Behaviours of natural organic matter in membrane filtration for surface water treatment — a review

A.W. Zularisam[a,b], A.F. Ismail[a,*], Razman Salim[c]

[a]Membrane Research Unit, Universiti Teknologi Malaysia, Skudai Johor, Malaysia
Tel. +60 (7) 553-5592; Fax: +60 (7) 558-1463; email: afauzi@utm.my
[b]Environmental Engineering Focus Group, Faculty of Civil and Environmental Engineering, Kolej Universiti
Kejuruteraan and Teknologi Malaysia, Gambang, Pahang, Malaysia
[c]Faculty of Civil Engineering, Universiti Teknologi Malaysia, Skudai Johor, Malaysia

Abstract

Membrane application in surface water treatment provides many advantages over conventional treatment. However, this effort is hampered by the fouling issue, which restricts its widespread application due to increases in hydraulic resistances, operational and maintenance costs, deterioration of productivity and frequency of membrane regeneration problems. This paper discusses natural organic matter (NOM) and its components as the major membrane foulants that occur during the water filtration process, possible fouling mechanisms relating to reversible and irreversible of NOM fouling, current techniques used to characterize fouling mechanisms and methods to control fouling. Feed properties, membrane characteristics, operational conditions and solution chemistry were also found to strongly influence the nature and extent of NOM fouling. Findings of such studies are highlighted. The understanding of the combined roles of controlling factors and the methods used is very important in order to choose and optimize the best technique and conditions during surface water treatment. The future potential of membrane application for NOM removal is also discussed.

Keywords: NOM; Fouling mechanism; Surface water treatment; Membrane filtration

1. Introduction

Increasing population and improper industrialization practices have led to detrimental surface and underground water pollution. This phenomenon has raised concern in the public for stringent environmental legislation and alternative technology in water treatment. The presence of free chlorine content that is used as a disinfectant in conventional treatment is found to react with residual natural organic matter (NOM). This reaction process has been found to have a tendency to form disinfection by-products (DBPs)

*Corresponding author.

such as trihalomethanes, haloacetics and other halogenated organics. DBPs are carcinogens, and direct exposure can lead to cancers, miscarriages and nervous system complications. Its small size, easier maintenance and superior water quality produced by membrane filtration has made this advanced technology possible to replace conventional treatment processes that consist of ozonation, precipitation, coagulation, flocculation, chlorination and gravel filtration [1]. In addition, the membrane filtration process offers the extra advantages over conventional treatment such as a small footprint, compact module, lower energy consumption, environmental friendliness and the capability of handling wide fluctuations in feed quality.

Membrane filtration processes involving microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) in potable water production have increased rapidly over the past decade. MF and UF are employed to remove microparticles and macromolecules, which generally include inorganic particles, organic colloids (i.e., microorganisms) and dissolved organic matter (DOM). However, the use of membrane processes does not directly eliminate the problem of DBPs; even though MF, UF, NF or reverse osmosis (RO) have excellent performance on the removal of microbial particles, the disinfection process is still necessary.

DOM is ubiquitous in natural surface waters and is often claimed as an important factor for both the reversible and irreversible fouling in water filtration [2–6]. As for other membrane applications, the preferred membrane materials for surface water filtration are mostly polymeric with a configuration ranging from flat sheet to hollow fibre (Table 1).

Fouling is the main obstacle in membrane filtration efficiency as it causes a reduction in 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. Therefore, a fundamental knowledge of the possible foulants and how they cause fouling is essential before any remediation work is carried out. In the present paper the characteristics of NOM fouling are reviewed during surface water filtration that relate to both reversible and irreversible fouling mechanisms. Discussion is also devoted to the chemistry of NOM, current techniques used to characterize foulants, fouling mechanisms, membrane characteristics, fouling control methods, feed properties, operational conditions and solution chemistry that have been reported to potentially influence the NOM fouling in surface water filtration.

2. Chemistry of NOM

It is vital to identify foulants and fouling mechanisms before membrane fouling can be alleviated. "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 the hydraulic resistance effect. Increments and variation of hydraulic resistances may come from a variety of organic substances, inorganic particles, colloids and microorganisms with different fouling behaviours.

Fouling behaviour is found to be significantly influenced by various chemical and physical factors of the foulants. The foulant can be characterized according to its molecular structure, surface charge, molecular size and functional groups. One of the most important identified foulants found in surface water filtration is NOM.

Table 1
Membrane characteristics for water treatment

Membrane materials	Configuration	Pore size	Reference
Sulfonated PES	Flat sheet (cross flow)	0.7 nm	[5]
Polyslphone	Plate and frame (cross flow)	10 kDa	[7]
Polysulfone	Flat sheet (cross flow)	10 kDa	[7]
Polypropylene	Hollow fibre (dead end)	0.2 µm	[8]
PES	Flat sheet (dead end)	100 kDa	[9]
Regenerated cellulose	Flat sheet (dead end)	100 kDa	[9]
PVDF	Flat sheet (dead end)	0.22 µm	[9]
Cellulose ester	Flat sheet (dead end)	0.22 µm	[9]
PAN	Hollow fibre (cross flow)	50 kDa	[10]
Metal	Plate and frame (submerged)	0.2 µm	[11]
Composite (PA+PS)	Flat sheet (cross flow)	0.65 nm	[12]
Polypiperazine	Flat sheet (spiral wound)	360 g/mol	[13]
PES	Flat sheet (spiral wound)	2000 g/mol	[13]
Polyethylene	Hollow fibre (submerged)	0.1 µm	[14]
PAN	Flat sheet (cross flow)	110 kDa	[15]
Polypropylene	Flat sheet (dead end)	0.2 µm	[16]
Polysulphone	Hollow fibre (cross flow)	0.01 µm	[17]
Sulfonated PES	Flat sheet (cross flow)	20 kDa	[18]
PVDF	Flat sheet (dead end)	0.22 µm	[19]
Regenerated cellulose	Flat sheet (cross flow)	3 kDa	[20]
Polyamide TFC	Flat sheet (cross flow)	8 kDa	[20]
Polypiperazine	Flat sheet (cross flow)	290 Da	[21]
Polypropylene	Hollow fibre (dead end)	0.2 µm	[22]
Polysulphone	Capillary (cross flow)	40 kDa	[23]
Polysulphone	Hollow fibre (cross flow)	100 kDa	[24]
PES	Flat sheet (dead end)	0.16 µm	[25]
Cellulosic	Hollow fibre (cross flow)	100 kDa	[26]
Acrylic	Hollow fibre (cross flow)	50 kDa	[26]
Polyethylene	Hollow fibre (dead end)	0.1 µm	[27]

In water NOM is a complex mix of particulate and soluble components of both inorganic and organic origin that vary from one source to another [16]. 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 and vegetative debris and autochthonous input such as algae. Among these components, DOM is found to have the most detrimental effect on membrane performance as it can result in irreversible foul-ing during surface water filtration. DOM is a ubiquitous constituent in natural waters and generally is comprised of humic substances; polysaccharides; amino acids; proteins; fatty acids; phenols; carboxylic acids; quinines; lignins; carbohydrates; alcohols; resins; and inorganic compounds such as silica, alumino-silicates, iron, aluminium, suspended solids and microorganisms (bacteria and fungus).

NOM that occur in natural brown water are polyphenolic molecules with MW ranging from 5,000 to 50,000 Dalton [23]. In particular, NOM

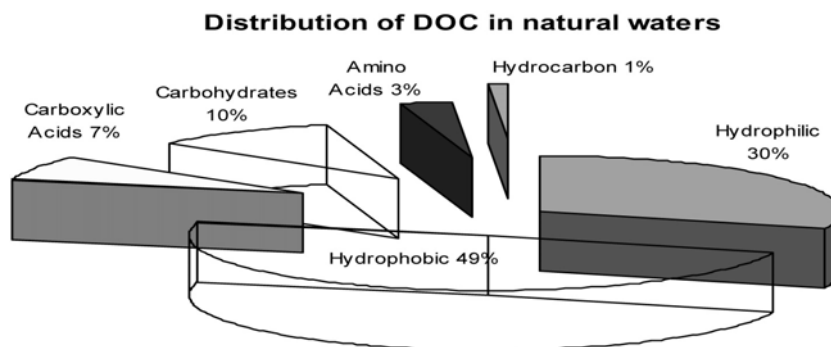**Distribution of DOC in natural waters**

Fig. 1. Fraction of NOM in surface water based on DOC [29].

can be fractionated into three segments: hydrophobic (humic substances), hydrophilic and transphilic fractions. The hydrophobic fraction represents almost 50% of dissolved organic carbon (Fig. 1) with larger MW. The hydrophilic fraction is composed of 25–40% of dissolved organic carbon (DOC) with lower MW (polysaccharides, amino acids, protein, etc.) and is operationally defined as a non-humic fraction. The transphilic fraction is comprised of approximately 25% DOC in natural water but with MW in between hydrophobic and hydrophilic fractions. A major fraction of the NOM arises from humic substances which are reported to represent 60–70% of TOC in soils and 60–90% of DOC in most natural waters [28]. This statement is found to be inconsistent with the information reported by Thurman [29] in Fig. 1, but this conflicting finding is not surprising since humic substance concentrations may vary with season and source [24].

Fan et al. [19] reported that the major fraction (over 50% of DOC) of NOM is composed of humic substances that are responsible for the colour of natural water. A humic substance is the predominant fraction of NOM and generally is divided into three categories: humic acid (HA), fulvic acids (FA) and humin. HA and FA are anionic polyelectrolyte with negatively charged carboxylic acid (COOH⁻), methoxyl carbonyls (C=O) and phenolic (OH⁻) functional groups.

Figs. 2 and 3 show both models of HA and FA structures. HA is soluble at higher pH — normally 10 — while fulvic acid is soluble in water at any pH [30]. Humin exists naturally as black in colour and is not soluble in water at any pH (Table 2). A humic fraction has been identified as the major foulant in membrane water filtration, which controls the rate and extent of fouling [31]. It causes more fouling than any other NOM component due to its adsorptive capacity on the membrane surface [32]. A study done by Mallevialle et al. [33] showed an organic matrix formed a structure of fouling layer that served as a glue for inorganic constituents. Similar results were reported by Kaiya et al. [27] in analyzing a deposited layer formed on a MF hollow fibre during filtration of Lake Kasumigaura water.

NOM deposition has been found as the dominant factor causing flux decline along with manganese constituents. A study by Mo and Huang [14] on the purification of 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, it was mainly due to biofouling. These studies found that organic foulants were of low MW and the primary inorganic substance was Ca^{2+}. Their investigations on membrane permeability recovery showed that alkaline cleaning was effective in removing organic foulants while acidic cleaning was more effective for inorganic scale. It has also
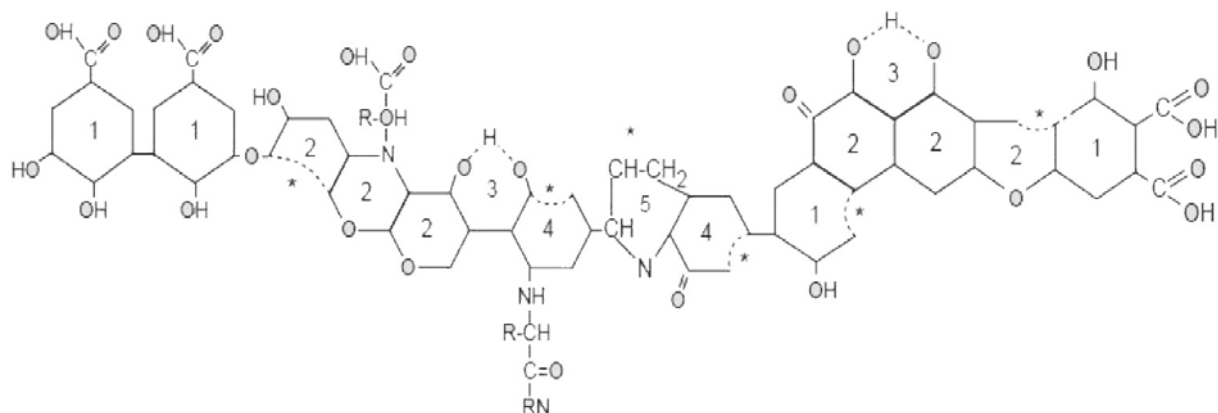
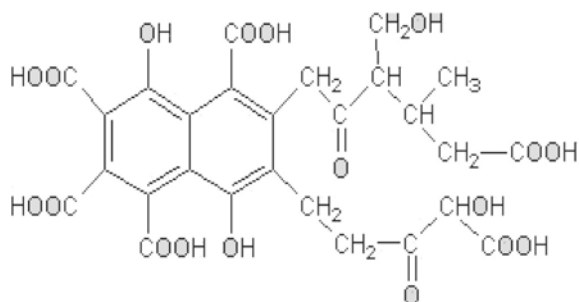Fig. 2. Schematic of humic acid model structure [35].

Fig. 3. Schematic of fulvic acid model structure [36].

Table 2
Physical and chemical characteristics of humic substances [35]

Fulvic acid		Humic acid		Humin
Light yellow	Yellow brown	Dark brown	Grey black	Black
	Increase in degree of polymerization			
	⟶			
2000	Increase in MW 300,000 and above			
45%	Increase in carbon content			62%
48%	Decrease in oxygen content			30%
1400%	Decrease in exchange acidity			500%
	Decrease in degree of solubility			
	⟹			

been shown that hydrophobic fraction of NOM causes much more fouling than hydrophilic fractions [34]. Nilson and DiGiano [34] 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 the DAX-8 showed a lower fouling effect. Humic macromolecules with higher hydrophobicity were found to favourably be adsorbed onto hydrophobic membranes than a hydrophilic fraction [34].

Previous studies done by many researchers showed humic substances caused irreversible fouling of membranes [25,37]. Yuan and Zydney [25] studied HA fouling on a 0.16 µm hydrophilic MF and found that aggregate HA was responsible for the initial stage of fouling. Furthermore, the fouling mechanism was substantially due to convective deposition with little internal pore adsorption. This finding is well supported by Schafer et al. [38] who observed that HA caused a 78% decline in flux compared to FA (15%). HA was observed to have a 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 behaviour, hydrophobia

and greater MW that led to the tendency to foul. A similar result was also reported by Lahoussine-Turcaud et al. [39] during UF observations with several organic and inorganic compounds from the Seine River. The flux decline observed was primarily due to HA deposition on the membrane surface.

The cellulose acetate membrane (hydrophilic) flux was twice as great as the hydrophobic poly-ethersulfone (PES) during UF of river water. The hydrophilic components were thought to have less of an impact on water quality than the humic fraction. However, recent studies done by Lin et al. [24] and Carroll et al. [22] have claimed that the non-humic fraction of NOM (hydrophilic and neutrals) materials was responsible in determining the rate and extent of flux decline. Carroll et al. [22] performed MF of hydrophobic hollow-fibre membranes with a single water source and concluded that the major cause of fouling was due to hydrophilic neutralily and not humic substances. Fan et al. [19] reported the order of fouling potential of NOM fraction as hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. They also found that hydrophobic membranes had the greatest fouling effect than hydrophilic membranes of similar size, suggesting that the fouling mechanism was governed by adsorption.

In addition, high MW components were identified as having the largest impact on membrane fouling compared to smaller DOM. This finding was well supported by the study carried out by Lee et al. [40] who found that polysaccharides and protein that have larger MW and lower UV to HPSEC–DOC/UV response significantly fouled their low-pressure (MF/UF) membrane. Polysaccharides are aldehyde derivatives of high polyhydric alcohols, which have neutral characters that can cause adsorption on a charged hydrophobic UF membrane [41]. The authors suggested that the large neutral NOM fractions were the prime foulants rather than humic substances. Speth et al. [42] in their study also found

hydrophilic neutrals fouled more than hydrophobic acids. This can be due to a bulky, macromolecular shape and neutral character of the polysaccharides that make it prone to foul and adsorb on membrane surface.

Lin et al. [24] studied the effect of fractionated NOM onto a negatively charged UF membrane and observed that both the large scale of hydrophobic and hydrophilic NOM components caused flux decline. However, the hydrophilic fraction was found to induce the worst fouling. Jarusutthirak et al. [43] in their study on the effect of effluent organic matter for UF membranes also found that the high MW of hydrophilic components was the prime contributor of NOM fouling. It can be claimed that NOM fouling was a result of low UV absorbing compounds and high MW hydrophilic components that occurred through adsorption mechanisms.

Inorganic particles can also affect the fouling behaviours of organic substances. The presence of inorganic particles such as clay minerals in surface water created a significant competition between NOM and inorganic particles to adsorb onto the membrane surface or in the pores. High surface areas of inorganic particles enhance the adsorption of organic substances on clay minerals and affect the fouling characteristic. This phenomenon either resulted in enhancing particle deposition on the membrane or a decrease of sorption of NOM onto the membrane and hence increase membrane permeability.

2.1. Effect of solution chemistry on NOM fouling

The extent of NOM fouling was also found to be strongly governed by ionic strength, pH and divalent cations [20]. NOM particles are seen to agglomerate more at low pH and in the presence of high multivalent cations concentrations. Contrarily, the particles stretch to more linear chains in low concentration, at neutral pH and low ionic strengths [44]. Many previous studies have shown that permeate flux is substantially reduced with

lower pH, high ionic strength and increasing divalent cation concentration [45]. Most of this behaviour could be explained by changes of intra- and intermolecular electrostatic gradients of the functional groups (COO- and COOH). Increasing ionic concentration changed rejection by buffering or shielding the charge on the solute molecules. This condition encouraged coiling and aggregation of NOM that led to higher apparent MW and surface area.

Hydraulic resistance of humic acid was found to increase at low pH, high ionic strength and in the presence of calcium ion. Calcium ions reduce the humic acid solubility and increase its aggregation by canceling (protonation) the negative charge effect of the functional group [20] or by bridging the negative membrane surface with the negative charge functional groups (carboxylic, phenolics and methoxy carbonyls) of humic substances. Braghetta et al. [46] claimed low pH and high ionic strength caused compaction of membrane pores size that restricts the entrance of solute through the membrane. It was also hypothesized that low pH and high ionic strength contribute to the reduced intermolecular electrostatic repulsion of NOM. Subsequently, molecules densely accumulated on the membrane surface which reduced pure water permeability.

Incremental surface water pH was found to alter the physical and chemical properties [23]. The authors ascribed the increase of UV_{254} absorbance to an increase in pH as a result of ionization of the carboxyl groups process that increased intramolecular repulsion and solubility. A decrease of UV_{254} absorbance values at low pH conditions was because NOM carboxyl groups were protonated and formed large complexes, which were less soluble and precipitated. The precipitation process removed most of the humic acid fraction and left only soluble fulvic acid in the solution. This hypothesis was proven from the result of the E_4/E_6 ratio (absorbance at 465 and 656 nm) that was inversely proportional with the value of obtained UV_{254} absorbance.

In a study of chemical and physical impact of NOM fouling in NF, Hong and Elimelech [3] found that fouling increased with increasing ionic strength, decreasing pH and with addition of Ca^{2+}. This finding was supported by Ghosh and Schnitzer [47] who found that it was due to lower intramolecular repulsion. A variation of this solution chemistry leads to changes in the net electrostatic charge of the humic's functional groups. Divalent cations specifically interact with humic functional groups and thus greatly reduce the NOM interchain repulsion between humic macromolecules. Reduction in the electrostatic repulsion later results in the formation of a densely packed fouling layer. The authors concluded that the rate of fouling is mainly controlled by the interplay between drag and electrostatic double layer repulsion in NF.

Jucker and Clark [48] explained the effect of electrolytes on humic substance aggregation in the form of apparent molecular weight (AMW). He found that humic substance's AMW distribution was shifting to a higher value at low ionic strength compared to results obtained at high ionic strength. This phenomena is probably due to the fact that humic substances are more compact at high ionic strength as a result of a contraction of the molecule which is caused by diminution of intramolecular electrostatic repulsion as the charges are neutralized [49]. Calcium concentration adsorbed on the membrane is found to be in proportion to the amount of humic substances adsorbed [50]. Therefore, calcium content in any surface water should be taken into account as excessive calcium presence definitely resulted in the substantial adsorption of humic substances on the membrane.

Hong and Elimelech [3] experienced a 50% flux decline after 70 h of filtration with a high permeation rate of 3.1×10^{-5} m/s and less than 10% with a low permeation rate (0.4×10^{-5} m/s). They found that a faster fouling rate happened at high ionic strength and with the addition of calcium ion. They hypothesized that both pheno-

mena were due to a reduction in electrostatic repulsion between the charged humic acids and the membrane. The same finding was observed by Bob and Walker [51] where they hypothesized that increasing the ionic strength led to a continous change in humic acid from uncoiled macromolecules to a fully coiled state. Coiled humic acids posed higher surface area and AMW that made it easier to be retained by the membrane. Subsequently, this increased the humic acid rejection, hydraulic resistance and fouling rate as well.

3. Identification of foulants

Researchers have used a number of techniques including inline attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectrometry, UV_{254} absorbance, HPSEC–DOC–UV, non-ionic macroporous ion exchange and pyrolysis–GC/MS to analyze and characterize membrane foulants.

3.1. ATR–FTIR

ATR–FTIR spectrometry provides insight into the nature of foulants in the membrane texture. It appears to be a valuable tool for foulant autopsies [16]. ATR–FTIR can also be used to determine the functional groups of certain unknown foulants which correspond to their vibrational energy of atomic bonds. Different functional groups absorb energy at different specific wavelengths that later can be translated into an intensity response. Frequent absorption bands seen are shown in Table 3 [52]. Nevertheless, this method may be insignificant in identifying certain functional groups when the absorption reading gives broad over-lapping bands. This phenomenon occurred due to the heterogeneity of natural water.

3.2. UV_{254} absorbance

Researchers [15,53,58] use UV_{254} absorbance to identify the permeate and retentate of rejected

Table 3
Common IR spectra for humic substances, polysaccharides and proteins [52]

Bands (cm^{-1})	Functional group
Humic substances:	
3400–3300	O-H stretching
	N-H stretching
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
Proteins group	
3300	Alcohol
1640	Alkene in aromatic
1540	Mono substituted amide
1100	Ether

compounds specifically for humic substances in unit of cm^{-1} or m^{-1}. The presence of unsaturated compounds generally produced a distinct colour and can therefore be detected by UV–Vis [4].

UV_{254} absorbance is sensitive to aromatic components and is an indicator for both HA and fulvic acid presence. Samples were first filtered through 0.2 μm to remove particulate matter and DI was used as a blank. The difference in reading of UV_{254} absorbance between feed and permeate

indicates the quantity of rejected humic substance by the membrane. Sspecific ultraviolet absorbance (SUVA) is a ratio of UV at the wavelength of 254 nm and DOC. High SUVA means high aromaticity or hydrophobicity of samples in the limited DOC. The permeate from membrane the filtration process with a high SUVA value conforms to most of the rejected compounds that are non-humic and that resulted in high values of UV_{254} in the permeate. Previous studies reported that SUVA of NOM from natural water or ground water was in the range of 2.4–4.3 L/mg-m to 4.4–5.7 L/mg-m, respectively [54].

3.3. HPSEC with online UV and DOC detection

The MW distribution of NOM was normally determined using high-performance liquid chromatography (HPSEC) with online UV and DOC detection [21]. The HPSEC contains a porous gel that allows separation of molecules based on their mass and MW. Smaller molecules access most of the pore volume while larger molecules that cannot pass the pores are eluted first. Subsequently, non-humic compounds with greater MW such as carboxylic protein and polysaccharides exhibit significant DOC peaks but with a low area of UV_{254} peak. On the other hand, humic fractions such as HA and fulvic acid exhibit high peaks with a molecular mass between 500 to 2000 Daltons with a high UV response.

3.4. Non-ionic macroporous ion exchange

The most common techniques for isolation of NOM fractions are gel filtration, UF and adsorption using non-ionic macroporous ion-exchange resins DAX-8 and XAD-4 [8,55]. The surface water is fractionated into hydrophobic, which is DAX-8 adsorbable; transphilic, which is XAD-4 adsorbable; and hydrophilic components, which pass through the DAX-8 and XAD-4 resin without any adsorption (Fig. 4).
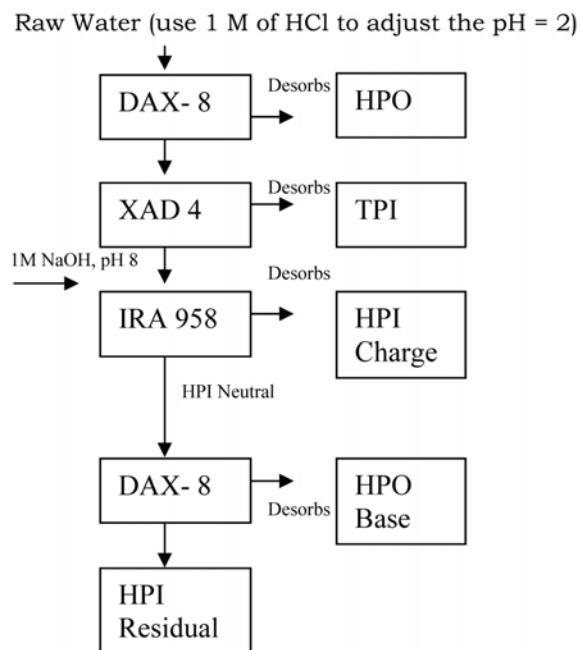

Fig. 4. Schematic diagram of HPO, TPI and HPI fractionation [8].

3.5. Pyrolysis–GC/MS

The application of pyrolysis and the GC/MS tool as an analytical method to characterize complex organic matter was successfully used by Speth et al. [42] and Jarusutthirak et al. [43]. A recent study done by Speth et al. [42] using pyrolysis with GC/MS showed that hydrophilic fractions of NOM were the major foulants for river water filtration.

The pyrolysis–GC/MS method was developed by Bruchet et al. [56]. This tool is useful for characterizing NOM in terms of biopolymers such as polysaccharides, polyhydroxyaromatics, amino sugar and protein when pyrolyzing refractory compounds released volatile fragments, which are separated and analyzed by GC/MS. Those fragments are then characterized by relative percentages according to their biopolymer. However, the pyrolysis–GC/MS technique is considered as a semi-quantitative technique due to variation of

fragments characteristics with their biopolymer structures. Besides that, almost 50% of the total peaks are classified as miscellaneous, and the standards used may also not effectively represent the classes of required compounds.

The ATR–FTIR and DOC fractionation methods using non-ionic macroporous ion-exchange resins such as DAX-8 and XAD-4 have been the most popular techniques used by many researchers to characterize NOM. But ATR–FTIR may generate unreliable IR spectra readings due to overlapping bands. On the other hand, DOC fractionation through ion-exchange resins (DAX-8 and XAD-4) exhibited total DOC recovery of less than 100%. This can be due to an improper elution procedure of DOC from the resins, or the commercial NOM did not represent actual NOM in the natural environment as it varies with season and origin.

4. Model interpretation

The extent of rejection of solutes by membranes 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 [6]. Fouling of membranes 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 (Table 4).

Bowen et al. [57] 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) cake starts to be built.

NOM fouling mechanisms on membrane processes are different and are dependent on membrane type. For MF, pore plugging, pore blockage and cake formation were found responsible for fouling that reduced pore size and increased rejection. In the case of UF, internal pore adsorption reduced the internal pore diameter and enhanced rejection, while in NF the fouling mechanism was mostly governed by cake deposition and concentration polarization.

The effect of adsorptive fouling on membrane filtration has been well explored and explained by many researchers [32], but the causes of fouling by dissolved NOM are still not well understood [22]. This is because NOM interactions with a membrane are complex due to many influential factors that govern the process such as solution chemistry (pH, ionic strength and water hardness), membrane characteristics (hydrophobicity, surface/pore charge, MWCO and morphology), operational conditions, inorganic presence and NOM characteristics (concentration, humic and non-humic fractions, charge, MW distribution). The contribution of NOM to fouling depends greatly on the natural water properties, characteristics of NOM and the type of pretreatment. The 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 [58,59].

NOM with a high content of colloidal matter can expedite fouling by forming a cake on the membrane surface or by precipitating and adsorbing (dissolved material) within the membrane pores. In the case of accumulation of retained materials on the membrane surface, the hydraulic resistance is related to the permeability of surface cake while for the adsorbing fouling of DOM, the filtration resistance is mainly governed by the size of membrane pores (effective membrane permeability). Altmann and Ripperger [60] stated that it was more difficult for large particles to foul the membrane surface than smaller particles. This

Table 4
Constant pressure filtration laws [49]

Law	Equation	Description
Complete blocking (pore blocking)	$V = \dfrac{J_0}{Kcb}\left(1 - e^{-kcbt}\right)$	Particles seal pores: $d_{particle} \approx d_{pore}$. Particulates do not accumulate on each other.
Intermediate blocking (long-term adsorption)	$V = \dfrac{J_0}{kib}\left[\ln\left(1 + kibt\right)\right]$	Particles accumulate on each other and seal membrane pores: $d_{particle} \approx d_{pore}$.
Standard blocking (direct adsorption)	$\dfrac{t}{v} = \dfrac{1}{J_0} + \dfrac{ksb}{J_0}\,t$	Particles deposit on the internal pore walls, decreasing the pore diameter: $d_{particle} < d_{pore}$.
Cake filtration (boundary layer resistance)	$\dfrac{t}{v} = \dfrac{kcf}{4J_0^2}\,v + \dfrac{1}{J_0}$	Particles are retained due to sieving and form cake on the surface; deposition occurs on other particles, membrane area is already blocked: $d_{particle} > d_{pore}$.

phenomenon is supported by the Kozeny equation that expresses the specific resistance (R_c) of an incompressible cake. Based on this equation, the cake-specific resistance increases when the diameter of deposited particles (d_p) decreases in size.

$$R_c = \frac{180\left(1 - \varepsilon_c\right)^2}{d_p^2\,\varepsilon_c^3} \tag{1}$$

where ε is the porosity of gel and d_p is the diameter of the particle deposited [32].

Membrane filtration performance is accessed through permeate flux and rejection parameters. These parameters are strongly correlated to the physicochemical properties of the feed solution. Unfortunately, surface water contains a complex feed solution of thousand heterogeneous particulate mixtures and soluble components that can lead to significant impact on membrane fouling. Among these components, DOM was found to have the most detrimental effect on membrane performance as it could result in irreversible fouling during surface water filtration. DOM has

been reported as the main cause of irreversible fouling in surface water filtration [33,61], and this fouling tendency is governed by solution chemistry, membrane characteristics and operational conditions. Laine et al. [61] found DOM adsorption as the most important parameter in membrane fouling in lake water, and this was true as many other researchers also claimed that polysaccharides, polyhydroxyaromatics, amino sugars and proteins were the significant fractions found in the cakes formed during membrane filtration.

Many researchers suggested that humic substances play a vital role in irreversible fouling of membranes. Maartens et al. [23] claimed UF membranes can remove NOM from natural brown water up to 98%, but this process had an impact on flux decline in the permeate volume that was due to an irreversible fouling mechanism. Hydrophobic interaction between the hydrophobic NOM fraction and a hydrophobic membrane may cause more flux decline than that of hydrophilic membranes. NOM with a variety of organic fractions of different hydrophobicity, hydrophilicity, molecular weight, sizes and charge densities gave

different interactions in membrane filtration. Yuan and Zydney [25] found that NOM adsorbed both inside the pores and on the membrane surface to form a cake layer. Cake layer formation is generally known to occur during surface water filtration using tight UF, NF and RO while pore blockage or direct adsorption usually happened using MF.

Cake layer formation is caused by an electrochemical interaction, and the degree of accumulation depends on a balance between convective transport of solutes towards the membrane and back-diffusion transport. The transport of large particles by drag force (convective force) is governed by an orthokinetic mechanism (inertial lift and shear induced diffusion). Inertial lift induced by the wall effect tends to reduce larger particles to the membrane especially at high cross flow velocity [32]. Furthermore, shear-induced diffusion is found to increase back transport of particles.

Both inertial lift and shear-induced diffusion involving back transport are functions of particle size. The larger the particle, the higher the possibility that it will be back transported [62]. On the other hand, back transport of small particles is controlled by Brownian diffusion, which has less effect compared to inertial lift and shear-induced diffusion. Subsequently, large particles in cakes tend to produce less resistance for the same mass deposited. Lahoussine-Turcaud et al. [39] describe NOM fouling as primarily governed by pore adsorption and gel formation. In their study, they experienced a 25% flux reduction for the first 5 min of 1 nm UF hollow fibre of 10 mg/L HA filtration and a further decline of flux (55%) after 300 min. They concluded that the first 5 min of rapid decline were due to irreversible adsorption of HA foulants. The continued flux decline was caused by HA gel deposition (reversible fouling) by convective transport. In another NOM–UF study carried out by Chang and Benjamin [63], it was shown that the cake deposition was the primary fouling mechanism to their

membrane flux decrement. This was proven by a SEM picture that showed most of the fouling occurred on the upper membrane surface. In that study they used a 10-nm UF hollow fibre with 4 mg/L NOM that gave a flux decline up to 80% after 20 h of filtration.

Some researchers used the zeta potential as a function of fulvic acid removal and an indicator for the degree of fouling mechanisms. Fu and Dempsey [64] used the addition of divalent cation (Ca^{2+}) to increase fulvic acid adsorption on a membrane surface. They experienced a decrease in zeta potential as more FA was rejected and increased in flux decline. The effect of particulates and adsorptive fouling on membrane performance were well described. However, fouling due to dissolved NOM–membrane interaction was not well described and is not yet well understood, though there are many reports that it is generally controlled by charge interaction and adsorptive behaviour.

Researchers have used different kinds of hydrophobic membranes and humic substances to prove that membrane fouling is due to adsorptive fouling. However, no NOM fouling was found when the membranes were running at moderate fluxes [44,65]. Cho et al. [66] claimed the ratio between flux and mass transfer coefficient was the dominant parameter that determines flux decline. They found NOM hydrophobicity and membrane materials did not significantly affect membrane fouling. Moreover, Howell et al. [67] found that critical flux was useful in reducing the fouling rate, and they also observed that using intermittent flux substantially helped to reduce long-term fouling.

All these findings support the theory that convection and diffusion dominate the extent and rate of flux declination rather than adsorptive or charge interaction between NOM and membranes. Schafer et al. [6] claimed that the rejection characteristics of membranes depend more on the current fouling state of the membrane and the nature of the foulant than on initial membrane

characteristics. In their study on NF membranes they found cation rejection was influenced by the charge of the precipitates on the membrane surface. Cations showed higher rejection compared to negatively charged low MW acids when the membrane was covered with a positive charge precipitate compared to more neutral or negative precipitates. Therefore, interaction and combined effects of NOM with the membrane matrix, membrane pore blockage and plugging, adsorption, precipitation, deposition and gel cake layer formation were the factors that determined the types of fouling mechanisms and the extent of flux reduction.

In summary, NOM adsorption or cake deposition on membrane surfaces is the result of physical, chemical and electrostatic interactions between NOM molecules and membrane surface properties. In physical adsorption it is caused by attractive dispersion forces that are relatively weak in comparison, while for chemical adsorption the electrons between NOM and membrane surface molecules are shared, which produce a relatively high strength bond. Electrostatic adsorption occurs between negatively charged functional groups of NOM and the membrane charged polymer.

5. Membrane materials

Membrane properties such as MWCO, pore size, surface charge and hydrophilicity/hydrophobicity play vital roles in determining the rejection, types of retained solutes, rate of flux reduction and types of membrane fouling mechanisms. A good knowledge of characterization of how membranes and foulants interact is foremost as this assists in avoiding membrane configurations that end up with irreversible adsorption.

Previous researchers have claimed that a hydrophobic membrane tends to foul more than a hydrophilic membrane while the membrane sur-

face a with positive charge tends to adsorb to negatively functional groups of NOM, thus increasing the potential of fouling. NOM adsorption is greater for hydrophobic membranes such as polysulphone and polyethersulphone than for hydrophilic membranes.

Laine et al. [61] observed better permeability occurring for more hydrophilic membranes (cellulose) than hydrophobic ones (acrylic) when running a static adsorption of surface water. The influence of hydrophobicity on flux rate does not only affect the NOM fouling patterns but also the membranes [34]. The study done by Nakatsuka et al. [68] showed that hydrophobic filtration membranes tend to foul, causing a much greater flux reduction than hydrophilic membranes. They found that cellulose acetate membranes (hydrophilic) had twice as large a flux as polyethersulfone during UF of river water.

Membranes with negative charge have been reported to reduce flux decline when the solute is also negatively charged [69]. Some researchers used chemicals to make the membrane surface covered with an anionic charge in order to reduce HA adsorption. Cho et al. [20] found that UF membranes with a negatively charged surface had a greater NOM rejection than the expected nominal MWCO performance. Although the used membrane was intrinsically hydrophobic, the adsorbed NOM found was less in quantity with less fouling.

There are two controlling factors that determine HA adsorption on the membrane surface: the electrostatic repulsion force due to a similarity in charge with the membrane, and adsorptive property due to its high hydrophobicity. Humic substances possess significant negative charges which prevent humic substances from being adsorbed onto the negatively charged membrane surface. However, in many cases reported membrane foulants could be hydrophobic materials as well [25,34,37]. This scenario occurred when hydrophobic interactions managed to overcome the electrostatic repulsion force between NOM

and the membrane. Adsorption of NOM on the membrane surface was found to alter membrane properties (hydrophilicity and surface potential charge). Membrane surface potential became more negative due to rapid adsorption of NOM (humic fraction) on hydrophilic membranes [70]. In addition, Wiesner and Aptel [32] reported that the membrane surface became more hydrophilic due to adsorption of NOM. It is therefore critical to choose suitable membrane materials that can result in low hydraulic resistance and high productivity.

Thus, it can be concluded that fouling is higher for negatively charged membranes when they are exposed to neutral (hydrophilic) materials and protein (bases) compared to high negatively charged materials (humic substances) though they possessed high adsorptive behaviour due to their high hydrophobicity.

6. Fouling control

Membrane efficiency in the filtration operation depends greatly on tedious management of fouling. Membrane fouling is the prime bottleneck that retards membrane effectiveness and wide application [14]. The usage of suitable fouling control techniques result in longer membrane life and lower operational costs. 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 and the 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 have been proven to recover completely initial membrane permeability. However, these procedures are expensive, can cause severe membrane damage, chemical contamination and may produce toxic by-product wastes [4,71].

In practical engineering, chemical cleaning is very effective in removing the deposited foulants and can be adopted as a long-term solution for inevitable fouling, but this procedure is out of the focus of this paper. The backwash technique is dependent on the nature of the fouling mechanism and is only suitable for backflushing a weakly adhered cake layer. In the case of pore plugging and pore adsorption (irreversible fouling), the consumption of chemical agents 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 [48].

Aluminium-based or iron-based coagulants have long been used to remove NOM in the conventional method [26]. Subsequently, coagulation pretreatment prior to membrane filtration was also used to enhance permeate quality, as MF and UF alone are inadequate [10,14,22,72,73]. Since MF/UF have their own limitations due to their larger 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 of meeting water quality requirements for NOM removal. However, Lahoussine-Turcaud et al. [39] stated that coagulation pretreatment could only reduce the rate of reversible fouling but not the irreversible fouling of low MW polysaccharide compounds. Carroll et al. [22] 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 were 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 [32]. Increase in particle size by coagulation helped to reduce foulant penetration into pores and formed a higher permeability cake on the membrane surface [58]. In addition, coagulation can also be used to assemble microorganisms with coagulated matter

though it is not as effective as other disinfectant agents.

Maartens et al. [23] suggested alteration of pH and application of metal ions as pretreatment techniques of feed water to reduce fouling of polysulfone UF membranes caused by natural brown water (NBW). NBW with pH 7 was sustained at 69% of its original flux after 300 min of filtration, whereas NBW with pH 2 was only 33%. In their experiment, using coagulants as pretreatment agents, they hypothesized that the presence of Al^{3+} and Ca^{2+} in the NBW would help to block the functional groups of NOM by forming large precipitated organic materials of metal ions and hence influence the potential of adsorptive behaviour of NOM membrane-binding activities. However, the results of their study indicated precoagulation with metal ions could not prevent membrane fouling, and, as a matter of fact, resulted in an increase of NOM adsorption and a much worse irreversible fouling mechanism. They explained that the increased fouling was due to the greater adsorption of NOM onto the PSF membrane (40 kD) caused by metal ion complexes. This finding was supported by another study, which also experienced an increase in fouling after coagulation [39].

Another chemical addition such as powdered activated carbon (PAC) has been found to reduce both cake deposition and DOC adsorption by rapid adsorption of dissolved foulants. PAC helps to improve hydraulic properties of cake by increasing its permeability and reducing compressibility. Most researchers [61,74] reported that the addition of PAC during membrane filtration helped decrease hydraulic resistance and irreversible fouling. A study done by Konieczny et al. [75] using PAC and granular activated carbon in the hybrid processes and PES found that they managed to reduce 99% TOC on ceramic membranes and 90% on PES membranes. However, Nilson and Digiano [48] and Lin et al. [31] found PAC adsorption to act adversely. They claimed PAC adsorption resulted in large and

more hydrophobic residuals that were detrimental to membranes. Lin et al. [31] reported the flux decline was due to small particles left by PAC adsorption.

Operating modes are important factors in optimizing membrane filtration. Operating conditions such as operating flux, TMP and CFV are the critical parameters that influence the efficiency of membrane filtration. In addition, there was a direct relationship between system performance and operating flux. Flux decline of constant pressure operation or TMP increases of constant flux operation can be taken as surrogate parameters of system performances. Many researchers [76,77] reported that running a membrane system with critical flux resulted in maximum flux without significant deterioration of system performance. Field et al. [78] defined critical flux as the maximum flux for which little or no fouling occurred. The operation of a membrane below or at the critical flux helped to reduce the fouling rate [67]. This statement was supported by Seidel and Elimelech [79] who claimed that the high fluxes imposed (40–60 L/m^2h), CFV and Ca^{2+} concentration have a significant impact on flux decline during 50 h of filtration operation. Thorsen [69] suggested that there is a critical flux at which the fouling rate starts to change with conditions at higher fluxes.

The fouling phenomenon is a function of convection and diffusion of solutes away from the membrane and is found to be linked with the hydrodynamic conditions of the system. The hydrodynamics of CFV play an important role in influencing NOM fouling. The hydrodynamics of crossflow membrane filtration, especially CFV, was observed to be capable of reducing NOM fouling at high CFV. CFV drags the back-transported particles off the membrane surface. The increment of CFV helps to increase the physical scouring effect at the membrane surface and improve back-transport into the bulk solution. Shear stress generated from this CFV helps to reduce the rate of cake deposition and the
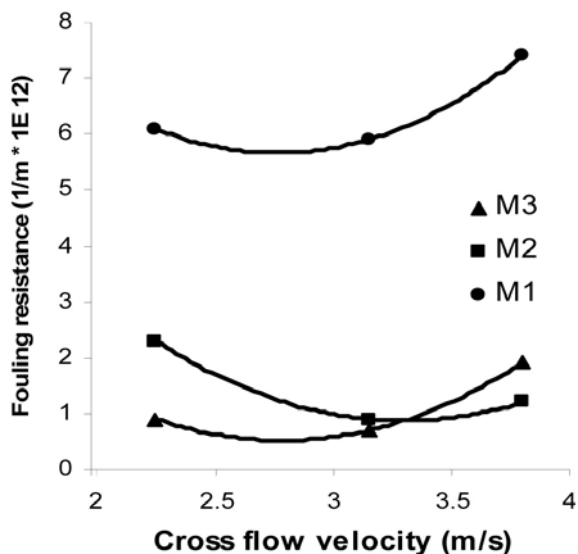
Fig. 5. Effect of CFV on hydraulic resistance [80].

Fig. 6. Variation of hydraulic resistance with filtrate flux for various CFVs [82].

resultant cake thickness. However, flux as a function of CFV is dependent on the imposed CFV value and particle size factors. Thomas et al. [80] reported that the increase of CFV above 3 m/s resulted in increased fouling resistance (Fig. 5). This was likely due to a more compact fouling layer and increased pore plugging caused by higher pressure. Previous study showed that CFV increased the small particle flux better than larger particles [71,81]. This phenomenon was due to particle classification at the membrane surface.

Increasing CFV with increment pump speed also generates finer colloidal particles, which can form a denser cake layer on the membrane surface. For an immersed membrane reactor the CFV is replaced by bubble aeration. The bubble acts directly against the fibres by colliding with and scouring the foulants. The bubble creates hydrodynamic effects that suppress the fouling layer. However, the efficiency of bubble aeration relies on the applied flow rate. A study done by Bouhabila et al. [82] showed that the air flow rate had a significant effect on hydraulic resistance, but this effect only worked for higher filtrate fluxes (Fig. 6).
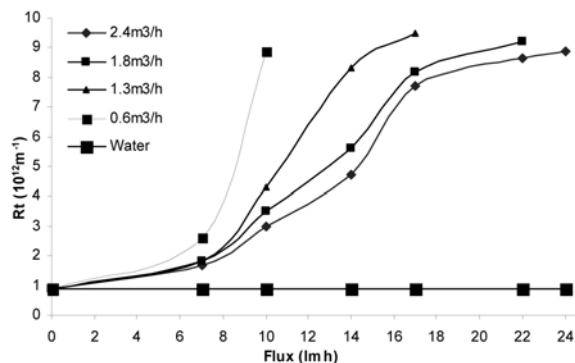
Hong and Elimelech [3] showed that the NOM fouling rate was substantially increased with an increasing initial permeation rate, particle concentration and TMP. This fouling condition was worsened when the operation was carried out for long hours.

7. Future direction of membrane filtration for surface water treatment

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 consumption. This technology becomes even more attractive when compact technology (small footprint) and careful water management are required with a critical water shortage problem to address. With the current technology, problems such as low membrane life, expensive membranes that are prone to fouling and questionable permeate quality are easily eased out. Currently, membrane potential has been specifically manipulated to their best application (Table 5).

However, there are still many technical challenges to optimize and make membrane technology more competitive in the market, especially for large-scale industries. There is a need for

Table 5
Specific use of membrane based on types [83]

Membrane type	Application
MF	Removes turbidity and microorganisms
UF	Removes viruses and large macromolecules recovery in water recycling
NF	Removes colour, large ions and higher flux than RO for surface water treatment
RO	Potable use and industrial reuse removal of small ions
MBR	Treat difficult waste possibly with specific organisms for special waste
Hybrid	UV–ozone–precoagulation or combined membrane systems becoming much effective than a single membrane

further research of advanced membrane materials that are resistant to both chemical and mechanical attacks during surface water treatment 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 parameters 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) is also vital and can be realized through using accurate process design and operating conditions. Furthermore, the proper selection of pretreatments, improvement of cleaning strategies and membrane systems with low energy requirements may help to position this technology to gain the confidence of the market.

8. Conclusions

Heterogeneity of NOM in surface water has made the nature and extent of fouling more difficult to control and predict. Membrane fouling is a phenomenon that cannot be prevented but can be minimized. Fouling of NOM occurs due to many factors and mechanisms. The factors affecting NOM and membrane interactions include NOM characteristics, operating conditions, membrane characteristics and solution chemistry.

NOM fouling occurs when dissolved organic or inorganic solute is adsorbed or deposited on the membrane. The adsorption mechanism happens more quickly compared to cake formation but depends on the membrane properties, ionic strength, pH and presence of divalent cations.

Solute deposition or gel formation occurs in parallel with the magnitude of 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. The presence of electrolyte composition, low pH and high ionic strength has been found to strongly enhance the degree and rate of fouling.

MF and UF are drinking water treatment processes that are particularly suitable for the removal of suspended solids and colloidal materials such as bacteria, algae, protozoa and inorganic particulates. However, these filtration types are less successful for the removal of dissolved contaminants, especially NOM in surface water. Coagulation was introduced to address this weakness as it has proven to be effective for decreasing hydraulic resistance, increasing critical flux and improving NOM removal.

There is still controversy over how NOM affects membrane fouling mechanisms. Some studies suggested that charge interaction and adsorptive behaviours are the responsible factors

that control NOM fouling, whereas others claim convective and diffusive particle transport that mainly dominate fouling in NOM filtration. As a matter of fact, many previous studies were done using various types of membranes and were operated at high fluxes in their experiments with regard to NOM fouling. These conditions contributed to physical accumulation due to convection, diffusion and adsorptive fouling. As a result, it was difficult to distinguish the dominant factor that was responsible for the fouling. Hence further study needs to be carried out in order to clarify this ambiguity and help in the proper selection of membrane properties and configurations, pretreatment, filtration process, operating conditions and cleaning conditions of surface water filtration so that the process can be operated economically and successfully.

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