THE EFFECT OF PRETREATMENT TO ULTRAFILTRATION OF BIOLOGICALLY TREATED SEWAGE EFFLUENT: A DETAILED EFFLUENT ORGANIC MATTER (EfOM) CHARACTERIZATION

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ABSTRACT

Ultrafiltration alone can remove only a portion of the effluent organic matter (EfOM) from biologically treated sewage effluent (BTSE). Use of pretreatment not only improves the EfOM removal but also reduces the membrane fouling. In this research, NTR 7410 ultrafiltration membrane was employed to remove EfOM from biologically treated sewage effluent. Different pretreatments namely $FeCl_3$ flocculation and powder activated carbon

(PAC) adsorption were evaluated. The highest removal of organic matter was observed when flocculation followed by adsorption was used as pretreatment.

The flocculation and adsorption removed 68.5% and 71.4% of hydrophobic organics, respectively. The molecular weight (MW) of the EfOM in BTSE ranged from 300 to about 400,000 daltons. After the flocculation pretreatment, majority of large MW organic matter was removed. The pretreatment of the flocculation followed by adsorption led to very high removal of both small and large organic matter. Further, this pretreatment led to practically no filtration flux decline.

Keywords: pretreatment, molecular weight distribution, effluent organic matter, ultrafiltration

1. INTRODUCTION

Wastewater reuse is being increasingly emphasized as a strategy for rational use of limited resources of freshwater and as a mean of safeguarding the deteriorating aquatic environment due to wastewater disposal. Although the secondary and tertiary treated wastewater can be discharged into waterways, it can not be used for non-portable reuse purposes without further treatment. Membrane processes can be successfully used in obtaining water of recyclable quality. However, the membranes are easily fouled by effluent organic matter (EfOM) present at high levels in wastewater. EfOM-fouling, defined as the accumulation and/or adsorption of organic materials on the surface, or in the pores of a membrane, affects the membrane performance including permeability and EfOM rejection (Speth et al., 1998).

Al-Malack and Anderson (1996) and Chapman et al. (2002) have studied the effect of flocculation on the performance of cross-flow microfiltraion of domestic wastewater and biologically treated effluent, respectively. Flocculation as pretreatment helped in reducing the membrane fouling. Abdessemed et al. (2000) 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. A detailed experimental study was conducted on a number of pretreatment methods to reverse osmosis (RO) in treating biologically treated sewage effluent (Kim et al., 2002). Among the pretreatment methods used, the UF was the best pretreatment to RO. A recent study conducted with flocculation and adsorption as pretreatment to crossflow microfiltration (CFMF) showed a significant reduction of flux decline with time (Guo et al., 2003). Another long-term study conducted with a submerged membrane-adsorption process indicated that the powdered activated carbon (PAC) adsorption helped in significant reduction in membrane fouling. This study indicated that membrane cleaning can be prolonged by several weeks by the PAC addition. Here, PAC functioned as a biosorption system, eliminating the need for frequent removal of PAC (Vigneswaran et al., 2003). The organics initially adsorbed onto PAC is biologically degraded thereafter.

None of these studies dealt with a detailed analysis of EfOM removed by different pretreatment methods. A detailed characterization of EfOM will help in the selection of a suitable pretreatment method and the optimum range of operation parameters of the pretreatment. In this study, three different pretreatment methods were evaluated in terms of their capability in removing EfOM and their role in reducing the membrane fouling. They are: (i) flocculation with $FeCl_3$, (ii) adsorption with PAC, and (iii) flocculation followed by adsorption. The colloidal organic matter, hydrophobic/hydrophilic organic matter and molecular weight size distribution of EfOM were measured in the effluent of the above pretreatment methods.

2. MATERIALS AND METHODS

2.1 Pretreatment methods

The present research was carried out with biologically treated sewage effluent drawn from the sewage treatment plant. The effect of PAC adsorption and $FeCl_3$ flocculation in removing EfOM was investigated. The removal of EfOM was studied in terms of TOC, UV absorbance at 254 nm (UVA_{254}), and specific UV absorbance (SUVA). SUVA represents the aromaticity of EfOM (Cho, 1998). The amounts of EfOM colloidal matter and hydrophilic and hydrophobic organic fractions were experimentally determined. The molecular weight sizes removed by different pretreatments were also analyzed.

2.1.1 Flocculation

The flocculation was carried out with ferric chloride ($FeCl_3$) of predetermined doses. The biologically treated sewage effluent was placed in six 1-liter containers, where known amounts of ferric chloride were added. The dose of $FeCl_3$ was added from 20 mg l^{-1} to 200 mg l^{-1}. The samples were then stirred rapidly for 1 minute at 100 rpm, followed by 20 minutes of slow mixing at 30 rpm, and 30 minutes of settling. The supernatant was analyzed for TOC to determine the optimum $FeCl_3$ dose and the molecular weight distribution of the organic matter present in them.

2.1.2 PAC adsorption

Adsorption with PAC was conducted using one liter of biologically treated sewage effluent. The PAC used in the experiments was washed with distilled water and dried in the oven at 103.5 °C for 24 hours. They were kept in a desiccator before using in the adsorption experiments. The characteristics of PAC used are given in Table 1. One gram per liter of PAC was stirred with mechanical stirrer at 100 rpm for 1 hour. The ambient temperature was 25 °C. The pretreatment of flocculation followed by adsorption was conducted with the same conditions of flocculation and adsorption. Flocculation was conducted first and the supernatant was added with adsorbent.

2.1.3 Ultrafiltration set-up

In this research, the cross flow ultrafilter unit (Nitto Denko Corp., Japan) was used to study the effect of pretreatment on the membrane performance. The membrane used in this study was NTR 7410 with an average pore size of 17,500 molecular weight cut off (MWCO) (Table 2) (Jarusutthirak and Amy, 2001). The schematic diagram of crossflow ultrafilter experimental setup is shown in Figure 1. The wastewater with and without pretreatment 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 ms^{-1} by means of by-pass and regulating valves. A pressure application is investigated in this study. A similar range of pressure and crossflow values was used by Thanuttamavong et al. (2002).

2.2 EfOM characterization

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

TOC was measured by using the Dohrmann Phoenix 8000 UV-persulphate TOC analyzer with an autosampler. All samples were filtered through 0.45 μm membrane prior to the TOC measurement. Thus, the TOC values 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. Specific UVA (SUVA values), which is the ratio between UVA_{254} and TOC was then calculated.

2.2.2 Colloidal organic fraction

The dialysis was performed with Spectra/Por-3 regenerated cellulose dialysis membrane bag (MWCO 3,500 daltons). The dialysis membrane was washed by soaking it in 4 liter of pure water for 24 hours. The wastewater sample was acidified with HCl to pH 1 and placed in the pre-washed dialysis membrane bag. It was dialyzed for 8 hours (each time) against three 4 liter portions of 0.1 N HCl (to remove salts and low MW of EfOM). It was then dialyzed until the silica gel precipitate is dissolved against 4 liter of 0.2 N HF. Finally, it was dialyzed for 12 hours (each time) against two 4 liter portions of pure water. This is to remove residual HF and fluosilicic acid. Finally, the sample was taken out the dialysis membrane from the last 4 l of dialysate of deionized water and measured for its TOC content. This represents the EfOM colloidal matter (with molecular weight range from 3,500 daltons to 0.45 µm). In wastewater engineering practice, organic matter of 3,500 daltons may be too small to be called as organic colloidal matter.

2.2.3 Fractionation of EfOM into hydrophobic and hydrophilic fractions

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-4 adsorbable; hydrophilic bases and neutrals) components. The remaining fraction escaping the XAD 4 is the hydrophilic component.

2.2.4 Molecular weight (MW) distribution

The wastewater effluent after each pretreatment was subjected to molecular weight (MW) distribution measurements. 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 distributions of organics. Standards of MW of various polystyrene sulfonates (PSS: 210, 1800, 4600, 8000, and 18000 daltons) were used to calibrate the equipment. Details on the measurement methodology are given elsewhere (Her, 2002).

3. RESULTS AND DISCUSSION

The EfOM removal by the different pretreatment methods was first measured in terms of TOC, SUVA and molecular weight distribution. As can be seen in the Table 3, the flocculation followed by adsorption led to the highest TOC removal. The TOC removal of the NTR 7410 UF membrane was only 43.6%, suggesting that EfOM in BTSE consists of significant quantity of organic matter of small molecular weight (MW) of less than 17,500 daltons. The SUVA values in the biologically treated sewage effluent was relatively lower than that in surface water, suggesting that aromaticity of EfOM is less compared to raw water. Her (2002) reported that SUVA value of Silver lake surface water was 4.5 $mg^{-1}m^{-1}l$.

3.1 Removal of colloidal organics

The organic colloidal portion in the secondary effluent with and without pretreatment of flocculation and adsorption was determined (Table 4). As can be seen from Table 4, more than 65% of organic colloidal matter was removed by flocculation. Here, the organic colloidal matter is defined as the one having a size between 3,500 daltons to 0.45 μm (a standard method to measure the colloidal portion in NOM or EfOM). This size may be too small to be removed by flocculation. On the other hand, adsorption removed only 30% of colloidal organic matter. The adsorption works on the principle of adhesion in proportion to porous adsorbing material and surface area (Murray, 1995). The mean pore diameter of PAC is 3 nm (Table 1) which is very small to remove the majority of colloidal organic matter.

3.2 Hydrophobic/hydrophilic organic fractions

The hydrophobic and the hydrophilic organic fractions were determined in the biologically treated sewage effluent before and after the treatment of flocculation and adsorption (Table 5). Table 5 shows that flocculation followed by adsorption resulted in high removal of both hydrophobic and hydrophilic organic matters. In principle, the flocculation and adsorption are used mainly to remove hydrophobic portions of large and small molecular weight organics, respectively. The removal of the hydrophilic portion of organics by flocculation may be due to large dose of $FeCl_3$ used (through sweep flocculation mechanism). The removal of the hydrophilic portion of organics by adsorption could be attributed to the physical affinity between hydrophilic organic molecules and PAC (through Vander Waals, electro static forces and chemisorption) (Benefield et al. 1982). 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 is usually found to be the most abundant fraction in all effluents, constituting 32 – 74% of the TOC and hydrophobic acids are the second most dominant portion, accounting for 17 – 28% (Imai et al. 2002). Thus, in this study, the hydrophobic and hydrophilic acids were chosen to identify the fractions.

3.3 Molecular weight size distribution

The molecular weight (MW) distribution of EfOM in BTSE was analyzed by using response (mV) data of HPSEC with elapsed time. The molecular weight of the EfOM ranged from 300 daltons to about 400,000 with the highest fraction of 300 – 5000 daltons. The points of inflection for the wastewater studied were found at the molecular weight of 98943, 53561, 4729, and 373 (Figure 2). They are denoted by A, B, C, and D in Figure 3. Here, it should be noted that the wastewater characteristics and the MW size distribution of the organic matter vary from season to season and from places to places. The secondary effluent of a wastewater treatment plant in Hawaii showed that the MW size distribution was from approximately 50,000 daltons to 100 with the highest fraction of 20,500 – 900 daltons (Her, 2002).

The response versus elapsed time graph was drawn for both flocculated and non-flocculated samples (Figure 2 (a)). Comparing the flocculation results at different doses of $FeCl_3$, the flocculation with optimum dose of $FeCl_3$ (120 mg l^{-1}) gave rise to the highest removal of organics. In addition to the removal of large molecular weight organics, it also removed a significant quantity of small MW organics. The mechanism of small molecular weight organic matter removal by flocculation with $FeCl_3$ is mainly through complexation of Fe at wide range of pH (5.5 – 7.5) (Vilge-Ritter et al., 1999). In the present experiment, the pH was between 7 - 7.5. Adsorption of small organic molecules on to Fe hydroxide also occurs at a neutral pH (Dempsey et al., 1984).

The MW distribution was also experimentally measured in the biologically treated effluent after the treatment of adsorption by PAC (Figure 2 (b)). As expected, PAC removed the majority of small MW organics. The PAC used had 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 the 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.

Figure 2 (c) also shows the MW distribution of EfOM in the effluent without and with a treatment of flocculation (20 minutes of flocculation followed by 30 minutes of settling) followed by adsorption (for 1 hour). This figure indicates that the treatment of flocculation followed by adsorption led to a high removal of both small and large organic matters. Especially, all of MW from 5000 to 400,000 could be removed by this pretreatment.

3.4 Ultrafiltration

The biologically treated sewage effluent was filtered through ultrafiltration unit with and without pretreatment. The direct filtration of biologically treated sewage effluent led to rapid filtration flux (J) decline with time (Figure 3). Here J_0 is the pure water filtration flux. The pretreatment of flocculation led to significant reduction of filtration flux decline compared to the pretreatment of PAC adsorption. This is due to higher reduction of colloidal matter and larger molecules by flocculation than by PAC adsorption (Figure 3 and Table 4). The flocculation also achieved a removal of a portion of small MW organics through the mechanisms of adsorption and complexation. The PAC adsorption played a major role in removing small molecular weight organics only. As can be seen in Table 4, the removal of the colloidal portion (between 3,500 daltons to 0.45 μm) by adsorption was not significant. The pretreatment of flocculation followed by adsorption led to the practically no filtration flux decline and superior TOC removal (more than 90% removal). Figure 4 presents the effluent (C) to influent (C_0) TOC ratio for different pretreatments.

4. CONCLUSIONS

The results obtained lead to the following conclusions.

1. The organic colloidal portion in the biologically treated sewage effluent was removed up to 65% by the pretreatment of flocculation. The PAC adsorption removed significant but less amount of organic colloids (less than 30%).

2. A significant amount of hydrophobic and hydrophilic fractions of organic matter could be removed by incorporating the pretreatment of flocculation and adsorption. The flocculation and adsorption removed 51.6% and 58.7% of hydrophilic and 68.5% and 71.4% of hydrophobic organic fractions, respectively.

3. The molecular weight of EfOM in the biologically treated sewage effluent ranged from 300 to about 400,000 daltons with the highest fraction in the range of 300 – 5,000 daltons.

4. After the pretreatment of flocculation, the removal of both large and small molecular weight organic matter was observed.

5. After the pretreatment of PAC adsorption, the majority of small MW organics was removed.

6. After the flocculation followed by adsorption, high removal of both small and large molecular weight organic matters was achieved (more than 88.2% of TOC removal).

7. The pretreatment of flocculation followed by adsorption led to practically no filtration flux decline of NTR 7410 membrane filtration.

5. ACKNOWLEDGEMENTS

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Table 1 Characteristics of powdered activated carbon (PAC) used (James Cumming & Sons Pty Ltd., Australia)

Table 2 Characteristics of NTR-7410 membrane used

Table 3 Organic removal by flocculation and adsorption (flocculation alone: 56.7%, adsorption alone: 65.4%, flocculation followed by adsorption alone: 89.4%, membrane used = NTR 7410; UF membrane with MWCO of 17,500 daltons, crossflow velocity = 0.5 m s^{-1}, pressure = 300 kPa)

Table 4 Organic colloidal portion (in TOC) in the secondary effluent with and without a treatment of flocculation and adsorption

Table 5 Hydrophilic, hydrophobic, and transphilic fractions in the secondary effluent after flocculation ($FeCl_3$: 120 mg $l^{-1}$and PAC: 1 g l^{-1})

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

Table 2 Characteristics of NTR-7410 membrane used

Code	Material	MWCO* (dalton)	Contact angle(°)	Zeta potential at pH 7 (mV)
NTR 7410	Sulfonated polysulfones	17,500	69	-98.63

* MWCO: molecular weight cut off

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	Quality of biologically treated effluent	Membrane without pretreatment (rejection, %)	Flocculation alone (rejection, %)	PAC adsorption alone (rejection, %)	Flocculation + adsorption + membrane (rejection, %)
TOC (mg l^{-1})	6.6	3.72 (43.6 %)	2.80 (57.6)	2.28 (65.4%)	0.61 (91.0%)
UVA_{254} (cm^{-1})	0.110	0.046	0.040	0.010	0.005
SUVA ($m^{-1}mg^{-1}l$)	1.661	1.237	1.429	0.438	0.641

Table 4 Organic colloidal portion (in TOC) in the secondary effluent with and without a treatment of flocculation and adsorption

	Colloidal portion of EfOM (TOC)	SUVA ($m^{-1}mg^{-1}l$)
Secondary effluent	4.04	1.287
After flocculation with 120 mg l^{-1} of $FeCl_3$	1.36	0.294
After adsorption with 1 g $l^{-1}$of PAC	3.18	0.440

Table 5 Hydrophilic, hydrophobic, and transphilic fractions in the secondary effluent after flocculation ($FeCl_3$: 120 mg l^{-1} and PAC: 1 g l^{-1})

Fraction	TOC of Secondary Effluent (ppm)	TOC of the effluent after flocculation (rejection, %)	TOC of the effluent after adsorption (rejection, %)	TOC of the effluent after flocculation followed by adsorption (rejection, %)
Hydrophobic	4.98	1.57 (68.5)	1.42 (71.4)	0.85 (82.9)
Transphilic	1.68	0.81 (62.9)	0.56 (66.9)	0.79 (53.0)
Hydrophilic	3.19	1.22 (61.8)	1.36 (57.4)	0.58 (81.8)

Figure 1 Schematic diagram of the fixed bed adsorption system

Figure 2 MW distributions of the secondary sewage effluent with and without pretreatments (a) flocculation, b) PAC adsorption and c) flocculation followed by adsorption)

Figure 3 Temporal variation of filtration flux with and without pretreatment (NTR 7410 ultrafiltration membrane, Nitto Denko Corp.) in the biologically treated sewage effluent sewage, operating pressure 300 kPa

Figure 4 TOC removal by ultrafiltration with and without pretreatment (NTR 7410 ultrafiltration membrane, Nitto Denko Corp.) in the biologically treated sewage effluent sewage, operating pressure 300 kPa

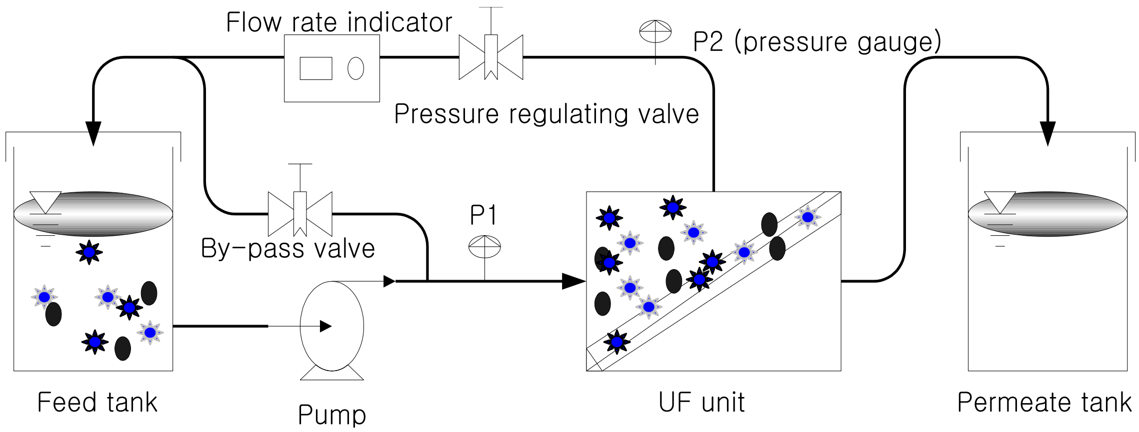
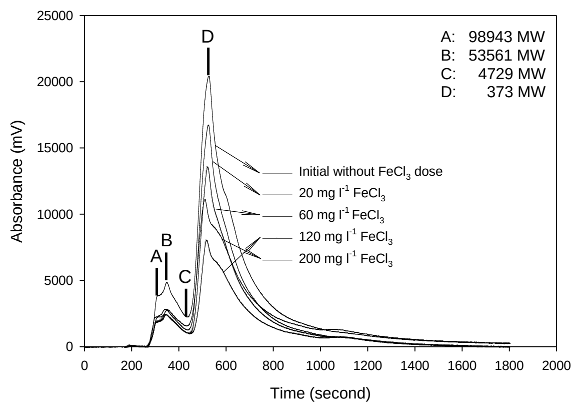
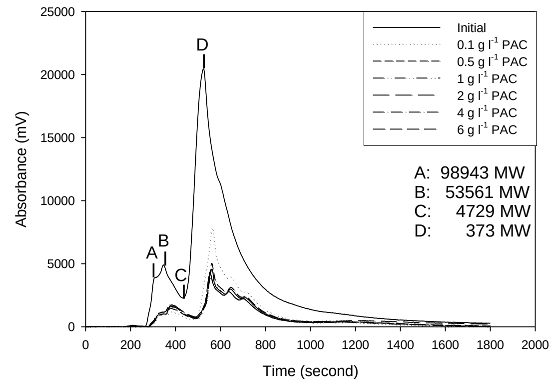


Figure 1 Schematic diagram of cross-flow UF unit used



a)



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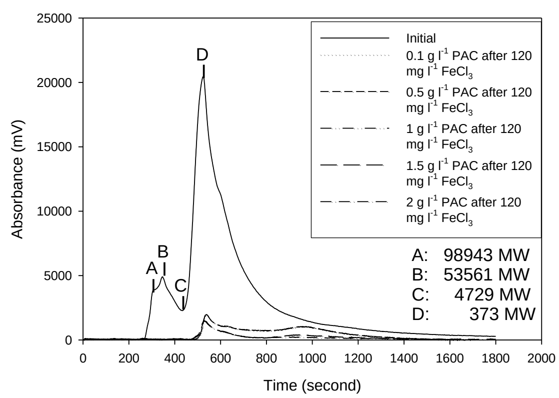

c)

Figure 2 MW distributions of the secondary sewage effluent with and without pretreatments (a) flocculation, b) PAC adsorption and c) flocculation followed by adsorption)

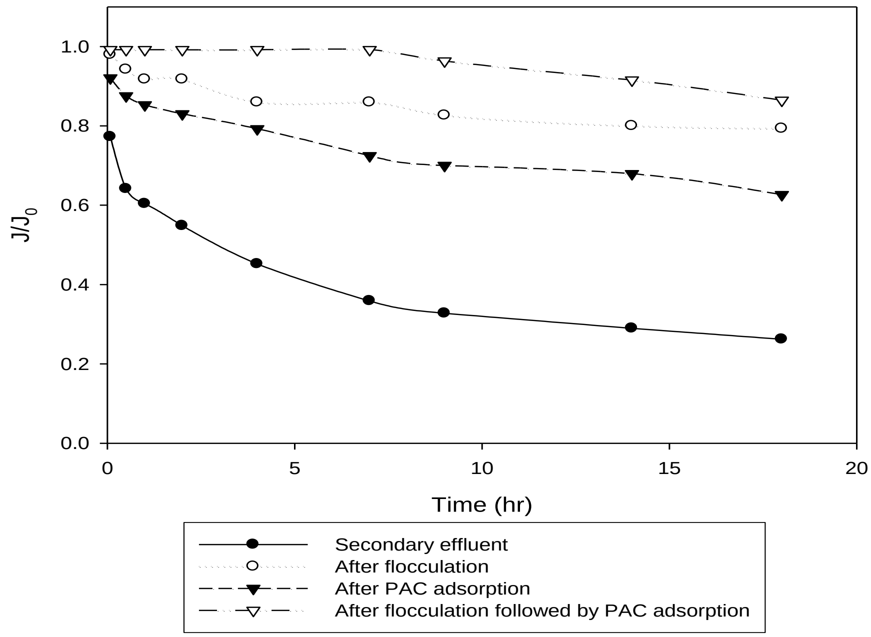

Figure 3 Temporal variation of filtration flux with and without pretreatment (NTR 7410 ultrafiltration membrane, Nitto Denko Corp., Japan) in the biologically treated sewage effluent, operating pressure 300 kPa

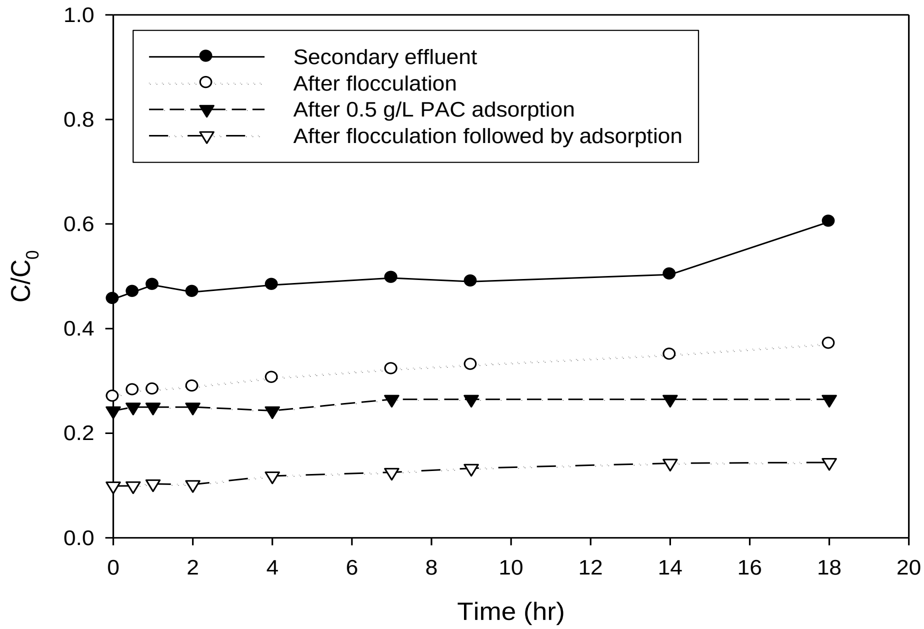

Figure 4 TOC removal by ultrafiltration with and without pretreatment (NTR 7410 ultrafiltration membrane, Nitto Denko Corp., Japan) in the biologically treated sewage effluent, operating pressure 300 kPa