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Application and Challenges of Membrane in Surface Water Treatment

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Abstract: Herein, we reviewed NOM and its components as the major membrane foulants during the separation and purification of water works. In addition, possible fouling mechanisms relating to NOM fouling, current techniques employed to characterize fouling mechanisms and methods to control fouling were briefly discussed. Conventional water treatment which involves a train of operating units such as coagulation, flocculation and sand filtration consumes substantial spaces and high Hydraulic Retention Time (HRT). Besides that it relies most on chemical consumption such as aluminium sulphate, ferric chloride and poly-aluminium chloride which end up as sludge waste contaminated with aluminium or ferric oxides. Furthermore, the chemical reaction between Natural Organic Matter (NOM) and disinfectant agent such as chlorine or chloramines has been extensively reported to form carcinogenic Disinfection By-Product (DBPs) which is potential in causing deleterious cancers diseases. Therefore, a more reliable and greener technology such as membrane technology has been employed as it possesses better capability in producing water of exceptional quality and practicality over the conventional treatment process. However, the widespread of this potential feature is significantly restricted by fouling issue which reduces its productivity, permeate quality and treatment performance.

Key words: NOM, water treatment, membrane fouling

INTRODUCTION

The need for water and wastewater treatments with regards to human consumption and industrial requirement are becoming more challenging as mankind continues to decline the finite water resources with more complex waste of pollutants contaminants. Looking at the most advanced water treatment process, it is apparent that the membrane technology is the today's state of the art. Small size in the plant, easier maintenance and superior water quality produce by membrane filtration has made this advanced technology possible to replace the conventional treatment processes (Clever *et al.*, 2000). Though, membrane technology is fairly new to the water industry but yet its growth in treatment applications is tremendous (Table 1). This is due to a steadily decreasing manufacturing cost, a relatively lower chemical consumption and low maintenance compared to conventional treatment. Membranes remove contaminants ranging from suspended solids, colloidal, dissolved organic solutes by physical retention, chemical adsorption and back diffusion. Dissolved organic matter is ubiquitous in natural surface water and often reclaimed (Youravong *et al.*, 2010; Mayani *et al.*, 2010;

Table 1: Overview pore size operating, volume treated and application by membrane processes

Process	Pore size (nm)	Operating pressure (Mpa)	Applications	Municipal drinking water production
MF	>50	0.05-0.5	Turbidity removal	500,000
UF	10	0.05-0.5	Turbidity, colloids and suspended solids removal	600,000
NF	<2	0.1-1.5	Dissolved solids, ions	1000,000
RO	Non-porous	5-8	Desalination of sea and brackish water	10000,000

Buetehorn *et al.*, 2010; She *et al.*, 2009; Berberidou *et al.*, 2009) as important factor for both the reversible and irreversible fouling in water filtration. Pressure driven membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and Reverse Osmosis (RO) allows the production of high quality drinking waters. The MF unit is widely used for turbidity or fine particles removal and is an ideal pretreatment for processes using tighter membranes. The MF can be operated in dead-end or crossflow filtration mode with latter being advantage of having tangential flow to sweep foulants off. But this high flow rate requires more energy and usually reserve for high solids water content. Apart

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of that, the UF only became popular in water treatment only recently, primarily due to its ability to remove bacteria or other microorganisms but it could only be effective either with a PAC or coagulant pretreatment which makes the operation more complex and generate a waste stream. Earlier studies using integrated conventional coagulation followed by direct membrane filtration or an inline coagulation combined with direct membrane filtration (Neubrand *et al.*, 2010; Beyer *et al.*, 2010; Mariam and Nghiem, 2010) have demonstrated effective control of fouling, improved membrane permeability and superior permeate quality despite having applied on low quality water sources. The NF is often more appropriate in water treatment as the product is not fully demineralized. The membranes used exhibited high organic removal but moderate calcium and alkalinity permeability made the process more economic compared to RO. However, the disadvantage of NF and RO are high energy cost, proper pretreatment and generation of waste streams that need further treatment prior to disposal. In spite of providing many advantages over the conventional treatment, fouling issue is the main challenge in membrane filtration efficiency as it causes reduction in permeates quality and filtration productivity. Productivity decline can be defined as a decrement in flux with time of operation due to the increment of hydraulic resistance. Productivity decline may also be interpreted as a need for additional energy supply to the filtration system so as to keep the system performance constant. Whereas fouling phenomenon is caused by particles smaller than membrane pores being adsorbed into the membrane pores then followed by particles of similar size to pore diameter before cake formation by deposited particles (Neubrand *et al.*, 2010; Ladner *et al.*, 2010). Therefore, a fundamental knowledge on the possible foulants and how they cause fouling are essential before any remediation works is carried out.

Applications

Microfiltration (MF): Microfiltration is used in a wide variety of industrial applications where particles of a size greater than 0.1 μm, have to be retained from a liquid. Applications include the sterilization and clarification of all kinds of beverages and pharmaceuticals and in particular pre-treatment for subsequent finer membrane filtrations, especially in water and wastewater treatment. Physical sieving is the major rejection mechanism for MF with water convecting through the membrane due to an applied TMP. The deposit or cake on the membrane can act as a rejecting layer and retain even smaller solutes than would be expected to be retained. Thus, a fouled MF membrane may have UF rejection characteristics and flux

may decline significantly due to build up of this deposit. Electrostatic interactions, dispersion forces and hydrophobic bonding may play some role in rejection.

Ultrafiltration (UF): Ultrafiltration and nanofiltration, in particular, are important processes for the removal of solutes, macromolecules (such as natural organic matter) pathogenic viruses and small colloidal materials in water and wastewater treatment. The production of potable water from seawater or brackish water by reverse osmosis has become increasingly important, especially in remote areas such as island, sea and inaccessible locations. The UF can as well be used for NF and RO pretreatment, which may lengthen the filtration cycle of these processes compared to a MF pretreatment. As MF, physical sieving is an important rejection mechanism in UF and convection dictates solvent passage. The deposit can also act as a self rejecting layer and charge interaction as well as adsorption may also play an important role. Rejection is usually evaluated with macromolecules of different MW such as dextran or proteins, which leads to the determination of MWCO.

Nanofiltration (NF): The NF is a process located between UF and RO. Some researchers refer NF as charged UF, softening membrane and low pressure RO. The NF is generally expected to remove 60 to 80% of hardness, 90% of color and all turbidity. The process has the advantage of low operating pressures compared to a significant to RO and high rejection of organics compared to UF or MF. However, the monovalent salt is not well retained to a significant extent as his is not normally required in water treatment of surface water. Rejection of membranes is usually evaluated by manufacturer with NaCl or $MgSO_4$ solution as opposed to MWCO speciation in the UF. Rejection mechanisms based on charge and size are important in NF. At neutral pH most NF membrane are negatively charges while at low pH they are mostly positive in charge. Physical sieving is the dominant rejection in NF for colloids and large molecules whereas the chemistries of solute and membrane become increasingly important for ions and lower molecular weight organics.

Reverse osmosis (RO): In RO the osmotic pressure of a solution has to be overcome by an applied transmembrane pressure (TMP) to achieve solvent flux and separation. Recovery (ratio of product per feed) has a high impact on flux and rejection and both decrease with increasing recovery. Physical sieving applies to colloids and large molecules. Besides that, RO rejection is mostly a function of the relative chemical affinity of the solute to the

membrane material. Ion rejection follows the lyotropic series which means that rejection is increased with increased hydrated radius of ion. The order of the ions however, may change due to ion pairing, complexation or other solute-solute interactions, thus difficult to predict rejection of ion mixtures. The rejection behavior in the presence of organic is still poorly understood and only trends can be noted. In general RO rejection is usually evaluated with NaCl or $MgSO_4$ solutions permeation.

Challenges: Membrane filtration processes involving microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and Reverse Osmosis (RO) have steadily gained importance in the environmental engineering separations over the past decade. Numerous improvements in the technology have caused widespread applications of this process in environmental, chemical, pharmaceutical and biomedical fields. However, several aspects of this evolving membrane technology has not yet been addressed conclusively and thus, potentially posing obstacles toward its wide adoption such as inevitable fouling problems, costs factor, know-how technology and unsuitable imported technology.

Know how technology: It is vital to identify membrane foulant and fouling mechanisms before membrane fouling can be alleviated or control. Clear fundamental knowledge on understanding and minimization of membrane fouling are important and can be realized though accurate process design and optimal operating conditions. Maintaining proper operating conditions, accurate pretreatment process, suitable cleaning solution or techniques and proper membrane selection for specific membrane application is the key preventative step to minimize membrane fouling and maintaining high membrane productivity. Apparently membrane efficiency in filtration operation depends greatly on tedious management of fouling. Membrane fouling is the prime bottleneck that retards the membrane effectiveness and wide application. The usage of suitable membrane design, construction, configuration and fouling control techniques will result in longer membrane life, lower operational and design costs. Membrane operating management comprises physical and chemical procedures. Physical methods such as intermittent backwashing, application of critical flux, critical TMP, intermittent suction operation, low TMP, high Cross Flow Velocity (CFV) and hydrodynamic shear stress scouring effect produce only temporary recovery of membrane flux and require high energy consumption. On the other hand, the application of effective chemical cleaning agents such as NaOCl, NaOH, HCl and HNO_3 has

been proven to completely recover the initial membrane permeability. However, these procedures are expensive, can cause severe membrane damage, chemical contamination and may produce toxic by-product wastes. Backwash technique is dependent on the nature of fouling mechanism and only suitable in back flushing weak adhered cake layer. In the case of pore plugging and pore adsorption (irreversible fouling), the consumption of chemical agent is more favourable. Surface water pretreatment prior to membrane filtration can be done either by adjusting the solubility of NOM or reducing the NOM concentration using precoagulation. Aluminium-based or iron-based coagulants had long been used to remove NOM in the conventional method. Subsequently pretreatment of coagulation prior to membrane filtration has also been employed to enhance the permeate quality as MF and UF alone are inadequate. Since, MF/UF has their own limitations due to their larger molecular weight cut off (MWCO) to the relative molecular mass of NOM, pretreatment processes such as coagulation and PAC would definitely help to improve these weaknesses and are capable to meet water quality requirements for NOM removal.

Fouling problems: Fouling is still the single most important problem that retards the widespread use of membrane separation processes as it could cause high operational and maintenance costs, lower productivity and permeate quality and high frequency of membrane regeneration. Membrane fouling can be defined as the decline in permeate flux or an increase in TMP. The flux decline results from a number of complex kinetic processes that lead to gradual deposition of solids on membrane surface or gradual blockage of the membrane pores. Four types of foulants may be distinguished: chemical foulants, which cause scaling, physical foulants, which are related to deposition of particles, biological foulants, which can form bio fouling and organic foulants, which can interact with the membrane. In general membrane with larger pores exhibit a greater flux decline compared to smaller one. This could be reason due to significantly higher intrinsic fluxes and the increased possibility of internal fouling. One important issue in membrane fouling is due to concentration polarization and cake formation of particulate materials. Concentration polarization is a phenomenon wherein there is a concentration of particles in a thin layer adjacent to the membrane which has the effect of reducing flow through the membrane. Cake formation is the accumulation of particulate matter on the membrane surface. Whereas pore blockage is due to deposition of foulant in the membrane pores.

Table 2: Cost and recovery of several membrane and hybrid filtration system

Process	Flux× 10^3 LMH	TMP Bar	Permeability LMH Bar	Recovery (%)	Total cost (US m^{-3})	Capacity (m^{3}d^{-1}×10^3)
Conventional	2-10	0.1-2.0	-	-	0.85-0.15	0.38-17
Conventional/ O$_3$/GAC	-	-	-	-	1.15-0.55	0.38-17
MF	0.1-1	0.3-2.1	60-250	90-98	0.1,0.21,0.27	8.7
UF	0.05-0.2	0.5-2.1	60-250	90-98	0.45,0.1,0.04	0.38-17
NF	0.01-0.1	5.2-8.6	5-10	75-95	0.85,0.34,0.16	0.38-17
RO	0.012-0.025	10.3-103	<5	<5	0.23-0.92	-
M/UF/NF	0.017-0.034	2.5-5	-	-	0.74	-

Cost factor: Membrane process and membrane technology have changed significantly in recent years. The required membranes characteristics depend greatly on the application and the desired permeate quality. As emerging technologies, there are many unknowns regarding the cost-effectiveness of membrane processes such as ultrafiltration (UF) and nanofiltration (NF) and RO for the potable water treatment. Uncertainty is related to the process performance and lack of design history. For example, the permeation rate that reasonably can be anticipated when treating raw water using a given membrane has great impact on the capital and operating costs that are estimated for a membrane installation. The RO membrane process produces water of exceptional quality but is found to be less cost effective compared to other membranes.

On the other hand, NF represents an interesting trade-off between the high energy requirement RO and the low rejection UF membrane. If water is turbid but not colored or polluted, MF is an attractive alternative due to its low cost operation. The RO process cost reduced by 30 to 40% after the development of MF pretreatment whereas it concluded their cost modeling with comments that cost is largely a function of flux as the flux determines the membrane area to be installed. At small design capacities (<20, 000 m^3), MF and UF costs were competitive with conventional treatment. The UF was less costly than MF for larger facilities (>20,000 m^3). The importance of particle size in cost evaluation was also pointed out where cost has been found to increase with particle concentration as well. The UF membrane was cost competitive with conventional treatment for low particle (up to 20 mg L^{-1}) if particles are 0.1 μm on average. The total treatment cost describing the capital and operating costs are shown in Table 2.

Efficacy of imported technology: Membrane technology for surface water treatment is considered to be the most promising development in water treatment as it could provide permeate quality far beyond the current regulatory requirement for potable water consumptions. However, lack of field experience, surface water database and knowledge on specific geographical surroundings,

the efficacy of imported membrane is therefore, questionable and may not be optimal to be directly applied in our tropical area. Although, this technology is even becoming more attractive with a package of a compact technology (small footprint) and superior permeate quality, problems related to low membrane life, expensive membranes that are prone to fouling and questionable permeate quality are still a major issues in membrane treatment process especially in our country. In particulars there are still many technical challenges which need further optimization so as to ensure membrane technology remain competitive in the market especially for large scale industry. There is a need for further research of advanced membrane materials that are resistant to both chemical and mechanical attacks during surface water treatment (such as Sg Bekok and Yong Peng water intake) as this would help in prolonging the membrane lifespan and induce long term performance. The identification of the best practices in terms of design, treatment configuration and operating parameter that suit to this tropical climate would help to project minimal capital for design, construction and operational costs. The development of clear fundamental knowledge on understanding and minimization of membrane fouling (due to NOM and particulates in surface water) are also vital and can be realized through employing accurate process design and operating conditions. Furthermore, proper selection of pretreatments, improvement of cleaning strategies and membrane system with low energy requirement may help to position this technology to reach market confidence.

SURFACE WATER FOULANTS

Foulant and its fouling mechanisms are extremely vital to be identified before one can alleviate the membrane fouling. Membrane fouling refers to both reversible and irreversible alteration in membrane properties. Reversible fouling means deposition of retained solutes on the membrane surface that generally exists as a gel cake layer. Irreversible fouling refers to adsorption or pore plugging of solutes in and within the membrane pore matrix. Concentration polarizations are the

accumulation of retained materials in the boundary layer above the membrane due to osmotic pressure and hydraulic resistance effect. Increment and variation of hydraulic resistances may come from variety of organic substances, inorganic particles, colloids and microorganisms with different fouling behaviors. The fouling behavior is significantly found to be influenced by various chemical and physical factors of the foulants. The foulant can be characterized according to their molecular structure, surface charge, molecular size and functional groups. One of the most important identified foulant found in surface water filtration is Natural Organic Matter (NOM). The NOM waters are a complex mix of particulate and soluble components of both inorganic and organic origin that vary from one source to others (Howe *et al.*, 2002). The NOM is a heterogeneous mixture with wide ranges in Molecular Weight (MW) and functional groups (phenolic, hydroxyl, carbonyl groups and carboxylic acid) and is formed by allochthonous input such as terrestrial, vegetative debris and autochthonous such as algae. Natural organic matters that occur in natural brown water are polyphenolic molecules with MW ranging from 5000 to 50000 Dalton (Maartens *et al.*, 1999). In particular, NOM can be fractionated into three segments; the hydrophobic fraction (humic substances), hydrophilic and transphilic. The hydrophobic fraction represented almost 50% of dissolved organic carbon (Fig. 1) with larger MW. The hydrophilic fraction composed 25-40% of Dissolved Organic Carbon (DOC) with lower MW (polysaccharides, amino acids, protein and etc.) and operationally defined as non-humic fraction. The transphilic fraction comprised approximately 25% of DOC in natural water but with MW in between hydrophobic and hydrophilic fractions. A major fraction of the NOM arises from humic substances and is reported to represent up to 60 to 70% of TOC in soils and 60 to 90% of DOC in most natural water. Fan *et al.* (2001) reported the major fraction (over 50% of DOC) of NOM is composed of humic substances and are responsible for

the natural water's color. A humic substance is the predominant fraction of NOM and generally is divided into three categories, which are Humic Acid (HA), Fulvic Acids (FA) and humin. The HA and FA are anionic polyelectrolyte with negatively charged of carboxylic acid ($COOH^-$), methoxyl carbonyls ($C=O$) and phenolic (OH^-) functional groups. Figure 2 and 3 show both models of humic acid and fulvic acids structures. Humic acid is soluble at higher pH normally 10 while fulvic acid is soluble in water under all pH. Humin is naturally exists in black color and does not soluble in water at any pH (Fig. 4). Humic fraction has been identified as the major foulant in membrane water filtration, which controls the rate and extent of fouling (Combe *et al.*, 1999). It causes more fouling than any other NOM components due to its adsorptive capacity on the membrane surface (Wiesner and Aptel, 1996). Study done by Mallevialle *et al.* (1989) showed organic matrix formed a structure of fouling layer that served as a glue for inorganic constituents. Similar results were reported by Kaiya *et al.* (1996) in analyzing deposited layer formed on a MF hollow fiber during filtration of Lake Kasumigaura water. The NOM deposition has been found as the dominant factor causing flux decline along with manganese constituent. Study by Mo and Huang (2003) on purification of
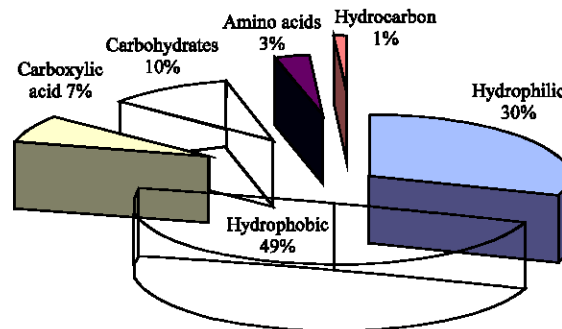

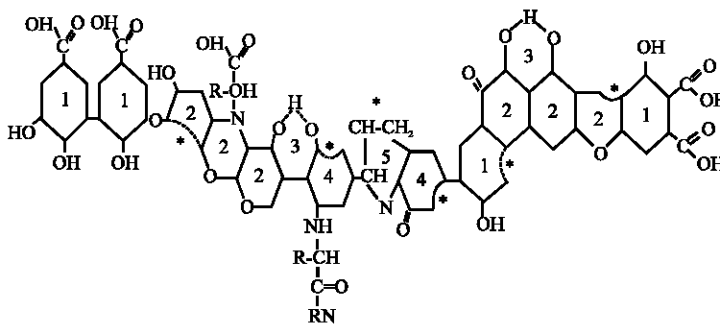Fig. 1: Fraction of NOM in surface water based on DOC (Thurman, 1985)

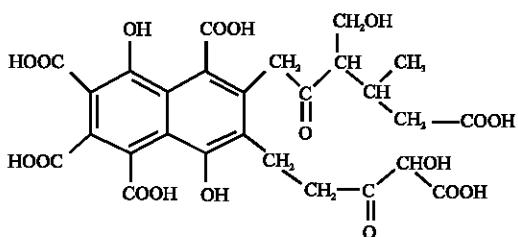Fig. 2: Schematic of humic acid model structure

Fig. 3: Schematic of fulvic acid model structure

Fig. 4: Physical and chemical characteristics of humic substances (Stevenson, 1982)

micro-polluted raw water revealed that fouling on the exterior surface was a combined effect of microorganisms and inorganic matter while on the inner surface was mainly due to the biofouling. They found the organic foulants were of low molecular weight and the inorganic was primarily represented by Ca^{2+} element. Their investigation on membrane permeability recovery showed that alkaline cleaning was effective in removing organic foulants while acidic cleaning was more effective on inorganic scales. It has also been shown that hydrophobic fraction of NOM causes much more fouling than hydrophilic fraction (Nilson and di Giano, 1996).

They performed NF of a hydrophilic membrane with aquatic NOM using DAX-8 to fractionate the NOM components. Hydrophobic fraction (absorbable to DAX-8) was mainly responsible for the permeate flux decline. On the other hand, the hydrophilic component which passed through DAX-8 showed less fouling effect. Humic macromolecules with higher hydrophobicity are found to favourably adsorb onto hydrophobic membrane than hydrophilic fraction (Jones and O'Melia, 2000). Earlier studies done by many researchers showed that humic substances caused irreversible fouling of membranes. Yuan and Zydney (1999) studied humic acid fouling on a 0.16 μm hydrophilic MF and found that aggregate humic acid was responsible for the initial stage of fouling. Furthermore, fouling mechanism was substantially due to convective deposition with little internal pore adsorption. This finding is well supported by

Schafer *et al.* (2001), who observed humic acid to cause 78% decline in flux compared to fulvic acid (15%). Humic acid was observed to give greater impact on membrane performance (irreversible fouling) than FA and hydrophilic fraction (reversible fouling). This scenario might be due to its high aromaticity properties, adsorptive behavior, hydrophobic and bigger molecular weight that lead to tendency of fouling. Similar result was also reported by Turcaud *et al.* (1990) during ultrafiltration observations with several organic and inorganic of Seine River. The flux decline observed was primarily due to humic acid deposition on the membrane surface. The cellulose acetate membrane (hydrophilic) flux was twice times greater than hydrophobic polyethersulfone (PES) during UF of river water. The hydrophilic components were thought to impact water quality less than the humic fraction, however recent studies done by Lin *et al.* (1999) and Carroll *et al.* (1999) have claimed that the non-humic fraction of NOM (hydrophilic and neutrals) materials were responsible in determining the rate and extent of flux decline. Carroll *et al.* (1999) performed MF of hydrophobic hollow fibre membrane with a single water source and concluded that the major cause of fouling was due to the hydrophilic neutral and not the humic substances. Fan *et al.* (2001) reported the order of fouling potential of NOM fraction as hydrophilic neutral >hydrophobic acids >transphilic acids >hydrophilic charged. They found that hydrophobic membrane had the most fouling effect than hydrophilic membrane of similar size suggesting that the fouling mechanism was governed by adsorption. In addition high molecules weight components had been identified as having the largest impact on membrane fouling compared to smaller DOM. This finding was well supported by study carried out by Lee *et al.* (2002). They found that polysaccharides and protein that have larger size of MW and lower UV to HPSEC-DOC/UV response, to significantly fouled their low pressure (MF/UF) membrane. Polysaccharides are aldehydes derivatives of high polyhydric alcohols, which have neutral characters that can cause adsorption on a charged hydrophobic UF membrane (Aiken *et al.*, 1992). They suggested that the neutral NOM fractions with larged sized were the prime foulants rather than humic substances. Speth *et al.* (2000) in their study also found hydrophilic neutrals fouled more than hydrophobic acids. It can be reasoned that since, polysaccharides (hydrophilic neutral) has a bulky macromolecular shape and with no electrostatic effect would definitely be prone to foul and adsorb on membrane surface. Lin *et al.* (1999) performed a study on the effect of fractionated NOM onto a negatively charge UF membrane and observed that both larged-sized molecules of hydrophobic and hydrophilic of NOM

components caused worsen flux decline. However, the hydrophilic fraction was found to induce the worst fouling. Jarusutthirak *et al.* (2002) in their study on the effect of effluent organic matter for UF membrane also found that the high molecular weight of hydrophilic component was responsible as the prime contributor of NOM fouling. It can be claimed NOM fouling was a result of low UV absorbing compounds and high molecular weight hydrophilic components that occurred through adsorption mechanisms. Inorganic particles can also affect the fouling behaviors of the organic substances. Presence of inorganic particles such as clay minerals in the surface water incurred a significant influence of competition between NOM and inorganic particles to adsorb onto the membrane surface or in the pores. High surface areas of inorganic particle enhance adsorption of organic substances on clays minerals and affect the fouling characteristic. This results in either enhancing particle deposition on the membrane or would decrease sorption of NOM onto the membrane and hence, increase the membrane permeability. But opposite finding was experienced by Hong and Elimelech (1997) when studied the effect silica (inorganic particle) on fouling of zirconia tubular membrane.

FOULANTS IDENTIFICATION IN SURFACE WATER TREATMENT

A number of techniques including inline Attenuated Total Reflection (ATR) Fourier transform infrared (FTIR) spectrometry, UV_{254}, SEC-DOC, DOC fractionation, pyrolysis-GC/MS, UF fractionation, SEM, SEM with Dispersive Spectrometer (EDS) and AFM to analyze and characterize membrane foulant. The ATR-FTIR spectrometry can provide insight of foulant nature in the membrane texture that appears to be a valuable tool for foulants autopsy (Her *et al.*, 2000). The FTIR can also be used to determine the functional groups of certain unknown foulants which corresponding to their vibrational energy of atomic bonds. Different functional group would absorb energy at different specific wavelength that latter can be translated in intensity response. Frequent absorption bands seen are shown in Table 3. But this method may also be insignificant in identifying of certain functional groups when the absorption reading gives broad overlapping bands. This phenomenon occurred due to heterogeneity of natural waters. Researchers (Aiken *et al.*, 1992; Kol and Konieczny, 2003) used UV_{254} absorbance at 254 nm to measure the permeate and retentate of rejected compounds specifically for humic substances.

Table 3: Common IR spectra for humic substances, polysaccharides and proteins

Bands (cm^{-1})	Functional group
Humic substances	
2940-2900	Aliphatic C-H stretching
1725-1720	Carboxylic acids
1660-1630	C=O stretching of amide group
1620-1600	Aromatic C=C
1590-1517	COO$^-$, N-H deformation
1460-1450	Aliphatic C-H
1400-1390	OH deformation, C-O stretching of phenolic OH
1280-1200	C-O stretching, OH deformation of COOH
1170-950	C-O stretching of polysaccharide
Polysaccharides group	
3400	Alcohol (1,2,3, Ar)
2940	Alkane
1480	Alkane
1370	1370 (starch)
1170	Tertiary alcohol
1120	Secondary alcohol
1040	Aliphatic ether
1000	Primary alcohol
775	Ethyl

The presence of unsaturated compounds would generally produce a distinct color and can therefore, be detected by UV-Vis (Bruchet *et al.*, 1990). The UV_{254} absorbance is sensitive to aromatic components and is an indicator for both humic acid and fulvic acid presence. Sample will first be filtered through 0.2 μm to remove particulate matter and DI is used as a blank. Difference in reading of UV_{254} absorbance between feed and permeate indicates the quantity of rejected humic substance by the membrane. The SUVA or specific ultraviolet absorbance is a ratio of UV at the wavelength of 254 nm and DOC. High SUVA means high aromaticity or hydrophobicity of sample in that limited DOC. Permeate from membrane filtration process which is found with high SUVA value is conforming that most of the rejected compounds are non-humic and that resulted in high value of UV_{254} in the permeate. Earlier studies reported that SUVA of NOM from natural waters or ground waters was in the range of 2.4-4.3 to 4.4-5.7 L mg^{-1} m, respectively (Krasner *et al.*, 1996; Gray *et al.*, 2004). The molecular weight distribution of NOM was normally determined using high performance liquid chromatography (HPSEC) with online UV and DOC detection (Schafer *et al.*, 2000). The HPSEC contains a porous gel that allows separation of molecules based on their mass and MW. Smaller molecules will access most of the pore volume while larger molecules that cannot pass the pores will be eluted first. Subsequently non-humic compound with large molecular weight such as carboxylic protein and polysaccharides will exhibit significant DOC peaks but with low area of UV_{254} peak. On the other hand, humic fraction such as humic acid and fulvic acid will exhibit high peaks with molecular mass
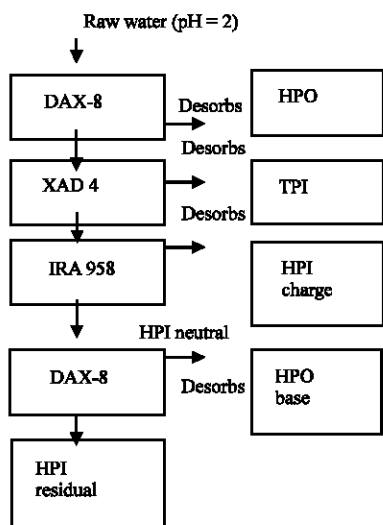
Fig. 5: Schematic diagram of HPO, TPI and HPI fractionation

between 500 daltons to 2000 daltons with high UV response. The most common technique for isolation of NOM fractions are gel filtration, ultrafiltration and adsorption using non-ionic macro-porous ion exchange resins DAX-8 and XAD-4 (Bowen *et al.*, 1995). The surface water is fractionated into hydrophobic (HPO) which is DAX-8 adsorbable, transphilic (TPI) fraction which is XAD-4 adsorbable and hydrophilic (HPI) components which pass through the DAX-8 and XAD-4 resin without any adsorption Fig. 5. Application of pyrolysis and GC/MS tool as an analytical method to characterized complex organic matter had been successfully employed by Speth *et al.* (2000) and Jarusutthirak *et al.* (2002). A recent study done by Speth *et al.* (2000) using pyrolysis with GC/MS showed that hydrophilic fraction of NOM were the major foulants for a river water filtration. Pyrolysis-GC/MS method was developed by Bruchet *et al.* (1990). This tool is useful for characterizing NOM in terms of biopolymers such as polysaccharides, polyhydroxyaromatics, amino sugar and protein. Pyrolysing process would casue refractory compounds to release volatile fragments, which are separated and analyzed by GC/MS. Those fragments are then characterized by relative percentages according to their biopolymer. However, pyrolysis -GC/MS technique is considered as a semi quantitative technique due to variation of fragments characteristics with their biopolymer structures. Beside that almost 50% of the total peaks would be classified as miscellaneous and the standards used also may not be effectively representing the classes of required compounds. The ATR-FTIR and DOC fractionation methods using non-ionic macro-porous

ion exchange resins such as DAX-8 and XAD-4 have been the most popular techniques used by many researches to characterize the NOM. But the ATR-FTIR may generate unreliable IR spectra readings due to overlapping bands. In addition, the DOC fractionation through ion exchange resins (DAX-8 and XAD-4) would exhibit total DOC recovery of less than 100%. This result can be reasoned due to improper elution procedure of DOC from the resins or the employed commercial NOM does not represent actual NOM in natural environment as it would vary with season and origin.

FOULING MECHANISMS IN SURFACE WATER TREATMENT

The extent of rejection of solutes by membrane is the most critical parameter in membrane filtration. For a clean membrane the extent of rejection is largely influenced by pore size whereas for a fouled membrane it is determined by the electrostatic interactions between the solute and membrane. Fouling of membrane is likely to happen in many instances due to a number of mechanisms such as pore blocking of solutes, cake deposition and precipitation of inorganic and organic particles at the membrane surface. Bowen *et al.* (1995) elucidated the consecutive steps of membrane blocking in flux decline during MF as follows: (1) the smallest pores are blocked by all particles arriving to the membrane, (2) the inner surfaces of bigger pores are covered, (3) some particles arriving to the membrane cover other already arrived particles while others directly block some of the pores and (4) a cake starts to be built. The NOM fouling mechanisms on membrane processes are different and are dependent upon membrane types. For MF, pore plugging, pore blockage and cake formation were found responsible for fouling that reduces pore size and increases rejection. In case of UF, internal pore adsorption reduces the internal pore diameter and enhances rejection while in NF the fouling mechanism is mostly governed by cake deposition and concentration polarization. Many researchers suggest humic substances play a vital role in irreversible fouling of membranes. Maartens *et al.* (1998) claimed UF membranes can remove NOM from natural brown water up to 98% but this progress impacted in flux decline in permeate volume that was due to irreversible fouling mechanism. Hydrophobic interaction between the hydrophobic NOM fraction and a hydrophobic membrane may cause more flux decline than that of hydrophilic membrane. The NOM with variety of organic fractions of different hydrophobicity, hydrophilicity, molecular weight, sizes and charge densities would give different interactions in membrane filtration. Yuan and Zydney

(1999) have found that NOM adsorbed both inside the pores and on the membrane surface to form a cake layer. A cake layer formation is generally known to occur during surface water filtration using tight UF, NF and RO while pore blockage or direct adsorption is usually happened when using the MF. A cake layer formation is caused by electrochemical interaction and the degree of accumulation is depending on a balance between convective transport of solutes towards the membrane and back diffusion transport. Transport of large particle by drag force (convective force) is governed by an orthokinetic mechanism (inertial lift and shear induced diffusion). Inertial lift induced by wall effect tends to reduce larger particle to the membrane especially at high CFV. Furthermore, the shear-induced diffusion is found to increase back transport of particles. Both of inertial lift and shear-induced diffusion involving backtransport are functions of particle size. The larger the particle the higher possibility it will be back transported (Chellam and Weisner, 1997). On the other hand, back transport of small particle is controlled by Brownian diffusion, which has less effect compared to inertial lift and shear induced diffusion. Subsequently large particle in cake tend to produce less resistance for the same mass of deposited. Turcaud *et al.* (1990) described that NOM fouling was primarily governed by pore adsorption and gel formation. In their study, they experienced 25% flux reduction for the first 5 min of 1 nm UF hollow fibre of 10 mg L^{-1} humic acid filtration and a further declination of flux (55%) after 300 min. They concluded the first 5 min rapid declination was due to irreversible adsorption of humic acid foulant. The continued flux decline was claimed to cause by humic acid gel deposition (reversible fouling) by convective transport.

MEMBRANE FOULING CONTROL

Membrane fouling is the prime bottleneck that retards the membrane effectiveness and wide application. Usage of suitable fouling control techniques will result in longer membrane life and low operation cost. Fouling control comprises physical and chemical procedures. Physical methods such as intermittent backwashing, application of critical flux, critical TMP, intermittent suction operation, low TMP, high Cross Flow Velocity (CFV) and hydrodynamic shear stress scouring effect produce only temporary recovery of membrane flux and require high energy consumption. On the other hand, application of effective chemical cleaning agents such as NaOCl, NaOH, HCl and HNO$_3$ have been proven to completely recover the initial membrane permeability. However, these procedures are expensive, can cause severe membrane damage, chemical contamination and may produce toxic by-product wastes. In practical engineering chemical cleaning is very effective in removing the deposited foulant and can be adopted as a long term solution for inevitable fouling but this procedure is out of focus of this study. Backwash technique is dependent on the nature of fouling mechanism and only suitable in back flushing weak adhered cake layer. In the case of pore plugging and pore adsorption (irreversible fouling), consumption of chemical agent is more favourable. Surface water pretreatment prior to membrane filtration can be done either by adjusting the solubility of NOM or reducing the NOM concentration using precoagulation. Aluminium-based or iron-based coagulants had long been used to remove NOM in the conventional method. Subsequently pretreatment of coagulation prior to membrane filtration had also been employed to enhance the permeate quality as MF and UF alone are inadequate. Since, MF/UF has their own limitations due to their larger Molecular Weight Cut off (MWCO) to the relative molecular mass of NOM, pretreatment processes such as coagulation and PAC would definitely help to improve these weaknesses and capable to meet water quality requirements for NOM removal. However, Turcaud *et al.* (1990) stated coagulation pretreatment could only reduce the rate of reversible fouling but not the irreversible fouling of low molecular weight polysaccharide compounds. Carroll *et al.* (1999) found that coagulation can be used as an efficient pretreatment to improve NOM removal and minimize fouling in MF of surface water. Coagulation of colloidal material and NOM are found to reduce the rate of fouling by aggregating fine particles that result in improving cake permeability, less dense, highly porous flocs and precipitation or adsorption of dissolved material into flocs. Increased in particle size by coagulation help to reduce foulant penetration into pores and forming a higher permeability cake on the membrane surface. Besides that coagulation can also be used to assemble microorganisms with coagulated matters though it is not as effective as other disinfectant agent. Maartens *et al.* (1998) suggested alteration of pH and application of metal-ions as pretreatments techniques of feed water as to reduce fouling of polysulfone UF membrane that was caused by Natural Brown Water (NBW). The NBW with pH 7 managed to sustain at 69% of its original flux after 300 min filtration whereas NBW with pH 2 was only 33%. In their experiment of using coagulants as pretreatment agents, they hypothesized that presence of Al^{3+} and Ca^{2+} in the NBW would help to block the functional groups of NOM by forming large precipitated organic material of metal-ions and hence, influence the potential of adsorptive behavior of NOM

membrane-binding activities. However, results of their study indicated precoagulation with metal-ions could not prevent membrane fouling but as a matter of fact resulted in an increased of NOM adsorption and a much worse irreversible fouling mechanism. They explained the increased fouling to the greater adsorption of NOM to the PSF membrane (40 kDa) caused by metal-ions complexes.

CONCLUSIONS

Fouling of NOM happens by many factors and mechanisms. Factor affecting NOM and membrane interactions include NOM characteristics, operating conditions, membrane characteristics and solution chemistry. The NOM fouling occurs when dissolved organic or inorganic solute adsorbs or deposits on the membrane. Adsorption mechanism happens more instantaneous and rapid compared to cake formation but depending on the membrane properties, ionic strength, pH and presence of divalent cation. Solute deposition or gel formation occurs parallel with the magnitude of a convective flux and the extent of concentration polarization. Hydrophobicity and electrostatic interactions between solute and membrane are also reported to be the dominant factors that affect the extent of NOM fouling. Presence of electrolyte composition, low pH and high ionic strength had been found to strongly enhance the degree and rate of fouling. The MF and UF are drinking water treatment processes, which are particularly suitable for the removal of suspended solids and colloidal materials such as bacteria, algae, protozoa and inorganic particulates. However, this type of filtration mode is less successful for the removal of dissolved contaminants especially NOM in the surface water. Coagulation had been introduced to address this weakness as it is proven effective for decreasing hydraulic resistance, increasing critical flux and improving NOM removal. There is still controversy over on how the NOM affects the membrane fouling mechanisms. Some studies suggested that charge interaction and adsorptive behavior are the responsible factors that control the NOM fouling whereas others claimed convective and diffusive particle transport that mainly dominate fouling in NOM filtration. As a matter of fact many earlier studies were done using various types of membranes and were operated at high fluxes in their experiment with regards to NOM fouling. These conditions would contribute to physical accumulation due to convection, diffusion and adsorptive fouling. As a result it as difficult to distinguish the dominant factor that responsible to the fouling. Hence, further study needs to be carried out in order to clarify this ambiguity and help in proper selection of membrane property, membrane configuration, pretreatment and operating conditions.

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