

MTE-6

Influence of Natural organic Matter (NOM) Characteristics On Membrane Rejection Mechanisms of Submerged Ultrafiltration Membrane Reactor

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Abstract

The main objective of this experiment is to study on the influence of NOM characteristics on the membrane rejection mechanisms. Polysulfone (PSF) membrane formed by a simple phase inversion technique was used in this research. The experiments were carried out through a hydrophobic 68 kDa MWCO polysulfone and a hydrophilic 50 kDa MWCO cellulose acetate of a submerged UF membrane reactor. The Ulu Pontian Kecil river water was fractionated into several components which were hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fractions using DAX-8 and XAD-4 ion exchange resins. The isolated surface water components were characterized by dissolved organic carbon (DOC), ultra violet absorbance at 254 nm (UV_{254nm}), specific ultraviolet absorbance (SUVA) or a measure of relative abundance of relative aromaticity, etc. The experimental results showed that the hydrophilic component of NOM to exhibit the worst flux decline despite lesser DOC and UV rejection compared to other fractions (HPO and TPI). The electrostatic interaction has been found to play a more influential role than steric hindrance mechanism when filtering nom fractions with a negatively charged membrane. The quantitative results of Resistance in-Series Model analysis on clean and fouled membranes elucidated that both reversible and irreversible fouling mechanisms occurred during surface water filtration.

Keywords: Fouling; NOM; Submerged ultrafiltration; Foulant; Surface water

Introduction

Membrane filtration processes involving microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) in potable water production have increased rapidly for the past decade and can potentially replace the conventional treatment process. Besides that, membrane filtration process does offer extra advantages over conventional treatment such as small footprint, compact module and capable of handling wide fluctuations in feed quality. MF and UF are employed to remove microparticles and macromolecules, which generally include inorganic particles, organic colloidal (i.e. microorganism) and dissolved organic matters (DOM). DOM is ubiquitous in natural surface water and often reclaimed [1-4] as important factor for both the reversible and irreversible fouling in water filtration. Unfortunately the presence of free chlorine content that is used as a disinfectant in the conventional treatment is found to react with this residual DOM consisting in the natural organic matter (NOM). This reaction process has been found to have tendency to form disinfection by product (DBPs). In this study the influence of NOM components characteristics to the fouling of a submerged ultrafiltration polysulfone membrane and fouling mechanisms were investigated. The potential foulants of NOM isolates which were detrimental to the employed submerged UF membrane were studied and identified by isolating the chosen surface water. The performance of membrane and the associated fouling mechanisms were examined based on NOM isolates rejection, flux declination, hydraulic series resistance.

Approach and Methods

Fabrication of UF membrane

The polysulfone polymer was supplied by Amoco Performance Product Inc. The additive polymer of PVP3000 was bought from Fluka Milwaukee while the solvent (DMEC) was purchased from Merck Darmstadt Germany. The PVP3000, solvent and PSF were sequentially mixed in a container until a homogenous mixture was achieved at a constant temperature of 60 °C. The formulated dope was then spun by using a forced convective dry/wet spinning technique under pressurized nitrogen gas. The membrane characteristic is shown in Table 1.

Table 1 - Characteristics of the experimental membranes

Parameter	MRUTM55	MRUTM66
Membrane type	Hollow fiber	Hollow fiber
Membrane material	Polysulfone (PSF)	Cellulose Acetate
Contact angle	56°	20°
MWCO	68 kDA	50 kDA
Surface property	Hydrophobic	Hydrophilic
Pure water specific flux (Lm ⁻² h ⁻¹ bar ⁻¹)	43 ± 5	85 ± 7

Table 2- Surface water characteristics

Source	Sungai Ulu Pontian, Johor
Coordinate	N1° 35.541', E103° 30.704'
DOC (mg/L)	6.8
UV ₂₅₄ (cm ⁻¹)	0.088
SUVA (L/mg.m)	1.29
Conductivity (µs/cm)	37

Table 3 DOC concentration of Sungai Ulu Pontian fractions (based on DOC and mass balance technique)

Fraction	DOC (mg/L)	DOC (%)
Hydrophobic (HPO)	2.38	35
Transphilic (TPI)	1.7	25
Hydrophilic (HPI)	2.6	38

Water quality

A soft and rich in NOM surface water (Table 2) was taken from Sungai Ulu Pontian Johor, Malaysia. The raw water was filtered by a 0.45 µm and fractionated into hydrophobic (HPO) fraction which is Supelite DAX-8 (Sigma-Aldrich) adsorbable, transphilic (TPI) which is Amberlite XAD-4 adsorbable and hydrophilic (HPI) components which pass

through the DAX-8 and XAD-4 resins without any adsorption (Table 3). The HPO and TPI components were collected after eluting the resins with 0.1 NaOH.

Membrane filtration operation and determination of hydraulic resistance

Ultrafiltration (UF) submerged reactor was used throughout this study and the experimental set-up is schematically illustrated in Figure 2. Initial flux of pure water permeate (J_{pwp}) was introduced to the membrane at TMP of 140 mmHg until the pure water permeability was stabilized. The DI water was replaced with a NOM fractional source at the same TMP of J_{pwp1} . The operational flux and flux decline were regularly measured throughout the experiment. Samplings for the UV₂₅₄ and DOC rejection were periodically taken until permeation reaches quasi-steady state conditions. The system was then replaced with DI water to remove (CP) layer and the second J_{pwp2} was measured. The system was back flushed thoroughly for 10 minutes [2] with DI water to remove all reversible adsorption layers before the third J_{pwp3} was measured and the membrane was taken out from the reactor. The foulants were extracted using 0.1 N NaOH for 3 hours followed by 0.1N HCl for another 3 hours solutions respectively [3]. The fourth J_{pwp4} was then measured to complete the Resistance in series model (Equation 1). The assumption on this model is made whereby the osmotic pressure is subsumed into the concentration polarization resistance.

$$J = \frac{\Delta P}{\mu(R_m + R_{cp} + R_c + R_a)} \quad (1)$$

where R_m is membrane intrinsic hydraulic resistance, R_{cp} is concentration polarization resistance, R_c is cake resistance, R_a is adsorption resistance.

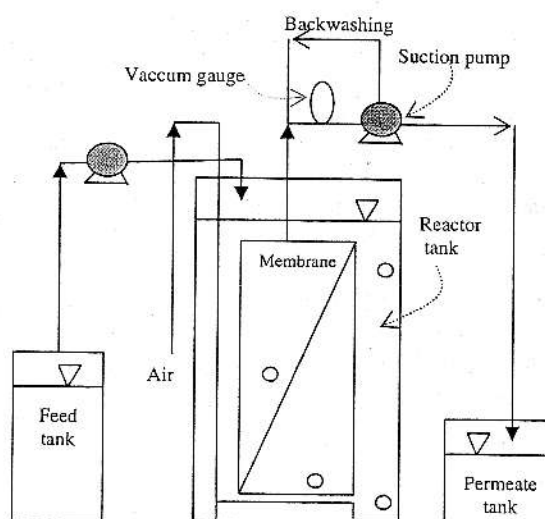


Figure 2-Schematic diagram of submerged UF reactor

Results and Discussion

Influence of NOM fractions on fouling characteristics

The Sungai Ulu Pontian exhibited a relatively low hydrophobic fraction concentration and therefore can be classified as a hydrophilic surface water type (Table 3). Surface water with SUVA less than $3 \text{ Lm}^{-1}\text{mg}^{-1}$ is classified as low-humic water [4]. The normalized permeate fluxes for the three fractions are shown in Figure 3. All the three fractions showed an obvious flux decline at the initial period of filtration. The fouling occurred in these cases were mostly attributed by the dissolved NOM.

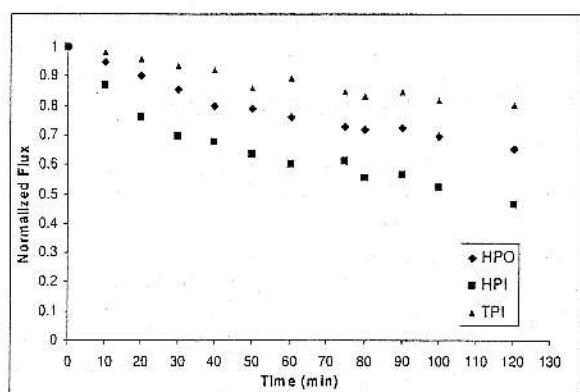


Figure 3-Flux profile of Sungai Ulu Pontian fractions by MRUTM55

The HPI fraction was found to perform the most significant fouling potential than other fractions and this finding could be taken as the most outstanding phenomenon observed in this study. The detrimental effect of HPI fraction to membrane permeability was even more pronounced as it showed greater flux decline and higher fouling rate than HPO and TPI components. However, this finding was contradictory with the results obtained by [5-6] where in their studies, the HPI components showed less fouling effect than humic fraction. Nevertheless the result presented here showed that the HPI exhibited the worst flux decline by approximately 54% of the initial flux after 120 minutes operation. On the other hand both HPO and TPI flux decline were about 35% and 20% in spite of having the same filtration duration. Thus it is worth noting that the HPI fraction was the prime foulant in NOM and was mainly responsible for fouling and major flux decline in surface water filtration. This could be reasoned from the low UV absorbing compound and high molecular weight component such as polysaccharides or polysaccharides types contained by the HPI fraction [7-8]. This finding was well supported

by studies carried out by done by Jarusutthirak [9] and Lin et al. [10] where they also found that the hydrophilic components cause more fouling potential than humic substances. Although the flux results showed the HPI fraction is the most detrimental foulant and exerted the worst flux decline but yet its DOC removal was the lowest (23%) in among other fractions. In this scenario the rule of thumb whereby normally highest flux decline would performance the best rejection did not occur. In fact it seems that the flux declination does not linearly parallel with the DOC removal and this case was even worsening when the UV_{254} removal was also the least. In this case apparently the HPI fraction is not only the most significant fouling potential but also would result in the worst membrane fouling (flux decline) and the lowest NOM removal (DOC and UV_{254} rejections). In addition the HPO fraction was found to be well rejected than other fraction in term of DOC and UV_{254} (Figure 4). This phenomenon is presumed to occur due to the electrostatic interaction between HPO fraction and the PSF membrane. HPO fraction contains mainly humic acid and fulvic acid that are anionic polyelectrolyte with negatively charged of carboxylic (COOH^-), methoxyl carbonyls (C=O) and phenolic (OH^-) [11]. Besides that, the PSF membrane was also widely reported by other researchers to have high negative charge density especially at higher pH as was employed in this experiment. Therefore less flux decline or higher HPO fraction was rejected by PSF membrane with regard to the charge repulsion between negative functional groups of HPO and negative surface charge of PSF membrane, respectively. Besides that the results of Figure 4 also showed that the UV_{254} removal were always higher than DOC rejection for all the three fractions. This could be again due to the tendency or preference of polysulfone membrane to repulse the high aromatic compound such as HPO fraction compared to other fractions and that it was shown high by the percentage of UV removal, meanwhile the DOC is not a specific measurement of certain compound but a total carbon concentration comprised by the three fractions.

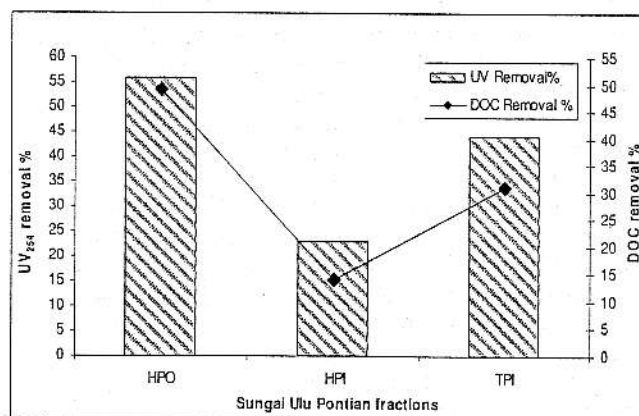


Figure 4 -UV₂₅₄ and DOC removal (%) of hydrophobic, transphilic and hydrophilic fractions by MRUTM55 membrane

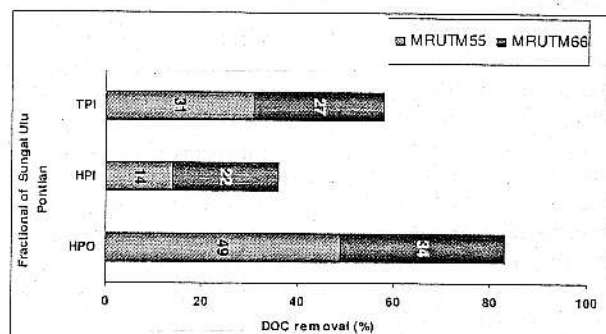


Figure 5-Comparison of DOC removal (%) between MRUTM55 and MRUTM66 on Sungai Ulu Pontian components

The effect of membrane characteristics on NOM rejection was further studied with a MRUTM66 membrane. This membrane has lower MWCO (58 kDa), more hydrophilic and less negative charge [12] compared to MRUTM55 membrane. From Figure 5 it was clearly shown that the MRUTM66 resulted in lesser DOC (%) rejection despite its lower MWCO than MRUTM55 membrane. This scenario is again presumably related to the shape, charge and size effects of NOM components towards the rejection mechanism of MRUTM66 membrane. In general the MRUTM66 increases the DOC rejection (%) of HPI fraction but decreases for both the HPO and TPI fractions when compared with MRUTM55. The HPI fraction removal (in term of % DOC rejection) by MRUTM55 was about 14% but increases to 22% when introduced to MRUTM66. However on overall the DOC removal was still dominated by HPO fraction followed by TPI and HPI fractions. Better removal in HPI fraction could be explained by the lower MWCO (50 kDa) employed by the MRUTM66 membrane whereas higher rejection of HPO and TPI than HPI component was due to higher intrinsic molecular weight (MW) possessed by both the fractions. Both the HPO and TPI fractions had been widely reported to have greater MW [13] or higher relative molecular mass [14] than HPI fraction by previous researchers. Furthermore the HPO fraction and TPI fraction have more complex molecules structures (aromatic shape) than HPI fraction (aliphatic structure) that made them easier to be excluded by the MRUTM66 membrane. During filtration with MRUTM66 most of the HPO fraction was successfully passing through the pores as the membrane was negatively less in charge and the electrostatic interaction between the functional groups of HPO and MRUTM66 (cellulose acetate) was no longer the rejection dominant mechanism. Thus it is worth to note here that the rejection mechanism imposed by the MRUTM66

was a steric exclusion hindrance while the MRUTM55 was an electrostatic repulsion mechanism. Based on the DOC removal (%) exhibited by all the NOM fractions of the Sungai Ulu Pontian, the order of rejection mechanisms is shown in Table 4.

Table 4- Dominant rejection mechanism on NOM fraction with different membrane (from most dominant to less dominant)

Membrane characteristics

- Negative Charged and hydrophobic membrane
Electrostatic interaction > Hydrophobicity > Steric exclusion
- Less negatively charged and hydrophilic membrane
Steric exclusion > Electrostatic interaction; Hydrophobicity

Effect of NOM fractions on Resistance in Series

Table 5- Percentage of fouling resistance to the total resistance (R_T) by NOM fractional components of Sungai Ulu Pontian

Fraction	Rm (%)	Rcp (%)	Re (%)	Ra (%)
HPO	59	22	3	16
HPI	55	1.08	12.5	30.9
TPI	65	5.34	19	7

The flux decline by NOM fractions were further quantitatively studied through resistance in series model (Equation 1). The explanation of flux decline caused by Sungai Ulu Pontian fractions was made by correlating their flux decline with the incurred fouling mechanisms and hydraulic resistances (Table 5). There seems to appear a relationship between the high fouling potential of HPI fraction and its high irreversible resistance (R_a). The HPI fraction has the highest R_a value (30.9%) and exhibited the worst flux decline in among the NOM fractions. Thus this severe flux decline was mostly attributed by the adsorption fouling mechanism of non-humic fraction (HPI) occurred during the filtration. This adsorption fouling mechanism can be described by saturation and precipitation processes of dissolved organic in the membrane pores; in this case it can be compounds derived from polysaccharide (neutral) and amino sugar [15]. This HPI fraction was expected to have the capability in passing through the membrane pores (HPI has an aliphatic structure) and not being able to be excluded by the steric hindrance mechanism as it was smaller than membrane MWCO (68 kDa). The normal molecular mass of HPI fraction found in river waters were reported [16-17] to be lower than 10 kDa. In addition, as the polysaccharide

does not have any ionizable functional group would definitely help them to easily overcome the electrostatic repulsion by the membrane. The precipitated HPI compounds would then adsorb onto the pores, constrict, reduce the pore sizes and to the extent of blocking it. This initial adsorption enhanced further mass accumulation of HPI that cover the pores and later lead to cake layer formation. This statement is well supported from the result of Table 5 that showed HPI fraction to have high cake resistance (12.5%). Meanwhile, the HPO fraction which has an aromatic structure showed the concentration polarization (CP) as the primary fouling mechanism to its flux declination (Table 6). This is supported by the highest Rcp (22%) possessed by HPO component compared to other fractions. Moreover there seems to be an underlying rejection mechanism that governs the preferential rejection of the HPO fraction by the PSF membrane that consequently led to high Rcp.

Table 6-Dominance fouling mechanism in NOM fractions as a function of hydraulic fouling resistance

Fraction	Primary fouling mechanism
HPO	Concentration Polarization
HPI	Adsorption
TPI	Cake formation

This result also indicates that the hydrophobicity interaction between HPO fraction and PSF membrane were found less significant in affecting the adsorptive fouling although previous studies [18-19] claimed that intrinsically hydrophobic membrane tend to adsorb NOM and foul more than hydrophilic membrane. This phenomenon could be well explained from the high humic content and negative charge (due to carboxylic and phenolic moieties) of HPO fraction that resulted in a significant rejection by the negative charge of polysulfone membrane. Therefore it can be hypothesized that there are two dominance factors which are responsible in determining the HPO adsorption and type of occurring fouling mechanism. The factors are adsorptive behaviour (due to hydrophobicity property) and the electrostatic repulsion interaction (due to similarity in charge with the membrane). HPO fraction possessed negative charges functional groups that prevent it from adhering or adsorbing onto the negatively charge membrane surface and therefore impacted in high Rcp. However in this experiment the HPO fraction did exhibit a significant adsorption fouling mechanism with adsorption resistance (Ra) 16% higher than TPI fraction. The Ra of HPO fraction showed higher value than TPI fraction (7%) despite its electrostatic interaction with the membrane. This scenario was believed to happen when the hydrophobic interactions was able to overcome the electrostatic repulsion incurred by the pressure gradient of

suction process. Thus for the HPO fraction, the adsorption mechanism could be taken as the secondary influential fouling mechanism after the concentration polarization. In general it could be summarized that fouling potential would be higher for the negative charge membrane when it is exposed to hydrophilic components compared to highly negative charge materials (HPO fraction) although they possessed high adsorptive tendency. The fouling mechanisms of the NOM fractions based on the hydraulic resistance can be disclosed as follows:

HPO Concentration > Adsorption > Cake formation
HPI Adsorption > Cake formation > Concentration polarization
TPI Cake formation > Adsorption > Concentration polarization

The responsible foulant that affect the membrane performance was the HPI fraction which was found to performance the worst flux decline during membrane filtration. Furthermore the adsorption fouling can be taken as the primary fouling mechanism that governed the membrane flux decline as the HPI fraction had the highest Ra. Therefore in future application, NOM hydrophobicity or aromaticity (feed source characteristic) and charge interaction (membrane property) can be employed as a quantitative predictor for NOM rejection and flux declination of membrane filtration of surface water.

CONCLUSIONS

Based on the results of this experiment several conclusions can be drawn out as follows:

- 1) Each of the Sungai Ulu Pontian NOM fraction caused substantial flux decline and the order of fouling potential based on flux decline was HPI>HPO>TPI
- 2) HPI and HPO fraction performed strong irreversible fouling due to their neutral property and hydrophobicity interaction with the membrane.
- 3) Charge interaction is more influential factor than hydrophobicity and steric exclusion mechanisms in determining the rejection, fouling mechanisms and the extent of flux decline.

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