Effect of Partial Flocculation and Adsorption as Pretreatment to Ultrafiltration

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In this study, the sufficiency of flocculation and adsorption with reduced doses of ferric chloride and powdered activated carbon (PAC) as pretreatment to ultrafiltration (UF) was investigated. A 50 mg/L dose of $FeCl_3$ and 0.5 g/L of PAC removed a majority of organic matter (OM; 88%), thus reducing the organic loading on UF that was used as posttreatment. Although flocculation with lower doses of $FeCl_3$ (10 mg/L) followed by PAC adsorption of 0.5 g/L and UF removed the same amount of organics (~88% OM), the majority of the OM removal was by the posttreatment of UF rather than by pretreatment, resulting in a significant decline of flux in UF. A detailed relative molecular mass (RMM) distribution analysis was made with flocculation, adsorption, and UF permeates. PAC adsorption decreased the majority of the relative intensity of smaller RMM of OM from the preflocculated water. Flocculation with <40 mg/L $FeCl_3$ was not sufficient to remove the relative intensity of the large RMM even after a postadsorption. The detailed analysis on weight-averaged RMM (M_w) indicated that the M_w values of OM in the wastewater and in the flocculated effluent were 29,800 daltons (initial), >25,000 (after flocculation with ≤40 mg/L $FeCl_3$), and <1000 (after flocculation with ≥50 mg/L $FeCl_3$).
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Introduction

Wastewater reuse will have a major impact in maintaining the environmental quality and the unrelenting pressure on conventional and natural freshwater sources. The most suitable processes for reuse are the membrane processes such as ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). UF is an effective process for the removal of colloidal matter, macromolecules, and pathogens. It removes only a part of dissolved organic matter (OM). Further, membrane fouling is the major problem in UF. Howe and Clark[1] reported that particulate matter (>0.45 μm) was relatively unimportant in fouling compared to dissolved matter in UF. Dissolved OM, ranging from 3 to 20 nm in diameter, appears to constitute the important membrane foulants.[1]

Many researchers found that $FeCl_3$ flocculation followed by powdered activated carbon (PAC) adsorption is one of the most effective pretreatments to membrane filtration.[2,3] Abdessemed and Nezzal[4] experimentally investigated the treatability of domestic wastewater by a coagulation–adsorption process using $FeCl_3$ and PAC. It removed 86% of chemical oxygen demand (COD) from domestic wastewater. Shon et al.[3] also observed that $FeCl_3$ flocculation followed by PAC adsorption removed 91% of dissolved organic carbon (DOC) from a biologically treated wastewater effluent. The $FeCl_3$ flocculation process can be used to aggregate colloids and suspended solids in the size range of 0.1–10 μm. A slight portion of small relative molecular mass (RMM) organic matter in the wastewater effluent can also be removed by complexation with ferric hydroxides. PAC adsorption can successfully remove the majority of the small RMM organic matter such as refractory organic matter, hydro-

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Table 1. Constituents of Synthetic Wastewater

Compound	Concentration (mg/L)	RMM (Da)	Fraction by DOC
Beef extract	1.8	300, 100, 70	0.065
Peptone	2.7	34,300, 100, 80	0.138
Humic acid	4.2	1500, 300	0.082
Tannic acid	4.2	6300	0.237
Sodium lignin sulfonate	2.4	12,100	0.067
Sodium lauryl sulfate	0.94	34,300	0.042
Arabic gum powder	4.7	900, 300	0.213
Arabic acid (polysaccharide)	5.0	38,900	0.156
$(NH_4)_2SO_4$	7.1		0
K_2HPO_4	7.0		0
NH_4HCO_3	19.8		0
$MgSO_4 \cdot 7H_2O$	0.71		0

phobic organic matter in the range of 200–3500 daltons (Da), and a small portion of the large RMM organic matter. Therefore, the pretreatment of flocculation followed by adsorption can remove the majority of dissolved organic matter in the wastewater.

Abdessemed and Nezzal[4] also stated from their experiments that flocculation is more beneficial than adsorption as pretreatment in terms of increase in permeate flux. There was an increase of 46.6% in permeate flux with flocculation and 22.2% with PAC adsorption. Shon et al.[3] showed that flocculation with an optimum dose of $FeCl_3$ of 68 mg/L improved the UF permeate flux by 50%. Al-Malack and Anderson[5] found the optimum $FeCl_3$ dose as 200 mg/L $FeCl_3$ at pH 9 to remove the organic matter in wastewater. The COD removal was 99.3%. According to the result of Aguiar et al.,[6] the optimum dose of coagulant was 2.1 $\pm$ 0.2 mg Fe per mg of total organic carbon (TOC).

PAC adsorption removed 60–75% of DOC from biologically treated wastewater effluent.[3,7] Lin et al.[8] studied the use of PAC adsorption at a dose up to 400 mg/L as pretreatment to remove humic substances of 20 mg/L in concentration. In their study, the PAC was ineffective in removing the RMM fractions of $<$300 or $>$17,000 Da. The flux decline in UF for the PAC-treated streams was worse than that without preadsorption.

In all the above studies, large doses of flocculants ($FeCl_3$) and PAC were used, which is not economical. Further, it will result in production of substantial amounts of sludge. In this study, a pretreatment of flocculation with reduced doses of $FeCl_3$ followed by adsorption with reduced doses of PAC was investigated in terms of flux decline in UF (used as posttreatment). Different RMM ranges of organic matter removed by different treatments were also studied. An attempt was made to optimize the pretreatment requirement based on the results of organic matter removal and effective RMM.

Experimental

Synthetic wastewater

This study was carried out with synthetic wastewater. The composition of the synthetic wastewater is presented in Table 1. This synthetic wastewater represents the biologically treated sewage effluent (BTSE).[9] Synthetic wastewater has a number of known compounds at known concentrations. The RMM of the mixed synthetic wastewater ranged from 300 to about 34,100 Da with the highest fraction of 900–1200 Da. Although sodium lignin sulfonate and tannic acid showed peaks at 12,100 and 6300 Da, respectively, the corresponding peaks were not found in the mixed synthetic wastewater, a phenomenon that may be explained by aggregations between OM and inorganic and/or organic compounds in the synthetic wastewater. Hong and Elimelech[10] found that the chemical composition of feed water greatly influenced the structure of OM. In the presence of high ionic strength and divalent cations, the OM structure was changed from a stretched and linear configuration to one that was coiled and compact. Verwey and Overbeek[11] reported that particle attraction and repulsion can be explained using DLVO (Derjaguin–Landau–Verwey–Overbeek) theory: (1) van der Waals (attraction) and (2) electrical double layer (repulsion). The wastewater used in this study has humics, tannic acids, polysaccharides, and divalent cations (such as magnesium). Thus, electrostatic interactions would change the RMM distribution, which will have a major impact on the flux decline.

Synthetic organic matter characterization

DOC was measured using a Dohrmann Phoenix 8000 ™ UV-persulfate TOC analyzer (Tekmar-Dohrmann, Mason, OH) equipped with an autosampler. All samples were filtered through a 0.45-μm membrane before DOC measurement. After pretreatment, the synthetic wastewater was examined for the RMM distribution of organics by high-pressure size-exclusion chromatography (HPSEC, Shimadzu Corp., Kyoto, Japan) with an SEC column (Protein-pak 125®, Waters Chromatography Division/Millipore, Milford, MA). Standards of RMM of various polystyrene sulfonates (PSS: 210, 1800, 4600, 8000, and 18,000 Da) were used to calibrate the equipment.

The RMM distribution represents a normalized fraction percentage, obtained by dividing each incremental height of the chromatogram with a sum of the heights when the chromatogram is divided into incremental mass intervals.[12,13] The molecular weight distribution (MWD) can also be represented by a UV response (mV intensity) with time. The latter representation is similar to that obtained with normalized fraction percentages, making it considerably easier to visualize the

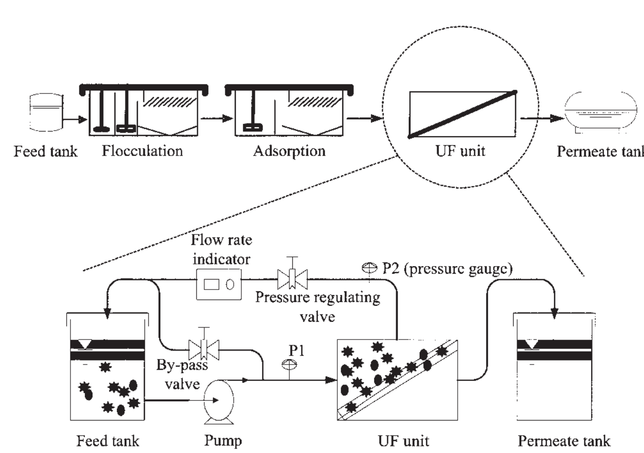


Figure 1. Partial flocculation followed by partial adsorption and UF unit.

Table 2. Characteristics of Powdered Activated Carbon (PAC) Used*

Specification	PAC-WB
Moisture content (%)	5 max
Surface area (m^2 g^{-1})	882
Nominal size	80% min finer than 75 micron
Type	Wood-based
Mean pore diameter (Å)	30.61
Mean diameter (μm)	19.71

*MD3545WB powder, James Cumming & Sons Pty. Ltd., Australia.

reduction of a peak of organic matter by different pretreatments, such as flocculation and adsorption. Thus, in this study both representations were used in interpreting organic removal by different pretreatments.

In general, UV absorbance at 254 nm detects limited components (mostly π-bonded molecules) of organic matter so this method is mostly applied to the MW estimations of humic and fulvic acids as well as hydrophobic (aromatic) organic matter. The UV detector used in this study had a limitation in detecting low UV-absorptivity components, such as proteins and polysaccharides. Thus, a relative intensity of UV response was used to interpret the results.[12,13] With an on-line DOC detector, all organic compounds can be recognized. According to a previous study, the RMM of 43,100 Da may be attributable to polysaccharide, 580 and 870 Da to humic substances, 300 Da to building blocks, 250 Da to acids, and <200 Da to amphiphilics.[14] Here, the building blocks refer to humic-substance hydrolysates (350–500 Da). Details on the measurement methodology are given elsewhere.[12,15]

Experimental setup of partial flocculation followed by partial adsorption and filtration

Figure 1 presents the experimental setup. Flocculation was first carried out with ferric chloride ($FeCl_3$) of different doses (10–68 mg/L). The samples were stirred rapidly for 1 min at 100 rpm, followed by 20 min of slow mixing at 30 rpm, and 30 min of settling. Adsorption with powdered activated carbon (PAC, 0.05–0.5 g/L) was then conducted using the preflocculated synthetic wastewater. The characteristics of PAC used are given in Table 2. A predetermined quantity of PAC was stirred with a mechanical stirrer at 100 rpm for 1 h. A prefilter (pore size 0.45 μm) was used to separate PAC particles before the application to UF unit.

In this study, the cross-flow UF unit (Nitto Denko Corp., Osaka, Japan) was used to study the organic removal from synthetic wastewater. The synthetic wastewater was pumped to a flat-sheet membrane module (effective membrane area 0.006 m^2). The operating pressure and cross-flow velocity were controlled at 300 kPa and 0.5 m/s by means of bypass and regulating valves. The Reynolds number and shear stress at the wall were 735 and 5.33 Pa, respectively. A Nitto Denko NTR-7410 membrane was used in this study (Table 3).

Results and Discussion

Removal of DOC by $FeCl_3$ flocculation and PAC adsorption

The efficiency of PAC adsorption and $FeCl_3$ flocculation was investigated in terms of dissolved organic carbon (DOC) removal from the synthetic wastewater (Figures 2i and 2ii). As can be seen in Figure 2i, DOC removal was the highest (78.2%) with the $FeCl_3$ flocculation at a dose of 68 mg/L. The optimum $FeCl_3$ dose was 68 mg/L from the laboratory jar test experiments. PAC also removed the DOC from 57.1 to 66.6% when PAC was added, at a dose of 1 to 2 g/L. For the synthetic wastewater used in this study, DOC removal was far better by flocculation than by adsorption, suggesting that the majority of organic matter (OM) in the synthetic wastewater is constituted of large molecular weight compounds.

Experiments were also conducted with the addition of partial optimum concentration of $FeCl_3$ and PAC to study the effect of reduced doses of chemicals in the DOC removal. The removal efficiency of OM by flocculation and adsorption at different doses and by posttreatment of UF is presented in Figure 3. For example, with the addition of an optimum dose of $FeCl_3$ and reduced doses of PAC (0.05–0.5 mg/L), removal of DOC from the synthetic wastewater was observed as follows: 82.6, 89.5, 89.8, and 92.2% for PAC doses of 0.05, 0.1, 0.3, and 0.5 g/L PAC, respectively. The above results indicate that PAC adsorption after flocculation with an optimum dose of $FeCl_3$ increased the removal of DOC. The increase was 15% when a PAC dose of 0.5 g/L was added. In the same manner, experiments were conducted with reduced doses of $FeCl_3$ and PAC. For instance, when the doses of $FeCl_3$ and PAC were kept at 30 mg/L and 0.5 g/L, respectively, removal of DOC was still high—up to 76%.

The posttreatment of UF had a significant effect in the removal of DOC for pretreated waters with lower $FeCl_3$ and PAC doses. For example, the posttreatment of UF led to additional DOC removal of 40% for the pretreated water with 10 mg/L $FeCl_3$ and 0.5 g/L of PAC. The pretreatment led to only 50% DOC removal, whereas the pretreatment followed by UF led to 90% removal. On the other hand, the pretreatment alone with 68 mg/L of $FeCl_3$ and 0.5 g/L of PAC led to >90% DOC removal, which allowed the posttreatment of UF to remove <4% additional DOC.

Flux decline of UF with pretreated wastewater

The performance of UF was also studied in terms of normalized permeate flux (J/J_0) with and without pretreatment (Figure 4). After the pretreatment of flocculation with the optimum dose of $FeCl_3$, the UF did not undergo any flux

Table 3. Characteristics of UF Membrane Used

Code	Material	MWCO* (daltons)	Contact Angle (°)	Zeta Potential at pH 7 (mV)	Specific Flux at 300 kPa (m/d)	R_m (Membrane Resistance, $\times 10^{12}$ m^{-1})
NTR 7410	Sulfonated polysulfones	17,500	69	−98.63	1.84	14.1

*MWCO, molecular weight cutoff.

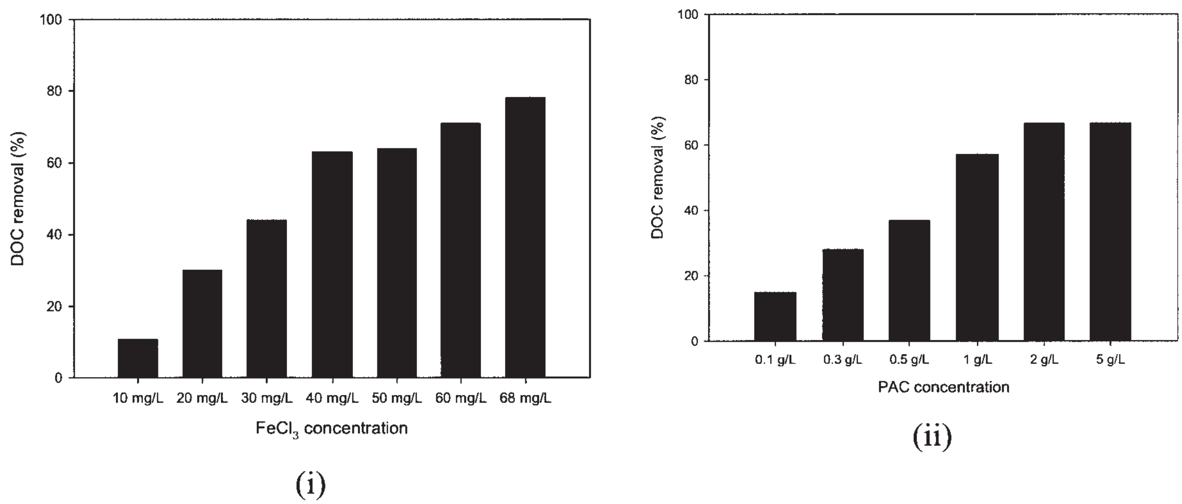


Figure 2. DOC removal by (i) $FeCl_3$ flocculation and (ii) PAC adsorption at different doses of $FeCl_3$ and PAC.

decline (Figure 4i). The pretreatment of PAC adsorption also helped in the reduction of flux decline. For example, the J/J_0 in the UF after a pretreatment of PAC adsorption (with 1 g/L) was from 1 to 0.71 after 6 h of operation (that is, 29% decline). The decline with no pretreatment was 0.66 (that is, 34% decline).

Figure 5 presents the permeate flux of UF with the wastewater that has undergone flocculation with 68, 50, 30, and 10 mg/L of $FeCl_3$ followed by PAC adsorption of known concentration of PAC. The flux decline was minimal, especially for preflocculated waters with $FeCl_3$ of $\geq$50 mg/L.

Relative molecular mass (RMM) distribution of organic matter

To understand the phenomenon of the flux decline, it is necessary to know the range of RMM of organic matter removed from the wastewater by flocculation, adsorption, and UF. This will help in the selection of a suitable pretreatment method and a correct membrane for a given application.[16]

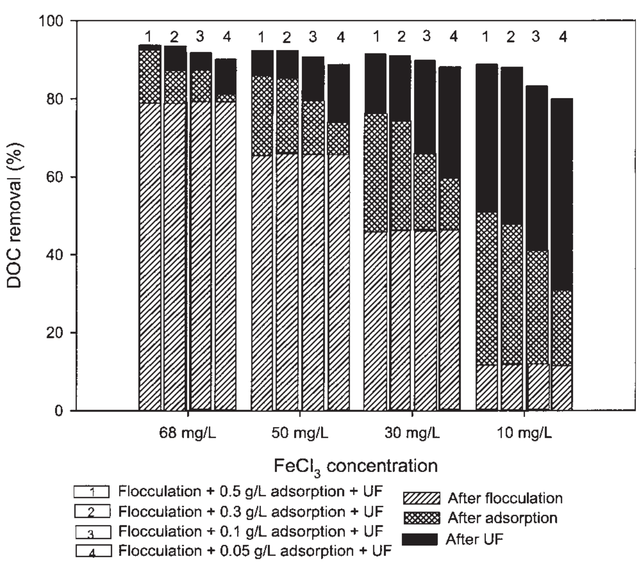


Figure 3. DOC removal of partial flocculation followed by partial adsorption and ultrafiltration.

UF membrane used: NTR-7410; MWCO: 17,500 Da; crossflow velocity: 0.5 m/s; transmembrane pressure: 300 kPa; Reynolds number: 735.5; shear stress: 5.33 Pa; DOC removal with UF alone: 75.3%.

Figures 6i and 6ii present the RMM distribution of OM [in terms of fraction percentage (peak heights divided by sum of peak heights) and UV response with time] in wastewater clarified with varying dosages of $FeCl_3$. It should be noted that settled flocs were removed and only supernatant was used in RMM distribution measurements. In some cases, peaks in the RMM distribution chart are higher after treatment than they were for raw wastewater. This is correct because peaks here do not represent absolute values but relative proportions. This is the reason that UV response (mV) with time is also presented along with these figures (Figure 6ii). The latter clearly shows removal of OM of different RMM values.

Flocculation with $FeCl_3$ in the 50 to 68 mg/L dosage range (near optimum dose) efficiently removed large RMM OM, tannic acid, sodium lignin sulfonate, sodium lauryl sulfate, and arabic acid (Figures 6i and 6ii). Focculation using higher doses of $FeCl_3$ also removed some smaller RMM OM compounds (600–1000 Da; that is, peptone, beef extract, and humic acid). The phenomenon of the small RMM OM removal (600–1000 Da) by $FeCl_3$ flocculation may be explained by the complexation of Fe.[17] However, the relative intensity of the smallest RMM (at 250 Da) was not reduced, showing that flocculation was not effective in removing small molecules. On the other hand, lower $FeCl_3$ dosages ($\leq$40 mg/L) did not decrease the relative intensity of all the large RMM organic compounds and the majority of small RMM compounds (Figures 6i and 6ii). The peaks corresponding to the relative intensity of the large RMM (36,300 Da) and small RMM (1000 and 900 Da) were clearly present in wastewater supernatant treated with <30 mg/L of $FeCl_3$. This trend of RMM distribution is in agreement with that of flux decline that occurred with 30 mg/L flocculation (Figure 4i). The relative intensity of the large RMM OM remaining in the synthetic wastewater may have been responsible for the flux decline. The indicative relationship between the particle size and the RMM is presented in Table 4. Perminova et al.[18] observed that large molecules (humic and fulvic acids) in the range of 4700–30,000 Da were responsible for the fouling of membranes by organic matter. Howe and Clark[1]

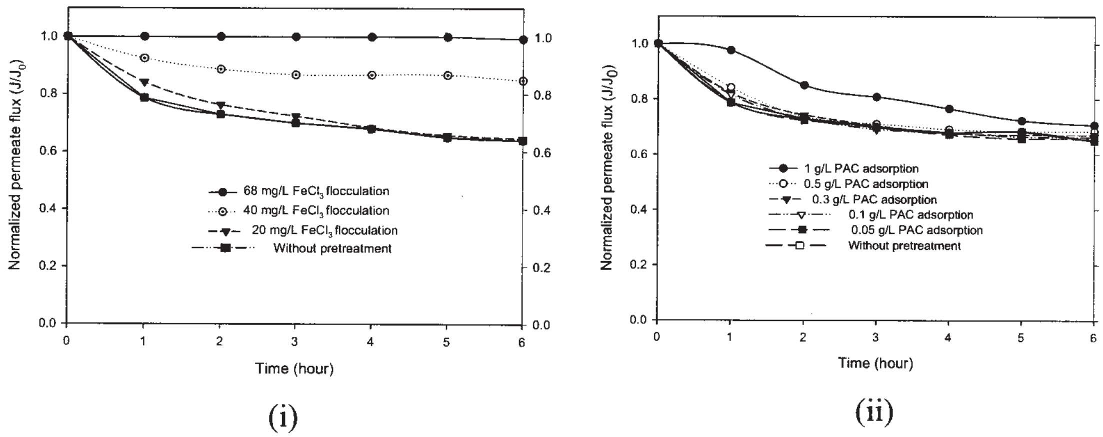


Figure 4. Temporal variation of filtration flux of different pretreatments with UF NTR-7410: (i) after PAC adsorption; (ii) after flocculation.

J_0 = 1.84 m/d at 300 kPa; cross-flow velocity: 0.5 m/s; MWCO: 17,500 Da; Reynolds number: 735.5; shear stress: 5.33 Pa.

found that the dissolved organic matter, which was smaller than about 3 nm, caused only minimal fouling.

Figures 6iii and 6iv present the RMM distribution of wastewater pretreated with PAC. Adsorption using larger PAC dosages (0.5 g/L) removed the majority of the relative intensity of the small RMM OM (200–600 Da). However, the majority of the relative intensity of larger RMM OM could not be removed by adsorption alone. The PAC used had a pore radius from 1 to

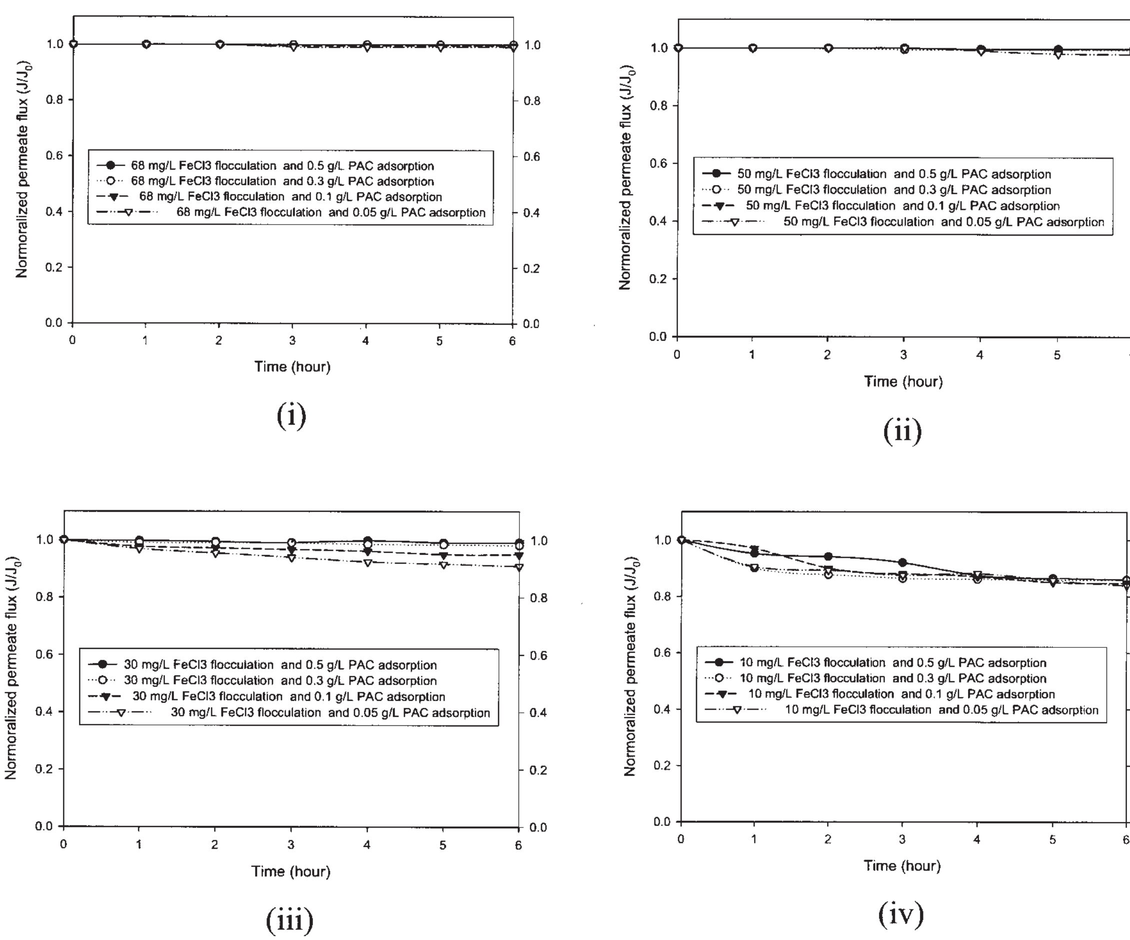


Figure 5. Temporal variation of filtration flux and DOC ratio with partial flocculation followed by partial adsorption with UF NTR-7410: (i) after 68 mg/L flocculation; (ii) after 50 mg/L; (iii) after 30 mg/L; (iv) after 10 mg/L.

J_0 = 1.84 m/d at 300 kPa; cross-flow velocity: 0.5 m/s; MWCO: 17,500 Da; Reynolds number: 735.5; shear stress: 5.33 Pa.

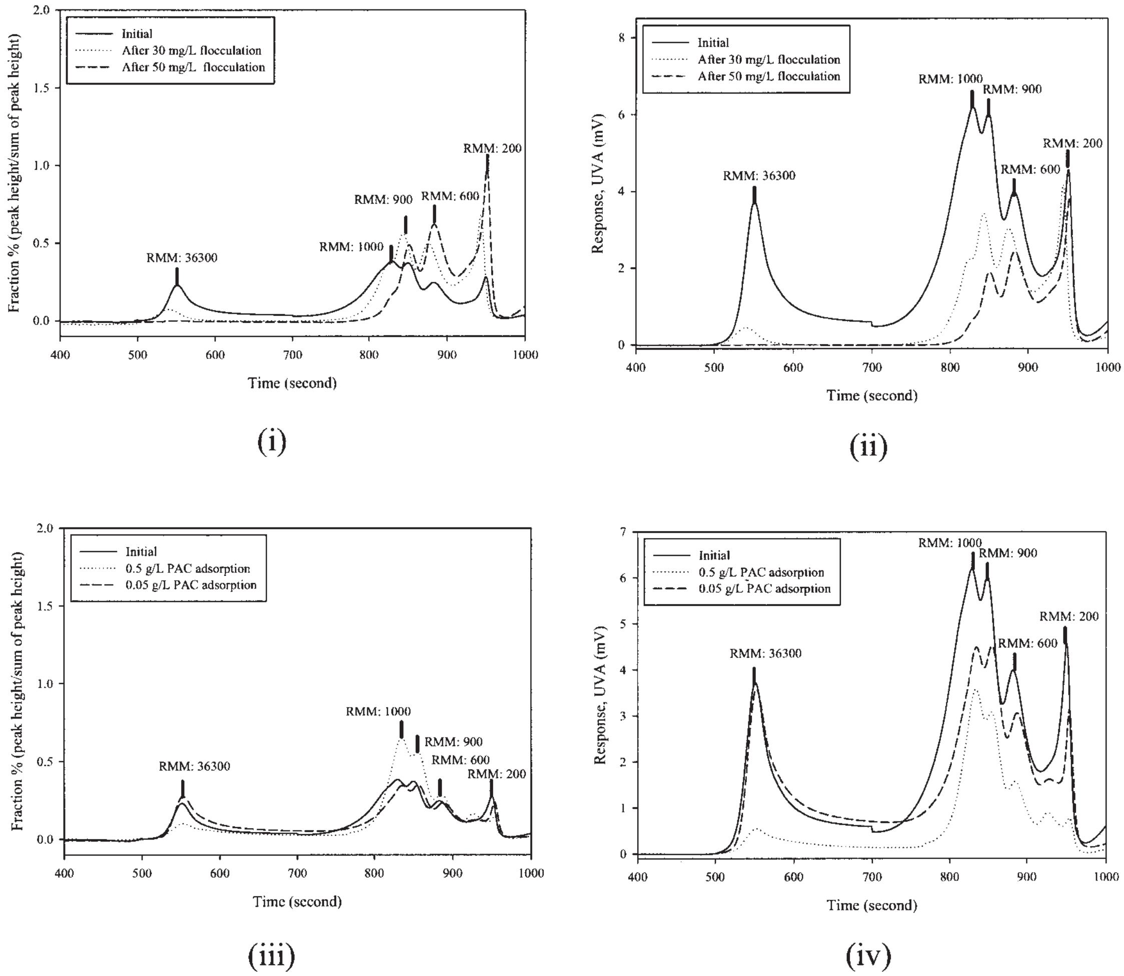


Figure 6. RMM distribution after (i) flocculation with the large $FeCl_3$ doses (fraction % vs. time); (ii) flocculation with small $FeCl_3$ doses (UV response vs. time); (iii) adsorption with large PAC doses (fraction % vs. time); and (iv) adsorption with small PAC doses (UV response vs. time).

5 nm with mean radius of 1.8 nm. The observed removal of a portion of a large RMM organics by PAC may have been a result of adsorption onto the larger pores, or the outer surface of PAC.[3] The RMM distribution results are consistent with the trend in flux decline (Figure 4ii).

Figure 7 shows the RMM distribution results after partial flocculation with 30 and 50 mg/L $FeCl_3$ doses and by partial adsorption. PAC adsorption removed the majority of smaller RMM of 900, 600, and 200 Da from wastewater preflocculated with more than 50 mg/L $FeCl_3$ (Figures 7i and 7ii). However, the peak corresponding to 1000 Da remained at high intensity, which indicates a difficulty in removing humic acid, tannic acid, and arabic gum powder (which has a peak at 1000 Da). Flocculation using <30 mg/L $FeCl_3$ was not sufficient to remove the large RMM OM, even after a postadsorption (Figures 7iii and 7iv).

Figure 8 presents the RMM distribution after $FeCl_3$ flocculation followed by PAC adsorption as pretreatment, and UF NTR-7410 filtration as posttreatment. The absolute disappearance of the relative intensity of OM at the peak corresponding to 36,300 Da was found after UF. Flocculation with a low dosage of 30 mg/L $FeCl_3$ and consecutive adsorption did not remove the majority of the large RMM OM. This resulted in relatively rapid flux decline in UF (Figure 5iii). Pretreatment with decreasing $FeCl_3$ doses increased the relative intensity of the peak corresponding to 1000 Da.

Table 5 presents the weight-averaged RMM (M_w) values of OM in the pretreated effluent and in the UF effluent. The M_w values of OM in the wastewater and in the flocculated effluent were 29,800 Da (initial), <1000 (after flocculation with ≥ 50 mg/L $FeCl_3$), and $>25{,}000$ (after flocculation with ≤ 40 mg/L

Table 4. Relationship between the Size (in nm and μm) and RMM (in Da)

Size (daltons)	Size (μm)	Size (nm)
500*	0.00039	0.39
1000*	0.00050	0.50
5000*	0.00085	0.85
7000*	0.00095	0.95
10,000*	0.00107	1.07
20,000*	0.00134	1.34
100,000**	0.01000	10.00
500,000**	0.05000	50.00

* The equation used to compute the size is: $Size\ (\mu m) = 0.0001\ (MW)^{0.3321}/2$.
**Adapted from Mulder.[19]

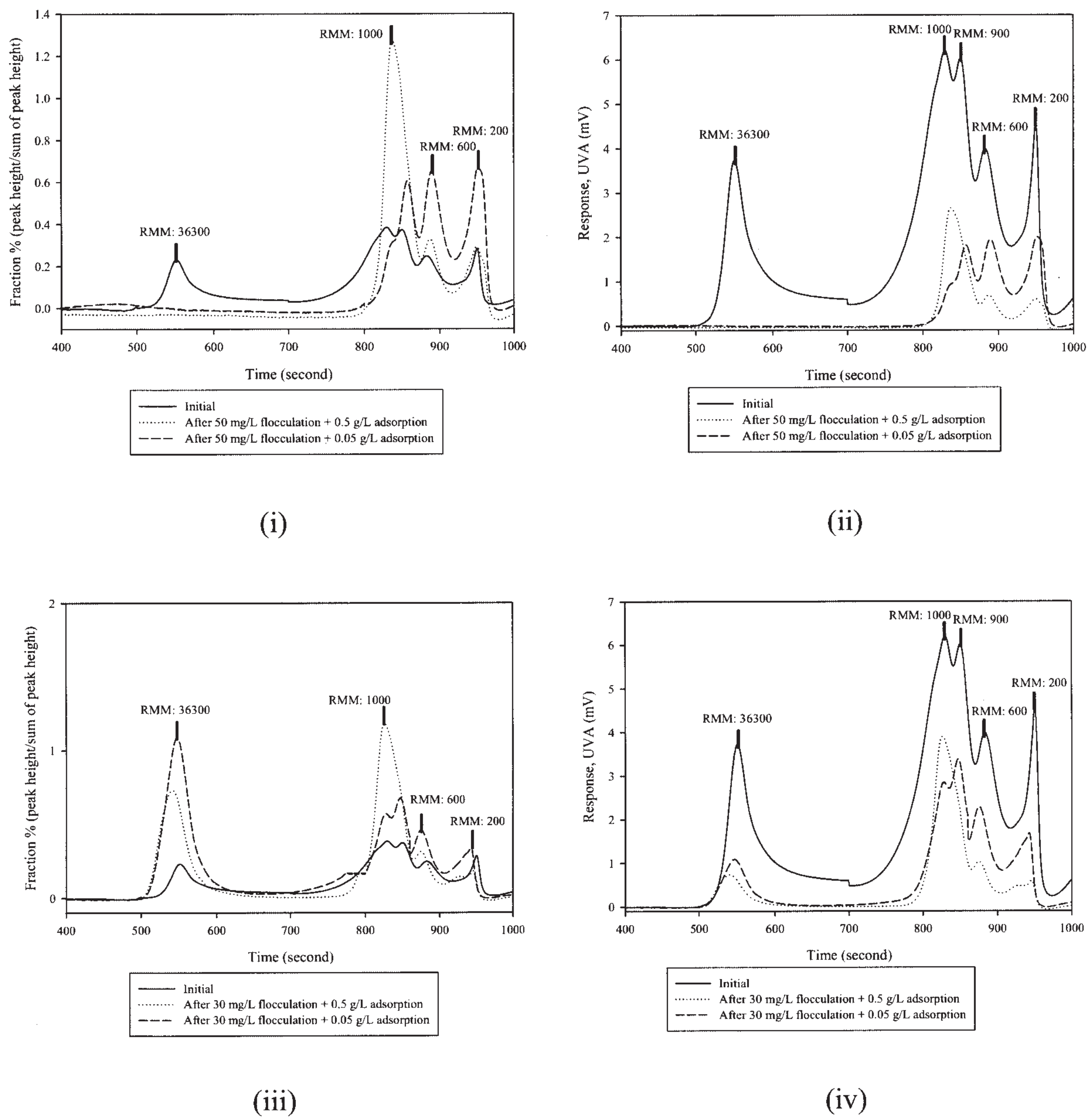


Figure 7. RMM distribution of organic matter after flocculation followed by PAC adsorption.

$FeCl_3$). Thus, a flocculation with >50 mg/L $FeCl_3$ and PAC adsorption is essential in removing large and small RMM OM for the synthetic wastewater in this study. The UF as posttreatment could not remove smaller RMM OM in a noticeable manner.

When the $FeCl_3$ concentration was decreased from 50 to 40 mg/L, the increase of M_w was significant. As the $FeCl_3$ concentration was further decreased from 40 to 20 mg/L, the increase of M_w values of OM was not so significant. The same trend was observed even with the PAC adsorption of the flocculated effluent (with $FeCl_3$ dose of 10–40 mg/L). This phenomenon is explained by the following two reasons: (1) the $FeCl_3$ dose of ≤40 mg/L was not sufficient to decrease the relative intensity of the large RMM OM; and (2) the PAC adsorbed only smaller RMM organic matter. When lower doses of $FeCl_3$ and PAC were used in the pretreatment, there was a significant difference in the M_w of the pretreated effluent and UF effluent. For example, when a $FeCl_3$ dose of 40 mg/L and a PAC dose of 0.5 g/L were used, the effluent from pretreatment had M_w = 25,000 Da. When this effluent was filtered through UF, the M_w decreased to 900 Da. This clearly shows that preflocculation with insufficient doses of flocculants delegates (or passes) the removal of large RMM organic matter to the posttreatment of UF. This, in turn, results in severe flux decline of membrane because the UF membrane fouling is mainly caused by large nanosized RMM organic matter.

A correlation between the amount of $FeCl_3$ dose and the M_w value is presented in Figure 9. The deviant crease circles show that the ranges of flocculant ($FeCl_3$) and adsorbent (PAC) are necessary to reduce the membrane fouling and to obtain superior DOC removal. Minimum concentrations of flocculant

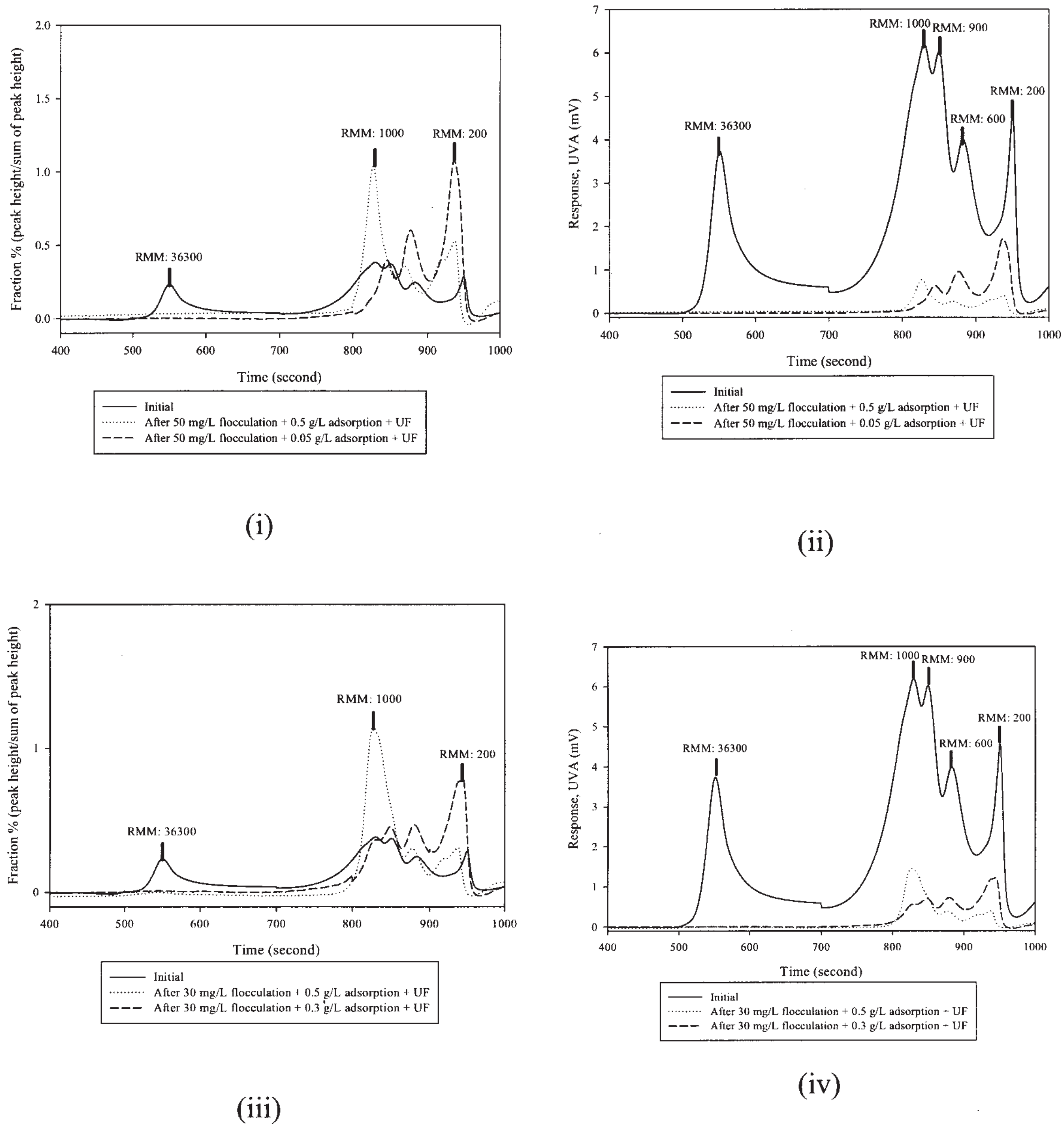


Figure 8. RMM distribution after flocculation and adsorption as pretreatment and UF as posttreatment.

J_0 = 1.84 m/d at 300 kPa; cross-flow velocity: 0.5 m/s; MWCO: 17,500 Da; Reynolds number: 735.5; shear stress: 5.33 Pa.

Table 5. Weight-Averaged RMM Values of Organic Matter after Pretreatment of Flocculation and Adsorption after Posttreatment of UF*

	PAC Concentration of 0.5 g/L	
$FeCl_3$ (mg/L)	After Semiflocculation Followed by PAC Adsorption	UF Permeate
68	1100	880
60	1100	870
50	1000	850
40	25,000	910
30	31,100	910
20	31,700	920
10	32,000	930

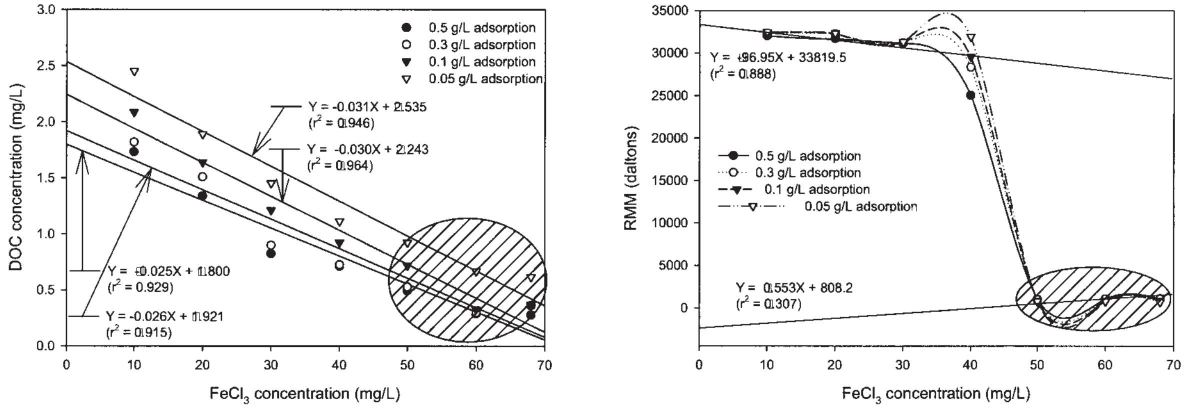
*All units: daltons.

($FeCl_3$) and adsorbent (PAC) are necessary to obtain high DOC removal and thus the minimum decreases in flux were 50 mg/L and 0.05 g/L, respectively, for the wastewater used in this study.

Conclusions

In this study, the sufficiency of flocculation and adsorption with reduced doses of ferric chloride ($FeCl_3$) and PAC as pretreatment to UF was investigated. The effectiveness of pretreatment was evaluated in terms of reduction in the decline of performance flux and the removal of organic matter of different RMMs. The finding can be summarized as follows:

(1) A $FeCl_3$ dose of <40 mg/L was not sufficient to decrease the relative intensity of the large RMM organic matter. $FeCl_3$ and PAC concentrations of 50 mg/L and 0.5 g/L, respec-



(i) (ii)

Figure 9. Correlation of partial flocculation concentration vs. DOC concentration and averaged-weight RMM: (i) $FeCl_3$ concentration vs. DOC concentration of partial flocculation followed by partial adsorption; (ii) $FeCl_3$ concentration vs. RMM of partial flocculation followed by partial adsorption.

J_0 = 1.84 m/d at 300 kPa; cross-flow velocity: 0.5 m/s; MWCO: 17,500 Da; Reynolds number: 735.5; shear stress: 5.33 Pa.

tively, removed a majority of DOC (88%), thus reducing the organic loading to UF used as posttreatment. Although flocculation with lower doses of $FeCl_3$ (10 mg/L) followed by PAC adsorption of 0.5 g/L and UF removed the same amount of organic matter, the majority of the DOC removal was achieved by the posttreatment of UF rather than by pretreatment. This resulted in a significant decrease of flux in UF. For example, 10 mg/L of $FeCl_3$ flocculation and 0.5 g/L of PAC adsorption removed only 50% of DOC, thus delegating UF to remove another 40% of DOC.

(2) Flocculation with $FeCl_3$ doses from 50 to 68 mg/L decreased the relative intensity of the majority of the large RMM organic matter, such as tannic acid, sodium lignin sulfornate, sodium lauryl sulfate, and arabic acid, and some of the small RMM organic matter. However, the relative intensity of the smallest RMM organic compounds (~300 Da) could not be removed by flocculation. The flocculation with lower $FeCl_3$ doses ($<$40 mg/L) could not remove the relative intensity of the large RMM organic matter (36,300 Da) even after a post-adsorption. Thus, the preflocculated effluent (with $<$40 mg/L $FeCl_3$) led to a significant decline of flux in UF operation. This also shows that the large RMM organic matter in the wastewater is the main cause for the flux decline in UF.

(3) PAC adsorption removed the relative intensity of the majority of smaller RMM of 900, 600, and 200 Da from the preflocculated water with $FeCl_3$ dose of $\geq$50 mg/L.

(4) The M_w values of OM in the wastewater and in the flocculated effluent were 30,000 Da (initial), $>$25,000 (after flocculation with $FeCl_3$ dose of $\leq$40 mg/L), and $<$1000 (after flocculation with $\geq$50 mg/L $FeCl_3$).

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Literature Cited

1. Howe K, Clark MM. Fouling of microfiltration and ultrafiltration membranes by natural waters. *Environ Sci Technol.* 2002;36:3571-3576.
2. Mameri N, Abdessemed D, Belhocine D, Lounici H. Treatment of fishery washing water by ultrafiltration. *AIChE J.* 1996;67:169-175.
3. Shon HK, Vigneswaran S, Kim InS, Cho J, Ngo HH. The effect of pre-treatment to ultrafiltration of biologically treated sewage effluent: A detailed effluent organic matter (EfOM) characterization. *Water Res.* 2004;38:1933-1939.
4. Abdessemed D, Nezzal G. Treatment of primary effluent by coagulation–adsorption–ultrafiltration for reuse. *Desalination.* 2002;152:367-373.
5. Al-Malack MH, Anderson GK. Coagulation–crossflow microfiltration of domestic wastewater. *J Membr Sci.* 1996;121:59-65.
6. Aguiar A, Lefebvre E, Rahni M, Beguebe B. Relationship between raw water TOC and the optimum coagulant dose (iron III chloride). *Environ Technol.* 1996;17:381-389.
7. Arana J, Melian JAH, Rodriguez JMD, Diaz OG, Viera A, Pena JP, Sosa PMM, Jimenez VE. TiO_2-photocatalysis as a tertiary treatment of naturally treated wastewater. *Catal Today.* 2002;76:279-289.
8. Lin CF, Huang YJ, Hao OJ. Ultrafiltration processes for removing humic substances: Effect of molecular weight fractions and PAC treatment. *Water Res.* 1999;33:1252-1264.
9. Seo GT, Ohgaki S, Suzuki Y. Sorption characteristics of biological powdered activated carbon in BPAC-MF (biological activated carbon–microfiltration) system for refractory organic removal. *Water Sci Technol.* 1997;35:163-170.
10. Hong S, Elimelech M. Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *J Membr Sci.* 1997;132:159-181.
11. Verwey EJW, Overbeek JTG. *Theory of the Stability of Lyophobic Colloids*. Amsterdam, The Netherlands: Elsevier Scientific; 1948.
12. Cho J, Amy G, Pellegrino J. Membrane filtration of natural organic matter: Factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane. *J Membr Sci.* 2000;164:89-110.
13. Lee S, Park G, Amy G, Hong SK, Moon SH, Lee DH, Cho J. Determination of membrane pore size distribution using the fractional rejection of nonionic and charged macromolecules. *J Membr Sci.* 2002;201:191-201.
14. Huber SA. Evidence for membrane fouling by specific TOC constituents. *Desalination.* 1998;119:229-234.
15. Her NG. *Identification and Characterization of Foulants and Scalants*

on NF Membrane. PhD Thesis. Boulder, CO: University of Colorado; 2002:40-49.
16. Tandanier CJ, Berry DF, Knocke WR. Dissolved organic matter apparent molecular distribution and number-average apparent molecular weight by batch ultrafiltration. *Environ Sci Technol.* 2000;34:2348-2353.
17. Vilge-Ritter A, Rose J, Masion A, Bottero JY, Laine JM. Chemistry and structure of aggregates formed with Fe-salts and natural organic matter. *Colloid Surf A.* 1999;147:297-308.
18. Perminova IV, Frimmel FH, Kudryavtsev AV, Abbt-Braun G, Hesse S, Petrosyan VS. Molecular weight characteristics of humic substances from different environments as determined by size exclusion chromatography and their statistical evaluation. *Environ Sci Technol.* 2003; 37:2477-2485.
19. Mulder M. *Basic Principles of Membrane Technology*. 2nd Edition. Boston, MA: Kluwer Academic; 1996.

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