_8H_{10}N_4O_2$	194.2	0.52 (i)	-0.63 (i)	-0.63
6	**Carbamazepine**	$C_{15}H_{12}N_2O$	236.3	-0.49 (c)	2.67 (c)	2.67
7	**DEET**	$C_{12}H_{17}NO$	191.3	2.0 (a)	2.18 (a)	2.18
8	**Dilantin**	$C_{15}H_{12}N_2O_2$	252.3	8.33 (a)	2.47 (a)	1.58
9	**Diphenyhydramine**	$C_{17}H_{21}NO$	255.4	8.98 (a)	3.27 (a)	1.78
10	**Fluoxetine**	$C_{17}H_{18}F_3NO$	309.3	10.05 (a)	4.05 (a)	1.5
11	**Oxybenzone**	$C_{14}H_{12}O_3$	228.2	9.7 (d)	3.79 (b)	1.59
12	**Primidone**	$C_{12}H_{14}N_2O_2$	218.3	-1.07 (i)	0.91 (i)	0.83
13	**Sulfumethoxazole**	$C_{10}H_{11}N_3O_3S$	163.2	5.6 (a)	0.89 (a)	-1.02
14	**Trimethoprim**	$C_{14}H_{18}N_4O_3$	290.3	7.12 (a)	0.91 (a)	0.76
15	**TCEP**	$C_9H_{15}O_6P$	250.2	7.66 (f)	1.44 (b)	1.05
16	**TCPP**	$C_9H_{18}O_4Cl_3P$	327.4	6.6 (g)	2.59 (b)	2.54
17	**TDCPP**	$C_9H_{15}Cl_6O_4P$	430.9	5.7 (i)	3.8 (h)	3.8

Table 5.5: Characteristics of trace organic compounds analyzed in ESI negative mode with LC-MS/MS

	Name of TOrC	Formula	Molecular mass (g/mole)	pKa	Log Kow	Log D (@ pH 7.5)
1	**Bisphenol A**	$C_{15}H_{16}O_2$	228.3	10.10 (a)	3.32 (a)	3.32
2	**Diclofenac**	$C_{14}H_{11}Cl_2NO_2$	296.15	4.15 (a)	4.51 (a)	1.16
3	**Gemfribizol**	$C_{15}H_{22}O_3$	250.3	4.7 (a)	4.77 (a)	1.97
4	**Ibuprofen**	$C_{13}H_{18}O_2$	206.3	4.91 (a)	3.97 (a)	1.38
5	**Naproxen**	$C_{14}H_{14}O_3$	230.3	4.15 (a)	3.2 (a)	-0.15
6	**Triclocarban**	$C_{13}H_9Cl_3N_2O$	315.6	12.77 (a)	4.9 (a)	4.9

7	**Ketoprofen**	$C_{16}H_{14}O_3$	254.3	4.45 (a)	3.12 (a)	-0.07
8	**Triclosan**	$C_{12}H_7Cl_3O_2$	289.5	8.1 (a)	4.76 (a)	4.66
9	**Sucralose**	$C_{12}H_{19}Cl_3O_8$	397.6	11.91 (e)	-1.0 (e)	-1
10	**Acesulfame**	$C_4H_5NO_4S$	163.15	5.67 (e)	-1.33 (e)	-3.17
11	**Methlyparaben**	$C_8H_8O_3$	152.15	8.4 (e)	1.66 (e)	1.61
12	**Propylparaben**	$C_{10}H_{12}O_3$	180.2	7.91 (e)	2.71 (e)	2.57

a) (Teerlink et al., 2012)
b) (Alturki et al., 2010)
c) (Knappe et al., 2007)
d) National Library of Medicine HSDB Database
e) www.druglead.com/cds/tcep.html
f) PATENT EP254733
g) (Sullivan, 2008)
h) Estimated
i) (Alturki et al., 2013)

5.4.5 Pre-coating and Filtration

Ceramic membranes were pre-coated at the beginning of the experiment in the first 2 minutes for the pilot scale. The solution of PAC in the form of slurry was first filtered to create a thin layer of SPAC on monolith ceramic membrane before starting feed water filtration. The pre-coat layer was then removed at the end of filtration by high backwashing flux and a new coating layer was introduced. The constant flux of 150 LMH was adopted for pilot scale experiments. Only atrazine (model micro-pollutant) and SPAC (pre-coat material) were selected for the pilot scale experiments with canal water as feed. Performance of SPAC was compared with NPAC (normal powdered activated carbon).

More detailed analysis was performed using wastewater effluent spiked with 29 TOrCs at the laboratory scale. Anopore ceramic membranes were pre-coated with SPAC or KCU 6 in a required dose prepared with Milli Q and pressurized (required dose) to the membrane before filtration. The initial trans-membrane pressure was set to 0.1 - 0.2 bar and was manually adjusted to maintain the average flux.

5.4.6 Samples collection, preparation and analysis

Samples volumes of 50 mL were collected periodically. Before being analyzed these samples were concentrated to 1 mL by using solid phase extraction (SPE). The concentrated samples were then transferred to the LC-MS/MS for further analysis.

5.4.7 Solid Phase Extraction (SPE)

SPE use a special solid phase as a sorbent to separate from liquid phase (Chang et al., 2009). Permeates and feed samples of 50 mL by volumes were extracted using SPE Dionex 280 Auto Trace instrument (Sunnyvale, CA). HLB cartridges (500 mg) from Waters Corporation (Millford, MA) were used as a media for extraction process. The cartridges were first preconditioned using 5 mL of MTBE followed by 5 mL of methanol and then 5 mL of Milli Q water. The procedure involves spiking the 50 mL sample with 100 µL of 100 ppb isotope stock solution. The samples were then placed onto the cartridges and rinsed with MilliQ water (5 mL) before drying for 1 hour using a stream of nitrogen. The dried cartridges were then eluted with 5 mL of 10% Methanol in MTBE (v/v). This was followed by elution with 5 mL of methanol into 15-mL calibrated centrifuge tubes. The extracted samples were then concentrated using a TurboVap® LV Evaporation System (Biotage, Charlotte, NC) with a moderate stream of nitrogen to produce a concentrated sample of about 500 µL. Vortex mixer was used to make sure that no residual is left and LC-MS grade methanol were used to make a sample of 1 mL.

5.4.8 Samples analysis using LC-MS/MS

All analyses were performed on an Agilent 1260 Infinity Liquid Chromatography (LC) unit with auto sampler connected to a mass spectrometer The detection limit of LC-MS/MS is 0.08 ng/l (Chang et al., 2009). A sample injection volume of 10 µL was used for all samples measurements. Two mobile phases were prepared differently based on operational modes. Ammonium formate at a concentration of 4 millimoles was injected into water comprising 0.1 % of formic acid, and also same concentration of ammonium formate was injected into methanol that has 1 % of formic acid. These solutions were used as mobile phases to buffer electrospray ionization (ESI) of the compounds in positive mode. The mobile phase for negative mode ESI analysis was 2 mM ammonium acetate in water and 2 mM ammonium acetate (AA) in methanol. The binary gradient supplying the mobile phases at a flow rate of 0.8 mL/min was set as follows: 90 % of AA was held for 30 seconds before being stepped down to 60 % at 30.6 seconds and dropped linearly to 5 % at 480 seconds. It is held at 5 % till 660 seconds, then decreased linearly to 90 % AA in 180 seconds followed by a 240 seconds equilibration step at 90 % AA, resulting in a total run time of 1080 seconds.

Mass spectrometry was done using an AB SCIEX QTRAP 5500 mass spectrometer (Applied Biosystems, Foster City, CA). Single compounds with concentration of 100 ppb were prepared. By applying the established optimal ionization polarity for each compound, samples were injected directly into the mass spectrometer. Scanning was performed over the range of 200 – 400 amu to determine the intensity peaks based on concentration of electrolyte. Optimization of compound-dependent parameters was performed automatically following instrument manufacturer’s instructions and the six most intense product ion peaks were displayed. The data were interpreted based on the calibration curve made from known concentrations of TOrCs.

5.5 Results

5.5.1 TOrCs removal from surface water with SPAC

The efficiency of S-PAC for removal of micro-pollutants was investigated. Two kinds of experiments were performed, batch experiment done with (i) PVDF membranes and (ii) ceramic membranes. In both cases the results were compared with N-PAC at the same dose. Schie canal water spiked with atrazine at representative dose of 2 µg/l. The flux was maintained to 150 L/m^{2}h in both cases. The details of the experiments are mentioned below.

5.5.1.1 Micro-pollutants removal with (NPAC/SPAC) pre-coated MF PVDF membranes

Batch tests (20 minutes contact time) were done with 2 µg/l atrazine and 15 mg/l of either SPAC or NPAC in Schie canal water, in order to determine the atrazine removal capacity of the PACs in competition with NOM (Figure 5.3).

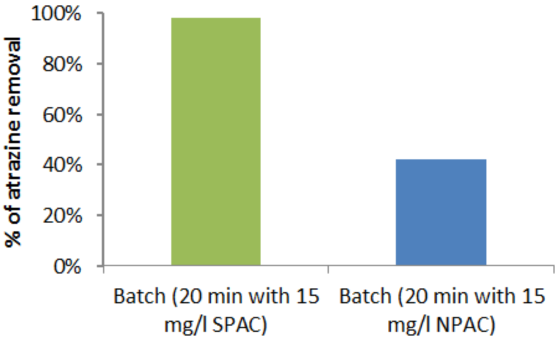


Figure 5.3: Atrazine Removal from Canal water @ 150L/m^2.h Flux on PVDF membrane pre-coated with PAC-Batch experiments

The results from Figure 5.3 show SPAC removed > 98 % of atrazine whereas 42 % removal was achieved with NPAC at the same dose (15 mg/l) and same retention time. This indicates that SPAC performance on micro-pollutants removal is very high compared with NPAC. Although when compared with other studies it was found that 5 mg/l of NPAC was able to reduce atrazine from 10 µg/L to 3 µg/L which is 70 %

removal (Crozes and Seacord, 2001). The low removal in canal water might be caused by high competition for adsorption site with NOM as the TOC of canal was quite high (15 mg/l) compared with surface water (2.5 mg/l) used by Crozes. This implies that the quality of raw water affects the removal rate of micro-pollutants.

5.5.1.2 Micro-pollutant removal with SPAC/NPAC pre-coated on Monolith Ceramic MF membrane – Pilot scale

A model micro-pollutant (Atrazine-2.2 ug/L) was spiked into the feed water. The ceramic membrane was pre-coated with SPAC or NPAC at the start of every filtration cycle. The dosing frequency was set to 6.7 l/h for 0.5 minute or less depending on dose required. Filtration started immediately after pre-coating at a constant flux of 150 L/m^{2}h and samples were collected periodically. The results of the experiments are shown below in Figure 5.4.

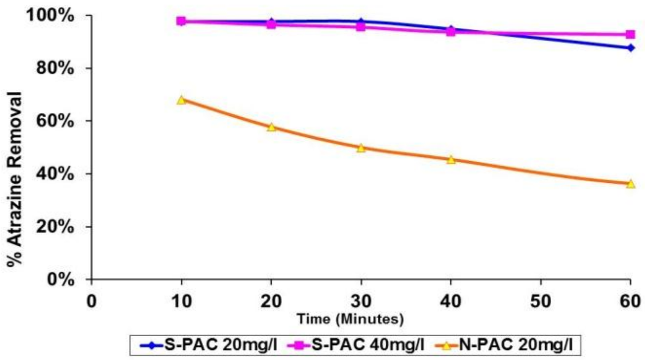


Figure 5.4: Atrazine Removal with Ceramic membrane pre-coated with S-PAC/N-PAC @150 L/m^2.h Flux

The MF ceramic membrane combined with SPAC pre-coats showed significant removal of micro-pollutants compared to NPAC (Figure 5.4). The removal of the atrazine after one hour filtration was > 95 % with both 40 and 20 mg/l of SPAC pre-coats, respectively, and 35 % with 20 mg/L NPAC (Figure 5.4). Continuous addition of PAC at a rate of 8 mg/l, resulted in a total dose of 576 mg/l in a UF + PAC system, achieved only 55 % of atrazine removal (Campos et al., 1998b).

5.5.2 Membrane Resistance increase on AAO100 membrane during TOrCs experiments: *Wastewater Effluents spiked with TOrCs*

The resistance of pre-coated membranes during wastewater effluents filtration was assessed as shown in Figure 5.5 below. KCU 6 showed a low increase of membrane resistance compared to SPAC at a dose of 30 mg/L. In previous chapters it was found that KCU 6 has a potential ability to remove biopolymers through adsorption to > 90 % at a dose of 30 mg/L. This was also achieved by SPAC at the same dose but the difference between the two is that SPAC involved two removal mechanisms. These mechanisms are adsorption and physical removal of biopolymers through the pre-coat layers. The voids between fine particles of SPAC layers are filled with biopolymers due to their bigger sizes, and eventually contributed to the total membrane resistance due to the increase of cake resistances.

At a dose of 10 mg/l, increase of resistances was observed when the KCU 6 started to exhaust. At this dose SPAC exhibited a low increase of membrane resistance at the end of filtration compared to KCU 6. But when the membrane alone was used, exponential increase of membrane resistance was observed. This increase was caused by membrane fouling due to NOM as discussed in previous chapters. Filtration of Milli Q water on pre-coated membrane with KCU 6 at a dose of 10 mg/l revealed that pre-coat layer has negligible contribution to the total increase of membrane resistance.

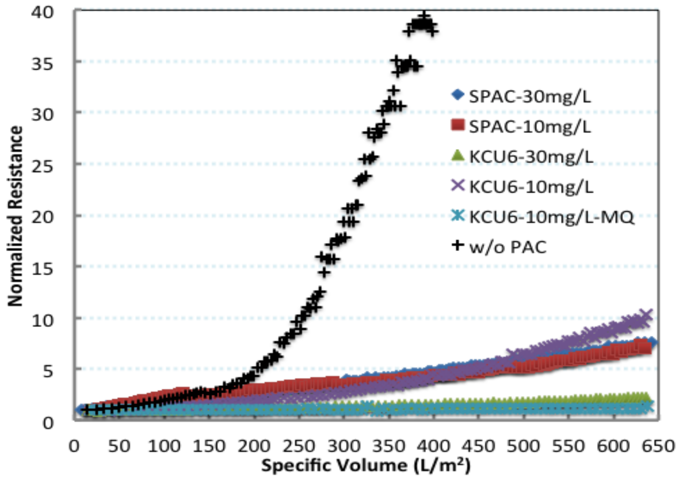
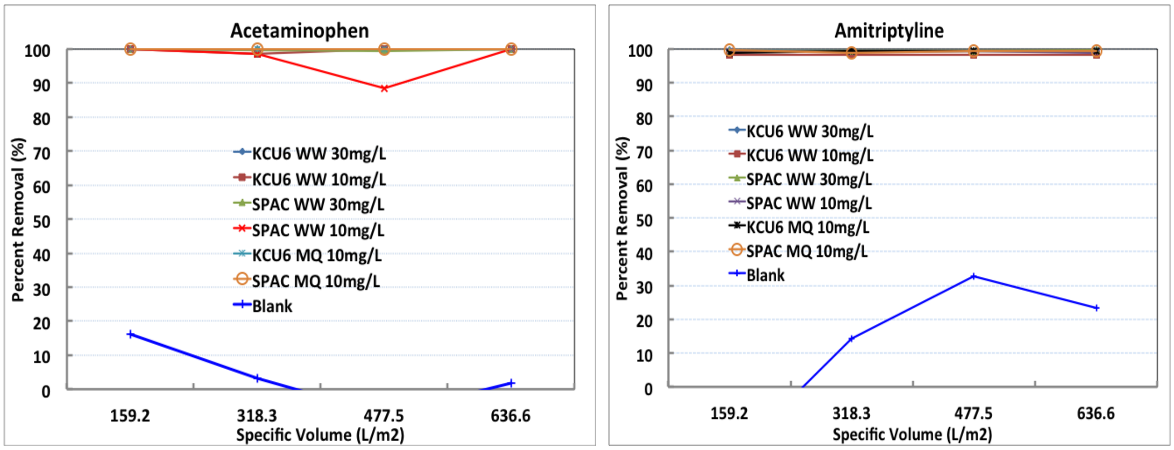


Figure 5.5: Increase of membrane resistances during wastewater effluent, and Milli Q spiked with TOrCs, filtration through pre-coated AAO100 membrane.

5.5.3 TOrCs removal with AAO100 Ceramic membrane pre-coated with SPAC/KCU 6

Pre-dosing and continuous dosing methods showed agreement in terms of TOrCs removal but much removal was observed in the early stages in case of pre-dosing (Campos et al., 1998b).

5.5.3.1 TOrCs breakthrough graphs measured by LC-MS/MS: ESI positive mode

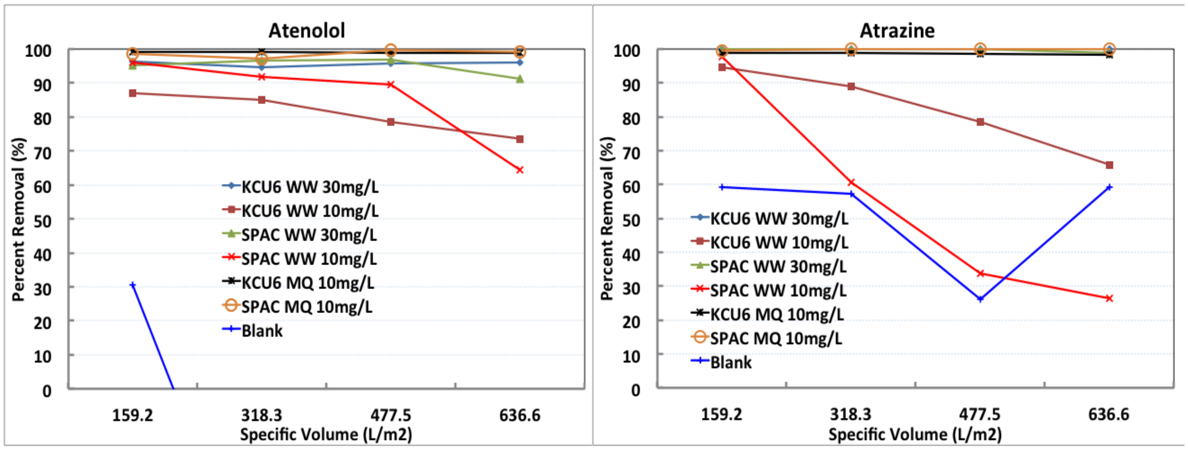


a: Acetominophen removal

b: Amotriptyline removal

Figure 5.6: Removal of (a) Acetominophen and (b) Amotriptyline with SPAC/KCU 6 pre-coats

Both KCU 6 and SPAC pre-coats at a dose of 30 mg/L removed almost 100 % of acetaminophen and amitriptyline (Figure 5.6a and 5.6b). Also a lower dose of 10 mg/L achieved high removal of acetaminophen and amitriptyline (> 99 %). The removal of acetaminophen was not affected by NOM competition in any case. An MBR combined with RO membrane achieved 98 % and 99 % of acetaminophen and amitriptyline removal, respectively, according to Alturki and co-workers studies (Alturki et al., 2010). Without PAC, the removal of acetaminophen and amitriptyline was below 16 % and 35 %, respectively. Adsorption through the membrane might be the removal mechanisms but in the case of amitriptyline, the trend showed that the removal increased as the fouling developed so pore constriction may influence the removal at a later stage.



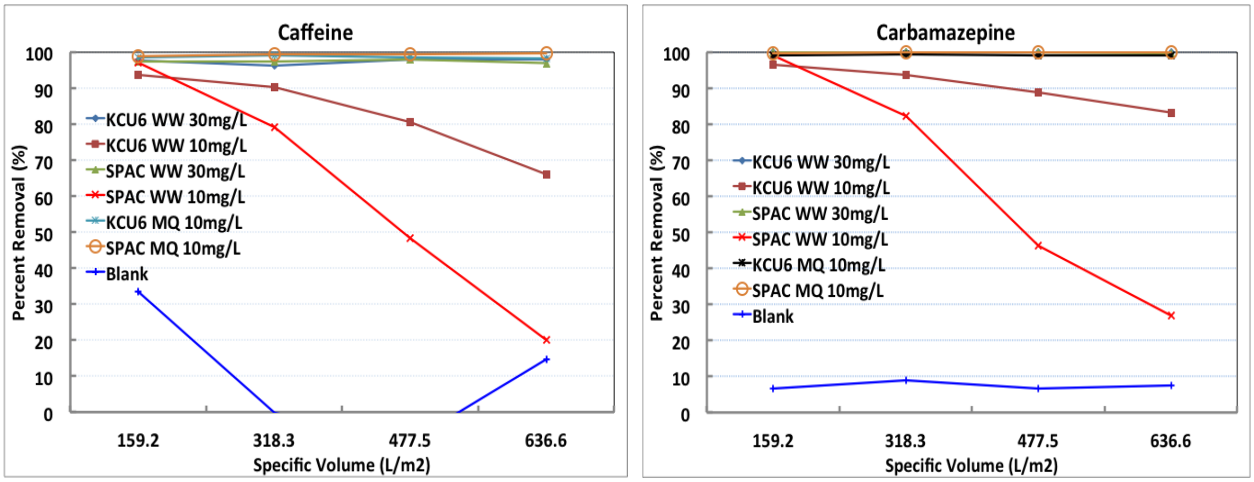
a: Atenolol removal **b**: Atrazine removal

Figure 5.7: Removal of (a) Atenolol and (b) Atrazine with SPAC/KCU 6 pre-coats

Atenolol removal with 30 mg/L pre-coats of KCU 6 and SPAC was 96 % and 94 %, respectively (Figure 5.7 a). This is close to other studies done by Alturki group using forward osmosis treatment where 99 % removal efficiency of atenolol was found (Alturki et al., 2013). With no competition 99 % removal was achieved in both cases. However, with competition the lower dose of 10 mg/L pre-coat of SPAC showed good removal at beginning (98 %) but dropped to 64 % at the end of filtration. It was also observed that KCU 6 at the lower dose achieved 87 % removal for the first sample collected and dropped gradually to 73 % at the end of filtration. With the membrane alone, 30 %

removal was observed in the initial stage and lowered to 0 % a when the fouling started to build up (Figure 5.7 a).

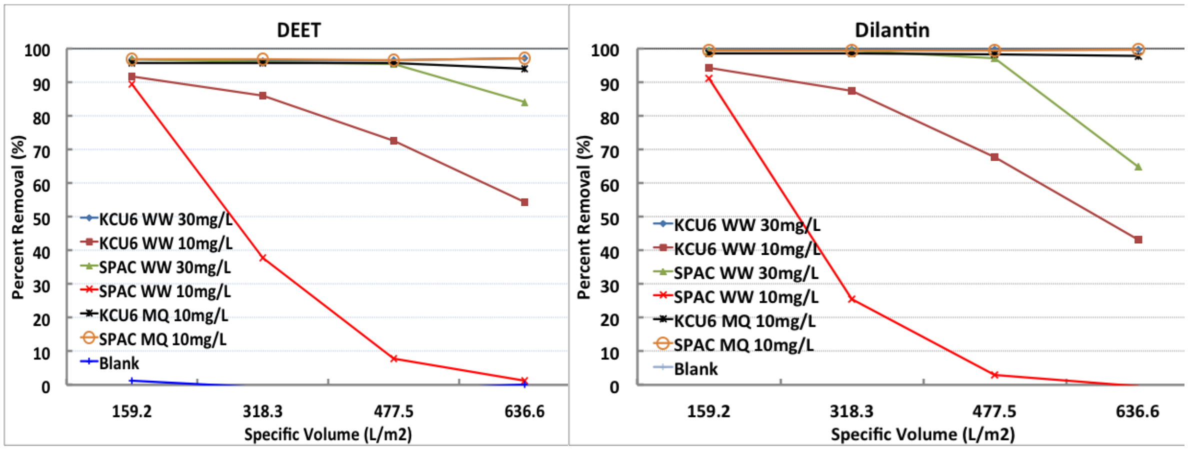
However, atrazine removal registered > 99 % with both KCU 6 and SPAC at 30 mg/L with competition and 10 mg/L without competition, respectively. Other complex treatment systems composed of slow sand filtration, ozone/hydrogen peroxide and biological activated carbon attained 92 % atrazine removal (Gerrity et al., 2011) which is less than the removal achieved by pre-coated ceramic microfiltration. Moreover, atrazine removal with the membrane alone was < 60 %. The substantial removal of atrazine with the membrane itself suggests that adsorption is a possible mechanism for this removal. Also atrazine could be adsorbed by macromolecules like biopolymers that are present in wastewater. When the dose is maintained at 10 mg/L, KCU 6 showed 94 % removal at the start of filtration and 66 % at the end while SPAC achieved 99 % removal and declined to 26 % at the end of filtration (Figure 5.7 b).



a: Caffeine removal **b**: Carbamazepine removal

Figure 5.8: Removal of (a) Caffeine and (b) Carbamazepine with SPAC/KCU 6 pre-coats

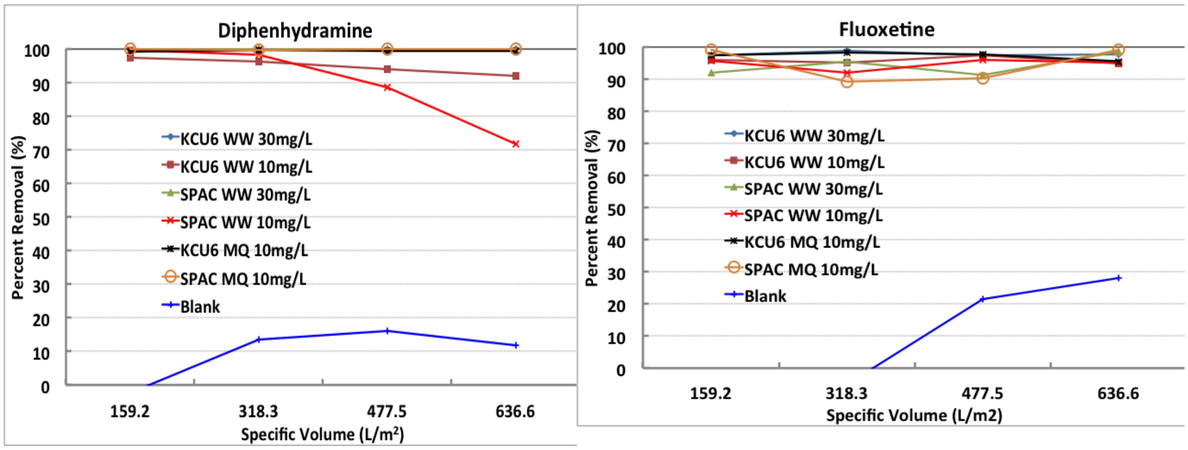
The results in Figure 5.8a showed both KCU 6 and SPAC at a dose of 30 mg/L maintained 99 % removal of caffeine. This rate of removal was also maintained under non-competition conditions with 10 mg/L doses for both. A high removal of caffeine was achieved in a sequential treatment unit composed of slow sand filtration, ozone and biological activated carbon (Gerrity et al., 2011). A low dose of 10 mg/L of SPAC achieved 97 % removal at the start but decline to 20 % removal at the end while the same dose of KCU 6 showed 94 % removal of caffeine at the beginning and dropped to 66 % at the final step of filtration. Without PAC the removal of caffeine was < 30 %. In the case of carbamazepine, high removal (> 99 %) was achieved with 30 mg/L for both PACs and 10 mg/L without competition (Figure 5.8 b). This level of removal is the same as what has been reported by Pisarenko and co-workers who determined the removal of carbamazepine using an ozone and RO hybrid system (Pisarenko et al., 2012). With competition, a low dose (10 mg/L) of KCU 6 showed 97 % removal of carbamazepine in the beginning and lowered to 83 % when the fouling increased. The same dose of SPAC achieved high removal in the initial stage of filtration (98 %) but declined to 27 % at the end of filtration (Figure 5.8 b). Carbamazepine removal was below 10 % with the membrane only.



a: DEET removal **b**: Dilantin removal

Figure 5.9: Removal of (a) DEET and (b) Dilantin with SPAC/KCU 6 pre-coats

The removal of DEET in non-competitive conditions was 95 % and 96 % with KCU 6 and SPAC, respectively (Figure 5.9 a) while dilantin removal was > 99 % with SPAC and 97 % with KCU 6 (Figure 5.9 b). Previous studies showed 98 % removal of DEET and 99 % of dilantin respectively (Gerrity et al., 2011, Alturki et al., 2010). The 96 % removal of DEET and > 99 % of dilantin was maintained with 30 mg/L of KCU 6 throughout the filtration under competitive condition (Figures 5.9 a and 5.9 b). Likewise, 30 mg/L of SPAC attained such levels of removal (96 % for DEET and 99 % for dilatin), which, however, declined to 84 % for DEET and 65 % for dilatin after a filtered specific volume of 475 L/m^2. DEET and dilatin removal in the competitive mode with a low dose of KCU 6 (10 mg/L) was not significant. The removal was 92 % and 94 % at the beginning for DEET and dilantin respectively which declined to 54 % and 43 %, respectively, at the end of filtration. However, poor removal was achieved by a low dose of SPAC (10 mg/L), which initially attained 89 % and 91 % removal of DEET and dilatin, respectively, which dropped to almost 0 % at the end of filtration for both (Figures 5.9 a and 5.9 b). The membrane alone did not remove both DEET and dilatin.

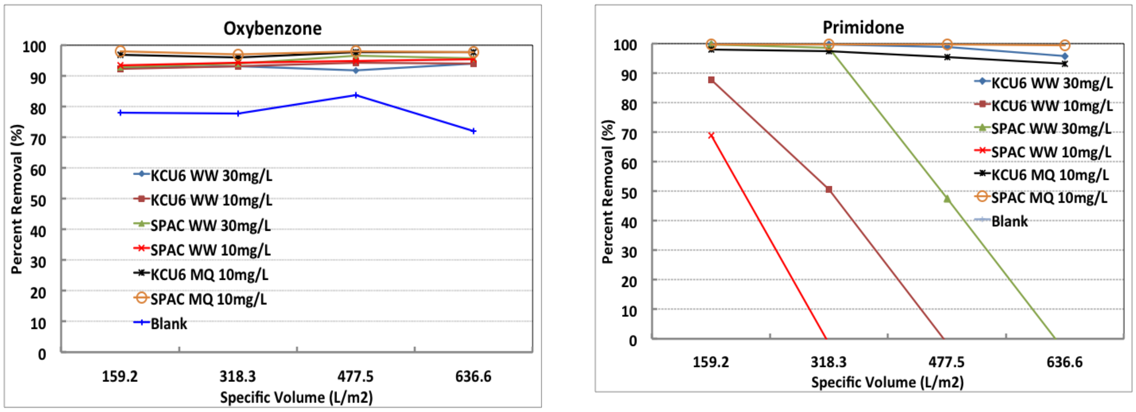


a: Diphenhydramine removal **b**: Fluoxetine removal

Figure 5.10: Removal of (a) Diphenhydramine and (b) Fluoxetine with SPAC/KCU 6 pre-coats

Significant removal of diphenhydramine (> 99 %) was achieved with a hybrid system of KCU 6 and SPAC pre-coats (30 mg/L) with ceramic MF membranes under competitive conditions. The same level of removal was attained without competition for both KCU 6 and SPAC (10 mg/L). When a low dose of 10 mg/L was applied, significant removal was still achieved with KCU 6 ranging from 97 % in the beginning to 92 % at the end while SPAC achieved 99 % in the beginning and 72 % at the end of filtration. Insignificant removal of < 16 % was achieved by the membrane alone (Figure 5.10 a).

Fluoxetine removal was > 90 % in all cases (with and without competition at 30 and 10 mg/L doses). Also the removal of fluoxetine with the membrane alone increased as the fouling increases (Figure 5.10 b). A number of studies have also shown high removal of fluoxetine in different treatment systems (Alturki et al., 2013, Gerrity et al., 2011).

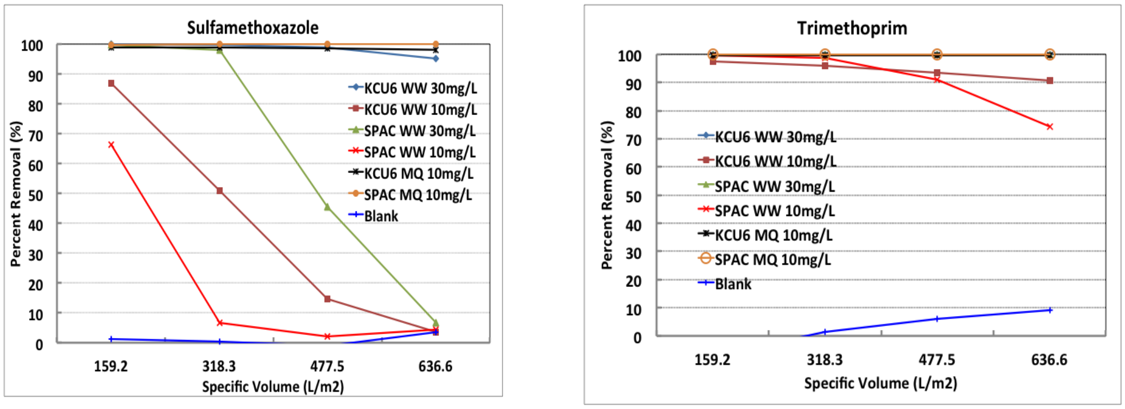


a: Oxybenzone removal

b: Primidone removal

Figure 5.11: Removal of (a) Oxybenzone and (b) Primidone with SPAC/KCU 6 pre-coats

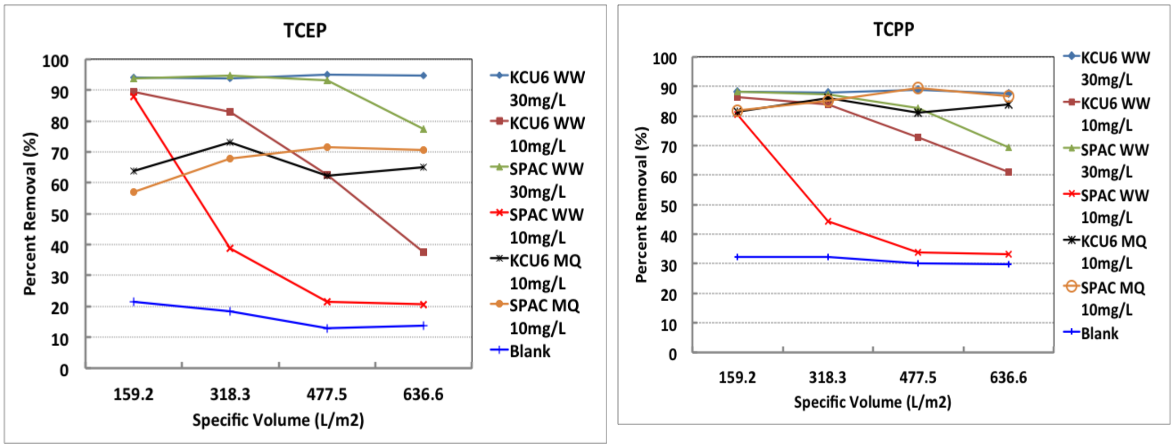
The removal of oxybenzone was > 90 % in all cases (with and without competition at 30 and 10 mg/L doses). Also high removal of oxybenzone (> 70 %) was achieved with the membrane alone, which suggests adsorption of oxybenzone by the ceramic membrane as a possible removal mechanism (Figure 5.11 a). SPAC at 30 mg/L in competitive condition showed good removal of primidone (99 %) in the first half of filtered volume but dramatically declined to 0 % at the end of filtration (Figure 5.11 b). Also KCU 6 and SPAC at 10 mg/L showed poor removal of primidone as the fouling developed (Figure 5.11 b). Only KCU 6 at 30 mg/L maintained good removal of primidone starting with 99 % and ending with 93 %. Previous studies also observed high removal of primidone in different treatments options (Gerrity et al., 2011, Pisarenko et al., 2012, Alturki et al., 2010). However, 100 % removal of primidone was achieved with 10 mg/L of SPAC without competition and 95 % with KCU 6 at the same dose and conditions (Figure 5.11 b).



a: Sulfamethoxazole removal **b**: Trimethoprim removal

Figure 5.12: Removal of (a) Sulfamethoxazole and (b) Trimethoprim with SPAC/KCU 6 pre-coats

High removal of sulfamethoxazole was achieved with SPAC and KCU 6, reaching 100 % and 98 %, respectively, without competition at a dose of 10 mg/L. A dose of 30 mg/l of KCU 6 attained 99 % removal in the beginning and 95 % at the end of filtration when TOrCs competed with NOM. In the literature, it was reported that > 99 % removal of sulfamethoxazole was achieved with SSF + Ozone/peroxide + BAC system (Gerrity et al., 2011). Good removal of sulfamethoxazole (98 %) was achieved with 30 mg/L of SPAC in the first half of filtered volume of wastewater effluents, but later dropped to 7 % in the second half of filtrate. Both KCU 6 and SPAC achieved no significant removal of sulfamethoxazole with a lower dose of 10 mg/L (Figure 5.12 a). In the case of trimethoprim, SPAC and KCU 6 with and without competition achieved 100 % removal. These findings were also supported by other studies that found high removal of trimethoprim from different treatments barriers (Gerrity et al., 2011, Pisarenko et al., 2012, Alturki et al., 2013, Alexander et al., 2012). When a low dose (10 mg/L) was used in a competitive adsorption scenario, KCU 6 achieved > 90 % removal while SPAC attained > 74 % removal (Figure 5.12 b). With the membrane alone, removal of both sulfamethoxazole and trimethoprim was < 10 % (Figures 5.12 a and 5.12 b).



a: TCEP removal

b: TCPP removal

Figure 5.13: Removal of (a) TCEP and (b) TCPP with SPAC/KCU 6 pre-coats

TCEP showed resistant characteristics for removal. Only KCU 6 pre-coats with 30 mg/L maintained high removal of 94 % throughout the filtration period followed by SPAC at the same dose, which achieved 94 % in the initial stage of filtration then declined to 77 % at the end of filtration. Without competition, both SPAC and KCU 6 attained about 70 % removal, respectively; at a pre-coat dose of 10-mg/L. Poor removal of TCEP was observed (< 20 %) with the membrane alone (Figure 5.13 a).

The removal of TCPP was about 30 % without PAC. A low dose of SPAC (10 mg/L) showed 80 % removal in the beginning and declined to 33 % at the end of filtration. KCU 6 at a low dose performed a little better by achieving 86 % removal of TCPP at the early stage of filtration and dropping to 61 % at the end of filtration. Without competition, both (SPAC and KCU 6) showed good removal of 85 % while a high dose of 30 mg/L of KCU 6 maintained 88 % removal of TCPP. However, SPAC at 30 mg/L showed 88 % removal at the start of filtration and 69 % at the end of filtration (Figure 5.13 b). In general, only KCU 6 pre-coat showed good removal of TCEP and TCPP at 30 mg/l dose. However, this was slightly lower compared with other treatments systems that removed 95 % and > 96 % of TCEP and TCPP, respectively (Gerrity et al., 2011).

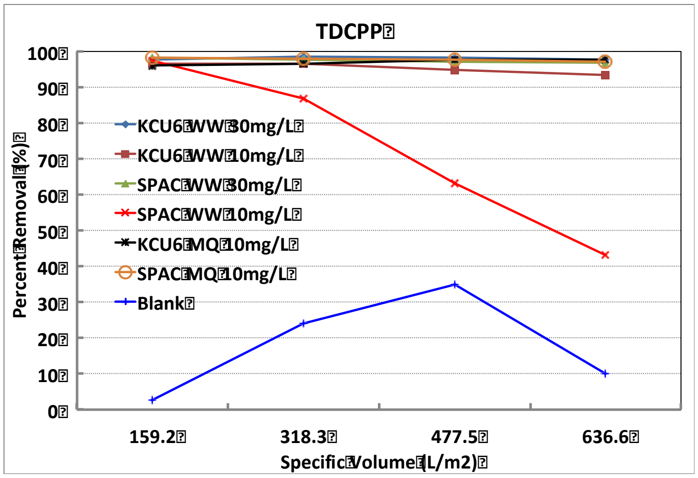
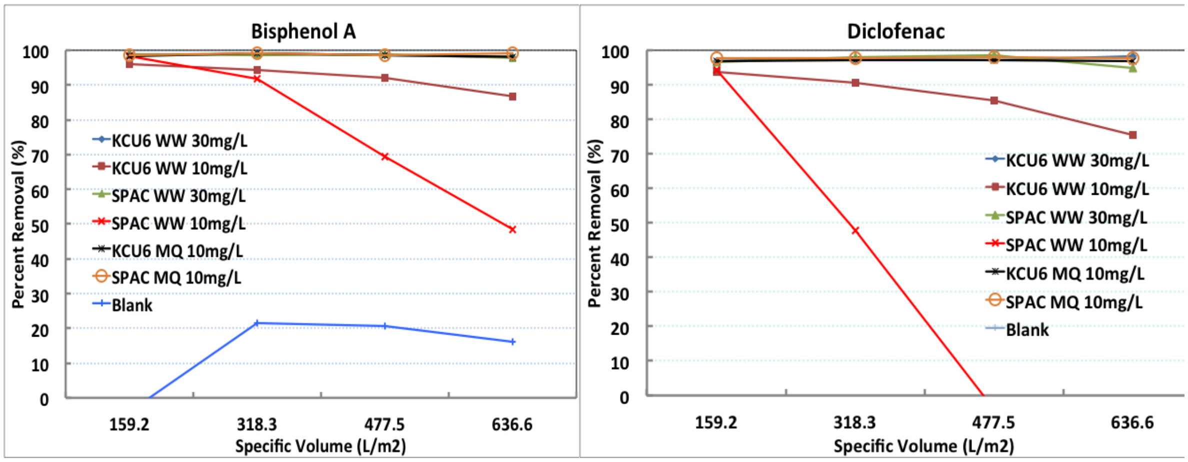


Figure 5.14: TDCPP removal with SPAC/KCU 6 pre-coats

High removal of TDCPP was achieved (> 97 %) with competition (at 30 mg/l) and without competition (at 10 mg/L) for both SPAC and KCU 6 (Figure 5.14). Also a low dose of 10 mg/L of KCU 6 pre-coat maintained high removal of TDCPP (> 93 %) from wastewater effluents while SPAC at the same dose showed strong performance in the beginning (98 %), which declined to 43 % at the end due to NOM loading.

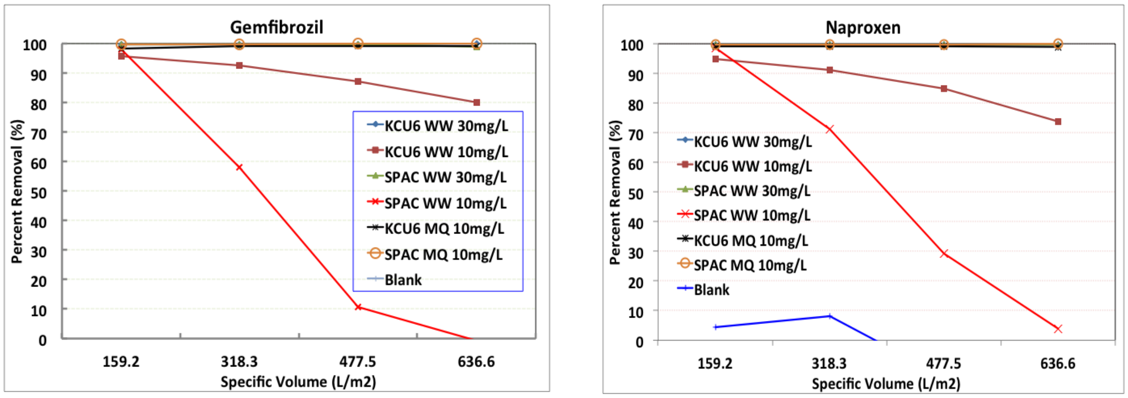
5.5.3.2 TOrCs breakthrough graphs measured by LC-MS/MS: ESI negative mode



a: Bisphenol removal **b**: Diclofenac removal

Figure 5.15: Removal of (a) Bisphenol and (b) Diclofenac with SPAC/KCU 6 pre-coats

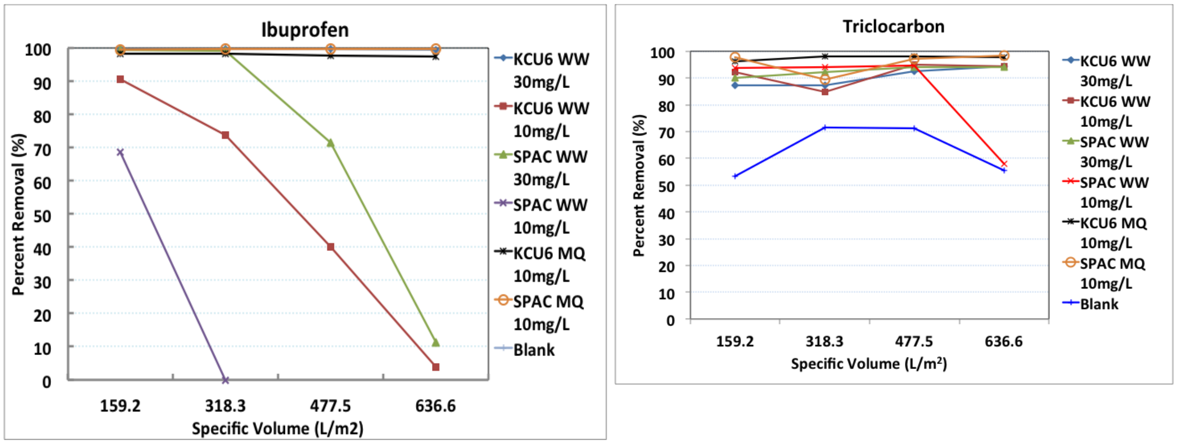
Bisphenol A and diclofenac were removed from wastewater to 99 % and 98 %, respectively, with KCU 6 and SPAC pre-coats at 30 mg/L (Figures 5.15 a and 5.15 b). Diclofenac removal (99 %) agreed with removal attained by a treatment system composed of a slow sand filter (SSF) system followed with ozonation (O_3) and biological activated carbon (BAC) (Gerrity et al., 2011). In contrast SSF + O_3 + BAC removed > 78 % of bisphenol A compared to 99 % removal achieved with the pre-coating technique. At a low dose of 10 mg/L pre-coats, the same levels of removal were achieved in the absence of NOM. In the presence of NOM, KCU 6 removed 96 - 87 % of bisphenol A and 94 – 75 % of diclofenac while SPAC at the same dose (10 mg/L) removed 99 – 49 % of bisphenol A and attained 94 % removal of diclofenac in the early stage, but suddenly decreased to 0 % after filtering the half of feed water (Figures 5.15 a and 5.15 b).



a: Gemfibrozil removal **b**: Naproxen removal

Figure 5.16: Removal of (a) Gemfibrozil and (b) Naproxen with SPAC/KCU 6 pre-coats

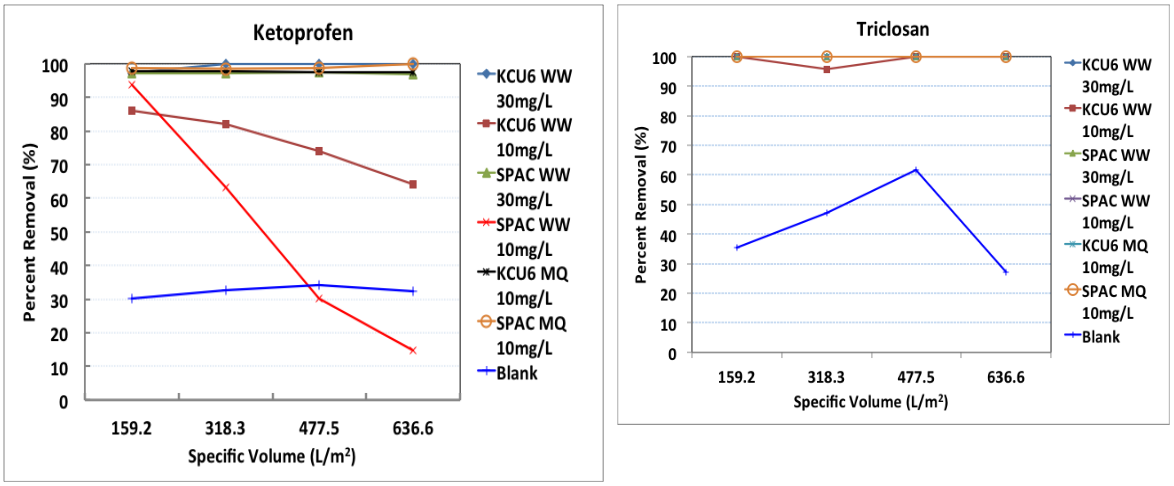
Both gemfibrozil and naproxen were well removed (100 %) from wastewater effluent with 30 mg/L of KCU 6 and SPAC pre-coats and from Milli Q water (100 %) with 10 mg/L of SPAC and KCU 6, respectively. The same degree of removal was achieved by an MBR + RO system (Alturki et al., 2010). When the KCU 6 dose was lowered to 10 mg/L pre-coats prior to wastewater filtration, 96 % gemfibrozil removal was achieved in the early stage, decreasing to 80 % in the latter stage while naproxen removal was 95 % in the beginning and declined to 74 % at the last stage of filtration. Poor removal of gemfibrozil and naproxen were observed with a low dose of SPAC that showed high removal in the beginning (99 %) but declined continuously to almost 0 % at the end of wastewater filtration (Figures 5.16 a and 5.16 b).



a: Ibuprofen removal **b**: Triclocarban removal

Figure 5.17: Removal of (a) Ibuprofen and (b) Triclocarban with SPAC/KCU 6 pre-coats

High level of removal of ibuprofen (almost 100 %) from wastewater was achieved with 30 mg/L of KCU 6 pre-coats throughout the experimental period. This level was also maintained with SPAC (10 mg/L) under non-competitive conditions as well as KCU 6 (98 % removal). But SPAC at 30 mg/L sustained high removal (99 %) only in the first half portion of filtration and declined to 11 % at the end of the filtration. This trend was also observed with a low dose of KCU 6 (10 mg/L) and it was worse with a 10-mg/L dose of SPAC (Figure 5.17 a). In the case of triclocarban, an average removal of 90 % was achieved for all cases (with and without NOM competition) except for a low dose of SPAC (10 mg/L) that showed removal of 58 % at the final stage of filtration (Figure 5.17 b). Also the membrane alone showed 53 – 72 % removal of triclocarban (Figure 5.17 b) but none for ibuprofen (Figure 5.17 a). High removal of ibuprofen and triclocarban (99 %) was achieved by the MBR system combined with RO (Alturki et al., 2010).

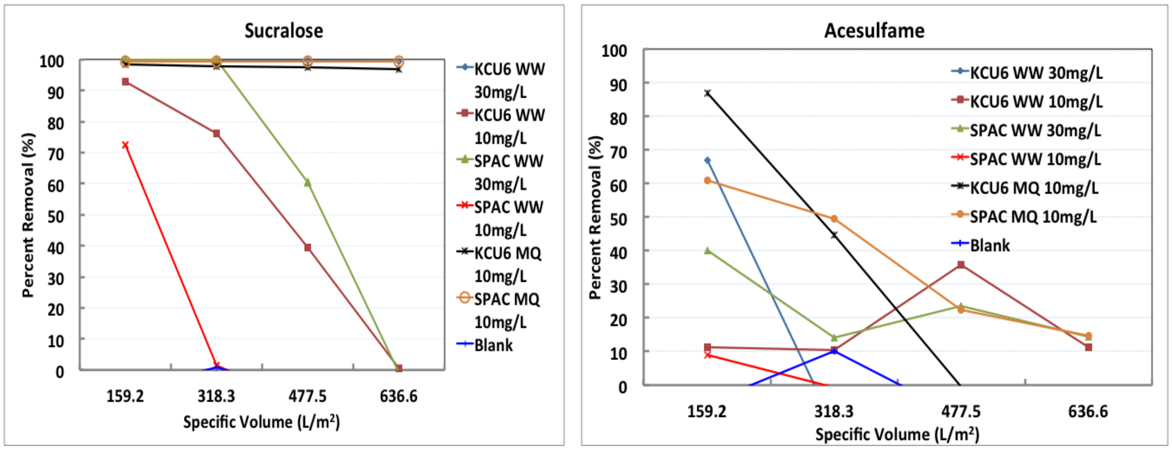


a: Ketoprofen removal **b**: Triclosan removal

Figure 5.18: Removal of (a) Ketoprofen and (b) Triclosan with SPAC/KCU 6 pre-coats

Figure 5.18a shows that KCU 6 at 30 mg/L and SPAC 10 mg/L removed almost 100 % of ketoprofen from wastewater and Milli Q water, respectively. However, SPAC (30 mg/L) and KCU 6 (10 mg/L) pre-coats, achieved high removal of ketoprofen (97 %) from wastewater and Milli Q water, respectively (Figure 5.18 a). The removal level achieved by both KCU 6 and SPAC pre-coats is far better than the amount removed by a forward osmosis process (90 %) as observed by (Alturki et al., 2013). However a low dose of 10 mg/L of KCU 6 pre-coat under competitive conditions attained 86 % removal in the early stage of filtration and declined to 64 % at the end of filtration. Alternatively, SPAC dose at 10 mg/L showed good removal in the beginning (94 %) but low removal at the end (15 %) as shown in Figure 5.18 a. Removal of ketoprofen from wastewater effluent was 30-34 % with the membrane alone (Figure 5.18 a).

Removal of triclosan was almost 100 % in all cases regardless of the low dose and high dose of KCU 6 and SPAC used as well as feed water (Miili Q and wastewater). But when the membrane alone was used without PAC pre-coating, significant removal (about 50 %) of triclosan from wastewater was observed (Figure 5.18 b). Triclosan is very hydrophobic and its removal was above 85 % after MBR treatment (Tadkaew et al., 2011).

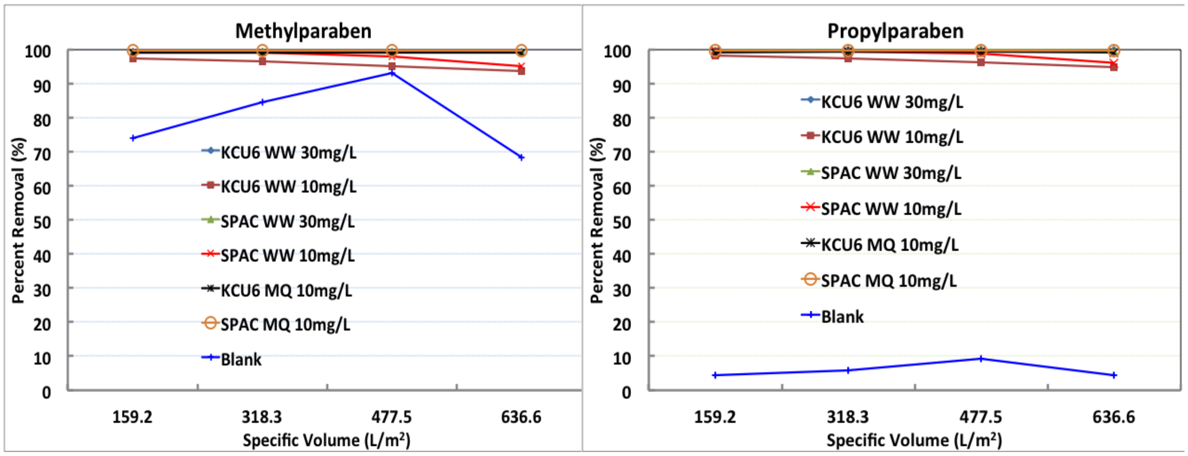


a: Sucralose removal **b**: Acesulfame removal

Figure 5.19: Removal of (a) Sucralose and (b) Acesulfame with SPAC/KCU 6 pre-coats

Significant removal of sucralose to almost 100 % from wastewater and Milli Q was achieved with 30 mg/L of KCU 6 and 10 mg/L of SPAC pre-coats, respectively. Also KCU 6 at 10 mg/L achieved 97 % removal of sucralose under non-competitive conditions

(Figure 5.19 a). SPAC at 30 mg/L dose maintained high removal (99 %) of sucralose until the middle of the filtration before declining to 0 % at the end of the filtration. A similar trend was also observed with a low dose of KCU 6 (10 mg/L). With 10 mg/L of SPAC the removal of sucralose was insignificant (Figure 5.19 a). Both KCU 6 and SPAC poorly removed acesulfame at 10 mg/L and 30 mg/L doses under all circumstances (with and without NOM competitions) as shown by Figure 5.19 b.



a: Methylparaben removal **b**: Propylparaben removal

Figure 5.20: Removal of (a) Methylparaben and (b) Propylparaben with SPAC/KCU 6 pre-coats

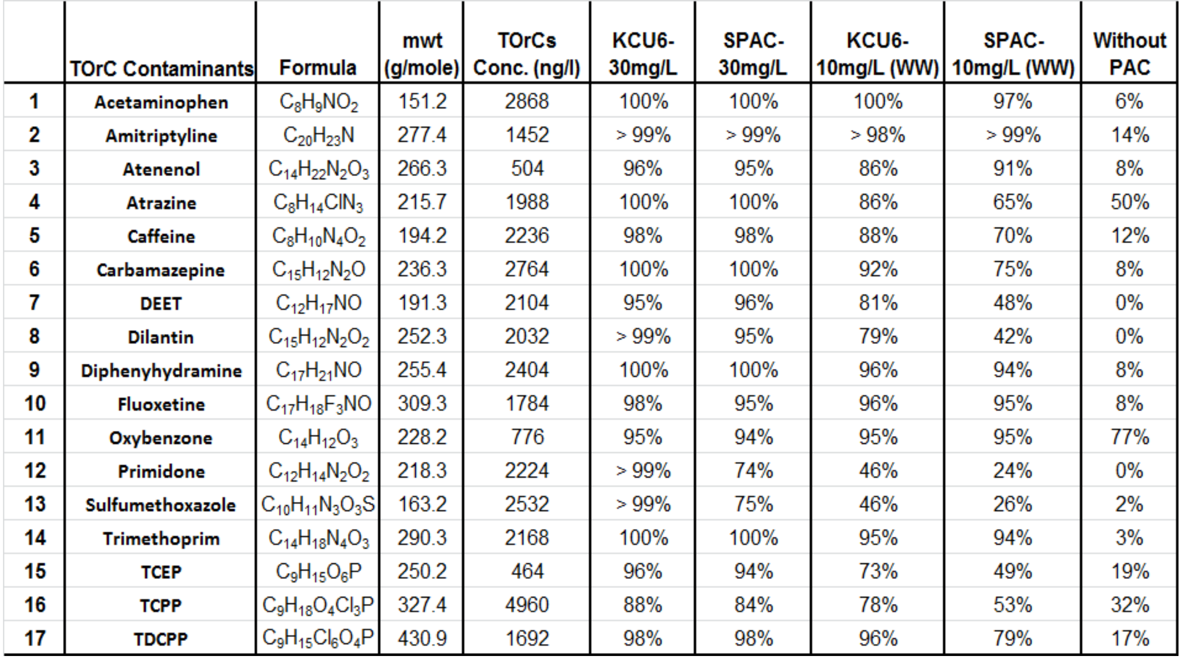
The highest removal of methylparaben, nearly 100 %, was achieved when 30 mg/L of SPAC and KCU 6 were applied to pre-coat the ceramic membrane prior to wastewater filtration. This high removal was also attained with 10 mg/L pre-coats of both KCU 6 and SPAC used as a barrier to remove micropollutants from Milli Q water. With a low dose of 10 mg/l, both KCU 6 and SPAC maintained significant removal of methylparaben from wastewater effluent to 95 % and 97 %, respectively (Figure 5.20 a). The removal of methylparaben was high, ranging between 68 – 93 % when membrane alone used. The trend showed that this removal increased as the fouling developed and decreased again when TMP was above 1 bar.

Almost 100 % removal of propylparaben was attained with 30 mg/L of SPAC and KCU 6 pre-coated on ceramic membrane prior to wastewater filtration. In the absence of NOM, 10 mg/L pre-coats of both KCU 6 and SPAC achieved 100 % removal of propylparaben (Figure 5.20 b). The results showed that a low dose of 10 mg/lof KCU 6 and SPAC maintained significant removal of propylparaben from wastewater effluent to 96 % and 98 % respectively (Figure 5.20 b). With the membrane alone, the removal of propylparaben was below 10 % (Figure 5.20 b).

5.6 Discussions of Results

The results of average removals of TOrCs with pre-coats layers of SPAC and KCU 6 are tabulated below (Table 5.6 and Table 5.7).

Table 5.6: TOrCs Removal measured with LC-MS/MS in ESI positive mode.



	TOrC Contaminants	Formula	mwt (g/mole)	TOrCs Conc. (ng/l)	KCU6-30mg/L	SPAC-30mg/L	KCU6-10mg/L (WW)	SPAC-10mg/L (WW)	Without PAC
1	Acetaminophen	$C_8H_9NO_2$	151.2	2868	100%	100%	100%	97%	6%
2	Amitriptyline	$C_{20}H_{23}N$	277.4	1452	> 99%	> 99%	> 98%	> 99%	14%
3	Atenenol	$C_{14}H_{22}N_2O_3$	266.3	504	96%	95%	86%	91%	8%
4	Atrazine	$C_8H_{14}ClN_3$	215.7	1988	100%	100%	86%	65%	50%
5	Caffeine	$C_8H_{10}N_4O_2$	194.2	2236	98%	98%	88%	70%	12%
6	Carbamazepine	$C_{15}H_{12}N_2O$	236.3	2764	100%	100%	92%	75%	8%
7	DEET	$C_{12}H_{17}NO$	191.3	2104	95%	96%	81%	48%	0%
8	Dilantin	$C_{15}H_{12}N_2O_2$	252.3	2032	> 99%	95%	79%	42%	0%
9	Diphenyhydramine	$C_{17}H_{21}NO$	255.4	2404	100%	100%	96%	94%	8%
10	Fluoxetine	$C_{17}H_{18}F_3NO$	309.3	1784	98%	95%	96%	95%	8%
11	Oxybenzone	$C_{14}H_{12}O_3$	228.2	776	95%	94%	95%	95%	77%
12	Primidone	$C_{12}H_{14}N_2O_2$	218.3	2224	> 99%	74%	46%	24%	0%
13	Sulfumethoxazole	$C_{10}H_{11}N_3O_3S$	163.2	2532	> 99%	75%	46%	26%	2%
14	Trimethoprim	$C_{14}H_{18}N_4O_3$	290.3	2168	100%	100%	95%	94%	3%
15	TCEP	$C_9H_{15}O_6P$	250.2	464	96%	94%	73%	49%	19%
16	TCPP	$C_9H_{18}O_4Cl_3P$	327.4	4960	88%	84%	78%	53%	32%
17	TDCPP	$C_9H_{15}Cl_6O_4P$	430.9	1692	98%	98%	96%	79%	17%

Table 5.7: TOrCs Removal measured with LC-MS/MS in ESI negative mode.

	Contaminants	Formula	mwt. (g/mole)	TOrCs Conc. (ng/l)	KCU 6 - 30 mg/L	SPAC- 30 mg/L	KCU6 - 10 mg/L	SPAC- 10 mg/L	Without PAC
1	**Bisphenol A**	$C_{15}H_{16}O_2$	228.3	1752	99%	99%	95%	84%	< 20%
2	**Diclofenac**	$C_{14}H_{11}Cl_2NO_2$	296.15	1884	98%	98%	90%	53%	0%
3	**Gemfribizol**	$C_{15}H_{22}O_3$	250.3	1616	> 99%	> 99%	93%	55%	0%
4	**Ibuprofen**	$C_{13}H_{18}O_2$	206.3	1672	99%	82%	67%	31%	0%
5	**Naproxen**	$C_{14}H_{14}O_3$	230.3	1580	> 99%	> 99%	90%	65%	5%
6	**Triclocarban**	$C_{13}H_9Cl_3N_2O$	315.6	132	92%	92%	90%	84%	60%
7	**Ketoprofen**	$C_{16}H_{14}O_3$	254.3	532	98%	98%	80%	60%	30%
8	**Triclosan**	$C_{12}H_7Cl_3O_2$	289.5	94.8	> 99%	> 99%	98%	> 99%	45%
9	**Sucralose**	$C_{12}H_{19}Cl_3O_8$	397.6	4560	> 99%	79%	68%	35%	0%
10	**Acesulfame**	$C_4H_5NO_4S$	163.15	11320	27%	27%	25%	4%	1.20%
11	**Methlyparaben**	$C_8H_8O_3$	152.15	1616	> 99%	> 99%	95%	99%	88%
12	**Propylparaben**	$C_{10}H_{12}O_3$	180.2	2488	> 99%	> 99%	98%	99%	6%

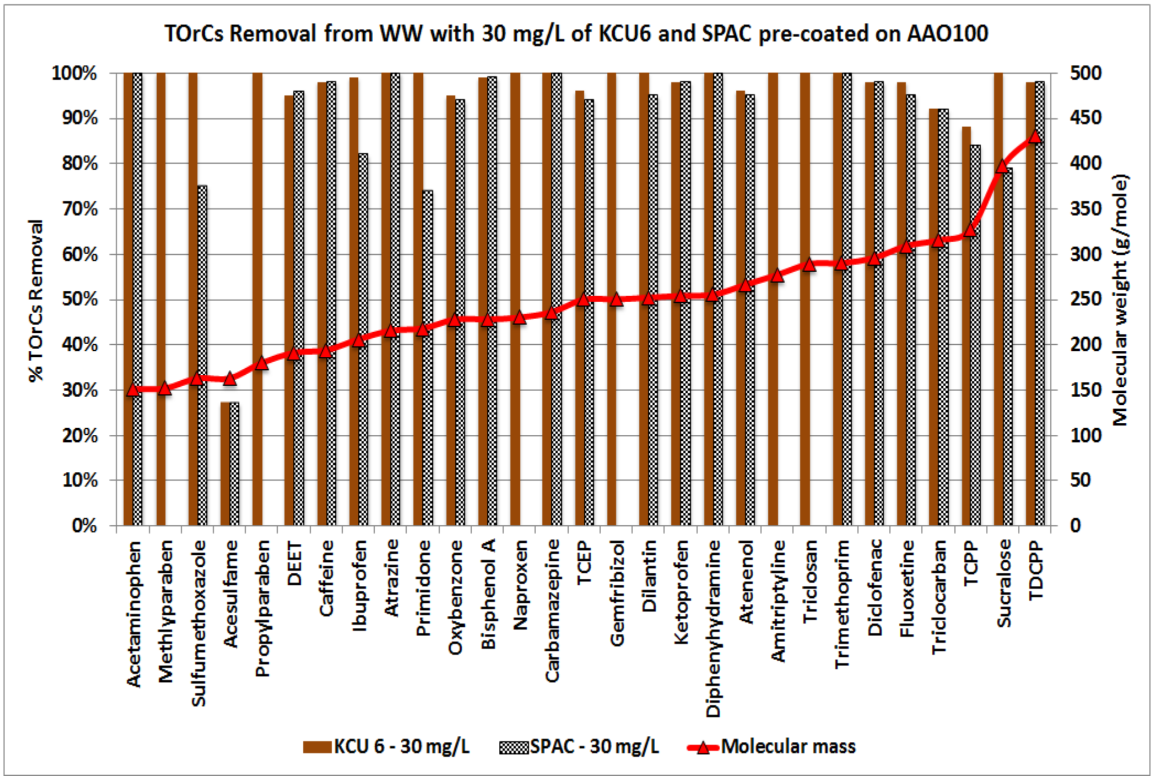


Figure 5.21: Trace organic compounds removed with 30 mg/L of SPAC and KCU 6 pre-coated on AAO100

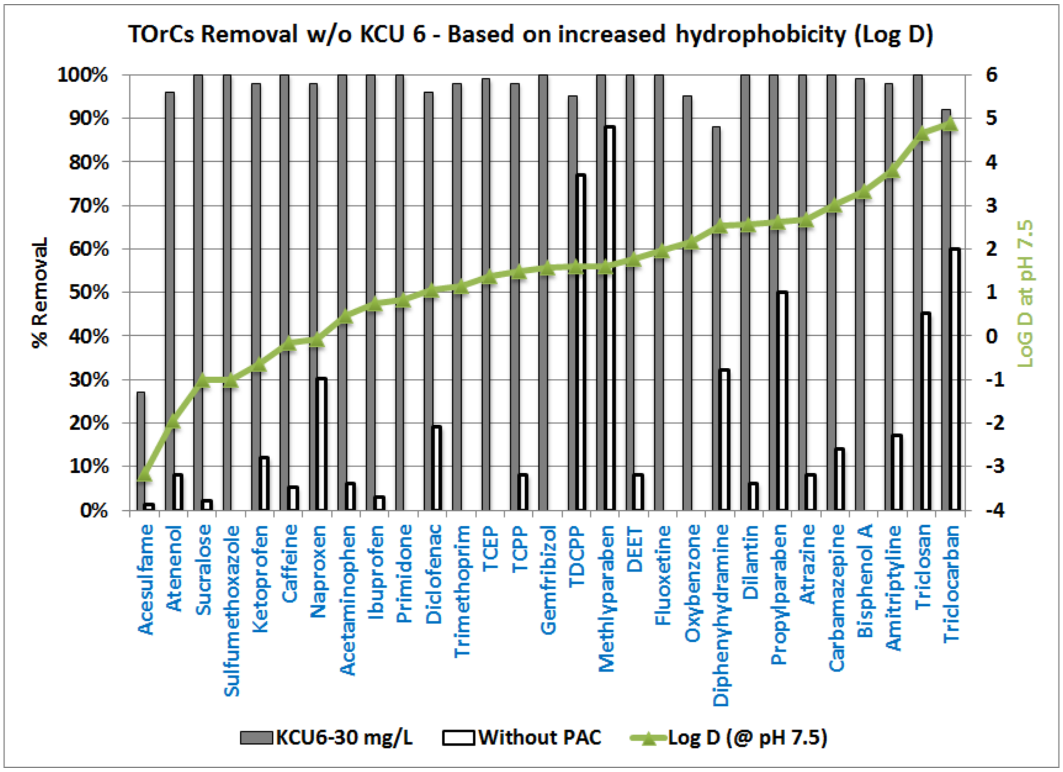


Figure 5.22: TOrCs Removal based on increased of hydrophobicity (Log D)

High removal of 95 % and above of trace organic compounds was achieved with KCU 6 at a dose of 30 mg/l pre-coated on the AAO100 membrane for 26 TOrCs out of 29 (Table 5.5 and Table 5.6). TCPP, triclocarban and acesulfame showed removals of below 95 %. However triclocarbon and TCPP showed better removal of 92 % and 88 %, respectively, compared with acesulfame that showed poor removal of only 27 %. Treatment of TOrCs with slow sand filters (SSF) followed by ozone or hydrogen peroxide and biological activated carbon (BAC) attained high removal of TOrCs (Gerrity et al., 2011) similar to the simple technique of ceramic membrane pre-coating with KCU6. High removal of > 99 % of carbamazepine, atrazine, primidone, trimethoprim, atenenol (> 97 %), TCEP (95 %) and TCPP (> 94 %) were achieved with RO combined with ozonation (Pisarenko et al., 2012).

SPAC at the same dose attained 95 % and above in 20 out of 29 TOrCs (Table 5.5 and 5.6). The nine trace organic compounds that showed less than 95 % removal are oxybenzone (94 %), TCEP (94 %), triclocarban (92 %), TCPP (84 %), ibuprofen (82 %), sucralose (79 %), sulfumethoxazole (75 %), primidone (74 %) and acesulfame (27 %). Other research found that the removal of primidone, sulfamethoxazole and carbamazepine with ozonation followed by slow sand filter was 70 %, > 80 % and > 98 %, respectively (Hübner et al., 2012).

When the dose was lowered to 10 mg/L, only acetaminophen, amitriptyline, diphenyhydramine, fluoxetine, trimethoprim, TDCPP, bisphenol A, triclosan, methylparaben and propylparaben attained 95 % removal and above for KCU 6. The same removal level was achieved with SPAC pre-coat at 10 mg/L except for diphenyhydramine (94 %), TDCPP (79 %) and bisphenol A (84 %) as shown in Table 5.5 and Table 5.6. The trend of removal of TOrCs is independent on the molecular weight (Figure 5.21) or increase of hydrophobicity above -1 of the log D value (Figure 5.22). The surface of activated carbon is relatively hydrophobic (Delgado et al., 2012). Hence it is expected that hydrophobic interaction between contaminant and activated carbon will increase the removal level.

The presence of NOM affects the TOrCs adsorption as both compete for adsorption sites. This is clearly shown by the difference observed in removal of TOrCs spiked into NOM-enriched water (wastewater effluent) compared to NOM-free feed water (Mill Q). The results revealed that 10 mg/ L of SPAC or KCU 6 in the absence of NOM completely removed almost all TOrCs (Figures 5.6 – Figures 5.20). However, only acesulfame exhibited low removal against PAC pre-coating even in the absence of NOM. This might be due to its extremely hydrophilic characteristics (Log D= -3.17 at pH of 7.5) as presented in Figure 5.22. Hydrophylic trace compounds break through granular activated carbon filter earlier than hydrophobic (Delgado et al., 2012).

In addition, pre-coating with KCU 6 or SPAC is a useful technique to deal with TOrCs, which provide better removal, compared to the coagulation process. Recently it was observed that acetaminophen, diclofenac, ibuprofen, naproxen, fluoxetine, sulfamethoxazale were only removed from 60 – 17 % by the coagulation based process (Alexander et al., 2012).

Significant removal was observed for some of the TOrCs when wastewater effluents spiked with TOrCs were filtered by the AAO100 ceramic membrane alone. These TOrCs include methylparaben (88 %), oxybenzone (77 %), triclocarban (60 %), atrazine (50 %) and triclosan (45 %) (Figure 5.21). There are two possible means of removal, one is adsorption to the membrane surface and the other one is adsorption to macromolecules like biopolymers or humic substances present in wastewater effluents. Alginate (used as model for biopolymers) was found to have greater ability to adsorb TOrCs compared to humic substance (Hajibabania et al., 2011).

Natural systems like soil treatment are good in removing some of TOrCs but failed to achieve significant removal in some of the TOrCs. A laboratory experiment involving a soil treatment column showed high removal of acetaminophen, atenolol and caffeine (> 80 %) with an observation of poor removal of primidone, TCEP, atrazine and carbamazepine (< 20%) as reported by (Teerlink et al., 2012). A system of a slow sand filter (SSF) combined with ozonation removed > 98 % of carbamazepine, > 80 % of sulfamethoxazole and ≈ 70 % of primidone (Hübner et al., 2012). In general, the novel PAC (KCU 6) showed better removal efficient of trace organic compounds compared to SPAC. Only acesulfame showed resistance to removal by both PACs in the presence and also absence of NOM.

5.7 Conclusions

In batch experiments, the results showed atrazine removal > 98 % for SPAC and 42 % removal for NPAC when 15 mg/l of SPAC or NPAC were mixed with Schie canal for 20 minutes. This signifies that SPAC performance for micro-pollutants removal is very high compared with NPAC. In pilot tests, both 40 mg/l and 20 mg/l of SPAC pre-coats maintained high average removal of 95 % while 20 mg/l of NPAC achieved an average removal of 50 %.

The novel PAC (KCU 6) at a dose of 30 mg/l, attained high removal of TOrCs (> 90 %) for most of the TOrCs analyzed with the exception of acesulfame (27 % removal) and TCPP (88 % removal). Acesulfame is very hydrophilic compared to the other trace organic compounds analyzed and this might be the reason for its poor removal. Good removal was also observed with 30 mg/L SPAC pre-coats as well. The results of this study show that molecular mass, charge, and hydrophobic character of TOrCs were not the key factors determining the fate of TOrCs removal in the PAC pre-coating approach. The presence of NOM and amount of pre-coat dose used were the key factors that influence the removal of TOrCs. The hybrid system of ceramic membrane and KCU 6 pre-coat achieved high levels of TOrCs removal that could be achieved with more costly systems such as MBR followed by RO or oxidation (ozone) with NF or RO. Therefore ceramic microfiltration membranes pre-coated with novel PAC (KCU 6) or SPAC is a simple and lower cost technology which is feasible for removal of TOrCs.

5.8 Recommendations

It is recommended to do further studies on the interaction between macromolecules present in wastewater effluents and TOrCs that showed good removal when the membrane alone is used. These compounds include methylparaben, oxybenzone, triclocarban, atrazine and triclosan. Therefore, two experiments are suggested one with Milli Q water and the other one with wastewater effluent both spiked with TOrCs before filtering by ceramic membranes alone.

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CHAPTER 6

6.0 Ceramic MF/UF membranes Filtration for Seawater Pretreatment: Successes and Challenges

Chapter is based on

Influence of Transparent Exopolymer Particles (TEP) on Fouling of UF Ceramic Membranes and Associated Flux Recovery after Membrane Cleaning

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Application of Ceramic Membranes for Seawater Reverse Osmosis (SWRO) Pre-treatment

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Ceramic Membrane Filtration for Seawater Pretreatment

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6.1 Summary

The use of low-pressure (microfiltration/ultrafiltration (MF/UF)) membranes has been well established in seawater pretreatment. Pretreatment of seawater is necessary for removal of organic, colloidal and particulate fouling materials to ensure better feed water quality of RO membranes. This particular chapter aimed to assess the performance of MF/UF ceramic membranes in seawater pretreatment. Anopore MF and UF ceramic membranes (AAO100 and AAO20) operated at constant pressure with a bench scale set up (0.1–0.2 bars) and a pilot plant equipped with monolith ceramic MF membrane from METAWATER operated at constant flux (150 LMH) were employed. Milli Q water was used for hydraulic backwashing (BW) to prevent cross contamination instead of seawater permeate in the case Transparent Exopolymers Particles (TEP) analysis for bench scale studies. Sodium hypochlorite was used for chemical enhanced backwashing (CEB) and chemical cleaning (CIP). Filtration cycles of 45-60 minutes were adopted for bench scale. A high backwashing flux of 1,500 LMH was applied for BW and CEB for 2 minutes. The membrane surfaces (fouled and cleaned) were analyzed with SEM, EDX and Epifluorescence Microscopy. Feed water was obtained from Red Sea water (Thuwal-Saudi Arabia). The increase of trans-membrane pressure (TMP) over time was monitored. The feed water and permeate were analyzed using a Silt Density Index (SDI) unit, turbidity meter and flow cytometer. The results showed that ceramic MF membrane filtration improved the SDI_{15} of seawater from 6.1 % per min to 2.1 % per min with the membrane alone. Further improvement to an SDI_{15} value of 1.9 % per min was achieved with an applied low dose of coagulant of 1 mg/L Fe^{3+}. A constant turbidity of 0.05 NTU was maintained for the filtrate throughout the filtration period. The removal of bacteria ranged from 3.7 logs (without coagulant) to 4 logs (with coagulant of 1 mg/L Fe). The low recovery after backwashing and high increase of TMP by the membrane alone was significantly controlled by coagulation at low dose (1 mg/L Fe^{3+}). Ceramic membranes after backwashing with Milli Q at high flux attained 10 - 15 % flux recovery. The use of CEB (sodium hypochlorite 3000 ppm) improved flux recovery to 80 % and 100 % after CIP. Membrane surface characterization with SEM, EDX and Epifluorescence showed the presence of particulates, microorganisms and transparent exopolymer particles (TEP) that are believed to contribute to fouling and flux decline. The low recovery after backwashing was attributed to the presence of TEP retained on the membranes that are hypothesized to be more sticky and difficult to be removed by hydraulic backwashing. TEP showed resistance against hydraulic backwashing resulting into low flux recovery. This suggests that TEP is a key factor in membrane fouling caused by seawater. The use of sodium hypochlorite for CEB played an important role in breaking up the structure of TEP and hence improved the flux recovery.

6.2 Introduction

The main advantages of ceramic membranes that make them attractive for seawater pretreatment is high flux during operation and backwashing. Feed water required for reverse osmosis (RO) membranes need to undergo a pretreatment step to prevent or reduce RO fouling. Although low-pressure membranes for seawater pretreatment are well established in terms of polymeric membranes; there is not much experience with ceramic membranes (CM). The objective of this study is to assess the performance of ceramic membranes for seawater pretreatment. Bench scale and pilot scale experiments using Red Sea water were carried out.

6.2.1 General Background

Pretreatment of seawater prior to RO membranes is necessary for effective operation of seawater reverse osmosis membranes (Sutzkover-Gutman and Hasson, 2010). Pretreatment is important since RO membranes are very sensitive to foulants such as colloids, inorganic scaling and biofouling development (Bonnélye et al., 2008). Severe fouling due to colloidal and dissolved organic matter may occur if RO is applied as a single system without a pretreatment step (Jeong et al., 2012). The role of pre-treatment is to remove or reduce algae, organics, and suspended and colloidal particles and ultimately produce better quality feed water for RO membranes (Cui et al., 2011). Two options of seawater pretreatment are available; conventional pretreatment using granular filters medium and low-pressure membranes (LPM). LPM provide stable water quality and currently is cost competitive with conventional pre-treatment systems (Remize et al., 2009).

LPM pretreatment prior to RO membranes provides consistent filtrate turbidity (< 0.1 NTU) and low Silt Density Index (SDI) value (< 3) as recommended for RO operation (Durham and Walton, 1999). Consistent permeate quality and turbidity removal of 99 % under a high flux of 450 LMH was achieved by a ceramic UF membrane (0.05 um pore size) made up with Zirconium dioxide (Xu et al., 2010). However, natural organic matter (NOM) removal by low pressure membranes alone is limited to 5 %, which is mostly high molecular weight NOM (Bonnélye et al., 2008).

NOM provides a substrate for micro-organisms (Pearce, 2007) and promotes both organic fouling (Prihasto et al., 2009) and biofouling (Ma et al., 2007b). Hence both bacteria and NOM need to be controlled to prevent RO fouling. LPM can significantly remove microorganisms such as bacteria (Jeong et al., 2012) due to their molecular weight cut-offs. Another foulant from seawater that recently has received a lot of attention is transparent exopolymer particles (TEP). TEP are found in more abundance in marine waters than surface waters (Villacorte et al., 2009, Hassler et al., 2011). Their binding effect is known to cause fouling (Passow, 2002) which is mostly irreversible.

Fouling in membranes systems increases operating and maintenance costs (Katsoufidou et al., 2008). Non-backwashable fouling which could not be reversed by hydraulic backwashing is the most problematic form of fouling in UF membranes (Kuzmenko et al., 2005). Natural organic matter (NOM) and extracellular polymeric substances (EPS) are known to be responsible for non-backwashable fouling (Katsoufidou et al., 2008).

EPS is composed mostly of proteins and carbohydrates (Wang et al., 2009) whereby the main portion of EPS is made up of carbohydrates rather than proteins (Zhang et al., 2008). EPS showed an affinity for binding with metals like copper, calcium, magnesium and lead (Bhaskar and Bhosle, 2006) as well as iron (Hassler et al., 2011) and form organic complexes with metals. EPS represents one of the foulants that are resistant to hydraulic cleaning (Liang et al., 2008). The source of transparent exopolymer particles (TEP) is from phytoplankton cells that release EPS which is later transformed into TEP.

TEP are high molecular weight organics made up of acidic polysaccharides (Passow, 2002); and their sticky nature (Passow and Alldredge, 1994) is attributed to highly negative charge (Zhou et al., 2010). The binding and attachment behaviour to surfaces is believed to be caused by electrostatic and hydrophobic interactions (Xu et al., 2011). Ceramic membranes made up of inorganic metals could be more prone to binding behaviour of TEP. Therefore, investigating the cleaning protocol that is effective for TEP removal is very crucial.

Back-washable fouling can be eliminated by hydraulic backwashing and air/water flushing while non-back-washable fouling requires chemical cleaning (Jiang et al., 2003). Ceramic membranes as in-organic membranes allow aggressive backwashing that theoretically enables removal of most of the particulates and colloidal matter attached to the membrane surface.

The efficiencies of chemical agents depend on concentration, soaking time and temperature (Kuzmenko et al., 2005, Raffin et al., 2011). Also combinations of two or more cleaning agents may provide better flux recovery. The use of caustic soda followed by sodium hypochlorite in chemical cleaning of UF polymeric membranes revealed high flux recovery instead of using a single chemical (Liang et al., 2008). However the selection of cleaning protocol is determined by water quality (feed) and nature of fouling (Porcelli and Judd, 2010). Ceramic membranes are more stable to chemicals since they can resist high acidic and basic conditions (Heijman et al., 2008). Therefore the only issue that needs consideration is the chemical cost.

In some cases after membrane cleaning with oxidizing agents, the permeability of the membrane increased above the original value due to increase of hydrophilicity of the membrane (Levitsky et al., 2011). The interaction of calcium with NOM increases the aggregation of NOM by forming NOM-Ca complexes found to influence the increase of flux decline (Katsoufidou et al., 2010).

Flux decline depends on quality of feed water (water composition) as well as membrane characteristics (e.g. charge, pore size, hydrophobic or hydrophilic behavior) and filtration flux (Cho et al., 2000). The nature of NOM (hydrophobic and hydrophilic) influences the flux recovery and flux decline in UF membranes. Membranes subjected to hydrophobic NOM water showed better flux recovery after chemical cleaning of the membrane (cleaned with sodium hydroxide or hydrochloric acid) than hydrophilic NOM water (Lee et al., 2001). Also hydrophilic NOM showed significant decline of flux (Lee et al., 2004). High permeability recovery after backwashing is attractive for membrane users, as such, investigating the cause of low permeability recovery and suggesting ways to improve permeability recovery is considered to be an issue of high priority.

The combination of coagulation with MF/UF membrane can eliminate the binding effect of TEP and increase the efficiency of ceramic membranes operation. It can also enhance the removal of NOM, bacteria and improve the SDI value of filtrate. Ceramic membranes, made up of in-organic materials, are a promising option to replace seawater conventional pretreatment and provide better and stable feed water quality. Therefore assessment of their performance for pretreatment of seawater is required.

6.3 Goal and Objectives

6.3.1 Goal

To assess the performance of the ceramic microfiltration membranes as a pretreatment option prior to seawater reverse osmosis (SWRO) membranes.

6.3.2 Objectives

- To determine SDI improvements after ceramic membrane filtration
- To assess bacterial removal and turbidity

- To control or reduce membrane fouling with in-line coagulation
- To assess the performance of backwashing (BW) with clean water or seawater permeate, chemical enhanced backwashing (CEB) and chemical cleaning (CIP) on flux recovery after membrane fouled with seawater filtration.
- To assess the influence of TEP on membrane fouling

6.4 Materials and Methods

6.4.1 Feed Water:

Seawater was obtained from the Red Sea at the King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi Arabia. The characteristics of the seawater are tabulated below (Table 6.1 and Table 6.2):

Table 6.1: Feed Water Quality – Red Sea

DOC (mg/l)	*UV (cm^{-1})*	*SUVA (L/mg-m)*	*Turbidity (NTU)*	*pH*	*Conductivity (ms/cm)*	*TDS (g/l)*	*Alkalinity (meq/L)*
1 – 1.2	0.012–0.02	1.2 – 1.5	0.5-5	8.2±0.1	60 - 70	30–39	7.6 - 11

Table 6.2: Red Seawater ionic composition

Ions	**Concentration**	**Ions**	**Concentration**	**Ions**	**Concentration**
Na^+	12,470 mg/L	Cl^-	22,199 mg/L	Br^-	67.8 mg/L
Mg^{2+}	1,436 mg/L	SO_4^{2-}	3,330 mg/L	Silica (as SiO2)	4 mg/L
Ca^{2+}	527 mg/L	Fe^{2+}	1.0 mg/L	Ba^{2+}	6 µg/L
Sr^{2+}	7.99 mg/L	Cu^{2+}	10 µg/L	Al^{3+}	90 µg/L

Synthetic seawater, which is free of TEP and a DOC level above the average level of Red Sea water, was studied to understand the role of TEP in a membrane fouling. Synthetic seawater (Table 6.3) was spiked with humic substances (0.6 mg/l) and a protein solution derived from bovine milk (0.7 mg/l) to introduce NOM of equivalent dose of 1.3 mg/l close to real NOM of red sea water. Also waste water effluents with DOC level of 5 mg/l was mixed with 50 % of Milli Q to lower the DOC to 2.5 mg/l, almost double to that of Red sea water was used to compare the efficiency of BW between membrane fouled with seawater and membrane fouled with wastewater effluent, respectively.

Table 6.3: Typical Feed Water Quality of Synthetic Seawater

Parameter	**Synthetic Seawater**
Turbidity (NTU)	0.05
DOC (mg/l)	1.5
UV (cm-1)	0.03
Ca^{2+} (mg/l)	531
Mg^{2+} (mg/l)	1,436

The ionic composition of Red Sea water is shown in Table 6.3

6.4.2 Membranes

Monolith ceramic membranes from METAWATER with a pore size of 0.1 µm and made of alumina were used for pilot scale experiments. For bench scale tests, flat sheet Anopore MF ceramic membranes (AAO100) with pore size of 0.1 um and Anopore UF ceramic membranes (AAO20) with pore size of 0.02 um were used. Both membranes are hydrophilic although they were manufactured by different methods. The METAWATER ceramic membrane was fabricated by sintering at a very high temperature while the Anopore ceramic membrane was fabricated by electrolysis. Membrane characteristics are shown in Table 6.4 below:

Table 6.4: Membranes characteristics

	AAO20	AAO100	METAWATER
Pore size	0.02 um	0.1 um	0.1 um
Contact angle	20^0	18^0	
Permeability (L/MH.bar)	1500	4500	1500
Size (diameter)	25 mm, 47 mm	25 mm, 47 mm	2.5 cm

6.4.3 Coagulant

Iron III chloride ($FeCl_3.6H_2O$), obtained from Aldrich- Sigma Company was used as a coagulant.

6.5 Experimental set-up and Filtration

The pilot plant from KWR (Netherlands) was employed to conduct the experiments (Figure 6.1). The pilot plant was operated at a constant flux of 150 LMH and backwashed with permeate at a high flux of 1,800 LMH after every 2 – 2.5 hours. The system is equipped with a backwashing vessel and pressurized inline gas (nitrogen) set to 4 bars, used for operation and air flushing. An aggressive backwashing flux of 1800 LMH for 15 seconds was applied for regular membrane hydraulic cleaning at the end of the filtration cycle. Backwashing was followed by air flushing (4 bars for 10 seconds) and forward flushing (300 LMH for 40 seconds) to complete physical cleaning of the membrane. Sodium hypochlorite (3 g/l), citric acid (1 %) and sodium hydroxide (0.1 M) were used for chemical cleaning (CIP) to restore the membrane permeability.

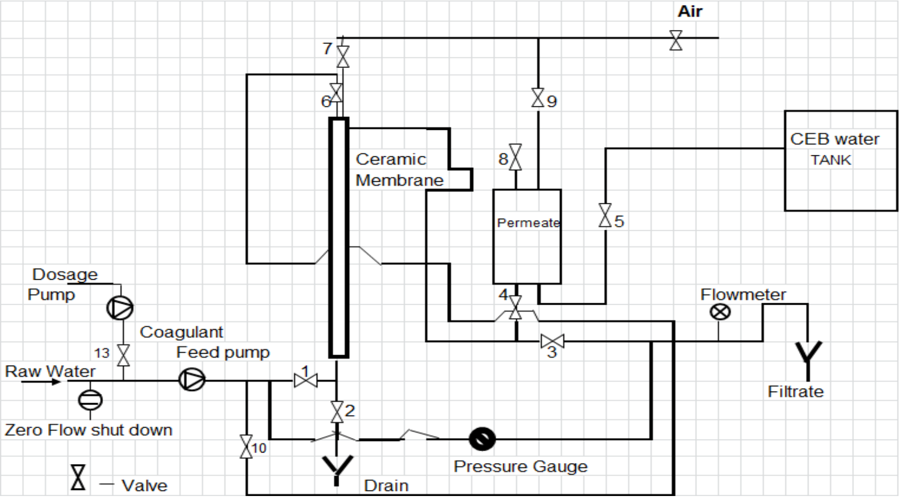


Figure 6.1: Layout of the Ceramic Pilot Plant

For bench scale experiments, an Amicon stirred cell was employed (Figure 6.2). The feed water was placed in a pressure vessel and nitrogen gas was used to pressurize the feed water through the membrane. The permeate water was collected in a beaker placed on a digital balance that also recorded the weight of the permeate water to establish the flux measurements.

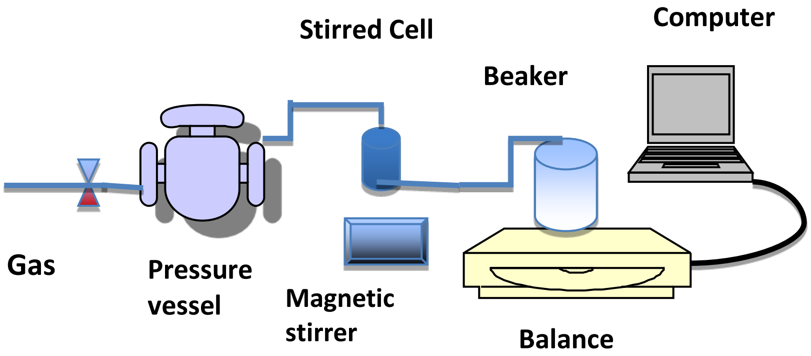


Figure 6.2: Schematic Layout of Amicon Stirred Cell

6.6 Methodology:

6.6.1 Pilot plant

A stock solution of $FeCl_3.6H_2O$ (121 mg/L) was prepared and placed in the dosing tank. The coagulant (iron III chloride) was then dosed in-line continuously at a dosing rate of 40 mL/minute to the feed water operated at 60 L/h to introduce an equivalent dose of 1 mg/L Fe to seawater. The pilot plant, which is equipped with static mixer, allowed solution to pass through and well mixed before being filtered in ceramic microfiltration.

6.6.2 Bench scale experiment protocol

The flat sheet UF membrane AAO20 was soaked in Milli Q for about 1 hour for conditioning before being used. The feed water was contained in a pressure vessel and the feed water (sea water) was filtered through the membrane placed in membrane cell. The duration of a filtration cycle was 60 minutes at constant pressure. The filtration was done at a constant pressure of 0.2 bars. Then the membrane was turned upside down and backwashed with Milli Q at a very high flux of 1500 LMH for 2 minutes. The flux decline before and after backwashing was assessed. For chemical enhanced backwashing (CEB) sodium hypochlorite (NaOCl) was used instead of Milli Q. Different concentrations of the sodium hypochlorite solution were applied to determine their influence on flux recovery after membrane cleaning. The results of flux recoveries after backwashing (BW) and CEB were compared.

Cleaning in place (CIP) was performed by using 3000 ppm of NaOCl. The fouled membranes were soaked in the chemical solution for at least one hour followed by Milli Q for about 5 minutes before being used for the new filtration cycle. The experimental conditions for bench scale experiments are in summarized Table 6.5 below.

Table 6.5: Operation conditions

	Initial Flux (LMH)	**Filtration time (Min.)**	**CEB/BW Flux (LMH)**	**Chemical for CEB**	**CIP**
AAO20	250 – 300	60	1,500	NaOCl (500 – 3000 ppm)	NaOCl (3000 ppm), HCl (pH 2) and Citric acid (1%)

6.6.3 SDI Test and Turbidity

Membrane filters from Millipore (HWAP) with a 0.45 um pore size was used. The membrane was placed on membrane holder and flushed with pure water for a few seconds at a pressure of 30 psi (2.1 bars) in order to remove air bubbles from the system as well as condition the membrane before the experiment. The time used to fill the first filtrate of 500 mL was recorded. After 15 minutes, a second sample of 500 mL of permeate was collected and the time taken was recorded to mark the SDI_{15} value. The following equation governs calculations for SDI_{15}.

$$SDI_{15} = \left[1 - \frac{T_i}{T_{15}}\right] X\ 100/15$$

Where Ti = Time used to collect first 500 mL, T_{15} = Time used to collect 500 mL after 15 minutes.

Turbidity of the feed water and permeates from the pilot plant was measured periodically by using a turbidity meter with a NTU scale unit.

6.6.4 Bacteria measurements

One millilitre (1 mL) of sample was collected from the bulk sample. Ten microliters (10 uL) of Na-EDTA was spiked into the sample and mixed well by a shaker and then warmed in a water bath at 35 C for 10 minutes. After 10 minutes passed, SYBR Green I (10 uL) was added and mixed well before warming the sample again for 10 minutes. The sample was then transferred to the Flow Cytometer for bacteria analysis.

6.6.5 TEP measurements

TEP by nature are transparent therefore, a special dye is needed to stain the TEP and make them visible. Alcian blue was used to stain the TEP. Alcian blue powder (0.1 g) 8GX (ordered from SIGMA-Aldrich) was dissolved in Milli Q (400 mL) followed by addition of acetic acid to make a solution of alcian blue at a pH of 2.5 and concentration of 0.025 %. The fouled membrane was first soaked in water for 1 minute and then soaked in the solution of alcian blue for 10 minutes and soaked again in Milli Q water for 5 minutes and then transferred to the Epi-fluorescence microscopy for qualitative TEP analysis in a bright field.

6.6.6 NOM Characterizations and Fouling Assessment

For NOM characterization, Liquid Chromatography with Organic Carbon Detection (LC-OCD) was used to detect the organic foulants. Fouling development was assessed based on flux decline under constant pressure filtration mode for the bench scale, and increase of membrane resistance under constant flux mode operation for the pilot scale. Membrane resistance was calculated based on the following equation

$$\mathrm{Rm} = \left[\frac{\partial P}{\mu J}\right]$$

Where ∂P – Trans-membrane pressure (N/m^2), µ - viscosity (Pa.s) and J – flux ($m^3/m^2.s$)

6.6.7 SEM and EDX analysis

The used and backwashed membranes were characterized by Scanning Electron Microscopy (SEM): QUANTA 3D FEG and NOVA NANO from FEI Company and Energy Dispersive X-ray Spectroscopy (EDX) from EDAX. Both samples for SEM and EDX were coated with gold ≈ 5 mm K575X from Quorum Tech.

6.6.8 Cleaning agents.

Milli Q water was used for BW of the fouled ceramic membranes instead of UF permeate to avoid cross contamination in the case of bench scale tests. Sodium hypochlorite was employed for CIP and CEB of Anopore Ceramic membranes (AAO). The efficiency of

NaOCl in terms of CIP was compared with other cleaning agents, citric acid (3 %) and hydrochloric acid (pH 2).

6.6.9 Zeta potential measurements

Zeta potential measurement of the ceramic membrane was done at different pH levels to find the isoelectric point by using Anton Par SurPASS instrument. Sodium chloride with a concentration of 1 millimole (1 mM) was used as the electrolyte under ambient temperature.

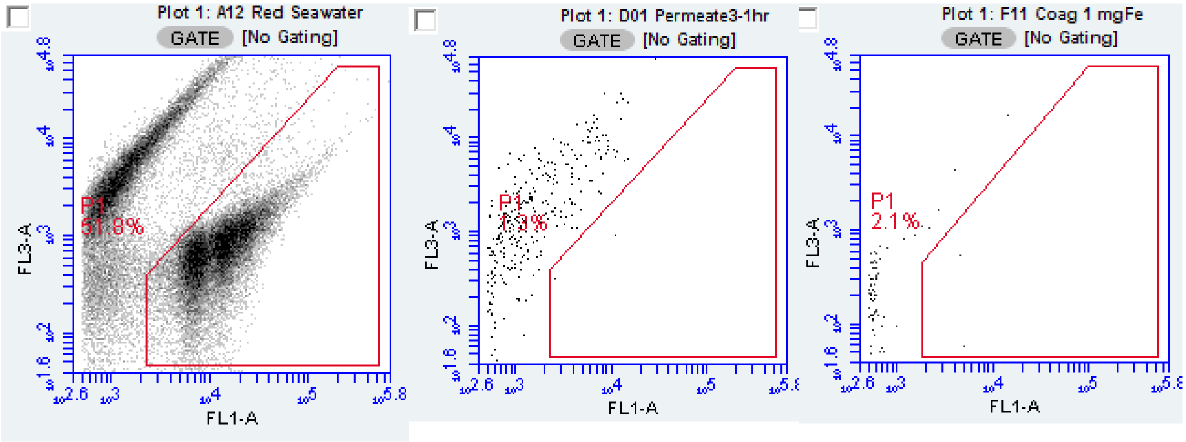
6.7 Results

6.7.1 Silt Density Index (SDI), Turbidity and Bacteria measurements (Pilot plant)

The feed water (seawater) and permeates of the ceramic membrane pilot plant operated at constant flux of 150 LMH, with and without coagulation (1 mg/L Fe), were collected for SDI, turbidity and bacteria measurements. The results are tabulated in Table 6.6.

Table 6.6: SDI, Turbidity and bacteria measurements

	Red Sea water	***CM Permeate without coagulation***	***CM Permeate with coagulation (1 mg/L Fe)***
SDI_{15} (% per min.)	6.1	2.1	1.9
Turbidity (NTU)	2	0.05	0.05
Number of bacteria in 50 uL	22,776	4	2



a b c

Figure 6.3: Numbers of bacteria measured from 50 uL of (a) Seawater (b) Ceramic MF Permeate and (c) Ceramic MF Permeate after coagulation with 1 mg/L Fe^{3+}

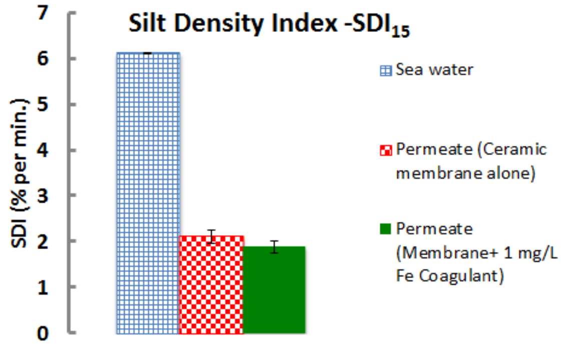


Figure 6.4: SDI_{15} *values of Seawater Ceramic MF Permeate and Ceramic MF Permeate after coagulation with 1 mg/L* Fe^{3+}

The SDI_{15} value of Red Sea water was found to be an average of 6.1 % min^{-1}. This value improved to 2.1 % min^{-1} after seawater filtration by the ceramic MF membrane and 1.9 % min^{-1} with coagulation (Table 6.6 and Figure 6.4). The measured SDI values of permeates met the recommended value of SDI (< 3) required for RO feed (Johir et al., 2009). The SDI improvement with the ceramic membrane alone showed better performance compared with a PVDF membrane of the same pore size that registered an SDI_{15} value of 3.17, although with coagulation an excellent SDI_{15} value of 0.75 was achieved (Yang and Kim, 2009).

The turbidity was also improved after ceramic membrane filtration and maintained at a constant value of 0.05 NTU in both cases (with and without coagulation) despite the variation of feed quality as shown by results in Table 6.6 above. This agrees with the requirement for RO feed that recommend turbidity to be < 1 NTU (Prihasto et al., 2009). The study conducted by Yang (Yang and Kim, 2009) also found a consistent turbidity value of 0.055 NTU of permeate when seawater was filtered with a PVDF MF membrane combined with 0.5 mg/L Fe coagulant.

Bacteria are known to play a key role in biofouling that is regarded as the worst type of fouling of RO membrane. Microfiltration membranes (including ceramic membranes) are good barriers for removing bacteria (Kim et al., 2005a). A flow cytometer, which is a quick and accurate method for bacteria measurement (Phe et al., 2005), was used to count the bacteria. The results shown in Table 6.6 and Figure 6.3 showed that bacteria removal by the ceramic membrane alone was 99.98 %, which slightly improved to 99.99 %, when coagulant (1 mg/L Fe) was applied. These results confirm that microfiltration membranes including ceramic membranes can remove bacteria to a significant level (Ericsson and Hallamans, 1994).

6.7.2 Fouling Management with inline coagulation: Pilot scale experiments

Despite the encouraging results achieved with ceramic membrane on reduction of SDI value, turbidity and bacteria removal that guarantee better feed for RO membranes, the ceramic membranes still suffered from fouling. Backwashing was not effective and irreversible fouling was also a problem. To mitigate the problem, in-line coagulation with iron III chloride was employed for improving operation and maintaining a low increase of trans-membrane pressure (TMP). A ceramic MF pilot plant was operated at constant flux of 150 LMH and backwashed with permeate every 2.5 hours. A comparison between operating with and without coagulation was carried out.

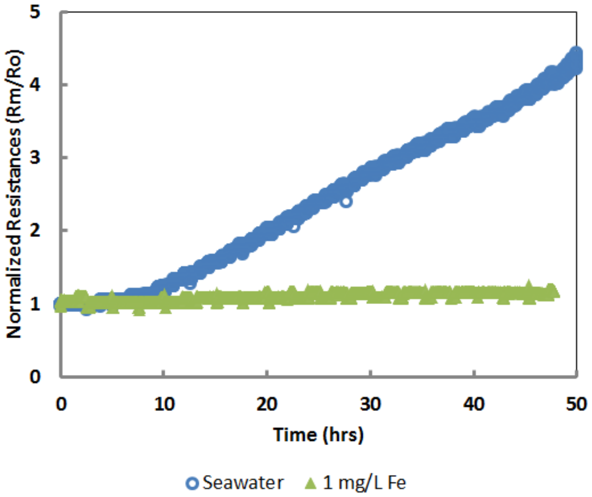
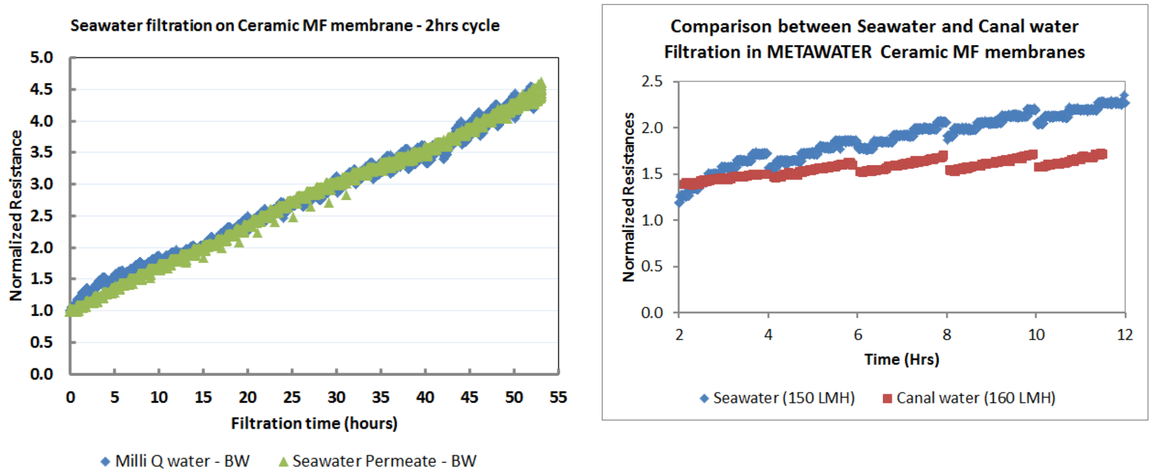


Figure6.5: Influence of in-line coagulation in membrane filterability

Coagulation improves filterability significantly and allows longer filtration cycles. Membrane resistance increased to 4.3 times after 50 hours of operation without coagulation and only increased to 1.3 times (after 50 hours) when a low dose of iron III chloride (1 mg/L Fe) was used (Figure 6.5) which maintained a low increase of membrane resistance.

Therefore it can be concluded that without coagulation, ceramic membrane filtration of seawater is not viable. The pilot study of ceramic membrane filtration done by the Cui group (Cui et al., 2011) recommended the use of coagulation, claiming that without coagulation ceramic membrane filtration of seawater is not feasible. Another study indicated that stable operation beyond one week was achieved with a low pressure membrane coupled with coagulation at a low dose of 1 mg/L Fe in seawater filtration (Brehant et al., 2002).

In pilot experiment studies, it was found that seawater filtration by ceramic MF membranes alone exhibited poor performance in backwash ability. Considering the DOC level of Red Sea water, which is close to 1 mg/L, and the turbidity of an average of 2 NTU (Table 6.1), poor recovery after backwashing is not expected based on the quality of feed water. It is expected that increase of flux/velocity during the cleaning process increases cleaning efficiency (Blanpain-Avet et al., 2009). But there was no significant flux recovery observed for ceramic membrane when operated alone without coagulation. The level of permeability recovery after backwashing was not changed even when Milli Q water was used to backwash instead of filtrate of ceramic MF membrane as shown by Figure 6.6 a below. Fouling was also observed to be more severe in a case of seawater filtration that have DOC of 1 mg/L compared to a surface water that have high DOC of about 5 mg/L as shown in Figure 6.6 b.



a. b.

Figure 6.6: (a) Seawater filtration on ceramic membranes backwashed with Milli Q water or seawater permeate (b) Comparison between seawater filtration and surface water filtration on ceramic MF membrane

Poor backwashing recovery could be attributed to the presence of sticky organic matter (TEP) that is known to be very persistent and difficult to be removed from membrane surface even after applying high backwashing flux. Therefore, bench scale experiments were conducted to study the fate of TEP before and after backwashing, enhanced backwashing with sodium hypochlorite and chemical cleaning with sodium hypochlorite. In marine waters, TEP are found in large quantity (Hassler et al., 2011) and their unique behavior of being very sticky (Passow, 2002) may cause hydraulic cleaning to be ineffective.

6.7.3 Flux Recovery after Backwashing (BW) and enhanced backwashing (CEB) with Sodium hypochlorite

Red sea water filtrations were done with the UF membrane at different initial fluxes and a filtration duration of 60 minutes as described in Tables 6.5. An Anopore UF membrane (AAO20) was backwashed with a sodium hypochlorite solution to study the performance of recovery rate of the CEB process. The results were compared with normal backwashing with Milli Q water. Flux recovery and decline was calculated based on the following equations.

$$Decline = 1 - \frac{J_f}{J_0}$$

Where J_0 is initial flux and J_f is final flux at the end of first filtration cycle.

$$\mathrm{Re}\,\mathrm{cov}\,ery = \frac{(J_{02} - J_{f1})}{(J_{01} - J_{f1})}$$

Where J_{01} is initial flux of 1st filtration cycle, J_{02} is initial flux of 2nd filtration cycle and J_{f1} is final flux of 1st filtration cycle.

6.7.3.1 Flux Recovery after Backwashing (BW) and enhanced backwashing (CEB) with Sodium hypochlorite: Red Sea filtration with AAO20

Red sea water was filtered through AAO20 membrane for 60 minutes at an initial flux of 225-250 LMH. The AAO20 membranes were backwashed with either Milli Q or a solution of diluted sodium hypochlorite (500 – 3000 ppm). A backwashing flux of 1500 LMH was used for 2 minutes. Table 6.7 below summarizes the results.

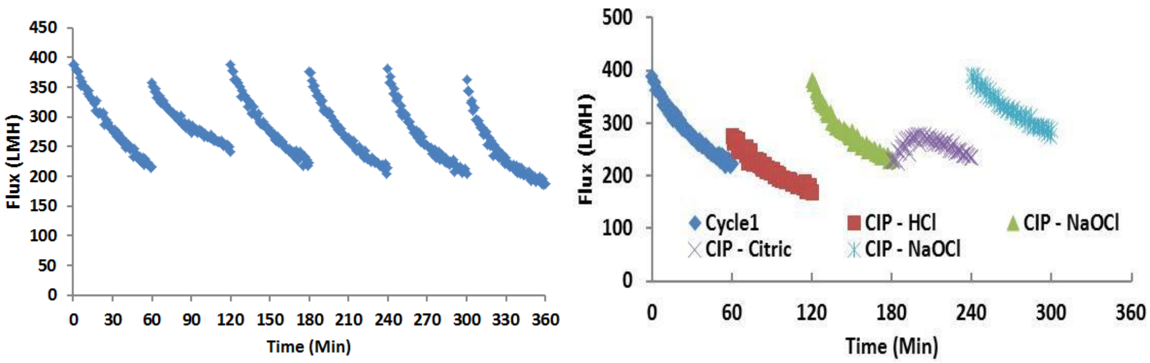
Table 6.7: Flux Recovery after BW/CEB of AAO20 membrane at Flux of 1500 LMH

BW(MQ)/CEB (NaOCl)	*Initial Flux – LMH (J_0)*	*Flux at 30 minutes (J_{30})*	*Flux at 60 minutes (J_{60})*	*Initial Flux after BW/CEB (J_{BW})*	*% Flux Recovery*
Milli Q	227.3	162.3	128	141.3	13
500 ppm (pH = 10.7)	231.1	164.2	122.2	170	44
1000 ppm (pH = 11)	229.2	162.3	124.1	187.2	60
1500 ppm (pH = 11.2)	229.2	170	133.7	194.8	64
2000 ppm (pH = 11.35)	239.7	163.3	111.8	197.7	67
3000 ppm (pH = 11.6)	242.6	179.5	129.9	219.6	80

The flux recovery after backwashing with Milli Q was 13 % and improved after enhanced backwashing with NaOCl to 43 - 80 %, increasing as the dose increased (Table 6.7). These results imply that the UF Anopore ceramic membrane after seawater filtration has a low recovery rate of fluxes even after high backwashing flux. But with the aid of chemicals like sodium hypochlorite, flux recovery improved significantly. Poor recovery of flux after hydraulic backwashing is similar to the study of the Kuzmenko group that found poor flux recovery (5 %) with a fouled UF membrane backwashed with DI water (Kuzmenko et al., 2005).

6.7.3.2 Flux recovery for AAO20 and Metawater Ceramic Membranes after CIP

CIP process involved soaking of AAO20 fouled membrane in sodium hypochlorite solution (3000 ppm) for one hour followed by Milli Q for 5 minutes. To compare the efficiency of sodium hypochlorite, other chemicals like hydrochloric acid (HCl) at pH 2 and citric acid 1% were used under the same cleaning protocol. Figures 6.7 (a) and 6.7 (b) below summarize the results.

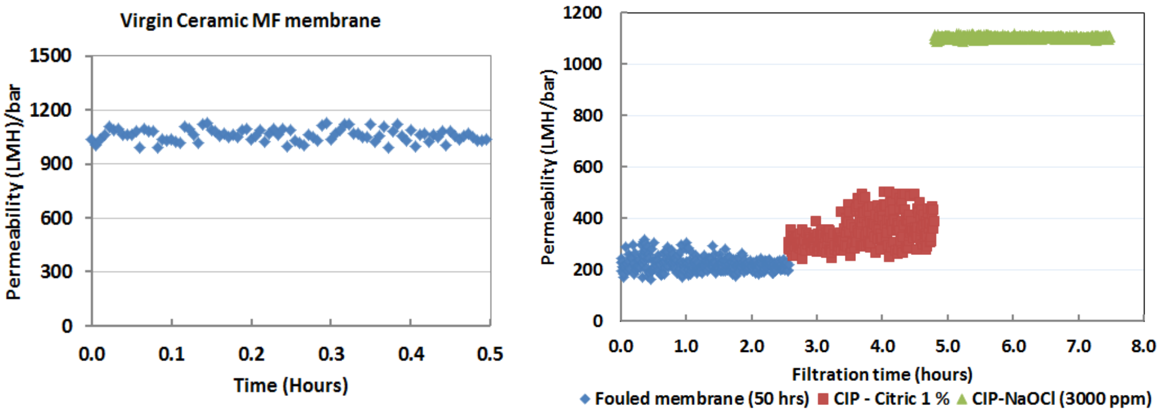


a: CIP of AAO20 membrane with 3000 ppm of NaOCl

b: CIP of AAO20 membrane with different chemicals

Figure 6.7: CIP of AAO20 UF membranes with (a) 3000 ppm of NaOCl and (b) different chemicals

The average flux recovery after CIP with NaOCl was 97% (Figure 6.7 a). Citric acid and hydrochloric acid showed insignificant flux recovery of 31 % for HCl and only 3 % in case of citric acid (Figure. 6.7 b). The pilot scale membrane (Metawater) after being fouled with seawater (50 hours filtration) was cleaned by soaked with citric acid (24 hours), flushed with Milli-Q water (5 minutes) and soaked with sodium hypochlorite (24 hours) and flushed again with Milli-Q water for 5 minutes. The results for the permeability recovery are presented in Figure 6.8 below.



a

b

Figure 6.8: (a) Permeability of the virgin ceramic MF membrane (METAWATER) and (b) Permeability of the fouled ceramic membrane before and after CIP

After 50 hours filtration of seawater, the permeability of the ceramic membrane declined from 1,100 LMH/bar to 220 LMH/bar (80 % decline). When the membrane was soaked in citric acid (1 %), permeability was slightly improved to average value of 345 LMH/bar, which is equivalent to 14 % recovery. However, complete permeability recovery (100 %) was achieved with sodium hypochlorite as shown above (Figures 6.8a and 6.8b). Other studies also found that sodium hypochlorite at pH 10 was very effective for restoration of flux to 100 % compared to other cleaning agents (Raffin et al., 2011). Acids (for chemical cleaning) are used to remove inorganic species and control mineral scaling which is also important for interruption of biofilm growth (Porcelli and Judd, 2010). The results of CIP (above) strongly suggest that the fouling of UF membranes after red sea filtration is mainly dominated by organics rather than inorganic fouling (Figures 6.7 and 6.8).

6.7.4 TEP images Analysis

6.7.4.1 AAO20 membrane fouled, backwashed, enhanced backwashed and chemical cleaned

The fouled membranes before backwashing, after backwashing and enhanced backwashing were analysed using epifluorescence microscopy after staining with alcian blue as described in the methodology. The images showing the membrane surfaces fouled with TEP were critically analysed.

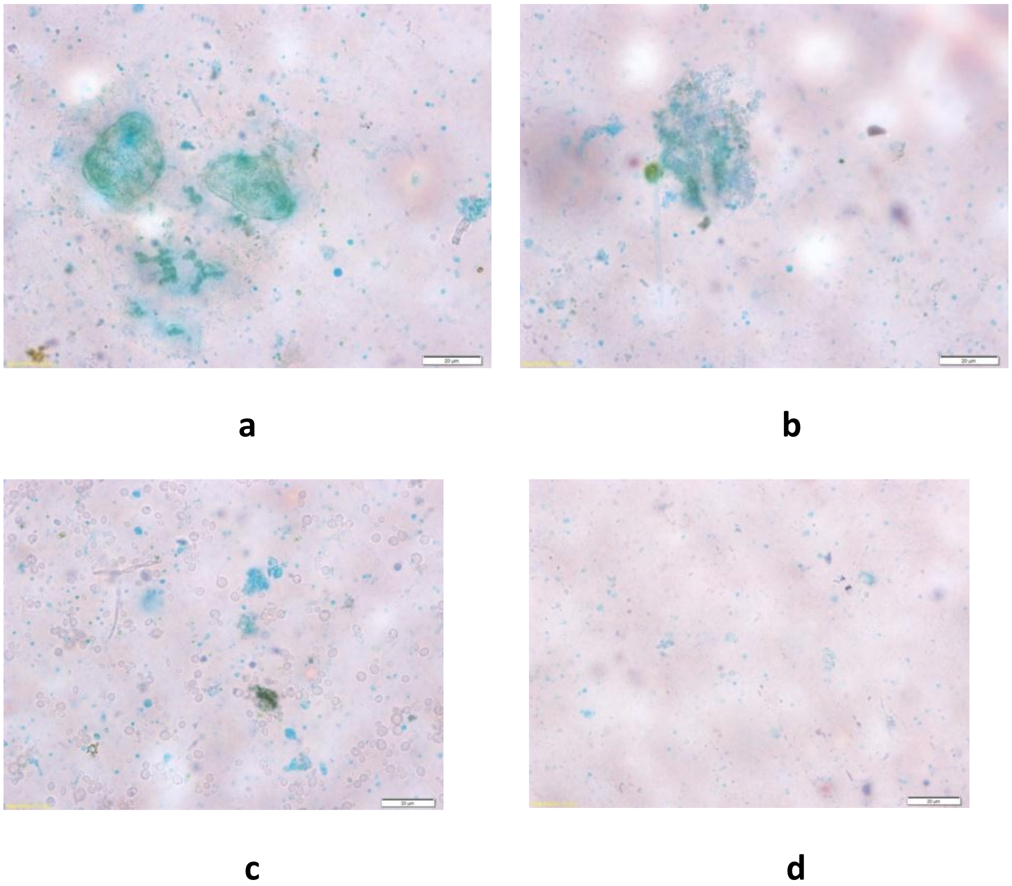


Figure 6.9: TEP on (a) fouled AAO20 membrane, (b) AAO20 Milli Q backwashed membrane, (c) AAO20 after CEB and (d) AAO20 after CIP

TEP were observed in abundance on the fouled membrane surface after Red sea filtration (Figure 6.9 a). Even after hydraulic backwashing at very high flux of 1500 LMH, most of the TEP still remained on membrane surface (Figure. 6.9 b). When CEB and CIP processes were performed on the fouled membrane, most of the TEP dissolved or were broken down into smaller components (Figures 6.9 c and 6.9 d). This is in agreement with other studies that described the ability of NaOCl to decompose NOM into small fractions of organic groups such as aldehydes (Porcelli and Judd, 2010). The membrane surfaces of alumina ceramic membranes are positively charged (Mullet et al., 1997a); and since TEP are strongly negatively charged they interact with the membrane surfaces by electrostatic attractions and strongly bind. Therefore the use of NaOCl at adequate pH for

CEB and CIP breaks the bond between foulants and the membrane surface by electrostatic repulsion so TEP can be released or broken down to small pieces. At very high pH, alumina ceramic membranes become negatively charge and therefore electrostatic repulsion between membrane and TEP is taking place.

6.7.4.2 AAO100 membrane fouled, backwashed, enhanced backwashed and chemical cleaned

Further studies on the fate of TEP after backwashing and chemical cleaning of the membranes were carried out using ceramic anopore MF membranes (AAO1000. The results of the studies are expressed in below figures (Figure 6.10 and Figure 6.11).

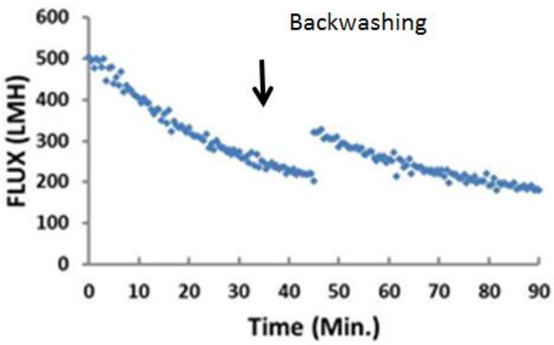
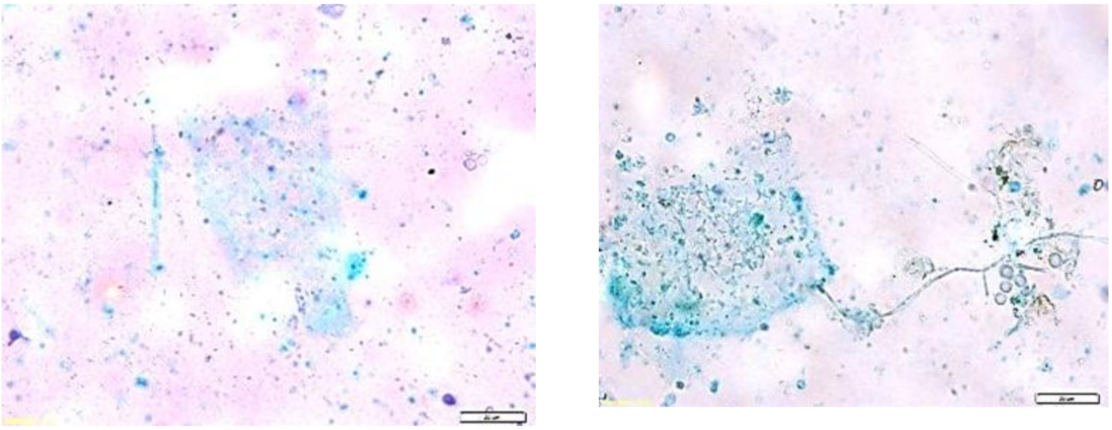
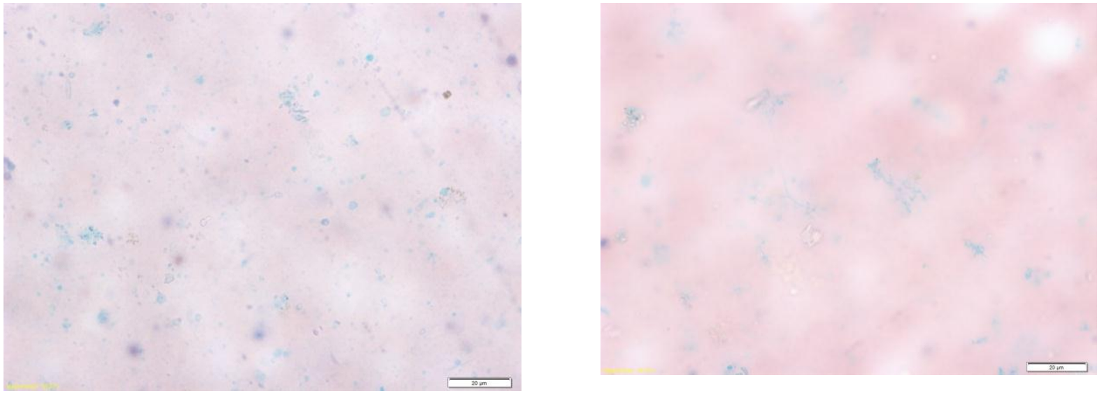


Figure 6.10: Flux decline and recovery for AAO100



(a) **(b)**



(c) (d)

Figure 6.11: TEP images on (a) AAO100 fouled membrane, (b) AAO100 backwashed membrane, (c) AAO100 after CEB with 1500 ppm of NaOCl (pH = 11.2) and (d) AAO100 after CIP with 3000 ppm NaOCl (pH = 11.6)

In a bench scale experiments, backwashing was found to be ineffective with recovery of about 10 % (Figure 6.10). A lot of TEP was found attached on the surface of the AAO100 ceramic MF membrane after one-hour filtration (Figure 11 a). Even after aggressive hydraulic backwashing at a flux of 1500 LMH, TEP was found to be resistant (Figure 11 b). Nevertheless chemically-enhanced backwashing (CEB) and chemical cleaning (CIP) both with sodium hypochlorite of 1500 ppm and 3000 ppm, respectively, removed the TEP on the membrane surface (Figure 11 c and 11 d). These results support the hypothesis that TEP is difficult to remove by hydraulic backwashing alone.

Also, it supports the notion that TEP was responsible for poor recovery of membrane flux after hydraulic backwashing since it can also serve as a matrix for other foulants. The isoelectric point of TEP is at a pH of 3 (Zhang et al., 2008) meaning it is highly electronegative while the Anopore membrane has an isoelectric point at pH of 8 (Figure 6.12).

Therefore, an alumina ceramic membrane possesses a positively charged surface that provides an opportunity for TEP attachment. This means that sodium hypochlorite promoted the detachment of the attached TEP from the membrane surface as shown in the images above. Moreover, the use of coagulation (as discussed in section 6.6.2) introduces positively ions that interact or agglomerate with TEP and prevent membrane fouling.

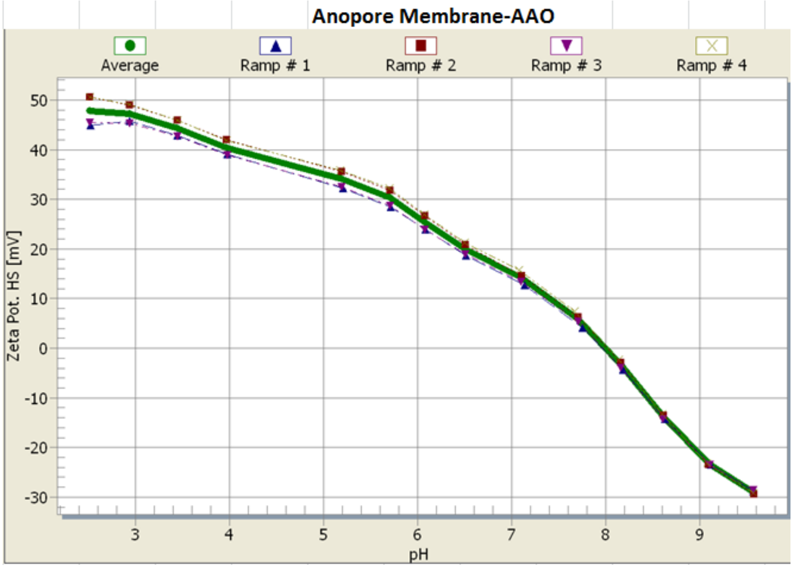


Figure 6.12: Zeta Potential of Anopore Ceramic membrane measured with 1 mM of NaCl electrolyte

6.7.5 Comparison of flux recovery with synthetic seawater and wastewater effluents.

Both synthetic seawater and waste water effluents were filtered through an AAO20 membrane for 1 hour and backwashed with Milli Q at very high flux (1500 LMH) for 2 minutes followed by the second filtration cycle of 1 hour. The filtrations were performed at a constant pressure (0.2 bars) and the flux recoveries were compared (Figure 6.13).

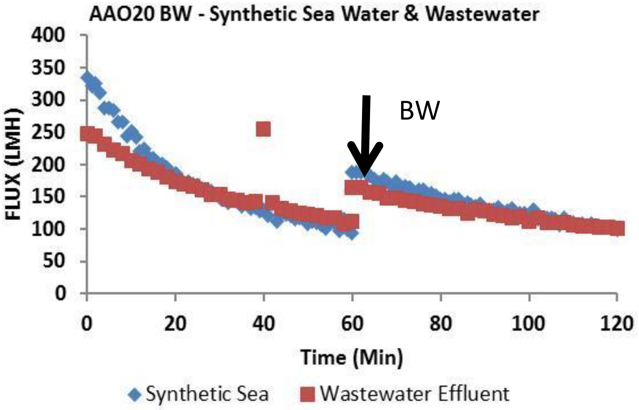
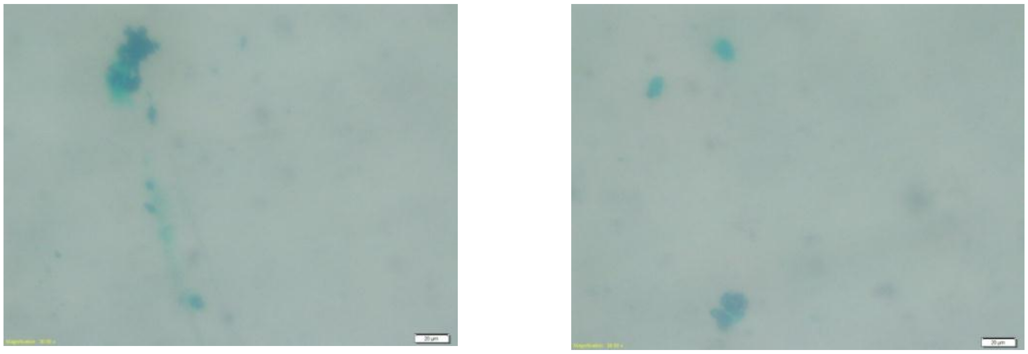


Figure 6.13: Flux Recovery of AAO20 after BW with Milli Q water – Synthetic and Wastewater Effluents

The initial flux of synthetic water was high compared with wastewater effluent probably due to higher concentration of NOM in wastewater effluents compared to synthetic water. However, the flux decline of synthetic seawater was faster than waste water effluents possibly due to availability of high contents of proteins from the synthetic seawater that influence severe fouling. In general, the flux recovery was about 40 % in both feed water after backwashing. Therefore it was 30 % better than seawater. This may be related to the absence of TEP in synthetic seawater and a different type and less TEP in wastewater that is hypothesized to be less sticky compared to TEP from seawater sources.



a: **b:**

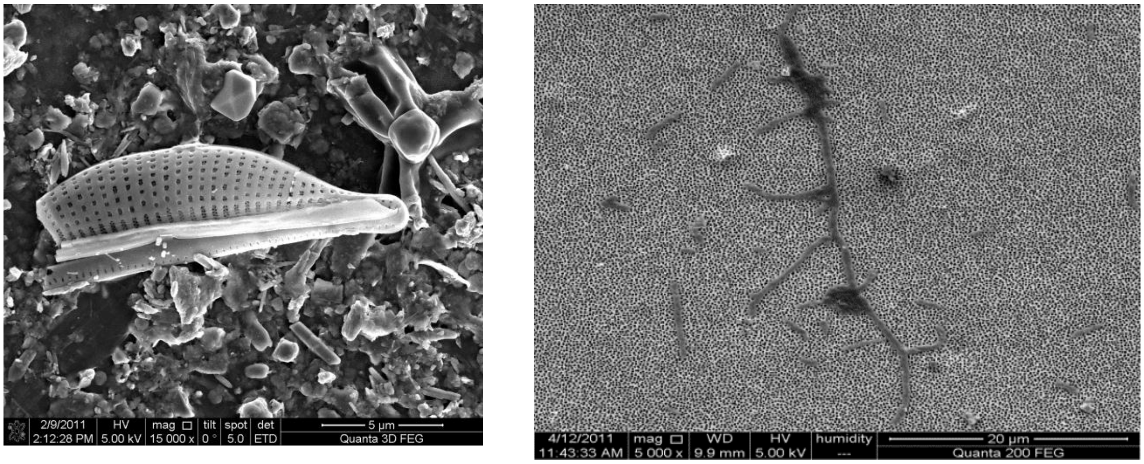
Figure 6.14: TEP originating from wastewater effluent on (a) AAO20 fouled membrane and (b) AAO20 membrane after backwashing.

Nevertheless, the images of the fouled AAO20 membrane with wastewater effluent (Figure 6.14 a) and the backwashed membrane with Milli Q (Figure 6.14 b) showed less

TEP on the membrane surfaces compared with membrane fouled with seawater (Figure 6.9).

6.7.6 SEM, EDX and TEP images of fouled and backwashed membranes

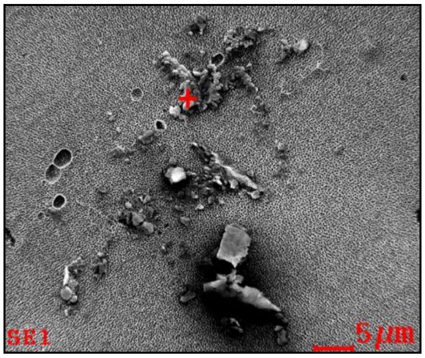
The membrane surface of the AAO20 membrane was analysed after Red Sea filtration to determine what kind of foulants were retained on the membrane. Scanning Electron microscopy (SEM), Energy Dispertive X-ray Spectroscopy (EDX), and Epifluorescence were employed. The results are shown in Figures 6.15 – 6.17 below:



(a) **(b)**

Figure 6.15: SEM images of fouled AAO20 membrane showing (a) diatom and (b) particulates

A diatom was observed on the fouled AAO20 membrane (Figure 6.15 a). Also, some particulates and colloidal matter still remained on the membrane surface after backwashing (Figure 6.15 b). Diatoms and inorganic minerals like iron and silica (Figure 6.15 (a) and Figure 6.16) contribute to the group of particulates and colloidal matter that fouled the membrane.



Element	Wt%
C	03.62
O	36.28
Na	00.28
Al	51.56
Si	01.20
P	02.53
Fe	04.54

Figure 6.16: SEM-EDX image of fouled AAO20 membrane composition of elements

TEP are considered to be responsible for binding these particulates and making backwashing ineffective. The image below (Figure 6.17) shows the diatom surrounded by TEP.

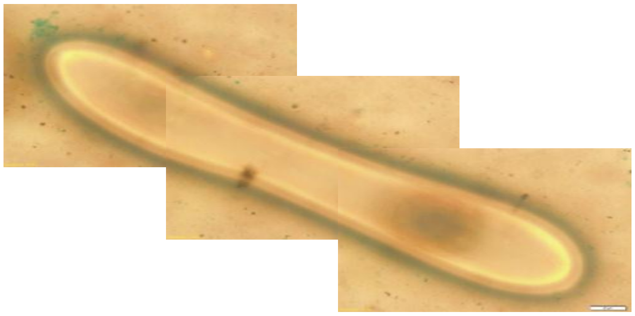


Figure 6.17: Diatom bound to and surrounded with TEP

Silica particulates, diatoms and TEP are possible colloidal foulants that contribute to the flux decline in Red sea water filtration by ceramic membranes.

6.7.7 Flux recovery improvement with coagulation

Red sea water was coagulated with 3 mg/L Fe before filtration through a AAO20 membrane for 60 minutes at an initial flux of 310 LMH. The AAO20 membrane was then turned upside down and backwashed with Milli Q water for 2 minutes at high flux of

1500 LMH before running a second filtration cycle. A control experiment (without coagulation) was done to compare the flux decline and flux recovery after backwashing. The results are tabulated below (Table 6.8).

Table 6.8: Flux decline of AAO20 membrane with/ without coagulation added in Red sea water

	AAO20 with coagulation (3 mg/L Fe)	**AAO20 without coagulation**
Initial Flux, J_0 (LMH)	313.2	311.3
Flux at 30 min, J_{30} (LMH)	288.4	194.8
Flux at 60 min, J_{60} (LMH)	265.5	137.5
Initial Flux after BW- J_{BW} (LMH)	270	154.7
% Flux Recovery after BW	20 %	10 %
% Flux Decline (1st Cycle)	15 %	56 %

It was observed that the use of a coagulant improved significantly the flux decline from 56 % to 15 %. Also flux recovery after backwashing was better (20 %) with coagulation compared with 10 % recovery without coagulation (Table 6.8). The coagulant may affects TEP by two mechanisms: first it acts as a barrier between TEP and the membrane surface and minimizes the contact; and secondly by formation of TEP coagulant flocs that minimize pore blocking and hence flux decline and flux recovery improved. The later mechanism is supported by other studies that found flocculation processes were more effective with iron III chloride than aluminum sulphate in formation of EPS coagulant flocs (Li et al., 2008). The interaction between membrane surface and TEP via electrostatic force is interrupted by the presence of metal ions. Ceramic membranes made up of inorganic metals could be more prone to binding behavior of EPS/TEP and the use of iron a coagulant can neutralize this effect by binding to the iron ions and forming flocs (Zhou et al., 2010) rather than binding to the membrane surface.

6.8 Conclusions and Recommendations

Ceramic microfiltration (MF) membranes achieved an average SDI_{15} value of 2.1 % per min, which pass the requirement for SDI value (< 3) for RO feed. This was further improved to SDI_{15} of 1.9 % per min when inline coagulation at a low dose of 1 mg/L Fe was applied. In addition, bacteria were completely removed by the use of 1 mg/L Fe coagulant. Stable and consistent filtrate turbidity of 0.05 NTU was achieved with and without coagulation despite turbidity fluctuations from seawater. Hydraulic backwashing with Milli Q was ineffective for the Anopore ceramic membrane in terms of flux recovery and TEP removal. TEP were found to be persistent after aggressive hydraulic backwashing that suggest having a high impact (compared to other NOM components) on the low flux recovery of ceramic MF/UF membranes in seawater filtration. Chemical enhanced backwashing (CEB) with sodium hypochlorite showed significant permeability recovery and TEP removal. This study suggests that there is interaction between TEP and colloidal, particulates and elements that make hydraulic backwashing to be ineffective to recover the flux of the fouled ceramic MF/UF membrane. Chemical cleaning with sodium hypochlorite can restore 100 % of membrane permeability of the fouled membranes. Membrane chemical cleaning with citric acid was not effective. TEP dissolved or broke in smaller components after CEB and CIP processes, suggesting that organic fouling with TEP is a dominant fouling mechanism. Coagulation decreases the sticking effect of TEP and improved both flux decline and recovery. Therefore for efficient and smooth operation of ceramic membranes the use of coagulation, even at a lower dose, is recommended. Also coagulant dose optimization based on removal of high molecular weight seawater NOM and flux is required. The use of hot water to backwash the fouled membrane should be considered in future studies to investigate its efficiency on the flux recovery after backwashing.

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CHAPTER 7

7.0 Coagulation Optimization of MF/UF Ceramic membranes Filtration in Seawater based on NOM characterization and Flux maintenance

Chapter is based on

Coagulation Optimization of Ceramic UF Membrane Filtration

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Application of Ceramic Membranes for Seawater Reverse Osmosis (SWRO) Pre-treatment

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7.1 Summary

The use of low-pressure membrane filtration for pre-treatment prior to reverse osmosis is becoming the accepted benchmark for desalination. The combination of chemical coagulation and micro- filtration (MF)/ultra-filtration (UF) is considered to be an effective pre-treatment for seawater prior to reverse osmosis (RO). Ceramic membranes are made of more chemically resistant materials than polymeric membranes which allow for more aggressive operation and cleaning. This part of research aimed to optimize coagulation pre-treatment using Fe (III) chloride prior to microfiltration and ultrafiltration ceramic membranes with a focus on fouling and natural organic matters (NOM) elimination. A constant pressure set up with stirred cells (10 mL) and a pressurized feed water vessel was used for bench scale experiments. Flat sheet ceramic membranes made of amorphous alumina (Aluminium oxide) with a pore size of 20 nm (AAO20) and 100 nm (AAO100), respectively, and polymeric MF and UF membranes (MF PVDF membrane with pore size of 100 nm and Mixed Cellulose Ester (MCE) membranes with a pore size of 25 nm) were used. Red Sea water and synthetic seawater were used as feed waters while iron III chloride was used as a coagulant. A TOC analyzer, UV absorbance spectrophotometer, LC-OCD Model 8 Chromatograph for Organics in Water, and Fluoromax 4 spectrofluorometer were used to analyze feed and permeates water. The fouling of the membrane was assessed by flux decline and increase of membrane resistances. The optimum dose of coagulant for high molecular weight NOM removal was found to be 3 mg/l Fe^{3+} and 4 mg/l Fe for UF ceramic membrane and MF ceramic membrane, respectively. However a low dose of coagulant between 0.5 – 1 mg/l Fe was found to be enough with respect to flux stabilization. The removal of high molecular weight components of NOM (biopolymers and humic substances) increased as the pH decreased. Ceramic UF membranes achieved a high removal of biopolymers ($\geq$ 60 %) and humics (> 50 %) when a coagulant of 3 mg/l of Fe^{3+} was applied at pH 4 and 5. Similar performance was observed for ceramic MF membranes. Therefore, a ceramic MF membrane should be considered as a pre-treatment option prior to RO membranes instead of UF membranes in order to minimize energy cost. Both UF membranes (AAO20 - ceramic & MCE - polymeric) achieved about 20 – 30 % removal of biopolymers but showed poor humic removal without a coagulant. With a coagulant, 50 – 60 % removal of biopolymers was achieved and humic substances removal was boosted to 40–50 % removal. Flux decline was improved with the use of a coagulant resulting in longer filtration cycles. Proteins showed more influence on flux decline than humic substances. Fluorescence Excitation Emission Matrix (FEEM) spectra confirmed the presence of protein- like and marine humic-like organic matter in Red Sea water. In conclusion, coagulation at favourable pH conditions can enhance removal of difficult components of NOM (biopolymers and humic substances) commonly known as a main source of fouling of membranes, while improving flux decline and lowering the frequency of membrane cleaning.

Continuous addition of iron III chloride (0.5 - 4 mg/L Fe) through inline coagulation showed almost complete control of irreversible fouling and reduces reversible fouling after 50 hours of operation, based on 2.5 hours intervals of filtration cycle. Also biopolymers removal improved to some extent based on the dose used and pH. For stabilization of flux a dose of 0.5 - 1 mg/L Fe^{3+} was sufficient. Reduction of high molecular weight NOM is essential for controlling or reducing irreversible fouling.

Therefore coagulation is recommended for smooth operation of ceramic membranes and for provision of low-fouling feed water prior to SWRO membranes.

7.2 Introduction

Seawater reverse osmosis is still an expensive process due to excessive use of energy during operation and later fouling development (Shon et al., 2008). The performance of sea water reverse osmosis (SWRO) membranes is highly dependent on the performance of pre-treatment methods (Profio et al., 2011). Conventional pre-treatment methods are still dominating in desalination (Voutchkov, 2010); however the use of integrated membrane systems incorporating low pressure membranes (LPM) appears to be the best option for SWRO pre-treatments (Vial and Doussau, 2003). The purpose of pre-treatment is to provide better and stable feed quality water to RO membranes (Ericsson and Hallamans, 1994) with less potential of fouling (Huang et al., 2009).

The use of low pressure membranes (MF/UF) in drinking water applications started in the early 1980's while, for sea water pre-treatment, it started at the end of the last century (Vial and Doussau, 2003). Remarkable improvements in membrane materials and operation of reverse osmosis (RO) membranes have been achieved although fouling remains as a major concern (Ma et al., 2007b). Fouling can increase operating costs and significantly shorten the membrane life (Johir et al., 2009). Low pressure membranes are regarded as an ideal option for sea water pre-treatment before RO membranes (Jezowska et al., 2009). The objective of pre-treatment prior to RO is to remove algae, suspended and colloidal particles, to reduce organics and provide better RO feed with less impact on fouling in RO membranes (Duan et al., 2003, Pearce, 2007).

Fouling of SWRO membranes can take place in the form of colloids/particulates, organic, in-organic (scaling) or biological (bio fouling) (Chiemchaisri et al., 2011). Adequate pre-treatments can reduce the risk of SWRO fouling, improving production and reducing frequencies of chemicals uses for membrane cleaning (Pearce, 2007). Normal colloidal and particulate matter, if not well eliminated with pre-treatment, tends to stay on the membrane surface and form cake layer fouling (Vela et al., 2008); while dissolved organic may cause pore blocking which is the worst form of fouling (Huang et al., 2009). Natural organic matter (NOM) also facilitates bio fouling in the presence of bacteria (Bonnélye et al., 2008). Scaling is not a common problem to LPM but is severe problem to high-pressure membranes. Therefore replacement of conventional pre-treatment method with LPM is required in order to provide more a robust barrier prior to seawater desalination.

The advantage of replacing the conventional pre-treatment with low pressure membranes is supported by the fact that conventional pre-treatment uses high dose of chemicals, produces more sludge and has a bigger footprint compared to UF/MF membrane systems (Teng et al., 2003). MF/UF systems provide stable water quality with simple design and operation (Busch et al., 2009). Moreover, MF/UF have become cost competitive to conventional pre-treatment method (Remize et al., 2009). MF and UF pre-treatment prior to RO provides a low Silt Density Index (SDI) value recommended for RO operation whereas conventional pre-treatment systems has failed to maintain SDI below 3 % per min or to remove particles < 10 um (Remize et al., 2009).

Many researchers used SDI as an indicator for RO feed (Remize et al., 2009, Vial and Doussau, 2003, Brehant et al., 2002, Zhang et al., 2006). It was reported that MF and UF membranes can reduce SDI to < 3 % per min and turbidity to < 0.2 NTU (Teng et al., 2003, Zhang et al., 2006). However, NOM removal is independent of SDI value since the SDI depends on particulates removed on 0.45 um filters whereas dissolved NOM can pass through. It was also reported that SDI and MFI failed to predict the fouling for water with high salinity (Hong et al., 2009). The study of (Remize et al., 2009) found that the DOC removal in low pressure membrane was less than the conventional granular media filtration pre-treatment.

NOM removal by UF/MF alone is limited to 5 % (mostly the high molecular weight), but with coagulation better removal can be achieved (Bonnélye et al., 2008). Hybrid system of MF/UF and coagulation reduces the fouling in both MF/UF membranes and RO membranes, improves flux and reduces cleaning frequencies of RO membranes (Pearce, 2007). Besides, pre-treatment through improved coagulation combined with UF membrane can lower turbidity to below 0.5 NTU and remove microbial populations more than 98 % (Ma et al., 2007a). This implies that membrane filtration is superior in terms of pathogen removal compared to conventional treatment (Alspach and Sakaji, 2007).

Alternatively, RO membranes are very sensitive to foulants such as colloids, inorganic scaling and biofouling (Bonnélye et al., 2008). Biofouling is a multistep process and begins after a clean membrane is exposed to micro-organisms, NOM and inorganic foulants (Ma et al., 2007b). NOM provides food to micro-organisms (Pearce, 2007) and promotes both organic fouling and biofouling. Also NOM causes high flux decline (Schäfer et al., 2000). Hence pre-treatment strategies should focus on reducing NOM in order to minimise (bio) fouling (Bonnélye et al., 2008).

Therefore, the efficient use of LPM can be achieved by combining their use with other pre-treatment techniques like coagulation. Coagulant doses of iron III chloride ranging between 1 and 10 mg/l as Fe are commonly used depending on the quality of feed water (Edzwald and Haarhoff, 2011). The coagulation process in a LPM system typically targets colloidal particles and natural organic matter removal (Voutchkov, 2010). The advantages of a hybrid pre-treatment process is to enhance removal of dissolved organics and maintain stable long-term operation of LPM and reduce fouling (Pearce, 2007). Ceramic membranes composed with inorganic materials may be the best option due to high production supported by high flux operation (Heijman et al., 2009). This chapter focuses on the optimization of the coagulation pre-treatment using Fe (III) chloride targeting fouling reduction, improvement of flux (permeability) and removal of organic matter as recommended in the previous chapter.

7.3 Goals and Objectives

7.3.1 Goal

To optimize the coagulation pre-treatment prior to ceramic membrane filtration of seawater by using iron III chloride based on filterability and removal of high molecular weight NOM.

7.3.2 Objectives

- To characterize and assess the influence of the high molecular weight NOM foulants responsible for ceramic membranes fouling by using LC-OCD and FEEM.
- To optimize coagulation processes based on coagulant dose, pH and filterability.
- To control/reduce fouling and improve membrane filterability.

7.4 Materials and Methods

7.4.1 Feed water

7.4.1.1 Red Sea water

Feed water was obtained from Red sea at King Abdullah University of Science and Technology in Thuwal Kingdom of Saudi Arabia. The Table 7.1 below shows the characteristics of the seawater:

Table 7.1: Feed Water Quality – Red Sea

DOC (mg/l)	**UV (cm^{-1})**	**SUVA (L/mg-m)**	**Turbidity (NTU)**	**pH**	**Conductivity (ms/cm)**	**TDS (g/l)**	**Alkalinity (mg/L CaCO3)**
1 – 1.5	0.012–0.02	1.2 – 1.5	0.1– 0.35	8.1–8.3	60 - 70	30– 39	130

The ion composition of Red Sea water is shown in Table 7.2

Table 7.2: Red Sea ionic strength

Ions	**Concentration**	**Ions**	**Concentration**	**Ions**	**Concentration**
Na^{+}	12,470 mg/L	Cl^{-}	22,199 mg/L	Br^{-}	67.8 mg/L
Mg^{2+}	1,436 mg/L	SO_4^{2-}	3,330 mg/L	SiO_2	4 mg/L
Ca^{2+}	527 mg/L	Fe^{2+}	1.0 mg/L	Ba^{2+}	6 µg/L
Sr^{2+}	7.99 mg/L	Cu^{2+}	10 µg/L	Al^{3+}	90 µg/L

7.4.1.2 Synthetic seawater

Synthetic seawater was prepared by dissolving salts in pure water (Milli Q) and stirred intensively with magnetic stirrer. The salts used were sodium chloride 99.99 % pure, calcium chloride dihydrate, magnesium sulfate tetrahydrate, magnesium chloride hexahydrate, potassium bicarbonate, potassium bromide and potassium chloride. The synthetic seawater was then spiked with humic acid and proteins solutions to simulate the seawater NOM. The ionic composition of the synthetic seawater is shown below in Table 7.3.

Table 7.3: Ions concentrations of Synthetic Sea water

Ions	Concentrations	Ions	Concentrations
Na^+	12,503 mg/L	Cl^-	21,992 mg/L
Mg^{2+}	1,436 mg/L	SO_4^{2-}	3,313 mg/L
Ca^{2+}	531 mg/L	$HCO3^-$	160 mg/L
Sr^{2+}	8 mg/L	Br^-	70 mg/L
K^+	368 mg/L		

7.4.2 Humic Acids and Proteins

A humic acid solution was prepared by dissolving 200 mg of the solid stock humic substance (from Aldrich-Sigma Co.) in one litre of pure water while stirring constantly. The solution was then filtered through 0.45 um filters to separate dissolved and particulates humics. A surrogate solution of proteins was derived by dissolving 500 mg of casein bovine milk (from Aldrich Chemical Company) in one litre of pure water. A few drops of dilute hydrochloric acid were added to a warm (50^0 C) stirred solution. The solution was constantly stirred for 15 hours to allow proteins to dissolve properly and then filtered through 0.45 um filters. Both (humic and protein filtered solutions) were measured to determine the DOC concentration by the TOC analyser.

7.4.3 Coagulant

Iron III chloride ($FeCl_3.6H_2O$) obtained from Aldrich- Sigma Company was used as a coagulant.

7.4.4 Membranes

Two types of UF membranes, an Anopore ceramic UF membrane (AAO20) with a pore size of 20 nm, and a polymeric membrane made up from Mixed Cellulose Esther (MCE) with a pore size of 25 nm, were used for bench scale experiments. Also, an Anopore ceramic MF membrane (AAO100) with 100 nm pore size was employed for bench scale experiments. An Alumina ceramic membrane with 0.1 µm pore size from METAWATER Co. Ltd of Japan was used for pilot testing. All membranes are highly hydrophilic.

7.4.5 NOM Characterizations and Fouling Assessment

For NOM characterization, a TOC Analyzer, UV absorbance, SUVA, Fluorescence Excitation Emission Matrix (FEEM), and Liquid Chromatography with Organic Carbon Detection (LC-OCD) were used to detect the organic foulants. Fouling growth was assessed based on flux decline under constant pressure filtration mode.

7.4.6 Experimental Set up

An Amicon stirred cell was employed to conduct the bench-scale experiments. The feed water was put in a pressure vessel, which was supplied by nitrogen gas that could be adjusted to the required pressure. The pressurized feed water was passed through the membrane placed in the stirred cell. The permeate water was collected in a beaker placed on a digital balance that measures the weight of the permeate water. The balance was connected to a computer and with the help of software the data from the balance were recorded at fixed time intervals. The layout of the set-up is shown in the Figure 7.1 below:

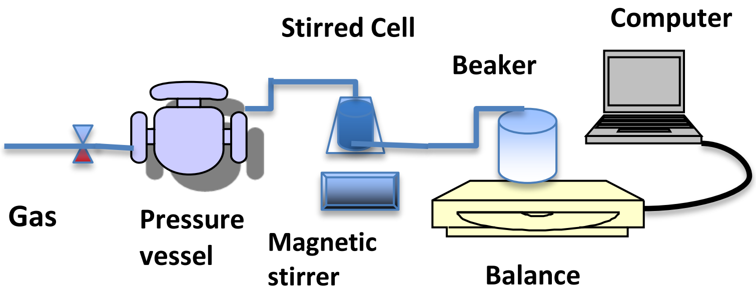


Figure 7.1: Schematic Layout of Amicon Stirred Cell

The pilot plant from KWR (Netherlands), equipped with ceramic microfiltration membrane from METAWATER (Japan), was used to conduct the experiments (Figure 7.2). The pilot was operated at constant flux mode and the system is equipped with a backwashing vessel and 4 bar nitrogen gas that is used for operation and air flushing. One cycle of filtration is composed of filtration, backwashing, air flushing and forward flushing. Filtration cycles of 2.5 hours were adopted for initial experiments. An aggressive backwashing flux of 1800 LMH for 15 seconds was applied for regular membrane hydraulic cleaning. This was followed by air flushing of 4 bars for 10 seconds and forward flushing of 300 LMH for 40 seconds to remove entrapped air. Sodium hypochlorite (3000 ppm), citric acid (1 %) and sodium hydroxide (0.1 M) were used for chemical cleaning (CIP) to restore the membrane permeability.

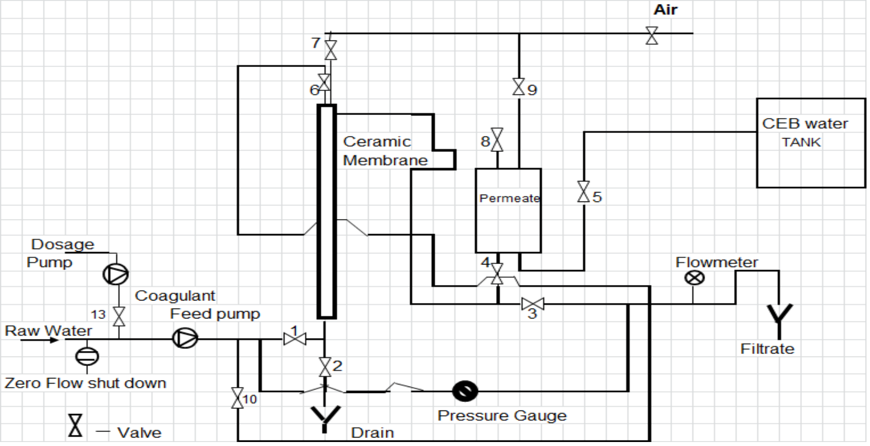


Figure 7.2: Layout of the Ceramic MF Pilot Plant

7.4.7 Coagulation protocol

7.4.7.1 Bench-scale coagulation protocol

The stock solution was prepared by dissolving 4.84 g of Iron III chloride in 500 ml of pure water. This is equivalent to 2 g/l of Fe^{3+} coagulant. Two litres of seawater were collected and spiked with required coagulant dose from the stock solution (ranged from 0

– 10 mg/L Fe) and placed in a jar test unit (Phipps & Bird Stirrer) for rapid mixing. The time set for rapid mix was 45 seconds at intensity of 300 rpm.

7.4.7.2 Pilot-scale coagulation protocol

A stock solution of $FeCl_3.6H_2O$ (ranging from 60.5 - 484 mg/L, depending on dose required) was prepared and placed in the dosing tank. The coagulant (iron III chloride) was then dosed in-line continuously at a dosing rate of 40 mL/minute to the feed water operated at 60 L/h to introduce an equivalent dose of 0.5 - 4 mg/L Fe to seawater. The pilot plant is equipped with internal static mixer prior to ceramic membrane to facilitate coagulation process.

7.5 Results and Discussions

7.5.1 NOM Characterization of Red Seawater by using LC-OCD

The composition of Red Sea water in terms of NOM was characterized by using LC-OCD. Table 7.4 below shows the representative NOM fractions of Red Sea water.

Table 7.4: Composition of NOM in Red Sea water

DOC (mg/l)	***Biopolymers (ppb)***	***Humics (ppb)***	***Building blocks (ppb)***	***Neutrals (ppb)***	***Acids (ppb)***
1.28	162	315	216	576	9
% Composition	12	25	17	45	1

Biopolymers contribute 12 % of the dissolved organic carbon (DOC) while the humic fraction contributes approximately 25 % of DOC of Red Sea water. Low molecular weight neutrals contribute more than 50 % of NOM in seawater. In order to understand the efficiency of the UF membrane and coagulant in NOM removal, the samples of permeate of AAO20 and MCE membranes were examined to determine NOM removal based on NOM fractions with and without coagulation. The details of the results are described in the subsequent sections.

7.5.2 Flux maintenance and NOM components removal with and without coagulation by UF membranes

7.5.2.1 Comparison of Flux decline and NOM removal: MCE membrane vs. AAO20 membrane

The Anopore UF ceramic membrane (AAO20) with average pore size 0.02 um and Mixed Cellulose Ester (MCE) with average pore size 0.025 um were employed to compare the efficiency of ceramic membranes in terms of flux decline and NOM removal. Both membranes were tested with and without coagulation and the removals of high molecular weight NOM were compared. The conditions for coagulation were described in section 7.3.7. The results for LC-OCD and flux decline are shown below (Figure 7.3):

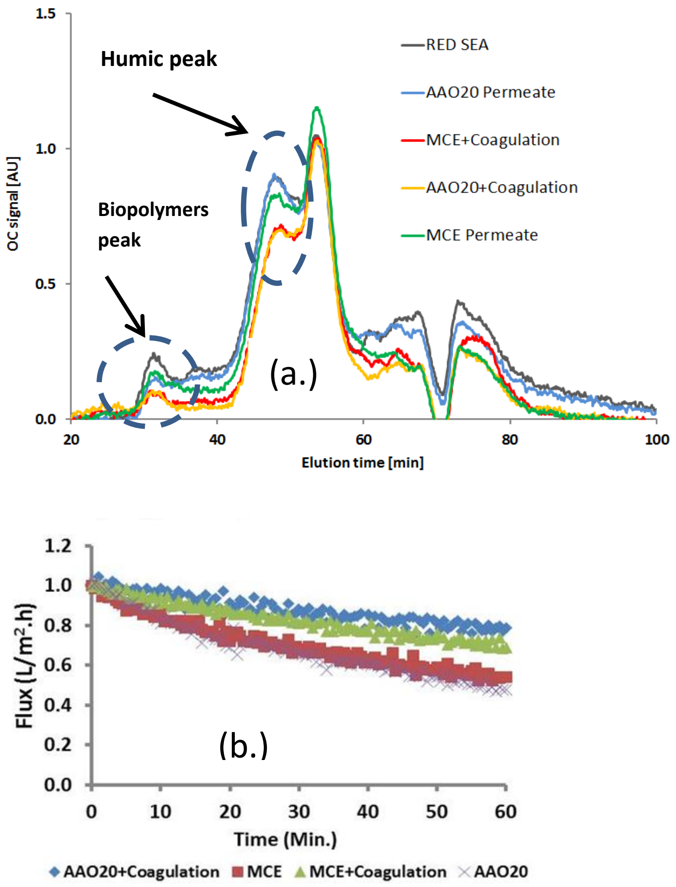
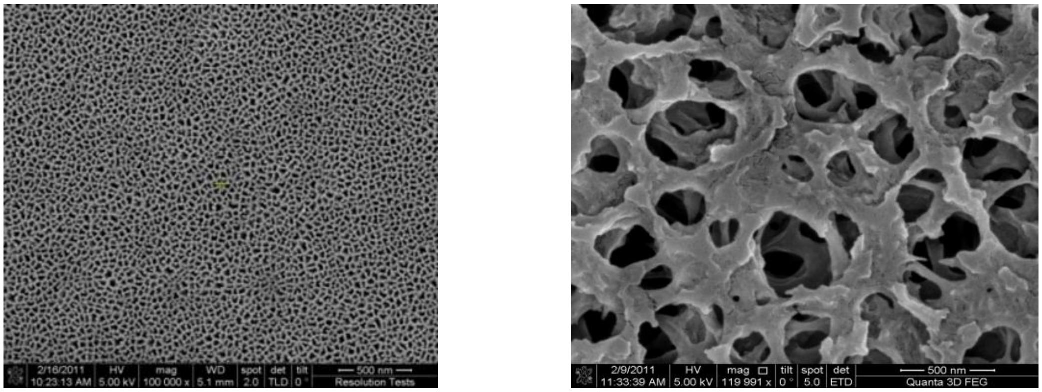


Figure 7.3: (a) OCD chromatograms and (b) Flux declines of seawater filtration with AAO20 and MCE membranes with and without coagulation (4 mg/L Fe)

The Ceramic UF Anopore membrane (AAO20) showed about 25 % removal of biopolymers and negligible humic substances removal without coagulant. While UF MCE membrane achieved 20 % removal of biopolymers and < 5 % removal of humic substances. The combination of UF membranes with coagulation (4 mg/l Fe) improved the removal of biopolymers to 60 % (AAO20) and 50 % (MCE) and from none (without coagulant) in case of humic substances to 45 % with coagulant (Figure 7.3 a). Humic acid and fulvic acid have lower electrical charges in sea water and can penetrate into MF and UF membranes, so their removal depends on effectiveness of the coagulation process prior to membrane filtration (Duan et al., 2009). The AAO20 ceramic membrane with coagulation performed better in terms of high molecular weight NOM removal as well as flux decline compared to MCE membrane. Ceramic membranes (AAO20) combined with 4 mg/l Fe^{3+} coagulant as Fe at an initial flux of 600 L/m^2h showed improvement of flux decline from 50 % without coagulant to 20 % with coagulant after 1-hour filtration. Alternatively, the polymeric membrane (MCE) under the same conditions showed less improvement of flux decline (from 50 % without coagulant to 30 % with coagulant) compared with the AAO20 membrane (Figure 7.3 b). This could be ascribed to the nature of pores, which are more homogeneous and cylindrical in shape in case of the AAO20 membrane and inhomogeneous in case of the MCE as shown by SEM images in Figures 7.4 (a) and 7.4 (b). However, these results show that there is not much statistically significant difference between the ceramic and polymeric membranes materials for the UF application with regard to flux decline and high molecular weight NOM removal.



a **b**

Figure 7.4: SEM images of (a) AAO20 membrane and (b) MCE membranes

A further study was carried out in order to understand which portion of NOM between biopolymers and humic substances is more influential in terms of membrane fouling. Synthetic seawater, which is free from TEP, was employed and the detail of the study is explained in below section.

7.5.3 Influence of Proteins and Humic substances for Flux decline in AAO20 membranes

The synthetic seawater was first mixed with humic alone to the concentrations of 1.3 mg/L, then protein alone (1.3 mg/L) and finally spiked with both protein and humic to the concentrations of 1.12 mg/L. All concentrations were confirmed by TOC analysis. The results of flux decline experiments showed that proteins have a stronger influence on flux decline than humic substances as shown by Figure 7.5. The flux decline with feed water spiked with humic substances alone was 27 % after one hour of filtration onto AAO20 membrane. About 80 % flux decline was observed with protein alone and 65 % decline when both protein and humic substances were used in equal proportion. This suggests that the biopolymers portion (i.e. proteins) plays a prominent role in flux decline in ceramic membranes compared with other NOM components. Protein particles are more susceptible to foul the MF/UF membranes by both mechanisms of pore blocking and cake formation that are attributed to the size of protein particles (> 20,000 Da) that are greater than humic substances particles (1000 – 20000 Da). These results agree with the work of (Campinas and Rosa, 2010) who showed that humic acid has less flux decline compared to extracellular organic matter (EOM) for a UF membrane.

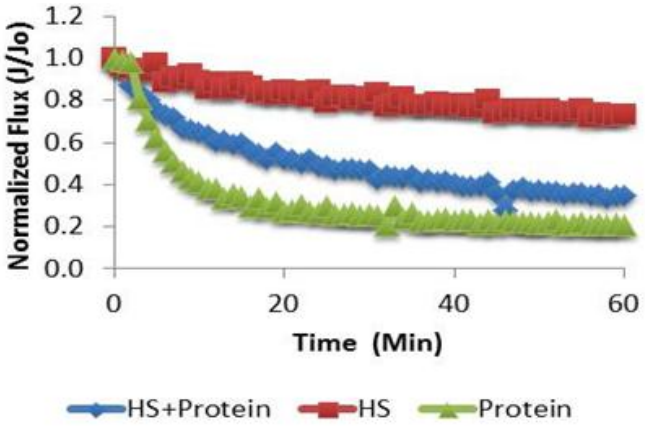


Figure 7.5: Influence of high molecular weight NOM components on Flux decline of AAO20 ceramic membrane (Initial Flux 350 LMH) using Synthetic seawater

Protein is a part of biopolymers, which can be also analysed with FEEM spectra in parallel with humic-like substances. A Fluoromax-4 Spectrofluorometer was employed for specific analysis of protein-like and humic-like organic matters available in both seawater and synthetic seawater before and after membrane filtration using UF Anopore ceramic membranes (AAO20) as described in section 7.4.4 below.

7.5.4 Characterizations of NOM by using Fluorescence Excitation Emission Matrix (FEEM): *Analysis of Red Sea water and Synthetic seawater*

A Fluoromax-4 Spectrofluorometer was employed to understand the presence and rejection of protein-like and humic-like components of NOM from Red sea and synthetic seawater before and after coagulation. FEEM in the presence of humic substances and proteins showed two peaks. These peaks are described as humic-like and protein-like organic matters. In a seawater marine humic-like peak is defined at an excitation/emission range of 310-330/400-420 nm and marine protein-like peak are found at an excitation/emission range of 270-280/300-350 nm (Salinas, 2011). However, for a synthetic seawater spiked with humic substances, the humic-like peak falls at an excitation/emission rage of 237-260/400-500 as described by (Henderson et al., 2009).

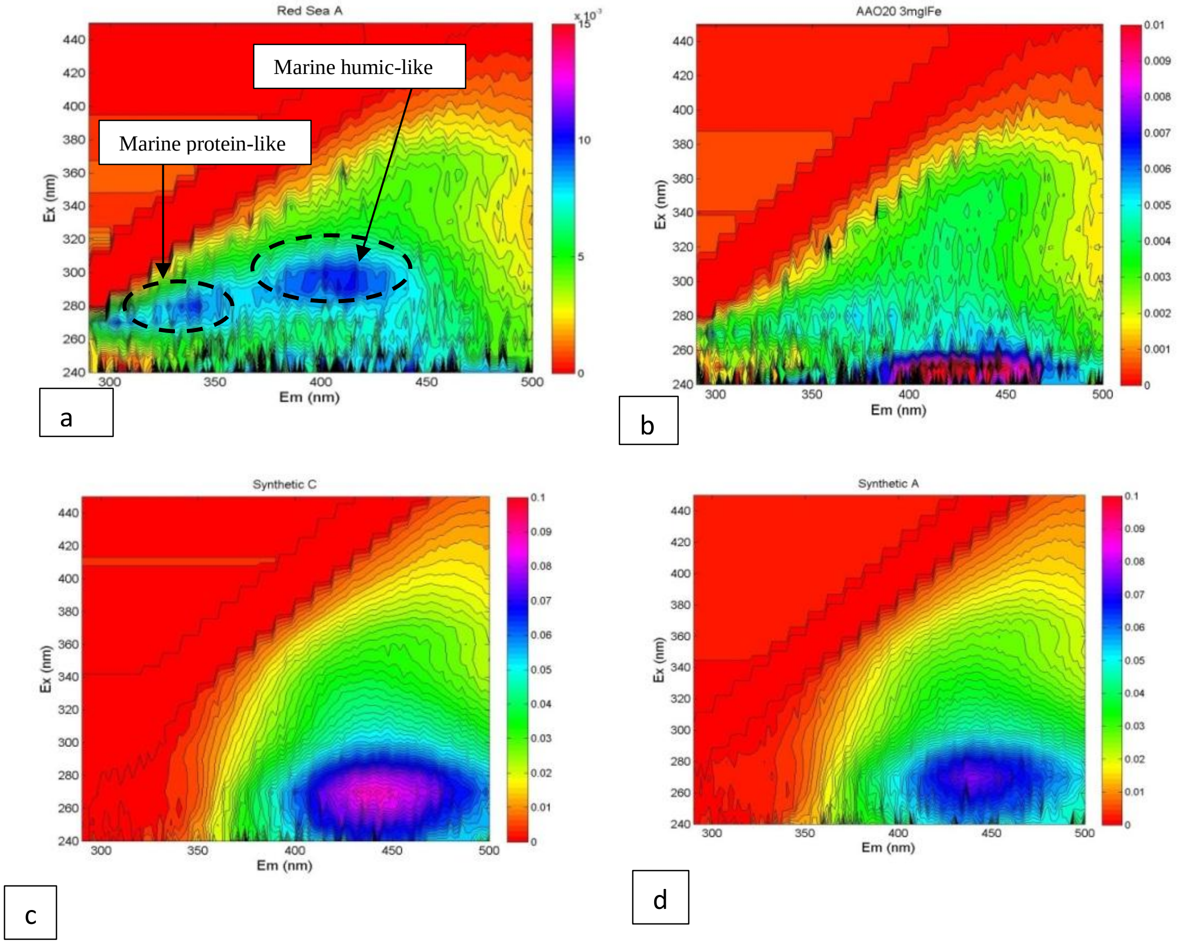


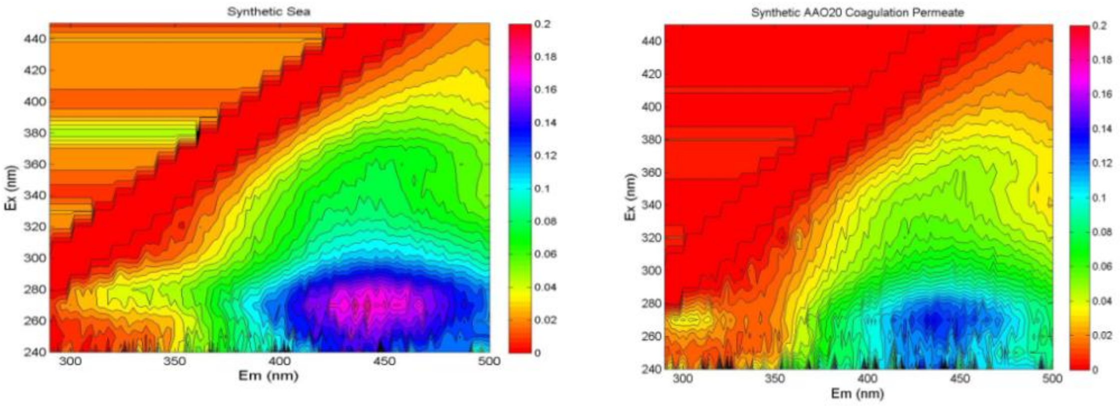
Figure 7.6: FEEM spectra for (a) Seawater, (b) AAO20 Seawater coagulated Permeate with 3 mg/L Fe, (c) Synthetic seawater spiked with 1.5 mg/L Humic substances and (d) AAO20 Synthetic seawater coagulated permeate with 4 mg/L Fe.

Figure 7.6 (a) above confirms the presence of marine humic-like and marine protein-like organic matter in Red Sea water. After coagulation with 3 mg/l as Fe, the peaks for marine protein-like and marine humic-like decreased significantly as shown by Figure 7.6 b. These results suggest that the AAO20 membrane with the aid of coagulation rejects significant amounts of marine humic and protein organic matters and this explains why a low flux decline was found after coagulation from previous data. Also these results correlate with LC-OCD results that show significant removal of the biopolymers fractions (which include proteins) and humic substances after the use of the coagulants. Furthermore, synthetic seawater was spiked with humic acid to the concentrations of 1.5 mg/l followed by coagulation with 4 mg/l Fe at a mixing intensity of 300 rpm for 45 seconds and filtered by the AAO20 membrane revealed significant results in terms of humic substances rejection. The results from Figure 7.6 c (synthetic seawater feed) and Figure 7.6 d (AAO20 permeate of synthetic seawater permeate after coagulation) showed 87 % rejection of humic substances (Table 7.5). These results suggest that in the absence of interaction and competition of other NOM constituents, humic substances removal might be increased with coagulant application.

Table 7.5: FEEM for Synthetic sea water and AAO20 permeate after coagulation (4 mg/l Fe)

	Ex/Em	***Intensity***	***% HS Rejection***
Synthetic Sea + HS (1.5 mg/l)	270/440	0.0855	
Permeate after coagulation	260/446	0.011	87

To demonstrate the influence and competition of other NOM components, synthetic seawater was spiked with humic substances and proteins to a concentration of 1.2 mg/L and 0.3 mg/L, respectively. The results of FEEM are shown in Figures 7.7 (a) and 7.7 (b) with a summary of results shown in Table 7.6.



(a) **(b)**

Figure 7.7: FEEM spectra of (a) Synthetic Seawater with 1.3 mg/L of Humic substances and 0.2 mg/L Protein (b) AAO20 Permeate of Synthetic seawater

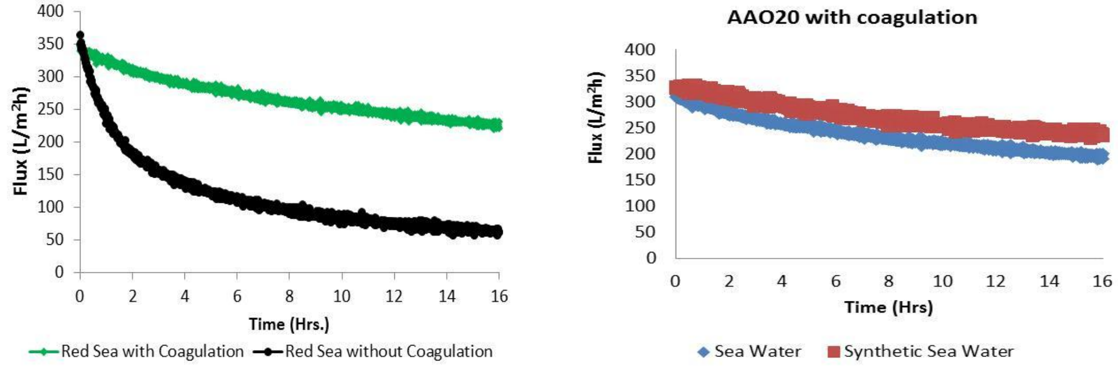
Table 7.6: FEEM peaks for Synthetic Sea water and AAO20 permeate after coagulation

	Humic-like (Ex/Em)	*Intensity*	*Protein-like (Ex/Em)*	*Intensity*
Synthetic Sea water	270/442	0.2	280/338	0.049
AAO20 permeate from coagulated synthetic seawater	270/444	0.12	270/334	0.021

The summary of the results in Table 7.6 showed that humic substance fluorescence rejection by AAO20 with coagulant (3 mg/L Fe) was about 40 % while protein rejection of fluorescence was about 43 %. The rejection of humic substances was probably affected by the presence of proteins since less rejection of humic substances was observed when both humic substances and proteins were added to the synthetic sea water compared with addition of humic substances alone.

7.5.5 Influence of long term filtration on Flux decline and improvement of membrane filterability with and without coagulation

Synthetic seawater (Table 2) was spiked with humic acid (0.7 mg/L) and a protein solution made up from bovine milk (0.6 mg/L) to imitate the concentration of dissolved organic matter (DOC) of Red Sea water ≈ 1.2 mg/L. A coagulant concentration of 3 mg/l as Fe was used and extended filtration (16 hours) was done. The results of flux decline were compared with Red Sea water as shown below:



(a) **(b)**

Figure 7.8: AAO20 Long terms filtrations (a) Seawater with and without coagulation and (b) synthetic seawater compared to seawater

Figure 7.8 a showed that with applied coagulation the flux decline after 16 hours of operation is equivalent to the flux decline achieved after one hour when Red Sea water filtered through AAO20 membrane without coagulant. Also, the results showed that the flux decline was 40 % and 30 % with Red Sea water and synthetic sea water after 16 hours of filtration for AAO20 combined with 3 mg/L as Fe coagulant, respectively (Figure 8 b). Hence the benefits of the coagulation process is not limited to the removal of high molecular weight NOM but is extended to longer filtration cycles which means less frequent use of chemicals for membrane cleaning. The coagulation process promotes longer life of the membrane with improved permeability and minimum fouling (Zeng et al., 2009). The advantages of operating ceramic membranes with coagulation were obvious. Therefore, for more economic and affordable operations using coagulation pre-treatment, optimization of the process is required.

7.5.6 Coagulation optimization based on Coagulant dose: Bench-scale experiments

7.5.6.1 Ceramic UF membrane (AAO20)

The use of coagulant showed an improvement in removing the high molecular weight fractions of NOM (biopolymers and humic substances) known to be the main fouling architects in membranes. To make it cost effective the coagulant dose needs to be optimized. The coagulant dose optimization experiments were carried out on the AAO20 under the previous described coagulation conditions (t = 45 seconds and 300 rpm). Serial doses of coagulant (1, 2, 3, 4 and 10 mg/l Fe) were used to determine the optimum dose. The initial flux was maintained at 350 LMH for all experiments. Samples (feed and permeates) were collected and measured by LC-OCD and the flux decline was monitored as shown below in Figure7.9:

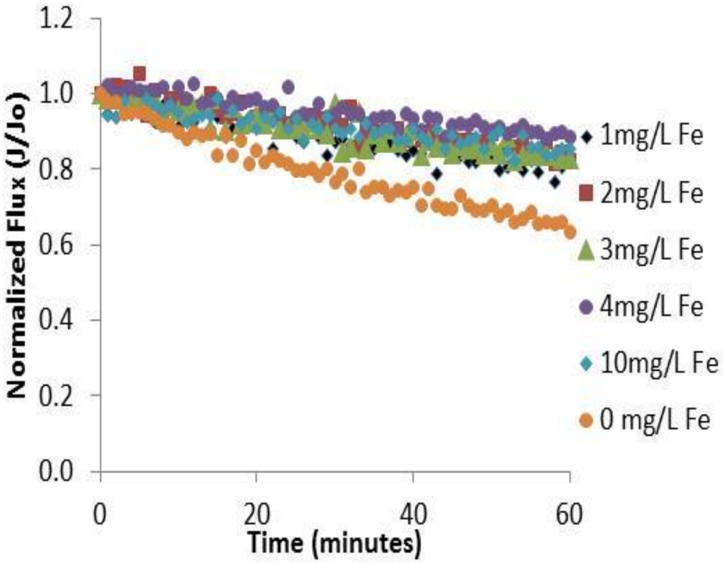


Figure7.9: Flux decline on AAO20 membranes at different coagulant doses (Jo ≤ 350 LMH).

Table 7.7 below shows the removal of high molecular weight NOM (biopolymers and humic substances) at different doses of iron III coagulants.

Table 7.7: Coagulant dose optimization for the AAO20 membranes

AAO20 + Coagulant (mg/L Fe)	Biopolymers (ppb)	Humic Substance (ppb)	DOC (mg/L)	pH
Seawater	156	445	1.1	8.1
0 (Membrane alone)	115	440	1.06	8.1
1	88	326	1.05	7.8
2	82	312	1	7.2
3	60	299	0.89	6.9
4	64	292	0.9	6.6
10	49	222	0.81	5.8

High molecular weight organic matter removal was enhanced by the use of coagulation prior to the AAO20 membrane filtration. Biopolymers removal was > 40% for all coagulant doses (1-10 mg/l Fe). This was increased to ≥ 60% with a coagulant dose ≥ 3 mg/l Fe^{3+} as shown by the results in Table 7.7. No significant variation was observed in terms of high molecular weight fractions of NOM removal between 3 – 10 mg/l of Fe coagulant dose. Hence, the optimum dose for high molecular weight NOM removal was found to be 3 mg/l Fe^{3+}. The optimum dose with respect to flux improvement is 1 mg/l Fe. An increase in the coagulant dose decreases the pH of feed water as shown in Table 7.7. Flux decline was maintained at 15 % after 1 hour of filtration despite using high dose (10 mg/l of Fe) or low dose (3 mg/l of Fe) coagulant. The flux decline becomes worse when no coagulant was used (37 %). This again indicates that pre-treatment of sea water with MF/UF combined with coagulation or adsorption can reduce fouling in RO (Brehant et al., 2002) due to reduction of the high molecular weight fraction of NOM. The improvement of the flux decline after coagulation is attributed to the substantial removal of biopolymers and humic substances (Figure 7.9). This implies coagulation plays an important role in fouling reduction (Huang et al., 2009).

7.5.6.2 Ceramic MF membrane (AAO100)

The coagulant dose based experiments were carried out on the AAO100 ceramic membranes. Serial doses of coagulant (0, 1, 2, 3, 4, 6 and 10 mg/l Fe) were used to determine the performance of the ceramic membrane under different coagulant doses. The initial flux was maintained at 500 LMH for all experiments and samples (feed and permeates) were collected and measured for LC-OCD, and the flux decline was monitored as shown by the results in Figure 7.10 below:

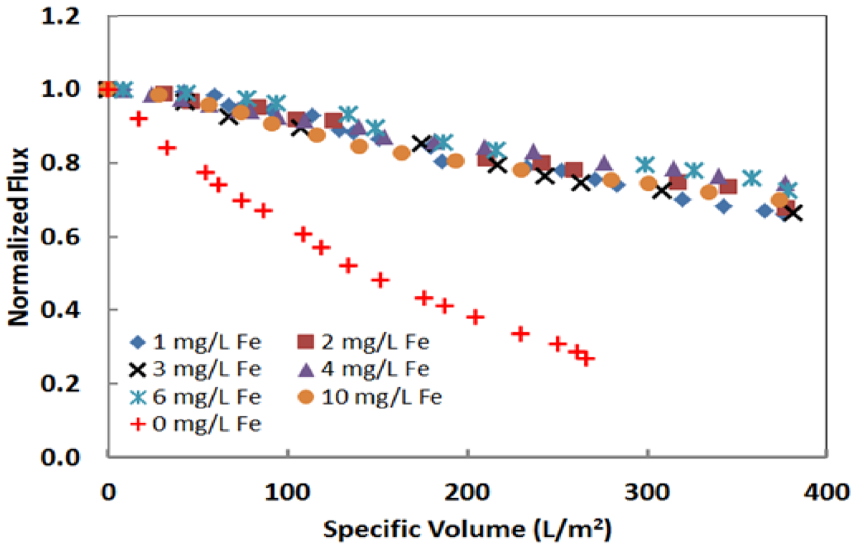


Figure 7.10: Flux decline on AAO100 membranes at different coagulant doses (Jo ≤ 500 LMH).

The results show that a low dose of 1 mg/L of iron coagulant improved the membrane resistances with no significant difference with high dose of 10 mg/L Fe. This confirms that for smooth operation of a ceramic membrane, a low dose of 1 mg/L is adequate. Furthermore, characterization of NOM components (focusing on high molecular weight NOM) from seawater and permeates of different coagulant doses were analyzed with LC-OCD, and the results are presented in Table 7.8 below.

Table 7.8: Coagulant dose optimization of the AAO100 membranes

AAO100 + Coagulant (mg/L Fe)	**Biopolymers (ppb)**	**Humic Substance (ppb)**	**DOC (mg/L)**	**pH**
Seawater	143	422	1.05	8.2
0 (Membrane alone)	99	389	1.05	8.2
1	93	365	0.91	8.0
2	77	334	0.94	7.7
3	83	350	0.89	7.2
4	75	268	0.78	6.9
6	66	290	0.88	6.6
10	65	255	0.78	6.2

Biopolymers removal was 31 % with the membrane alone without coagulant, which was slightly improved to 35 % with a low dose of 1 mg/l Fe^{3+} coagulant. The removal increased to 48 % and 55 % with doses of 4 and 10 mg/l Fe^{3+}, respectively. Humic substances removal increased from 8 % (without coagulant) to 40 % when a high dose of 10 mg/l Fe^{3+} was used (Table 7.8). A low dose of 1 mg/l Fe^{3+} coagulant improved removal of humic substances to only 14 % as shown by the results in Table 7.8 while the overall DOC removals for all coagulants were not significant. However, the coagulation process improved flux decline significantly regardless of the amount of coagulant dose (Figure 7.10). Thus improvement of the flux decline after coagulation was achieved even with a low dose of iron III chloride (1 mg/l Fe). Also, NOM components removal increased with an increase of coagulant dose although no huge impact was observed on flux decline related to NOM removal. Therefore the optimum dose with respect to high molecular weight NOM removal for ceramic MF membrane is 4 mg/l Fe and 1 mg/l Fe with respect to flux maintenance.

7.5.7 Coagulation Optimization based on coagulant pH: Bench-scale experiments

7.5.7.1 AAO20 Ceramic UF membranes

Changes in pH have a significant influence on the coagulation process with regards to flux decline and NOM removal. To access the influence of pH in the coagulation process, the optimum dose obtained in Section 7.4.6.1 (3 mg/l Fe) was used to determine the optimum pH by using AAO20 membranes. The coagulation conditions remained the same and hydrochloric acid (37 % HCl) and sodium hydroxide (1 M NaOH) were used to adjust the pH of feed water. Initial flux of feed water filtration was set to 350 L/m^2.h. Samples of feed water and permeates were collected for LC-OCD measurements and the flux decline was monitored by measuring the change in weight per unit time of permeate. The results for LC-OCD and flux decline under different pH conditions are shown in Figure 7.11 and Table 7.9 below:

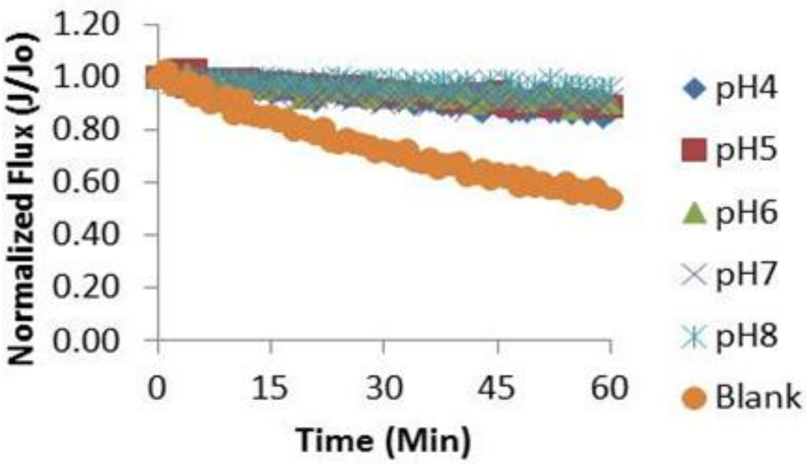


Figure 7.11: Flux decline based on different pH at the same coagulant doses (3 mg/L Fe) and Initial Flux ≤ 350 LMH

Table 7.9 below shows the removal of high molecular weight organic matter after coagulation with a dose of 3 mg/L Fe at a different pH levels.

Table 7.9: pH optimization for coagulant of 3 mg/L as Fe

	DOC (mg/l)	Biopolymers (ppb)	High mwt HS (ppb)	% Removal Biopolymers	% Removal H.S
Red Sea	1.45	168	434		
Without coagulant	1.38	140	407	17	6
pH 4	1.01	60	185	64	57
pH 5	1.03	67	199	60	54
pH 6	1.16	85	254	49	41
pH 7	1.13	97	260	42	40
pH 8	1.13	86	297	49	32

The overall DOC removal was observed to be about 5 % without coagulant and improved to about 25 % after coagulation. The removal of high molecular weight NOM fraction was found to increase as the pH decreases with optimum results obtained at pH of 5 (Table 7.9). However, the highest removal of biopolymers and humic substances was achieved at pH 4. Flux decline showed good performance at pH 7 and pH 8 (Figure 7.11). This is attributed to the formation of hydrolysis species of iron that adsorb high molecular weight NOM at pH 7 - 8 that formed a porous cake layer with good filterability. Alternatively, at low pH, the formation of precipitate of organic and iron complexes might block the membrane pores, which leads to more flux decline at low pH. The study conducted by (Duan et al., 2002) found that effective coagulation was observed at high pH (9-10) when saline water containing humic acid was coagulated with aluminium sulphate compared with coagulation of a surface water. This leads to the conclusion that the chemistry of the feed solution affects the mechanism of coagulation. Also pH impacts the surface charge of the ceramic membranes. The isoelectric point of alumina is around pH 8-9 (Mullet et al., 1997, Huisman et al., 1998), so a decrease of pH progressively increases the positive surface charge.

In general, coagulation at favorable pH boosted removal of high molecular weight fractions of NOM. These results are supported by several other studies (Vial and Doussau, 2003, Bonnélye et al., 2008) that found NOM removal to be around 5 % (mainly from high molecular weight fractions) after MF/UF membranes filtration, but with enhanced coagulation more removal can be achieved.

7.5.7.2 AAO100 Ceramic MF membrane

Based on optimum dose of 4 mg/L Fe coagulant obtained for AAO100 membrane with respect to NOM removal; the optimum pH for coagulation based on optimum dose iron III chloride was determined by bench scale experiments under constant pressure mode. The study was focused on removal of high molecular weight NOM (biopolymers and humic substances). The DOC level of Red Sea water used to conduct experiments was 1.12 mg/L, including a biopolymers content of 0.143 mg/L and humic substances of 0.39 mg/L, as measured by LC-OCD. Figure 7.12 below shows the results for pH optimization with 4 mg/L Fe coagulant applied in seawater.

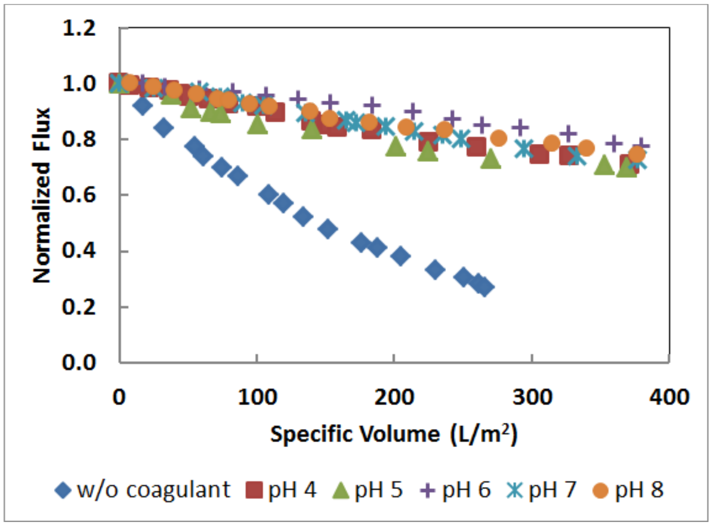


Figure 7.12: Flux decline of AAO100 membranes at different pH conditions with 4 mg/l Fe coagulant

Table 7.10 below shows the effect of pH in seawater coagulation in terms of high molecular weight NOM removal at different pH levels.

Table 7.10: Effect of pH in seawater coagulation (4 mg/L Fe) in terms of NOM removal in AAO100 membrane flitration

	DOC (mg/l)	Biop. (ppb)	Humics (ppb)	% Removal DOC	% Removal Biopolymers	% Removal Humics
Red Sea	1.12	144	389			
pH 4	0.79	48	159	29%	67%	59%
pH 5	0.63	61	150	44%	58%	61%
pH 6	0.69	63	208	38%	56%	47%
pH 7	0.78	75	268	30%	48%	31%
pH 8	0.82	73	327	27%	49%	16%
Membrane alone	1.03	95	365	8%	34%	6%

When the optimum dose was tested at different pH conditions, the removal of biopolymers and humic substances was increased as the pH decreased. The removal was significantly increased for humic substances from 16 % at pH 8 to 60 % at pH 4 (Table 7.10). Also, biopolymers removal increased from 49 % at pH 8 to 67 % at pH 4 (Table 7.10). Removal mechanisms are pH dependent; at low pH precipitation is dominant while at high pH the adsorption mechanism is dominant (Duan et al., 2002). Coagulation causes compression of the electrical double layer and aggregation of the particles thereby increasing the possibility of removal for both NOM and particles (Edzwald and Haarhoff, 2011). The study conducted by (Duan et al., 2003) using humic acid as a model contaminant, confirms that the removal of humic acid depends on coagulant dose and pH.

Previous studies have shown that iron III chloride coagulation removed more biopolymers than humic substances (Shon et al., 2008). However this study showed that both biopolymers and humic substances from seawater are moderately removed by coagulation combined with ceramic membranes. Acidic conditions for the feed water not only have an advantage in the coagulation process (i.e. removal of high molecular weight NOM) but also can play an important role in reducing scaling in an RO system. The flux decline based on pH trends was not significant (Figure 7.12). Low flux decline was observed at pH 6. Therefore it can be concluded that the coagulation process at pH 4 - 5 improved the removal of high molecular weight NOM, in particular humic substances, and yet maintains the flux decline close to a minimum value obtained at pH 6.

Further studies were also conducted with pilot-scale to confirm the results obtained from the bench-scale experiments in particular with optimization of a coagulant dose based on flux maintenance. High and low doses were applied with in-line coagulation under constant flux operations at a flux of 150 LMH. Also, longer filtration cycles up to 4 hours was applied for longer duration of filtration without chemical cleaning as described by the below section.

7.5.8 Dose optimization with inline coagulation – Pilot scale experiments

The advantages of iron III chloride over aluminium sulphate as a coagulant is that its solubility is low over a wide range of temperature and pH (Edzwald and Haarhoff, 2011). A low dose of a coagulant (0.5 – 1 mg/l Fe^{3+}) was enough for stabilization of flux (Figure 7.13). This agrees with previous results of bench scale studies that found 1 mg/l Fe dose was sufficient for improvement of flux decline. The results also showed that reversible fouling was significantly reduced and the backwashing was very effective (Figure 7.13).

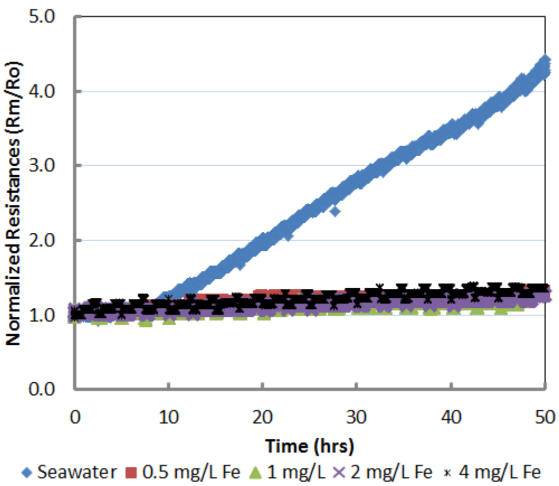


Figure 7.13: Seawater Filtration on Ceramic MF membrane w/wo coagulation in different doses at constant flux of 150 LMH

The use of coagulation significantly reduces the fouling and maintains stable operation and hence reduces the use of chemicals for membrane cleaning. Previous studies also found that coagulation, even at a low dose of 1 mg/L Fe, can maintain steady operation for more than one week (Brehant et al., 2002). This will reduce the operating cost of ceramic membranes if used as a pre-treatment process and also provide better feed for an RO membrane with less loading of high molecular weight NOM. The benefit of coagulation is noteworthy even at a low dose of 0.5 mg/L Fe as shown in Figure 7.14.

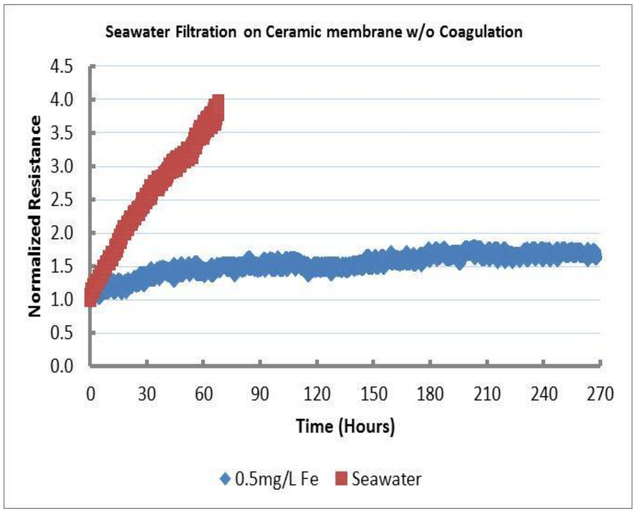


Figure 7.14: In-line coagulation of seawater with 0.5 mg/L Fe – Pilot scale

After 60 hours of operation (2.5 days) with a 2 hours interval of backwashing, the membrane alone reached a 4-fold increase in membrane resistance at a constant flux of 150 LMH. This means that after 2 days of operation with the membrane alone, chemical cleaning is required. But with the use of a low dose of coagulant (0.5 mg/L Fe), the increase of membrane resistance was significantly decreased to 1.7-fold after 270 hours (11.25 days) with an extended backwashing interval of 4 hours (Figure 7.14). These results imply that, with coagulation, longer filtration time with high permeability can be achieved without frequent chemical cleaning. The permeability of the fouled membrane measured after 50 hours of filtration without coagulation and with coagulation of 1 mg/L Fe dose was 220 LMH/bar and 740 LMH/bar respectively (Figure 7.15).

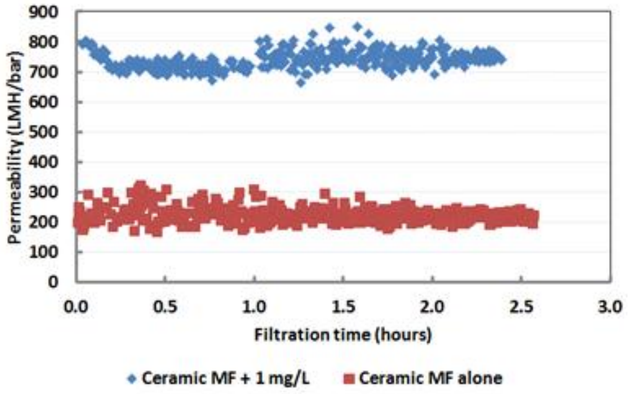


Figure 7.15: Permeability of fouled membrane (50 hours filtration) with coagulation (1 mg/L Fe) and without coagulation

7.6 Conclusions

The optimum dose for iron (III) chloride coagulant was found to be 3 mg/l Fe for ceramic UF membrane and 4 mg/l Fe for ceramic MF membrane based on high molecular weight NOM removal. In terms of flux decline, 1 mg/l was found to be an optimum dose. However flux stabilization was achieved with in-line coagulation at a dose of 0.5 mg/l Fe using the pilot-scale unit. The removal of high molecular weight NOM increased as the pH decreased and it was at an optimum at pH 5. Coagulation improves flux decline significantly and allows longer filtration cycles. This implies that the frequency of chemical cleaning for RO membranes and MF/UF membranes could be lowered. Also coagulation boosted the removal of the high molecular weight fraction of NOM. LC-OCD results showed that ceramic membranes alone could remove 20-30 % of biopolymers without coagulant while humic substances were poorly removed. But with coagulant, significant removal of biopolymers and humic substances was achieved by 60 % and 50 %, respectively. Fluorescence excitation emission analysis of Red Sea water confirms the presence of marine protein-like and marine humic-like organic matter as possible foulants. Bench scale studies revealed that the biopolymers fraction contributes significantly to fouling and flux decline.

7.7 Recommendations

- More research is needed to determine the cost effectiveness of coagulant use for MF/UF prior to RO membrane and to compare the costs of membrane cleaning with or without coagulation.
- The capabilities of other coagulants in terms of NOM removal and flux decline improvement in comparison to iron III chloride need to be assessed to choose the most appropriate coagulant for seawater pre-treatment.

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CHAPTER 8

8.0 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

8.1.1 Removal of Natural Organic Matter (NOM) and Effluent organic matter from surface water and wastewater effluents respectively

This research focused on removal of NOM, in particular high molecular weight organic matter as well as effluent organic matter. The biopolymers fraction of NOM is known to cause severe fouling in low-pressure membranes, which has a direct impact on operational and maintenance cost. Another fraction of NOM which is humic substances that also constitute a high molecular weight group after biopolymers; may contribute to membrane fouling but it is of concerns when passing through the low pressure membrane and fouling nanofiltration or reverse osmosis membranes dedicated for wastewater reuse or seawater treatment. Therefore, humic substances removal is also encouraged. Commercial powdered activated carbon (PAC) has been successful used for removal of trace organic compounds but not successful in removal of high molecular weight NOM especial biopolymers. A pre-coat approach, which allows maximum contact between contaminants and activated carbon, was proposed to be used in combination with ceramic membranes. Based on pre-coat approach two techniques for removal of biopolymers were demonstrated.

The first technique is the use of a submicron powdered activated carbon (SPAC) pre-coat. SPAC was produced by grinding commercial powdered activated carbon (PAC) into very fine particles by using novel mill. Fine particles increase the surface area of PAC, which increases the kinetics of adsorption. The potential of SPAC does not depend on adsorption alone but also on sieving characteristics that are made up with a pre-coat layer. The pre-coat layer creates bed pores with an average diameter of 0.4 µm. These spaces can entrap some of biopolymers by physical means and increase removal of biopolymers. With two possible mechanisms combined together (adsorption and straining), biopolymers removal of > 85 % from surface water was achieved.

High rejection of protein-like organic matter (93 %) and humic-like organic matter (82 %) was observed with fluorescence excitation emission analysis (FEEM) when 40 mg/L of SPAC was used to pre-coat a monolith ceramic membrane prior to canal water filtration. Furthermore, transparent exopolymers particles (TEP) were significantly reduced to 70 % from canal water. DOC removal was also increased from 5 % (without pre-coat) to 50 % with SPAC pre-coat. When SPAC was applied in treatment of wastewater effluents, a pre-coat dose of 30 mg/L attained 80 % removal of biopolymers.

In a second technique, a new and novel PAC was developed in collaborative project between King Abdullah University of Science and Technology (KAUST) and Cornell University. This novel PAC (KCU 6) is characterized by large pores structure (maximum 33 nm) and large BET surface area (1,280 m^2/g) compared to commercial PAC, properties which positively influence adsorption of biopolymers. It was observed that > 90 % of biopolymers were removed from wastewater effluent when the wastewater was filtered by a pre-coated ceramic membrane at a dose of 30 mg/L. Removal of other NOM components was also good when KCU 6 used as pre-coat. This was later confirmed with FEEM results that showed rejection of > 85 % of protein-like organic matter and > 70 % of humic-like organic matter. Comparison of the pre-coating results with 0.45 um filters (that allows NOM to pass through) and 0.1 um ceramic membranes coated with KCU 6, revealed that the removal of NOM components is mainly taking place in pre-coating layers through an adsorption process.

In seawater pre-treatment, coagulation prior to ceramic MF membrane filtration was applied. The use of coagulation (Iron III chloride) combined with ceramic membrane improved the removal of high molecular weight NOM. A coagulant dose of 3 mg/L Fe at pH 5 with ceramic UF membrane showed 60 % and 54 % of biopolymers and humic substances, respectively. It was also observed that 4 mg/L Fe coagulants at pH 4 achieved a high removal of biopolymers (67 %) and humic substances (59 %) when ceramic MF membrane was used. Fluorescence excitation emission analysis of Red Sea water confirmed the presence of marine protein-like and marine humic-like organic matters as a possible foulants. Also, transparent exopolymers particles (TEP) were found to be a significant foulant in seawater based on epi-fluorescence image analysis. These organic foulants were significantly controlled with the use of coagulation that also reduced membrane fouling.

8.1.2 Fouling Control/reduction and membrane cleaning

Ceramic membrane alone can remove about 50 % of biopolymers from wastewater effluent. The removal is mainly taking place in membrane pores, which, however, caused blockage resulting in an increase of membrane resistance or fouling. The novel PAC (KCU 6) used in bench scale experiments was successful in preventing the fouling of the membrane when used as a membrane pre-coat.

KCU 6 has a wide range of mesopores with a maximum size of 33 nm that allow biopolymers to be well adsorbed and lowers significantly membrane resistances. It was found that a dose of 30 mg/L of KCU 6 maintained a low increase in membrane resistance compared to commercial PACs. KCU 6 showed potential ability to control fouling in ceramic MF membranes and increase significantly the filterability of the membrane by maintaining the high flux operation even at a lower dose of 10 mg/L.

In surface water treatment, it was found that 40 mg/L of SPAC pre-coated on monolith ceramic membrane (pilot plant) controlled the membrane fouling. This could be associated with high removal of biopolymers achieved by SPAC, which is associated with straining and adsorption mechanisms as described earlier. When the dose is lowered to 20 mg/L or 10 mg/L of SPAC, fouling is poorly controlled with reduction of 46 % and 7 %, respectively. Therefore a dose below 20 mg/L of SPAC is not recommended for fouling reduction.

When ceramic membranes are used in pretreatment of seawater, the flux recovery after backwashing of the membrane, using either seawater permeate or Milli-Q water was found to be not effective. Epifluorescence images showed the presence of transparent exopolymer particles (TEP) on the surface of the membrane after aggressive backwashing. These sticky materials (TEP) are strong enough to adhere other foulants that surrounding the TEP. TEP are negatively charged while ceramic membranes, made up of alumina, are positively charged which provides a good environment for strong binding to each other as well as other foulants (colloidal and particulates).

Chemical enhanced backwashing (CEB) with sodium hypochlorite showed significant permeability recovery and TEP removal. This study suggests that there is interaction between TEP, colloids and particulates that make hydraulic backwashing to be ineffective to recover the flux of the fouled ceramic MF/UF membrane. Chemical cleaning with sodium hypochlorite can restore 100 % of membrane permeability of the fouled membranes. Cleaning of membranes with citric acid was not effective which supports the notion that inorganic fouling was not critical. TEP dissolved or broke into smaller components after CEB and CIP processes (with sodium hypochlorite), suggesting that organic fouling with TEP is a dominant fouling mechanism in seawater. To limit the interaction of TEP and the surface of a ceramic membrane, in-line coagulation using iron III chloride was introduced. A low dose of 0.5 – 1 mg/L Fe was found to control both reversible and irreversible fouling of ceramic membranes mainly caused by the influence of TEP.

8.1.3 Removal of trace organic compounds (TOrCs)

The novel PAC, KCU 6, at a dose of 30 mg/l, accomplished a high removal of TOrCs > 90 % for 27 out of 29 models TOrCs. The remaining TOrCs, which are TCPP and acesulfame, reached an average removal of 88 % and 27 %, respectively. Acesulfame is highly hydrophilic compared to other trace organic compounds analyzed and this might be the reason for poor removal. Poor removal of acesulfame was also observed in the absence of NOM, which implies that TOrCs competition with NOM has no influence on removal of acesulfame.

Good removal was also observed with 30 mg/L SPAC pre-coats as well. Out of 29 TOrCs model compounds, 23 compounds achieved > 90 % removal. The remainder of the TOrCs showed removals below 90 % removal: ibuprofen (82 % removal), sucralose (79 %), acesulfame (27 %), primidone (74 %), sulfumethoxazole (75 %) and TCPP (84 %). Most of these compounds are hydrophilic (log D < 1) with the exception of ibuprofen and TCPP which, however, showed much better removal > 80 %. Without NOM competition, the adsorption of these compounds was > 90 % except for acesulfame (< 40 %) and TCPP (85 %).

Molecular masses, charge and hydrophobic behaviors of TOrCs were not the key factors determining the fate of TOrCs adsorption. The presence of NOM and amount of pre-coat dose used were the key factors that influence the removal of TOrCs.

In conclusion, the hybrid system of ceramic membrane and KCU 6 pre-coat achieved a high level of TOrCs removal that could be only otherwise be achieved with sophisticated and expensive schemes such as a membrane bioreactor (MBR) combined with reverse osmosis (RO) or oxidation (ozone) with nanofiltration (NF)/reverse osmosis (RO). Therefore ceramic microfiltration membranes pre-coated with the novel PAC (KCU 6) or SPAC is a simple, affordable and low cost technology, which is viable for removal of TOrCs.

8.1.4 Ceramic membrane for pre-treatment of seawater

Ceramic microfiltration (MF) membranes achieved an average SDI_{15} value of 2.1 % per min, which meets the requirement for SDI value (< 3) for RO feed. With the use of coagulant at a dose of 1 mg/L Fe, the SDI value improved to 1.9 % per min. In addition, bacteria were almost completely removed by ceramic membrane alone or when combined with in-line coagulation at continuous dosing of 1 mg/L Fe coagulant. Stable and consistent filtrate turbidity of 0.05 NTU was achieved with and without coagulation despite turbidity fluctuations in the seawater. Coagulation decreases the sticking effect of TEP and improved both flux decline and recovery.

8.1.5 Membrane properties and pre-coat materials

Interaction between membrane properties, feed water qualities and pre-treatment materials may positively or negatively affect operation and maintenance of membranes. Ceramic membranes made of alumina have a positively charge surface that favors binding with TEP during seawater filtration. They are hydrophilic membranes and exhibit high permeability compared to polymeric membranes. Scanning electron microscopy (SEM) images showed that ceramic Anopore membranes have uniform and homogeneous pores compared to polymeric membranes, which suggests high permeability and more effective backwashing could be achieved with ceramic Anopore membranes. However, the Metawater ceramic membrane exhibited non-uniform pores, which, reflects to the different methods, used during fabrication. Moreover, atomic force microscopy (AFM) images showed that ceramic Anopore membranes have a smooth surface compared to PVDF MF membranes and hence they are expected to be less prone to cake layer fouling.

The novel PAC (KCU 6), has a large BET surface area and wide distribution of pores with considerably bigger pores compared to other PACs, and hence showed good sorption capabilities of biopolymers. Elemental analysis of different powdered activated carbons (PACs) showed similarity in composition between novel PACs (KCUs) and parent material of SPAC (SASuper) so this was not considered as a key factor that affected adsorption in this study. The particles sizes of PACs suggest that no penetration of PAC or pore blockage of membranes pores is expected during pre-coating or filtration. The effective particles size of SPAC is 1.4 µm and the maximum pore size of the ceramic MF membrane is 0.19 µm which signifies that SPAC will not pass through the membranes pores and 100 % pre-coating could be achieved.

8.2 Recommendations

- It is recommended to further ground a novel PAC (KCU 6) into fine particles, which would aim to combine physical and adsorption mechanisms, and scale up the study from bench scale to pilot scale.
- In case of TOrCs removal, it is recommended to do further studies on the interaction between macromolecules present in wastewater effluents and TOrCs that showed good removal when the membrane alone is used. These compounds include methylparaben, oxybenzone, triclocarban, atrazine and triclosan. Therefore, two experiments are suggested one with Milli-Q water and the other one with wastewater effluent both spiked with TOrCs before filtering by ceramic membranes alone.
- More research is needed to determine the cost effectiveness of coagulant use for MF/UF prior to RO membrane and to compare the costs of membrane cleaning with or without coagulation.
- The abilities of other coagulants in terms of NOM removal and flux decline improvement in comparison to iron III chloride need to be assessed and final select the most appropriate coagulant for sea water pre-treatment.