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Foulant Analyses of Ultrafiltration (UF) Membrane Fouled with Natural Organic Matter (NOM) of Ulu Pontian River and Bekok Dam Reservoir

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ABSTRACT An autopsy procedure has been carried out on both clean and fouled polysulfone (PSF) UF membranes with prime intention to investigate the relative effect of NOM fouling onto the membrane characteristics and as well as to identify the primary NOM component that possessed the major fouling potential. A PSF membrane has been fouled with feeds of Bekok Dam reservoir and Ulu Pontian river. Results of foulant analyses showed that the membrane was mainly fouled by the organic NOM fraction of hydrophilic character. In fact, the hydrophilic fraction was found to play a more significant role as the primary foulant that were hypothesized to be responsible for the substantial flux decline during membrane water treatment. Comparatively there were distinctive changes in membrane characteristics from the perspective of contact angle, SEM analysis and membrane zeta potential of NOM fouled membrane, thus adequately supporting the evidence of membrane fouling by the responsible foulant. In particular the membrane wettability and surface charge have been found to decrease significantly after being fouled with both NOM source waters, as a matter of fact the Ulu Pontian river showed greater decrement of membrane properties compared to its counterpart the Bekok Dam reservoir. Thus this observation implied that most of the membrane surface has been covered-up by the non-humic component which could possibly be the primary membrane foulant as it was significantly found to adhere most on the membrane surface. ATR-FTIR analysis revealed that hydrophilic components such as the polysaccharides-like substances, alcoholic compounds and aliphatic amide of protein groups as the responsible materials covering the membrane surface.

ABSTRAK Satu prosedur otopsi telah dijalankan ke atas membran polisulfina (PSF) yang bersih dan yang dikotorkan bertujuan untuk mengenalpasti kesan relatif pengotoran NOM ke atas sifat membran dan komponen NOM yang mempunyai potensi pengotoran yang tinggi. Membran PSF telah dikotorkan dengan air Empangan Bekok dan Sungai Ulu Pontian. Keputusan analisa kekotoran menunjukkan membran telah mengalami pengotoran yang tinggi berpunca dari komponen NOM yang bersifat hidrofilik. Tambahan pula komponen hidrofilik telah didapati berperanan penting sebagai pengotor utama dan telah hipotesiskan sebagai punca kepada penurunan fluk membran. Secara perbandingannya terdapat perubahan ketara kepada sifat membran dari perspektif sudut sentuhan, analisis SEM dan keupayaan zeta yang membuktikan kekotoran membran. Secara terperincinya keterbasahan membran dan cas permukaan telah didapati menurun secara drastik setelah dikotorkan oleh kedua-dua sumber air, malahan pengotoran oleh Sungai Ulu Pontian telah menunjukkan penurunan yang lebih tinggi berbanding sumber air dari Empangan Bekok. Hasil pemerhatian ini menunjukkan hampir keseluruhan permukaan membran telah diliputi oleh bahan bukan humik yang bertanggungjawab sebagai bahan kotoran utama. Analisis ATR-FTIR mendedahkan bahawa komponen hidrofilik seperti bahan polisakarida, komponen alkohol dan kumpulan amida protein sebagai bahan yang bertanggunggjawab memenuhi permukaan membran.

(Membrane, NOM, Foulant, Membrane autopsy)

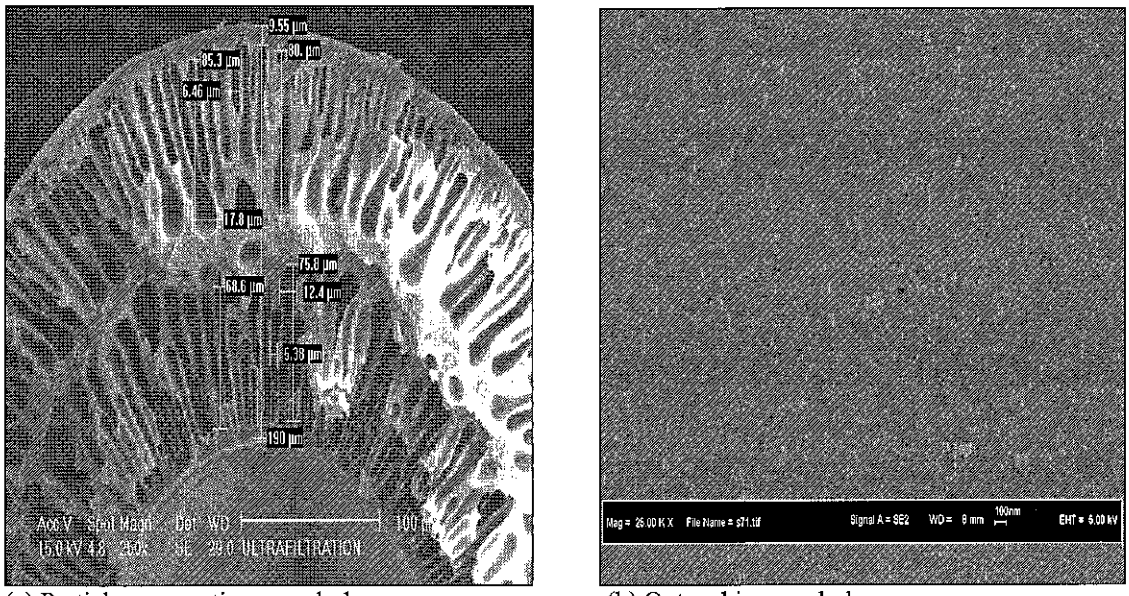
INTRODUCTION

MF and UF have been intensely researched both with respect to the development of membrane which is less prone to fouling as well as membrane processes applications that work under optimal operating parameters. In spite of acting as a precursor to disinfection by products (DBP), natural organic matter (NOM) that ubiquitously occurs in drinking water sources is problematic that it rigorously has been claimed as the distinctive "culprit" for fouling problem in water filtration [1 - 4]. NOM which composed variety of particulate and soluble organic/inorganic compounds have been widely reported as the primary foulant agent during surface water filtration especially in drinking water production. The hydrophobic fraction of NOM has been specifically identified as the main membrane foulant in water filtration as it possessed higher aromaticity properties and greater adsorptive character due to its high hydrophobicity characteristics [5]. These statements were in agreement with Schafer et al. [6] who observed that humic acid exhibited greater flux decline and caused irreversible fouling than that of the hydrophilic fraction (reversible fouling). On the other hand, the hydrophilic fraction was thought to result in minor contribution of organic matter fouling compared to the hydrophobic fraction, however recent studies done by several researchers Lin et al. [7] have revealed that the hydrophilic NOM fraction has played a significant role in the extent and rate of membrane fouling. In this study the potential foulants of NOM source containing waters such as Bekok Dam reservoir and Ulu Pontian river were initially characterized by DOC, UV_{254nm}, and SUVA before being filtered with an immersed ultrafiltration 68 MWCO PSF membrane. New and fouled membrane specimens were further analyzed for membrane wettability changes, zeta potential, FTIR analyses and SEM for qualitative morphological study. Subsequently distinctive differences in membrane characteristics were supposed to be of great help in indicating the relative impact of NOM and its critical composition that were responsible for fouling the UF membrane.

MATERIAL AND METHODS

Membranes and Filtration Procedure

An ultrafiltration membrane with a MWCO of 68 kDa was employed in the membrane filtration experiment with NOM sources water of Bekok Dam reservoir and Ulu Pontian river. The home-made membrane was spun by a simple phase inversion technique with water as a non-solvent coagulant and bore fluid solution. An exclusive formula which combined polysulphone (PSF), PVP and DMAc has been used to produce an asymmetric hollow fiber membrane. Membrane properties were characterized for contact angle, pure water permeability (*Jpwp*), zeta potential and molecular weight cut-off (MWCO). Figure 1 show the SEM of clean PSF membrane whilst Table 1 illustrates the membrane properties. As can be inferred in Figure 1, the as-spun PSF membrane from the phase inversion process exhibited typical asymmetric structure with developed macro pores and finger like structures that acted as micro porous mechanical support. In particular the asymmetric membrane showed pronounced morphologies with an apparent dense top layer and porous sublayer which present in the form of sponge, finger like and macro voids structures. A finger like structure was evenly formed when DMAc/water was used as the solvent/non-solvent pairs with polysulfone polymer. The cross section of the PSF as-spun fiber showed a finger like structure that started from the outer edge of the nascent fiber to the middle of cross section. Moreover the NOM source water was filtered by the spun UF membrane in a submerged configuration (Figure 2) with a constant TMP of 250 mmHg. A 13 L feed reservoir was employed to provide continuous supply for permeate extraction. The fouled membrane was later subjected to zeta potential, contact angle and ATR-FTIR measurements for organic foulant analysis.



(a) Partial cross section morphology (b) Outer skin morphology

Figure 1. SEM images of clean asymmetric PSF membrane morphological

Table 1. Properties speciation of home-made membrane

MEMBRANE	UF POLYSULPHONE
Type	Hollow fiber
Contact angle °	56°
MWCO (kDa)	68
Zeta potential (pH 7)	-27 mV
Jpwp ($Lm^{-2}h^{-1}bar^{-1}$)	43± 5
OD (μm)	600

NOM SOURCE WATER

Selected Malaysian natural surface water of Bekok Dam reservoir and Ulu Pontian river were used in this study. The qualities of these waters are shown in Table 2. Sample was preserved by adding 10% (by volume) of nitric acid before stored in refrigerator of 3 °C. The Bekok Dam water exhibited higher SUVA possession than that of the Ulu Pontian river, thus implied that the hydrophobic properties of Bekok Dam was greater than the Ulu Pontian river. In fact this finding also revealed that the Bekok Dam was relatively more hydrophobic NOM source water compared to its counterpart the Ulu Pontian river. This observation was consistent with the humic fraction (%DOC) analyses after the DAX-8 fractionation procedure. The hydrophobic (HPO) concentration for Bekok Dam and Ulu Pontian river were 47% and 35%, respectively. This comparison apparently denoted that the Ulu Pontian river contained higher hydrophilic fraction than Bekok Dam reservoir. Therefore these observations clearly suggesting that the Ulu Pontian river was relatively more hydrophilic NOM source water compared to Bekok Dam.

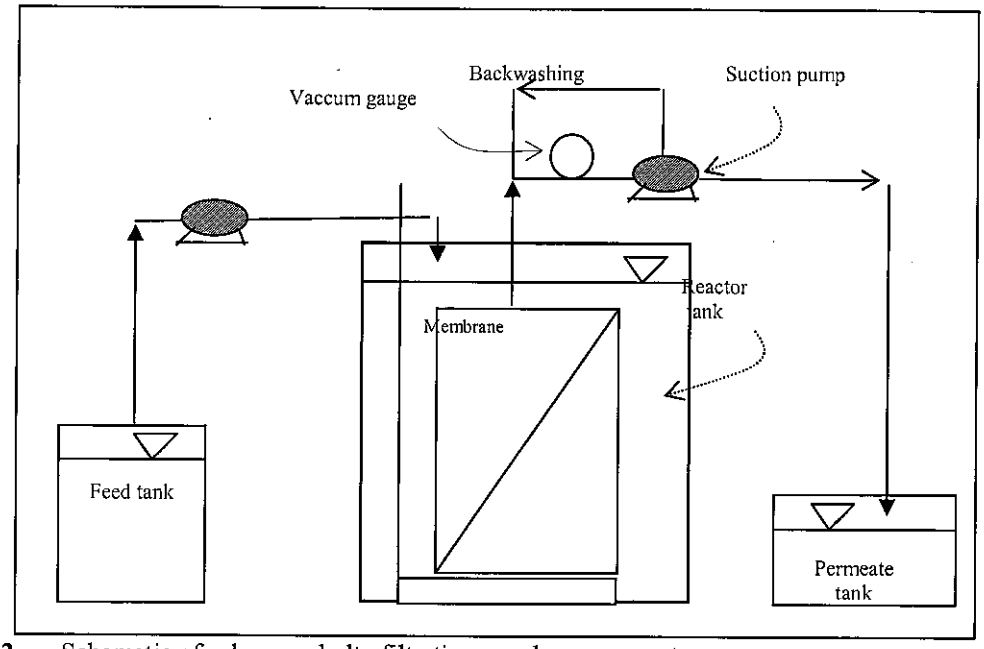


Figure 2. Schematic of submerged ultrafiltration membrane apparatus

Table 2. Water quality and DOC concentrations of NOM fractions for the Bekok Dam and Ulu Pontian river

	ULU PONTIAN RIVER	BEKOK DAM RESERVOIR WATER
Coordinates	N1° 35.541', E 103° 30.704'	N2° 6.933, E103° 4.344'
DOC (mg/L)	6.7	8.04
SUVA (L/mg.m^{-1})	1.29	2.82
pH	7.03	7.74
Conductivity (μS/cm)	56	72
Mn^{2+} (mg/L)	0.0414	0.0017
Ca^{2+} (mg/L)	1.22	1.56
Al^{3+} (mg/L)	0.0396	0.0267
UV_{254nm}	0.087	0.227
SUVA (L/mg.m)	1.27	2.39
HPO fraction (%)	35	47
HPO DOC (mg/L)	2.38	4.71

RESULTS AND DISCUSSION

Membrane Autopsy by Contact Angle Assessment

Relative changes of membrane property by NOM adsorption onto the membrane surface or into the membrane pores was studied through quantitative measurement of membrane's contact angle which technically depicted the character of foulant substances. As can be inferred from Table 3, both NOM containing surface waters have been found to induce lower contact angle for fouled membrane compared to the clean PSF membrane. The contact angle of fouled PSF membrane has been found to decrease from 56° to 48° when it was filtered with relatively high hydrophilic surface water or Ulu Pontian river. However, contact angle of fouled membrane filtered with relatively more hydrophobic NOM source water (Bekok Dam reservoir) was only found to slightly reduced from 56° to 53°. In general a decrease in contact angle was primarily influenced by a deposition of organic foulant onto the membrane surface. In this case it can be seen that the degree of contact angle reduction was commonly attributed by the composition of NOM source water which was essentially related to the humic and non-humic distribution. Higher reduction in contact angle performed by the Ulu Pontian river adequately depicted the influence of non-humic

compound in governing the type of responsible membrane foulant. In particular this phenomenon implied the involvement of selective interactions between the hydrophilic NOM compound and the membrane surface. Hydrophilic NOM constituent is commonly described as colloidal and macromolecules of polysaccharides-like substances, amino sugar and protein groups [8]. These compounds are inherently neutral or possessed positive charge in natural solution chemistry between pH 6 and pH 8. Subsequently these characteristics enhance relatively higher affinity of adsorption or deposition of hydrophilic NOM onto the negatively charged PSF membrane surface (-27 mV).

Table 3. Contact angle characterization of clean and fouled membrane

	CONTACT ANGLE
Clean membrane	56
Fouled with Ulu Pontian river (SUVA: 1.27 L/mg.m)	48
Fouled with Bekok Dam reservoir (SUVA: 2.39 L/mg.m)	53

MEMBRANE AUTOPSY BY ZETA POTENTIAL

The results of zeta potential for clean and NOM fouled PSF membrane with source waters is tabulated in Table 4. The zeta potentials of fouled membrane exhibited a decrease in surface charge (less negative) measurements by both the NOM source waters. However, relatively more hydrophilic NOM containing source water (Ulu Pontian river) showed higher reduction in surface charge than relatively less hydrophilic water (Bekok Dam reservoir). Thus the result of Table 4 implied that the covering organic foulant was either neutral or positive charged compound. In particular the neutral components in NOM can be closely corresponded to non-humic fraction or hydrophilic fraction of polysaccharide groups such as chitin, cellulose and amino sugar [9] whereas the positive NOM component reflected to the base compounds such as primary protein and secondary protein groups. Therefore factor potentially reducing the membrane surface charge could be strongly correlated with the accumulation of organic matter with neutral/base properties such as contained by the hydrophilic NOM. This hypothesize is consistent with the relative concentration of the hydrophilic presence in the source water, such as used in this study. As a matter of fact, the zeta potential of fouled membrane decreased proportionally with the relative increment of NOM hydrophilicity of source water. This phenomenon significantly denoted that, membrane fouling or solute foulant which was responsible in controlling the extent of fouling or changing the relative property of membrane surface was primarily originated from the hydrophilic fraction within the bulk NOM.

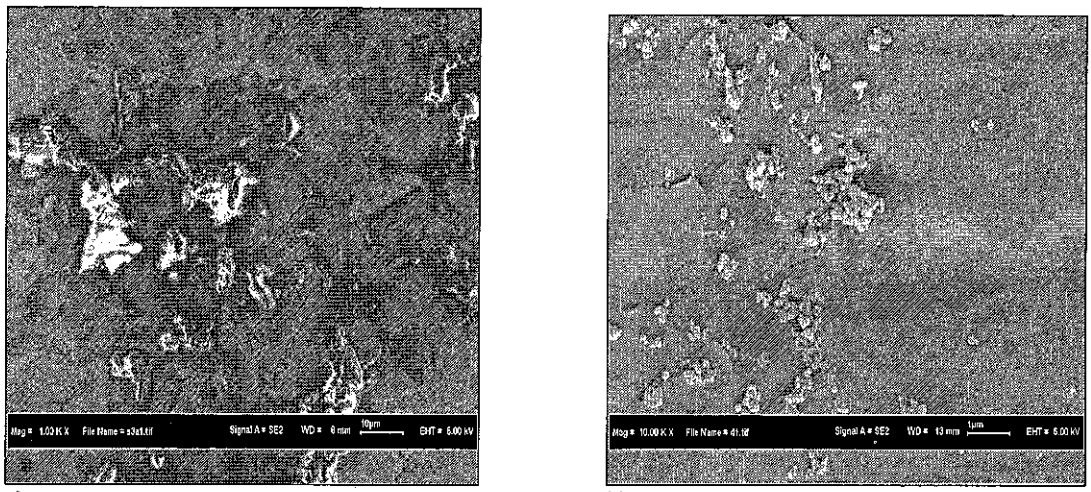
Table 4. Zeta potential curves of clean and fouled PSF membranes by streaming potential

	ZETA POTENTIAL (mV)
Clean membrane	-27
Fouled with Ulu Pontian river (SUVA: 1.27 L/mg.m)	-4
Fouled with Bekok Dam reservoir (SUVA: 2.39 L/mg.m)	-16

MEMBRANE AUTOPSY BY MORPHOLOGICAL ANALYSIS

Morphological surfaces of interior and exterior of fouled UF membrane were observed under SEM analysis for the purpose of qualitative measurement of details membrane structural. Figure 3 elucidates that the surface of membrane fouled with Bekok Dam reservoir was fully covered with NOM materials however, the membrane which was fouled by Ulu Pontian river showed clearer membrane surface with only minor NOM accumulation around the membrane. This phenomenon could be explained by the fact that NOM adsorption or fouling mechanism was significantly governed by the NOM source characteristics. Bekok Dam possessed higher hydrophobic content which can be correlated with humic substances that have greater hydrophobicity or adsorptive tendency onto the hydrophobic membrane surface such as used in this experiment. In addition the humic components were also relatively bigger in molecular weight or molecular mass [2] than the hydrophilic NOM component, thus subsequently led them easier to be excluded and retained by the membrane. Therefore the membrane fouled with Bekok Dam reservoir was mostly attributed by cake deposition or reversible fouling instead of pore adsorption (irreversible fouling). In the case of Ulu Pontian river, there was only little cake layer deposition seen on the membrane surface fouled with Ulu Pontian water compared to Bekok Dam water, thus the responsible fouling was most probably occurred due to pore adsorption on the pore matrix or within the pore

size. It is hypothesized that the interaction between the polymeric PSF membrane and relatively high hydrophilic NOM source water such as Ulu Pontian river promoted better pore adsorption fouling mechanism, as its dominant hydrophilic component was relatively smaller and neutral, thus resulted in NOM passing through the membrane without much influence of steric hindrance resistance and charge repulsion.



a) b)

Figure 3. SEM micrograph of UF membrane fouled with a) Bekok Dam b) Ulu Pontian river

MEMBRANE AUTOPSY BY FTIR ANALYSIS

Fouled membrane would exhibit changes in the absorbance intensity of the clean membrane which suggesting that a new functional groups of foulant was covering the original membrane. ATR-FTIR was used to study on any significant spectra differences (in term of absorbance intensity and new emerged IR spectra) between the clean and fouled membrane. In fact, the membrane autopsy works using FTIR may also assist in identifying the foulant functional groups which is beneficial to support the evidence of NOM fouling associating with humic substances or non-humic components as the major foulants. Figure 4 illustrates the subtraction of FTIR spectrum of Bekok Dam and Ulu Pontian river that fouled PSF membrane (the PSF membrane spectrum has been digitally subtracted). Generally both NOM source containing waters exhibited absorption bands at 1012.9 cm^{-1}, 1013.2 cm^{-1}, 1077.2 cm^{-1}, 1106.3 cm^{-1}, which corresponded to C-O bonds associating with primary alcohols, ethers and polysaccharides-like substances [9, 10, 11]. In particular, peaks at these wave numbers significantly reflected a hydrophilic character of organic materials as the membrane foulants. In fact the peak observed at 741 cm^{-1} (ethyl), 1166.8 cm^{-1} (tertiary alcohol), 1170.5 cm^{-1} (tertiary alcohol), 1147.8 9 cm^{-1} (secondary alcohol) and 1148.8 cm^{-1} (secondary alcohol) by both NOM sources, were further reinforcing the presence of polysaccharides or polysaccharide-like as the primary membrane foulants. However the Ulu Pontian water exhibited higher absorbance intensity, suggesting greater foulant density compared to PSF membrane fouled with Bekok Dam. The absorption peak at 1654.5 cm^{-1} and 1580.9 cm^{-1} (by Ulu Pontian river) corresponded to C=O stretching of amide I band and N-H bonding of amide II band, reflecting possible occurrence of proteins and N-acetylaminosugars [8, 9]. In comparison, the Bekok Dam showed similar spectral pattern at wave number of 1654.5 cm^{-1} and 1586.8 cm^{-1} (but with less intensity), which attributed to primary and secondary amides of protein groups. In summary fouling by the Ulu Pontian river and Bekok Dam depicted significant contribution of hydrophilic NOM character such as polysaccharide, polysaccharide like substances and protein groups as the major foulants. Greater foulant absorbance intensity was apparent for PSF membrane fouled with relatively more hydrophilic NOM source water (Ulu Pontian river) compared to more hydrophobic NOM source water (Bekok Dam reservoir).

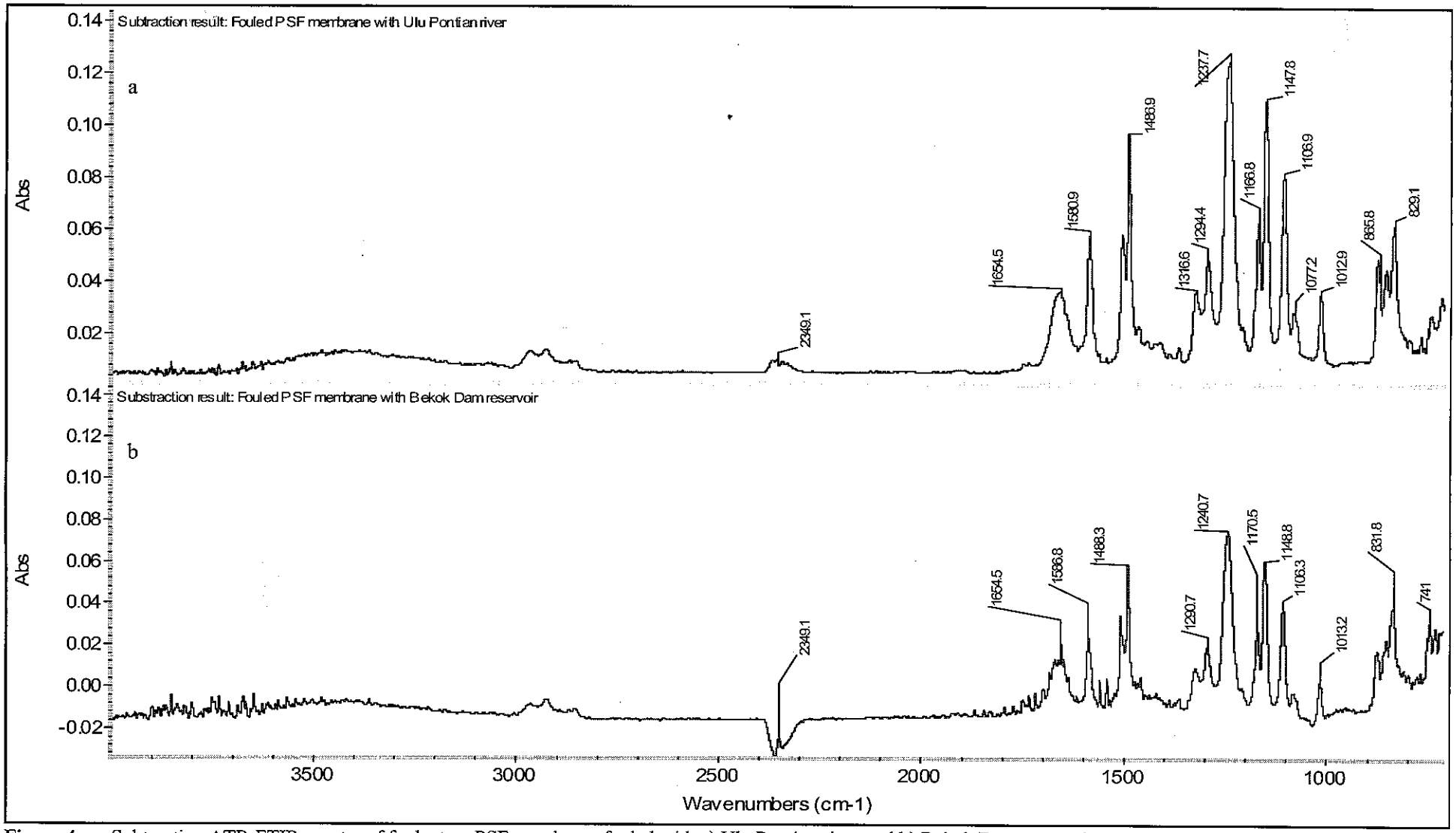


Figure 4. Subtraction ATR-FTIR spectra of foulant on PSF membrane fouled with a) Ulu Pontian river and b) Bekok Dam reservoir

CONCLUSIONS

Based on the above findings several conclusions could be drawn as follows:

i. Reduction of contact angle (becoming more hydrophilic) of both source waters was essentially influenced by the hydrophilicity of NOM source possession as more hydrophilic water such Ulu Pontian river exhibited greater deduction compared to Bekok Dam.

ii. Membrane fouled with Ulu Pontian river showed clearer membrane surface which suggesting pore adsorption mechanism instead of cake deposition such as shown by the Bekok Dam reservoir. Difference pattern in fouling mechanism was mostly governed by NOM constituent property such as Ulu Pontian river which has greater possession of smaller MW and more neutral character of hydrophilic NOM source than that of Bekok Dam.

iii. Zeta potential of fouled membrane exhibited significant decrement (less negative) after being filtered with NOM source water especially by the Ulu Pontian river, thus indicated that the hydrophilic NOM was mainly the responsible organic foulant that was covering the membrane surface.

iv. It was also shown that NOM components that reduce contact angle and decrease zeta potential were also found as the primary materials covering the membrane surface, thus implied that the polysaccharide, polysaccharide like substances, alcoholic compounds and aliphatic amide of protein groups of hydrophilic components as the primary foulants contributed to membrane fouling, irrespective of the NOM source.

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ABBREVIATIONS

DMAc	-	Dimethylacetamide
DOC	-	Dissolved Organic Carbon
NOM	-	Natural Organic Matter
PSF	-	Polysulfone
PVP	-	Poly Vinyl Pyrolidone
UV_{254nm}	-	UV absorbance at 254nm
SUVA	-	Specific UV_{254nm}