Membrane Chemical Cleaning: From Art to Science

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Abstract

Membrane chemical cleaning is an integral part of operation for micro- and ultrafiltration systems in the water industry and has significant impact on process operations. However, this issue has not been adequately addressed primarily for two reasons: 1) cleaning protocols are typically recommended from membrane manufacturers and some cleaners are proprietary; 2) the issues of membrane fouling are poorly understood and related to site-specific water quality issues. As advances in aquatic chemistries and the analytical tools of membrane fouling occur, a broad understanding of the interactions between fouling materials and membranes, among fouling materials, and between fouling materials and cleaning chemicals becomes possible, although there still are many gaps in the understanding of the basic chemistry of fouling. This paper will present the basic chemistry of membrane fouling and cleaning, physical and chemical conditions that have significant impacts on cleaning efficiency, and the compatibility of membrane materials with different cleaning alternatives. Three case studies will be used as examples.

Membrane fouling is a complicated phenomenon and typically results from multiple causes. In spite of its complexity, electrostatic and hydrophobic/hydrophilic interactions that involve both membrane and fouling materials are recognized to have significant bearing, especially for the more-difficult-to-clean membrane fouling dominated by natural organic matter (NOM) and microbial activities. Electrostatic interactions occur among functional groups of membranes, fouling materials, and water primarily through dissociation, which strongly depend on the pH, ionic strength, and concentrations of multivalent cations in the solution. Hydrophobic/ hydrophilic interactions are functions of structure similarities between membranes and fouling materials, the types and density of functional groups on both membrane surfaces and fouling materials, and solubility of molecules of fouling materials. As analytical techniques and knowledge of structural details of NOM progress, the structure-solubility correlations for synthetic compounds can be extended to natural organic matter with modifications to provide a rough assessment on the hydrophobic nature of NOM.

Types and major functions of commonly used cleaning chemicals are discussed, focusing on how cleaning chemicals interact with fouling materials. Caustic can increase solubility of solutes by hydrolysis and solubilization. Oxidants such as free chlorine are able to oxidize NOM and increase hydrophilicity by increasing the amount of oxygen-containing functional groups such as carboxyl and phenolic groups. Because caustic can change the configuration of natural organic matter and make the fouling layer into a looser and more open structure, the combination of caustic and free chlorine enhances cleaning. Acids and EDTA are effective cleaners for scale compounds and metal oxides though solubilization and chelating. A surfactant performs more complicated and multiple functions. Surface coating/conditioning is considered to have major impact on fouling dominated by NOM.

Concentration, cleaning time, temperature, and hydrodynamic conditions during the cleaning are important factors affecting cleaning efficiency. Mass transfer barriers within the fouling layer are likely to be the rate-limiting factor. Creating favorable hydrodynamic conditions to facilitate mass transfer is likely to enhance the efficiency of cleaning. Temperature has a significant impact on both the efficiency and rate of membrane cleaning, presumably by changing the reaction equilibrium, by enhancing the reaction kinetics, and by increasing the solubility of solutes.

Another important aspect is chemical compatibility of membrane media and other filter components to cleaning chemicals. A membrane made of high chemical tolerance would allow greater freedom in selecting the composition, strength of cleaning solutions, as well as the conditions for cleaning.

Introduction

For the most part of 20th century, the goals for drinking water treatment have been primarily focused on removal of particles, inactivation of pathogens, and improvements of aesthetic quality. However, the discoveries of adverse health impacts of disinfection-by-products and the disinfection-resistant pathogens such as *Cryptosporidium* oocysts in later part of the century are having profound impact on the drinking water treatment practices used for almost a century, and are fundamentally reshaping the industry. Membrane filtration is a one of the promising technologies to help the industry effectively remove microbial contaminations without increasing the concentrations of disinfection-by-products in drinking water.

One of major problems in the operation of membrane process is membrane fouling. Membrane fouling is referred to the flux decline of a membrane filter caused by the accumulation of certain constituents in the feed water on the surface of the membrane or in membrane matrix. Certain fouling materials can be removed by hydraulic means such as filter backwash or scrubbing; most can be removed by chemical means such as Cleaning-In-Place (CIP), or chemical cleaning. Chemical cleaning is an integral part of membrane process operation that has a profound impact on the performance and economics of membrane processes. Currently, practices of chemical cleaning are mostly based on recommendations from membrane manufactures. Some of them supply proprietary cleaners while others use commercial chemicals. This paper is an attempt to provide some insights on how cleaning chemicals and fouling materials interacts, therefore, it hopefully will cast some lights on how and why chemical cleaning works. The scope of the paper focuses on low-pressure membrane process, namely microfiltration (MF) and ultrafiltration (UF), because they are the most widely used membrane processes in drinking water treatment.

Membrane Fouling

Type of Membrane Fouling, Water Quality Indicators, and Control Measures

According to the type of fouling materials, four categories of membrane fouling are generally recognized. They are (a) inorganic fouling/scaling, (b) particle/colloids fouling, (c) microbial fouling, and (d) organic fouling. A brief description on the nature of fouling, relevant water quality as indicators, and control measures are summarized below for each type of membrane fouling.

Inorganic Fouling/Scaling

Inorganic fouling or scaling is caused by the accumulation of inorganic precipitates such as metal hydroxides, and “scales” on membrane surface or within pore structure. Precipitates are formed when the concentration of chemical species exceeding their saturation concentrations. Scaling is a major concern for reverse osmosis (RO) and nanofiltration (NF). RO and NF membranes reject inorganic species. Those species form a concentrated layer in the vicinity of membrane-liquid interface - a phenomenon referred to “concentration polarization”. For microfiltration (MF) and ultrafiltration (UF), inorganic fouling due to concentration polarization is much less profound, but can exist most likely due to interactions between ions and other fouling materials (i.e., organic polymers) via chemical bonding. Some pretreatment processes for membrane filtration such as coagulation and oxidation, if are not designed or operated properly, may introduce metal hydroxides on membrane surface or within pore structure. Inorganic fouling/scaling can be a significant problem for make-up water of caustic solutions prepared for chemical cleaning.

Particulate/colloid Fouling

Algae, bacteria, and certain natural organic matters fall into the size range of particle and colloids. However, they are different from inert particles and colloids such as silts and clays. To distinguish the different fouling phenomena, particles and colloids here are referred to biologically inert particles and colloids that are inorganic in nature and are originated from weathering of rocks.

In most cases, particles and colloids do not really foul the membrane because the flux decline caused by their accumulation on the membrane surface is largely reversible by hydraulic cleaning measures such as backwash and air scrubbing. A rare case of irreversible fouling by particles and colloids is that they have smaller size relative to membrane pore size. Therefore, those particles and colloids can enter and be trapped within the membrane structure matrix, and not easily be cleaned by hydraulic cleaning.

Microbial/Biological Fouling

Microbial fouling is a result of formation of biofilms on membrane surfaces. Once bacteria attach to the membrane, they start to multiple and produce extracellular polymetric substances (EPS) to form a viscous, slimy, hydrated gel. EPS typically consists of heteropolysaccharides and have high negative charge density. This gel structure protects bacterial cells from hydraulic shearing and from chemical attacks of biocides such as chlorine.

Severity of microbial fouling is greatly related to the characteristics of the feed water. Water quality parameters that indicate the potential of microbial fouling are classified into three categories:

(a) Parameters indicating the abundance of microbes,
(b) Parameters indicating nutrient availability,
(c) Parameters indicating environmental conditions for microbial growth,

Organic Fouling

Organic fouling is profound in membrane filtration with source water containing relatively high natural organic matters (NOM). Surface water (lake, river) typically contains higher NOM than ground water, with exceptions. For source water high in NOM, organic fouling is believed to be the most significant factor contributed to flux decline (Mallevialle et al., 1989; Lahoussine-Turcaud et al, 1990). Microfilters usually remove insignificant amount of organic matter, as measured by dissolve organic carbon (DOC). DOC as an indicator for organic fouling is probably neither proper nor adequate. Efforts to identify the effects of subgroups of NOM on membrane fouling have yet been able to draw definitive conclusions.

The effects of various operating strategies against different types of fouling are summarized in Table 1. As indicated in Table 1, chemical cleaning is an effective control strategy for all types of membrane fouling.

Table 1. Effects of Operating Strategies on Membrane Fouling

Type of Fouling	**Effects of Operating Strategy**			
	Hydraulic Cleaning	**Feed Chlorination**	**Feed Acidification**	**Chemical Cleaning**
Inorganic	-	-	++	++
Particulate	++	-	-	++
Microbial	+	++	+*	++
Organic	-	+	-	++

Note: - No effects or have negative effects. + Some positive effects, ++ Positive effects
* in conjunction of feed chlorination.

How Fouling Affect Membrane Flux

The effect of membrane fouling can be examined through a simplified model – Hagen-Poiseuille equation:

$$J = \frac{ed_p^{2}\Delta P}{32dm} \qquad \text{Equation (1)}$$

Where: *J:* flux
ε: porosity of the membrane (ratio of the membrane pores area to total membrane area),
dp: mean pore diameter of the membrane,
DR: trans-membrane pressure,
d: effective thickness of the membrane,
m: viscosity of fluid.

Hagen-Poiseuille equation is a special form of Darcy equation where: (1) flow within membrane pores is in laminar flow regime, and (2) the pores are round in shape. This equation can be expanded to non-round pores by replacing *dp* in Equation (1) with hydraulic diameter D_H (the ration of section area of flow to wetted perimeter). That is:

$$J = \frac{eD_H^{2}\Delta P}{32dm} \qquad \text{Equation (2)}$$

According to Equation (2), for given trans-membrane pressure and fluid viscosity, the flux of a membrane depends on (1) porosity of the membrane, *e*, (2) hydraulic diameter of the flow channel in pores, D_H, and (3) the effective thickness of the membrane, *d*.

When a membrane is fouled, porosity decreases, hydraulic diameter decreases, and effective thickness increases. If J_0, e_0, D_{H0}, and d_0 represent flux, porosity, hydraulic diameter, and effective thickness of a "clean" membrane, respectively, the influence of membrane fouling on flux can be expressed by the flux ratio of the fouled membrane and the clean membrane, J/J_0:

$$\frac{J}{J_0} = \frac{(e/e_0)(D_H/D_{H0})^2}{(s/s_0)} = (\frac{e}{e_0})(\frac{D_H}{D_{H0}})^2(\frac{d}{d_0})^{-1} \qquad \text{Equation (3)}$$

Three terms on the right-hand side of Equation (3) correspond to three fouling mechanisms: pore blocking, and, internal pore plugging, and cake filtration, respectively (Cheryan, 1998). The impacts of last two terms on flux reduction are graphically presented in Figure 1 in which e/e_0 is unity. Since the effect of e/e_0 on J/J_0 is linear, the response surface in Figure 1 will move downward to (1 - e/e_0) unit when e/e_0 is less than 1.0.

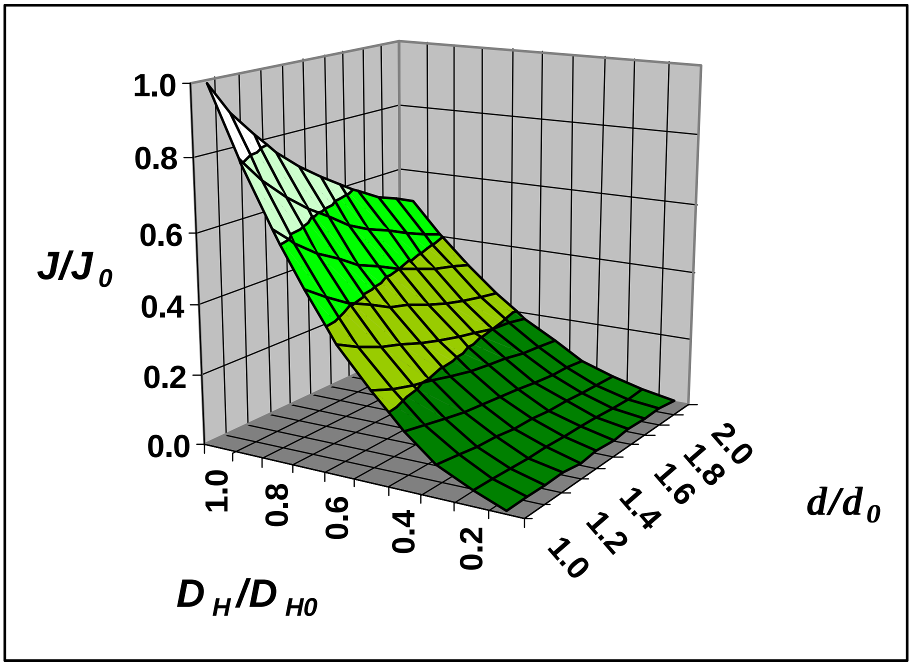

Figure 1. J/J_0 as a function of D_H/D_{H0}, and d/d_0 (e/e_0 = 1.0)

Figure 1 shows a steep decline of flux along the axis of D_H/D_{H0}, indicating that internal pore plugging would cause greater hydraulic resistance than cake formed on membrane surface. This is intriguing when one considers the fouling caused by natural organic matters. Because most of natural organic matters have sizes less than pore diameters of MF and UF used in drinking water filtration, adsorption of natural organic matters on the membrane is a plausible mechanism. It has been reported that pores appeared to be more preferable sites for adsorption (Jucker and Clark, 1994). That may explain why organic fouling typically causes more severe flux decline than particle/colloidal fouling (Lahoussine-Turcaud et al, 1990), which is most likely to foul the membranes through mechanisms of pore blocking and cake formation. It should be noted that the increase in membrane thickness due to the accumulation of foulants is not physical thickness of the fouling layer, but a hydraulically equivalent of an increase in thickness of clean membrane. This is because fouling layer and clean membrane may have different permeability.

In reality, more than one mechanisms of membrane fouling may occur simultaneously. In addition, the relationship of flux decease and the changes in ε, D_H and *d* cannot be established because they are very difficult to measure experimentally. Therefore, alternative procedures have to be established to quantify the impacts of fouling. One commonly used approach is to lump all factors affecting flux except trans-membrane pressure into one resistance term to form so-called resistance model:

$$J = \frac{\Delta P}{R} \qquad \text{Equation (4)}$$

Membrane Chemical Cleaning

The key issue to understand membrane fouling and cleaning is to understand interactions a) between fouling materials and membrane, b) between cleaning chemicals and fouling materials, c) between cleaning chemicals and membrane, and d) among the fouling materials.

Interactions Between Fouling Materials and Membrane

Membrane fouling is a complicated phenomenon of which causes of fouling are multiple and poorly understood. The core of the issue is interactions between fouling materials and membrane, and between fouling materials themselves. It has been recognized that electrostatic interaction and hydrophobic/hydrophilic interaction between membranes and fouling materials have a significant bearing on membrane fouling. This is particularly true to more difficult fouling problems caused by adsorption of natural organic matters and biopolymers on the membrane. The balance between the forces of electrostatic repulsion and hydrophobic adhesion determines the outcomes of membrane fouling, as well as the efficiency of chemical cleaning

Electrostatic Interactions

Surface charge of membrane media is the results of ionization of particular functional groups existed on the membrane surface (e.g., carboxyl and amine). Because ionization of a functional group depends on pH, surface charge of a particular membrane is also pH-dependent. In pH range of typical natural waters, most membranes appear to have a neutral to negative net surface charge. On the other hand, colloids, particles, and dissolved organic matters typically carry negative charges at the pH of natural water. Therefore, there is a tendency of electrostatic repulsion between membranes and those constituents.

Natural organic matter, a major factor of membrane fouling, typically contains about 50% humic substances. Aquatic humic substances (AHS) are polyprotic acids (Malcolm, 1985). Major acidic functional groups include carboxylic and phenolic functional groups. About 70% - 80% of total acidity is from carboxylic groups, and rest is from phenolic hydroxyl groups, as illustrated by a typical titration curve of HAS in Figure 2 (adapted from Thurman, 1985)

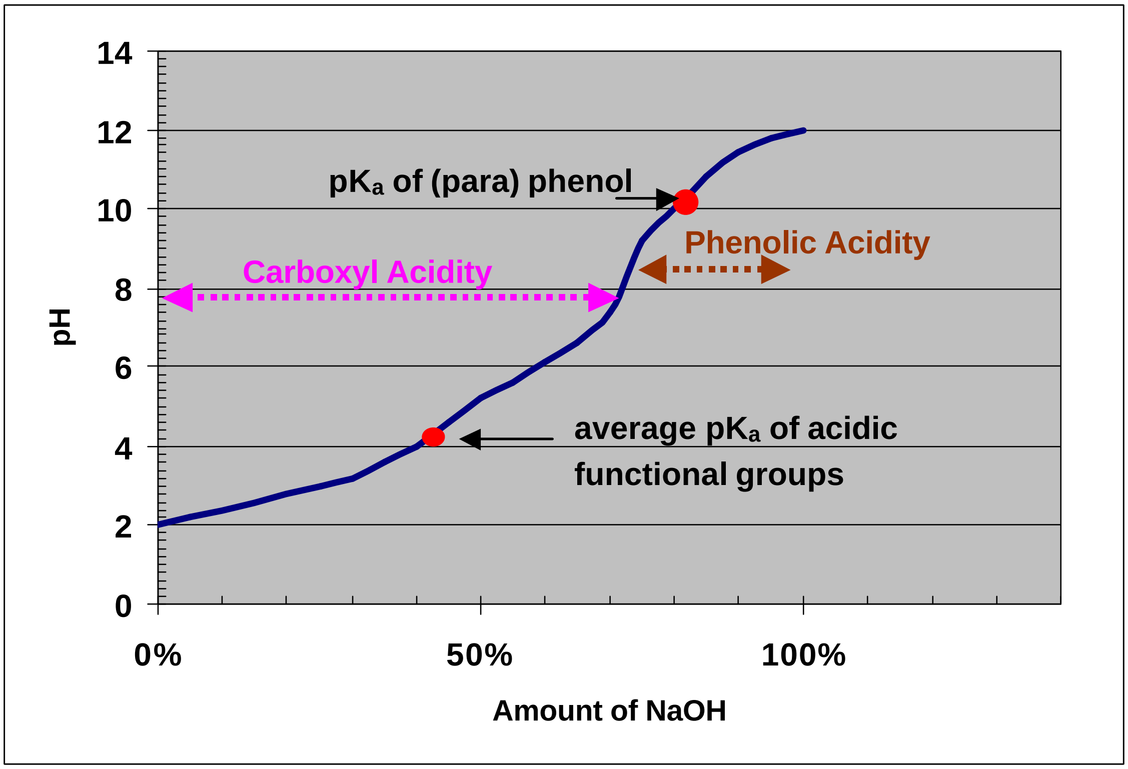

Figure 2. Titration of aquatic humic substances (adapted from Thurman)

As illustrated in Figure 2, over two thirds of acidic functional groups dissociates at pH of natural waters. During chemical cleaning, the pH of caustic cleaning solutions is typically above 12. At this pH, all but a very few ionic functional groups would dissociate and carry negative charges.

Conditions other than pH may also affect the interactions between fouling materials and membranes. For example, high ion strength of a solution can compress “double electric layer” of colloids, which could reduce their repulsion to negatively charged membranes. Another example is divalent cations, which can act as “salt bridge” between a negatively charged membrane and other negatively charged species in the fluid by charge neutralization. It has been reported that high ion strength and high calcium concentration increased the tendency of membrane fouling (Clark and Junker, 1993; Hong, 1996).

As discussed above, membranes and most fouling materials are likely to carry negative charges. Therefore, electrostatic repulsion is a major force to keep membrane and fouling materials apart. By the same logic, membrane cleaning can be enhanced by increasing electrostatic repulsion by increasing the charge density of fouling materials.

Hydrophobic Interaction

Hydrophobic interaction can be described as “like attracts likes”. That is, there is a natural tendency of attraction between membranes and solutes with similar chemical structures. Hydrophobic attraction results from van der Waals force between molecules.

It is estimated that the van der Waals energy per CH_2 group is approximately 2.5 kJ/mol (Somasundaran et al., 1964). For a 12-C organic segment, the van der Waals cohesive energy is approximately 30 kJ/mol, which exceeds the electrostatic repulsion energy from the dissociation of one charge group. In other words, if there is only one charged functional group in an organic compound and the number of C-atoms of the compound is greater than 12, the energy of hydrophobic adhesion starts to exceed the energy of electrostatic repulsion, resulting adhesion of the compound to a hydrophobic surface such as membrane. Hydrophobic adhesion is important mechanism for fouling dominated by NOM because generally high molecular weight of NOM in comparing to their charge density provides great potential for hydrophobic adhesion. Thurman and Malcolm (1979) found that this "one-in-twelve" rule is also applicable to the separation of NOM by XAD resin: if there is at least one ionic functional group per 12 carbon atoms in a molecule, then the molecule has solubility such that it can be isolated on the XAD resin and eluted in a NaOH solution.

Hydrophobicity of membrane media is usually characterized by (water) contact angle. The greater the contact angle, the more hydrophobic of a membrane medium is. The measurement of water contact angle is affected by many factors including material, manufacturing process, roughness of the membrane surface, the purity of water, and even the techniques used by individual investigators. A plot according to the data from Cheryan (1998) is depicted in Figure 3, which represents an approximate order of hydrophobicity of various membrane media. The mean and standard deviation are used in Figure 3 whenever more than one measurement for the same medium is available.

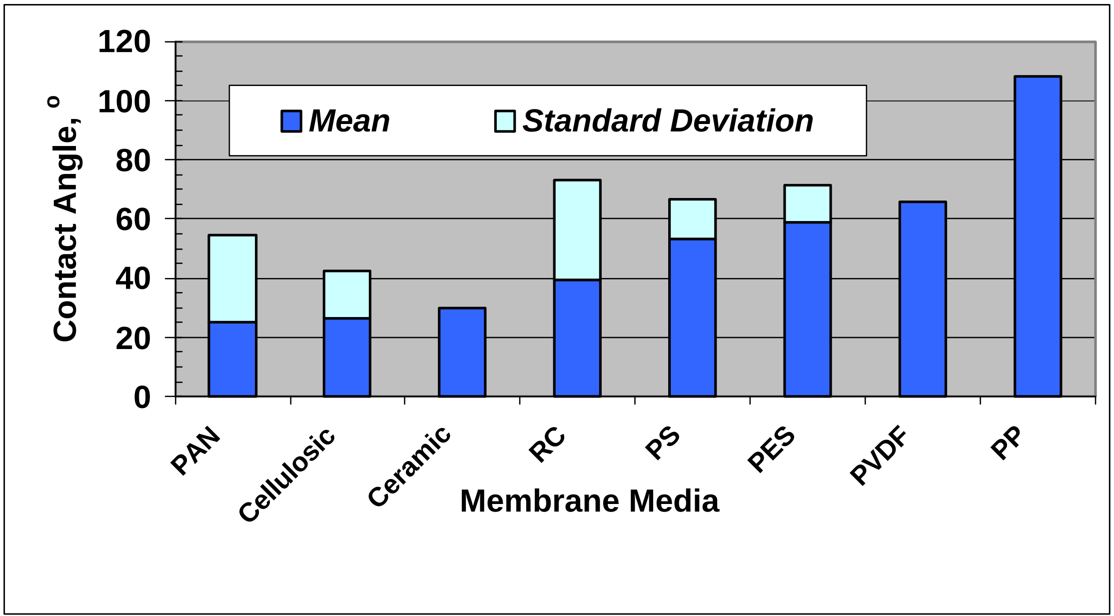

Figure 3. Hydrophobicity of various membrane media (data from Cheryan, 1998): PAN- polyacrylonitrile, RC-regenerated cellulose, PS – polysulfone, PES – polyethersulfone, PVDF – polyvinylidene fluoride, PP – polypropylene

It is not surprising to find great discrepancy in contact angle even within the "same" membrane medium. This is because manufacturing processes that are collectively termed as "hydrophilization" can significantly modify hydrophobicity of a membrane. One good example is that a relatively hydrophobic PVDF membrane can be made more hydrophilic by surface modification through a proprietary oxidation step.

Hydrophobicity of a solute can be characterized by its octanol-water partition coefficient, K_{OW}, or aquatic solubility, Ks (Stumm and Morgan, 1996). Typically, the values of K_{OW} of chemical species are inversely proportional to their solubility in water, K_S (Schwazenbach et al., 1993). In general, the higher the hydrophobicity of a chemical spices, the higher its potential to foul membrane. Figure 4, adapted from Schwarzenbach et al. (1993), depicts median values of K_{OW} and K_S of some representative compounds

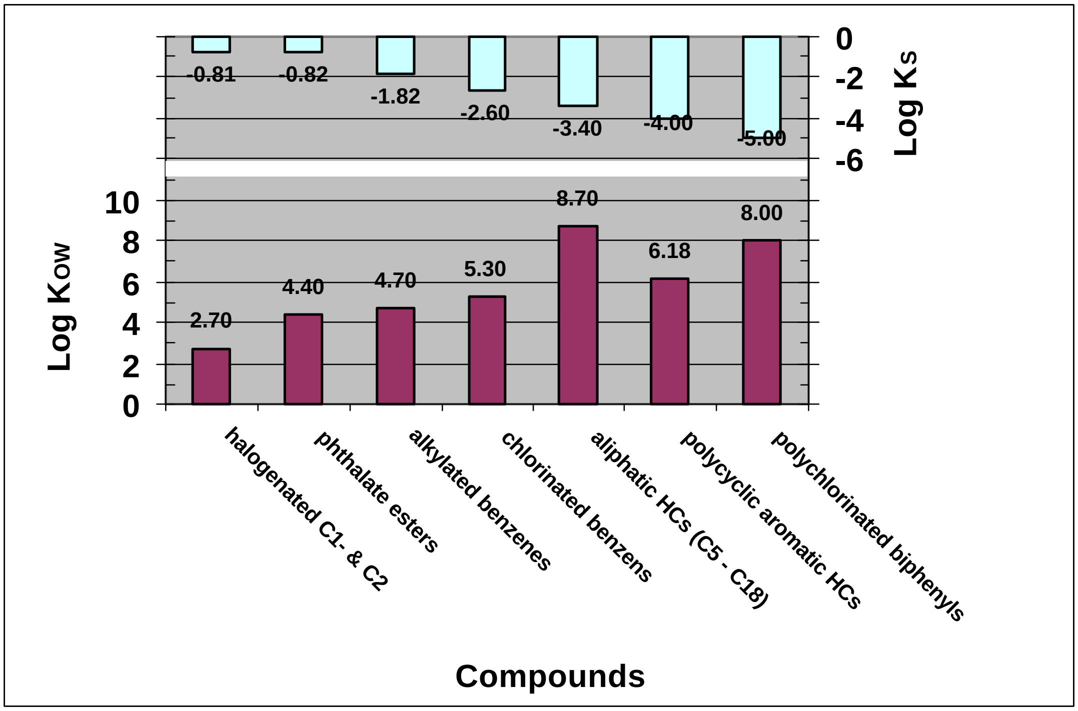

Figure 4. Median values of K_{OW} and K_S of representative compounds (Adapted from Schwarzenbach et al., 1993)

Figure 4 illustrates the underline principle for the relationship between hydrophobicity of a particular group of compounds and their structure. As expected, hydrophobicity will increase with the increase in molecular weight and the decrease in polarity of molecules. An extensive discussion on how chemical structure affects hydrophobicity can be found in Schwarzenbach et al. (1993).

With the exception of aliphatic hydrocarbons (C5 – C18), the relation ship between median values of log K_S and log K_{OW} is largely inversely proportional, as shown in Figure 5.

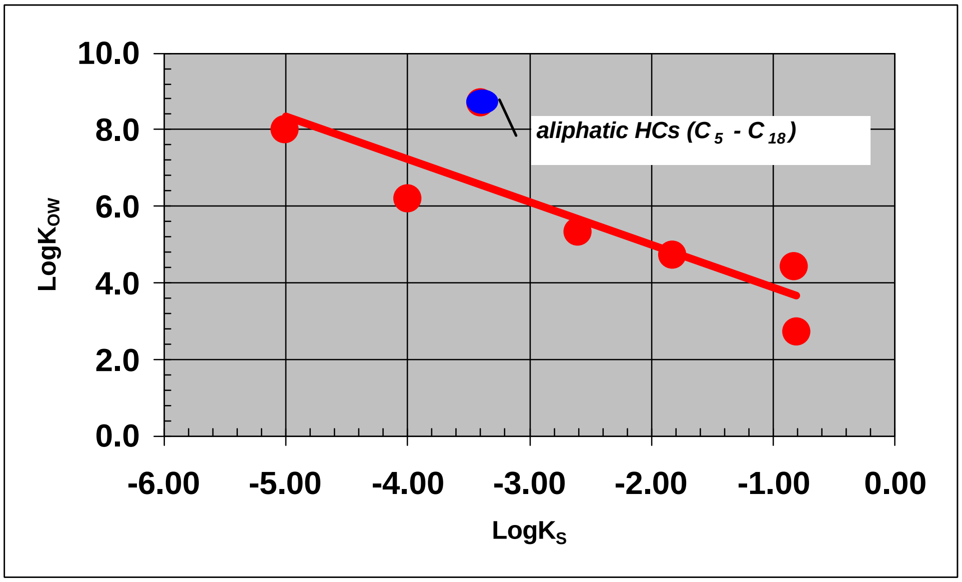

Figure 5. Relationship of Log K_{OW} and Log K_S of representative compounds

The principles of the relationship between chemical structure and hydrophobicity, as indicated in Figure 4, are also applicable to natural organic matter. However, because natural organic matter is much more heterogeneous and complicated, there has been not enough information to develop a clear-cut relationship as that in Figure 4 for natural organic matter. In general, aquatic natural matter has a much higher molecular weight on average. While the number of C-atoms per charged functional group might be well below 12 on average (Thurman, 1985), those charged functional groups is not necessarily distributed evenly on carbon backbones. Therefore, in the regions where mass-to-charge ratio is high, hydrophobic adsorption could dominate.

Naturally, analytical methods that give more details on the structures of natural organic matter would generate insights on the hydrophobic/hydrophilic nature of a particular group of organic matter. Fractionation with nonionic XAD can divide natural organic matter into hydrophobic and hydrophilic fractions. Depending upon the nature of organic matter, this method can generally isolate 50% to 90% of dissolved organic carbon in natural water samples (Thurman et al., 1978, Groué and Leenheer, 1997). Another method to provide structural information is “Bruchet Grouping”, which classifies natural organic matter into four groups by pyrolysis - gas chromatography – mass spectrometry (pyrolysis-GC-MS). The subgroups of organic matter classified by this method include polysaccharides, polyhydroxyaromatics, aminosugars, and proteins (Gadel and Bruchet, 1987; Bruchet et al., 1990). Although the pyrolysis-GC-MS is only considered as semi-quantitative and only identifies about 5 -15% of dissolved organic carbon, it provides some insights on the structure and possible origin of natural organic matters. The third valuable method is ^{13}C-nuclear magnetic resonance spectrometry (^{13}C-NMR). This method provides information for carbon functionality such as aromatic-C, aliphatic-C, carboxylic-C, phenolic-C, etc. The cross correlation of pyrolysis-GC/MS and ^{13}C-NMR indicated the following (Groué and Leenheer, 1997):

(a) The percentage of carboxylic-C increases with hydrophilicity, while the percentage of aromatic-C increases with hydrophobicity;
(b) Aromaticity is strongly correlated to the content of polyhydroxyaromatics and the carbon-to-nitrogen (C/N) ratio;
(c) The content of protein and aminosugars is reversibly correlated to the C/N ratio.

From those results, one can conclude that polyhydroxyaromatics, although sometimes only a minor constituent of natural organic matters, is the most hydrophobic and would have strong adhesion on membranes that are relatively hydrophobic. This seems to be in agreement with results of some lab and field studies (Jacangelo et al, 1992; Grozès et al., 1993).

In aquatic environments where oxygen is abundant, biochemical modification to the natural organic matters usually lead to more oxygen-containing functional groups on the carbon backbones. The important functional groups include carboxylic acids, enolic hydrogen, quinone, alcoholic hydroxyl, ether, ketone, aldehyde, ester, lactone, amide, and amine (Thurman, 1985). The existence of these functional groups typically increases hydrophilicity of natural organic matter by increasing charge density, and by formation of hydrogen bonds with water molecules. This is very important for understanding the chemical cleaning because the effectiveness of cleaning is greatly related to its ability to increase charge density of foulants, therefore to make them less adhesives to membranes.

Conceptual Model of Membrane Fouling and Cleaning

For membrane fouling dominated by the adsorption of natural organic matter, and dominated by microbial causes to a less extent, the fouling and cleaning can be illustrated by a simple conceptual model as in Figure 6.

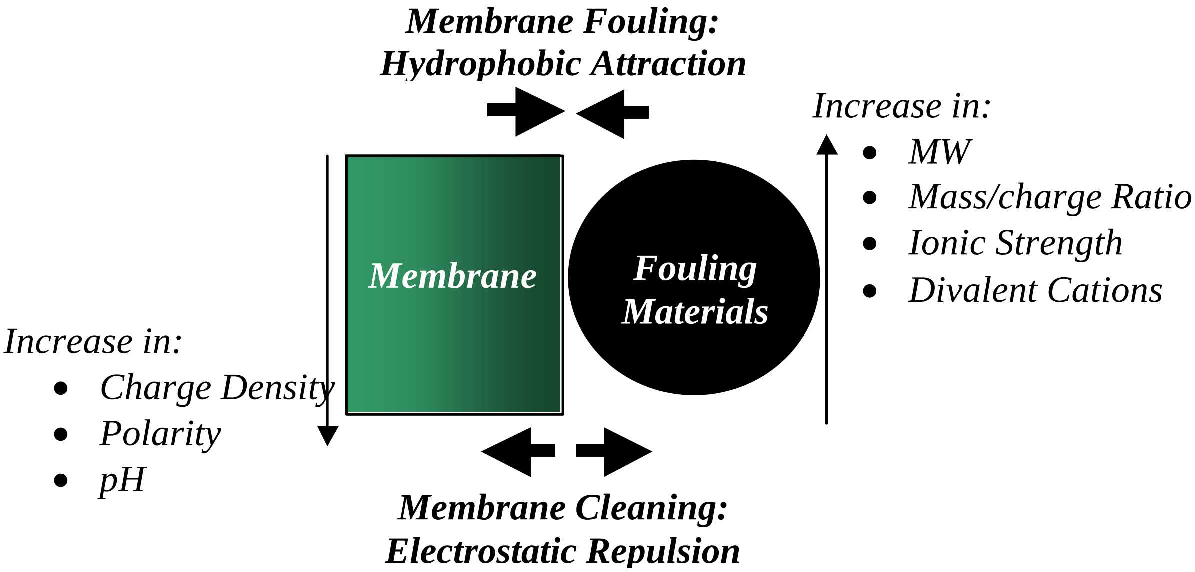

Figure 6. Conceptual Model of Membrane Fouling and Cleaning

The balance between hydrophobic attraction and electrostatic repulsion essentially determines if a membrane is being fouled or being cleaned. As molecular weight and mass/charge ratio of solutes, ionic strength, and the concentration of divalent cations increases, hydrophobic attraction tend to increase, so does the potential of membraen fouling. On the other hand, increases in charge density and polarity of solutes, and pH will increase electrostatic repultion between the membrane and solutes, which reduces the adhesion between membrane and fouling materials and enhances the cleaning efficiency. The model is simplistic in a sense that it only focus on major interactions – electrostatic repulsion and hydrophobic attraction - between membrane and fouling materials. The model considers other possible interactions between membrane and fouling materials such as hydrohgen bonds and dipolar moment as secondary. In addition, the model does not address hydrodanymic aspect of mass transport, which is also important to membrane fouling, but beyond the scope of the paper. Nevertheless, the model provides a conceptual framwork on understanding of the chemical aspects for membrane fouling and cleaning, which is the focus of the paper.

Membrane Cleaning Chemicals

Once the cause of membrane fouling is identified, various cleaning chemicals can be used to remove fouling materials from the membrane and to restore the membrane flux. Chemicals commonly used for cleaning MF and UF membranes in water industry fall into five categories, as summarized in Table 2. A more detailed discussion is followed for each of cleaning chemicals.

Table 2. Major Categories of Membrane Cleaning Chemicals

Category	Major Functions	Typical Chemicals
Caustic	Hydrolysis, solubilization	NaOH
Oxidants/Disinfectants	Oxidation, disinfection	NaOCl, H_2O_2, peroxyacetic acid
Acids	Solubilization	Citric acid, nitric acid
Chelating Agents	Chelation	Citric acid, EDTA
Surfactants	Emulsifying, dispersion, surface conditioning	Surfactants, detergents

<u>Caustic</u>

Caustic is typically used to clean membranes fouled by organic and microbial foulants. The function of caustic is two-fold: (1) hydrolysis, and (2) solubilization. There are a number of organic materials including polysaccharides, and proteins can be hydrolyzed by caustic. The hydrolysis of polysaccharides is the reason why cellulose-based (cellulose, a simple polysaccharide, consists of thousands of glucose linked by 1,4’-β-glycoside bounds) membranes have to be used in a limited pH range. Proteins are also hydrolyzed by caustic. Tertiary structures of proteins are likely to be disrupted and proteins are reduced to peptides. Fats and oils also react with caustic through saponification, generating water-soluble soap micelles.

A very important function of caustic is to increase negative charges of humic substances. Therefore, they are easier to be removed from membranes. As mentioned before, humic substances contain many functional groups that are organic acids. Their acidity ranges from pKa (negative logarithm of the dissociation constant) of 1.2 (oxalic) to 13 (phenol), with an average pKa of 4.2 (Thurman, 1985). During caustic cleaning, pH of cleaning solution can be as high as 13. At this pH, even the weakest phenolic groups would dissociate by 50%. As a result, the negative charges on organic molecules increase to a great extent, so does their solubility. For example, when carboxyl (-COOH) is converted into carboxylate ($-COO^-$) at alkaline conditions, solubility increases nearly three orders of magnitude (Thurman, 1985). Phenolic groups are typically associated with the most hydrophilic portion of NOM and likely to have strong adhesion to membranes. Hydrophilizing this portion of organic matter undoubtedly weakens the bound between membrane and those fouling materials. In addition, the molecules of nature organic matter are likely to have stretched, linear configuration due to the repulsion between negative charged functional groups (Stumm and Morgan, 1996; Hong and Elimelech, 1997). This change in molecule configuration creates a loose fouling layer that allows an easier access for chemicals to penetrate the inner portion of fouling layer, therefore facilitates mass transfer, and enhances the efficiency of cleaning.

Oxidants

Most common oxidants used for membrane cleaning include chlorine and hydrogen peroxide. The oxidation of organic polymers generates more oxygen-containing functional groups such as ketone, aldehyde, and carboxylic acids. As discussed before, the existence of these functional groups generally increases hydrophilicity of their parent compounds. Therefore, oxidation reduces the adhesion of fouling materials to membranes. The chlorination of aquatic humic substances by NaOCl at alkaline conditions (pH = 12) yields three major classes of products: (a) non-chlorinated substituted aromatics, (b) non-chlorinated substituted straight chain acids, and (c) chlorinated straight chain acids. These products were considered as the part of cross-linking structure and ring rupture of activated aromatic structures (Havlik et al., 1979; Christman et al., 1980). Among the non-chlorinated substituted aromatics many are aromatic di-, tri-, and tetracarboxylic acids. The increase in abundance of carboxylic groups on aromatic rings increases negative charges of natural organic matter at alkaline pH conditions due to the dissociation of these acids.

Quite often, oxidants are mixed with caustic to form a cleaning “cocktail”. This practice seemed to be anti-intuitive because chlorine and hydrogen peroxide are known to be more powerful oxidants at acidic conditions. There are four reasons to mix oxidants, specifically chlorine with caustic:

(1) To enhance cleaning efficiency. The mixture provides a synergy for NOM dominated fouling because fouling layer tends to have more open structure at caustic conditions due to the change in configuration as discussed before. This synergy provides more access to chlorine to reach inner layer of fouling materials, facilitates the mass transfer and reactions between chlorine and fouling materials, and enhances the cleaning efficiency.

(2) To control of excess oxidation to membranes and other module components. At acidic conditions, chlorine is such a strong oxidant that the potential of damage to membrane and other filter components increases to a great extent. Mixing chlorine with caustic will prevent excess oxidation by chlorine.

(3) To simplify the equipment and operation of membrane cleaning. Both caustic and oxidants are needed for efficient membrane cleaning. Mixing them allows the cleaning to be conducted in one step.

(4) Reduce the health hazards of cleaning operation. Chlorine at acidic conditions has a tendency to migrate to gas phase, as governed by following reactions:

$$H^+ + OCl^- \Leftrightarrow HOCl \qquad \text{Equation (5)}$$

$$HOCl + HCl \Leftrightarrow Cl_2(aq) + H_2O \qquad \text{Equation (6)}$$

$$Cl_2(aq) \Leftrightarrow Cl_2(g) \qquad \text{Equation (7)}$$

Where $Cl_2(g)$ and $Cl_2(aq)$ are chlorine concentration in gas-phase and water (mol/L), respectively. As pH increases, equilibriums of three equations would shift towards to the left hand. Therefore, chlorine concentration in gas-phase [$Cl_2(g)$] decreases.

Acids and Chelating

Acids are used primarily for removing scales and metal dioxides from fouling layers. When membrane is fouled by iron oxides, citric acid is very effective because it not only dissolves iron oxides precipitates, but also forms complex with iron. In addition, some of organic compounds such as polysaccharides and proteins also hydrolyze. If there is coexistence of divalent cations (calcium, for example) and natural organic matters, “salt bridge” effect of divalent cations can cause a denser and more adhesive fouling layer. The removal of divalent cations by either acids or chelating reagent such as EDTA can also improve the cleaning of membranes fouled by organic foulants (Hong and Elimelch, 1997).

Surfactants

Surfactants are compounds that have both hydrophilic and hydrophobic structures. They can form micelles with fat, oil, and proteins in water and help to clean the membranes fouled by these materials. Some surfactants may also interfere hydrophobic interactions between bacteria and membranes (Paul and Jeffery, 1984; Ridgway et al., 1985, Ridgway, 1988; Rosenberg and Doyle, 1990). In addition, surfactants can disrupt functions of bacteria cell walls. Therefore, surfactants affect fouling dominated by the formation of biofilms.

One interesting but less clear aspect is how surfactants affect membranes fouling dominated by NOM. For the sake of simplicity, let’s consider the interaction of a hydrophobic membrane and a nonionic surfactant with a linear configuration, i.e., a hydrophilic head and a hydrophobic tail. Because the surfactant is nonionic, the interaction between the membrane and the surfactant is dominated by hydrophilic/hydrophobic reaction. Since the membrane is hydrophobic, hydrophobic tail of the surfactant is preferably adhered to the membrane surface and hydrophilic head is orientated towards aquatic phase. This arrangement is like to have the membrane a hydrophilic “coating”, resulting in a more hydrophilic membrane. In fact, soaking in surfactant has been used as a method for surface modification to improve hydrophilicity or wetting ability of certain membranes.

Operating Parameters Affecting Cleaning Efficiency During Chemical Cleaning

Because membrane cleaning is essentially conducted through chemical reactions between cleaning chemicals and fouling materials, factors that affect the mass transfer and chemical reactions such as concentration, temperature, length of cleaning period, and hydrodynamic conditions all affect cleaning efficiency.

When selecting cleaning conditions, one of the most important considerations is if the conditions for cleaning are compatible with membrane media and other components of the membrane filters and systems. Chemical compatibility of membrane and other filter components and systems limits the type and the maximum allowable concentration of a chemical to be used during cleaning. Membranes made from materials with high chemical resistance allow more flexible selections of the type and the concentrations of cleaning chemicals in dealing with various types of fouling problems

Concentration of cleaning chemicals can affect both the equilibrium and the rate of reaction. Unlike reactions occurred in liquid phase, reactions between cleaning chemicals and fouling materials occur in the interface of liquid and a (solid) fouling layer. The concentration profile of cleaning chemicals within the fouling layer is a function of the concentration of cleaning chemicals in the bulk liquid phase. Therefore, the concentration of cleaning chemicals not only needs to maintain the reasonable reaction rate (kinetics need), but also needs to overcome mass transfers barrier imposed by the fouling layer. In practice, the concentrations of cleaning chemicals are usually high enough to satisfy the kinetic need. It is mass transfer that sets the lower boundary for the concentration of cleaning chemicals.

Temperature can affect membrane cleaning by (1) changing the equilibrium of a chemical reaction, (2) changing the reaction kinetics, and (3) changing the solubility of fouling materials and/or reaction products during the cleaning. Generally, an elevated temperature promotes better membrane cleaning. Again, one should check compatibility of membrane and other filter components regarding temperature during cleaning.

As discussed previously, membrane cleaning involves mass transfer of chemicals to the fouling layer and the reaction products back to the bulk liquid phase. Therefore, hydrodynamic conditions that promote contacts between cleaning chemicals and fouling materials during the cleaning are preferred. From mass transfer point of view, dynamic cleaning involving circulating cleaning solutions through the system can be more effective than simply static cleaning such as soaking. This may be particularly important for the fouling materials embedded in membrane matrix. In static cleaning conditions, the transport mechanism is primarily through diffusion. Maximizing concentration gradients of both cleaning chemicals and reaction products and shortening the distance of diffusion by bringing fresh chemicals close to the vicinity of the fouling materials would enhance the cleaning.

Case Studies

Four case studies are presented to illustrate some points discussed previously.

Case 1: Effects of Cleaning Chemical Composition

To investigate the effect of different compositions of cleaning solution, a study was conducted in which a hollow-fiber membrane filter used in a field test for five months was acquired and hollow fiber samples were removed from the housing. The feed water to the filter was surface water. The water is relatively hard, but has low turbidity, medium TOC, and occasional algae bloom. Characteristics of the feed water are presented in Table 3.

Table 3. Characteristics of Feed Water Quality in Figure 5

Item	Sample No.	Range (Min. – Max.)	Mean	Std. Dev.
Turbidity, NTU	176	0.5-2.9	1.1	0.4
PH	18	7.7 – 8.7	8.1	0.3
Alkalinity, mg/L $CaCO_3$	18	37 - 65	54	9
Calcium, mg/L	6	69 - 76	73	4
TOC, mg/L	18	1.22 – 2.99	1.86	0.52
UV_{254}, cm^{-1}	18	0.01 – 0.09	0.02	0.02

The clean water flux was used as an indicator measuring the “cleanness” of fibers samples. The water used for measuring clean water flux was DI water filtered through UF. Clean water flux of fiber samples as received were first measured. Then fibers were cleaned with various schemes (caustic alone, NaOCl alone, caustic plus NaOCl). After cleaning, clean water flux was measured again. Changes in flux following different cleaning schemes were compared, as depicted in Figure 7, which were based on the average of four to five duplicates.

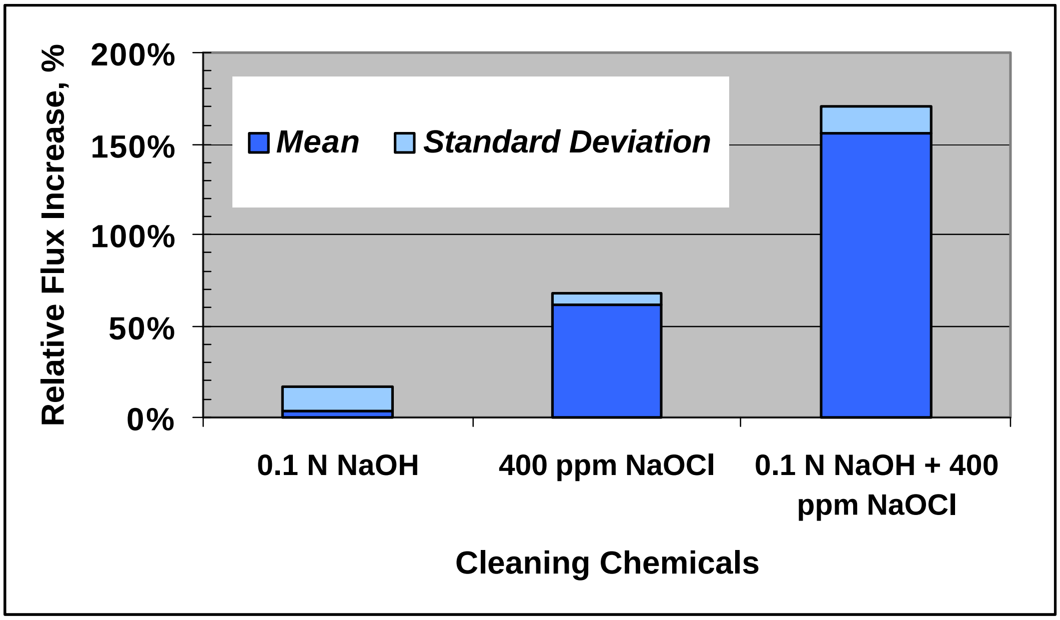

Figure 7. Comparison of effects of cleaning chemicals on flux

As depicted in Figure 7, cleaning with 0.1 N NaOH alone did not show any effect. Cleaning with 400 ppm NaOCl increased flux by 60%. However, the cleaning with the combination of two chemicals increased flux by over 150%. Clearly, the combination of caustic and NaOCl is the most effective cleaning scheme for membrane fouled by this particular feed water. A possible explanation for this is that almost all ionic functional groups of fouling materials were carboxylic and dissociated at low pH already. Therefore, increase in pH by caustic alone does not increase charge density. Relatively low UV absorbency at 254 nm indicates low aromaticity of NOM, thus a low number of phenolic groups in this water, which is in consistence with the assumption of the nature of ionic functional groups. NaOCl oxidized the fouling material and created more ionic functional groups, possibly including both carboxylic and phenolic groups. The increase in charge density increases electrostatic repulsion and made cleaning more efficient. With the combination of NaOCl and caustic, charge density increased farther due to the dissociation of phenolic groups at high pH. Therefore, highest cleaning efficiency was achieved.

Case Study No. 2: Effects of Concentration of Cleaning Chemicals on Cleaning

As discussed previously, caustic and oxidants have different functions in chemical cleaning. The combination of both chemicals can generate synergy for effective cleaning. This case study presents the results of hollow fiber cleaning studies for samples taken from two different test sites that have different water quality characteristics, as summarized in Table 4. Site A is a surface water of low hardness and organic matters. Site B is surface water with high hardness, moderate organic matters.

Table 4. Water Quality Characteristics of Two Sites

Water Quality Parameter	Site A		Site B	
	Range	Average	Range	Average
Turbidity, NTU	1 – 5	2	1.1 – 3.8	1.8
PH	7.6 – 7.9	7.7	7.7 – 8.8	8.1
Alkalinity, mg/L $CaCO_3$	-	-	122 - 162	142
Calcium, mg/L	8 – 14	12.7	69 – 76	73
Hardness, mg/L $CaCO_3$	50 – 70	57	240 - 297	267
TOC, mg/L	0.3 – 0.5	0.4	1.22 – 2.99	1.86
UV_{254}, cm^{-1}	0.005 – 0.011	0.007	0.01 – 0.09	0.02
Color, CU	1 – 5	2	4 – 90	29

Concentrations of caustic and oxidant (NaOCl) were varied to form different combinations of caustic/oxidant mixture. The effectiveness of cleaning as a function of different combinations of cleaning solution was gauged based on the flux recovery as new fibers and presented in Figures 8 and 9 for Site A and B, respectively.

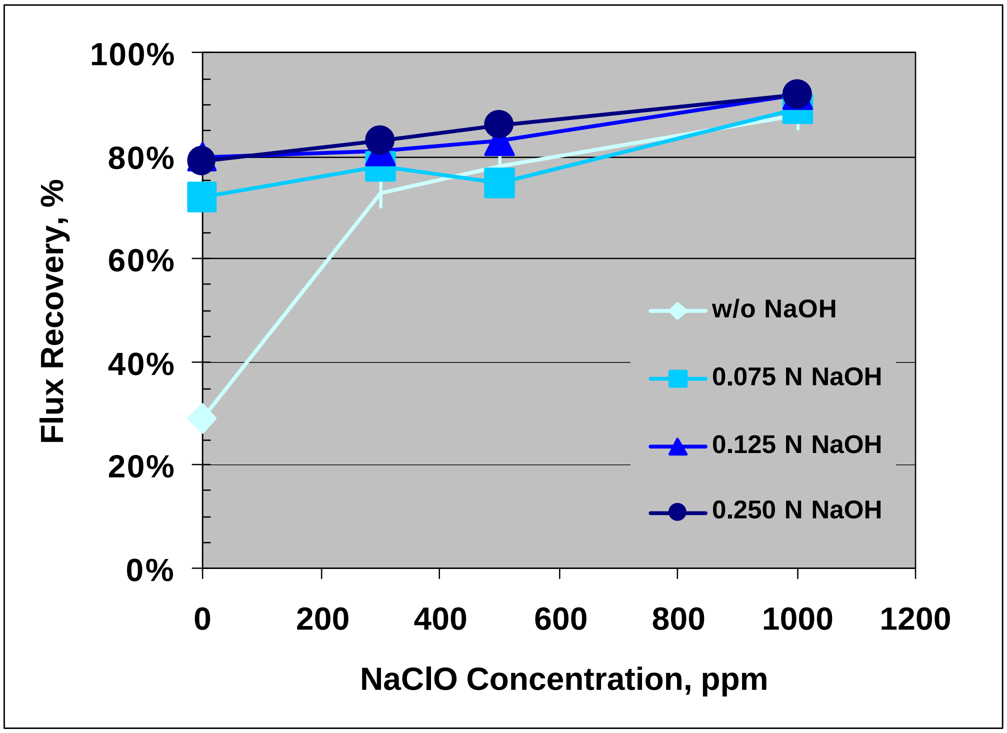

Figure 8. Effects of NaOCl and NaOH concentrations on cleaning of hollow fiber samples taken from Site A.

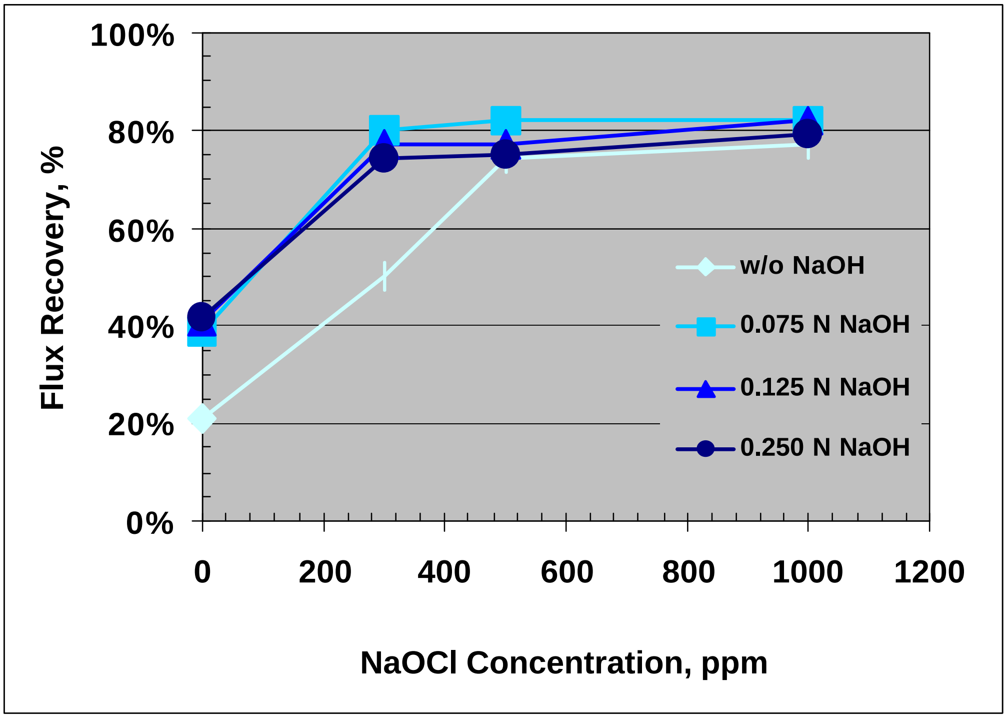

Figure 9. Effects of NaOCl and NaOH concentrations on cleaning of hollow fiber samples taken from Site B.

It is interesting to note the difference in cleaning effectiveness for different combinations of caustic/chlorine concentrations for two sites. For Site A, flux recovery generally increased as concentrations of both caustic and NaOCl increased. Caustic alone was quite effective to clean fouled membranes, generating 70+% flux recovery. As the concentration of NaOCl increased, the effect of caustic concentration on effectiveness of cleaning started to diminish, but still measurable at 1,000 ppm NaOCl. For Site B, on the other hand, the effect of NaOH concentration on cleaning was insignificant except for zero caustic concentration. There seemed to be a threshold concentration for caustic between 0 to 0.075 N. Once the threshold value is satisfied, excess caustic does not have significant effect anymore. In addition, there seemed to also have a threshold concentration of NaOCl between 300 ppm to 500 ppm. Beyond this threshold concentration, the improvements in flux recovery were rather marginal. Compared to the samples from Site A, flux recovery of samples from Site B reached a pseudo-maximum around 80%.

Different effects of cleaning chemical concentrations on effectiveness may attribute to the difference in fouling materials. The feed water of Site A contains low organic matters, low metals, and probably low hydrophobic humic substances judged by low values of TOC and UV_{254} data. Therefore, addition of NaOCl did not improve flux recovery significantly as for samples from Site B. On the other hand, membranes from Site B seemed to have fouling materials that could not been cleaned with caustic/chlorine solutions, such as metal oxides deposits. Part of evidence supporting this assumption was the presence of the calcium, magnesium, aluminum, and iron on the membrane outer surface before the chemical cleaning, and the absence of those cations after the membrane was cleaned by citric acid following caustic/chlorine cleaning. It is also possible that those multivalent cations might form salt bridges between molecules of organic matter, and made fouling layers dense and hard to penetrate by cleaning solutions. Nevertheless, a two-step cleaning procedure involving caustic/chlorine cleaning followed by citric acid cleaning was able to restore the flux of membrane to a satisfactory level (94+%).

Case Study No. 3: Effect of Temperature on Chemical Cleaning

Temperature can affect both equilibrium, and kinetics of a reaction. An indirect effect of temperature on reaction equilibrium and reaction is that elevated temperature generally increases the solubility of chemical species with a few exceptions (calcium and magnesium carbonates, for example). The effect of temperature on cleaning hollow fiber samples from a field test is depicted in Figure 10, where a high strength cleaning solution (5,000 ppm NaOCl plus 0.25 N NaOH) was used to clean severely fouled membranes.

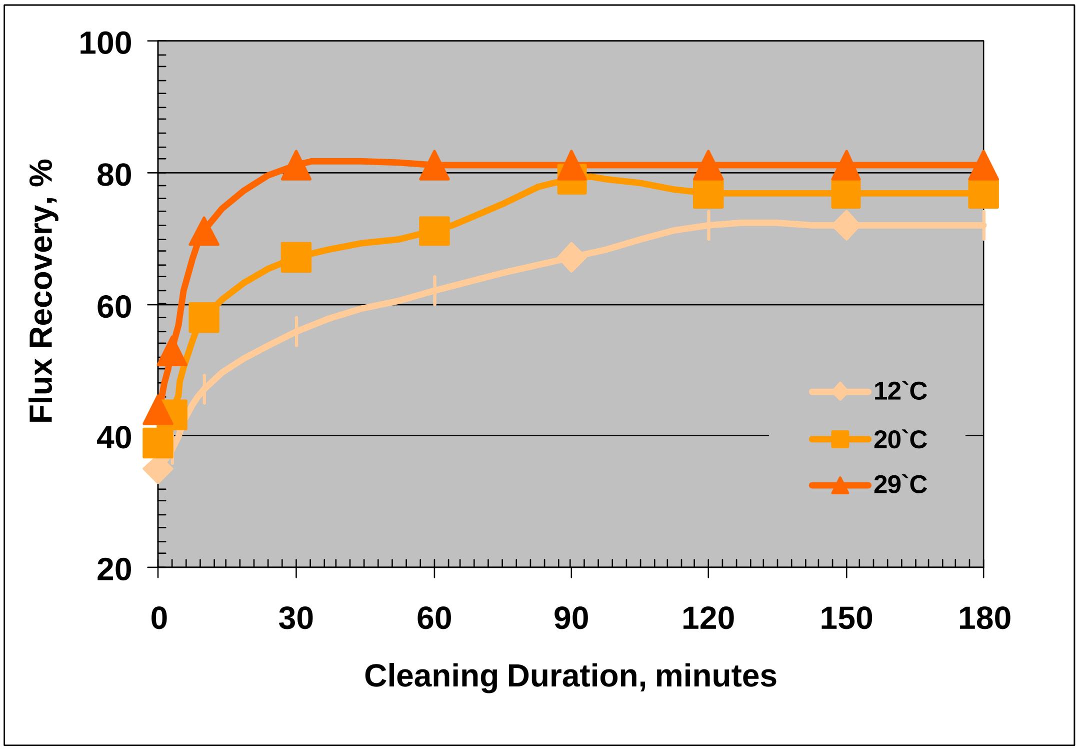

Figure 10. Effect of temperature on chemical cleaning of hollow fiber samples Cleaning solution: 5,000 ppm NaOCl + 0.25 N NaOH

As expected, higher temperature can affect both the pseudo-maximum of flux recovery and the time to reach a certain flux recovery. The effect is more profound for shorter cleaning durations less than 2 hours that is commonly used in practice. It should be noted that the test was conducted with a high strength cleaning solutions. It can be expected that the effect of temperature is more significant if the strength of the cleaning solution is reduced.

Summary and Conclusions

Membrane chemical cleaning is an integral part of operation for MF and UF applications in water industry and has significant impact on process economics. However, this issue has not been adequately addressed, partially because cleaning protocols are typically recommended from membrane manufactures and some cleaners are proprietary, partially because the issues of membrane fouling and cleaning are poorly understood and site-specific. As the advances in aquatic chemistries and analytical tools of fouling materials are gained increasingly, a broad understanding of the interactions between fouling materials and membranes, among fouling materials, and between fouling materials and cleaning chemicals starts to become possible, although there still are many gaps in chemistry details needed to be filled.

Membrane fouling is a complicated phenomenon and typically resulted from multiple causes. In spite of its complexity, electrostatic and hydrophobic/hydrophilic interactions that involves both membrane and fouling materials are recognized to have significant bearing, especially for more difficult membrane fouling dominated by organic materials and microbial activities. Electrostatic interactions occur among functional groups of membranes, fouling materials, and water primarily through dissociation and polarization, which strongly depend on the pH, ionic strength, and concentrations of divalent, multivalent cations in the solution. Hydrophobic/hydrophilic interactions are functions of structure similarities between membranes and fouling materials, the types and density of functional groups on both membrane surfaces and fouling materials, and solubility of molecules of fouling materials. As progresses in analytical techniques and in knowledge in structural details of natural organic matter, the structure-solubility correlations for synthetic compounds can be extended to natural organic matter with some reservations to provide a rough assessment on the hydrophobic nature of the latter.

The balance between hydrophobic attraction and electrostatic repulsion essentially determines if a membrane is being fouled or being cleaned. A simplified conceptual model is proposed to describe the effects of hydrophobic attraction and electrostatic repulsion on membrane fouling and cleaning. As molecular weight and mass/charge ratio of solutes, ionic strength, and the concentration of divalent cations increases, hydrophobic attraction tend to increase, so does the potential of membraen fouling. On the other hand, increases in charge density and polarity of solutes, and pH will increase electrostatic repultion between the membrane and solutes, which reduces the adhesion between membrane and fouling materials and enhances the cleaning efficiency.

Types and major functions of commonly used cleaning chemicals are discussed. The emphasis is on how cleaning chemicals interact with fouling materials. Four case studies are also presented for illustrating the points. Caustic can increase solubility by hydrolysis and solubilization. Because caustic can change the configuration of natural organic matters and make the fouling layer has a looser and more open structure, the combination of caustic and NaOCl enhances cleaning. Acids and EDTA are effective cleaners for scaling and metal oxides though solubilization and chelating. The function of surfactant is more complicated and multiple. Surface coating/conditioning is considered to have major impact on fouling dominated by natural organic matters, as demonstrated in both lab and field studies. However, the impact of surfactants lost in product water can limit the application of this technique.

Concentration, cleaning time, temperature, and hydrodynamic conditions during the cleaning are important factors affecting cleaning efficiency. Mass transfer barrier within the fouling layer is likely to be the rate-limiting factor. Creating favorable hydrodynamic conditions to facilitate mass transfer is likely to enhance the efficiency of cleaning. Temperature has a significant impact on both the efficiency and rate of membrane cleaning, presumably by changing the reaction equilibrium, by enhancing the reaction kinetics, and by increasing the solubility of solutes.

One important aspect is chemical compatibility of membrane media and other filter components to cleaning chemicals. A membrane made of high chemical tolerance would allow greater freedom in selecting the composition, strength of cleaning solutions, as well as the conditions for cleaning.

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