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Transparent exopolymer particle (TEP) fouling of ultrafiltration membrane systems

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ABSTRACT

An abundant form of extracellular polymeric substances (EPS) called transparent exopolymer particles (TEP) was recently regarded by Berman and Holenberg (T. Berman and M. Holenberg, Don't fall foul of biofilm through high TEP levels, Filtrat. Separat., 42 (2005), 30-32) as a major initiator of biofilm formation on membrane surfaces, which can eventually lead to biofouling. The TEP method applied here was an adapted version of the spectrophotometric technique developed by Passow and Alldredge (U. Passow and A.L. Alldredge, A dye-binding assay for the spectrophotometric measurement of transparent exopolymer particles (TEP), Limnol. Oceanogr., 40(7) (1995) 1326-1335). The main modifications were to the calibration procedure. TEP can be visualized by staining with alcian blue, a dye specific for acidic polysaccharides. The amount of TEP can be semi-quantified by measuring the absorbance of the dye that complexed with polysaccharides in water samples. Since TEP is a very complex polysaccharide, a commercially available polysaccharide: Gum Xanthan was used to standardize the amount of alcian blue dye bound to TEP and therefore express concentrations of TEP in terms of Xanthan equivalents per liter (μg X_{eq}/L). For the calibration, TOC measurements were made in order to relate the TOC removed by filtration to the amount of Xanthan (μg) retained in the filter. Biopolymer LC-OCD analyses were also employed for some of the samples in order to support the TEP results. Using the modified TEP method, the presence of TEP was assessed in the feed water and at various points along the treatment lines of two integrated membrane systems (IMSs) treating surface water and secondary wastewater effluent. Results showed that significant amounts of TEP were present in surface water (~990 μg GX/L) and secondary wastewater effluent (~270 μg GX/L). TEP removal efficiencies of 100% were measured for ultrafiltration (UF). TEP (>0.4 μm) removal efficiencies of *ca.* 70% were measured with in-line coagulation employing a *high* coagulant dose (10 mg Al^{3+}/L) in surface water. Significantly lower TEP removal efficiencies (*ca.* 27%) were observed with in-line coagulation employing a *low* coagulant dose (1.5 mg Al^{3+}/L) in secondary treated effluent. Biopolymer LC-OCD analyses also revealed removal of high molecular weight biopolymers by UF and in-line coagulation in both IMS.

1. Introduction

Fouling and cleaning are serious operational problems in ultrafiltration (UF) and reverse osmosis membrane systems. Fouling of UF/MF membrane systems is usually controlled by (in-line) coagulation [1,2]. In NF/RO systems, conventional pre-treatment, *i.e.* coagulation/sedimentation/filtration or membrane pre-treatment, *i.e.* (in-line) coagulation followed by UF/MF [3–5] are known to effectively reduce

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membrane fouling. In addition, biological activated carbon filtration has been shown to reduce the fouling potential of RO feedwater [6,7]. However, which type of foulant is targeted by each pre-treatment step and how effective each type of pre-treatment is in removing foulants is still not clearly understood.

One of the major causes of membrane fouling in UF/MF systems is the sticky extracellular polymeric substances (EPS), which has a major role in microbial growth and aggregation on the membrane surface [8,9]. An abundant form of EPS called transparent exopolymer particles (TEP), was cited by Berman and Holenberg [10] as the major initiators of biofilm formation in membranes which can eventually lead to biofouling. TEP is known to be abundant in fresh and marine water in the particulate-colloidal range (2–200 μm) [11–16]. TEP can also cause particulate/colloidal fouling of the spacer and/or membrane in RO/NF systems if they are not removed during pre-treatment. TEP are sticky and transparent particles that exhibit characteristics of gels, and consist predominantly of acidic polysaccharides [14]. Although polysaccharide fouling had been reported by Kennedy et al.[17], the role of exopolysaccharide particles like TEP on the fouling of membranes is still not well understood.

Operationally, TEP is defined as transparent particles that form from acid polysaccharides and are stainable by alcian blue [18]. TEP tend to disappear with the addition of glucosidase [19], confirming that they consist predominantly of sugars. Due to its transparent character, TEP escapes detection by microscopy and was largely unnoticed for many years. To better assess its presence, Passow and Alldredge [20] developed a semi-quantitative technique using spectrophotometry to measure TEP. They measured TEP based on particles retained on 0.4 μm polycarbonate filters, which bond with the cationic dye alcian blue. Alcian blue can stain both sulfated and carboxylated polysaccharides [21,22] at a specific pH [23] and concentration [20,24]. Another method to measure TEP developed by Arruda-Fatibello et al. [24], also uses the alcian blue staining technique while introducing centrifugation to separate suspensions of TEP–alcian blue precipitate from the dye solution. Until now, both methods have been applied in the field of marine sciences and not in membrane applications.

The main goal of this research was to measure TEP and for this purpose an existing method [20] was employed and adapted. In addition, pre-treatment performance in integrated membrane systems (IMSs) with respect to TEP removal was assessed.

2. Materials and methods

The methodology adapted in this study was the spectrophotometric technique described by Passow and Alldredge [20], but with some modifications. The principal modification was on how the amount of Gum Xanthan (GX) retained on the filters was determined. The GX was used to standardize the amount of dye bound to TEP. TOC measurements were employed in order to relate the TOC removed by filtration to the amount of GX (μg) retained on the filter.

2.1. Apparatus and materials

Filtrations were carried out in a pump-controlled Sartorius Vacuum Filtration System using Whatman Ø 47 mm polycarbonate filters (0.40 μm pore size) as filter media. Absorbance was measured in a Perkin Elmer UV-Vis Spectrometer Model Lambda 20. TOC were measured in a TOC analyzer O.I. Analytical Model 700.

The staining solution was prepared with alcian blue 8GX (C.I.N. 74240) Standard Fluka (Fluka). Standard stock solution was prepared with GX (G1253) from Sigma. All solutions and reagents were prepared with water from Millipore Ultra-Pure Water System Milli-Q Plus 185.

2.2. Spectrophotometric measurement

Water samples (50–90 mL) were gently filtered through 0.40-μm polycarbonate filter at low and constant vacuum of 150 mm of Hg. The retained particles on the filters were stained with 500 μl of a 0.02% aqueous staining solution of alcian blue 8GX in 0.06% acetic acid (pH 2.5). After staining, the filters were rinsed once with ultra-pure water to remove excess dye. The rinsed filters were then transferred into 25-mL beakers. Six milliliters of 80% H_2SO_4 were added to the filters and they were soaked for 2 h. The beakers were gently swirled 3–5 times during this period. After soaking the filters, the absorbance of the acid solution was measured using a UV spectrometer, equipped with a 1-cm cuvette using ultra-pure water as a reference at 787 nm.

Filter media and sample turbidity may influence the absorbance of the acid solution. To correct the absorbance, two separate filters were tested. One of the filters was stained with alcian blue (filter blank) and the other one was used to filter the sample (sample blank). Both filters were soaked in the acid solution for 2 h and the absorbance was measured thereafter, as previously described. The absorbance of the sample was then corrected by subtracting the absorbance of

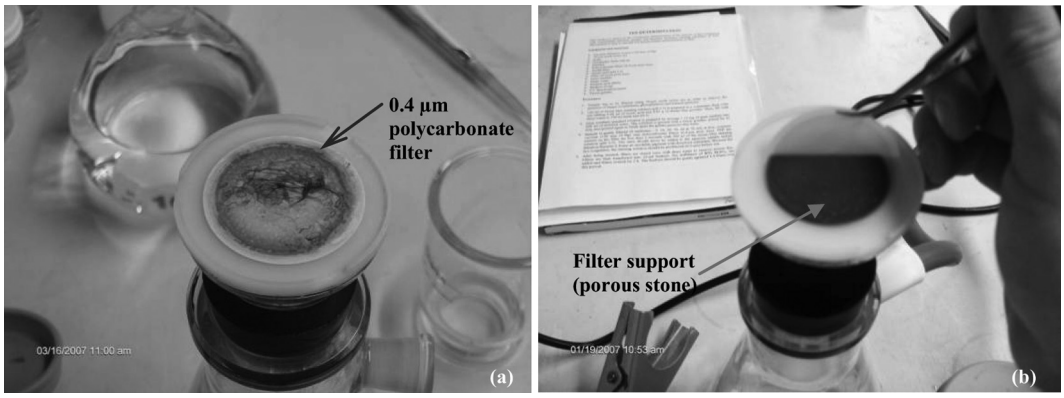

Fig. 1. (a) Gum Xanthan retained on polycarbonate filter and stained with alcian blue solution and (b) filter after staining with alcian blue (blank filter).

the blank filter. The absorbance results were linearly related to the amount of stainable material (TEP) present in the sample.

2.3. Calibration of the staining solution

The alcian blue staining solution was known to show variations (between batches) in terms of purity and solubility, and subsequent measured absorption of samples usually varied in different batches of staining solution [20]. Thus, calibration of the staining solution was necessary. The standard calibration solution was prepared by mixing 15–20 mg of GX into 200 mL of Milli-Q water. The solution was stirred for 30 min with a magnetic stirrer to break apart the gel-like particles (TEP) that formed.

Dilutions of GX were prepared from the standard stock solution. The same procedure as outlined by Passow and Alldredge [20] was employed using these solutions (Fig. 1). However, instead of measuring the amount of GX retained on the 0.4 µm filter, TOC was measured for each dilution of standard solution and its filtrate, after passing through a 0.4 µm filter. From the amount of organic carbon removed by filtration, the amount of GX retained on the filter was calculated by relating the organic carbon removed to its molecular formula $(C_{35}H_{49}O_{29})_n$. This can be computed according to $W_{GX} = (TOC_{unfilt} - TOC_{filt}) \times V_{GX} \times 0.45^{-1}$; where W_{GX} is the weight of GX retained in the filter (µg GX), TOC_{unfilt} is the total organic carbon of GX solution (µgC/L), TOC_{filt} is the total organic carbon of filtered GX solution (µgC/L) and V_{GX} is the volume of filtered GX solution (L). One microgram of GX contains approximately 0.45 µg of carbon. From the results, the calibration factor f_x was computed using the equation: $f_x = \overline{W}_{GX} \times \left(\overline{GX}_{787} - B_{787}\right)^{-1}$; where $\overline{W}_{GX}$ is the average weight of GX retained in the filter, $\overline{GX}_{787}$ is the average absorbance for the different dilutions of GX and B_{787} is the filter blank absorbance. The standard calibration line was then plotted by relating corrected absorbance ($GX_{787} - B_{787}$) against the weight of GX retained, W_{GX} (Fig. 2). Different calibration lines and calibration factors were used for samples stained with different batches of staining solution.

2.4. TEP concentration

The standard calibration line was used to express TEP concentration in terms of GX following the equation: $C_{TEP} = (A_{787} - B_{787} - T_{787}) \times f_x \times (V_f)^{-1}$; where C_{TEP} is TEP concentration in µg GX/L, A_{787} is the absorbance of the sample, B_{787} is the absorbance of filter blank, T_{787} is the absorbance of sample blank, f_x is the calibration factor of the staining solution in µg GX and V_f is the filtered volume of the sample in litres.

3. Results and discussion

3.1. Validation of the TEP method

To validate the methodology used with the modified spectrophotometric method, different sample

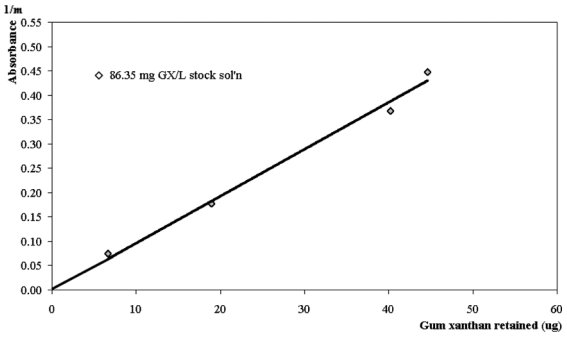

Fig. 2. Gum Xanthan standard calibration line.

volumes (same water sample) of Delft canal were filtered through 0.4 μm polycarbonate filters. Four sample volumes were considered (30, 50, 70 and 90 mL) in order to compare the TEP results. Also, absorption due to turbidity was analyzed. TEP concentrations obtained from sample volumes 50, 70 and 90 mL, were quite similar although for 90 mL, filtration time was longer and filters started to clogged. For sample volume of 30 mL, C_{TEP} was quite low compared to other sample volumes. The absorbance due to turbidity was 0.03 irrespective of the volume, and was considered to be negligible compared to the absorbance due to the sample. Thus, sample volumes of 50–90 mL were used for all TEP measurements and absorbance due to turbidity was neglected in low turbidity water.

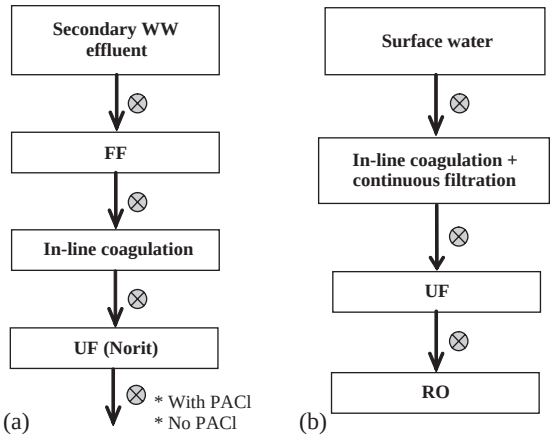

Fig. 3. (a) IMS pilot plant in Veendam treating secondary wastewater effluent and (b) North Water IMS plant treating surface water. *Note:* Cross dots represents sampling points.

3.2. Assessment of TEP removal in two IMSs

Samples were taken from two IMS plants located in Drenthe, The Netherlands namely: IMS pilot plant treating secondary wastewater effluent from the Veendam WWTP and the full-scale IMS plant of North Water treating surface water (Fig. 4). Samples along both treatment lines were analyzed to determine the presence of TEP following the methodology developed in this study.

Results showed that TEP was present in both surface water (~990 μg GX/L) and secondary wastewater effluent (~270 μg GX/L). Surface water showed higher concentration of TEP than the secondary effluent as TEP is known to be abundant in untreated surface water. The presence of TEP in secondary wastewater effluent can be attributed as a result of the biological wastewater treatment. This means that polysaccharides could be produced during this treatment step and consequently TEP were formed, although not in the same rate as in surface waters. Passow [15] explained that even though TEP are exopolymers, not all EPS occur as TEP (>0.4 μm) or can form TEP. TEP formation depends on the chemical composition of TEP precursors (which are in fact colloidal TEP particles ranging in size from 0.4 μm down to 0.001 μm), the species releasing them and growth conditions.

Assessing the removal of TEP along the treatment lines showed effective removal by in-line coagulation and very good removal by UF. For the treatment line treating surface water employing in-line coagulation and continuous filtration, the removal of TEP was 70% while the remaining fraction of TEP was totally removed by UF. For the treatment line treating secondary effluent, the fuzzy filter (FF) removed 19% of TEP, in-line coagulation removed 27% of TEP and UF removed all the remaining TEP. In general, both treatment lines showed good removal of TEP, although removal by in-line coagulation varied significantly. The variation can be attributed to the difference in coagulant dose which was 1.5 mg Al^{3+}/L for the pilot plant (treating secondary effluent – line (a) in Fig. 3) and 10 mg Al^{3+}/L for the full-scale IMS plant (treating surface water – line (b) in Fig. 3). Thus, further research on the optimal coagulant dose, pH, and coagulation conditions is required if optimal TEP removal with low coagulant doses.

To get a better picture of how effective in-line coagulation was in reducing reversible and irreversible fouling, operational data of UF in the Veendam IMS pilot plant (Fig. 4, Tables 1 and 2) was analyzed. The operational data illustrated the variation in the UF membrane resistance over time. It was observed that when in-line coagulant was dosed, the membrane resistance during filtration was lower and the frequency of chemical cleaning was reduced compared with the situation when coagulant was not added. For example, employing in-line coagulation pre-treatment (1.5 mg Al^{3+}/L), the membrane resistance due to *reversible fouling* increased by 11% (from 3.6E+12 m^{-1} to 4.0E+12 m^{-1}) over a period of 30 h while without in-line coagulation pre-treatment, it increased by 28% (from 3.6E+12 m^{-1} to 4.6E+12 m^{-1}) in a period of just 4 h.

In terms of irreversible fouling, with in-line coagulation pre-treatment (1.5 mg Al^{3+}/L), membrane resistance with increased by 8% (from 3.3E+12 m^{-1} to 3.55E+12 m^{-1}) over a period of 30 h while without in-line coagulation pre-treatment, it increased by 30% (from 3.3E+12 m^{-1} to 4.3E+12 m^{-1}) in a period of just 4 h. With low dosage of coagulant (1.5 mg Al^{3+}/L), performance of the UF filter improved by about eight

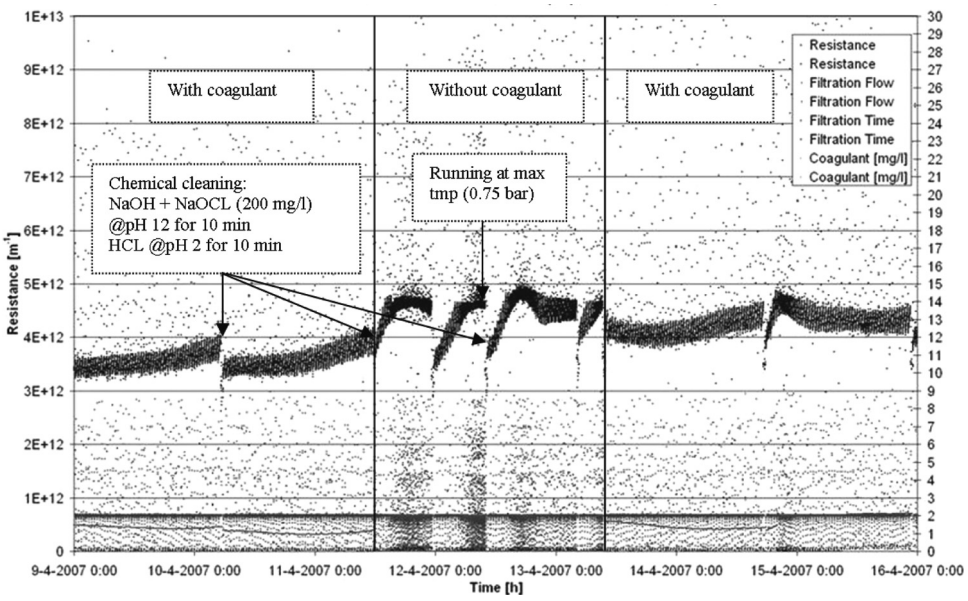

Fig. 4. Operational data of UF in Veendam IMS pilot plant illustrating reversible and irreversible fouling of membranes with and without the addition of coagulant.

times compared to without coagulation, and the effectiveness of backwashing was improved by in-line coagulation (1.5 mg Al^{3+}/L).

Biopolymer LC-OCD analyses (DOC-LABOR, Germany) were employed for samples collected in both treatment lines in order to support the TEP results. The LC-OCD chromatograms of secondary effluent showed two regions with high peaks, one peak for biopolymers and the other one for humic substances (Fig. 5). The longer the elution time of the chromatogram peak, the lower the molecular weight (MW) of the corresponding fraction. Biopolymers were within the higher MW fractions, most of which were more than 710 kDa. Zooming in to the biopolymer fraction (Fig. 5), revealed two peaks with elution times of 85 and 92 min, the first peak of which was only found in secondary effluent samples. The biopolymer peak with elution time below 85 min can be attributed to TEP due to the fact that they were removed along the treatment steps while no significant removal on other biopolymer fractions which is of lower MW.

With respect to the surface water samples, the reason of the absence of TEP-like peak could be due to the way the analysis was carried out. Samples were prefiltered through 0.45 μm filters in the LC-OCD analysis. The MW of TEP in surface water could be larger than the superior limit (about 710 kDa) of the range in which the analysis was developed and for that it could not be found in the results. Looking back at the TEP results, only 4% of TEP measured in surface water was within the 0.40–0.45 μm range while for secondary effluent about 15% of TEP measured was on the same range. This could well indicate that the TEP found in surface water are of higher MW than those found in secondary effluent. TEP are important for many aspects of particle dynamics in aquatic systems which stems from their central role in coagulation and sedimentation of particles [15,18]. The relatively shorter retention time

Table 1
TEP removal in an IMS pilot plant (Veendam) treating secondary waste water effluent (line (a) in Fig. 3)

Sample	Replicates	Filtered vol. (mL)	TEP concentration				% TEP removal
			μg GX		μg GX/L		
Feed water (secondary effluent)	2	50	13.5	±2.1	270	±42	19
Fuzzy filter filtrate	2	50	11.0	±1.1	220	±22	
After in-line coagulation (1.5 mg Al^{3+}/L)	2	50	8.0	±0.8	160	±16	27
UF permeate	2	50	0.0	±0.0	0	±0	100

Table 2
TEP removal in North Water IMS plant treating surface water (line (b) in Fig. 3)

Sample	Replicates	Filtered vol. (mL)	TEP concentration				% TEP removal
			μg GX		μg GX/L		
Feed water (surface water)	2	50	49.5	±6.4	990	±127	70
After in-line coagulation (10 mg Al^{3+}/L) and continuous sand filtration	2	50	15.5	±0.7	310	±14	
UF permeate	2	50	0.0	±0.0	0	±0	100

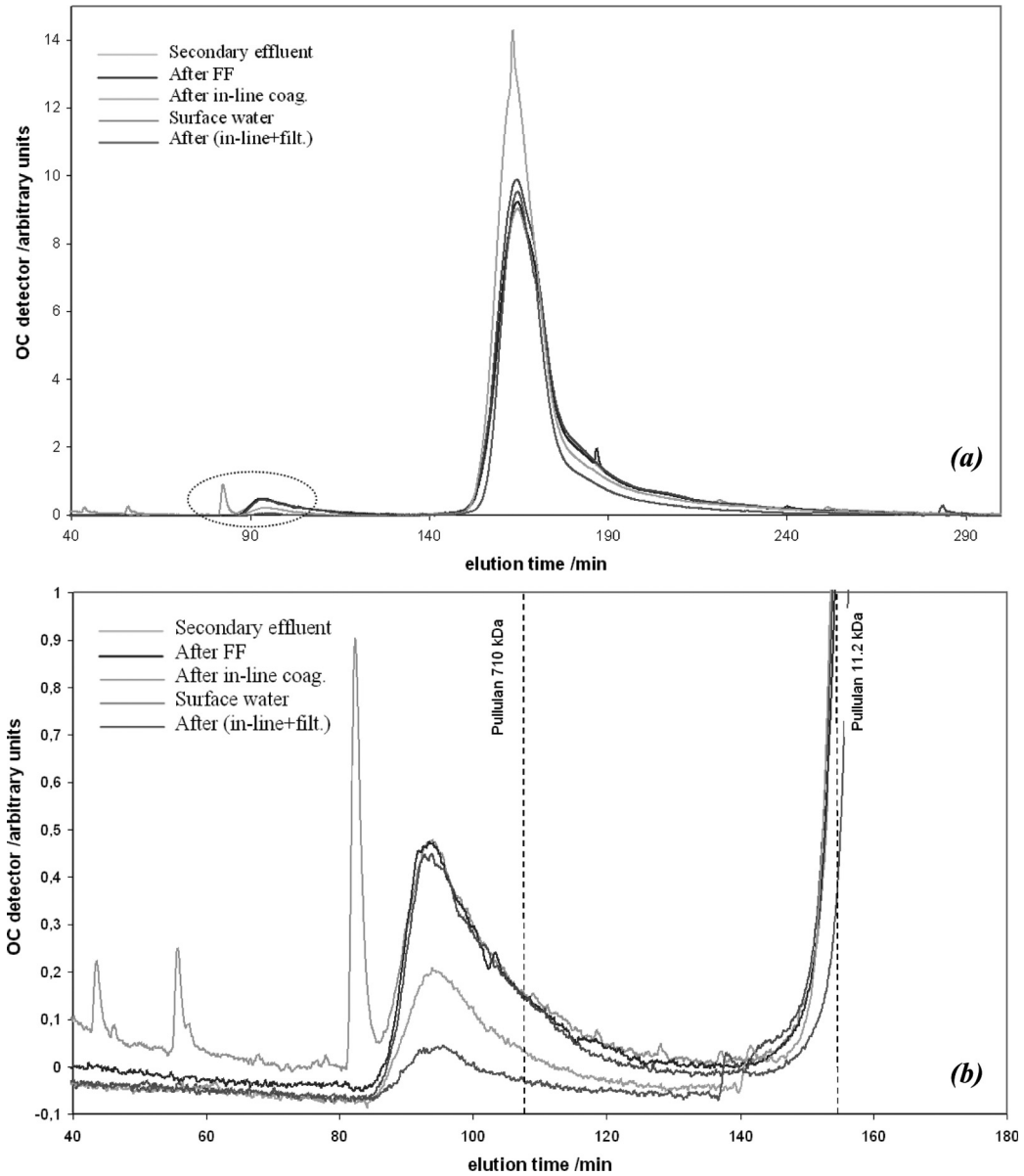

Fig. 5. LC-OCD chromatograms of biopolymers through the treatment lines: (a) showing the biopolymers (left) and humic peaks (right) and (b) a zoom view of the high molecular biopolymers fraction.

(compared to surface water) between the released of the TEP precursors from biological wastewater treatment, where TEP believed to originate in secondary effluent samples, allow less time for TEP to coagulate into larger forms. Thus, TEP in secondary effluent is expected to have lower MW than those in surface water.

4. Conclusions

- A modified spectrophotometric method to measure TEP (size >0.4 μm) was applied in this study to measure TEP in surface water and secondary wastewater effluent. Significant amounts of TEP were found in surface water (~990 μg GX/L) and secondary wastewater effluent (~270 μg GX/L).
- TEP (>0.4 μm) removal efficiencies of *ca.* 70% were measured with in-line coagulation employing a *high* coagulant dose (10 mg Al^{3+}/L) in surface water. Significantly lower TEP removal efficiencies (*ca.* 27%) were observed with in-line coagulation employing a *low* coagulant dose (1.5 mg Al^{3+}/L) in secondary treated effluent. In all cases, 100% removal of TEP (>0.4 μm) was measured after UF.
- Operational data from a UF plant treating secondary treated effluent showed an 11% increase in membrane resistance due to *reversible* fouling in a 30 h period of operation with in-line coagulation pre-treatment (1.5 mg Al^{3+}/L). However, when no coagulant was employed, the membrane resistance increased by 28% in just 4 h. In the same way, the *irreversible* fouling resistance increased by 7% over a 30 h period of operation with in-line coagulation pre-treatment (1.5 mg Al^{3+}/L). However, when no coagulant was employed, the irreversible fouling resistance increased by 30% in just 4 h.
- Using optimal coagulant dose and pH and coagulation conditions (shear rate, flocculation time etc.) is critical in minimizing/eliminating the effect of TEP fouling in UF, and a thorough study of these aspects is required to optimize TEP removal in IMS.
- In this study, TEP was only determined in the particulate-colloidal range by retention onto 0.40 μm polycarbonate filters. Further studies are required to determine if TEP colloidal precursors (which can be as small as 1-3 nm in diameter and hundreds of nanometers long) can cause membrane fouling.

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