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Characteristics of dissolved organic matters in submerged membrane bioreactor with low-concentration Cr(VI)

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ABSTRACT

Hexavalent chromium (Cr(VI)) is a common heavy metal, but is hazardous to the environment and human body. Low concentration of Cr(VI) (0.4 mg/L) is ubiquitous in municipal wastewaters of China. However, little is known about its effects on dissolved organic matter (DOM) in submerged membrane bioreactors (MBRs). The effects of low concentration of Cr(VI) on the characteristics of DOM in submerged MBRs were investigated in this study. Compared with control MBR conditions, results showed that low-concentration Cr(VI) caused an increase in concentrations of dissolved organic carbon, polysaccharides, and proteins. Low-concentration Cr(VI) also increased the concentrations of humic substances and protein-like substances, and inhibited the formation of macromolecules (over 500 kDa) in DOM, further enhancing membrane fouling. The low molecular weight (<500 kDa) DOM led to irreversible membrane pore blocking and serious membrane fouling. Additionally, the shifting of DOM functional groups (shift from 3,200 to 3,700 cm^{-1}, shift from 1,640 to 1,626 cm^{-1}, minor change at 1,383.4 and 671–601.4 cm^{-1}) indicated that amino, carboxyl, and sulfonate functionalities were involved in the connection between Cr(VI) and DOM.

Keywords: Dissolved organic matter; Low-concentration Cr(VI); Wastewater treatment; Membrane bioreactor

1. Introduction

Dissolved organic matter (DOM) is the dissolved, soluble, and non-settleable organic matter that results from substrate metabolism and biomass growth and decay during biological wastewater treatment (the fraction of organics that pass through a 0.45 μm pore size membrane) [1–3]. DOM is mainly present in the liquid phase of activated sludge and is comprised of a variety of chemically complex organic compounds including polysaccharides, proteins, humic acids, etc. [1–3]. In wastewater treatment and sludge reuse, DOM is used to adsorb toxic pollutants, especially heavy metal ions [4,5]. DOM is also the precursor to disinfection by products [6]. According to recent studies [6–8], DOM is considered to be one of the primary culprits in the issue of membrane fouling. Consequently, DOM plays a significant role in the wastewater treatment, especially biological processes with activated sludge.

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Although chromium (Cr) is a common heavy metal, it is hazardous to the environment and the human body [9–11]. The most common form of Cr produced by industrial processes is Cr(VI), which is mobile in the environment and highly toxic [12]. Cr(VI) can cause variations in bacterial behavior and exacerbate the accumulation of high molecular weight (MW) organic matter [13,14]. Cr(VI) severely inhibits catabolic reactions in non-acclimated activated sludge, but primarily inhibits anabolic reaction in acclimated biomass [12]. Municipal wastewater in China contains low-concentration Cr(VI) (0.2–0.5 mg/L) [15], and the average Cr(VI) concentration remains at 0.4 mg/L [7,16]. Therefore, a large amount of Cr(VI) pollution is flowing into municipal wastewater treatment systems in China. Low-concentration Cr(VI) has become one of the major heavy metal problem in the municipal wastewater system. However, the characteristics of DOM in the activated sludge with low-concentration Cr(VI) are still limited.

This study aims to characterize DOM in a submerged membrane bioreactor (MBR) activated sludge system with low-concentration Cr(VI) using parameters including DOM composition, MW, and functional groups. To study the effects of Cr(IV) on DOM characteristics, a lab-scale MBR was set up and operated for over 70 d with synthetic wastewater containing 0.4 mg/L Cr(VI). A second MBR was run under similar conditions, only without Cr(VI) addition, to serve as the control. The relationship between DOM and membrane fouling was also studied.

2. Materials and methods

2.1. MBR operating conditions

A laboratory-scale submerged MBR (MBR-Cr(VI)), with an effective volume of 3.0 L (20 cm × 10 cm × 25 cm of length × width × height), was fed with synthetic wastewater containing low-concentration Cr(VI). The reactor was seeded with 3.0 g/L mixed liquid suspended solid (MLSS) aerobic activated sludge from the aerobic tank of the anoxic/aerobic process in a municipal wastewater plant (Quyang Wastewater Treatment Plant, Shanghai, China). Properties of the seeded activated sludge are shown in Table 1. MBR-Cr(VI) was equipped with a hollow fiber membrane module with an effective filtration area of 100 cm^2 and a nominal pore size of 0.4 μm (Li-tree Company, Suzhou, China). Filtration occurred in an intermittent suction cycle of 10 min on and 2 min off. The hydraulic retention time was 8 h. The sludge retention time, MLSS, and mixed liquor volatile suspended solids (VSS) were 30 d, 3.4 ± 0.6 g/L, and 2.5 ± 0.3 g/L, respectively. Air (0.6 m^3/h) was supplied continuously under the membrane modules. An identical, parallel reactor (MBR-Blank) was operated at same conditions without Cr(VI) addition. The sludge retention time, MLSS, and VSS were 30 d, 3.6 ± 0.1 g/L, and 2.8 ± 0.5 g/L, respectively, for MBR-Blank. The two reactors were operated continuously for over 70 d.

Table 1
DOM properties of the seeded activated sludge

Properties	Seeded activated sludge
DOC (mg/g VSS)	2.0 ± 0.2
$UV_{254\ nm}$ (cm^{-1})	0.1 ± 0.0
SUVA (L/(mg m))	1.0 ± 0.1
Polysaccharide (mg/g VSS)	1.7 ± 0.3
Protein (mg/g VSS)	9.1 ± 0.4

The synthetic wastewater, as defined in previous literature [7,17], was prepared every 2 or 3 d. Considering the average Cr(VI) concentration in municipal wastewater [18], the influent concentration of Cr(VI) was maintained at 0.4 mg/L for MBR-Cr(VI) using a stock solution (100 mg/L) K_2CrO_4 as the Cr(VI) source.

2.2. Analysis of DOM characteristics

All DOM samples were filtered through a 0.45 μm filter (SCAA-101, ANPEL, China) from the supernatant of activated sludge in MBRs [19,20]. Several analytical parameters, including dissolved organic carbon (DOC), UV absorbance at 254 nm ($UV_{254\ nm}$), specific UV absorbance (SUVA = $UV_{254\ nm}$/DOC), major functional groups, MW, were measured three times every 7 d to characterize DOM. A total organic carbon (TOC) analyzer (TOC-V_{VPN}, Shimadzu, Japan) was used to determine the DOC concentration. To measure humic substances and aromatic compound content in the DOC, $UV_{254\ nm}$ and SUVA, respectively, were measured via UV–vis spectrophotometer (4802 UV/VIS, UNICO, USA). The carbohydrate and protein contents of the DOM were analyzed by the phenol–sulfuric acid method and Bradford method, respectively [21,22]. After 24 h freeze-drying pretreatment, the major functional groups of organic matters in DOM were also measured three times per seven days by Fourier transform infrared (FTIR) spectroscopy (Nicolet 5700, Thermo Electron Corporation, USA). MW distribution of DOM was analyzed by a gel filtration chromatography analyzer (LC-10ADVP, Shimadzu, Japan). Three-dimensional excitation–emission matrix (EEM) fluorescence spectroscopy of DOM was determined by a luminescence spectrometry (F-4500FL spectrophotometer, Hitachi, Japan) as previously described [23].

2.3. Analysis of other parameters

Cr(VI), chemical oxygen demand (COD), ammonia, total nitrogen (TN), VSS, and MLSS were analyzed according to the standard methods [24].

3. Results and discussion

3.1. Operation performance of MBR

The average characteristics of the influent and the effluent for MBR-Cr(VI) and MBR-Blank are summarized in Table 2. The COD removal efficiencies of both the two MBRs are approximately 90%. Both MBRs achieved excellent NH_4^+-N removal efficiencies, and the NH_4^+-N concentrations of the effluents of both MBRs are maintained below 1.00 mg/L. Additionally, COD and NH_4^+-N removal efficiencies in both MBRs were stable. Based on the above results, low-concentration Cr(VI) has no obvious influence on the removal of COD and NH_4^+-N in MBR. Because the MBRs are strictly aerobic in this study, TN removal is mainly due to bacterial growth. The decrease in TN removal in MBR-Cr(VI) suggests that low-concentration Cr(VI) inhibits bacterial growth. The 60% Cr(VI) removal efficiency of MBR-Cr(VI) indicates that an MBR cannot completely remove Cr(VI) in wastewater at the average 0.4 mg/L Cr(VI) concentration.

3.2. Constituents of DOM

DOM, a complex consisting of soluble organic compounds, is characterized by the concentrations of various constituents (Table 3) including DOC, humic substances ($UV_{254\ nm}$), aromatic compounds (SUVA), etc. MBR-Cr(VI) has a higher DOC concentration, $UV_{254\ nm}$ value, and SUVA value than MBR-Blank. MBR-Cr(VI) exhibited higher polysaccharide and protein contents in the DOM, indicating that more polymers and proteins are released from the cell, likely as a result of cell lysis caused by the toxicity of low-concentration Cr(VI) [25]. The higher $UV_{254\ nm}$ value of DOM in MBR-Cr(VI) suggests that more humic substances are present in DOM when exposed to Cr(VI). Gu and Chen [26] and Vaiopoulou and Gikas [12] reported that humic substances worked as an effective strategy to improve the biological transformation and degradation of toxins. In the same way, humic substances may be attributing to Cr(VI) removal, leading to higher humic substance content in the DOM of MBR-Cr(VI). Additionally, Gu and Chen [26] reported that the pure culture for removing Cr(VI) was enhanced with addition of humic substances, especially the relative aromatic compounds. Higher SUVA values in the DOM of MBR-Cr(VI) indicate that aromatic compounds may be contributing to the removal and rapid immobilization of Cr(VI), but also that mixed bacteria secreted aromatic compounds to resist and reduce Cr(VI).

Table 3
DOM properties in two MBRs[a]

Properties	MBR-Cr(VI)	MBR-Blank
DOC (mg/g VSS)	4.6 ± 0.7	1.9 ± 0.3
UV_{254nm} (cm^{-1})	0.2 ± 0.0	0.1 ± 0.0
SUVA (L/(mg m))	1.8 ± 0.2	1.2 ± 0.2
Polysaccharide (mg/g VSS)	4.3 ± 0.1	1.8 ± 0.1
Protein (mg/g VSS)	17.3 ± 0.1	8.4 ± 0.4

[a] All the values represent mean ± SD ($n = 20$, the DOM properties in two MBRs were analyzed every 7 d in over 70 d operation. Every sample was measured twice).

3.3. Fluorescence characteristics of DOM

The three-dimensional EEM fluorescence spectra of DOM in the two MBRs (Fig. 1) show three main peaks. The first main peak is observed at the

Table 2
Average characteristics of the influent and the effluent water for the two MBRs (mg/L)

Items	MBR-Cr(VI)			MBR-Blank		
	Influent	Effluent	Removal (%)	Influent	Effluent	Removal (%)
COD	291.4 ± 41.1	24.6 ± 12.8	92 ± 5	285.0 ± 52.3	29.3 ± 10.4	90 ± 5
NH_4^+-N	13.0 ± 2.5	0.9 ± 0.6	93 ± 4	13.6 ± 3.0	0.7 ± 0.5	95 ± 3
NO_3^--N	1.5 ± 0.9	14.7 ± 6.1	–	1.2 ± 0.7	13.7 ± 2.3	–
TN	18.2 ± 3.4	16.7 ± 2.7	8.4 ± 5.6	17.5 ± 2.6	14.2 ± 3.6	19 ± 10
Cr(VI)	0.4 ± 0.1	0.1 ± 0.1	61 ± 18			

Note: All the values represent mean ± SD ($n = 70$, the data were measured every day during the experiment).

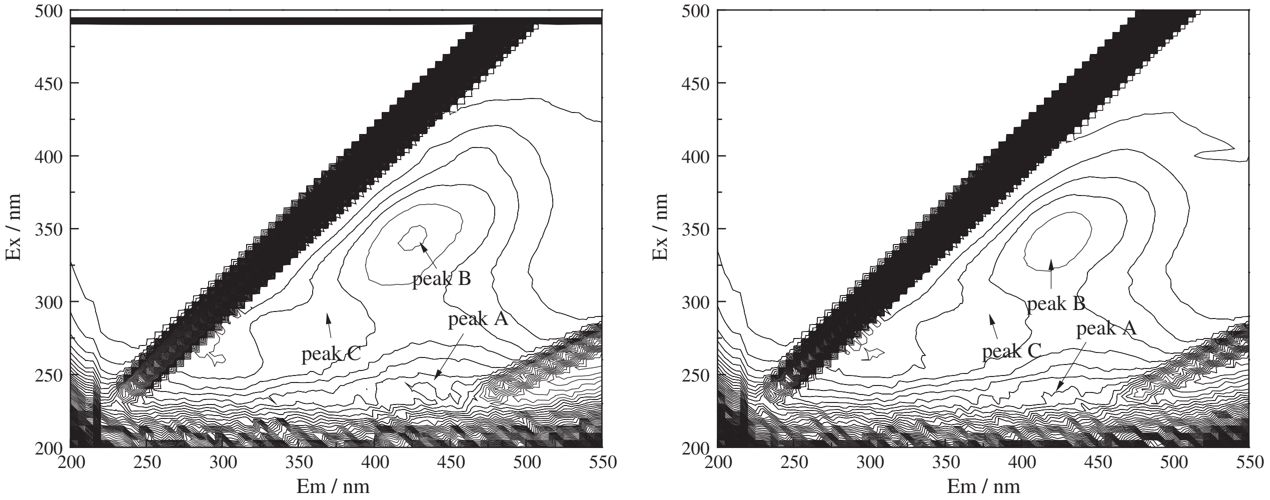

Fig. 1. EEM fluorescence spectra of DOM in (a) the MBR-Cr(VI) and (b) the MBR-Blank.

excitation/emission wavelengths (Ex/Em) of 245/420 nm (Peak A), which has been previously reported as a fulvic acid-like peak [27]. The second main peak, at the Ex/Em of 340/420 nm (Peak B), is related to visible humic acid-like substances [28]. The third main peak, around the Ex/Em of 280/355 nm (Peak C), is associated with the protein-like substances [27,29]. Additionally, several other peaks with relatively high fluorescence intensity are observed in Fig. 1. Those peaks mainly appear in the region of excitation wavelengths 200–225 nm, which are related to aromatic protein substances [28].

The fluorescence parameters of the spectra, including peak location, fluorescence intensity, and the corresponding peak substances (Table 4), were used for quantitative analyses. In the MBR-Cr(VI), higher intensity of the three main peaks was observed than in MBR-Blank, indicating that the presence of low-concentration Cr(VI) increases the concentrations of the fulvic acid-like, protein-like, and visible humic acid-like substances in DOM. This phenomenon is consistent with the results in Section 3.2. Low-concentration Cr(VI) did not, however, change the percent composition of the components in DOM measured via fluorescence. It has been shown that high-concentration Cr(VI) causes crucial variations on both the component percentage and the structure of organic matter, probably due to the adsorption of Cr(VI) onto organic matter and the subsequent precipitation of the matter [30]. Conversely, low-concentration Cr(VI) only increases the component concentration of DOM, without changing the distribution of components.

3.4. MW distribution of DOM

The MW distributions of DOM in the two MBRs are summarized in Fig. 2. The fraction of molecules within the ranges of <50 and 100–500 kDa in MBR-Cr(VI) exceeds those in MBR-Blank. The compounds over 500 kDa compose a major portion (over 50%) in DOM of MBR-Blank. In MBR-Cr(VI), the majority of substrates in DOM are in the range of <500 kDa. This result suggests that the presence of low-concentration Cr(VI) decreases the MW of DOM molecules.

Table 4
Fluorescence spectral parameters of DOM in the two MBRs[a]

Peaks	Ex/Em	MBR-Cr(VI) FI[b]	MBR-Blank FI	Existing substances
Peak A	245/420	39.9 ± 1.3	16.1 ± 2.5	Fulvic acid-like
Peak B	340/420	30.6 ± 0.8	17.7 ± 1.1	Protein-like
Peak C	280/355	19.5 ± 1.5	9.2 ± 0.8	Visible humic acid-like

[a] All the values represent mean ± SD ($n = 15$, EEM analysis was thrice carried out on day 25, 35, 48, 60, and 70 during over 70 d operation. Every sample was measured thrice).

[b] FI: fluorescence intensity.

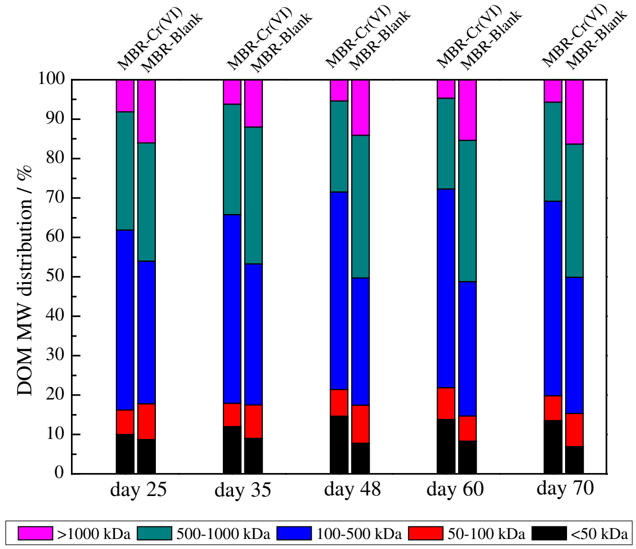

Fig. 2. MW distributions of DOM in the two MBRs.

In order to better understand the effects of low-concentration Cr(VI) on the MW distributions of DOM, the evaluations of number-average molecular weight (M_n), weight-average molecular weight (M_w), and the coefficient of M_w distribution (M_w/M_n), according to Fig. 2, are employed in this study. M_w, M_n, and M_w/M_n ratio of DOM are 107.58 kDa, 11.06 kDa, and 9.72, respectively, in MBR-Cr(VI). The M_w, M_n, and M_w/M_n ratio of DOM are 361.21 kDa, 40.15 kDa, and 8.99, respectively, in the MBR-Blank. DOM of MBR-Blank has a much broader MW distribution than that of MBR-Cr(VI). M_w of DOM changes from 361.21 to 107.58 kDa due to low-concentration Cr (VI). This result, along with Fig. 2, indicates that low-concentration Cr(VI) inhibits the formation of macromolecular (over 500 kDa) DOM. Previous studies indicated that organic matter formed macromolecules when exposed to high-concentration (>10 mg/L) Cr(VI) as a result of microbial aggregation and heavy metal binding [30,31]. The low MW DOM induced by low-concentration Cr(VI) leads to irreversible membrane pore blocking, which has been reported in previous work [7].

3.5. Major functional groups of DOM analysis

The FTIR spectra of DOM in the two MBRs are illustrated in Fig. 3. The broad region around 1,626.4 cm^{-1} is assigned to stretching vibration of C=O and C=N amide I. The peak at 1,540.5 cm^{-1} corresponds with N–H deformation and C=N stretching amide II. These two peaks indicate the observed material is a protein-like substrate [7,27]. The transmittance peaks at 3,413.5 and 1,145.5 cm^{-1} correspond to the stretching of O–H bonds and C–O stretching, respectively. The peak at 1,740 cm^{-1} represents the asymmetrical stretching vibration of COO$^-$ [27]. The peak at 1,383.4 cm^{-1} is typical for phenolic OH$^-$, COO$^-$, and CH$_3$COO$^-$, and the peak in the vicinity of 1,454.2 cm^{-1} is indicative of the C–H bonds in the alkanes class [7].

In Fig. 3, intensity variations and position shifts of the peaks for MBR-Cr(VI) are observed. From the FTIR spectrum of DOM in MBR-Cr(VI), a relative increase in responses was observed between 3,200 and 3,700 cm^{-1}, predicting the increase in free hydroxyl groups in the DOM. The shifting of peak at 1,640–1,626.4 cm^{-1} indicates the involvement of N–H of amines and C–O of amides in DOM of MBR-Cr(VI). The minor change of peaks at the region 1,383.4 and 671–601.4 cm^{-1} suggests the involvement of sulfonate group and –C–C– group, respectively. Therefore, low-concentration Cr(VI) has a crucial influence on functional groups of DOM, especially amino, carboxyl, and sulfonate groups, which is consistent with the former study [32]. Li et al. [33] reported that amino groups played an important role in Cr(VI) removal due to the physical interactions between the positively charged amino groups ($-NH_3^+$) and negatively charged Cr(VI) ($Cr_2O_7^{2-}$). Cr(VI) removal is also related to ion exchange, physical adsorption, surface precipitation, complexation with functional groups, and chemical reactions with surface sites [34].

3.6. Correlation between DOM and membrane fouling

As our previous work [7] shows, low-concentration Cr(VI) causes a transmembrane pressure jump and leads to membrane fouling (Fig. 4), especially irreversible membrane pore blocking. This study further demonstrates the correlation between DOM and serious membrane fouling under low-concentration Cr(VI) exposure. Sections 3.2 and 3.3 show that humic substances and protein-like substances, as compared to polysaccharides, exhibit an increase in concentration with the 0.4 mg/L Cr(VI) addition. This substantial increase in concentration suggests that humic substances and protein-like substances play a more important role in membrane fouling when low-concentration Cr(VI) is present. Previous literature [35–37] also considers the effects of humic substances and protein-like substances in DOM aggravate membrane fouling. Wang et al. [38] and Hong and Elimelech [39] reported that substances with amino and carboxyl

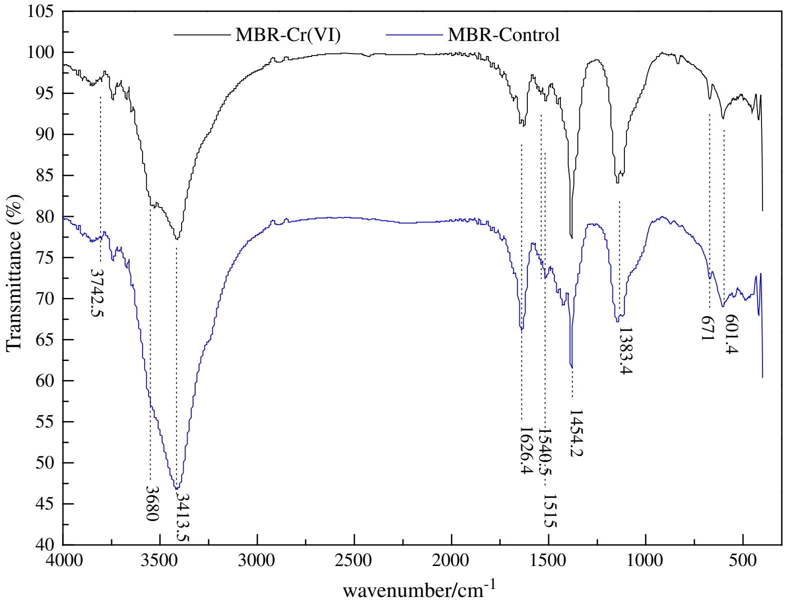

Fig. 3. FTIR spectra of DOM in the two MBRs.

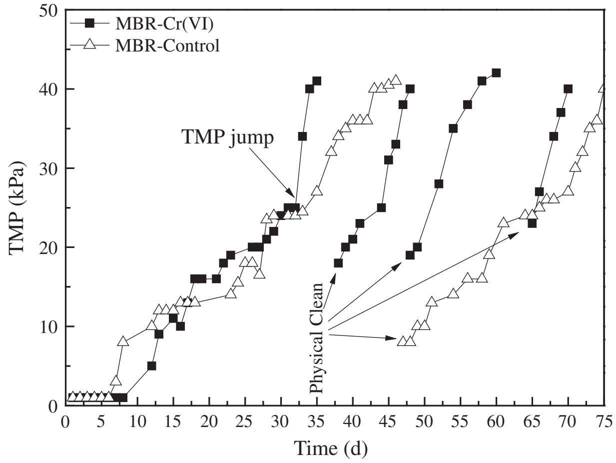

Fig. 4. Variation of transmembrane pressure (TMP) in MBR-Cr(VI) and MBR-Blank [7]

groups could also cause membrane fouling. Therefore, variation functionalities of amino and carboxyl groups caused by low-concentration Cr(VI) (Section 3.6) are probably involved in membrane fouling. Additionally, the low MW DOM (Section 3.5) in MBR-Cr(VI) enhanced the membrane pore blocking, leading to serious membrane fouling. Consequently, changes in DOM characteristics, due to the amendment of low-concentration Cr(VI), aggravate membrane fouling.

4. Conclusions

Effects of low-concentration Cr(VI) (0.4 mg/L) on the characteristics of DOM in submerged MBR activated sludge systems were investigated in this study. Low-concentration Cr(VI) led to higher concentrations of dissolved organic carbon, polysaccharides, and proteins in DOM. The increase in concentrations of humic substances and protein-like substances and the inhibition of macromolecule (over 500 kDa) formation enhanced membrane fouling. The low MW (<500 kDa) DOM led to the irreversible membrane pore blocking, which also resulted in serious membrane fouling. The observed shifts in DOM functional groups indicated that amino, carboxyl, and sulfonate functionalities were involved in the connection between Cr(VI) and DOM.

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