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**Ferrous iron/peroxymonosulfate oxidation as a pretreatment
for ceramic ultrafiltration membrane: Control of natural
organic matter fouling and degradation of atrazine**

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1 ABSTRACT

2 Ferrous iron/peroxymonosulfate (Fe(II)/PMS) oxidation was employed as a
3 pretreatment method for ultrafiltration process to control membrane fouling caused
4 by natural organic matter, including humic acid (HA), sodium alginate (SA), bovine
5 serum albumin (BSA), and their mixture (HA-SA-BSA). To evaluate the mechanism
6 of fouling mitigation, the effects of Fe(II)/PMS pretreatment on the characteristics of
7 feed water were examined. The degradation of atrazine (ATZ) was also investigated
8 and the species of generated radicals were preliminarily determined. Under the test
9 exposure (15 and 50 μM), Fe(II)/PMS pretreatment effectively mitigated membrane
10 fouling caused by HA, SA and HA-SA-BSA mixture, and the performance improved
11 with the increase of Fe(II) or PMS dose; whereas aggravated BSA fouling at lower
12 doses and fouling alleviation was observed only at a higher dose (50/50 μM). The
13 fouling mitigation was mainly attributed to the effective reduction of organic
14 loadings by coagulation with *in-situ* formed Fe(III). Its performance was comparable
15 or even slightly higher than single coagulation with Fe(III), most likely due to the
16 oxidation by Fe(II)/PMS process. Fe(II)/PMS oxidation showed better performance
17 in reducing DOC and UV_{254} , fluorescence intensities of fluorescent components and
18 UV-absorbing compounds than single coagulation. In addition, Fe(II)/PMS
19 pretreatment was efficient in ATZ degradation due to the generation of sulfate and
20 hydroxyl radicals, whereas coagulation was ineffective to remove it.

21 **Key words:** Ferrous iron/peroxymonosulfate (Fe(II)/PMS), ceramic ultrafiltration
22 (UF) membrane, natural organic matter (NOM), membrane fouling, atrazine (ATZ)

1. Introduction

Ultrafiltration (UF) membranes are being increasingly used in water and waste water treatment due to their effective retention of microorganisms, suspended particles, colloids, and some macromolecules (Jermann et al., 2007; Peter-Varbanets et al., 2009). Compared with polymeric UF membranes, ceramic UF membranes are emerging and promising in the field of water treatment because of their inherent advantages, such as higher mechanical and chemical stability, longer lifespan and increasing cost competitiveness (Lee et al., 2013; Lee and Kim, 2014). However, membrane fouling which may lead to more energy consumption and reduced productivity is still a critical obstacle for the further widespread application of ceramic UF membranes (Cheng et al., 2017). It was generally considered that natural organic matter (NOM, mainly including humic-like substances, polysaccharides, proteins, and lipids) was still one of the most problematic membrane foulants (Guo et al., 2009; Yuan and Zydney, 2000). Among various NOM fractions, the high molecular weight (MW) biopolymers such as proteinaceous substances and polysaccharides were identified as the main NOM components for UF membrane fouling (Zhang et al., 2015a). Some typically possible mechanisms were regarded as contributors to membrane fouling, including the formation of loose cake layer and impermeable gel layer, pore blocking and pore narrowing due to adsorption of organic matter (Qu et al., 2012; Zhang et al., 2015b).

A common approach to mitigate membrane fouling caused by organic matter is feed water pretreatment prior to membrane filtration, which can remove the organic

foulants with high fouling tendency or transform them into smaller fragments with low fouling potential (Gao et al., 2011; Huang et al., 2009). The widely used pretreatment methods for membrane fouling control mainly include coagulation/flocculation (Yu et al., 2013), adsorption (Li et al., 2014), oxidation (Van Geluwe et al., 2011), and their combinations (Wang et al., 2016). Although the common pretreatment methods showed certain effect on membrane fouling control, there are still problems occurring in the practical application. Zhang et al. (2015a) observed that coagulation pretreatment using aluminium chlorohydrate (ACH) achieved a remarkable reduction in both total and irreversible fouling resistance, whereas it was ineffective for removing algal toxin microcystin-LR. Shao et al. (2016) reported that powdered activated carbon (PAC) and humic acid (HA) exhibited a significant synergistic fouling effect by forming a fouling layer together on the membrane surface in PAC-UF hybrid process. Our previous study (Cheng et al., 2016) indicated that pre-ozonation with low doses efficiently alleviated membrane fouling caused by HA and sodium alginate (SA) by converting high-MW molecules into smaller ones, which could pass through membrane pores and deteriorate the permeate quality.

To solve these problems, ferrous-activated peroxymonosulfate (PMS), which is one of the sulfate radicals ($\text{SO}_4^{\bullet-}$)-based advanced oxidation processes (AOPs), was put forward as a pretreatment alternative for ceramic UF membrane in this study. It was reported that (Antoniou et al., 2010) PMS has a lower energy of the lower unoccupied molecular orbital (LUMO), which means that PMS is more easily to be

activated by accepting e^- than the other two peroxides, hydrogen peroxide (H_2O_2) and persulfate (PDS). Owing to high activity, relatively lower cost and environmentally friendly nature, Fe(II) has been selected as an ideal activator of PMS (Zou et al., 2013). Rastogi et al. (2009a) reported that Fe(II)/PMS system showed a relatively higher reactivity for the degradation of 4-chlorophenol (4-CP) compared to Fe(II)/PDS and Fe(II)/ H_2O_2 . In previous studies, Fe(II)/PMS process has been utilized to degrade organic compounds such as polychlorinated biphenyls (PCBs) (Rastogi et al., 2009b) and 2,4-dichlorophenol (2,4-DCP) (Anipsitakis and Dionysiou, 2004) in aqueous solutions. To achieve a higher activation efficiency, previous research on Fe(II)/PMS oxidation were mainly performed under acidic conditions to avoid the formation of ferric oxyhydroxides through hydrolysis (Ji et al., 2015; Rastogi et al., 2009b). However, very little effort has been put on the study of *in-situ* formed Fe(III), which could be used as a coagulant in neutral conditions. Moreover, the cost of Fe(II) salts is considerably lower than Fe(III) salts. To this end, Fe(II)/PMS process can be regarded as a combination of oxidation by $SO_4^{\cdot-}$ and coagulation by Fe(III), which might simultaneously mitigate membrane fouling and improve the permeate quality. Considering that ceramic membrane can withstand the severe oxidizing environment in the presence of residual oxidants and radicals, it is of particular interest to integrate Fe(II)/PMS oxidation with ceramic membranes. However, to the best of our knowledge, very limited work has been done in this field.

The objective of this study was to investigate the effect of feed water

pretreatment by Fe(II)/PMS on mitigating membrane fouling caused by different NOM fractions, including HA, SA and bovine serum albumin (BSA), as well as their mixture (HA-SA-BSA). The impact of Fe(II)/PMS pretreatment on membrane fouling was evaluated by (1) flux decline and reversibility analysis, (2) characterization of the organic matter by various methods, and (3) comparing with single coagulation by Fe(III). Furthermore, the effect of Fe(II)/PMS and coagulation on the removal of atrazine (ATZ) was investigated and the species of generated radicals were preliminarily determined. The results were expected to illustrate the feasibility of Fe(II)/PMS pretreatment on UF membrane fouling control and the improvement of permeate quality.

2. Materials and methods

2.1 Materials and reagents

HA, SA, BSA, and ATZ were purchased from Sigma-Aldrich (USA). Potassium peroxymonosulfate ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), *tert*-butyl alcohol (TBA) and methanol were supplied by Aladdin Chemicals (Shanghai, China). All other reagents were of reagent grade quality and purchased from Bench Chemicals (Tianjin, China). HA, SA and BSA were chosen for preparing the feed solutions to represent humic substances, polysaccharides and proteins in natural waters, respectively. HA stock solution (2.0 g/L) was prepared by dissolving 2.0 g of HA in 800 mL NaOH (0.01 mol/L), followed by stirring for 24 h and adjusting pH to 7.0, and then the solution was diluted to 1000 mL with ultrapure water. The SA and BSA stock solutions (2.0 g/L) were prepared by dissolving 2.0 g of SA and BSA in 1000

mL ultrapure water, respectively, and then stirring for 12 h. The stock solution of ATZ (100 μ M) was prepared by dissolving ATZ in ultrapure water, and then stirring for 72 h. The stock solutions of FeSO₄ and PMS were freshly prepared by dissolving weighed amounts of FeSO₄ and PMS in ultrapure water, and standardized by inductively coupled plasma optical emission spectrometry (ICP-OES) and the iodometric method (Ball et al., 1967), respectively. These stock solutions were stored in dark place. The employed concentrations of HA, SA and BSA samples with individual fractions were all 10.0 mg/L, while the HA-SA-BSA mixture with the concentration of 5.0-5.0-5.0 mg/L was utilized to investigate the combined fouling of different organic fractions. In the experiment of ATZ removal, the water sample was prepared by spiking 1.0 μ M ATZ into a 10.0 mg/L HA solution. All samples employed in the experiment were prepared by diluting stock solutions with ultrapure water (18.2 M Ω ·cm) produced by a Milli-Q purification system (Millipore, USA), and the pH values were adjusted to 7.0 ± 0.1 prior to the experiment.

2.2 Experimental setup

The pretreatment experiments were performed in 500 mL triangular flasks at room temperature ($25 \pm 1^\circ\text{C}$). The reactions of Fe(II)/PMS oxidation were initiated by adding certain doses of PMS into water samples containing Fe(II) at desirable concentrations. By contrast, the desired Fe(III) doses were added into water samples to start the reaction of coagulation. In this study, PMS doses of 15 or 50 μ M, and initial Fe(II) concentrations of 15 or 50 μ M were employed. The pretreatments were conducted in batch mode with rapid mixing for 1 min at 200 r/min, followed by slow

mixing for 20 min at 50 r/min. After that, the pretreated water samples (without removal of the precipitate) were immediately used for membrane filtration.

Filtration tests were carried out using a flat sheet ceramic UF membrane with molecular weight cut-off of 50 kDa. The characteristics and images of the employed membrane are shown in [Table S1](#) and [Fig. S1](#). A schematic representation of the UF filtration experimental setup is illustrated in [Fig. S2](#). UF experiments were conducted in a filtration cell with an effective volume of 120 mL in dead-end mode at a constant transmembrane pressure (TMP) of 50 kPa, which was maintained through a nitrogen gas bottle connected to the filtration cell. For each experiment, a piece of ceramic flat sheet membrane was placed at the bottom of the cell with its filtration layer towards the feed water. During filtration, the permeate flux was monitored using an electronic balance (BSA3202S, Sartorius, Germany) and the output data was periodically recorded via a data acquisition system. In this study, hydraulic backwash was utilized for membrane cleaning. Backwash was performed by applying a higher pressure (approximately 150 kPa) on the permeate side, forcing the permeate water back through the membrane to the feed side. As a result, the cake layer attached on membrane surface was lifted and detached from ceramic membrane. Membrane fouling analysis was calculated through the UF membrane filtration experiment, which are described in detail in Section 2.3.

2.3 Fouling analysis

The distribution of fouling resistance was calculated using the resistance-in-series model ([Lin et al., 2009](#)), as shown in [Eq. \(1\)](#):

$$R_t = TMP/(\mu J) = R_m + R_{ir} + R_r \quad (1)$$

where, TMP is the transmembrane pressure (Pa); μ is the dynamic viscosity (Pa·s); J is the permeate flux (m/s); R_t , R_m , R_{ir} and R_r are the total hydraulic fouling resistance, intrinsic membrane resistance, hydraulic irreversible fouling resistance and hydraulic reversible fouling resistance (m^{-1}), respectively.

R_m was calculated through the filtration of ultrapure water and the permeate flux was recorded as J_0 , as shown in Eq. (2):

$$R_m = TMP/(\mu J_0) \quad (2)$$

R_t was calculated according to the final permeate flux (J_1) after filtration of water samples, as shown in Eq. (3):

$$R_t = TMP/(\mu J_1) \quad (3)$$

After each hydraulic backwash, the average ultrapure water flux of cleaned membrane was recorded as J_2 . Hence, R_r and R_{ir} were calculated according to Eqs. (4) and (5), respectively.

$$R_r = TMP/(\mu J_1) - TMP/(\mu J_2) \quad (4)$$

$$R_{ir} = R_t - R_m - R_r = TMP/(\mu J_2) - TMP/(\mu J_0) \quad (5)$$

In addition, four classic fouling models, including complete blocking, standard blocking, intermediate blocking and cake filtration (Qu et al., 2014) were employed to better understand the fouling behavior of different NOM fractions.

2.4 Analytical methods

Dissolved organic carbon (DOC) was analyzed using a total organic carbon (TOC) analyzer (multi N/C 2100, Jena, Germany) after filtering the sample by 0.45

177 μm membrane. Ultraviolet absorbance (UV_{254}) was measured using an UV/vis
178 spectrophotometer (T6, Puxi, China) in terms of UV absorbance at the wavelength
179 of 254 nm. The fluorescence excitation-emission matrices (EEMs) of organic matter
180 were characterized by a fluorescence spectrophotometer (F7000, Hitachi, Japan)
181 with a 1 cm cuvette. EEMs were generated by scanning over excitation (Ex)
182 wavelengths of 200-450 nm at 5 nm increments and emission (Em) wavelengths of
183 250-550 nm at 1 nm increments. In order to remove most of the Raman scatter peaks
184 in fluorescence spectra, an EEM of ultrapure water was subtracted from each sample
185 EEM. In addition, the area under the Raman scatter peak (Ex=350 nm and
186 Em=381-426 nm) of an ultrapure water sample (run the same day) was employed for
187 Raman normalization and the obtained fluorescence intensities in this study were in
188 Raman units (R.U., nm^{-1}) ([Murphy et al., 2010](#)). A high-performance size exclusion
189 chromatography with UV detection (HPSEC-UV) was utilized to measure the
190 apparent MW distributions. The measurement was performed using a
191 high-performance liquid chromatograph (HPLC) (Agilent 1200) coupled with a
192 TSK-gel G4000PW_{XL} silica gel column (7.8×300 mm, 10 μm) (TOSOH, Japan).
193 The mobile phase for HPSEC was phosphate buffer solution (0.1 mol/L NaCl, 0.002
194 mol/L K_2HPO_4 and 0.002 mol/L KH_2PO_4 , pH=6.85), and the flow rate was
195 controlled at 0.3 mL/min. More details about the measurement can be found in our
196 previous paper ([Cheng et al., 2016](#)). Moreover, ATZ was also analyzed by the HPLC
197 coupled with a Spherisorb S5 ODS2 column (4.6×250 mm, 5 μm) (Waters, USA)
198 using UV detection at 225 nm. The mobile phase was composed of ultrapure water

and methanol with ratio of 30:70 (v/v) at a flow rate of 1.0 mL/min, and the column temperature was set at 30°C.

3. Results

3.1 Effect of Fe(II)/PMS pretreatment on membrane fouling

3.1.1 HA fouling

The effect of Fe(II)/PMS pretreatment on HA fouling of ceramic UF membrane was investigated and the results are shown in Fig. 1. As illustrated in Fig. 1(a), untreated HA resulted in significant flux decline, and the terminal specific fluxes were reduced to 0.55 and 0.47 during the first and second filtration cycle, respectively. Feed water pretreated by Fe(II)/PMS oxidation with the dose of 15/15 μM obviously improved membrane flux. Increasing the initial concentration of PMS to 50 μM slightly improved the flux and a higher Fe(II) dose (50 μM) led to a greater flux improvement. The flux curve became almost horizontal after treatment by Fe(II)/PMS with the molar ratio of 1:1 (50/50 μM), indicating that best flux improvement was achieved at this dose level, which was comparable to coagulation with 50 μM Fe(III). Under different doses, Fe(II)/PMS pretreatment significantly improved permeate flux with a promotion of terminal specific flux from 0.47 to 0.66-0.93.

Fig. 1

As shown in Fig. 1(b), untreated HA caused most severe reversible and irreversible membrane fouling with the fouling resistance of 0.443 and 0.425×10^{12} m^{-1} , respectively. When the sample was pretreated by Fe(II)/PMS, both reversible

and irreversible fouling significantly reduced by the rate of 23.5%-83.5% and 68.9%-96.5%, respectively. It was suggested that more irreversible fouling was reduced compared with reversible fouling. The reversible fouling resistance of pretreated HA by 50/50 μM Fe(II)/PMS was slightly lower than that of the sample pretreated by 50 μM Fe(III). In addition, the regression results using classic fouling models are shown in [Table 1](#) and [Fig. S3](#). As for untreated HA, the correlation coefficient (R^2) values were 0.682, 0.997, 0.768 and 0.842 for complete blocking, standard blocking, intermediate blocking and cake filtration, respectively, indicating that the main mechanism for flux decline caused by HA was standard blocking. When HA was treated by Fe(II)/PMS prior to filtration, R^2 values for the models significantly increased except for standard blocking, indicating the decreasing roles played by standard blocking. As for HA, Fe(II)/PMS pretreatment exhibited an excellent performance in improving membrane flux, reducing both reversible and irreversible fouling, and decreasing the role of standard blocking.

3.1.2 SA fouling

[Fig. 2\(a\)](#) illustrates that Fe(II)/PMS oxidation dramatically improved the permeate flux in the filtration of SA. The performance improved with the increase of Fe(II)/PMS dose and the best performance was observed at the dose of 50/50 μM , by which the specific flux increased from 0.24 and 0.20 to 0.66 and 0.63 at the end of the first and second cycle, respectively. [Fig. 2\(b\)](#) shows that untreated SA induced more severe reversible fouling compared with irreversible fouling. This result was consistent with previous studies ([Cheng et al., 2016](#); [Li et al., 2014](#)) which reported

that SA mainly caused significant external fouling due to the formation of cake/gel layer. This part of fouling could easily be removed by hydraulic backwash and the flux was recovered immediately. It can also be seen that the reversible fouling gradually decreased with the increase of Fe(II) and PMS doses, whereas the irreversible fouling increased to varying degrees at relatively lower doses and began to decrease until the maximum dose reached. In addition, compared with pretreatment by 50/50 μM Fe(II)/PMS, the same dose of Fe(III) showed similar efficiency in reducing the total fouling resistance. The regression results (Table 1) indicated that the fouling mechanism of untreated SA was mainly ascribed to the combination of standard blocking ($R^2=0.999$) and cake filtration ($R^2=0.998$). After treatment by Fe(II)/PMS, the R^2 values for cake filtration decreased to 0.996 and 0.982, implying that the pretreatment decreased the role of cake filtration. These results indicated that Fe(II)/PMS showed a significant effect for mitigating membrane fouling by SA and decreasing the role of cake filtration, irrespective of the increase of irreversible fouling resistance at lower Fe(II)/PMS doses.

Fig. 2

3.1.3 BSA fouling

As shown in Fig. 3(a), the membrane was severely fouled by untreated BSA and the specific flux rapidly declined in the initial filtration stage. Instead of improving membrane flux, Fe(II)/PMS pretreatment at lower doses caused more serious flux decline. When the Fe(II)/PMS dose increased to 50/50 μM , the permeate flux was improved with a promotion of terminal specific flux from 0.19

and 0.13 to 0.38 and 0.28 during the first and second cycle, respectively. The promotion effect was comparable to single coagulation with 50 μM Fe(III). It can also be seen that the flux was difficult to be recovered through hydraulic backwash. Fig. 3(b) shows that untreated BSA caused both severe reversible and irreversible fouling. Although the total fouling resistance changed with the change of Fe(II)/PMS dose, the distribution of reversible and irreversible fouling changed little. Table 1 shows that standard blocking played a major role in BSA fouling with the R^2 value of 0.995. Fe(II)/PMS pretreatment with the dose of 15/15 μM decreased the R^2 values for complete blocking, intermediate blocking and cake filtration, whereas the dose of 50/50 μM significantly increased the values. The effect of Fe(II)/PMS pretreatment on BSA fouling was closely associated with its dose. Specifically, relatively higher doses of Fe(II)/PMS (under the tested exposure) apparently alleviated membrane fouling, whereas fouling aggravated at lower doses.

Fig. 3

3.1.4 HA-SA-BSA fouling

Since humic substances, polysaccharides and proteins are usually simultaneously present in natural waters, the mixture of HA-SA-BSA was employed to investigate the effect of Fe(II)/PMS pretreatment on the combined fouling. As shown in Fig. 4(a), Fe(II)/PMS dramatically improved the flux and the terminal specific flux increased from 0.15 to 0.40, 0.45, 0.55 and 0.79 with the doses of 15/15, 15/50, 50/15 and 50/50 μM , respectively. Furthermore, Fe(II)/PMS oxidation with the dose of 50/50 μM led to a higher flux improvement than coagulation with 50 μM

Fe(III) (0.64 cf. 0.58). As shown in Fig. 4(b), membrane fouling caused by untreated sample was dominated by reversible fouling, which could be eliminated through hydraulic backwash. All fouling resistances, including the total, reversible and irreversible fouling resistances gradually decreased with the increase of Fe(II)/PMS dose, indicating that Fe(II)/PMS was efficient for alleviating membrane fouling caused by the mixture of HA, SA and BSA. As shown in Table 1, the untreated sample both fit the models of standard blocking ($R^2=0.999$) and cake filtration ($R^2=0.990$). Fe(II)/PMS pretreatment decreased the R^2 values for cake filtration to 0.857 and 0.962, suggesting that the fouling mitigation was mainly ascribed to the removal of cake layer on membrane surface.

Fig. 4

3.2 Characterization of the feed water pretreated by Fe(II)/PMS

3.2.1 DOC and UV₂₅₄

DOC and UV₂₅₄ were tested to characterize the total dissolved organic matter and the organics containing unsaturated bonds or aromatic chromophores (primarily humic substances), respectively (Leenheer and Croué, 2003). The variations of DOC and UV₂₅₄ for the UF feed water treated with Fe(II)/PMS and Fe(III) were examined, and the results are illustrated in Fig. 5. In terms of HA, PMS alone (50 µM) exerted a minor influence on DOC removal. A higher DOC reduction was achieved for the higher Fe(II) dose at the same dose of PMS. With the Fe(II) dose increased from 15 to 50 µM, the DOC removal rate increased from 26.8% to 56.8% and 40.8% to 93.0% under the PMS doses of 15 and 50 µM, respectively. In addition, Fe(II)/PMS showed

a higher efficiency in DOC removal than Fe(III) at the same Fe dose (26.8% cf. 20.0% and 93.0% cf. 86.6%). It seemed that the *in-situ* formed Fe(III) was slightly more effective than the dosed Fe(III) in DOC removal, most likely due to the oxidation by Fe(II)/PMS process. Previous studies (Guan et al., 2009; Lee et al., 2009) also reported similar findings in arsenic and phosphate removals. The DOC removals for SA and the mixture presented similar rules as that of HA. As for BSA, only treatment with 50/50 μM Fe(II)/PMS or 50 μM Fe(III) led to an obvious DOC removal. As shown in Fig. 5(b), the removals of UV_{254} were in similar trends as that of DOC. Under different Fe(II)/PMS doses, the UV_{254} levels were decreased from 0.367 and 0.173 cm^{-1} to 0.014-0.177 and 0.013-0.097 cm^{-1} for HA and the mixture, respectively. These results suggested that Fe(II)/PMS pretreatment led to significant removal of DOC and UV_{254} at proper doses, and the removal rates were slightly higher than by single coagulation with the same dose of Fe(III).

Fig. 5

3.2.2 Fluorescence EEM spectra

To investigate the performance of Fe(II)/PMS and Fe(III) pretreatments for fluorescent components removal, the fluorescence EEM spectra of HA, BSA and the mixture were obtained (Fig. S4). Since polysaccharides cannot be detected using fluorescence spectroscopy (Shao et al., 2014), SA was not investigated here. As shown in Fig. S4, there are three significant peaks in the spectra, including HA/Mixture1 (Ex/Em: 260/430 nm, humic-like substances), BSA1/Mixture2 (Ex/Em: 275/340 nm, tryptophan-like protein substances) and BSA2/Mixture3

(Ex/Em: 225/340 nm, tryptophan-like protein substances) (Chen et al., 2003). The normalized fluorescence intensities of each peak for the UF feed water treated with Fe(II)/PMS and Fe(III) are illustrated in Fig. 6. In terms of humic-like substances, the fluorescence intensities of HA reduced from 0.57 to 0.05, 0.02, 0.25 and 0.12, while that of Mixture1 reduced from 0.39 to 0.06, 0.02, 0.16 and 0.07 after treated with 15/15 μM Fe(II)/PMS, 50/50 μM Fe(II)/PMS, 15 μM Fe(III) and 50 μM Fe(III), respectively. At the same dose of Fe, Fe(II)/PMS oxidation showed significantly better performance in reducing the fluorescence intensities of humic-like and tryptophan-like protein substances than single coagulation with Fe(III). The results suggested the formation of some oxidative radicals during the Fe(II)/PMS process, which reduced fluorescence intensities by changing the fluorescence characteristics of each NOM fraction (discussed in Section 4).

Fig. 6

3.2.3 Size exclusion chromatography

The apparent molecular weight distributions of UV-absorbing compounds in the UF feed water treated with Fe(II)/PMS and Fe(III) were determined by HPSEC-UV (Fig. 7). It should be noted that the UV detector only detects limited components (mostly π bonded molecules) of organic matter, and some molecular size fractions can only be measured using a DOC detector (Her et al., 2002a; Her et al., 2002b). Therefore, the HPSEC-UV method was used only for limited qualitative analysis in this study. The sample of untreated HA contained humic substances, building blocks (breakdown products of humic substances (Henderson et al., 2011))

and low MW organic matter. Besides, the untreated mixture also included biopolymers (high MW substances), which was caused by the addition of protein and polysaccharide. After treatment with Fe(II)/PMS or coagulation, the peaks of humic substances, building blocks and low MW organic matter in both HA and the mixture were significantly reduced, whereas the peak of biopolymers in the mixture disappeared. The results indicated that both Fe(II)/PMS and coagulation were efficient for removing UV-absorbing compounds over a wide MW range. As for Fe(II)/PMS treatment, the overall UV absorbance gradually decreased with the increase of Fe(II)/PMS dose (under the exposure of 15 and 50 μ M). Coagulation with Fe(III) exhibited a similar trend as Fe(II)/PMS oxidation. For both HA and the mixture, the overall UV response of Fe(III) coagulated sample was higher than that of Fe(II)/PMS treated feed water (at the same dose of Fe), indicating that the high UV-absorbing compounds in HA and the mixture were more susceptible to the treatment of Fe(II)/PMS than coagulation by Fe(III).

Fig. 7

3.3 Effect of Fe(II)/PMS pretreatment on ATZ degradation

Due to the high effectiveness for the control of grassy weeds, broad leaf and algae, ATZ (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) has been one of the most widely used herbicides around the world (Graymore et al., 2001). However, ATZ is toxic and harmful to humans and animals, which exhibits a high potential to contaminate the source of drinking water (Nelkenbaum et al., 2009). To this end, ATZ was employed to investigate the oxidation characteristic of Fe(II)/PMS

pretreatment and justify its applicability for water quality control during herbicides pollution.

The concentrations of ATZ in the feed and permeate were measured, and the results are shown in Fig. 8(a). After coagulation with Fe(III) (15 and 50 μ M), the concentrations of ATZ remained unchanged, indicating that coagulation was ineffective for ATZ removal. The result was consistent with previous studies (Alizadeh Tabatabai et al., 2014; Zhang et al., 2015a), which reported that coagulation exerted minor effect on the removal of small organic molecules. PMS alone (50 μ M) exhibited a poor efficiency with the removal rate of less than 9%. By contrast, Fe(II)/PMS oxidation with a dose of 15/15 μ M significantly reduced ATZ concentration with a removal efficiency of 72.2%, and increasing the dose of PMS to 50 μ M led to a higher efficiency (85.6%). However, the removal efficiency significantly decreased to 35.9% when the Fe(II) dose increased to 50 μ M. Similar results were reported by the study of Rastogi et al. (2009b), which showed that excessive Fe(II) could be detrimental for the degradation efficiency of Fe(II)/PMS process. This was caused by the competition of generated radicals between Fe(II) and ATZ, which reduced the concentration of radicals reacted with ATZ. When Fe(II)/PMS dose increased to 50/50 μ M, the removal rate reached up to 98.2% and the residual ATZ was almost undetectable. The permeate ATZ concentration of ceramic UF membrane was slightly lower than that in the feed (the removal rate lower than 10%). Since the molecular size of ATZ (MW=215.68) was much smaller than the pore size of UF membrane, and it was difficult to be rejected by the

membrane through size exclusion, therefore the rejection was likely due to the mechanisms of adsorption or electrostatic repulsion (Li et al., 2014). Considering the low retention rate by single membrane filtration, Fe(II)/PMS pretreatment played an important role in the removal of ATZ.

Fig. 8

In addition, TBA and methanol were employed as radical scavengers to preliminarily identify the species of generated radicals in the Fe(II)/PMS process. TBA was a strong hydroxyl radical ($\cdot\text{OH}$) scavenger due to the high rate constant ($k_{\cdot\text{OH}, \text{TBA}} = 3.8\text{-}7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), whereas it was less sensitive to $\text{SO}_4^{\cdot-}$ ($k_{\text{SO}_4^{\cdot-}, \text{TBA}} = 4.0\text{-}9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) (Cong et al., 2015). By contrast, methanol reacts with both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$. Under the Fe(II)/PMS dose of 50/50 μM , the ATZ removal rate decreased from 98.2% to 43.7% and 32.6% in the presence of 1 mM TBA and 1 mM methanol, respectively (Fig. 8(b)). When the addition of TBA and methanol both increased to 2 mM, the corresponding removal rates further reduced to 36.3% and 26.6%, respectively. Similar result was observed at the Fe(II)/PMS dose of 15/15 μM , suggesting that TBA inhibited the effect of $\cdot\text{OH}$ and methanol inhibited both the effects of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$. This result indicates the presence of both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ in the process of Fe(II)/PMS oxidation.

Besides ATZ, some other trace organics, including sulfamethoxazole, sulfamethazine, sulfamethoxydiazine and *p*-chloronitrobenzene were also investigated. The details about the experiment and the results are shown in Text S1 and Fig. S5, respectively. It can be seen that Fe(II)/PMS pretreatment also

significantly improved the removal efficiencies of these organics, whereas conventional Fe coagulation was ineffective for removing them. The results indicated that the removal performance of Fe(II)/PMS was not restricted to ATZ. The detailed reaction mechanism will be discussed in Section 4.

4. Discussion

The above results demonstrated that Fe(II)/PMS oxidation was a promising pretreatment method to simultaneously control membrane fouling and ensure product water quality for ceramic UF membrane (under appropriate exposure). The principal reactions in the Fe(II)/PMS process and second-order rate constants are summarized in Table 2. Since the flux improvement was comparable or slightly higher than coagulation with Fe(III), the *in-situ* formed Fe(III) (reaction 1) most likely played a major role in fouling mitigation. As shown in Table 3, the PMS concentration decreased rapidly within 1 min and remained nearly constant in the last 20 min, indicating that Fe (III) was formed immediately after the addition of PMS, irrespective of the Fe(II)/PMS dose. This could be interpreted by the fast reactions between Fe(II) and PMS. The molar ratio of Fe(II) and PMS played an important role in PMS consumption and the formation of Fe(III). At the same dose of Fe(II) (50 μM), the residual Fe concentration could be reduced from 27.2 to 4.8 μM with the PMS dose increased from 15 to 50 μM , indicating that PMS was a limiting reagent to produce Fe (III) (Table 3). Excessive Fe(II) or PMS caused the waste of reagents and the optimal molar ratio of Fe(II)/PMS was 1:1.

The *in-situ* formed Fe(III) could be functioned as a coagulant, which was able

to form larger flocs after reacting with water through charge neutralization and sweep-coagulation (Gao et al., 2011). A proper dose of Fe(II)/PMS could reduce the organic loading of feed by forming settable flocs with a larger size, which was much bigger than the pore size of ceramic UF membrane and rejected by the membrane. Accordingly, membrane fouling caused by different NOM fractions was significantly reduced under optimal doses. However, although SA fouling was significantly mitigated, an increase of irreversible fouling resistance was still observed under lower Fe(II)/PMS doses. This was caused by the formation of some micro-flocs, which increased the occurrence of pore blocking/constriction. Due to the narrow MW distribution of BSA, lower doses of Fe(II)/PMS led to the formation of more micro-flocs, which fully blocked membrane pores to cause significant flux reduction. Ma et al. (2014) reported similar results when studying the effect of low dose of coagulant on the performance of UF membrane. As for HA-SA-BSA mixture, since proteins (BSA) could be encapsulated by humic substances (HA) because of the electrostatic attraction (Tan et al., 2008), lower doses of Fe(II)/PMS still improved the membrane flux.

Coagulation with *in-situ* formed Fe(III) efficiently reduced the levels of DOC and UV₂₅₄ of feed water and the organic loadings for ceramic UF membrane, which were responsible for membrane fouling control. Activation of PMS by Fe(II) led to the formation of SO₄^{•-} (reaction 1), which was transformed into [•]OH under alkaline conditions (reaction 2), and [•]OH also reacted with sulfate groups and oxidized them to SO₄^{•-} at strong acidic conditions (reaction 3). Therefore, both SO₄^{•-} and [•]OH were

presented in the Fe(II)/PMS process under the current experimental conditions. Because of the oxidation characteristics, $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ showed better performance in reducing fluorescence intensities of fluorescent components and UV-absorbing compounds than coagulation with Fe(III). In addition, $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ oxidation also contributed to the removal of DOC and UV_{254} levels of the feed water, therefore Fe(II)/PMS pretreatment was slightly more effective than single coagulation in membrane fouling mitigation.

Due to the high reaction rate between the generated radicals and ATZ (reactions 6 and 7), Fe(II)/PMS oxidation was also very effective in ATZ degradation. The reactions of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ with ATZ led to dealkylation and produced some intermediate products, including desethyl-atrazine, desisopropyl-atrazine, acetaldehyde and acetone (Lutze et al., 2015). However, excessive Fe(II) was detrimental for the degradation efficiency of ATZ because it consumed the generated $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ (reactions 4 and 5). As shown in reactions 8 and 9, $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ differ considerably in their reaction rates with HA ($k_{\text{SO}_4^{\cdot-}, \text{HA}} = 6.8 \times 10^3 \text{ L mgC}^{-1} \text{ s}^{-1}$, $k_{\cdot\text{OH}, \text{HA}} = 1.4 \times 10^4 \text{ L mgC}^{-1} \text{ s}^{-1}$). Since $\cdot\text{OH}$ reacts more fast with HA than $\text{SO}_4^{\cdot-}$, ATZ was degraded more efficiently by $\text{SO}_4^{\cdot-}$ than by $\cdot\text{OH}$ in the presence of HA. Due to the higher selectivity of $\text{SO}_4^{\cdot-}$ than $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$ -based AOPs have advantages over common AOPs ($\cdot\text{OH}$ -based) for ATZ degradation in the presence of organic matter. In the Fe(II)/PMS process, $\text{SO}_4^{\cdot-}$ was favorable for destruction of reactive organic contaminants, while $\cdot\text{OH}$ contributed to the degradation of $\text{SO}_4^{\cdot-}$ -refractory organics, this complementarity led to an enhanced efficiency for contaminants degradation. In

terms of coagulation, it was very effective to control membrane fouling caused by high MW organic matter and maintain the permeate flux, whereas ineffective for the removal of micropollutants (e.g. ATZ).

Overall, this study demonstrated that Fe(II)/PMS oxidation was an effective pretreatment for UF process, which simultaneously mitigated membrane fouling by different NOM fractions and controlled permeate water quality during ATZ pollution. However, it should be noted that the results obtained were based on surrogate organic foulants, which might have some discrepancies with real water samples (Li et al., 2014). Moreover, although ceramic membrane is promising for membrane water treatment, polymeric membrane is still the mainstream. To this end, Songhua River water and polyethersulfone membrane were employed to verify the effectiveness of Fe(II)/PMS pretreatment. Fig. S6 shows that although the efficiency of Fe(II)/PMS pretreatment varied with the source of feed water to some extent, it was still effective for mitigating membrane fouling by real water samples. Its effectiveness for polymeric membrane was also verified (Fig. S6), indicating that the value of the pretreatment was not only restricted to ceramic membrane. From the standpoint of full-scale applications, Fe(II)/PMS oxidation is generally considered to be more expensive than traditional coagulation process due to the relatively higher cost of PMS, even though the cost of Fe(II) is lower than Fe(III). In addition, this study was conducted in a batch system, and the obtained results might be inconsistent with continuous operation since the accumulation of organic foulants on the membrane was a long-term process. Therefore, more detailed cost analyses and

continuous operation should be further conducted for its full-scale applications.

5. Conclusions

In this study, the effects of feed water pretreatment by Fe(II)/PMS oxidation on UF membrane fouling control and the characteristics of different NOM fractions were investigated. The effect of Fe(II)/PMS pretreatment for ATZ degradation was also studied to exam its oxidation characteristic. The following conclusions can be drawn:

(1) Fe(II)/PMS pretreatment significantly mitigated membrane fouling caused by HA, SA and HA-SA-BSA mixture, and the performance improved with the increase of Fe(II) or PMS dose (under the exposure of 15 and 50 μM). Lower doses of Fe(II)/PMS aggravated membrane fouling caused by BSA, and fouling mitigation was observed only at a higher dose (50/50 μM). The fouling control performance was comparable or even slightly higher than single coagulation with the same dose of Fe(III), most likely due to the oxidation by Fe(II)/PMS process.

(2) In the process of Fe(II)/PMS, *in-situ* formed Fe(III) played an important role in the reduction of DOC and UV_{254} for different NOM fractions, which were responsible for membrane fouling control. Compared with coagulation by Fe(III), Fe(II)/PMS showed better performance in reducing DOC and UV_{254} , fluorescence intensities of fluorescent components and UV-absorbing compounds.

(3) Fe(II)/PMS was effective in the degradation of ATZ (98.2% at 50/50 μM) due to the presence of both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$, whereas coagulation exerted minor influence on removing it. The retention rate of ATZ by single membrane filtration was lower than 10%, and Fe(II)/PMS pretreatment made major contributions to ATZ

removal.

(4) PMS was a limiting reagent to produce Fe (III) and radicals from Fe (II) oxidation. Excessive Fe(II) or PMS caused the waste of reagents and excessive Fe(II) was also detrimental for ATZ degradation. The molar ratio of 1:1 for Fe(II) and PMS was optimal for both membrane fouling control and ATZ removal.

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688 **Tables**

689 **Table 1** Correlation coefficient (R^2) values of regression analyses for membrane
 690 fouling by different water samples.

NOM fraction	Feed Fe(II)/PMS dose (μM)	Complete blocking	Standard blocking	Intermediate blocking	Cake filtration
HA	0/0	0.682	0.997	0.768	0.842
	15/15	0.857	0.999	0.895	0.927
	50/50	0.955	0.999	0.956	0.957
SA	0/0	0.845	0.999	0.962	0.998
	15/15	0.878	0.998	0.958	0.996
	50/50	0.940	0.999	0.964	0.982
BSA	0/0	0.481	0.995	0.740	0.920
	15/15	0.432	0.981	0.652	0.856
	50/50	0.823	0.999	0.919	0.976
Mixture	0/0	0.609	0.999	0.883	0.990
	15/15	0.615	0.999	0.748	0.857
	50/50	0.947	0.999	0.955	0.962

691

692 **Table 2** Principal reactions in the Fe(II)/PMS process.

No.	Reaction	Rate constant	Reference
1	$\text{Fe}^{2+} + \text{HSO}_5^- \rightarrow \text{Fe}^{3+} + \text{SO}_4^{\cdot-} + \text{OH}^-$	$3.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	(Rastogi et al., 2009b)
2	$\text{SO}_4^{\cdot-} + \text{OH}^- \rightarrow \cdot\text{OH} + \text{SO}_4^{2-}$	$(6.5 \pm 1.0) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	(Ji et al., 2014)
3	$\cdot\text{OH} + \text{SO}_4^{2-} \rightarrow \text{SO}_4^{\cdot-} + \text{OH}^-$	$1.18 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	(Khan et al., 2013)
4	$\text{Fe}^{2+} + \text{SO}_4^{\cdot-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-}$	$3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	(Rastogi et al., 2009b)
5	$\text{Fe}^{2+} + \cdot\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$	$4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	(Khan et al., 2013)
6	$\text{SO}_4^{\cdot-} + \text{ATZ} \rightarrow \text{products}$	$(2.6\text{-}3.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	(Yang et al., 2015)
7	$\cdot\text{OH} + \text{ATZ} \rightarrow \text{products}$	$(2.5\text{-}3.0) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	(Yang et al., 2015)
8	$\text{SO}_4^{\cdot-} + \text{HA} \rightarrow \text{products}$	$6.8 \times 10^3 \text{ L mgC}^{-1} \text{ s}^{-1}$	(Lutze et al., 2015)
9	$\cdot\text{OH} + \text{HA} \rightarrow \text{products}$	$1.4 \times 10^4 \text{ L mgC}^{-1} \text{ s}^{-1}$	(Lutze et al., 2015)

693 **Table 3** PMS consumption with time and residual Fe during Fe(II)/PMS

694 pretreatment. Experimental condition: $[\text{HA}]_0 = 10 \text{ mg/L}$, $\text{pH} = 7.0$.

$[\text{Fe(II)}]_0$ (μM)	$[\text{PMS}]_0$ (μM)	PMS concentration variation with time (μM)				Residual Fe (μM)
		1 min	5 min	10 min	21 min	
15	15	1.6	1.4	1.3	1.3	2.3
15	50	36.2	34.9	34.2	34	1.1
50	15	1.0	ND	ND	ND	27.2
50	50	3.5	3.1	2.8	2.8	4.8

695 ND, not detected.

696

697 **Figure Captions**

698 **Fig. 1** Effects of Fe(II)/PMS pretreatment on membrane fouling by HA: (a) Flux
699 decline and (b) Reversibility. Error bars represent standard deviations (n=3).

700 **Fig. 2** Effects of Fe(II)/PMS pretreatment on membrane fouling by SA: (a) Flux
701 decline and (b) Reversibility.

702 **Fig. 3** Effects of Fe(II)/PMS pretreatment on membrane fouling by BSA: (a) Flux
703 decline and (b) Reversibility.

704 **Fig. 4** Effects of Fe(II)/PMS pretreatment on membrane fouling by HA-SA-BSA
705 mixture: (a) Flux decline and (b) Reversibility.

706 **Fig. 5** DOC (a) and UV_{254} (b) levels of the UF feed water with and without
707 treatment with Fe(II)/PMS and Fe(III) coagulation.

708 **Fig. 6** Fluorescence intensity of each component for the UF feed water with and
709 without treatment with Fe(II)/PMS and Fe(III) coagulation.

710 **Fig. 7** HPSEC chromatograms of the UF feed water with and without treatment with
711 Fe(II)/PMS and Fe(III) coagulation: (a) HA, (b) HA-SA-BSA mixture.

712 **Fig. 8** Removal of ATZ: (a) effect of Fe(II)/PMS and Fe(III) pretreatments on the UF
713 feed and permeate, (b) effect of TBA and methanol on the Fe(II)/PMS process.

714 Conditions: $[ATZ]_0 = 1 \mu M$, $[HA]_0 = 10 \text{ mg/L}$, $pH = 7.0 \pm 0.1$.

Fig. 1 Effects of Fe(II)/PMS pretreatment on membrane fouling by HA: (a) Flux decline and (b) Reversibility. Error bars represent standard deviations (n=3).

Fig. 2 Effects of Fe(II)/PMS pretreatment on membrane fouling by SA: (a) Flux decline and (b) Reversibility.

Fig. 3 Effects of Fe(II)/PMS pretreatment on membrane fouling by BSA: (a) Flux decline and (b) Reversibility.

Fig. 4 Effects of Fe(II)/PMS pretreatment on membrane fouling by HA-SA-BSA

mixture: (a) Flux decline and (b) Reversibility.

Fig. 5 DOC (a) and UV₂₅₄ (b) levels of the UF feed water with and without treatment with Fe(II)/PMS and Fe(III) coagulation.

Fig. 6 Fluorescence intensity of each component for the UF feed water with and without treatment with Fe(II)/PMS and Fe(III) coagulation.

734 **Fig. 7** HPSEC chromatograms of the UF feed water with and without treatment with
735 Fe(II)/PMS and Fe(III) coagulation: (a) HA, (b) HA-SA-BSA mixture.

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Fig. 8 Removal of ATZ: (a) effect of Fe(II)/PMS and Fe(III) pretreatments on the UF feed and permeate, (b) effect of TBA and methanol on the Fe(II)/PMS process. Conditions: $[\text{ATZ}]_0 = 1.0 \mu\text{M}$, $[\text{HA}]_0 = 10.0 \text{ mg/L}$, $\text{pH} = 7.0 \pm 0.1$.

Graphical Abstract