Effects of low-concentration Cr(VI) on the performance and the membrane fouling of a submerged membrane bioreactor in municipal wastewater treatment

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Abstract

The effects of low-concentration Cr(VI) (0.4 mg/L) on the performance of a submerged membrane bioreactor (SMBR) in municipal wastewater treatment, as well as membrane fouling were investigated. Compared with the SMBR for control municipal wastewater, the SMBR for Cr(VI)-containing municipal wastewater had higher soluble microbial products (SMP) concentration with lower molecular weights, and smaller sludge particle sizes. Furthermore, low-concentration Cr(VI) induced membrane fouling, especially the irreversible membrane pore blocking, which markedly shortened the service life of membrane.

Keywords: Submerged membrane bioreactor; Hexavalent chromium; Municipal wastewater; Membrane fouling; Membrane pore blocking

Nomenclature

SMBR	submerged membrane bioreactor
SMP	soluble microbial products
EPS	extracellular polymeric substances
TMP	trans-membrane pressure (kPa)
HRT	hydraulic retention time: HRT is a measure of the average length of time that a soluble compound remains in an activated-sludge process bioreactor.
SRT	solids retention time: SRT is the average time the activated-sludge solids are in the system. It is an important design and operation parameter for the activated-sludge process.
MLSS	mixed liquor suspended solids (mg/L): MLSS is the concentration of suspended solids in activated sludge process. It is an important part of the activated sludge process to ensure that there is a sufficient quantity of active biomass available to consume the applied quantity of organic pollutant at any time.
MW	molecular weight
R	total membrane resistance
R_m	intrinsic membrane resistance
R_p	pore blocking resistance
R_c	fouling layer resistance

Introduction

Hexavalent chromium (Cr(VI)) is well known to impose adverse influence on the biological performance of the conventional activated sludge systems at different Cr(VI) concentrations, such as treatment efficiency and microbial composition (Stasinakis et al. 2003; Stasinakis et al. 2003; Zhao et al. 2009; Vaiopoulou et al. 2012). In an activated sludge system, activated microorganisms are the bacteria and protozoa (mainly bacteria) used for the biodegradation of pollutants in biological process. The activated microorganisms and their biomass combined to form balls in the bioreactor, which are usually called sludge flocs. Cr(VI) can affect the particle size distribution of sludge flocs, although some conflicting results have been reported (Stasinakis et al. 2003). Madoni et al. and Stasinakis et al. found that high-concentration of Cr(VI) (5-400 mg/L) could induce acute reduction of oxygen uptake rate and decrease the maximum growth rate of activated sludge bacteria (Madoni et al. 1999; Stasinakis et al. 2003). Although the presence of Cr(VI) in the range of 1-20 mg/L only causes a small loss of organic substrate removal (Samaras et al. 2009), a significant inhibition of ammonia nitrogen removal can be observed at 0.5 mg/L Cr(VI) because autotrophic nitrifiers are more sensitive to Cr(VI) than heterotrophic microorganisms (Stasinakis et al. 2003).

A membrane bioreactor is the combination of a membrane process, such as microfiltration, with an activated sludge bioreactor. Compared with conventional activated sludge processes, a membrane bioreactor has many advantages, such as a smaller footprint, higher volumetric load, lower sludge production and better effluent quality. As submerged membrane bioreactor (SMBR) is one of the major type membrane bioreactors, its membrane module is submerged directly in the bioreactor and the filtration takes place in the bioreactor. In SMBR, Cr(VI) has a similar impact on the microbial activities as in the conventional activated sludge systems. Cr(VI) can influence the sludge morphology, which further affects membrane filtration (Zhao et al. 2009; Vaiopoulou and Gikas 2012). Membrane fouling variations at high Cr(VI) concentration have been reported (Zhao et al. 2009; Amiri et al. 2010). High-concentration Cr(VI) can significantly aggravate membrane fouling, as the microorganisms stimulated by Cr(VI) excrete a great amount of soluble microbial products (SMP) and extracellular polymeric substances (EPS) (Malamis et al. 2009; Samaras et al. 2009; Vaiopoulou and Gikas 2012).

Cr(VI) concentrations lower than 1 mg/L has been reported to reduce filamentous microorganisms in the conventional activated sludge system, which results in the appearance of pin-point flocs and free-dispersed bacteria (Stasinakis et al. 2003). Additionally, a poor settling property of the sludge is also observed at low-concentration Cr(VI) (lower than 1 mg/L). According to the investigations, the municipal wastewater in China contains low-concentration Cr(VI) (0.2-0.5 mg/L) (Chen et al. 2003; Cheng 2003), and the yearly average Cr(VI) concentration remains at 0.4 mg/L (Stasinakis et al. 2003; Zhao et al. 2009). Tons of Cr(VI) pollution is diluted with domestic wastewater and flowing into municipal wastewater treatment system in China. Additionally, the maximum permitted Cr(VI) concentration of industrial effluent in China is 0.5 mg/L (EPA 2002). Cr(VI) has become one of the major heavy metals in the municipal wastewater (Liu et al. 2005). Although the effect of low-concentration Cr(VI) (lower than 1 mg/L) on the pollution removal of SMBR has been reported by Zhao et. al. (2009), the effect of low-concentration Cr(VI) on membrane fouling is less studied. In view of the relationship between membrane fouling and microbial community, low-concentration Cr(VI) may have some special effects on SMBR performance (Xia et al. 2010; Xia et al. 2012). To our best knowledge, the effect of low-concentration Cr(VI) (average value is 0.4 mg/L in municipal wastewater) on the performance and the membrane fouling in SMBR is unclear and needs further study.

This study aimed to investigate the effects of low-concentration Cr(VI) (0.4 mg/L) on the performance of a lab-scale SMBR feeding with Cr(VI)-bearing municipal wastewater (Cr(VI) concentration of 0.4 mg/L). The comparison study was made by using a control SMBR in treating non-Cr(VI) containing municipal wastewater. The performances of the SMBRs were evaluated in terms of the trans-membrane pressure (TMP), the production of SMP and EPS, and particle size distribution of sludge flocs. In addition, the contributions of membrane pore blocking, gel layer fouling and cake layer fouling to the total membrane fouling were examined using membrane fouling resistance analysis. The Fourier transform infrared analysis of foulants and the scanning electron microscopy-energy-dispersive X-ray analyzer anaylses of membrane were also carried out to elucidate the effects of low-concentration Cr(VI) (0.4 mg/L) on the performance of the SMBR as well as the membrane fouling.

Materials and methods

Experimental set-up and operation

As Figure 1 showed, a lab-scale SMBR (SMBR-Cr(VI)) with a working volume of 3.0 L was used. A polyvinylidene fluoride (PVDF) hollow fiber membrane module (pore size 0.4 μm) with a total surface area of 0.01 m^2 (Litree Company, China) was equipped in the reactor and the constant flux was set at 45 L/(m^2·h) (LMH). Air (0.6 m^3/h) was supplied continuously through a perforated pipe under the membrane module. The influent was fed by a peristaltic pump controlled by a distributing pan. Filtration was carried out in an intermittent suction mode with 10-min suction followed by 2-min release. Hydraulic retention time (HRT) and solids retention time (SRT) were kept at 8.0 h and 30 days, respectively. Mixed liquor suspended solids (MLSS) were maintained at 3430±540 mg/L during the operation. Considering the yearly average Cr(VI) concentration in municipal wastewater (Zhao et al. 2009), the concentration of Cr(VI) was maintained at 0.4 mg/L in SMBR-Cr(VI) using a stock solution (100 mg/L) K_2CrO_4 as Cr(VI) source. A same parallel SMBR (SMBR-Control) was operated at identical conditions without Cr(VI) addition.

Figure 1

The inoculating sludge was drawn from the aerobic tank in the Quyang wastewater treatment plant (Shanghai, China), which treats about 60000 m^3/d of domestic wastewater using anaerobic-anoxic-oxic (A^2/O) process. The reactors with inoculating sludge were firstly operated under the relevant conditions to achieve a steady state. Then they were equipped with the new membrane modules and worked as SMBRs to start the following experiments. When TMP reached 40 kPa, the membrane module was removed and washed with tap water to remove the cake layer (physical cleaning). The synthetic municipal wastewater was composed of 250 mg/L glucose, 250 mg/L corn starch, 57 mg/L NH_4Cl, 28 mg/L peptone, 52.8 mg/L KH_2PO_4, 9 mg/L $MgSO_4 \cdot 7H_2O$, 3.66 mg/L $MnSO_4 \cdot H_2O$, 0.55 $FeSO_4 \cdot 7H_2O$ and 8 mg/L $CaCl_2$ (Miura et al. 2007; Xia et al. 2010). $NaHCO_3$ with a concentration of 120 mg/L was used to maintain the pH at 7.0-7.5. The average characteristics of influent and effluent water in both of the SMBRs are summarized in Table 1.

Table 1

Extraction and measurement of EPS

Extraction of SMP, loosely bound EPS and tightly bound EPS were performed according to a modified thermal extraction method (Jiang et al. 2013). A 40 mL activated sludge mixed liquor was first centrifuged (MILTIFUGE X1R, Thermo Electron Corporation, USA) at 6000 g for 5 minutes. Then the supernatant was filtered through a 0.45 μm filter (SCAA-101, ANPEL, China) to get SMP. The remaining sludge was re-suspended in 40 mL of 0.9% NaCl solution, treated by ultrasound (DS510DT, 40 kHz, 300W, Shangchao, China) for 8 minutes and then shaken at 150 rpm for 10 minutes. After the final centrifugation at 8000 g for 10 minutes, the organic matter in the supernatant was regarded as the loosely bound EPS of the sludge. The sludge pellet left in centrifuge tube was re-suspended in 40 mL of 0.9% NaCl solution, and retreated by ultrasound for 4 minutes. The suspension was heated at 80 ^{o}C for 30 minutes and then centrifuged at 12000 g for 20 minutes. The supernatant was regarded as tightly bound EPS of the sludge. As SMP, loosely bound EPS and tightly bound EPS have been normalized as the concentration of carbohydrate and protein, they were measured by the phenol-sulfuric acid method and Branford method, respectively (Xia et al. 2012). Molecular weight (MW) distributions of SMP, loosely bound EPS and tightly bound EPS were studied by a gel filtration chromatography analyzer (LC-10ADVP, Shimadzu, Japan).

Resistance analysis

When TMP reached 40 kPa and the membrane was considered to be fouled, the membrane resistance analysis was performed in triplicate every time. Based on the resistance-in-series model on the relationship between permeate flux and TMP (Lee et al.

2001), the hydraulic resistance could be calculated according to the following equation:

$$R = R_m + R_p + R_c = \frac{\triangle P}{\mu J} \tag{1}$$

Where R_m is the constant resistance of the clean membrane, R_p is the resistance due to pore blocking, and R_c is the fouling layer resistance caused by concentration polarization and cake layer. $\triangle P$ is TMP, μ is viscosity of the liquor, and J is permeate flux. The methods to measure the resistances of the membrane were as follow: (1) R_m: the flux and TMP of the new membrane module were measured using deionized water before the operation. (2) R: after the operation, the flux and TMP of the membrane module were measured in SMBR. (3) R_p+R_m: after removing the cake attached on the membrane surface by washing the membrane with tap water (physical clean method), the flux and TMP of the membrane module were measured using deionized water. (4) R_c: $R_{m,}$ and R_p were subtracted from R to get R_c. From these values, R, R_m and R_p+R_m of each SMBR could be obtained using Eq. (1).

Additional analysis

Particle size distribution of sludge flocs was carried out using a focused beam reflectance measurement (Eyetech particle size and shape analyzer, Ankersmid, Holland). The organic substance information of foulants was determined with a Fourier transform infrared spectrometer (Nicolet 5700, Thermo Electron Corporation, USA). Analyses of particle size distribution, MW and Fourier transform infrared were performed in triplicate. Inductively coupled plasma mass spectrometry (ICPMS 7700, Agilent, USA) was employed to measure Cr(VI) concentration. Measurements of chemical oxygen demand (COD), total nitrogen (TN), ammonia (NH_4^+-N) and MLSS were performed according to Chinese National Environment Protection Agency (NEPA) standard methods (NEPA 1997). When TMP increased up to 40 kPa, membrane modules were used for both morphology and construction analysis by scanning electron microscopy (XL30, Philips, Netherlands) coupled with an energy-dispersive X-ray analyzer (Oxford Isis, UK).

Results and discussion

Variations of TMP and SMP concentration

The development rate of TMP is an important index to evaluate membrane filterability in SMBR systems as it can directly reflect the extent of membrane fouling. TMP variations of SMBR-Cr(VI) and SMBR-Control are presented in Figure 2. The results indicated that low-concentration Cr(VI) (0.4 mg/L) had a crucial impact on the membrane fouling behavior, which was consistent with the report of Zhao et al.(2009). TMP variations of SMBR-Cr(VI) were characterized by two-phase fouling phenomenon, namely a slow TMP rise followed by a rapid rise. Both SMBR-Cr(VI) and SMBR-Control initially displayed a similar trend and exhibited a fouling rate (dTMP/ dt) of 1.33 kPa/d at the beginning of 30 days. TMP increased slowly during this period. However, a fast TMP jump (7.51 kPa/d) occurred at 32th day in the SMBR-Cr(VI), which gave the signal of severe membrane fouling. TMP jump might result from sudden changes of the cake layer structure. A recent investigation confirmed that TMP jump was closely related to a sudden increase of the SMP concentration at the bottom of cake layer (Hwang et al. 2008). In addition, SMP were released from bacterial to form a protective barrier for preventing harmful effects of heavy metals (Pal et al. 2008; Samaras et al. 2009). After physical cleaning, TMP in SMBR-Cr(VI) and SMBR-Control decreased about 21 and 34 kPa, respectively, indicating that the pore blocking in SMBR-Cr(VI) was more severe than that in MBR-Control. Compared with SMBR-Control, the higher fouling rate (about 7.21 kPa/d) in SMBR-Cr(VI) further confirmed the severe pore blocking in SMBR-Cr(VI). Thus, low-concentration Cr(VI) (0.4 mg/L) could cause severe membrane fouling through the cake layer structure change, which not only enhanced pore blocking, but also increased the concentration of SMP.

Figure 2

SMP in MBR also plays a significant role in membrane fouling (Meng et al. 2009; Tian et al. 2011) and Cr(VI) removal (Kilic et al. 2008). During filtration, SMP from the bulk attaches to the membrane surface, blocks membrane pores, and forms a gel layer. Figure 2 showed the variations of SMP concentration in SMBR-Cr(VI) and SMBR-Control. The SMP concentration increased gradually along with the development of TMP in two SMBRs, which was consistent with the fact that both composition and concentration of organic matter in SMP has great impact on membrane fouling (Le-Clech et al. 2006). Figure 3 revealed that protein was the main component of SMP, and the protein concentration of SMP in SMBR-Cr(VI) was higher than that in SMBR-Control. The protein concentration with high-concentration (over 50 mg/L) Cr(III), which was considered as the toxic substance for bacteria, was about 12.69 mg/L (Malamis et al. 2009). SMBR-Cr(VI) had a similar protein concentration, indicating that low-concentration Cr(VI) (0.4 mg/L) could also be toxic to bacteria. As can be seen, once Cr(VI) in the influent of SMBR promoted the release of protein by microorganisms in the system. Therefore, low-concentration Cr(VI) (0.4 mg/L) can increase the protein concentration of SMP, which can further arouse a TMP jump and aggravate severe membrane fouling.

Figure 3

Particle size distributions of sludge particles

The particle size distributions of the sludge particles in SMBR-Cr(VI) and SMBR-Control are presented in Figure 4. The sludge particles of SMBR-Cr(VI) had a narrower range profile of size distribution, and the mean particle size of SMBR-Cr(VI) was smaller than that of SMBR-Control. Statistical results of the sludge particle distributions are summarized in Table 2. In SMBR-Cr(VI), about 75% of the particles was distributed in the size range of 10-50 μm, and 22% of particles was in the size range from 0 to 10 μm. However, in SMBR-Control, over 50% sludge particles fell between the particle range of 50-200 μm with few particles in the range of 0 to 10 μm.

Figure 4

Table 2

The results indicated that low-concentration Cr(VI) (0.4 mg/L) would cause smaller particles distributed in the 0-50μm range. The results might be due to the reduction of the filamentous microorganism concentration and the significant increase of planktonic bacteria population in the mixed liquor. Moreover, EPS was reported to bond Cr(VI) more easily than planktonic bacteria (Pal and Paul 2008; Vaiopoulou and Gikas 2012). Thus, the formation of larger sludge particles was inhibited due to the absence of EPS for the combination of bacteria and EPS. Hence, low-concentration Cr(VI) (0.4 mg/L) could inhibit the formation of large particles, because of its influence on microorganism community structure and EPS. In addition, small particles generally have a strong tendency to deposit on the membrane surface for cake layer formation and penetrate into membrane pores, further leading to pore blocking. Thus, the results are in line with the explanation of severe membrane fouling observed in SMBR-Cr(VI) through the variations of TMP and SMP concentration.

MW distributions of SMP and EPS

As a significant factor indicating the performance and membrane fouling of SMBR (Wang et al. 2009), the MW distributions of SMP and EPS in two SMBRs were investigated with gel filtration chromatography (Figure 5). SMBR-Cr(VI) had lower MW molecules of SMP, while the MW molecules of loosely bound EPS and tightly bound EPS in two SMBRs were almost similar. Low-concentration Cr(VI) (0.4 mg/L) could affect microbial metabolism, synthesis of biomolecules, and the microorganisms in activated sludge (Vaiopoulou and Gikas 2012), which play key roles in the release and structure of EPS (Laspidou et al. 2002). Recent studies also showed that a possible reduction mechanism of Cr(VI) toxic effects might relate to the presence of soluble EPS in activated sludge (Kilic and Donmez 2008; Pal and Paul 2008; Parvathi et al. 2008). In this study, the variations MW of SMP, loosely bound EPS and tightly bound EPS in two SMBRs were different as above mentioned, which had never reported. This observation indicated that low-concentration Cr(VI) (0.4 mg/L) in SMBR mainly affected the MW distribution of SMP by causing the release of more lower MW molecules. There was no effect on loosely bound EPS or tightly bound EPS. Additionally, a big proportion of low MWs could lead to a severe membrane fouling in SMBR-Cr(VI) through pore blocking.

Figure 5

Fourier transform infrared analysis of foulants

The Fourier transform infrared spectra of the foulants on the membranes in two SMBRs are presented in Figure 6. The spectra showed a broad region of adsorption around a peak at 3434.5 cm^{-1}, which was due to the stretch of the O-H bond in hydroxyl functional groups, as well as a sharp peak at 2930.6 cm^{-1}, which was attributed to the stretch of the C-H bonds (Maruyama et al. 2001). Furthermore, there was a peak at 1635.2 cm^{-1} which was unique to the protein secondary structure, called amides I, indicating the presence of proteins in membrane fouling. A broad peak at 1047.6 cm^{-1} was due to polysaccharides or polysaccharide-like substances (Meng et al. 2007). However, there were some differences in the major components between the foulants of two SMBRs. Compared with foulants in SMBR-Control, the lack of 1544.7 cm^{-1} peak in SMBR-Cr(VI), which was unique to the amides II protein secondary structure (Meng et al. 2007), indicated the absence of some proteins in the foulants as a result of low-concentration Cr(VI) (0.4 mg/L).

Figure 6

Analysis of membrane fouling resistance

Total membrane resistance (R) includes intrinsic membrane resistance (R_m), pore blocking resistance (R_p) and fouling layer resistance (R_c) (Lee et al. 2001). Although several papers had studied on the effect of chromium on the membrane fouling, the conclusions were contradictory (Dialynas et al. 2009; Zhao et al. 2009). Besides, only few reports discussed the influence of Cr(VI) on each fouling resistance and the membrane fouling mechanism. As shown in Table 3, total membrane resistance and membrane layer resistance of SMBR-Cr(VI) were 2.05 and 1.91 times of those of SMBR-Control, respectively. Moreover, the fouling layer was the main component contributing to the total membrane resistance in SMBR-Cr(VI), illustrating that

SMBR-Cr(VI) suffered from severe membrane fouling because of the cake layer fouling. According to the recent studies, high-concentration SMP could cause severe cake layer fouling. The deposited biopolymers could promote easier and faster bacterial adhesion, and SMP could trap particles more tightly on the membrane (Chu et al. 2005; Meng et al. 2009). The TMP jump (As shown in Section "***Variations of TMP and SMP concentration***") also supported the hypothesis that the severe membrane fouling in SMBR-Cr(VI) was due to the high-concentration SMP around the cake layer. The TMP variations after physical cleaning indicated severe pore blocking in SMBR-Cr(VI).

Table 3

As shown in Table 3, R_p in SMBR-Cr(VI) was 8.94 times higher than that of SMBR-Control. Table 3 shows the resistance distributions of the membrane filtration in SMBR-Cr(VI) and SMBR-Control. The percentage of R_p to R in SMBR-Cr(VI) was about 10.85%, which is 4.84 times of that in SMBR-Control (2.24%). All these results indicated that low-concentration Cr(VI) (0.4 mg/L) induced severe membrane pore blocking. The toxicity of Cr(VI) could cause the appearance of pin-point flocs and planktonic microorganisms and some damage to the cells. Thus, the small size organic matter could block the membrane pores, as suggested by Zhao et al. (2009). According to some previous conclusions (Lyko et al. 2008; Meng et al. 2009; Shon et al. 2009), the high-concentration and low-MW SMP could lead to severe membrane pore blocking and membrane filtration reduction. Since membrane pore blocking is the initial phase of particulate fouling and irreversible fouling, and is considered to be the most severe fouling (Meng et al. 2007; Guo et al. 2012), the resistance results indicated that low-concentration Cr(VI) (0.4 mg/L) could complicate the irreversible membrane fouling and shorten the service life of membrane module.

Membrane morphology and construction

Scanning electron microscopy images (Figure 7) were taken to identify the morphology of membrane fouling on the membrane surface. The membrane surface of SMBR-Cr(VI) was covered by a cake layer with a thickness around 8.62 μm. Nevertheless, a thinner cake layer (4.35 μm) was covered on the membrane surface of SMBR-Control. These data demonstrated that low-concentration Cr(VI) (0.4 mg/L) had a crucial effect on cake-layer fouling by increasing of cake layer thickness.

Figure 7

Element analysis of the surface cake layer was further performed to determine the chemical components of the layer. The elements of C, O, N, Na, K, Mg, Ca, Si and Cr were detected in the cake layer of SMBR-Cr(VI) and SMBR-Control (Table 4). Although the relative contents of Mg, Ca and Si in the layer were small, these elements contributed significantly to the cake layer formation. Mg, Ca and Si could bridge the deposited cells and biopolymers and then formed a dense cake layer when they pass through the membranes (Huang et al. 1998; Meng et al. 2007). Additionally, the contents of Ca decreased from 8.26% to 2.60%, but there was little variation of those of Mg and Si. The decrease of Ca content in cake layer indicated that low-concentration Cr(VI) (0.4 mg/L) might promote the bridging and flocculation between Ca^{2+} and the biopolymers, which will aggravate membrane fouling. Large amounts of carbon, representing organic foulants, were observed in the cake layer of SMBR-Cr(VI). The organic foulants coupled with the inorganic precipitation could accelerate the cake layer formation, which resulted in severe pore blocking and shortened the lifespan of membrane module. The large amount of carbon was also consistent with the result that low-concentration Cr(VI) (0.4 mg/L) induced an increase in SMP(Seen in Figure 2 and Figure 3). It was also found that the relative content of Cr in foulants was small, because Cr(VI) concentration was low.

Table 4

Conclusions

The performance of SMBR and membrane fouling were evaluated using municipal wastewater with low-concentration Cr(VI) (0.4 mg/L). That concentration had no apparent side effects on treatment efficiency but led to the mean size decrease of the sludge particles. Low-concentration Cr(VI) (0.4 mg/L) increased SMP concentration and reduced mean MW molecules. There was no such tendency for either loosely bound EPS or tightly bound EPS. All analyses on contributing factors towards membrane fouling showed that low-concentration Cr(VI) (0.4 mg/L) induced severe cake layer fouling. Moreover, it could aggravate the membrane pore blocking and the irreversible membrane fouling, thereby shortening the service life of membrane module.

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Table Captions

Table 1 Average characteristics of the influent and the effluent for SMBR-Cr(VI) and SMBR-Control

Table 2 Particle size distributions in SMBR-Cr(VI) and SMBR-Control

Table 3 Results of the membrane filtration resistances in SMBR-Cr(VI) and SMBR-Control

Table 4 Element analyses of the cake layer in SMBR-Cr(VI) and SMBR-Control (Wt (%))

Table 1

Average characteristics of the influent and effluent water for SMBR-Cr(VI) and SMBR-Control. All the values represent mean ± SD (n=70).

Parameters	SMBR-Cr(VI)			SMBR-Control		
	Influent (mg/L)	Effluent (mg/L)	Removal (%)	Influent (mg/L)	Effluent (mg/L)	Removal (%)
COD	291.4±41.1	24.6±12.8	91.54±4.84	285.0±52.30	29.30±10.44	89.72±4.96
NH_4^+-N	12.96±2.49	0.86±0.58	93.35±4.10	13.62±3.02	0.72±0.54	94.68±3.39
TN	18.22±3.42	16.69±2.67	8.37±5.58	17.45±2.63	14.20±3.60	18.67±9.61
Cr(VI)	0.38±0.07	0.13±0.06	60.85±17.84	-	-	-

Table 2
Particle size distributions in SMBR-Cr(VI) and SMBR-Control.

Parameters	Particle size (µm)	Particle size distribution (%)				
	Mean	<10µm	10-50µm	50-100µm	100-200µm	>200µm
SMBR-Cr(VI)	28.63±10.83	22.15	74.99	2.82	0.03	0.01
SMBR- Control	57.57±21.14	0.01	49.13	15.83	23.03	12.00

Table 3

Results of the membrane filtration resistances in SMBR-Cr(VI) and SMBR-Control.

Resistance	$R(10^{12}\ m^{-1})$	$R_m\ (10^{12}\ m^{-1})$	$R_m / R(\%)$	$R_P(10^{12}\ m^{-1})$	$R_p / R(\%)$	$R_c(10^{12}\ m^{-1})$	$R_c / R(\%)$
SMBR-Cr(VI)	7.33±0.41	0.135±0.091	1.84±0.29	0.795±0.351	10.85±0.94	6.40±0.365	87.31±1.48
SMBR-Control	3.57±0.22	0.140±0.053	3.92±0.58	0.080±0.007	2.24±0.71	3.35±0.281	93.84±1.05
$R_{Cr(VI)}/R_{Control}$	2.05	0.96	-	9.94	-	1.91	-

$R_{Cr(VI)}/R_{Control}$: Resistances of SMBR-Cr(VI)/ Resistances of SMBR-Control.

$n_{SMBR\text{-}Cr(VI)}=12$, $n_{SMBR\text{-}Control}=6$; when TMP reached 40kPa, resistance analysis was performed in triplicate.

Table 4

Element analyses of the cake layer in SMBR-Cr(VI) and SMBR-Control (Wt(%))

Element	C	N	O	Na	Mg	Si	K	Ca	Cr
SMBR-Cr(VI)	57.36±2.13	6.00±0.30	31.00±1.22	0.19±0.03	0.41±0.02	1.20±0.09	0.34±0.03	2.60±0.95	0.31±0.07
SMBR-Control	41.16±1.43	7.20±0.45	39.83±2.34	0.43±0.05	0.50±0.09	1.29±0.15	1.33±0.16	8.26±1.33	-

n=24, 8 spots were measured and each spots were analyzed in triplicate.

Figure Captions

Figure 1 A schematic of submerged membrane bioreactor (SMBR)

Figure 2 Variations of the trans-membrane pressure (TMP) and soluble microbial products (SMP) concentrations in SMBR-Cr(VI) and SMBR-Control

Figure 3 Variations of carbohydrate and protein concentrations of soluble microbial products (SMP) in SMBR-Cr(VI) and SMBR-Control

Figure 4 Particle size distributions of sludge samples in SMBR-Cr(VI) and SMBR-Control

Figure 5 Molecular weight (MW) distributions of (a) SMP, (b) loosely bound EPS, (c) tightly bound EPS in SMBR-Cr(VI) and SMBR-Control

Figure 6 Fourier transform infrared spectra of fouling on the membrane in SMBR-Cr(VI) and SMBR-Control

Figure 7 Scanning electron microscopy images of membrane. (a) the cross-section image of virgin membrane; (b) the cross-section image of fouled membrane in SMBR-Cr(VI); (c) the cross-section image of fouled membrane in SMBR-Control

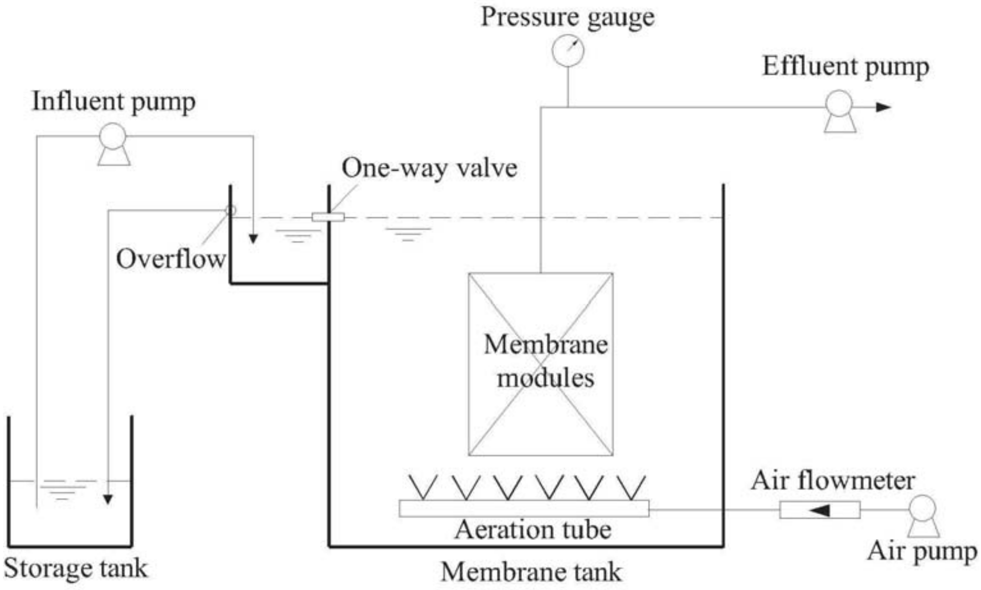


Figure 1 A schematic of submerged membrane bioreactor (SMBR) (SMBR-Cr(VI) with low-concentration Cr(VI) (0.4 mg/L) and SMBR-Control without Cr(VI) were run at the same condition in two similar reactors, respectively.)

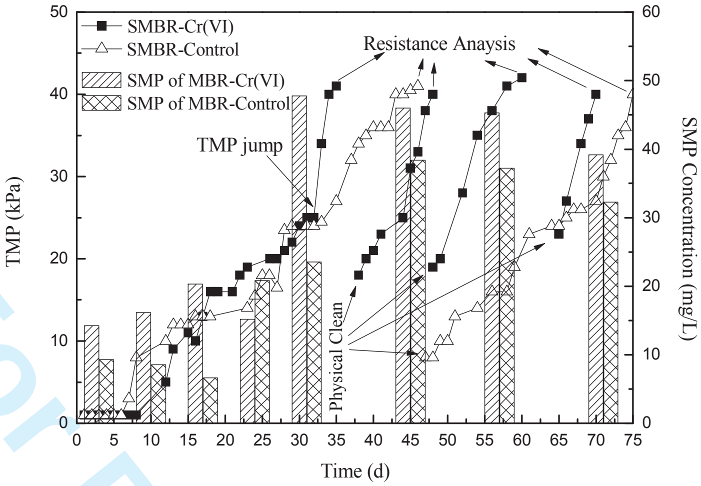


Figure 2 Variations of the trans-membrane pressure (TMP) and soluble microbial products (SMP) concentrations in SMBR-Cr(VI) and SMBR-Control (SMBR-Cr(VI) had a TMP jump at day 32th. The resistance analysis was carried out at day 35th, 48th, 60th, 70th for SMBR-Cr(VI) and day 46th, 75th for SMBR-Control, when the TMP reached 40 kPa. The physical cleaning was performed at day 38th, 48 th, 65 th for SMBR-Cr(VI) and at day 47th for SMBR-Control. Rapid SMP increase occurred during 25th to 30th in SMBR-Cr(VI).)

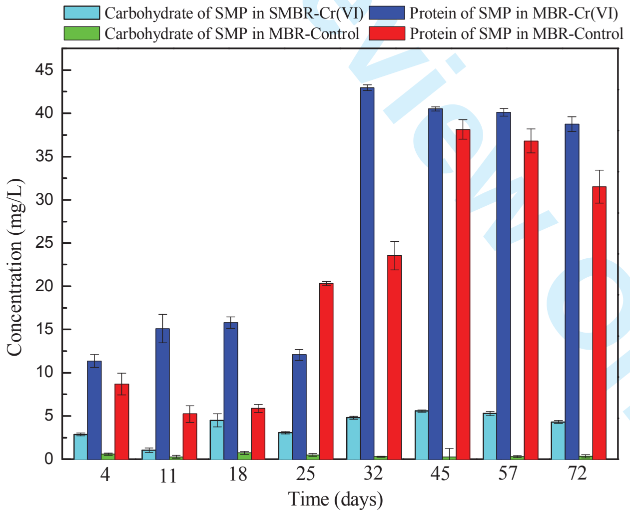


Figure 3 Variations of carbohydrate and protein concentrations of soluble microbial products (SMP) in SMBR-Cr(VI) and SMBR-Control (Because SMP was excreted by the microorganisms in sludge, its concentration depended on the microorganism behaviors to the surrounding condition, such as toxicity shock. The physical and chemical clean was done outside two SMBRs. It caused no effects on the microorganism behaviors. Thus, the differences between the SMPs in the two SMBRs were due to low-concentration Cr(VI) (0.4 mg/L).)

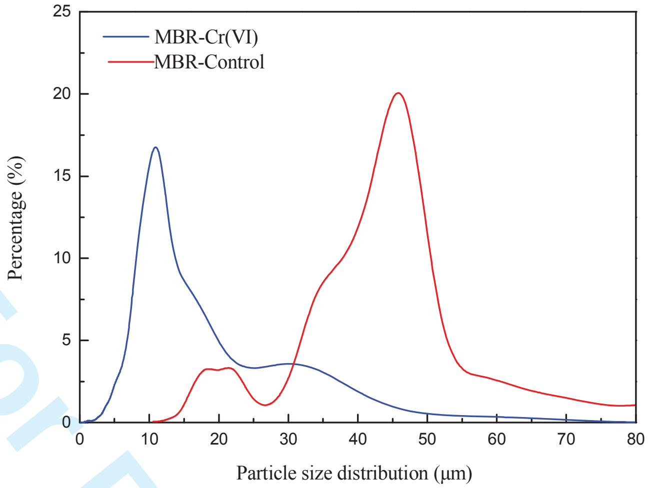


Figure 4 Particle size distributions of sludge samples in SMBR-Cr(VI) and SMBR-Control

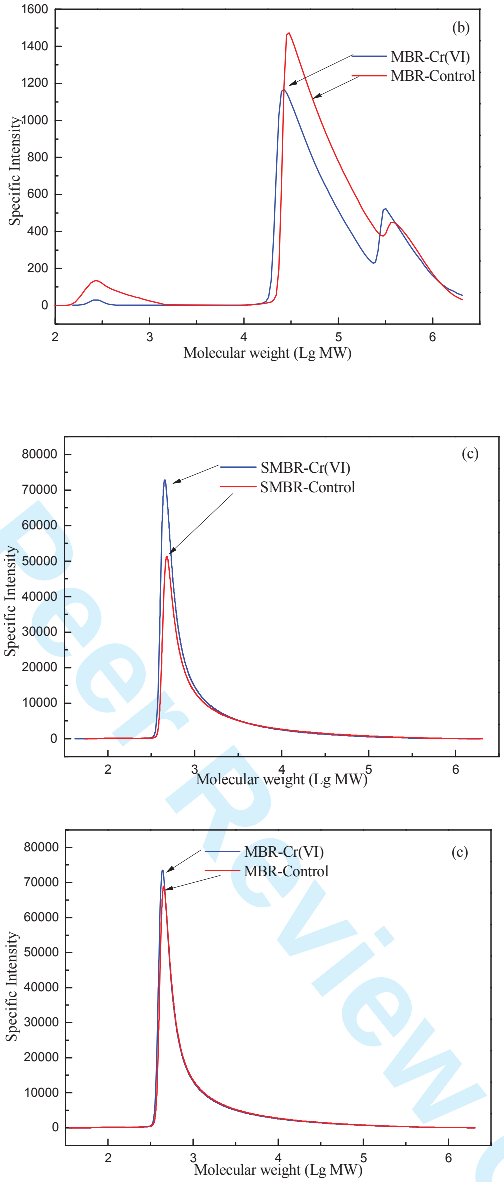


Figure 5 Molecular weight (MW) distributions of (a) SMP, (b) loosely bound EPS, (c) tightly bound EPS in SMBR-Cr(VI) and SMBR-Control

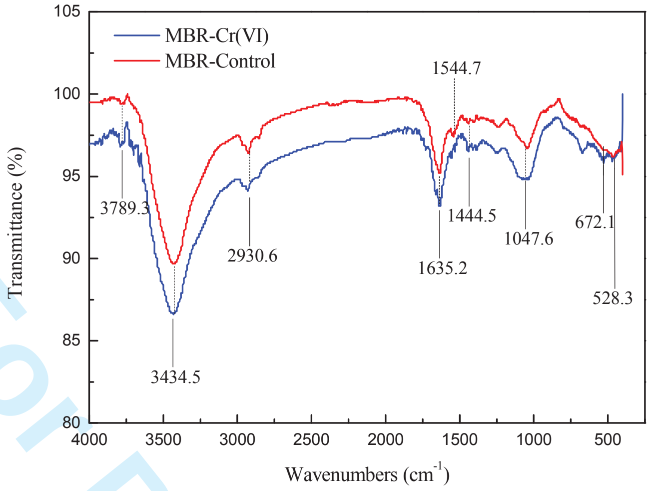
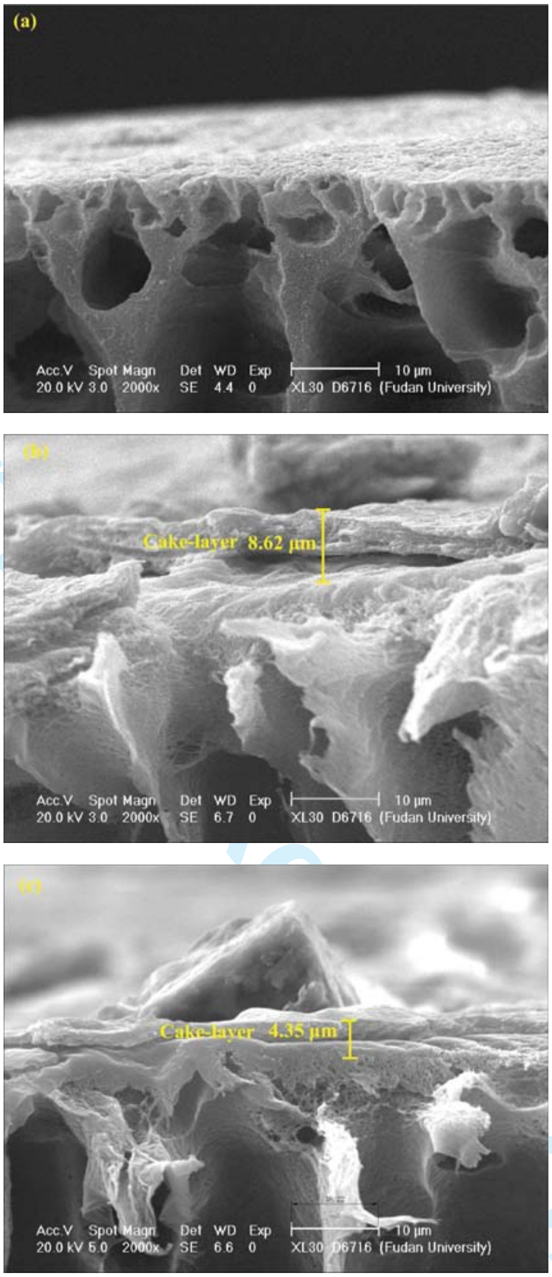


Figure 6 Fourier transform infrared spectra of fouling on the membrane in SMBR-Cr(VI) and SMBR-Control



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