INFLUENCE OF FLOCCULATION AND ADSORPTION AS PRETREATMENT ON THE FOULING OF ULTRAFILTRATION AND NANOFILTRATION MEMBRANES: APPLICATION WITH BIOLOGICALLY TREATED SEWAGE EFFLUENT

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ABSTRACT

Membrane fouling is a critical limitation on the application of membranes to wastewater reuse. This work aims to understand the fouling phenomenon which occurs in ultrafiltration (UF; 17500 molecular weight cutoff (MWCO)) and nanofiltration (NF; 250 MWCO) membranes, with and without pretreatment. For this purpose, the molecular weight (MW) distribution of the organics has been used as a parameter to characterize the influent, the permeate and the foulant on the membrane surface. The variation of foulant concentration on the membrane due to pretreatment of the influent by flocculation and/or adsorption was investigated in detail.

With the UF membrane, the peak of the MW distribution of organics in the permeate depended on the pretreatment; for example, the weight-averaged MW (M_w) of 675 daltons without pretreatment shifted down to 314 daltons with pretreatment. In the case of the NF membrane, the M_w of organics in the permeate was 478 daltons (without pretreatment) and 310 (with flocculation followed by adsorption). The M_w of the organics in the foulant on the membrane surface was 513 daltons (UF) and 192 (NF) without pretreatment and 351 (UF) and 183 (NF) after pretreatment with flocculation followed by adsorption, respectively. Without the pretreatment, the foulant concentration was higher on both membranes. The difference was more significant on the UF membrane than on the NF membrane.

For both membranes, the flocculation-and-then-adsorption pretreatment proved very effective.

Keywords: adsorption, biologically treated sewage effluent, effluent organic matter, flocculation, foulant, nanofiltration, pretreatment, ultrafiltration,

INTRODUCTION

Wastewater reuse is increasingly seen as an essential strategy for making better use of limited freshwater, and a means of preventing deterioration in the aquatic environment from wastewater disposal. Although secondary- and tertiary-treated wastewater can be discharged into waterways, it cannot be used for nonpotable purposes without further treatment. For this, membrane processes are now being successfully used to obtain water of recyclable quality.

Even though membrane processes can effectively remove a variety of contaminants from biotreated sewage effluent (BTSE), membrane foulants (i.e., sparingly soluble inorganic compounds, colloidal or particulate matter, dissolved organics, chemical reactants, and microorganisms) can reduce the water flux through a membrane by as much as 90% (*1*). Pretreatment of BTSE prior to its application to membrane processes will reduce cell deposition, and subsequent biogrowth due to dissolved organic matter (*2,3*). Pretreatment also reduces the

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need for frequent chemical cleaning, which is a major factor impacting on membrane life. From these perspectives, pretreatment offers great potential for improving the efficiency of membrane processes.

Flocculation, powdered activated carbon (PAC) adsorption, and granular activated carbon (GAC) biofiltration can remove most of the solutes and organic colloids present in BTSE; and hence, they can be used as successful pretreatment processes. Al-Malack and Anderson (4), Chapman et al. (5), and Abdessemed et al. (6) have studied the effect of flocculation and adsorption as pretreatment on the performance of cross-flow microfiltraion (MF) and ultrafiltration (UF) of domestic wastewater and BTSE, respectively. Al-Malack and Anderson (4) from their experiments with BTSE found that flux values improved with the addition of alum at an optimal dose of 80 mg/L. This flux improvement was attributed to the agglomeration of particles which could then be easily removed by shearing action. Chapman et al. (5) indicated that the floating medium flocculator (a static flocculator) with ferric chloride addition produced filterable flocs of about 20 μm, resulting in the removal of 45% of the suspended solids, 97% of phosphorus, and 45% of the organics from the BTSE. Abdessemed et al. (6) have shown that adsorption is efficient in removing the effluent organic matter (EfOM), while flocculation allows UF to perform as well as MF membranes by producing higher permeate flux. The characteristics of the dominant transport mechanism in UF and nanofiltration (NF), effects of pH and ionic strength on organic matter, and transport of fractions were investigated by Lee et al. (7). Zhang et al. (8) have studied the

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fouling of membranes and removal of natural organic matter (NOM) in a PAC adsorption/membrane hybrid system in treating drinking water. They suggested that increased doses of PAC and SiO_2 led to a steady increase of fouling as the NOM linked PAC or SiO_2 particles to one another, and to the membrane surface, so that the particles became part of the foulant. None of these studies discussed the importance of detailed analysis of the EfOM removed by different pretreatment methods. A detailed characterization of the EfOM in the foulant will help in selecting a suitable pretreatment method and in defining the optimum range of operational parameters for pretreatment. Characterization of membrane fouling also has a significant impact on the cost, design, and operation of membrane technology.

To characterize the foulants on the membrane surface, scanning electron microscopy (SEM), pyrolysis-GC/MS, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), etc, have been used (*1,8,9*). Yuan and Zydney (*10*) have shown that NOM (e.g., humic and fulvic acids) is a major foulant during UF of surface water. Carbohydrates, proteins, and polyhydroxyaromatics also are found to cause membrane fouling in this surface water application (*1*). This viscous film layer – which has to be removed by physical cleaning - was responsible for most of the flux decline. The viscous foulant material remaining has been related to biological fouling. The characteristics of the fouling matter are thus dominated by biological growth (cells themselves and extracellular materials) (*1*). A number of studies have also shown that the colloidal fouling rate increases with the ionic

strength of the solution, feed colloidal concentration and permeate water flux through the membrane surfaces (*11-13*).

None of the above studies attempted to characterize the EfOM in terms of molecular weight (MW) distribution. Information on MW distribution has a number of advantages:

    i)   a more fundamental understanding of the complex interactions that occur in the unit operations and treatment process,

    ii)   process selection and evaluation to develop improved techniques, and

    iii)   determination of an applied membrane MW cutoff (MWCO) for targeted pollutants, etc.

The main objective of this study was to investigate the variation in the membrane (UF and NF) foulant characteristics (in terms of MW) after the BTSE had undergone different pretreatments. The pretreatments used prior to the application of the UF and NF were: (i) flocculation with $FeCl_3$, (ii) adsorption with PAC, (iii) flocculation followed by adsorption (Floc-Ads), and (iv) GAC biofiltration. All the effluents after pretreatments and filtrations were characterized in terms of MW distribution. The main role of pretreatment is the simultaneous enhancement of removal efficiency and the reduction of fouling potential. However, optimizing the pretreatment is also an economic necessity. MW distribution can be used as an index in the optimization of the pretreatment.

MATERIALS and METHODS

Bio-treated sewage effluent (BTSE)

The study was conducted with BTSE drawn from a sewage treatment plant. The wastewater treatment is a medium-sized activated sludge unit (25,000 m^3/d). The characteristics of the BTSE used are presented in Table 1. The hydraulic retention time and the sludge age were 6 h and about 8 days, respectively. The molecular weight (MW) of the BTSE ranged from 250 daltons to about 3573 with a large fraction ranging from 250 daltons to 520 (during the period of the experiments). A high performance size exclusion chromatography and ultraviolet absorbance (HPSEC-UVA) detection were used in this study. In general, the MW distribution of this BTSE ranged from 200 daltons to 50,000 in winter, while it was from 200 daltons to 3000 in summer and spring. This also varies from place to place, with the characteristics of the sewage and with the operational conditions of the sewage treatment plant. For example, the range of MW of the BTSE was 300 daltons to 400,000 (with a peak between 300 daltons and 3,000) in Gwangju, (Korea), whereas it was 100 daltons – 50,000 in Hawaii (USA) with a peak between 900 daltons and 20,500 (*14*).

Table 1 Characteristics of the biologically treated sewage effluent (BTSE) used

Pretreatment methods

Flocculation

Flocculation was carried out using the optimum dose (120 mg/L) of ferric chloride (FeCl$_3$) predetermined by standard jar tests. Ferric chloride was chosen in these experiments as it is capable of removing both colloidal organic matter and phosphorus. The BTSE was placed in a 1 L container and an optimum dose of ferric chloride was added. The sample was stirred rapidly for 1 min at 100 rpm, followed by 20 min of slow mixing at 30 rpm, and 30 min of settling. The molecular weight distribution of the organic compounds present in the supernatant was also measured.

PAC adsorption

The PAC used in the experiments was washed with distilled water and dried in an oven at 103.5 °C for 24 h. It was kept in a desiccator before use in the adsorption experiments. The characteristics of the PAC are given in Table 2. For the adsorption experiments, 1 g of PAC was added to 1 L of BTSE and the

resulting mixture stirred with a mechanical stirrer at 100 rpm for 1 h. For studying the pretreatment of Floc-Ads, the experimental conditions were similar to those of flocculation and adsorption alone, respectively. Flocculation took place first, and the adsorbent was added to the supernatant obtained after flocculation and settling. During the PAC adsorption experiment, the contact time was too short (1 h) for any biogrowth to occur, so the pretreatment of adsorption can be considered as physical adsorption.

Table 2 Characteristics of powdered activated carbon (PAC) (James Cumming & Sons Pty Ltd., Australia) and granular activated carbon (GAC) (Calgon Carbon Corp., USA) used in this study

GAC biofiltration

A GAC biofilter column was used for long-term bioadsorption experiments. The filter column had ports for influent feeding, effluent collection, and backwashing. The column was packed with 20 g (bed depth of 7 cm) of GAC (Figure 1). The physical properties of the GAC are shown in Table 2. A shallow bed depth was chosen to attain quick biofilm formation and acclimatization. The GAC bed was acclimatized at a constant filtration rate of 1 m/h. The filter was backwashed (to attain up to 30% bed expansion) for approximately 5 min every 24 h of the filtration run. The backwashing was done to remove suspended solids removal. Only negligible amounts of biofilm were washed out during this operation. After

45 days of operation of the biofilter, 4 L of the effluent was collected from the biofilter and used as a feed to UF. Here, the main mechanism is biosorption.

Figure 1 Schematic drawing of the fixed bed GAC biofilter

Crossflow filtration set-up

A cross-flow membrane filtration unit (Nitto Denko Corp., Japan) was used to study the effect of pretreatment on the membrane performance. The schematic diagram of the cross-flow ultra- and nanofilter experimental setup is shown in Figure 2. Both permeate and concentrate were recycled back to the feed tank except for the sample withdrawn for DOC measurement. The characteristics of the feed may be considered as constant during the experiment. Each experiment was conducted over a period of 18 h. New membranes were used in each experiment to avoid the effect of residual fouling and to compare the results obtained under different conditions. Wastewater, with and without pretreatment, was pumped into a flat sheet membrane module (effective membrane area of 0.006 m^2). The operating transmembrane pressure and cross-flow velocity were controlled at 300 kPa and 0.5 m/s by means of bypass and regulating valves. The Reynold's number and shear stress at the wall were 735.5 (laminar flow) and 5.33 Pa, respectively. The membranes used in this study were NTR 7410 and LES 90 (Table 3). Contact angle measurements using the sessile drop method with a contact angle meter (Tantec, Co., USA) were used to determine an index

for membrane hydrophobicity; 20 µL of Milli-Q water was dropped onto the dried membrane surface and the contact angle was measured within approximately 10 s. The ξ potential of the different membranes was measured by the electrophoresis method (ELS 8000 Otzca, Japan) using polylatex in 10 mM NaCl solution as a standard particle. The pH of the solution was adjusted with 0.1 N HCl and NaOH.

Figure 2 Schematic drawing of cross-flow UF/NF unit

Table 3 Characteristics of UF and NF membranes used

EfOM characterization methods

Total organic carbon (TOC) and UV absorbance (UVA)

TOC was measured by using the Dohrmann Phoenix 8000 UV-persulfate TOC analyzer equipped with an autosampler. All samples were filtered through 0.45 µm membrane prior to the TOC measurement. Thus, the TOC obtained are, in fact, dissolved organic carbon (DOC) values. UV absorbance was measured using a UV/Visible spectrophotometer at 254 nm. Here too, the samples were filtered through a 0.45 µm filter prior to measurement. The specific UVA (SUVA) values, which is the ratio between UVA_{254} and DOC, was then calculated.

XAD fractionation of EfOM

XAD-8 and XAD-4 resins were used for fractionating EfOM into hydrophobic EfOM (XAD-8-adsorbable, mostly hydrophobic acids with some hydrophobic neutrals) and transphilic EfOM (XAD-4 adsorbable; hydrophilic acids) components. The remaining fraction escaping the XAD-4 was the hydrophilic component (*15*).

Foulant concentration

The adsorbed EfOM concentration of the fouled membrane surfaces was measured, after washing of the membranes with 0.1 N NaOH solution. The DOC concentration in the solution was then measured. The NaOH solution desorbs hydrophobic and hydrophilic acids, most of the microorganisms, and EfOM with calcium complexes from the fouled membranes (*11*). Since the inorganic contribution in the dried film layer is usually low (less than 15%) (*1*), the removal of inorganic compounds was not considered in this study. When the fouled membranes were soaked in NaOH solution for 2 days, the permeate flux recovered up to more than 95%. NaOH cleaning was selected because the wastewater used in this study contained a high amount of humic compounds. The efficiency of different cleaning chemicals in desorbing foulants was compared in a previous study, and NaOH was found to be the most suitable agent (*16*). Both reversible and irreversible fractions of EfOM were found to be

desorbed and dissolved into NaOH solution. Earlier studies also indicated that NaOH is a suitable cleaning agent for membranes fouled with organic matter. Acid washing is mainly suitable for membranes fouled with inorganic matter. Therefore, in this study, the membrane samples were soaked in 0.1 N NaOH solution and stirred periodically for 2 days to desorb the EfOM component from the membrane surface.

Molecular weight (MW) distribution

HPSEC (Shimadzu Corp., Japan) with an SEC column (Protein-pak 125, Waters Milford, USA) was used to determine the MW distribution of organic matter. All the samples were previously filtered on a 0.45 µm filter prior to the DOC measurement. This procedure also protects the HPSEC column. Standard solutions of different polystyrene sulfonates (PSSs) with known MW (210, 1800, 4600, 8000, and 18000 daltons) were used to calibrate the equipment. Thus, the range of SEC column used in this study is MW = 100 daltons to 0.45 µm. Details on the measurement methodology are given elsewhere (*14*). The MW can be classified into three groups: i) number-averaged molecular weight, ii) weight-averaged molecular weight, and iii) z-average molecular weight. The number-averaged molecular weight, called the "median", can be calculated as follows:

$$M_n = \sum_{i=1}^{n}(N_i M_i) / \sum_{i=1}^{n}(N_i)$$

The weight-averaged molecular weight, can be calculated from the following equation:

$$M_w = \sum_{i=1}^{n}(N_i M_i^2) / \sum_{i=1}^{n}(N_i M_i)$$

where N_i is the number of molecules having a molecular weight M_i and i is an incrementing index over all molecular weights present.

RESULTS and DISCUSSION

Wastewater characteristics

Hydrophobic and hydrophilic fractionations and effectiveness of the pretreatments

It is important to characterize the BTSE in terms of fractionation. The EfOM removal achieved by the different pretreatment methods used in this study was first measured in terms of hydrophobic and hydrophilic fractions. Organic fractions in BTSE can be categorized into six classes: hydrophobic acids, bases and neutrals and hydrophilic acids, bases and neutrals. In particular, the hydrophilic fraction was found to be the most abundant fraction in all effluents, constituting 32 – 74% of the DOC. Hydrophobic acids were the second most dominant portion, accounting for 17 – 28% of the DOC (*17*). Thus, in this study, the hydrophobic, transphilic, and hydrophilic acids were chosen to identify the fractions. The hydrophobic and the hydrophilic organic fractions were determined in BTSE before and after the various pretreatments studied (Figure 3). GAC biofiltration and Floc-Ads were effective in

removing the hydrophobic fraction. Removal of hydrophilic fraction was also effective using the pretreatment of Floc-Ads. Transphilic fraction removal was about 50% (in terms of DOC) for all the pretreatments, which means that it is not possible to remove the majority of the transphilic fraction using chemical treatment. Theoretically, flocculation and adsorption are expected to remove mainly the hydrophobic fraction of large and small molecular weight organics, respectively. However, some hydrophilic fraction was also removed by flocculation and adsorption. The removal of the hydrophilic fraction of organics observed by flocculation may be due to the large dose of $FeCl_3$ used. They may have been removed by a sweep flocculation mechanism. The removal of the hydrophilic fraction of organics by adsorption can be attributed to the physical affinity between hydrophilic organic molecules and PAC (through van der Waals and electrostatic forces and chemisorption) (18).

Figure 3 Hydrophilic, transphilic and hydrophobic concentrations in BTSE after different pretreatments (Floc: flocculation, GAC: GAC biofiltration, PAC: PAC adsorption, Floc+PAC: flocculation followed by PAC adsorption)

Experiments with the UF membrane

DOC removal

The EfOM removal was first measured in terms of DOC. As can be seen in Figure 4, the DOC removal by the NTR 7410 UF membrane was only 43.6%, suggesting that a significant portion of EfOM in the BTSE consists of low molecular weight (MW) compounds much smaller than 17,500 daltons. On the other hand, the DOC removal is significant considering the fact that MWCO of the membrane is larger than the weight-averaged MW of the EfOM in the BTSE. This may be due to the influence of a number of parameters such as pore size distribution, surface charge effect of the membrane, physicochemical affinity of organic pollutants toward the membrane (hydrophobicity of the membrane, solute-solute and solute membrane interactions), and hydrodynamic characteristics of the membrane system (such as cross-flow velocity). Further, similar results were obtained with the same membrane in a previous study (*15*). Here the researchers observed a DOC removal of 30 to 60% although the weight-averaged MW in the water was only about 1300 daltons. Adsorption (by either the PAC or GAC biofilter) was found to be more efficient in removing DOC than flocculation as a pretreatment.

With the PAC adsorption as a pretreatment, the MW distribution in the effluent ranged from 3000 to 200 daltons. However, in the effluent of the GAC biofilter, some large MW organics (35,000 daltons) did remain (Figure 5): they are probably extracellular polymer substance (EPS) such as polysaccharides and proteins present in the BTSE (which were produced by microorganisms in the biofilter). These molecules may have been responsible for the permeate flux decline in the UF observed after biofiltration. (Figure 8). Even though the DOC

removal by GAC is better than that with PAC adsorption, the flux decline of GAC biofiltration is higher than that of PAC adsorption. Pretreatment of Floc-Ads led to a DOC removal as high as 90.1%. In this case, the additional removal by the posttreatment of UF was negligible (Figure 4).

Figure 4 Effect of different pretreatment methods in terms of DOC removal (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number.: 735.5, shear stress: 5.33 Pa)

In one set of experiments, UV absorbance and DOC were measured for the same samples. This permitted us to calculate SUVA (UVA/DOC), which is an index of aromaticity of organic matter. Normally, the surface waters and groundwaters have an SUVA value in the range of 3.0 to 6.0 $m^{-1}mg^{-1}L$ (15). In the present experiment, the SUVA value of the wastewater before and after the treatment was less than 2.00 $m^{-1}mg^{-1}L$, which means that the majority of organic compounds in the BTSE are nonaromatic compounds. The results summarized in Table 4 show the organic removal by different pretreatments.

Table 4 DOC and SUVA values by flocculation and adsorption. (membrane used = NTR-7410; UF membrane with MWCO of 17,500 daltons, crossflow velocity =0.4 m/s, pressure = 300 kPa)

MW distribution

The MW distribution of the soluble organic matter was measured after each pretreatment and in the UF effluent (Figure 5). The efficiency of UF was lower for smaller MW components. When a pretreatment was provided, the additional organic matter removed by UF as posttreatment was not significant (around 1.6% - 17.1%). The phenomenon of removal of small MW organic matter by flocculation with $FeCl_3$ is mainly due to complexation of Fe at a wide range of pHs (5.5 − 7.5) (*20*). The adsorption of small organic molecules onto iron hydroxide also occurs at a neutral pH (*21*).

Figures 5 (a) and 5 (b) confirm that adsorption (both GAC biofilter and PAC adsorption) removes the majority of organics except the fraction corresponding to MW 330 daltons: this might correspond to non humic substances and hydrophilic components. Figure 5 (a) shows that the pretreatment of Floc-Ads is very efficient (except for this fraction) and makes the additional removal by posttreatment of UF negligible. A previous study on the MW distribution of biologically treated effluent related different organic compounds and the MW range: a fraction of large MW (about 30,000 daltons) corresponds to polysaccharides, proteins, and aminosugars originating from cell components during biological processes and a fraction of small MW (about 250 daltons to 3,000) includes humic substances (3,000 daltons to

about 800), building blocks (around 500 daltons), acids (about 200 daltons), and amphiphiliic compounds (less than 200 daltons) (*19*). Here, the building blocks refer to humic substance - hydrolysates (350-500 daltons), which are more acidic than fulvic acids and are intermediates in the degradation process of fulvic acids such as low MW organic acids.

Figure 5 MW distributions of the soluble EfOM after different pretreatments; a) UF alone, GAC biofilter, and Floc-Ads, b) after flocculation and PAC adsorption (membrane used = NTR 7410 UF with a MWCO of 17,500, crossflow velocity = 0.5 m/s and transmembrane pressure = 300 kPa)

Experiments with the NF membrane

DOC removal

NF alone and Floc-Ads had nearly the same efficiency in terms of DOC removal (Figure 6). The removal efficiency of NF is only slightly improved by a pretreatment of flocculation and adsorption.

Figure 6 Organic removal by NF with and without pretreatment (membrane used = LES 90, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa)

MW distribution analysis of NF effluent

The results obtained (Figure 7) confirm that the NF membrane alone and with the pretreatment of flocculation/adsorption removed all the MW fractions except the soluble organic matter around MW = 330 daltons, which is only partially removed.

Figure 7 MW distributions of the soluble EfOM with different pretreatments; LES 90 with a MWCO of 250 before and after pretreatment (crossflow velocity = 0.5 m/s and transmembrane pressure = 300 kPa)

Comparison of UF and NF performances

UF and NF performances were compared in terms of organic removal efficiency (DOC) and normalized permeate flux (J/J_0). The flux decline is due to membrane fouling which depends on the composition of the feed and hydrodynamic conditions. In the present experiments, the hydrodynamic conditions were fixed to a predetermined value. Thus, the flux decline is mainly related to the feed composition. The feed composition is influenced by the pretreatment. A fast decline of the permeate flux with time necessitates more frequent backwashing and chemical cleaning, which decrease the membrane life and increase the cost of operation (*22*).

The operation of UF membranes can be improved by pretreatment (Figure 8 (a)). For example, Floc-Ads as pretreatment resulted in an increase of the initial permeate flux from 32.9 L/(m^2 h) without pretreatment to 108.4 L/(m^2 h). The UF NTR 7410 filtration without pretreatment resulted in rapid filtration flux decline with time. When the large MW (Figure 5) was removed by flocculation and Floc-Ads, the rate of decline of the flux was minimized. The PAC adsorption or GAC biofiltration alone as pretreatment did significantly reduce the permeate flux decline to the extent of the above pretreatments. This may be due to the MW distribution. The pretreatment of Floc-Ads led to practically no filtration flux decline and superior DOC removal (Figure 8 (b)).

On the other hand, in the NF experiments the direct application of NF without any pretreatment showed a similar filtration flux compared to that with pretreatment (Figure 8 (c)). The flux ratio (J/J_0) was only marginally higher with pretreatment. The removal efficiency was also similar with and without pretreatment (Figure 8 (c)). Thus, from this result it can be concluded that NF membranes may be operated for polishing BTSE without any pretreatment. However, the permeate flux is relatively small (permeate flux = 22.9 L/(m^2 h) with a transmembrane pressure of 300 kPa).

Figure 8 Temporal variation of filtration flux and DOC ratio with and without pretreatment; a) UF NTR 7410 permeate flux (J_0 = 3.01 m/d at 300 kPa; crossflow velocity = 0.5 m/s), b) UF NTR 7410 DOC ratio, c) NF LES 90 (J_0 = 0.77

m/d at 300 kPa; crossflow velocity = 0.5 m/s; C and C_0 = the effluent and influent DOC values; J_0 = pure water permeate flux)

Characterization of foulants on membrane surfaces

DOC concentration of the foulant

The adsorbed EfOM foulants of the fouled membrane surfaces were analyzed after washing of the membranes with 0.1 N NaOH solution. After pretreatment of Floc-Ads, the UF gave the low foulant concentration (Figure 9 (a)). The trend of foulant concentration was strongly proportional to the flux decline (Figure 8) on the UF membrane. On the other hand, the foulant concentration on the NF surface was much lower than that of UF (Figure 9 (b)).

Figure 9 DOC concentration of adsorbed EfOM on the fouled membrane surfaces after different pretreatments (a) EfOM concentration adsorbed on the UF membrane and b) on the NF membrane)

Tables 5 and 6 show the number-averaged and weight-averaged MW values of the foulants on different membranes, with and without pretreatment. The pretreatment of flocculation and/or adsorption reduced not only the amount of foulants on the membrane but also the MW of the foulants. The weight-averaged

MW of the foulants shifted from 675 daltons (without pretreatment) down to 400 – 300 (with pretreatment).

Table 5 MW values of foulants on the UF membranes (initial BTSE - number-averaged (median value) MW (M_n*): 759 daltons, weight-averaged MW (M_w**): 1158 daltons and polydispersivity (P*** = M_w/M_n): 1.53)

Table 6 MW values of foulants on the NF membrane (initial number-averaged (median) MW (M_n*): 759 daltons, weight-averaged MW (M_w**): 1158 daltons and polydispersivity (P*** = M_w/M_n): 1.53)

Foulant interpretation

The main groups of macromolecules in wastewater are polysaccharides, proteins, lipids, and nucleic acids (*23*). EfOM smaller than MW = 10^3 daltons includes carbohydrates, amino acids, vitamins, and chlorophyll. Persistent chemical compounds found in BTSE such as dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyl (PCB), and other toxic substances of public health significance are also low molecular weight compounds (*24,25*). Thus, as the foulants on the UF and NF membrane surfaces have been found to be in the range of MW = 183-513 daltons, this fouling may be assumed to be due to adsorption of recalcitrant matter, carbohydrates, amino acids and fatty acids (*26*). Although the MWCO of UF is large (17,500 MWCO), the foulants are small in size (MW = 386

daltons). This may be due to interaction between EfOM and the membrane pores. The foulant MW (d_p) to membrane MWCO (d_m) ratio is only 4.3 (where d_p = particle diameter and d_m = membrane pore diameter) because a 17,500 MWCO of UF corresponds to a pore size of about 1.3 nm and MW = 386 daltons MW corresponds to 0.3 nm. With such a ratio, strong interaction with the walls of the pores can be expected (*27*). Further, in this study, the samples were filtered by 0.45 µm membranes before DOC measurement, whereas the studies claiming that the main foulants during UF and NF are humic and fulvic acids (MW = 4,700 – 30,400 daltons) did not use prefiltration with a 0.45 µm membranes (*28*).

ACKNOWLEDGEMENTS

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Table 1 Characteristics of the bio-treated sewage effluent (BTSE) used

Table 2 Characteristics of powdered activated carbon (PAC) (James Cumming & Sons Pty Ltd., Australia) and granular activated carbon (GAC) (Calgon Carbon Corp., USA) used in this study

Table 3 Characteristics of UF and NF membranes used

Table 4 DOC and SUVA values by flocculation and adsorption. (membrane used = NTR-7410; UF membrane with MWCO of 17,500 daltons, crossflow velocity =0.4 m/s, pressure = 300 kPa)

Table 5 MW values of foulants on the UF membranes (initial BTSE - number-averaged (median value) MW (M_n^*): 759 daltons, weight-averaged MW (M_w^{**}): 1158 daltons and polydispersivity ($P^{***} = M_w/M_n$): 1.53)

Table 6 MW values of foulants on the NF membrane (initial number-averaged (median) MW (M_n^*): 759 daltons, weight-averaged MW (M_w^{**}): 1158 daltons and polydispersivity ($P^{***} = M_w/M_n$): 1.53)

Table 1 Characteristics of the bio-treated sewage effluent (BTSE) used

DOC (mg/L)	COD (mg/L)	pH	NO$_3$-N (mg/L)	TN (mg/L)	TP (mg/L)	Conductivity (µS/cm)
6.5 -10.4	16- 25.5	6.8 – 7.5	2.3 – 8.2	23.2 - 40	2.2 - 5	200 - 584

Table 2 Characteristics of powdered activated carbon (PAC) (James Cumming & Sons Pty Ltd., Australia) and granular activated carbon (GAC) (Calgon Carbon Corp., USA) used in this study

Specification	PAC-WB	GAC
Surface area (m^2/g)	882	1001.2
Mean pore diameter (Å)	30.61	22.55
Micropore volume (cm^3/g)	0.34	0.269
Mean diameter (μm)	19.7	750
Product code	MD3545WB powder	F-400

Table 3 Characteristics of UF and NF membranes used

Code	Material	MWCO[*] (daltons)	Contact angle(°)	Zeta potential at pH 7 (mV)	PWP[**] (L/m^2•h)	R$_m$ (membrane resistance, x 10^{12} m^{-1})
UF NTR 7410	Sulfonated polysulfones	17,500	69	-98.63	125.5	14
NF LES 90	Aromatic polyamides	250	54	-67.2	32.1	33

[*] MWCO: molecular weight cut off

[**] PWP: pure water permeability at 300 kPa

Table 4 DOC and SUVA values by flocculation and adsorption. (membrane used = NTR-7410; UF membrane with MWCO of 17,500 daltons, crossflow velocity =0.4 m/s, pressure = 300 kPa)

	Quality of bio-treated effluent	Membrane without pretreatment	Flocculation + membrane	GAC biofilter + membrane	PAC adsorption + membrane	Flocculation + adsorption + membrane
DOC (mg/L)	6.9	3.89	2.03	1.14	1.68	0.68
UVA_{254} (cm^{-1})	0.130	0.047	0.010	0.005	0.006	0.004
SUVA ($m^{-1}mg^{-1}L$)	1.884	1.208	0.493	0.439	0.357	0.588

Table 5 MW values of foulants on the UF membranes (initial BTSE - number-averaged (median value) MW (M_n^*): 759 daltons, weight-averaged MW (M_w^{**}): 1158 daltons and polydispersivity ($P^{***} = M_w/M_n$): 1.53)

UF	Permeate (daltons)			Foulants (daltons)		
	M_n^*	M_w^{**}	P^{***}	M_n^*	M_w^{**}	P^{***}
UF alone	495	675	1.36	415	513	1.24
Flocculation + UF	355	404	1.14	403	415	1.03
PAC adsorption + UF	330	379	1.15	384	399	1.04
GAC biofilter + UF	324	327	1.01	375	387	1.03
Floc. + Ads. + UF	301	314	1.04	348	351	1.01

Table 6 MW values of foulants on the NF membrane (initial number-averaged (median) MW (M_n^{*}): 759 daltons, weight-averaged MW (M_w^{**}): 1158 daltons and polydispersivity ($P^{***} = M_w/M_n$): 1.53)

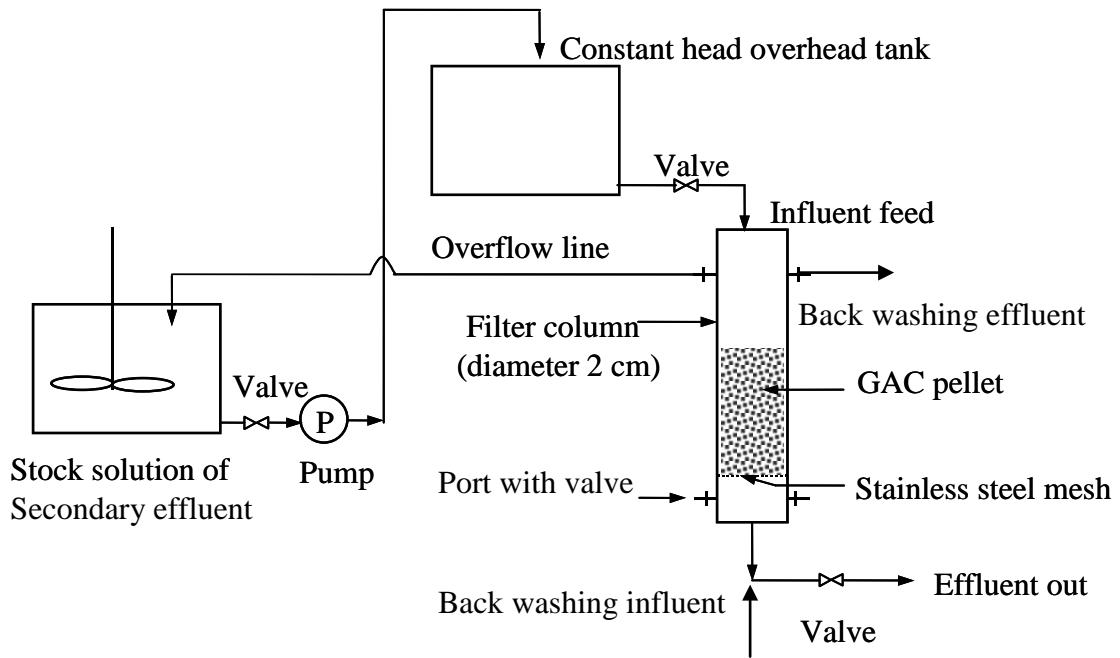| NF	Permeate (daltons)			Foulants (daltons)		
	M_n^{*}	M_w^{**}	P^{***}	M_n^{*}	M_w^{**}	P^{***}
NF alone	392	478	1.22	189	192	1.01
Floc. + Ads. + NF	302	310	1.03	182	183	1.01

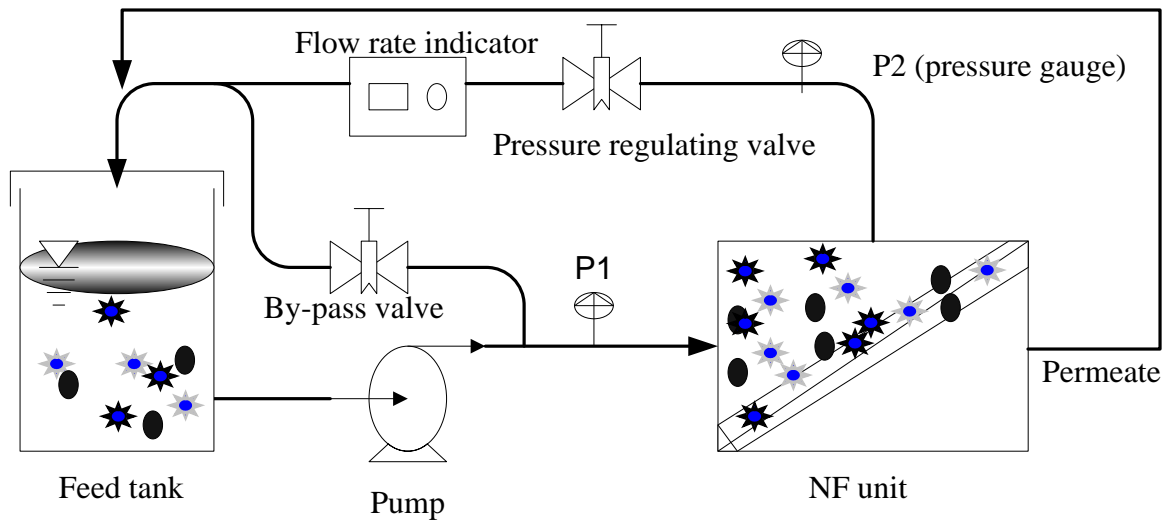Figure 1 Schematic drawing of the fixed bed GAC biofilter

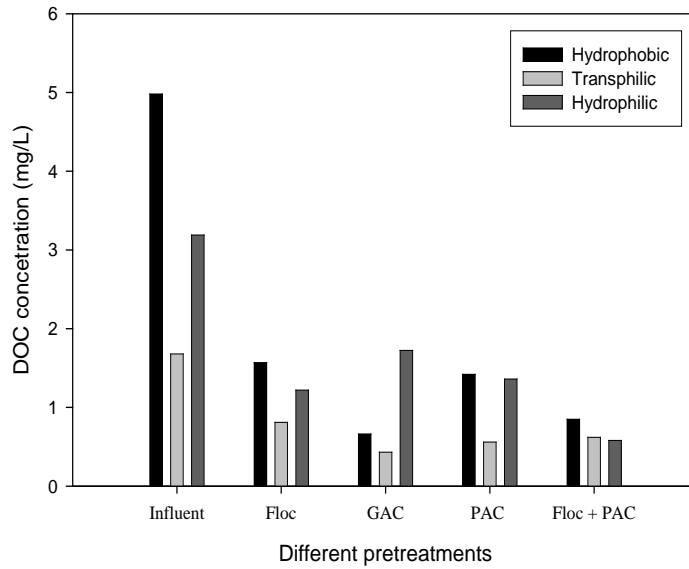Figure 2 Schematic drawing of cross-flow UF/NF unit

Figure 3 Hydrophilic, transphilic and hydrophobic concentrations in BTSE after different pretreatments (Floc: flocculation, GAC: GAC biofiltration, PAC: PAC adsorption, Floc+PAC: flocculation followed by PAC adsorption)
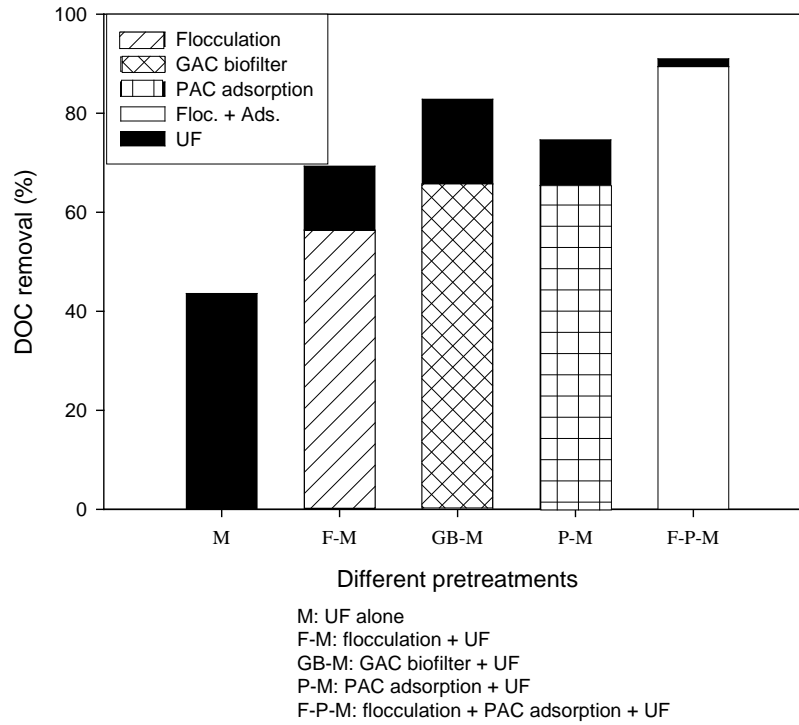
Figure 4 Effect of different pretreatment methods in terms of DOC removal (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number.: 735.5, shear stress: 5.33 Pa)
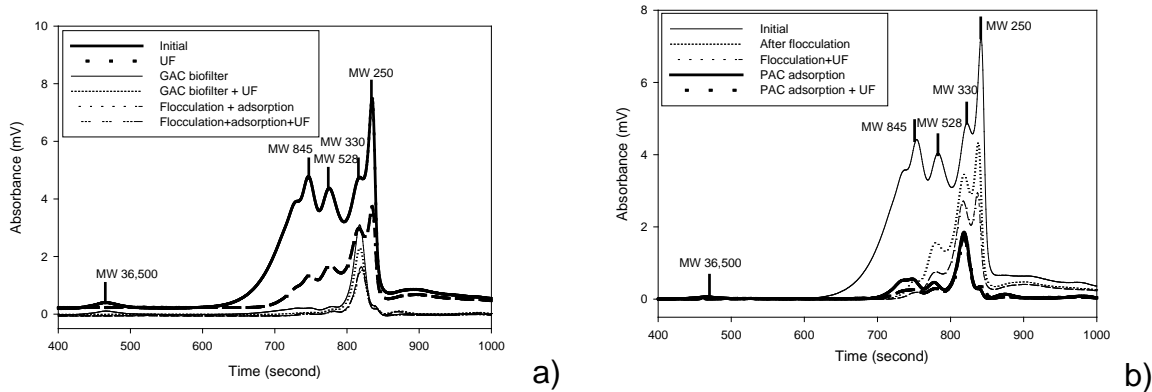
Figure 5 MW distributions of the soluble EfOM after different pretreatments; a) UF alone, GAC biofilter, and flocculation followed by adsorption b) after flocculation and PAC adsorption (membrane used = NTR 7410 UF with a MWCO of 17,500, crossflow velocity = 0.5 m/s and transmembrane pressure = 300 kPa)
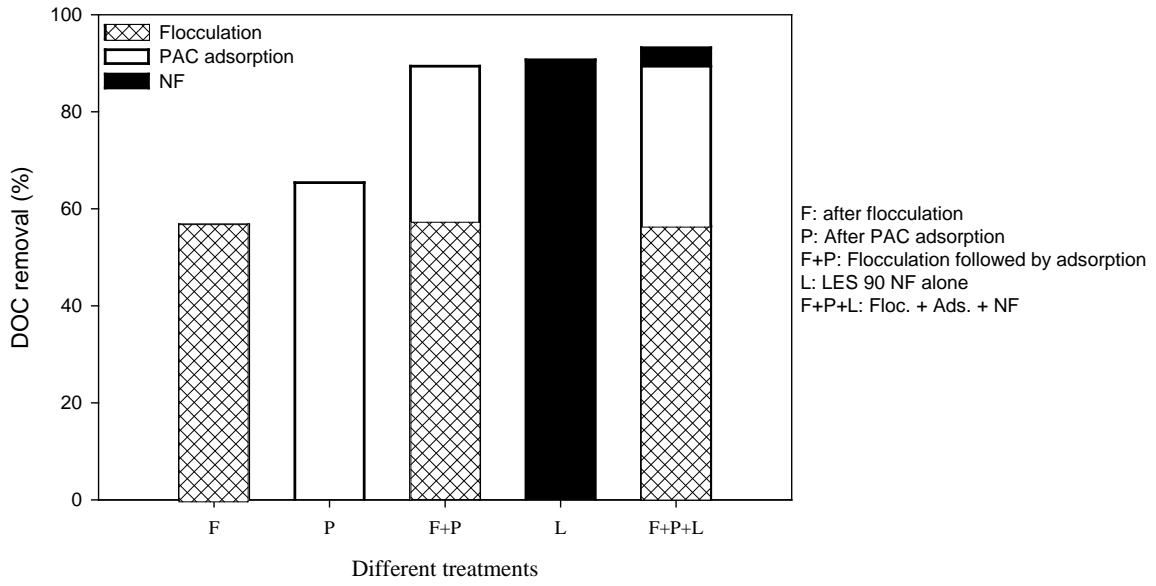
Figure 6 Organic removal by NF with and without pretreatment (membrane used = LES 90, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa)

Figure 7 MW distributions of the soluble EfOM with different pretreatments; LES 90 with a MWCO of 250 before and after pretreatment (crossflow velocity = 0.5 m/s and transmembrane pressure = 300 kPa)

Figure 8 Temporal variation of filtration flux and DOC ratio with and without pretreatment; a) UF NTR 7410 permeate flux (J_0 = 3.01 m/d at 300 kPa; crossflow velocity = 0.5 m/s), b) UF NTR 7410 DOC ratio, c) NF LES 90 (J_0 = 0.77 m/d at 300 kPa; crossflow velocity = 0.5 m/s; C and C_0 = the effluent and influent DOC values; J_0 = pure water permeate flux)

Figure 9 DOC concentration of adsorbed EfOM on the fouled membrane surfaces after different pretreatments (a) EfOM concentration adsorbed on the UF membrane and b) on the NF membrane)

Figure 1 Schematic drawing of the fixed bed GAC biofilter

Figure 2 Schematic drawing of cross-flow UF/NF unit

Figure 3 Hydrophilic, transphilic and hydrophobic concentrations in BTSE after different pretreatments (Floc: flocculation, GAC: GAC biofiltration, PAC: PAC adsorption, Floc+PAC: flocculation followed by PAC adsorption)

Figure 4 Effect of different pretreatment methods in terms of DOC removal (UF membrane used = NTR 7410; MWCO of 17,500 daltons, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa, Reynold's number.: 735.5, shear stress: 5.33 Pa)

Figure 5 MW distributions of the soluble EfOM after different pretreatments; a) UF alone, GAC biofilter, and flocculation followed by adsorption b) after flocculation and PAC adsorption (membrane used = NTR 7410 UF with a MWCO of 17,500, crossflow velocity = 0.5 m/s and transmembrane pressure = 300 kPa)

Figure 6 Organic removal by NF with and without pretreatment (membrane used =

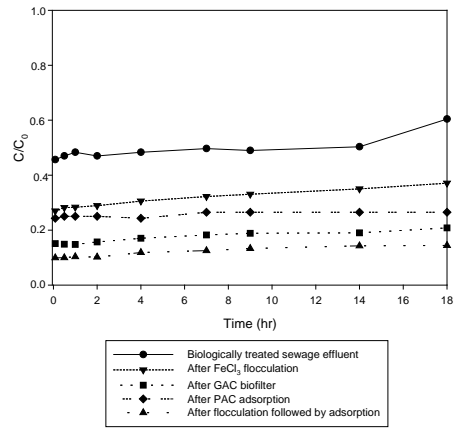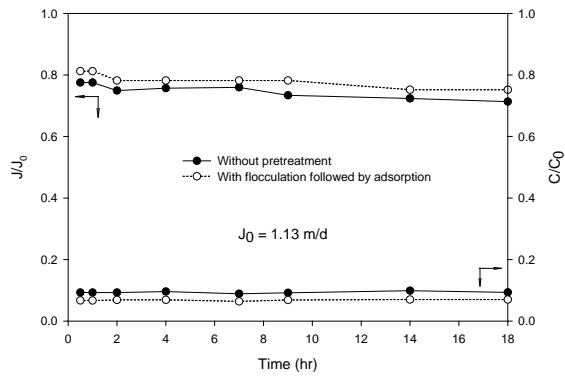LES 90, crossflow velocity = 0.5 m/s, transmembrane pressure = 300 kPa)

Figure 7 MW distributions of the soluble EfOM with different pretreatments; LES
90 with a MWCO of 250 before and after pretreatment (crossflow velocity = 0.5
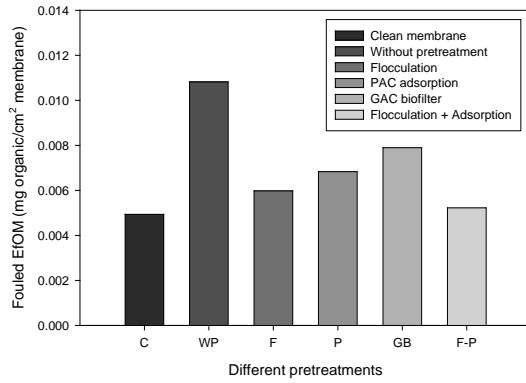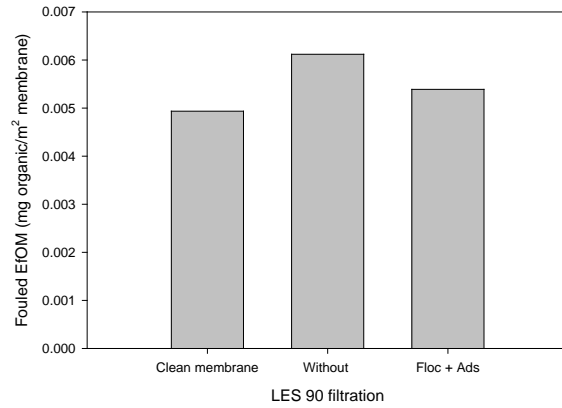m/s and transmembrane pressure = 300 kPa)

a)

b)

c)

Figure 8 Temporal variation of filtration flux and DOC ratio with and without pretreatment; a) UF NTR 7410 permeate flux (J_0 = 3.01 m/d at 300 kPa; crossflow velocity = 0.5 m/s), b) UF NTR 7410 DOC ratio, c) NF LES 90 (J_0 = 0.77 m/d at 300 kPa; crossflow velocity = 0.5 m/s; C and C_0 = the effluent and influent DOC values; J_0 = pure water permeate flux)

a)

b)

Figure 9 DOC concentration of adsorbed EfOM on the fouled membrane surfaces after different pretreatments (a) EfOM concentration adsorbed on the UF membrane and b) on the NF membrane)