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Cyanobacterium removal and control of algal organic matter (AOM) release by UV/H_2O_2 pre-oxidation enhanced Fe(II) coagulation

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ABSTRACT

Harmful algal blooms in source water are a worldwide issue for drinking water production and safety. UV/H_2O_2, a pre-oxidation process, was firstly applied to enhance Fe(II) coagulation for the removal of *Microcystis aeruginosa* [*M. aeruginosa*, 2.0 (±0.5) × 10^6 cell/mL] in bench scale. It significantly improved both algae cells removal and algal organic matter (AOM) control, compared with UV irradiation alone (254 nm UVC, 5.4 mJ/cm^2). About 94.7% of algae cells were removed after 5 min UV/H_2O_2 pre-treatment with H_2O_2 dose 375 μmol/L, $FeSO_4$ coagulation (dose 125 μmol/L). It was also certified that low residue Fe level and AOM control was simultaneously achieved due to low dose of Fe(II) to settle down the cells as well as the AOM. The result of $L_9(3)^4$ orthogonal experiment demonstrated that H_2O_2 and $FeSO_4$ dose was significantly influenced the algae removal. UV/H_2O_2 induced an increase of intracellular reactive oxidant species (ROS) and a decrease in zeta potential, which might contribute to the algae removal. The total microcystins (MCs) concentration was 1.5 μg/L after UV/H_2O_2 pre-oxidation, however, it could be removed simultaneously with the algae cells and AOM. This study suggested a novel application of UV/H_2O_2-Fe(II) process to promote algae removal and simultaneously control AOM release in source waters, which is a green and promising technology without secondary pollution.

1. Introduction

In 2007, the “green monster” invaded Taihu, China's third largest lake, which provides drinking water for over 2 million people, and turned it into a toxic nightmare while cutting off the normal water supply of Wuxi for 8 days (Guo, 2007). Currently, the “green monster”-cyanobacterial blooms have already become a notorious and serious environmental phenomenon (Paerl and Paul, 2012) and have attracted worldwide concerns, because these blooms are gradually becoming the greatest threat to water quality, public health and aquatic ecosystems (Brooks et al., 2016). *Microcystis aeruginosa* (*M. aeruginosa*), one of the prominent and ubiquitous cyanobacterial species, is the chief culprit of harmful blooms in aquatic environments with eutrophication (Lapointe et al., 2015). During the blooms, *M. aeruginosa* seriously influences water treatment processes by plugging the filtration tanks/membranes. Furthermore, the algal organic matter (AOM) released from algae cells, such as toxins, substances causing taste and odor, and precursors of disinfection by-products (DBPs), can deteriorate water quality and be harmful to humans, animals and aquatic biota (Lui et al., 2011). The effective removal of cyanobacteria is critically important for preventing these issues.

Various methods have been proposed to remove *M. aeruginosa*, such as ultrafiltration (Tan et al., 2008), air flotation (Teixeira and Rosa, 2006), copper sulfate inhibition (Hullebusch et al., 2002), coagulation and sedimentation. Generally, ultrafiltration and air flotation can remove different algae species with high rates of above 90%. However, these methods are usually hindered by the heavy investment and operational cost. Copper sulfate inhibition usually requires large doses, and the residual copper would affect other aquatic biota (Hullebusch et al., 2002). Traditional coagulation and sedimentation is one of the mainstream processes in drinking water plants, but it cannot effectively remove algae due to the low density, high mobility, negatively charged surface and diverse morphology of algae cells (Teixeira and Rosa, 2006). Strategies such as increasing coagulant doses can improve the removal of algae, but may also result in unacceptably high level of coagulant residue, which possibly leads to secondary pollution.

Pre-oxidation is a feasible and popular process to enhance algae removal (Ma et al., 2012a,b). By addition of oxidants, such as Cl_2, O_3,

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$KMnO_4$, ClO_2, persulfate and ferrate, pre-oxidation could assist coagulation by changing zeta potential, destroying the organic coating and inactivating algae cells, resulting in a higher removal efficiency of algae in the subsequent sedimentation (Henderson et al., 2008). For example, ClO_2, Cl_2 and O_3 treatments could increase the removal efficiency of *Chlamydomonas*, *Euglena gracilis* and *Scenedesmus quadricauda*, by 90%, 95% and 99%, respectively (Steynberg et al., 1996; Plummer and Edzwald, 2002). However, most pre-oxidation technologies require a long contact time with algae cells. For instance, to achieve removal efficiencies of 75%, 95.8% and 98.2%, pre-Cl_2, Fe^{2+}-activated persulfate and UV-activated persulfate pre-oxidation methods require 20, 60 and 120 min, respectively (Ma et al., 2012b; Gu et al., 2017; Wang et al., 2016). Moreover, it takes 150 min to settle down 82.3% *M. aeruginosa* cells after pre-oxidation by $KMnO_4$ (Ma et al., 2012a). The longer contact time not only prolongs the treatment process but also increases the risk of releasing undesirable compounds (Lin et al., 2016). Extensive pre-oxidation can cause lysis of algae cells to release the intracellular organic matter (IOM), which can elevate the risk of formation of DBPs and probably inhibit coagulation (Ma et al., 2012a). Therefore, these factors should be carefully considered before applying strong oxidants. Ideal pre-oxidation methods should be moderate to balance the need to avoid extensive pre-oxidation with improving algae removal efficiency. Finally, the addition of some chemical oxidants, such as $KMnO_4$, persulfate and ferrate, could have residual effects, and consequently influence the drinking water quality (Hullebusch et al., 2002). Therefore, developing a new technology aiming to solve the present problems is important and necessary.

Advanced oxidation processes (AOPs) generate strong oxidant-hydroxyl radicals (•OH). They can react rapidly and almost non-selectively with most organic compounds (Liu et al., 2012), therefore have the potential for removing *M. aeruginosa* and AOM at the same time. Combined ultraviolet irradiation (UV, 254 nm UV-C) and H_2O_2 process, as one of AOPs, is widely studied because of its high removal efficiency on contaminants and non-polluting nature (Lee et al., 2017). UV is widely applied in water treatments for its powerful penetration and lethality on cells (Wolfe, 1990). H_2O_2 is a common and widely used chemical for disinfection and water treatment. One of its potential merits compared with other oxidants is environmental friendliness as it degrades to water and oxygen without producing persistent toxic chemicals or byproducts that cause aesthetic odor or color issues. A previous study reported that UV irradiation treatment can effectively impair algae cells and did not involve the addition of any harmful chemicals into water (Tao et al., 2013). It was demonstrated that UV irradiation could inactivate algae by damaging its photosynthesis system, which might exert a positive effect on its removal (Cordi et al., 1997). Alam et al. also found that UV radiation may increase the specific gravity of the cells and thus may adversely affect the ability of the cells to remain in suspension (Alam et al., 2001). Meanwhile, a suitable dose of H_2O_2 could affect the cell integrity of *M. aeruginosa*, cause lipid oxidation and decrease the stability of the cell membrane (Xu et al., 2006; Huo et al., 2015). Therefore, UV/H_2O_2 is expected to be a promising pre-oxidation technology to improve coagulation efficiency for algae removal, due to its strong ability to inactivate algae cells and suppress their growth (Zhang et al., 2017) without any secondary pollution. However, there are no publications investigating UV/H_2O_2 assisted coagulation for algae removal.

In this study, UV/H_2O_2 was firstly used as a pre-oxidation process to assist the subsequent Fe(II)-coagulation-sedimentation process to remove *M. aeruginosa* and AOM. The effects of some critical parameters, including the optimum doses of Fe(II), UV irradiation time, H_2O_2 concentration and reaction time, on the *M. aeruginosa* removal efficiency were investigated. The specific objective is to study the effects of UV/H_2O_2 on the changes in *M. aeruginosa* characteristics including surface properties and the morphology and integrity of cells. The residual Fe concentration after sedimentation was also analyzed to help evaluate the safety of UV/H_2O_2 technology. This study demonstrates that UV/H_2O_2 might be a potential pretreatment process to assist coagulation for the algae removal as well as AOM release control.

2. Materials and methods

2.1. Materials

An axenic strain of *M. aeruginosa* (No. FACHB-905) isolated from Dianchi Lake, China was obtained from the Institute of Hydrobiology, Chinese Academy of Science. All chemicals used in the study were of analytical grade. All solutions were prepared with deionized water. H_2O_2 and ferrous sulfate ($FeSO_4$) solutions were prepared just before experiments.

2.2. Experimental design

2.2.1. Pre-oxidation experiments

The *M. aeruginosa* cells were harvested in the exponential phase and diluted with deionized water to a concentration of 2.0 ($\pm$0.5) $\times$ 10^6 cell/mL. Pre-oxidation experiments were carried out in a cylindrical reactor equipped with a low-pressure UV lamp (254 nm, 8 W, GL Type, XiashiWanhua Co., China) at an average irradiance of 18.0 μW/cm^2 at room temperature (Li et al., 2017).

The UV irradiation time was designed as 0, 1, 4, 5 and 6 min (corresponding to 0, 1.1, 4.3, 5.4 and 6.5 mJ/cm^2) to study the effects of UV doses on algae removal. H_2O_2 pre-oxidation proceeded continuously for 5 min with the different UV irradiation time during the process.

For the contribution of different H_2O_2 concentrations, the H_2O_2 stock solution was added to the reactor containing algae cells to the desired concentrations of 0, 125, 250, 375 and 750 μmol/L, while the pre-treated time of UV/H_2O_2 remained at 5 min.

And for the effects of H_2O_2 pre-oxidation time, 0, 2.5, 5, 10 to 15 min were tested, with the same H_2O_2 dose of 375 μmol/L and UV irradiation for 5 min. For the oxidation time less than 5 min, UV lamp turned on firstly to irradiate 5 min. During the process, H_2O_2 solution stock was dosed to obtain the desired time. On the other hand, H_2O_2 and UV was dosed simultaneously. The UV lamp was turned off after 5 min and H_2O_2 can contact 10 or 15 min.

During all the processes, the solution was homogenized by a magnetic stirrer at a speed of 200 rpm. Samples receiving only stirring but no UV and/or H_2O_2 treatment were set as the control.

2.2.2. Coagulation and sedimentation experiments

After pre-oxidation, 400 mL solution was transferred into a 500 mL beaker immediately. After adding $FeSO_4$ solution into the beaker, coagulation and sedimentation experiments were undertaken using a programmable jar tester (MY3000-6N, Meiyu, China) at room temperature. The reaction solution was rapidly mixed at 250 rpm for 1 min followed by slow mix at 50 rpm for 10 min. After settling for 20 min, clarified supernatant samples were withdrawn from sampling ports 2 cm below the water surface and divided into several subsamples to be analyzed.

2.3. Analytical methods

2.3.1. Density of cells and removal efficiency

M. aeruginosa cell density was determined by optical density at 680 nm (OD_{680}), which was positively correlated to cell number, using a UV–vis spectrophotometer (L6S, Lengguang, China) (Dai

et al., 2009). The removal efficiency was expressed based on the variation in *M. aeruginosa* cell density using the following formula.

$$R = (OD_{680}i - OD_{680}a)/OD_{680}i \times 100\%$$

where $OD_{680}i$ and $OD_{680}a$ are the initial and final density of *M. aeruginosa* cells, respectively.

2.3.2. Determination of K^+ and residual Fe

Measurements of K^+ leaking from *M. aeruginosa* were taken according to the methods of Gu et al. (2017). An inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 8000, PerkinElmer, USA) was used to determine the concentrations of K^+ and residual Fe.

2.3.3. TOC concentration

The supernatant samples were centrifuged at 4000 rpm for 10 min, and then filtered through a cellulose acetate membrane with a pore size of 0.45 μm for the subsequent analysis of total organic carbon (TOC) (TOC-L, Daojin, Japan).

2.3.4. Zeta potential and intracellular reactive oxidant species (ROS) measurement

After pre-oxidation treatments, about 3 mL algae samples were used to analyze the changes of zeta potential (Zetasizer Nano, England). Another 10 mL algae suspension was sampled and immediately added to $Na_2S_2O_3$ to terminate reactions. Then, 1.0 μL of 2′,7′-dichlorofluorescein diacetate (DCFH-DA) solution was immediately added to these treated cultures to the final concentration of 100 μM. The samples were incubated at room temperature in the dark for 1 h, and then measured using a fluorescence spectrophotometer (F-97, Lengguang, China) with an Ex/Em = 498/522 (Rastogi et al., 2010; Jia et al., 2017). The signal strength of the control was subtracted from those of the treated samples, and the results were taken as the indication of ROS levels in algae cells induced by oxidation or irritation. The ROS level in this study especially refers to intracellular ROS.

2.3.5. Scanning electron microscopy (SEM)

The treated and control groups of the *M. aeruginosa* cells suspension were centrifuged at 4000 rpm for 10 min, and the supernatant was discarded. The precipitates were retained for SEM analysis (VEGA TS 5136 MM, TESCAN Brno s.r.o., Czech Republic).

2.3.6. Microcystins (MCs) concentration

Samples from various stages, including before pre-oxidation, after pre-oxidation but before coaugulation, and after coaugulation were centrifuged at 4000 rpm for 10 min. The supernatant was filtered through a 0.22 μm pore size membrane filter to obtain an extracellular MCs sample. The total MCs concentrations were evaluated using the enzyme-linked immunosorbent assay (ELISA) method with the kit (Product No. 520011, Abraxis, Warminster, PA) (Metcalf et al., 2000). All analyses were conducted in triplicate.

3. Results and discussion

3.1. Comparison of UV, H_2O_2 and UV/H_2O_2 pre-oxidation on *M. aeruginosa* removal

Fig. 1 shows the removal rates of *M. aeruginosa* after Fe(II) coagulation enhanced by different pre-treatments. Three methods were employed, i.e. UV alone (5 min), H_2O_2 (375 μmol/L for 5 min), and their combination (5 min), and the Fe(II) concentration was varied from 75 to 175 μmol/L. An approximate removal rate of 1.8% was observed with UV irradiation at different Fe(II) doses,

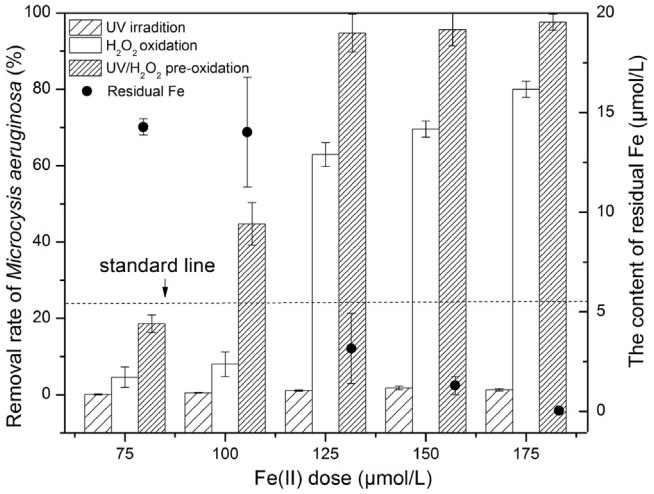

Fig. 1. Comparison of three pre-treatments on *Microcystis aeruginosa* removal rate and residual Fe under UV/H_2O_2-Fe(II) at different Fe(II) dose. The time for three pre-treatments is 5 min. Initial algae cell density: 2.0 (±0.5) × 10^6 cells/mL. H_2O_2 dose 375 μmol/L. The error bars represent the standard deviations from duplicate tests. The standard line is the Fe content in drinking water.

indicating UV irradiation alone could not promote the removal rate significantly within 5 min. The removal rate was improved from 4.5% to 80.0% by H_2O_2 alone when the initial Fe(II) dose increased from 75 to 175 μmol/L. However, this seemed to be limited for H_2O_2 pre-oxidation alone under these conditions. It may be higher with an increased Fe(II) dose, but that would increase the cost and possibly cause secondary pollution in water. Fig. 1 shows that the UV/H_2O_2 pretreatment achieved removal efficiencies of 94.7%, 95.7% and 97.6% with Fe(II) doses of 125, 150 and 175 μmol/L, respectively. Although the removal efficiency improved slightly when the dose increased from 125 to 175 μmol/L, it was accompanied by 40% increase in Fe(II) dosage. Therefore, taking economic cost into account, an optimum Fe(II) dose was found to be 125 μmol/L. Furthermore, the Fe(II) dosage in the study was less than that of published reports. For instance, a dose of 197.4 μmol/L of Fe(II) was required to remove 89.7% of *M. aeruginosa* with a density of 1 × 10^6 cells/mL when using $KMnO_4$ pre-oxidation (Ma et al., 2012a). Consequently, compared with the other two pre-treatments, it could be easily concluded that the UV/H_2O_2 process could efficiently enhance the coagulation-sedimentation process to remove algae cells (over 94.7%) with a lower Fe(II) dose within 5 min.

H_2O_2 is a common oxidant and decomposes into water and oxygen gas spontaneously, and the reaction is shown in Equation (1) below (Zuorro et al., 2013). H_2O_2 could affect cell surface charge and morphology to cause the cells to settle down easily in the subsequent coagulation (Equation (2)) (Barroin and Feuillade, 1986) ('cell*' represents the algae cells oxidized by H_2O_2). In the subsequent Fe(II) coagulation process, the residual H_2O_2 could react with Fe(II), which not only avoids extensive oxidation, but also simultaneously forming in situ Fe(III). This is the well known Fenton reaction, whose mechanisms are presented in Equations (3) and (4). It was reported that the in situ Fe(III) has larger reactive surface area and can be continuously introduced as fresh coagulant. Such a method has been suggested to benefit the growth of flocs, and remove algae more effectively than Fe(II) and one-off dosing of Fe(III) (Ma et al., 2012a). Therefore, the algae removal rate of H_2O_2-enhanced Fe(II) coagulation was higher than that of UV irradiation, due to its greater inactivation of algae cells and production of more in situ Fe(III).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (1)$$

$$H_2O_2 + \text{cell} \rightarrow \text{cell}^* + \text{AOM} \quad (2)$$

$$Fe(II) + H_2O_2 \rightarrow \text{in situ } Fe(III) + OH^- + {\bullet}OH \quad (3)$$

$$Fe(II) + {\bullet}OH \rightarrow \text{in situ } Fe(III) + H_2O \quad (4)$$

The UV/H_2O_2 process is one of the AOPs which can produce hydroxyl radicals, an oxidant with a stronger oxidation capacity than H_2O_2. The reactions are shown in Equations (5)–(7) (Tureli et al., 2010). Some of the hydroxyl radicals could be induced by the direct UV photolysis of H_2O_2 (at $\lambda = 200–280$ nm), while some was produced through the subsequent reactions shown in Equations (5)–(7). When UV is applied together with H_2O_2, the hydroxyl radicals produced can impact the algae cells more significantly than H_2O_2 alone, as shown in Equation (8) (The 'cell**' represents the algae cells inactivated by hydroxyl radicals during the UV/H_2O_2 process). In this process, Fenton reaction also occurs according to Equations (3) and (4), which benefit the subsequent coagulation. Therefore, UV/H_2O_2 as pre-oxidation can enhance coagulation and remove algae more efficiently than UV or H_2O_2.

$$H_2O_2 + h\nu \rightarrow 2\ {\bullet}OH \quad (5)$$

$${\bullet}OH + H_2O_2 \rightarrow H_2O + {\bullet}HOO \quad (6)$$

$${\bullet}HOO + H_2O_2 \rightarrow H_2O + {\bullet}OH + O_2 \quad (7)$$

$${\bullet}OH + \text{cell} \rightarrow \text{cell}^{**} + \text{AOM} \quad (8)$$

The variations of residual Fe with different Fe(II) doses after UV/H_2O_2 pre-oxidation enhanced Fe(II) coagulation are presented in Fig. 1. The residual Fe decreased rather than increased with the increase of initial Fe addition. They were lower than the standard of Fe in drinking water (5.4 μmol/L, GB5749-2006), with values of 3.2, 1.3 and 0.04 μmol/L under the coagulant doses of 125, 150 and 175 μmol/L, respectively. The results are consistent with Ma et al. (2012b), who also demonstrated that the residual alum decreased with the increase of initial alum dose when using pre-chlorination. Some studies suggested that this phenomenon might be related to AOM released from *M. aeruginosa*. In water, the AOM, especially those with a high protein content, can make contact with coagulants to form protein-coagulant complexes (Pivokonsky et al., 2006). When less coagulant is added, the AOM would hinder the cross-linking and clustering of Fe-hydroxide polymers (Jekel and Heinzmann, 1989). In contrast, sufficient coagulants benefit the cross-linking and clustering of Fe-hydroxide polymers to settle down with the Fe coagulant. The results demonstrated that UV/H_2O_2 enhanced Fe(II) coagulation could efficiently remove *M. aeruginosa* in water, with less coagulant dosage and without secondary pollution, which is a green and promising technology.

3.2. Evaluation of different process parameters on M. aeruginosa removal

3.2.1. Contribution of UV irradiation

Fig. 2 shows the contribution of UV irradiation time from 0 to 6 min (0, 1.1, 4.3, 5.4 and 6.5 mJ/cm^2) to *M. aeruginosa* removal in the Fe(II) coagulation-sedimentation process (H_2O_2 dose 375 μmol/L, Fe(II) dose 125 μmol/L). H_2O_2 pre-oxidation time was fixed at 5 min continuously, and the UV lamp was turned on earlier or later to obtained the desired treatment time. The removal rate was enhanced from 62.9% to 94.7% when the UV irradiation time was prolonged from 0 to 5 min, while that of 6 min decreased slightly.

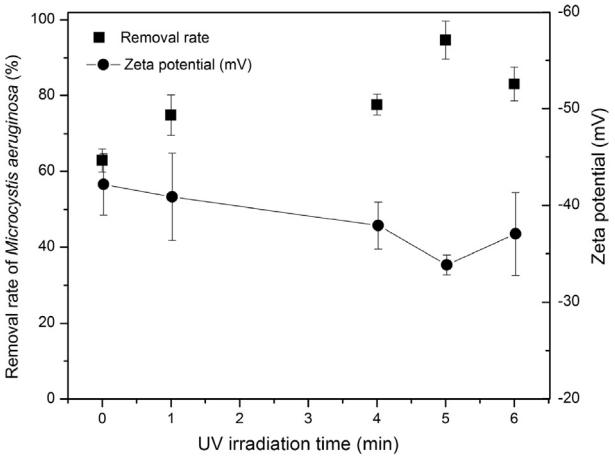

Fig. 2. The variations of removal rates and zeta potentials with UV irradiation time. Initial algae cell density: 2.0 (±0.5) × 10^6 cells/mL. H_2O_2 dose 375 μmol/L. $FeSO_4$ dose 125 μmol/L. Initial zeta potential: −53.5 mV. The H_2O_2 pre-oxidation continuously proceeded to 5 min with different UV irradiation time. The error bars represent the standard deviations from duplicate tests.

This indicates that an appropriate time of UV irradiation improves the removal rate.

Alam et al. found that UV radiation may increase the specific gravity of the cells, and thus may adversely affect the ability of the cells to remain in suspension (Alam et al., 2001). Fig. 1 demonstrated that *M. aeruginosa* cells were not removed efficiently by UV alone. However, Fig. 2 indicates that the algae cells were removed at a relatively low rate under lower UV irradiation with H_2O_2, while a higher removal rate could be achieved by increasing the UV irradiation time. A similar result was obtained by Ou et al. (2011) that different UV irradiation had different impact on algae cells. But in this study, the effect of UV was further enhanced by H_2O_2 pre-oxidation. The higher removal efficiency was attributed to the synergistic effects of UV/H_2O_2, which can produce hydroxyl radicals [shown in Equations (5)–(7)], to inactive the cells more effectively. And in the coagulation process, the inactive cells could be well settled down by the in situ Fe(III).

It is reported that the decreases in the absolute value of cells' zeta potential by pre-oxidation are vital to improve coagulation (Chen and Yeh, 2005). In Fig. 2, the zeta potential indicates a constantly decreasing tendency when the UV irradiation time increased from 0 to 5 min. In contrast, a slight increase was observed from 5 to 6 min. The surface of algae cells using only H_2O_2 treatment (375 μmol/L for 5 min, UV irradiation for 0 min) was highly negatively charged, with a zeta potential of −54.5 mV. The surface of 5 min sample, on the other hand, was neutralized to −33.8 mV by 5.4 mJ/cm^2 of UV/H_2O_2. Therefore, UV/H_2O_2 pre-oxidation did decrease the zeta potential of algae cells, which probably led to better performance in coagulation and sedimentation, and the effect was positively correlated with pre-oxidation time to certain extent. Therefore, when appropriate H_2O_2 dose is added, UV irradiation was an important factor affecting the removal rate, by directly increasing the specific gravity and decreasing the zeta potential.

Different pre-oxidation treatments have various effects on the zeta potential of algae cells. It was reported that permanganate pre-oxidation and pre-chlorination didn't have an obvious effect on the surface charge of *M. aeruginosa* cells (Chen and Yeh, 2005). However, UV/persulfate (PS) pretreatment could effectively change the surface properties of the cells (Chen et al., 2017). It was also found

that ozone caused a reduction in the electrophoretic mobility of *Scenedesmus* cells, perhaps due in part to the changes in the exterior portions of the cells wall (Lee et al., 2017). At this point, it can be inferred that UV irradiation with H_2O_2 oxidation altered the outside membrane of *M. aeruginosa*, which was to some extent reflected by the changes in zeta potential. Furthermore, UV/H_2O_2 pre-oxidation as well as UV/PS and ozone have a greater influence on the outside of the algae membrane than permanganate pre-oxidation and pre-chlorination.

3.2.2. Contribution of H_2O_2 concentration on *M. aeruginosa* removal

The algae cell integrity could be destroyed after being exposed to a large dose of H_2O_2 for a long time (Huo et al., 2015). Therefore, it was necessary to explore the optimum H_2O_2 dose that could be used as moderate pre-oxidation to assist in removing algae and to simultaneously control the AOM release. As shown in Fig. 3, the effects of H_2O_2 concentration from 0 to 750 μmol/L on *M. aeruginosa* removal with the Fe(II) coagulation-sedimentation process were investigated. The UV irradiation without H_2O_2 barely enhanced the coagulation process, and the removal rate of *M. aeruginosa* was approximately 1.1%. The removal rate remarkably increased from 1.1% to 94.7% with increasing H_2O_2 doses to 375 μmol/L, but then decreased to 90.9% under 750 μmol/L H_2O_2. The TOC in the supernatant after coagulation-sedimentation was also presented in Fig. 3. It could be seen that TOC decreased with increasing H_2O_2 doses, and all fell below 1.4 mg/L, which was lower than the safety level in drinking water (5 mg/L, GB5749-2006).

Fig. 3 presents that the optimum H_2O_2 dose was 375 μmol/L. An excessive H_2O_2 dose would probably destroy the cells in the pre-oxidation process, which might make the algae cells difficult to settle down. In addition, the excessive H_2O_2 might decompose to O_2, which would impact the settlement of the algae cells in the coagulation-sedimentation process. During the experiments, it was observed that gas bubbles were produced in the mixed solution with higher H_2O_2 doses. Furthermore, it is reported that the decomposition rate of H_2O_2 is greater with increasing H_2O_2 concentration (Zuorro et al., 2013). Therefore, higher H_2O_2 dose would pose a negative effect on both processes. On the other hand, an H_2O_2 dose less than 375 μmol/L could be insufficient to react with Fe(II), which would directly decrease the algae removal rate.

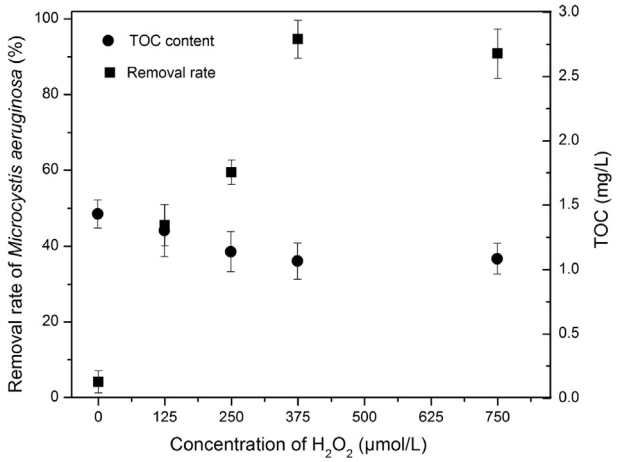

Fig. 3. Effects of H_2O_2 concentration on *Microcystis aeruginosa* and TOC removal. Initial algae cell density: 2.0 (±0.5) × 10^6 cells/mL. UV irradiation combined with H_2O_2 pre-oxidation for 5 min $FeSO_4$ dose of 125 μmol/L. The error bars represent the standard deviations from duplicate tests.

3.2.3. Contribution of H_2O_2 pre-oxidation time on *M. aeruginosa* removal

The effects of H_2O_2 pre-oxidation time on *M. aeruginosa* removal were also illustrated (Fig. 4). The UV irradiation time was fixed at 5 min, while H_2O_2 pre-oxidation time varied from 0 to 15 min. UV/H_2O_2 combination inactivated *M. aeruginosa* cells, and the residual H_2O_2 oxidized Fe(II) to form in situ Fe(III), which can remove cells effectively. The removal rate notably increased from 48.7% to 94.7% when the H_2O_2 treatment time was prolonged from 0 to 5 min, while a decline was observed with longer treatment time. The residual Fe content is also presented in Fig. 4. It increased with the prolonging of H_2O_2 contact time, and was 3.2 and 37.5 μmol/L when reacting for 5 and 15 min, respectively. The variation in residual Fe may be related to AOM release caused by the long time H_2O_2 oxidation.

Fig. 4 shows that the optimum contact time is a vital factor influencing the removal rate, and there is a balance between the amount of H_2O_2 consumed in the pre-oxidation process and that in the coagulation process. The short pre-oxidation time (less than 5 min) would directly lead to insufficient contact between hydroxyl radicals and algae cells in the pre-oxidation process, and excessive H_2O_2 in the coagulation-sedimentation process. This insufficient contact would result in less inactivation of *M. aeruginosa* cells, which limits its assistance in the coagulation-sedimentation process. The excessive H_2O_2, reacting with a finite amount of Fe(II), could cause residual H_2O_2 in the coagulation-sedimentation process. It might stimulate the self-decomposition of H_2O_2 to generate O_2. The gas rises from the mixed solution in the direction opposite to sedimentation, which hinders the growth and sedimentation of flocs. On the other hand, if the contact time is too long, more hydroxyl radicals and H_2O_2 can engage in the inactivation of *M. aeruginosa* cells in the pre-oxidation process, leaving insufficient dosage to oxidize Fe(II) in the coagulation-sedimentation process.

In addition, the individual contributions of $FeSO_4$ dosage, H_2O_2 dosage, UV irradiation time and H_2O_2 oxidation time on the *M. aeruginosa* removal efficiency were investigated by single factor analysis. The optimum process parameters were determined by an $L_9(3)^4$ orthogonal experiment, as shown in Table S1. The regression coefficient R in Table S1 ranged from high to low in the following order: H_2O_2 dose > $FeSO_4$ dose > UV irradiation time > H_2O_2

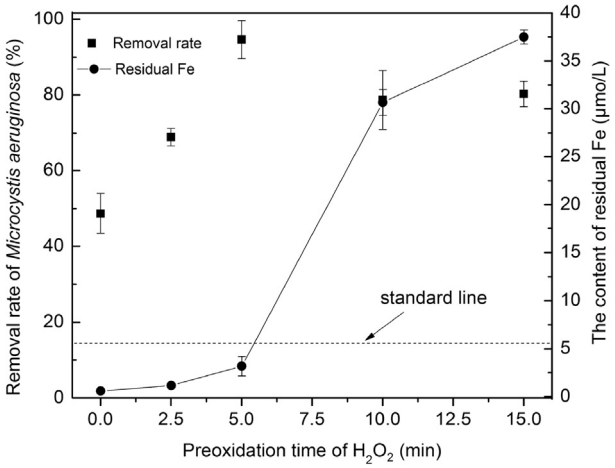

Fig. 4. Effects of H_2O_2 pre-oxidation time on *Microcystis aeruginosa* removal and residual Fe content. ▲: Removal rate. Initial algae cell density: 2.0 (±0.5) × 10^6 cells/mL. UV irradiation time maintained for 5 min while H_2O_2 pre-oxidation time varied from 0 to 15 min H_2O_2 dose 375 μmol/L. $FeSO_4$ dose 125 μmol/L. The error bars represent the standard deviations from duplicate tests. The standard line is the Fe content in drinking water.

oxidation time, which demonstrated that the $FeSO_4$ dose and H_2O_2 dose significantly influenced the removal efficiency. Table S1 indicates that the optimal level requires 175 μmol/L of $FeSO_4$ and 750 μmol/L of H_2O_2 ($A_9B_6C_1D_1$). However, considering both economic and time costs, the optimal conditions for *M. aeruginosa* removal are considered as 125 μmol/L of $FeSO_4$, 375 μmol/L of H_2O_2, and UV irradiation combined with H_2O_2 oxidation for 5 min ($A_1B_1C_1D_1$). The F-ratio was used in the variance test to evaluate whether the impact factors were statistically significant (Wang et al., 2016). The F-values indicated that the order of effects was consistent between the variance analysis and intuitive analysis.

3.3. Effects of pre-oxidation on the physiology of M. aeruginosa

To further understand the effects of UV irradiation only, H_2O_2 pre-oxidation only and UV/H_2O_2 on *M. aeruginosa*, the change in physiological characteristics after pre-oxidation was investigated.

3.3.1. Morphology of M. aeruginosa

The effects of different pre-oxidation processes on the morphology of *M. aeruginosa* cells were determined by SEM. Fig. 5 gives a fairly clear view of the cells morphology changes with SEM images after pre-treatments. Fig. 5(a) presents the spherical shapes and smooth surfaces of *M. aeruginosa* cells, which are in accordance with other studies (Ma et al., 2012b). When *M. aeruginosa* cells were treated with UV irradiation for 5 min (5.4 mJ/cm^2), the majority of algae cells were still spherical and intact, but some of the cell walls began to wrinkle [seen in Fig. 5(b)]. This was also in accordance with Wang et al. (2015). In addition to the effects on *M. aeruginosa*, similar results were reported in the diatom *Cyclotella spec.*, green algae *Micrasterias*, red macroalgae and *Palmaria palmata* and *Odonthalia dentata* (Meindl and Lütz, 1996). However, Fig. 5(c) shows that in the presence of H_2O_2 (375 μmol/L dose), some of the cells appeared to be distorted with cell inclusion leaking. When they were exposed to UV/H_2O_2 for 5 min, the spherical surface of a small number of algae cells was damaged with a remarkable alteration in morphology, resulting in the leakage of intracellular materials [Fig. 5(d)]. This indicated that UV/H_2O_2 pre-oxidation process could alter the morphology of a small number of *M. aeruginosa* cells to the greatest extent, compared with UV irradiation and H_2O_2 oxidation alone.

A previous study reported that UV/PS treatment could lead to the complete loss of the cellular structure within 120 min (Wang et al., 2016). In addition, discharge plasma oxidation could cause the majority of algae cells to show extensive damage to the cell membrane after exposure for 10 min (Zhang et al., 2014). Compared with these oxidation methods, the UV/H_2O_2 pre-oxidation process was more moderate and effective. This process could affect algae cells within 5 min, and cause morphology alteration on only a small scale, which is significant for the control of AOM and MCs release.

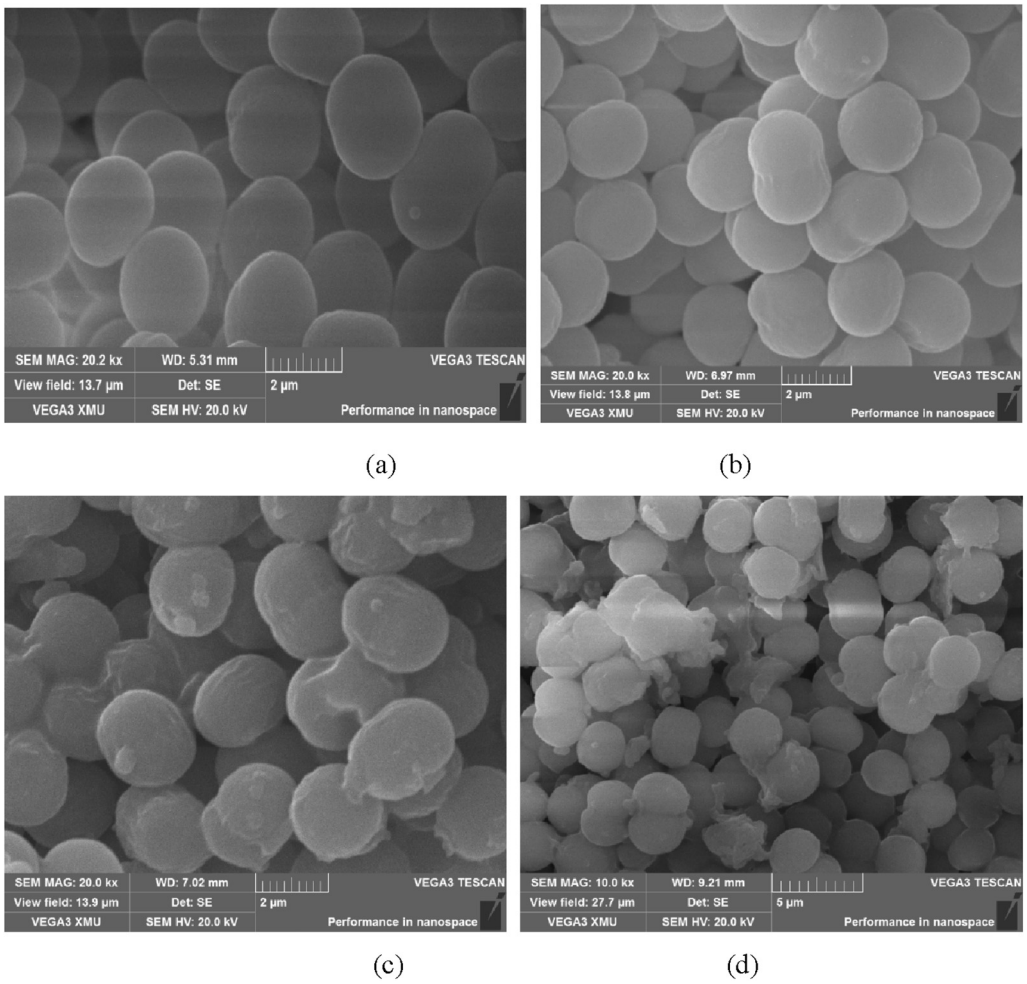

Fig. 5. SEM images of *Microcystis aeruginosa* after pre-treatments. (a) Control group, (b) UV irradiation, (c) H_2O_2 pre-oxidation, (d) UV/H_2O_2 pre-oxidation. Initial algae cell density: 2.0 (±0.5) × 10^6 cells/mL.

3.3.2. K^+ release

Potassium (K) is a key element in the cell membrane of *M. aeruginosa* (Gu et al., 2017). Consequently, the extent of cell membrane integrity can be evaluated using the level of K^+ released from cells. Therefore, the damage to cell membrane by various treatments was indicated using K^+ release (Fig. 6). The treatments were ranked in terms of K^+ release as follows: UV/H_2O_2 > H_2O_2 > UV irradiation > control. The greatest damage to cells was caused by UV/H_2O_2 pre-oxidation, as shown by the maximum amount of K^+ released, which is in accordance to the change of cell morphology (Fig. 5). It was reported that 62.6% K^+ was released from *M. aeruginosa* cells by a $Na_2S_2O_8$ and $FeSO_4$ activation system (Wang et al., 2016), which was in agreement with the present results (approximately 62.0% K^+ released).

3.3.3. Intracellular ROS level

Some ROS could be produced by algae cells during normal metabolism, and are involved in the regulation of many physiological processes (Rastogi et al., 2010). Moreover, the intracellular ROS level is as an indicator of cell stress and is used to evaluate the level of stress or even damage in cells (He and Häder, 2002). The intracellular ROS production could be stimulated by various environmental stresses such as exposure to UV irradiation (including UV-B, UV-A) (He and Häder, 2002), and some chemical substances (such as methyl jasmonate, sulfathiazole and anthraquinone) (Kim et al., 2009). Elevated levels of intracellular ROS are highly deleterious to cell structures and functions, and can alter or inactivate their biochemical functions (Alam et al., 2001; He and Häder, 2002). In this study, the changes of intracellular ROS under different treatments are presented in Fig. 7. The UV/H_2O_2 pre-oxidation resulted in the highest intracellular ROS level, compared with UV irradiation and H_2O_2 pre-oxidation alone. The values of DCF-fluorescence were 235 and 113 after UV irradiation and H_2O_2 pre-oxidation, respectively, while it increased to 1057 after UV/H_2O_2 pre-oxidation. The results indicated that UV/H_2O_2 pre-oxidation had synergistic effects, that could interfere with normal metabolism and inactivate the cells. When cells were exposed to a UV/H_2O_2 environment, oxidative damage to lipids/proteins by H_2O_2 could cause serious conformational changes in the cytomembrane, which improved H_2O_2 diffusion and the subsequent UV penetration (Wang et al., 2015). Such processes induced more production of intracellular ROS, which in turn further increases the damage to cell structure and impair cellular activity.

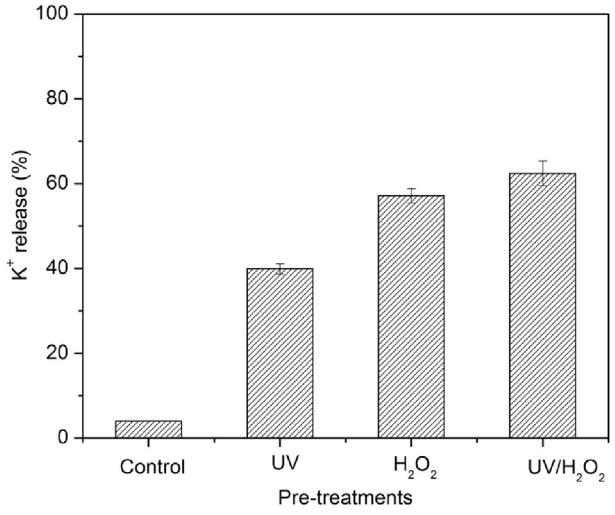

Fig. 6. Release of K^+ under different pre-treatments. Initial algae cell density: 2.0 (±0.5) × 10^6 cells/mL. UV irradiation time 5 min H_2O_2 dose 375 μmol/L. H_2O_2 pre-oxidation 5 min. The error bars represent the standard deviations from duplicate tests.

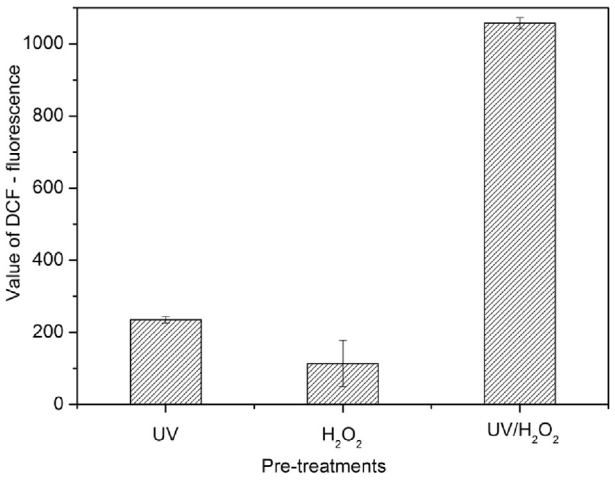

Fig. 7. Changes of intracellular ROS (measured by value of DCF-fluorescence) with different pre-treatments. Initial algae cell density: 2.0 (±0.5) × 10^6 cells/mL. UV irradiation time: 5 min H_2O_2 dose 375 μmol/L. H_2O_2 pre-oxidation for 5 min. The error bars represent the standard deviations from duplicate tests.

3.4. AOM release and control

3.4.1. TOC changes and control

Fig. 8 shows the TOC changes in *M. aeruginosa* suspensions during different treatments. For samples after pre-treatments, the lowest value of TOC was observed with UV irradiation alone for 5 min (1.3 mg/L), indicating that UV-induced release of AOM was limited. This phenomenon also demonstrated that UV irradiation only produced limited damage on the structure of *M. aeruginosa* cells (Wang et al., 2016). The results were verified by the change of cells morphology shown in Fig. 5(b). It was mentioned before that the algae removal rate was only 1.1% using the UV irradiation alone. The TOC results further demonstrate that AOM could not effectively settle down using Fe(II) coagulation either enhanced by UV alone. In contrast, after H_2O_2 and UV/H_2O_2 pre-oxidation, TOC were 1.6

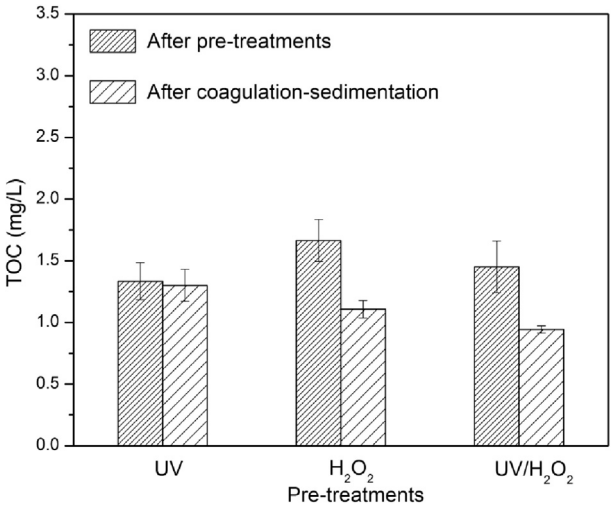

Fig. 8. Changes of TOC with different pre-treatments. Initial algae cell density: 2.0 (±0.5) × 10^6 cells/mL. UV irradiation time 5 min H_2O_2 dose 375 μmol/L. H_2O_2 pre-oxidation 5 min $FeSO_4$ dose 125 μmol/L. The error bars represent the standard deviations from duplicate tests.

and 1.4 mg/L, respectively. However, these two pre-treatments resulted in lower TOC levels than UV after coagulation-sedimentation. H_2O_2 and UV/H_2O_2 pre-oxidation could enhance Fe(II) coagulation to improve cell removal rates to 80.0% and 94.7%, respectively (section 3.1). In addition, TOC was lower than 1.0 mg/L after the UV/H_2O_2-Fe(II) process, possibly because of the in situ Fe(III) formed, which can settle down the cells and TOC simultaneously. A previous study also proved that organic matter could be degraded by the hydroxyl radicals produced during the Fenton reaction (Wang et al., 2016). Therefore, AOM degradation by the hydroxyl radicals induced during the Fenton reaction could also occur, leading to a further decrease in TOC.

Fig. 3 also shows the variations of TOC with the different concentration of H_2O_2 after sedimentation. Without H_2O_2, the TOC level was the highest among all the samples, a value similar to that shown in Fig. 8. With increasing H_2O_2 concentration, a declining trend was observed for the TOC level, strongly suggesting that the reduction of TOC was caused by more hydroxyl radicals under UV/H_2O_2 combination.

The guideline for TOC in drinking is different in different countries. In China, the standard level for TOC in drinking water is 5 mg/L (GB5749-2006), while it is 4 mg/L in America and Germany (Guidelines for feed water, 2011). In any event, TOC after Fe(II) coagulation-sedimentation in this study met the guidelines.

3.4.2. Release and control of MCs

The concentrations of MCs in water before and after coagulation are shown in Table 1. MCs were released from *M. aeruginosa* cells after pre-treatments, but degraded or settled down in the subsequent coagulation process. The MCs could be effectively removed from water and their potential threat was eliminated totally by the pre-oxidation enhanced Fe(II) coagulation.

MCs are intracellular chemical compounds that can be released into the bulk liquid when algae cells are stressed or dead (Sakai et al., 2009). According to the SEM images, a very small portion of algae cells showed alteration on the cells surface after UV irradiation. It was possible that some cells are negatively affect or even killed, leading to release of MCs. As shown in Table 1, it is interesting that the MCs concentrations with H_2O_2 and UV/H_2O_2 pre-oxidation were lower than that of UV irradiation. One possible reason is that UV/H_2O_2 provided abundant H_2O_2 and hydroxyl radicals, which degraded MCs by oxidation. This observation is supported by a previous study (He et al., 2012).

Furthermore, after pretreatments, MCs can be further removed through degradation or sedimentation with the formation and growth of the flocs in the coagulation-sedimentation process. The final MCs levels were all below 0.1 μg/L for all the three treatments. Therefore, UV irradiation alone was accompanied by negligible algae and TOC removal, but could achieve high MCs elimination. Attempts have been made to shed light on this phenomenon. Some researchers have reported that extracellular polymeric substances (EPS), which mainly consist of polysaccharides, proteins and some macromolecular carbohydrates such as DNA, lipids and humic substances, can act as photosensitizers (Hessen and Donk, 1994; Alam et al., 2001). When UV irradiates on algae cells, their EPS maybe turn into photosensitizers, which have a long-lasting residual oxidizing ability (Alam et al., 2001). During coagulation, the residual oxidative effect from UV irradiation might continue to degrade the MCs. Therefore, even though these MCs could not be settled with cells, they could be eliminated in UV pre-treated samples. After MCs degradation, the EPS photosensitizers could not be degraded themselves and revert to their original forms. Such compounds were not removed due to the poor coagulation efficiency. Therefore, the TOC in water is higher with UV irradiation-Fe(II) coagulation, as shown in Fig. 8.

During the UV/H_2O_2-Fe(II) process, the subsequent addition of Fe(II) stimulated Fenton reaction, where the residual H_2O_2 oxidized Fe(II) to form in situ Fe(III) and degrade the AOM and MCs. Meanwhile, the in situ Fe(III) may not only hydrolyze to form Fe-AOM complexes, but also attach and bind to the negatively charged cell surfaces. Therefore, it was more effective to promote the growth and settlement of flocs, resulting in a high removal rate of *M. aeruginosa* cells, AOM and MCs. On the other hand, the hydroxyl radicals induced during Fenton reaction could degrade the AOM, especially the MCs, leading to a further decrease in TOC and MCs.

The significant finding of the present work is that UV/H_2O_2 could effectively inactivate *M. aeruginosa* cells without large-scale cell damage, and the cells and AOM could be simultaneously and efficiently removed without secondary pollution. Additionally, the degradation and the settlement of AOM and MCs both contributed to their decrease in water, which was probably due to Fenton reaction. The effects and significance of this process is being studied in detail, to give a clearer view on the mechanism of UV/H_2O_2-Fe(II) process.

4. Conclusion

The UV/H_2O_2-Fe(II) process is demonstrated to be a highly effective technology for the removal of *M. aeruginosa* cells without secondary pollution. This is attributed to the combined effects of UV/H_2O_2 pre-oxidation and the continuous formation of in situ Fe(III) in the UV/H_2O_2-Fe(II) process. The results have verified that it is a green and promising technology, which is indicated by the higher removal rate of *M. aeruginosa* (94.7%) and lower Fe(II) dosage (125 μmol/L) as well as lower TOC and Fe residuals in water. The optimum pre-oxidation is moderate, which can effectively inactive cells and avoid the extensive oxidation leading to the release of large amounts of AOM and MCs. Furthermore, in situ Fe(III) was likely formed simultaneously to effectively removed algae cells, AOM and MCs. The residual Fe, TOC and MCs contents were lower than the guidelines after coagulation-sedimentation. The results demonstrated the UV/H_2O_2-Fe(II) process is a promising technology for drinking water treatment. Additional research is needed to assess the feasibility of the UV/H_2O_2-Fe(II) process in pilot- or full-scale drinking water treatment plants.

Table 1
The variations of MCs contents in water before and after Fe(II) coagulation.

Treatments	MCs concentration (μg/L)		
	Before pre-oxidation	After pre-oxidation	After Fe(II) coagulation
UV irradiation	≤0.1	1.9 (±0.2)	≤0.1
H_2O_2 oxidation		0.9 (±0.1)	≤0.1
UV/H_2O_2 oxidation		1.5 (±0.1)	≤0.1

Note: The time for three pre-treatments is 5 min H_2O_2 dose 375 μmol/L.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2017.12.020.

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