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Distribution and transformation of molecular weight of organic matters in membrane bioreactor and conventional activated sludge process

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ABSTRACT

The distribution and transformation of molecular weight (MW) of organic matters in a pilot-scale submerged membrane bioreactor (MBR) and a conventional activated sludge (CAS) process was studied in order to better understand organic pollutant behaviours and removal mechanisms in the two processes. Gel filtration chromatography (GFC) images of the CAS process showed that the influent wastewater had relatively large MW molecules and a narrow MW distribution while the dissolved organic matters (DOM) in the anaerobic, anoxic, oxic basins and the effluent water demonstrated a broad MW distribution. MW distribution in the MBR system illustrated that the organic matters with high MW molecules were degraded into relatively low MW organic substances, whereas DOM in the oxic basin had a little part of high MW molecules produced by microorganisms during the metabolism of substrates. There is a lack of those high MW molecules in the effluent water due to the retention of the macromolecules by the membrane. Test results also showed that in both the CAS process and the MBR the majority of molecules in the influent wastewater with MW between 100 kDa and 500 kDa were mainly transformed into the molecules with MW between 10 kDa and 100 kDa.

1. Introduction

Membrane bioreactor (MBR) process is an emerging and promising technology by using membranes in combination with traditional biological treatment. Membranes in the ultrafiltration or microfiltration range can prevent the loss of biological solids and high molecular weight solutes from a bioreactor [1], thus enabling the independent control of sludge retention time (SRT) and hydraulic retention time (HRT) and retaining a high concentration sludge biomass. This yields advantages such as smaller footprint, less sludge production and better effluent quality, etc. compared with conventional activated sludge (CAS) process.

It has been widely reported that, compared with CAS system, better pollutant removal efficiency could be achieved in MBRs for the treatment of municipal and industrial wastewater [2–4]. To date, a lot of literature has been published regarding to the organic removal performance, sludge characteristics, operational conditions and so on, and illustrated the differences and similarities between MBRs and CAS system [5–8]. Several mechanisms may exist through which MBRs are in favor of enhanced biotransformation and mineralization of organic pollutants. Physical retention by the membranes is one of the positive factors [5]. Besides that, it is also attributed to longer SRTs which are always adopted in MBRs compared to CAS [7,8]. This allows for adaptation of microorganisms in general and of potentially slow growing specialist bacteria in particular, which will establish a more diverse microbial community with broader physiological capabilities in the system [9]. Thirdly, the increased microorganism concentration in MBRs leads to an intensification of biological processes and may improve the interaction between microorganisms and the chances of genetic information exchange [10]. The higher biomass concentration also results in lower food to microorganism (F/M) ratio, which is conducive to more complete mineralization of organic substances in MBRs. Although those intensive efforts mentioned above are very helpful to understand the removal mechanisms of organic substances and to classify the performance differences between MBRs and CAS systems, there is a lack of sufficient information on the molecular weight (MW) distribution and transformation in MBRs and CAS processes for the treatment of wastewater. A detailed characterization of MW distribution and transformation will deepen the understanding of organic removal patterns and mechanisms in these two wastewater treatment processes.

Fractionating wastewater components into different MW fractions gives detailed information about wastewater characteristics and helps in the design of appropriate treatment processes [11,12]. Gel filtration chromatography (GFC) (or called as size exclusion chromatography or gel permeation chromatography) separates macromolecules according to their hydrodynamic volume, which is defined by the Stokes radius. Gel filtration columns consist of

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porous polymer beads designed to have pores of different sizes. When a mobile phase is passed through the column, particles with small hydrodynamic volumes have a longer path length as they equilibrate into the pores of the beads more often than those with large hydrodynamic volumes, which will result in their separation [13]. There are many applications of GFC technology. In group separations, high or low molecular weight components are removed from the sample, for example in desalting or buffer exchange [13,14]. Recently, it has been used for quantitative determination of pollutant concentration in wastewater [15]. The application of GFC technology to the research on MW of organic matters in wastewater and in the wastewater treatment processes could advance our knowledge on the organic pollutant behaviours and removal pathways.

In this study, a pilot-scale anoxic/oxic submerged MBR (A/O-MBR) for the treatment of real municipal wastewater at an existing biological nutrient removal (BNR) wastewater treatment plant (WWTP) was established and operated in order to verify the MW distribution and transformation in the MBR and to compare it with the BNR WWTP. Detailed MW distributions and characterization of the influent wastewater, the dissolved organic matters (DOM) in mixed liquors of treatment units and the effluent were carried out by employing the GFC technology. The results obtained in this study are expected to provide an insight into the differences and similarities between MBR and CAS process based on MW distribution and transformation.

2. Materials and methods

2.1. WWTP and pilot-scale MBR

The process of the Quyang municipal WWTP of shanghai, China (see Fig. 1), is comprised of primary treatment and secondary treatment (activated sludge process, i.e., nitrification, denitrification and phosphorous elimination in A/A/O tanks). The wastewater passed through coarse and fine screens, an aerated grit chamber, primary clarifiers, A/A/O tanks and secondary clarifiers. The secondary effluent was discharged into Shajing Gang River close to the WWTP after filtration in biological aerated filters (BAF) (not shown in Fig. 1). The treatment capacity of the WWTP was about 60,000 m^3/d and the main operational parameters [16] are summarized in Table 1.

The pilot-scale A/O-MBR as shown in Fig. 1, which was located at the WWTP, consisted of an effective volume of 160 L anoxic and 480 L oxic zone. Nine flat sheet membrane modules (SHZZ-MF, Zizheng Environmental Inc., Shanghai, China) were mounted vertically in the oxic zone. The membranes were made of polyvinylidene fluoride (PVDF) membrane with a mean pore size of 0.20 μm. The effective filtration area for each module was 0.7 m^2. Air was monitored by a flow-rate meter and supplied through the air diffuser which was below the membrane modules in order to supply oxygen demanded by the microorganisms and to induce a cross-flow velocity (CFV) along membrane surfaces. After passing through a 0.9-mm pore-sized stainless bar screen, wastewater from the grit chamber outlet in the WWTP was supplied into the anoxic zone, and the mixed liquor of the anoxic zone then flowed into the oxic zone by gravity. The quality of the influent wastewater (grit chamber effluent of the CAS process) of the MBR is listed in Table 2. The influent pump was controlled by a water level sensor to maintain a constant water level in the bioreactor. The constant flux operation mode

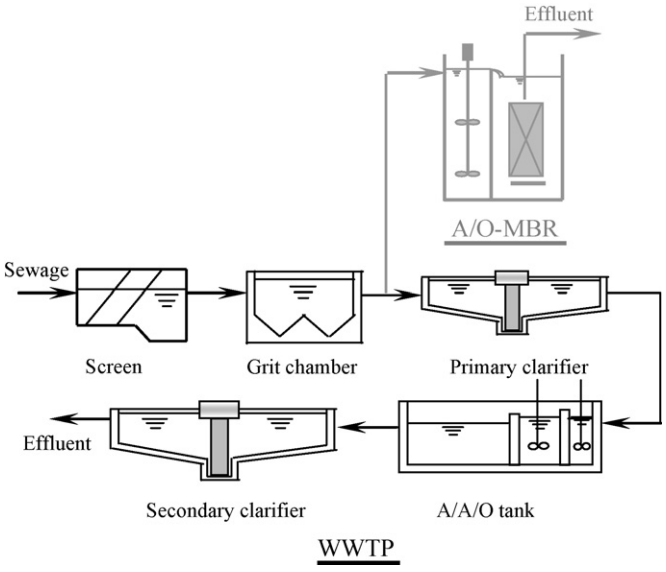

Fig. 1. Flow diagram of the WWTP and the pilot-scale MBR.

Table 2
Influent wastewater characteristics of the MBR.

Items	Concentration
COD (mg/L)	361.0 ± 221.0
TN (mg/L)	45.6 ± 20.6
NH_3-N (mg/L)	27.4 ± 11.6
TP (mg/L)	8.8 ± 3.6
SS (mg/L)	280.0 ± 220.0
pH	6.9 ± 0.6

Values are given as mean concentration ± standard deviation; number of measurements: n = 43.

Table 1
Operational parameters of MBR and the WWTP.

MBR		WWTP [16]	
Treatment capacity (m^3/d)	10	Treatment capacity (m^3/d)	60,000
Membrane flux (L/(m^2 h))	25	H_L of primary clarifier (m^3/(m^2 h))[a]	3.5
Effluent suction cycle (min)[b]	10/2	H_L of secondary clarifier (m^3/(m^2 h))[a]	1.1
Anoxic zone HRT (h)	1.3	Anaerobic zone HRT (h)	1.5
Oxic zone HRT (h)	3.9	Anoxic zone HRT (h)	1.5
SRT (d)	40	Oxic zone HRT (h)	4.7
Oxic zone DO (mg/L)	1–3	SRT (d)	10
Anoxic zone DO (mg/L)	<0.4	MLSS (g/L)	2.5
MLSS (g/L)	15–18	Ns (kg BOD_5/(kg MLSS d))[c]	0.2
Ns (kg BOD_5/(kg MLSS d))[c]	0.04–0.05	R[d]	0.5–1.0
R[d]	3	r[e]	2–3

[a] H_L, hydraulic load.
[b] It means a suction cycle of 10 min suction and 2 min relaxation (non-suction) was performed.
[c] Ns represents sludge organic load.
[d] R, return rate of mixed liquor from oxic zone to anoxic zone.
[e] r, return rate of sludge.

Table 3
Average characteristics of treated water and removal efficiencies of MBR and CAS.

Items	MBR		CAS	
	Concentration (mg/L)	Removal efficiency (%)	Concentration (mg/L)	Removal efficiency (%)
COD	22.0 ± 16.0	93.9 ± 5.1	35.5 ± 5.5	88.6 ± 5.3
TN	15.0 ± 5.6	77.3 ± 8.4	18.1 ± 3.8	72.0 ± 6.3
NH_3-N	1.9 ± 1.1	95.2 ± 2.7	2.5 ± 2.1	93.4 ± 5.0
TP	4.0 ± 1.8	68.0 ± 14.1	1.7 ± 0.4	86.1 ± 8.5
SS	0.0	100	11.4 ± 3.6	94.8 ± 6.2

Values are given as mean concentration ± standard deviation; number of measurements: n = 43 for MBR and n = 9 for CAS.

was employed in the MBR. The membrane-filtered effluent was obtained by suction using a pump connected to the modules. The effluent flow-rate and the TMP were monitored by a water meter and a pressure gauge, respectively. The operating conditions of the MBR are also listed in Table 1. During this study, the temperature in the mixed liquor of the two processes was between 23 and 27 °C.

2.2. Analytical methods

Measurements of chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP), ammonia (NH_3-N), and pH in the influent wastewater and the effluent, mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) in the system were performed according to Chinese NEPA standard methods [17]. The number of measurements (n) is clearly indicated in Tables and Figures. Dissolved oxygen (DO) concentration in the reactor was measured by a dissolved oxygen meter (Model YSI 58, YSI Research Inc., OH, USA). Extracellular polymeric substances (EPS) were extracted from biomass according to the thermal treatment method reported by Chang and Lee [18].

DOM samples, which were obtained by filtering 100 mL of the collected wastewater samples, mixed liquors, and EPS solutions with a filter paper with a mean pore size of 0.45 μm, were fractionated by GFC analyzer. The GFC system consisted of a TSK G4000SW type gel column (TOSOH Corporation, Japan) and a liquid chromatography spectrometer (LC-10ATVP, SHIMADZU, Japan). Polyethylene glycols (PEGs) with MW of 1,215.0 kDa, 124.7 kDa, 11.84 kDa and 0.62 kDa (CAS number: 25322-68-32, Merck Chemicals Inc., Germany) were used as standards for calibration [19]. The elution at different time intervals was collected by an automatic fraction collector and automatically analyzed by using a UV spectroscope and a dissolved organic carbon (DOC) analyzer to obtain a MW distribution curve.

3. Results and discussion

3.1. Pollutant removal performance in MBR and CAS process

Table 3 summarizes the average characteristics of treated water in the MBR and in the CAS process. It can be seen that the removal of COD, NH_3-N, TN and suspended solids (SS) was quite successful in the pilot-scale MBR. About 60% TP removal was also achieved in the MBR during the experiment. Compared with CAS system, MBR showed its advantages in the removal of COD, TN, NH_3-N and SS; however, with regard to TP removal, the CAS system which was employed A/A/O process achieved better removal efficiency than that of the A/O-MBR.

3.2. MW distribution of organic matters in MBR and CAS processes

3.2.1. MW distribution of organic matters in CAS system

In principle, larger MW molecules are excluded earlier than smaller ones, which is due to the fact that large MW organic matters are unable to travel through the gel pores. High correlation between the exclusion time and the MW, as shown in Fig. 2, could be obtained.

The GFC chromatograms of DOM in the influent wastewater (grit chamber effluent), in the mixed liquors of the anaerobic basin, the anoxic basin, the oxic basin and in the effluent water of the CAS system in the WWTP are shown in Fig. 3. The GFC chromatograms of DOM in the primary clarifier effluent (data not shown) were almost the same as those of DOM in the influent wastewater, and thus the transformation of MW in DOMs from primary clarifiers to grit chambers was not discussed in detail here.

The GFC results revealed the similarity of MW distribution of DOM in the samples collected in CAS system, i.e., two main peaks of chromatograms were detectable. It also illustrated their differences on MW distribution of DOM in various treatment units. GFC images of DOM in the anaerobic, anoxic, oxic basins and in the effluent water each had a low intensity peak around 22 min which was absent in GFC profiles of the influent DOM. The specific MW distribution of DOM among them was also varied. It could be observed that the peaks in chromatograms of DOM in the influent wastewater (grit chamber effluent) only appeared between 10 and 15 min while other chromatograms showed much broader distribution. The chromatograms of DOM in the anaerobic basin and the anoxic basin showed part of molecules distributed before 10 min. It demonstrated that high MW molecules, according to the correlation between exclusion time and MW as illustrated in Fig. 2, existed in the anaerobic and anoxic basins while they were absent in the influent wastewater. It could be inferred that the high MW molecules were produced by microorganisms during substrate metabolism and/or released during cell lysis and decay [20]. In the meantime, compared with MW distribution of the influent wastewater, GFC images of DOM in the anaerobic and anoxic basins illustrated that the peaks appeared at longer elution time, which indicated that the majority of molecules in the anaerobic and anoxic basins were of relatively smaller MW than those in the influent wastewater. It could be due to the fact that the influent large MW molecules were metabolized into low MW organics by

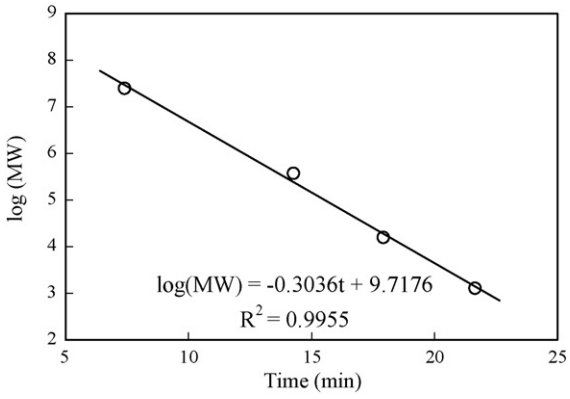

Fig. 2. Relationship between log (MW) and exclusion time.

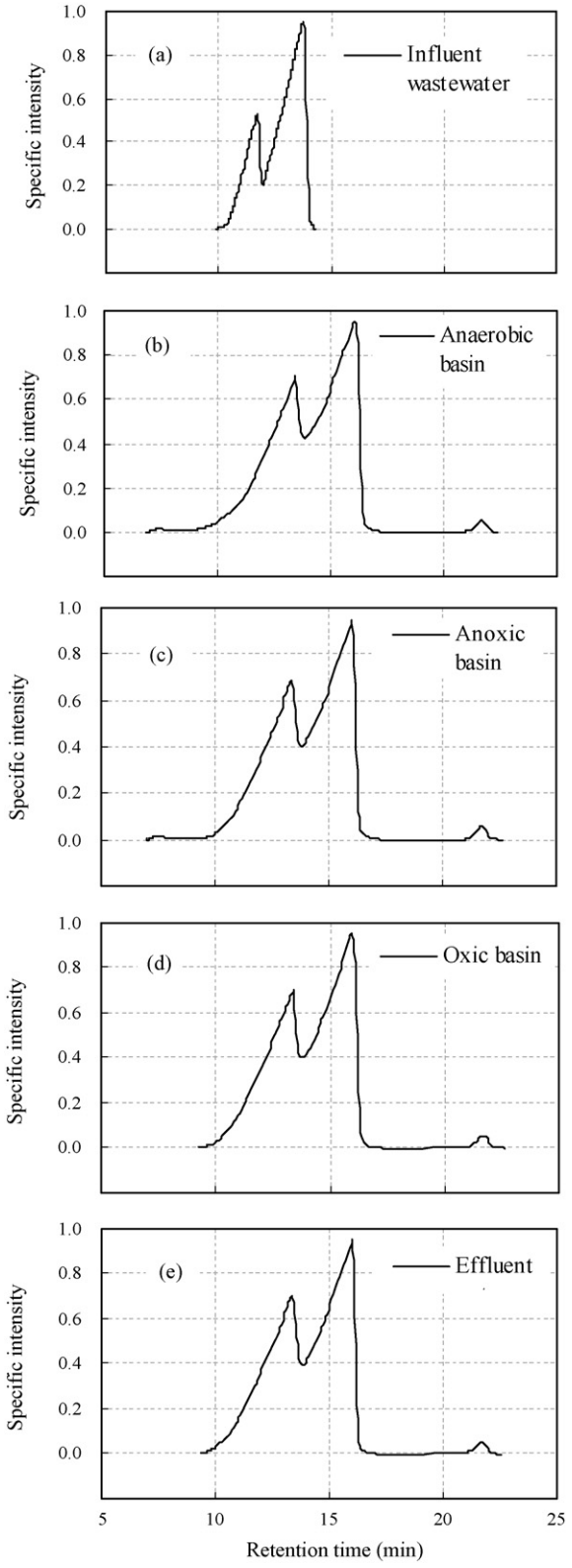

Fig. 3. GFC chromatograms of DOM in CAS system. (a) Influent wastewater (grit chamber effluent); (b) anaerobic basin; (c) anoxic basin; (d) oxic basin; (e) effluent water.

microorganisms [21]. In comparison with MW distribution of DOM in the anaerobic and anoxic basins, MW distribution of DOM in the aerobic basin and the effluent lacked the part of distribution before 10 min, and the mechanisms were worthy of further investigating.

Table 4
MW, M_w and M_n distributions of organic matters in CAS system.

Items	MW (kDa)	M_w (kDa)	M_n (kDa)	M_w/M_n
Influent wastewater	80.9–2,176.5	342.9	209.2	1.64
DOM of anaerobic basin	0.2–21,528.4	251.1	17.6	14.3
DOM of anoxic basin	0.15–202,07.8	235.4	16.8	14.0
DOM of oxic basin	0.16–3,657.7	189.5	16.6	11.4
Effluent water	0.18–3,222.7	195.0	19.1	10.2

In order to better understand MW distributions of the CAS system, number-average molecular weight (M_n), weight-average molecular weight (M_w) and the coefficient of MW distribution in terms of M_w/M_n were used in this study. A low coefficient of M_w/M_n indicated that organic substances had a narrow distribution of MW [22]. Table 4 presents the MW distributions of DOM in the influent wastewater, in the mixed liquor of the anaerobic basin, the anoxic basin, the oxic basin, and in the effluent water. It can be seen that the influent wastewater had a much narrower distribution of MW, of which the M_w/M_n was 1.64. During the anaerobic treatment, the MW distribution featured a broad distribution with M_w/M_n 14.3. It could also be found that the MW distribution of DOM tended to become narrow as the wastewater was treated in sequence from anaerobic to anoxic and to oxic conditions (M_w/M_n from 14.3 to 14.0 to 11.4). This corresponded well to the findings reported by Huang et al. [19].

3.2.2. MW distribution of organic matters in the MBR

Fig. 4 shows the GFC chromatographs of DOM in the MBR system. Compared with DOM in the influent wastewater, DOM in the anoxic basin of the MBR system had relatively low MW distribution with a sharp peak appearing after 15 min (see Fig. 4(b)). It indicated that the influent DOM was partly degraded into small molecules. However, DOM in the oxic basin showed different MW distribution characteristics particularly the distribution before 10 min in Fig. 4(c), which demonstrated that DOM in the oxic basin had part of large MW molecules. It could also be observed from Fig. 4(d) that the high MW molecules (indicated by the elution time before 10 min) existing in DOM of the oxic basin did not present in the effluent DOM. The absence of high MW molecules, in particular over 1,869.7 kDa, in the membrane effluent was attributed to the retention effects of the membrane and to the adsorption of the gel layer formed on membrane surfaces [22]. The major part of low MW molecules existing in DOM of the oxic basin could permeate through the gel layer and membrane pores, thus resulting in the soluble COD in the effluent of the MBR. Chen and Liu [23] also reported that a low MW fraction was present in the effluent of an MBR for the treatment of landfill leachate.

Table 5 summarizes the MW, M_w, M_n of DOM in the MBR system. It could be seen that M_w/M_n of DOM in the anoxic basin was larger than that in the influent wastewater, indicating that DOM in the anoxic basin had a broader distribution than that of the influent DOM after the degradation. From the M_w/M_n coefficient shown in Table 5, it was obvious that DOM in the oxic basin had much broader distribution of MW with M_w/M_n 1,037.5 compared with MW distribution of the effluent DOM of M_w/M_n 3.15. The high MW molecules in DOM of the oxic basin (over 1,869.7 kDa) were absent in the effluent, which is mainly due to the retention of

Table 5
MW, M_w and M_n distributions of organic matters in MBR.

Items	MW (kDa)	M_w (kDa)	M_n (kDa)	M_w/M_n
Influent wastewater	80.9–2,176.5	342.9	209.2	1.64
DOM of anoxic basin	11.5–1,689.6	162.2	53.5	3.03
DOM of oxic-MBR	6.1–382,000.0	4,9036.1	47.3	1,037.5
Effluent water	10.9–1,869.7	164.3	52.2	3.15

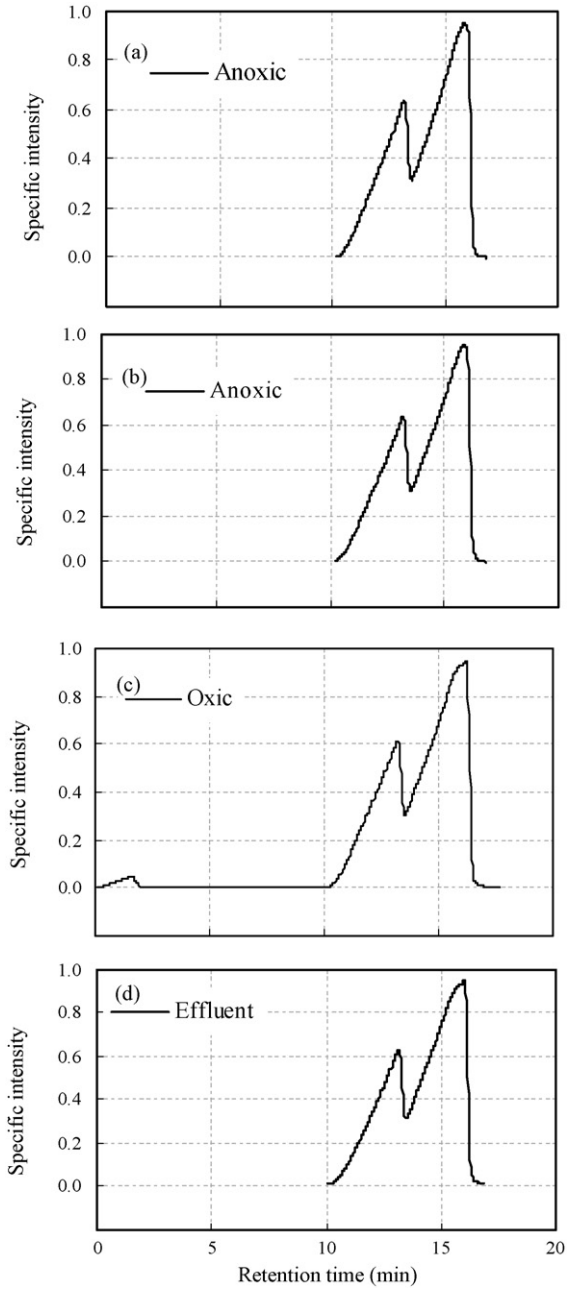

Fig. 4. GFC chromatograms of DOM in MBR. (a) Influent wastewater (grit chamber effluent); (b) anoxic basin; (c) oxic basin; (d) effluent water.

macromolecular substances by the membrane and by the fouling layer on the membrane surfaces [24].

In MBRs, the aeration intensity is generally higher than that of CAS system in order to induce a high cross-flow velocity along membrane surfaces to control membrane fouling. Thus, the mixed liquors of MBRs are subject to higher shearing stress. It has been reported that high shear intensity could result in the breakage of microbial flocs and the release of EPS [25,26]. EPS are usually accepted as macromolecules with a matrix of substances such as polysaccharides, proteins and humic acids, etc., and the release of those substances could result in a broad distribution of MW in the oxic basin.

It could be observed that there were similarities of the GFC profiles, i.e., two main peaks, between the CAS process and the MBR if the overall comparison between them was conducted. The similarity of GFC images was found to be interrelated to the

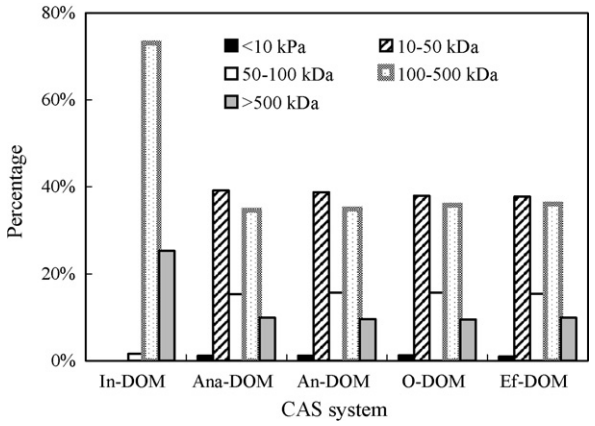

Fig. 5. MW transformation in CAS process.

influent wastewater if we analyzed them in combination with Figs. 3 and 4. Therefore, the similarity of the GFC chromatograms could be assumed as the typical "fingerprint of biological treatment of this kind of wastewater". Quantitative analysis of the fingerprint images could be further conducted according to the spectral intensity. It has to be pointed out that if the influent wastewater properties are different, various specific "fingerprint" of GFC images might be obtained, e.g., Lyko et al. [27] detected three main peaks as the "fingerprint" of DOM in a full-scale municipal MBR.

It is worth noting that operational parameters such as SRT, temperature, etc. could also influence the MW distribution of organic matters in MBR and CAS processes. A higher MW fraction of organic matters in supernatants (carbohydrates and humic acids) was observed at lower SRT in submerged MBRs [24,28]. It was reported that the maximum macromolecular peak intensities were found at low temperature in supernatants of a full-scale MBR for municipal wastewater treatment, while at higher temperature the peak intensities were significantly lower (up to 70% lower peak intensities) [27]. However, the information about the specific effects of SRT and temperature on MW distribution of organic matters in CAS system is still very limited, which should be further investigated.

3.3. MW transformation of CAS and MBR system

The MW distributions of DOM in the influent (In-DOM), DOM in the anaerobic basin (Ana-DOM), DOM in the anoxic basin (An-DOM), DOM in the oxic basin (O-DOM) and DOM in the effluent (Ef-DOM) in the CAS process are illustrated in Fig. 5. It could be found that molecules with MW <10 kDa and with MW in the range of 10–50 kDa were absent in the In-DOM while they did exist in Ana-DOM, An-DOM, O-DOM and Ef-DOM. These findings suggested that the molecules with large MW of 100–500 kDa and >500 kDa of In-DOM were metabolized and degraded by microorganisms into relatively low MW molecules such as 10–50 kDa and <10 kDa. In the meantime, the molecules with MW ranging from 50 kDa to 100 kDa in Ana-DOM, An-DOM, O-DOM and Ef-DOM had a percentage of 15.2–15.6% among the total molecules, whereas in In-DOM the molecules with 50–100 kDa only accounted for 1.6%. It could be inferred that the majority of molecules in In-DOM which had MW of 100–500 kDa and over 500 kDa were mainly transformed into 10–100 kDa molecules in Ana-DOM, An-DOM, O-DOM and Ef-DOM during the treatment process.

In the MBR system, the molecules with MW <10 kDa were absent in In-DOM, An-DOM, Ef-DOM (about 0.1% percentage in O-DOM) (see Fig. 6). Compared to the CAS process, it showed similar transformation of molecules with MW 100–500 kDa and >500 kDa of In-DOM, which were degraded into lower MW molecules

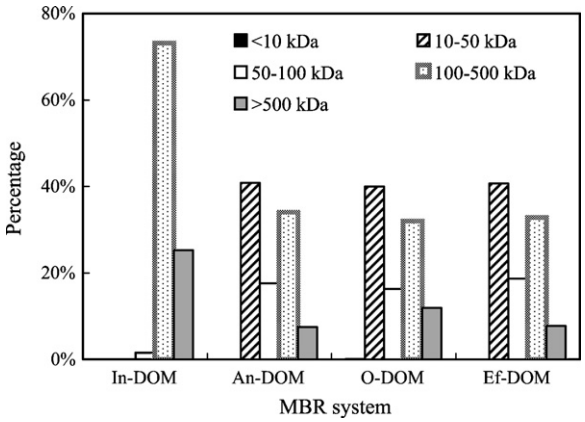

Fig. 6. MW transformation in MBR system.

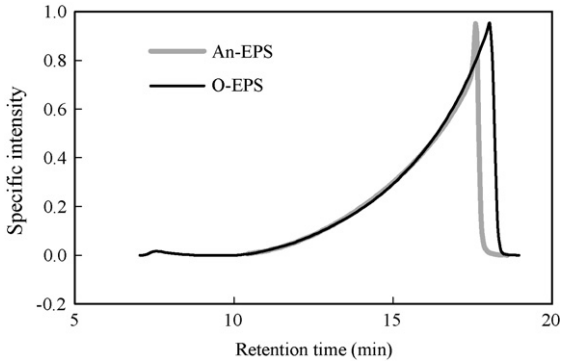

Fig. 8. GFC chromatograms of EPS in MBR.

(10–100 kDa) in the MBR system. It should be noted that the macromolecules with MW >500 kDa increased in O-DOM in comparison to those in An-DOM and then decreased in Ef-DOM, which confirmed the retention of macromolecular substances by the membrane as discussed above.

The similarities and differences of organic matter MW transformation in the CAS process and the MBR system may correspond to the organic removal mechanisms in these two processes. The bacterial metabolism plays a major role in the removal of organic substances in both CAS and MBR processes, which contributes to the similar transformation of MW of organic matters. However, the MBR system could enhance the organic removal efficiency by employing the membrane and longer SRT compared to the CAS process [29]. The retention of macromolecular by the membrane, as indicated by the difference of organic matter MW transformation between these two processes, facilitates the removal of organic matters (microorganisms could degrade them, to some extent, at longer SRT) and improves the effluent water quality of MBRs.

3.4. MW distribution of EPS in CAS and MBR processes

In biological wastewater treatment processes, EPS are excreted by microorganisms at the presence of organic materials in wastewater and/or produced from cell lysis and hydrolysis, which play a crucial role in the structure and functions of microbial aggregates [30,31]. Fig. 7 shows GFC chromatograms of EPS in the anaerobic basin (Ana-EPS), EPS in the anoxic basin (An-EPS) and EPS in the oxic basin (O-EPS) in the CAS process. MW of Ana-EPS and O-EPS both mainly distributed between 10 and 15 min, and MW of An-EPS illustrated a relatively broad distribution (elution time between 10 and 19 min). Peaks of Ana-EPS, An-EPS and O-EPS could be seen at elution time 12.8, 16.7 and 13.5 min, respectively, suggesting the peak MW of 240.4 kDa, 12.1 kDa and 144.9 kDa based on the correlations of MW and elution time as shown in Fig. 2. The macromolecular peaks which appeared in EPS were reported to consist of polysaccharides associated with proteins or colloids [27]. The differences of MW distribution of Ana-EPS, An-EPS and O-EPS might be due to the change of microbial physiology under various environmental conditions and thus the release of EPS with specific characteristics. Hong et al. [32] found that the EPS composition and quantity were varied as aerobic conditions were changed to anoxic in a submerged MBR for synthetic wastewater treatment.

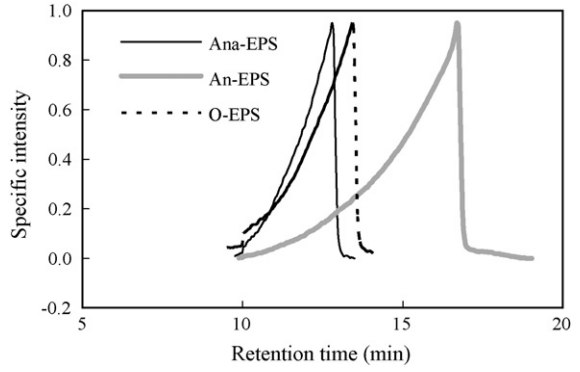

Fig. 7. GFC chromatograms of EPS in CAS process.

The GFC chromatograms of An-EPS and O-EPS in the MBR system are illustrated in Fig. 8. Compared to the CAS system, An-EPS of the MBR showed similar MW distribution with An-EPS in the CAS system; however, O-EPS of the MBR demonstrated a broad distribution of MW and GFC chromatograms distributed between 7 and 19 min. In combination with the GFC image of O-DOM of the MBR (see Fig. 4), a linkage of MW distribution might be found between O-DOM and O-EPS. It could be inferred that the macromolecules in O-DOM, which were detected neither in the influent DOM nor in the anoxic phase, were excreted from the microorganisms under oxic conditions. As discussed above, the macromolecular compounds could be separated by the membrane and thus caused membrane fouling, which was in agreement with the report that the increase of macromolecular compounds significantly influenced the sludge dewaterability and thus membrane fouling in pilot-scale and full-scale MBRs [27,33]. GFC analysis of this study also confirmed the macromolecules of EPS excreted by microorganisms could finally be released into mixed liquor as DOM.

EPS samples extracted from various biomass, in particular for different wastewater treatment, may have different GFC profiles. Nagaoka and Nemoto [34] reported that the EPS solution featured three main peaks at 100 kDa, 500 kDa and 2,000 kDa in an intermittently aerated MBR for synthetic wastewater treatment, whereas in our study only one peak appeared in the GFC images of EPS in both the MBR and CAS systems for real municipal wastewater treatment. Two main GFC peaks of soluble EPS were observed in the study of Lyko et al. [27], i.e., one peak was located at about 7 min and the other at 9–9.7 min in terms of elution time in several municipal MBR plants in Germany.

In our study, similar GFC profiles of EPS were obtained in the MBR and the CAS process. It could be inferred that the similarity of the GFC profiles between the two systems could be due to the fact that the same municipal wastewater was treated, which corresponded to other researchers' reports [28]. In our study, EPS MW of the MBR (2.2–2,912.3 kDa) and the CAS system (2.4–18,968.2 kDa) was comparable to the MW range reported by other researchers [27,34]. It should be pointed out that many parameters such as SRT, temperature, gas sparging, substrate composition, loading rate, etc.

[27,28,35,36] can influence the EPS concentration and composition in the mixed liquors of both MBR and CAS processes, and thus could affect the MW distribution of EPS. Further study on the correlations of operational parameters and EPS properties in terms of MW distribution, release of macromolecules, etc. is needed in order to better understand fouling mechanisms and to control or mitigate membrane fouling caused by EPS.

4. Conclusions

GFC analysis of the CAS process showed that the influent wastewater had relatively large MW molecules and a narrow MW distribution while the DOM in the anaerobic basin, the anoxic basin, the oxic basin and the effluent water demonstrated a broad MW distribution including larger and smaller MW molecules than that of the influent wastewater.

MW distribution of the MBR system illustrated that organic matters with high MW molecules were degraded into low MW organic substances, and DOM in the oxic zone consisted of a little part of much larger MW molecules which were produced by microorganisms during the metabolism of organic matters. It was also observed that there was a lack of these high MW molecules in the effluent water due to the retention of macromolecules by the membrane.

It was also found that in both the CAS system and the MBR the majority of molecules in the influent wastewater with MW 100–500 kDa were mainly transformed into the molecules with MW 10–100 kDa in the treatment process and in the effluent water.

In the CAS system, EPS in the anaerobic and the oxic basin had a relatively narrow distribution while An-EPS showed a broad distribution. The An-EPS of MBR had similar MW distribution with An-EPS in the CAS process while O-EPS in the MBR showed a much broader MW distribution. A linkage of MW distribution could be found between O-DOM and O-EPS in the MBR.

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