Performance of Flocculation and Adsorption Pretreatments to Ultrafiltration of Biologically Treated Sewage Effluent: the Effect of Seasonal Variations

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Abstract: The effect of seasonal variations on ultrafiltration (UF) following pretreatment was investigated in terms of organic removal, removal of fraction, and molecular weight (MW) distribution. The MW range of effluent organic matter (EfOM) in biologically treated sewage effluent during winter (BTSE-W) consisted of large MW. However, the MW ranged from 3000 to 200 daltons in biologically treated sewage effluent in the summer (BTSE-S). During filtration experiments of BTSE-S, the UF NTR 7410 filter showed rapid flux decline with time without pretreatment. $FeCl_3$ flocculation removed the hydrophobic (HP) and hydrophilic (HL) fractions with different trends. In winter the HP fraction was removed up to 68.5%, whereas during the summer season, the HL fraction was removed by up to 59.8%. Flocculation removed large MW organics together with small MW, while PAC removed the majority of small MW organics. The flux decline with adsorption was also more severe than that with flocculation. Considering MW distribution, when large MW was removed by flocculation, the flux decline was

minimized, whereas PAC adsorption which removed small MW still decreased the permeate flux.

Keywords: Adsorption, biologically treated sewage effluent, flocculation, pretreatment, ultrafiltration

INTRODUCTION

With increasing water shortages wastewater reuse is becoming increasingly important. Although biologically treated sewage effluent (BTSE) is commonly discharged into waterways, it cannot be reused for domestic or industrial purposes without additional treatment. Membrane separation processes offer many advantages in water reuse technologies; however, their wider use is still hindered by high operating costs, which are mostly due to membrane organic fouling problems (1–3).

The composition of effluent organic matter (EfOM) is a combination of those of natural organic matter (NOM), soluble microbial products (SMPs), and trace harmful chemicals. Most of the NOM originates from drinking water, which is one of the major components in wastewater, while SMPs come from biological treatment and non-biodegradable organic matter (4). Of particular interest are recalcitrant organic chemicals which are resistant to biodegradation, and thus challenging to remove during typical wastewater treatment. Some micro-contaminants associated with wastewater effluent may cause adverse impacts to aquatic and human health if the compounds are present in recycled water. Some of the organic compounds of concern include: disinfection by-products (DBP), N-nitrosodimethylamines (NDMA), pesticides, herbicides, pharmaceuticals, and endocrine disrupting chemicals (EDCs) (5).

Jarusutthirak et al. (6) found that the colloidal fraction indicated higher membrane flux decline and fouling on UF membranes primarily due to the effects of pore blockage. Hydrophobic and transphilic fractions from BTSE influenced less fouling and flux decline than the colloids due to their molecular size as well as electrostatic repulsion between organic acids and the membrane surface. This membrane organic fouling can be significantly reduced by flocculation and powdered activated carbon (PAC) adsorption. These processes are able to remove most of the solutes and organic colloids present in BTSE. Abdessemed et al. (7) have studied the effect of flocculation and adsorption as pretreatment on the performance of cross-flow microfiltraion (MF) of domestic wastewater and BTSE, respectively. They experimentally showed that the flocculation-adsorption process removed 86% of chemical oxygen demand from domestic wastewater. In this study, $FeCl_3$ and powdered activated carbon were used at a dose of 40 mg l^{-1} and 20 mg l^{-1} respectively.

Characteristics of EfOM in BTSE vary from place to place and from season to season. For example, the range of molecular weight (MW) of

BTSE was 300 daltons to 400,000 (with a peak between 300 daltons and 3000) in Gwangju (Korea) (4), whereas it was 100 daltons–50,000 in Hawaii (USA) with a peak between 900 daltons and 20,500 (8). However, none of the previous studies discussed the influence of seasonal variations in terms of detailed analysis of the EfOM removed by pretreatment methods. A detailed characterization of EfOM during the seasons will help in selecting the most suitable pretreatment method, and in defining the optimum range of operational parameters for pretreatment.

In this study, the chosen pretreatments used prior to the application of UF were flocculation with $FeCl_3$, and adsorption with PAC. The UF permeates were characterized in terms of organic matter, MW distribution, and fraction (hydrophobic, transphilic, and hydrophilic).

METHODS

Biologically Treated Sewage Effluent

The study was conducted with BTSE drawn from a sewage treatment plant during the summer (BTSE-S) and winter (BTSE-W) seasons. The wastewater treatment plant is of medium size (25,000 m^3/d) and uses activated sludge technology. The average hydraulic retention time and the sludge age were 6 hours and about 8 days, respectively.

Flocculation and Adsorption

Flocculation was carried out using the optimum dose of ferric chloride ($FeCl_3$) as predetermined by standard jar tests. Ferric chloride was chosen in these experiments, since it can remove both colloidal organic matter and phosphorus efficiently. BTSE samples were placed in 1 L beakers and an optimum dose of ferric chloride was added by injection. The samples were stirred rapidly for 1 minute at 100 rpm, followed by 20 minutes of slow mixing at 30 rpm, and 30 minutes of settling. The molecular weight distribution of the organic compounds present in the supernatant was also measured. For the adsorption experiments, one gram of PAC was added to 1 L of BTSE and stirred with a mechanical stirrer at 100 rpm for one hour. The characteristics of PAC used are given in Table 1.

Membrane Unit

Figure 1 presents the experimental schematic of the cross-flow ultrafiltration (UF) unit used in the study. BTSE was pumped to the membrane module. New membranes were used in each experiment to avoid the effect of
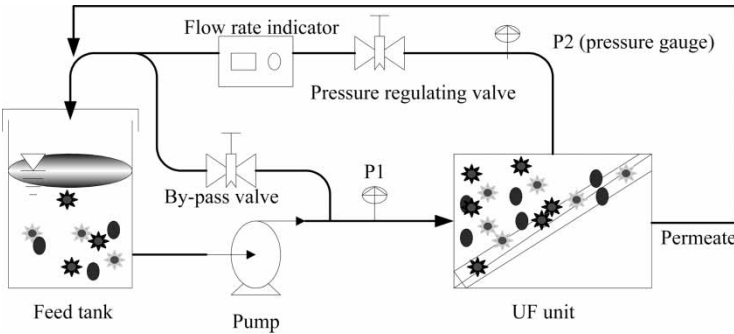
Table 1. Characteristics of powdered activated carbon (PAC) used (James Cumming & Sons Pty Ltd., Australia)

Specification	PAC-WB
Iodine number (mg g^{-1} min^{-1})	900
Ash content (%)	6 max.
Moisture content (%)	5 max.
Bulk density (kg m^{-3})	290–390
Surface area (m^2 g^{-1})	882
Nominal size	80% min finer than 75 micron
Type	Wood based
Mean pore diameter (Å)	30.61
Micropore volumn (cm^3 g^{-1})	0.34
Mean diameter (μm)	19.71
Product code	MD3545WB powder

residual fouling and to compare the results obtained under different conditions. The operating transmembrane pressure and cross-flow velocity were controlled at 300 kPa and 0.5 m/s by means of by-pass and regulating valves. The Reynold's number and shear stress at the wall were 735.5 (laminar flow) and 5.33 Pa, respectively. The major specifications of the NTR 7410 (Nitto Denko Corp., Japan) membrane are shown in Table 2.

Total Organic Carbon (TOC)

TOC was measured by using a Dohrmann Phoenix 8000 UV-persulphate TOC analyzer, equipped with an autosampler. All samples were filtered via 0.45 μm membranes prior to TOC measurements. Thus the obtained results, in fact, are dissolved organic carbon (DOC) values.

Figure 1. Experimental set-up of the cross-flow membrane system.

Table 2. Characteristics of UF membrane used

Code	NTR 7410
Material	Sulfonated polysulfones
MWCO[a] (daltons)	17,500
Contact angle (°)	69
Zeta potential at pH 7 (mV)	−98.63
PWP[b] at 300 kPa (m^3/m^2d)	1.84
R_m (membrane resistance, $\times 10^{12}$ m^{-1})	14.1

[a]MWCO: molecular weight cut off.
[b]PWP: pure water permeability.

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), transphilic EfOM (XAD-8 nor XAD-4 adsorbable; hydrophilic acids) components. The remaining fraction escaping the XAD-4 consists of hydrophilic components (9).

Molecular Weight Distribution

High pressure size exclusion chromatography (HPSEC, Shimadzu Corp., Japan) with a SEC column (Protein-pak 125, Waters Milford, USA) was used to determine the MW distribution of organic matter (10). All the samples were previously filtered on a 0.45 μm filter prior to the DOC measurement. This laboratory procedure also protects the HPSEC column. Standard solutions of different polystyrene sulfonates with known MW (PSS: 210, 1800, 4600, 8000, and 18,000 daltons) were used to calibrate the equipment. Thus, the range of SEC column used in this study is from about 100 daltons to 0.45 μm sizes.

RESULTS AND DISCUSSION

Characteristics of BTSE-W and BTSE-S

The DOC of BTSE-W and BTSE-S were about 10.5 mg/L and 6.5 mg/L, respectively. The SUVA values varied from about 2.2 (BTSE-W) to about 1.4 (BTSE-S). MW distributions of EfOM during the winter (BTSE-W) and summer (BTSE-S) seasons are illustrated in Fig. 2. The MW range of EfOM shows 50,000 to 200 daltons in BTSE-W. On the other hand, the MW is distributed from 3000 to 200 daltons with the highest response in
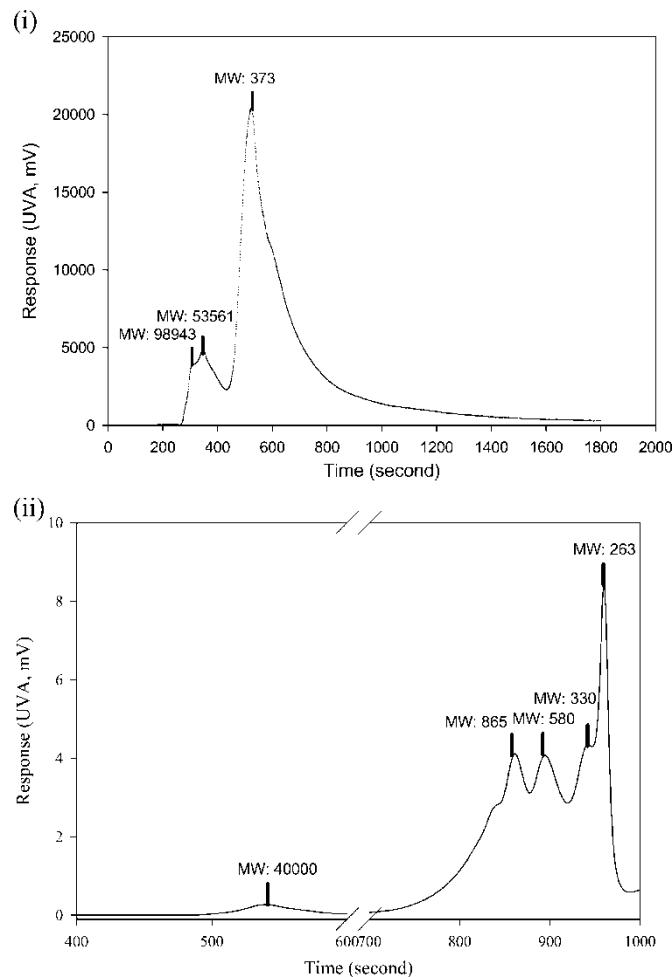
Figure 2.   MW distribution of (i) BTSE-W and (ii) BTSE-S.

BTSE-S. Figure 3 presents HP, TP, and HL fractions in BTSE-W and BTSE-S. BTSE-W mainly consisted of the HP fraction, whereas BTSE-S included a higher portion of the HL fraction. This difference may be due to seasonal temperature variations, since biological treatment is significantly affected by temperature (11).

Removal of DOC and Fractions by Flocculation and Adsorption

The EfOM removal by the different pretreatment methods was first measured in terms of DOC. As shown in Fig. 4, DOC removal by PAC adsorption was higher than by FeCl$_3$ flocculation. This may be due to a large amount of small
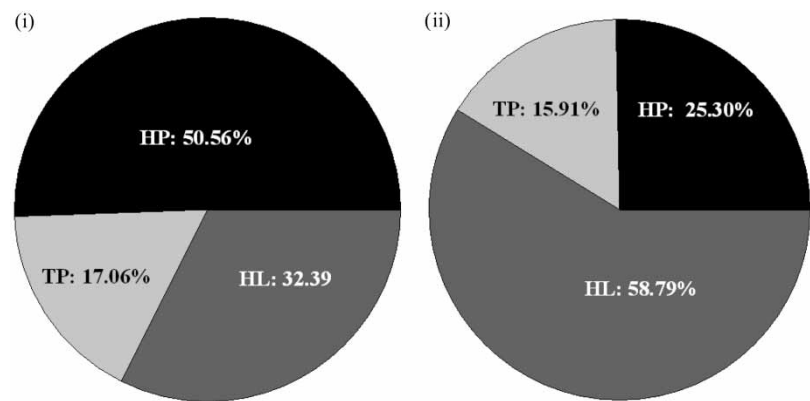
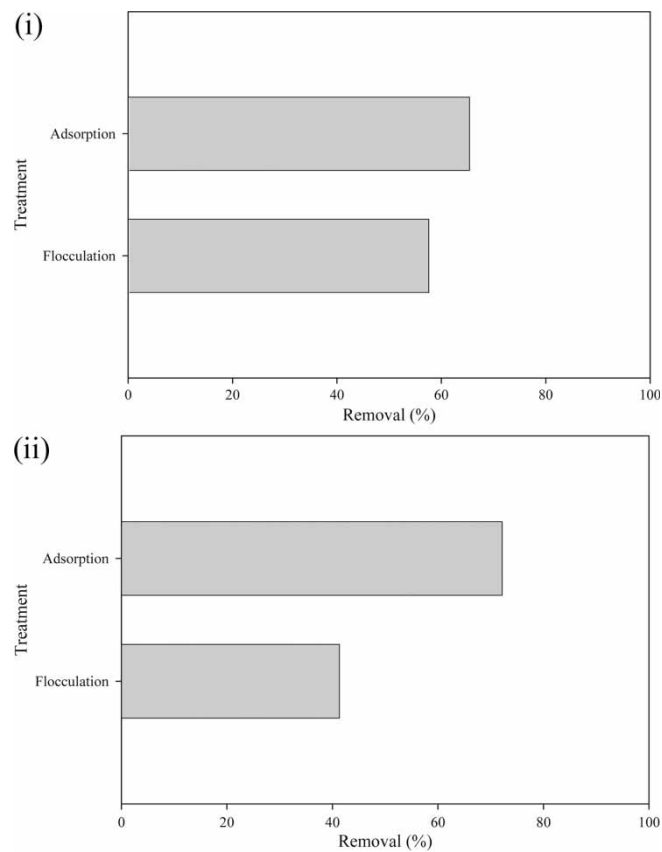*Figure 3.* HP, TP, and HL fractions in (i) BTSE-W and (ii) BTSE-S used in this study.

Figure 4. DOC removal of different pretreatments with the optimal doses of flocculent and PAC in (i) BTSE-W and (ii) BTSE-S.

Table 3. HP, TP, and HL fractions in BTSE-W (FeCl$_3$: 41 mg-Fe/L and PAC: 1 g/L)

Fraction	DOC of BTSE-W (ppm)	DOC of the effluent after flocculation (rejection, %)	DOC of the effluent after adsorption (rejection, %)
HP	4.98	1.57 (68.5)	1.42 (71.4)
TP	1.68	0.81 (62.9)	0.56 (66.9)
HL	3.19	1.22 (61.8)	1.36 (57.4)

MW present in BTSE. In general, PAC adsorption preferentially removes small MW (4).

The HP and HL organic fractions were determined in the BTSE-W before and after treatment by flocculation and adsorption (Table 3). It is generally accepted that flocculation and adsorption mainly remove HP portions of large and small MW organics, respectively. The removal of the HL portion of organics by flocculation may be due to the dose of FeCl$_3$ used, through the sweep flocculation mechanism. The removal of the HL portion of organics by adsorption could be attributed to the physical affinity between hydrophilic organic molecules and PAC through van der Waals and electrostatic forces, and chemisorption (12).
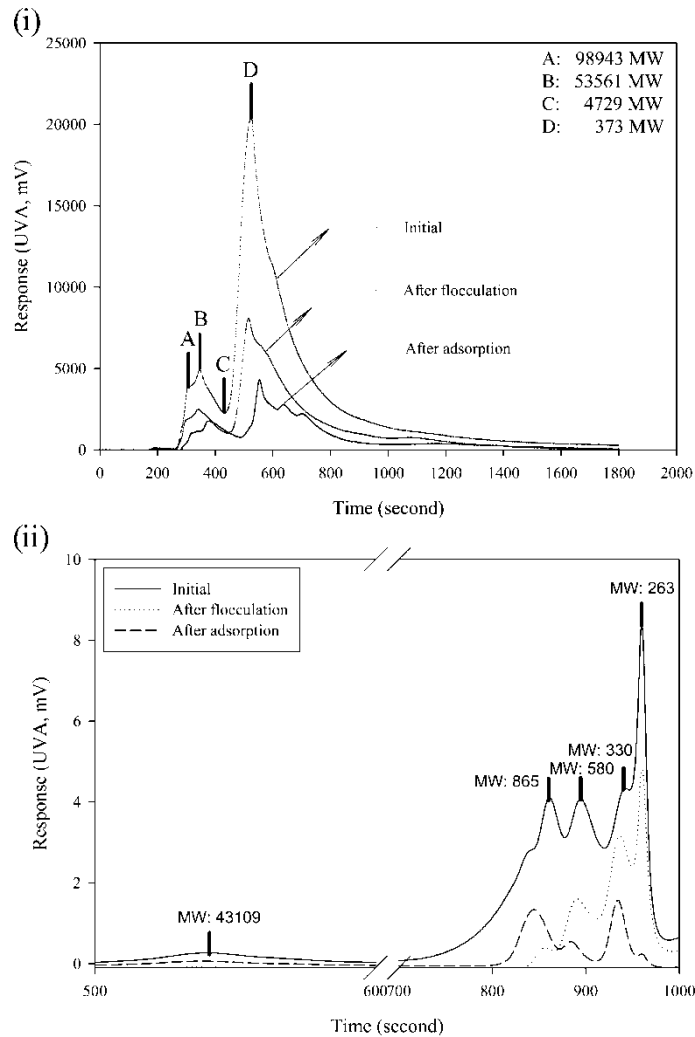
Table 4 presents the removal of different fractions by different pretreatments of BTSE-S. PAC adsorption removed the large amount of the HP compounds from BTSE samples collected in both seasons. This may be due to the HP characteristics of PAC, so that PAC adsorption favorably removed HP fractions. However, FeCl$_3$ flocculation removed HP and HL fractions with different trends. In the winter HP was removed by up to 68.5%, whereas in the summer season HL was removed by up to 59.8%. This is probably due to ion charge effects, since flocculation preferably removes fractions with higher negative charges.

MW Distribution Results

MW distribution of EfOM in BTSE-W was analyzed by using response (mV) data of HPSEC with elapsed time (Fig. 5), denoted as A, B, C and D.
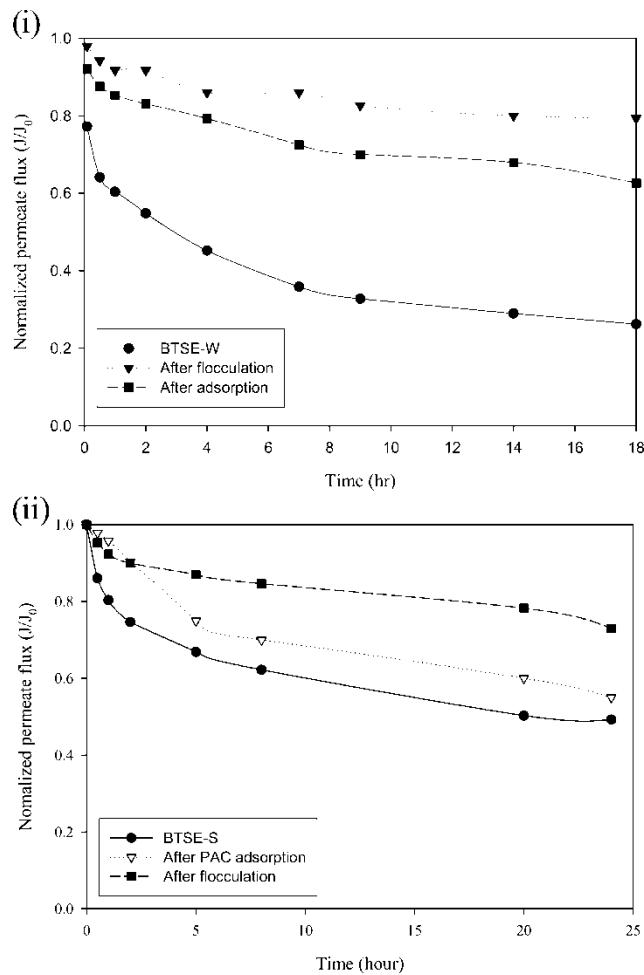
Table 4. Removal of HP, TP, and HL fractions in BTSE-S (FeCl$_3$: 28 mg-Fe/L and PAC: 1 g/L)

Fraction	DOC of BTSE-S (ppm)	DOC of the effluent after flocculation (rejection, %)	DOC of the effluent after adsorption (rejection, %)
HP	1.645	0.999 (39.3)	0.460 (72.0)
TP	1.034	0.802 (22.4)	0.282 (72.7)
HL	3.822	1.540 (59.7)	1.258 (67.1)

Figure 5. MW distribution of EfOM after FeCl$_3$ flocculation and PAC adsorption in (i) BTSE-W and (ii) BTSE-S.

The response versus elapsed time graph was drawn for both flocculated and non-flocculated samples (Fig. 5). In addition to the removal of large MW organics, it also removed a significant quantity of small MW organics. The mechanism of small MW organic matter removal by flocculation with FeCl$_3$ is mainly through complexation of Fe for wide range of pH (5.5–7.5) (13). In the present experiments the pH varied between 6.0 and 7.5. Adsorption of small organic molecules on Fe hydroxide also occurs at a neutral pH (14). MW distribution was also experimentally measured in BTSE-W

(i)

(ii)

Figure 6. Temporal variation of filtration flux with and without pretreatment in (i) BTSE-W and (ii) BTSE-S (UF NTR 7410, $J_0 = 3.01$ m/d at 300 kPa; crossflow velocity $= 0.5$ m/s; $J_0 =$ pure water permeate flux).

after PAC adsorption treatment (Fig. 5). As expected, PAC removed the majority of small MW organics. The PAC used in the experiments has a pore radius from 1 to 5 nm with mean radius of 1.8 nm. The removal of large MW organics by PAC can be explained as adsorption onto the larger pores of PAC. In addition, some of the larger MW organics may have been retained on the outer surface of PAC.

Detailed MW distribution of BTSE-S samples following pretreatment are shown in Fig. 5. MW distribution of BTSE-S comprised of small (260 daltons, 580 and 870) and large (43,110 daltons) MW, with peaks at 260 daltons

showing the highest responses. Ferric chloride ($FeCl_3$) flocculation and PAC adsorption with optimum doses were used as treatment methods. As shown in Fig. 5, flocculation alone could not remove the majority of small MW (260 daltons, 330 and 580); while adsorption alone could not remove large MW compounds (330 daltons, 870 and 43,110).

UF Performance Associated with Pretreatment

UF performances associated with flocculation and adsorption pretreatment of BTSE-W and BTSE-S were compared by normalized permeate fluxes (J/J_0), where J_0 denotes pure water permeate flux. The operation of UF membranes using BTSE-W and BTSE-S was improved following pretreatment (Fig. 6). During filtration experiments of BTSE-S with no pretreatment, the UF NTR 7410 membranes showed rapid flux decline with time (Fig. 6). The flux decline with adsorption was also more severe than that with flocculation, which can be explained by MW distribution characteristics. When the large MW was removed by flocculation, the flux decline was minimized, however, PAC adsorption as pretreatment, which removes the small MW, decreased the permeate flux. Thus, for the studied wastewater, it is important to remove the large MW to minimize the flux decline.

CONCLUSIONS

The effect of pretreatment and UF filtration was investigated in terms of removal of DOC, removal of different fractions of organic matter and MW distribution. BTSE-W mainly consisted of the HP fraction, whereas BTSE-S included a higher portion of the HL fraction. EfOM in BTSE-W consisted of large MW (50,000 to 200 daltons) matter, whereas BTSE-S had smaller (3000 to 200 daltons) MW matter. PAC adsorption removed the large amount of the HP compounds from BTSE samples collected in both seasons. However, $FeCl_3$ flocculation removed HP and HL groups with different trends. During the winter season HP was removed up to 68.5%, whereas in the summer season HL was removed up to 59.8%. During filtration experiments of untreated BTSE-S, the UF NTR 7410 filtration membranes showed rapid flux decline with time. The operation of UF membranes using BTSE-W and BTSE-S was improved by the pretreatment of flocculation. The flocculation as pretreatment led to large MW removal, which in turn resulted in the reduction of UF flux decline.

ACKNOWLEDGEMENTS

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