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Removal of *Microcystis aeruginosa* and control of algal organic matters by potassium ferrate(VI) pre-oxidation enhanced Fe(II) coagulation

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Abstract−The problem of cyanobacteria blooms during potable water production has generated wide concern. Ferrate(VI) serving as a pre-oxidation tactic was first applied to enhance conventional Fe(II) coagulation for *Microcystis aeruginosa*-laden water treatment at lab scale. Results demonstrated that ferrate(VI) pre-oxidation could successfully destabilize algae cells through destroying the protective organic layer. The residual ferrate(VI) together with post-added Fe(II) could provoke a comproportionation reaction, where large amounts of Fe hydrolyzates [$Fe(OH)_3$] are formed. The in-situ $Fe(OH)_3$ with abundant reactive surface is responsible for the promotion of flocs growth by facilitating the clustering and cross-linking of algal organic matters (AOM) and cyanobacteria cells, simultaneously resulting in satisfactory reductions in OD_{680}, turbidity and UV_{254}. Overdose of ferrate(VI) could cause severe cell destruction along with the release of intracellular organic matter (IOM), which may impair the water quality by increasing the concentration of dissolved organic carbon (DOC) and the disinfection by-products formation potential (DBPFP). Meanwhile, considering the Fe residual in settled water, the optimal ferrate(VI) dose (20 μM) and Fe(II) dose (80 μM) were proposed. Besides, the synergistic effect of both the degradation by ferrate(VI) and the adsorption by in-situ $Fe(OH)_3$ contributed to the removal of DOC and Microcystin-LR. This study suggests that ferrate(VI) might be a potential candidate for pre-treatment to assist Fe(II) coagulation when addressing algae-laden water.

Keywords: *Microcystis aeruginosa*, Fe(II) Coagulation, Potassium Ferrate(VI), Algal Organic Matters, Disinfection By-products

INTRODUCTION

With the increasing amount of wastewater being discharged from domestic sewage as well as industrial and agricultural production in the whole world, the mass of nutrients, including organic components (primarily containing nitrogen and phosphorus) and inorganic trace elements (primarily contain boron, cobalt and molybdenum), has caused serious eutrophication [1,2], which can lead to intractable cyanobacterial blooms in water bodies, threatening the ecological balance and human health [3]. As one of the most representative species of algae during seasonal algal blooms, *Microcystis aeruginosa* (*M. aeruginosa*) has captured widespread attention owing to its considerably adverse effects on drinking water treatment plants (DWTPs) [4,5]. The special physiological structures and characteristics, such as strong hydrophilicity, low specific gravity, negatively charged surface and high mobility make algae cells remarkably stable in water and difficult to remove by conventional water treatment processes [6]. Furthermore, algae cells impair the water processing system and the pipe network mainly by clogging the filter tank, releasing IOM, and infiltrating into the water pipes [7]. And in addition to producing hazardous microcystins with severe hepatotoxicity, algal organic matters (AOM) released into water have also proven to be important precursors for the disinfection by-products (DBPs) [8].

To achieve a satisfactory algae removal rate, strategies like membrane filtration [9], ultrasonic inactivation [10], copper sulfate inhibition [11], as well as doubly increasing coagulants, are usually employed in practical applications. However, the introduction of membrane and ultrasound may be hindered by the high capital outlay and operational costs. With respect to copper sulfate inhibition, large amounts of copper dosage may result in excess copper residual and negatively influence other aquatic microorganisms [12]. The way to increase the dosage of coagulant may also cause excessive coagulant residual, which possibly leads to unacceptable secondary pollution. Traditional coagulation-sedimentation is still the core of current water treatment processes in DWTPs, especially in the developing countries [13]. In view of the inefficiencies in cyanobacteria aggregation and AOM rejection by conventional Fe/Al-based coagulation, novel and effective assistant technology to enhance algae removal has been needed to be investigated urgently.

Recently, various pre-oxidation methods such as $KMnO_4$ [14], O_3 [15], and UV/chlorine [16], were successively reported and appear to be overwhelmingly promising for *M. aeruginosa*-laden water purification. The mechanisms of such pre-oxidation techniques have been evidenced to be oxidative stress-induced alterations in cell surface properties and its physiological activity. Nevertheless,

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pre-treatments of sole $KMnO_4$ or O_3 tend to cause excessive oxidation of algae cells, accompanied with undesired release of IOM, which is not in favor of coagulation and likely to deteriorate the effluent water quality [14,15]. Qi et al. [17] proposed a novel strategy to adjust the pre-oxidation degree by the integration of Fe(II) and $KMnO_4$, which achieved high removal efficiencies of algae cells and AOM due to the moderate destruction on algae cells without significant IOM release. As for the introduction of UV in many coupled technologies, undoubtedly, it requires high funds to reconstruct the existing facilities in DWTPs. Additionally, the steric hindrance of algae cells dispersed in *M. aeruginosa*-laden water affects the diffusion and mass transfer of UV in aqueous solution, which may result in lower UV utilization [18]. Alternatively, with high standard redox potentials of 2.2 and 0.72 V NHE separately in acidic and basic solutions, ferrate(VI) has the potential to deal with *M. aeruginosa*-laden water treatment fittingly [19]. It is well known that the actual water body during seasonal algal blooms is weakly alkaline, and the relatively low redox potential generated by ferrate(VI) under such condition is advantageous for avoiding excessive oxidation of algae cells. Furthermore, ferrate(VI) is also accepted as a non-polluting oxidant and has long been widely used in practical applications of water treatment. Zhou et al. [20] demonstrated that the dual roles of ferrate(VI) (oxidation-based algae inactivation and the formed in-situ Fe(III)-induced self-coagulation) were responsible for the significant enhancement in algae removal. However, previous studies on algae removal by ferrate(VI) were carried out under the ideal conditions where the simulated algae suspension only contains extracted cells without AOM. To date information about efficacy of ferrate(VI) on the more realistic simulated water (*M. aeruginosa* cells and AOM coexist) is still lacking. Moreover, there might be some synergistic effect when using ferrate(VI) to enhance conventional Fe(II) coagulation for *M. aeruginosa*-laden water treatment, and the principal reactions occurring in the combined system are shown in Eqs. (1)-(2). To be specific, the ferrate(VI)/Fe(II) process is expected to facilitate the production of in-situ Fe(III) and further benefit the coagulation of *M. aeruginosa*. However, there are no investigations focusing on ferrate(VI) assisted Fe(II) coagulation for *M. aeruginosa*-laden water treatment.

In this study, ferrate(VI) was first employed as a pre-oxidation chemical to assist Fe(II) coagulation to handle with *M. aeruginosa*-laden water. The removal efficiencies of *M. aeruginosa* and AOM, changes of algal characteristics including zeta potential, cell viability and surface morphology, as well as the flocs properties after coagulation-sedimentation under different Fe(II) and/or Ferrate(VI) doses were investigated. Furthermore, the DBPs formation potential (DBPFP) of chlorinated sample was also detected to help evaluate the safety of ferrate(VI) enhanced Fe(II) coagulation process.

$$FeO_4^{2-} + H_2O \rightarrow Fe(III) + O_2 + OH^- \quad (1)$$

$$FeO_4^{2-} + Fe^{2+} + H_2O \rightarrow Fe(III) + OH^- \quad (2)$$

MATERIALS AND METHODS

1. Material

M. aeruginosa (FACHB-912) was provided by the Institute of Hydrobiology, Chinese Academy of Sciences. The BG-11 media was used for expanding cultivation of *M. aeruginosa*, and the temperature was controlled at 25 °C constantly, accompanied with the periodic illumination pattern of 14 h dark : 10 h light. *M. aeruginosa* in the exponential growth phase was employed to prepare the simulated algae-containing solution with a cell density of 2×10^6 cells/mL by diluting with deionized water (no pH adjustment).

SYTOX green nucleic acid stain was obtained from Thermo Fisher Scientific (USA). Microcystin-LR (MC-LR) ELISA kit was provided by MedChemExpress (USA). All the other chemicals used were of analytical or chromatographic grade and purchased from Macklin Biochemical Co., Ltd. (China). The free chlorine (HClO) stock solution was prepared by diluting 5% sodium hypochlorite and standardized periodically according to the APHA Standard Methods [21]. The potassium ferrate stock solution was freshly prepared before each experiment, and the actual concentration of ferrate(VI) was determined by spectrophotometry [22].

2. Experimental

The enhanced Fe(II) coagulation-sedimentation experiments initiated by ferrate(VI) pre-oxidation were carried out with 200 mL of simulated algae suspension in a 250 mL glass beaker. Ferrate(VI) with desired doses from 0 to 50 μM was first added for the pre-oxidation process. After reaction with stirring at 250 rpm for 3 min, the stock solution of $FeSO_4$ was dosed with the designed concentration ranging from 0 to 120 μM. The coagulation conditions were set as follows: rapid mixing at 250 rpm for 1 min followed by medium mixing at 100 rpm for 2 min and slow mixing at 40 rpm for 10 min. After settling for 20 min, sufficient supernatant samples were withdrawn from 2 cm below the water surface for subsequent experiments and detections, and before which $Na_2S_2O_3$ was used to quench the reaction. The measurements included optical density at 680 nm (OD_{680}), turbidity, UV_{254}, DOC, Zeta potential, Fe residual, MC-LR and DBPFP. Following, the rest of the settled precipitates were divided into two subsamples. The first subsample was subjected to rapid stirring at 250 rpm for 5 min to obtain the redispersed algae suspension, which was subsequently used to test the cell integrity. Another subsample was subjected to floc characterization after centrifugation and drying. All jar tests were conducted on a programmable jar tester (ZR4-6, ZhongRun, China) and at 25 °C room temperature. During the chlorination experiments, sodium hypochlorite was dosed according to Cl_2 : TOC mass proportion of 3 : 1, and the solution pH was adjusted to 7.0 with KH_2PO_4-NaOH buffer. Then, the samples were placed in an incubator (FYQHX-I, Kexi, China) and chlorinated for 72 h at 25 °C in the dark. Finally, excess ascorbic acid was used to quench the reaction solutions for DBPFP assessments.

3. Analytical Method

To evaluate the effect of ferrate(VI)/Fe(II) process on *M. aeruginosa* cells, flow cytometry (CytoFLEX, Beckman Coulter, USA) was employed for the cell integrity test following the method of Qi et al. [17]. The death of algal cell is accompanied by irreversible damage to the cell membrane, which allows SYTOX to penetrate and stain, and emits green fluorescence. However, for living algae cells, the auto-fluorescence of intact intracellular chlorophyll can show red. These two fluorescences were collected at 530 and 630 nm channels, respectively, and the data were collected and analyzed using the matched CytExpert software.

According to the method of Naushad et al. [23,24], the flocs after centrifugation were transferred to an air oven (BGX-6050, Puxia, China) and dried at 40 °C for 72 h. Following, the samples were observed with a scanning electron microscopy (JSM-7800F, JEOL, Japan).

The supernatants after centrifugation were filtered through a 0.22 μm pore size CA membrane to prepare the samples of extracellular MC-LR and DBPs precursors. The method of double-antibody one step sandwich elisa assay was used to detect the MC-LR concentration. According to the methods of USEPA 551.1 [25] and 552.3 [26], DBPFP were quantified by liquid/liquid extraction with methyltertiary-butyl-ether (MTBE) followed by gas chromatography (6890N, Agilent, USA) equipped with an electron capture detector, and the collected data were analyzed using the Chemstation B.02 software.

OD_{680} and UV_{254} were determined by measuring the absorbance value at 680 and 254 nm separately with an UV-vis spectrophotometer (DR6000, HACH, USA). A multiple parameter meter (Multi 3630IDS, WTW, Germany), and zetasizer (Litesizer™ 500, Anton paar, China) were used to measure the pH/turbidity and zeta potential, respectively. An inductively coupled plasma optical emission spectrometer (700 Series, Agilent) and a TOC/TN analyzer (Multi N/C 2100 S, Jena, Germany) were separately used to measure the concentration of Fe ion and DOC.

RESULTS AND DISCUSSION

1. Effect of Ferrate(VI) Dose on Coagulation

Fig. 1 shows the removal efficiency of *M. aeruginosa* by ferrate(VI) pre-oxidation enhanced Fe(II) coagulation under different ferrate(VI) doses ranging from 0 to 50 μM. It indicates that the process of single Fe(II) coagulation without addition of ferrate(VI) was not capable of treating *M. aeruginosa*-laden water, which only realized very limited removal rates of 2.9%, 0.8% and 9.1% for OD_{680}, turbidity and UV_{254}, respectively. This relatively high UV_{254} removal rate seemed to be related to the Fe-AOM chelates with large molecular weight formed after Fe(II) addition, which were partially rejected by membrane filtration process during the sample pretreatment before UV_{254} detection. When the simulated algae suspension was pretreated by ferrate(VI), great aid effects were observed. The best coagulation performance with the removal rates of 88.2%, 89.1% and 36.4% for OD_{680}, turbidity and UV_{254}, was obtained under the ferrate(VI) dose of 20 μM. There are two likely interpretations for the promotion. First, the oxidative stress induced by ferrate(VI) pretreatment led to the desorption of the organic protective layer on the surface of algae cells [27], which accordingly caused a decrease in the absolute value of zeta potential (Fig. 1), and this charge neutralization phenomenon was demonstrated to be very beneficial for cell destabilization [28]. Additionally, the in-situ Fe(III) generated from the self-decomposition of ferrate(VI) and the comproportionation reaction with Fe(II) could serve as an efficient coagulant to remove *M. aeruginosa* and the AOM [29,30]. The newly formed Fe(III) has been widely certified to be more advantageous to promote floc growth than pre-formed Fe(III) [14,27].

However, excessive ferrate(VI) of above 30 μM may result in serious cell breakage accompanied by significant release of IOM [14, 20], which was certified to be adverse for coagulation. As seen in Fig. 1, overdose of ferrate(VI) led to the obvious decrease in algae removal efficiency. It is noteworthy that the zeta potential decreased from −5.39 mV to −11.26 and −21.85 mV when the ferrate(VI) dose increased from 20 to 30 and 50 μM, respectively. The results indicated that excessive oxidation by ferrate(VI) endowed the algae cell's surface a strong capacity to consume positively charged Fe(II) coagulant and adversely affect coagulation process. A similar phenomenon was observed by Liu et al. [15] that the zeta potential of algae cells substantially decreased when excessive $KMnO_4$ and O_3 were added for pre-oxidation. It could be concluded that cell breakage under excessive oxidation exposure and the accompanied IOM release contributed to the decrease in zeta potential. On the other hand, as we all know, UV_{254} is a good indicator to symbolize the

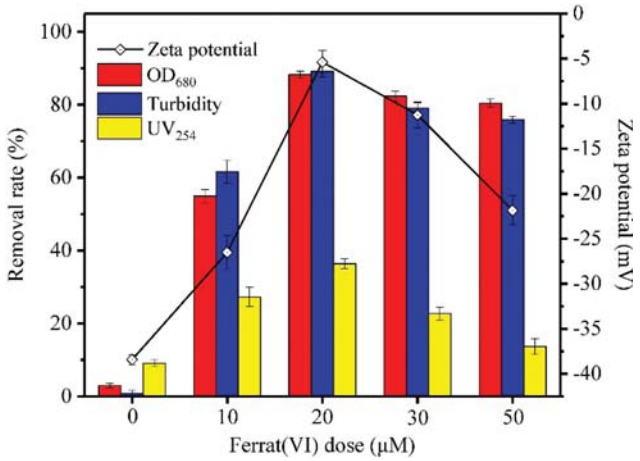

Fig. 1. Effect of ferrate(VI) dose on the variations of algae removal rate and zeta potential. Conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial zeta potential −41.75 mV, initial pH 8.38, temperature 25 °C, Fe(II) dose 80 μM. Error bars represent the standard deviations (n=3).

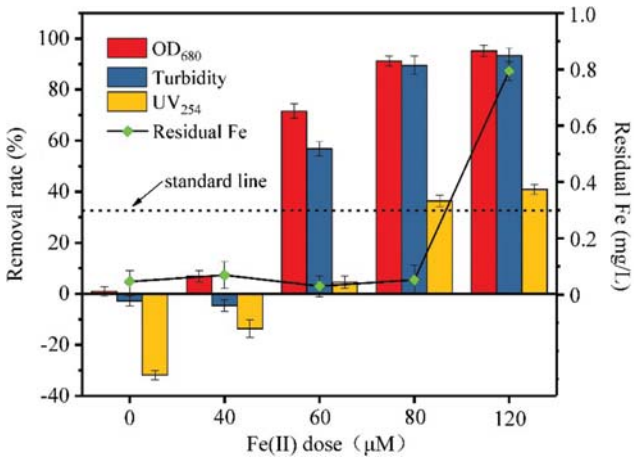

Fig. 2. Effects of Fe(II) concentration on *M. aeruginosa* removal and residual Fe content. Conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.41, temperature 25 °C, ferrate(VI) dose 20 μM. Error bars represent the standard deviations (n=3).

organic matter possessing aromatic structures or unsaturated carbon bonds [31]. As a result, a distinct decline in UV_{254} removal was observed, and the removal performance was likely compromised by the non-negligible IOM release at ferrate(VI) dose of above 30 μM (Fig. 1).

2. Effect of Fe(II) Dose on Coagulation

The contribution of Fe(II) dose on coagulation during *M. aeruginosa*-laden water treatment was also illustrated. As seen in Fig. 2, only 0.98% of *M. aeruginosa* settled down after the sole ferrate(VI) treatment at a dose of 20 μM, which indicates that Fe(II) played an important role in the ferrate(VI)/Fe(II) process, and the coagulation performance induced by the ferrate(VI) self-decomposition to in-situ Fe(III) was negligible without the addition of Fe(II). Even under this dose, the sole ferrate(VI) treatment caused further deterioration of water quality, which was reflected in the increase in turbidity and UV_{254} by 2.7% and 31.8%, respectively. It was reported that about 20%-30% of algae cells were removed by sole ferrate(VI) treatment at an equal dose [20], which was inconsistent with the present results. Establishment of an environment without AOM by repeatedly extracting algae cells is probably the reason for the differences in comparison with our study. Moreover, a similar removal performance was observed by subsequently introducing 40 μM Fe(II) (Fig. 2). The results show little to no improvement for coagulation by ferrate(VI)/Fe(II) process under a relatively low Fe(II) dose, which was inferred to be attributed to the desorption of adsorbed organic matter (S-AOM) on the algae cell surface, release of IOM, and inefficiency of flocs formation [32-34]. However, when the Fe(II) dose was elevated to 60 μM, the coagulation performance was dramatically enhanced as that the removal rates of OD_{680}, turbidity and UV_{254} were substantially increased to 71.6%, 56.8% and 4.5%, respectively. To further elevate Fe(II) dose, higher removal efficiencies were obtained. Nevertheless, the coagulation performance in terms of OD_{680}, turbidity and UV_{254} improved slightly when the Fe(II) dose increased from 80 to 120 μM.

Fig. 2 also shows the changes of residual Fe under various Fe(II) doses during ferrate(VI) enhanced Fe(II) coagulation process. The residual Fe was kept at a low level of below 1.0 mg/L when the Fe(II) doses were less than 80 μM. However, a surge in Fe residual occurred when the Fe(II) dose increased to 120 μM, at such condition the Fe concentration reached 0.794 mg/L, which exceeded the maximum allowable Fe concentration in drinking water (0.3 mg/L, GB5749-2006) [35]. This phenomenon was proposed to be attributed to the fast consumption of ferrate(VI) and alkalinity, which makes it difficult for the excessive Fe(II) to form ferric hydroxides and thus could not been separated from water. Therefore, the optimum dosage of Fe(II) was recommended to be 80 μM; under such condition, the ferrate(VI)/Fe(II) process achieved high removal rates of 91.2%, 89.5% and 36.4% for OD_{680}, turbidity and UV_{254}, respectively.

3. Effect of Ferrate(VI)/Fe(II) Process on Algal Integrity and Flocs Morphology

To further investigate the influence of ferrate(VI)/Fe(II) process on algal integrity, the proportions of damaged cells under different ferrate(VI) doses were tested by flow cytometer (Fig. 3). In the control, only 3.5% of *M. aeruginosa* ruptured during sole Fe(II) coagulation process. When introducing the pre-oxidation of ferrate(VI), the mortality rate of algae cells increased from 14.3% to 88.4% as

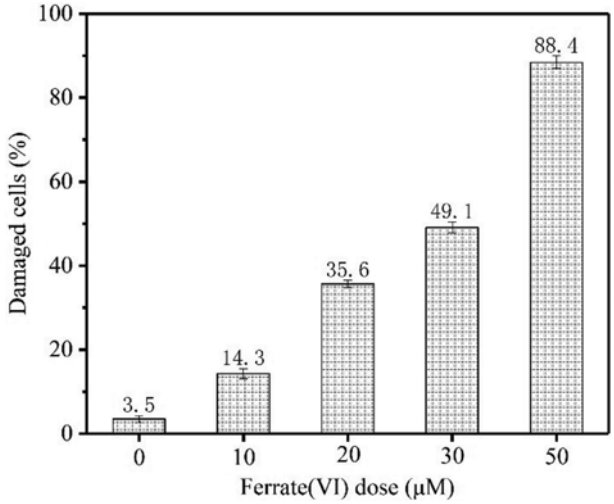

Fig. 3. Effect of ferrate(VI) dose on the damage of algal integrity. Conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.38, temperature 25 °C, Fe(II) dose 80 μM. Error bars represent the standard deviations (n=3).

ferrate(VI) dose increased from 10 to 50 μM. Previous studies suggested that although the pre-oxidation methods can enhance the removal of *M. aeruginosa*, the choice of oxidant species and dosage should be fully considered to avoid severe cell lysis caused by excessive pre-oxidation, whereby the leaked IOM would significantly impair coagulation [7,17,27]. Therefore, the coagulation performance depends on the trade-off between the cell destabilization and IOM release, and the ideal pre-oxidation should be moderately controlled. Combined with the results shown in Fig. 2, one could conclude that ferrate(VI) pre-oxidation-induced 35% of damaged cells was acceptable because the best coagulation efficiency was achieved at this dose. However, further elevating ferrate(VI) doses to 30 and 50 μM, the resulting damaged cell proportions of 49.1% and 88.4% led to the obvious reduction of coagulation performance, especially in the aspect of UV_{254} removal (Fig. 1 and Fig. 3). This implies that at high ferrate(VI) dose of above 30 μM, the negative effects of IOM release caused by excessive pre-oxidation have substantially offset the removal capacity of organic matter by flocs adsorption during ferrate(VI)/Fe(II) process. However, the limited IOM release caused by 35% cell destruction (at a ferrate(VI) dose of 20 μM) can be well digested and removed by the ferrate(VI)/Fe(II) process.

SEM images were also captured to further visually certify the degree of damage on algae cells, and the enhancement of coagulation performance, the morphology of flocs including cyanobacteria cells and Fe hydrolyzates after ferrate(VI)/Fe(II) process with different ferrate(VI) dose is illustrated in Fig. 4. In the control [Fig. 4(a)], a fairly clear view of the cyanobacteria cells with spherical shapes as well as a large number of amorphous and tiny Fe hydrolyzate colloids adhering to their surfaces were presented. It further indicates that the sole Fe(II) process was incapable of forming large and dense algae-iron flocs and resulted in a poor coagulation performance, which was in accordance with the results in Fig. 1. When 10 μM ferrate(VI) was added prior to Fe(II) dosing, the majority

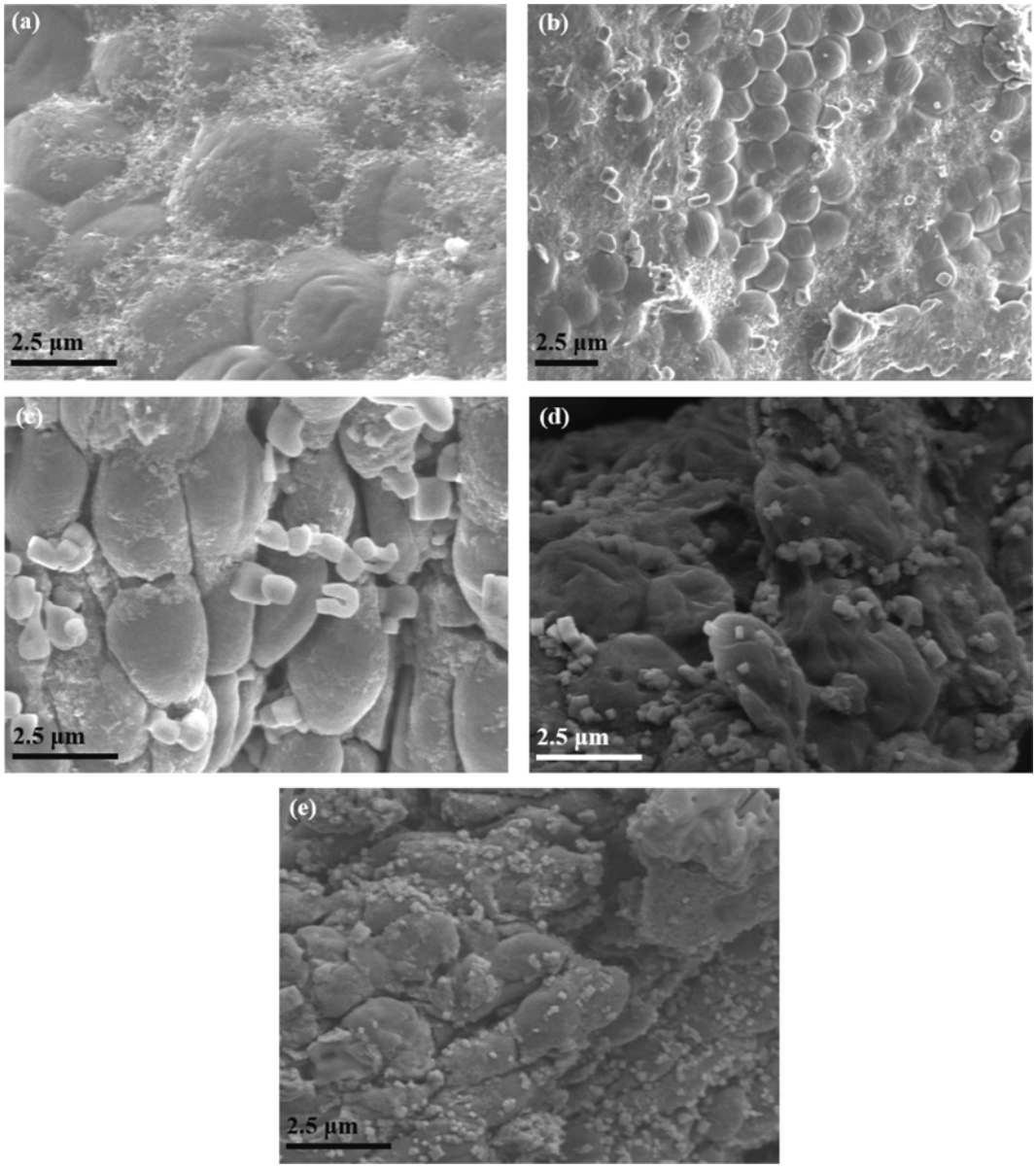

Fig. 4. SEM images of algal flocs and cell surface morphology after Fe(II) coagulation-sedimentation with ferrate(VI) pre-oxidation at a dose of (a) control, (b) 10 μM, (c) 20 μM, (d) 30 μM, (e) 50 μM. Initial algae cell density: 2.0×10^6 cells/mL, Fe(II) dose 80 μM.

of cyanobacteria cells maintained a spherical and intact shape, but many iron crystals with large sizes surrounding the cell surface began to appear and multiply [Fig. 4(b)]. Furthermore, at ferrate(VI) dose of 20 μM [seen in Fig. 4(c)], more and larger iron crystals were generated and cross-linking large numbers of cyanobacteria cells to form denser algae-iron flocs, though their shapes became elliptical. Ma et al. [14] reported that the in-situ formed Fe hydrolyzates [$Fe(OH)_3$] with more plentiful reactive surface area could significantly promote algae flocs growth by facilitating the clustering and cross-linking of AOM and cyanobacteria cells. Therefore, the synergistic effect produced in the of ferrate(VI)/Fe(II) process, including not only the effective inactivation of cyanobacteria cells by oxidative stress of ferrate(VI), but also the enhanced formation of well agminated hydrolyzates (iron crystals) through the rapid reactions between ferrate(VI) and Fe(II), was attributed to the favorable coagulation-sedimentation performance and excellent algae removal efficiency. However, Fig. 4(d) shows that under a higher ferrate(VI) expose (30 μM), most cyanobacteria cells have undergone severe distortions and lost their spherical structure, which was suspected that the un-neglected release of IOM has occurred [36, 37]. More acute cell destruction was observed in Fig. 4(e). When the cyanobacteria cells were exposed to 50 μM ferrate(VI), though abundant iron crystals were produced, the surface of most algae cells was damaged with remarkable rupture, which was bound to cause a large amount of leakage of IOM. Consequently, SEM results are well consistent with those presented by the flow cytometry, and they indicate that ferrate(VI) dose of 20 μM is the optimal equilibrium point to ensure a moderate oxidation, under such conditions

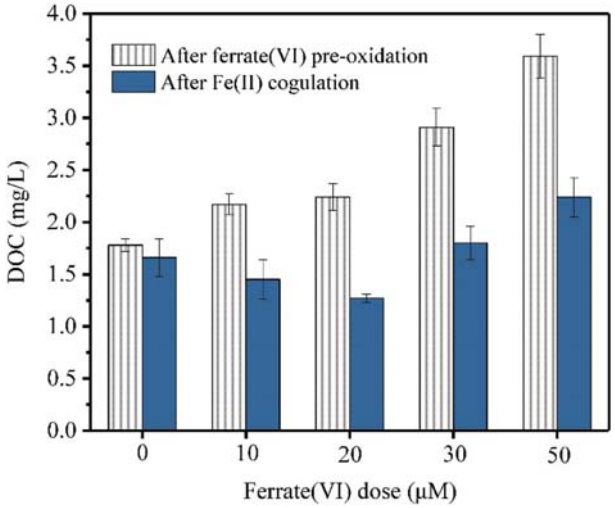

Fig. 5. The variations of DOC concentration before and after Fe(II) coagulation-sedimentation. Conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.38, temperature 25 °C, Fe(II) dose 80 μM. Error bars represent the standard deviations (n=3).

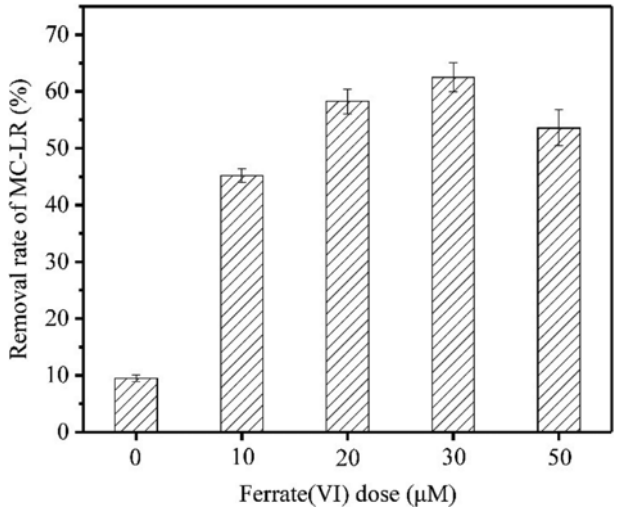

Fig. 6. Effect of ferrate(VI) dose on the removal rate of MC-LR after Fe(II) coagulation-sedimentation. Conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.38, temperature 25 °C, Fe(II) dose 80 μM. Error bars represent the standard deviations (n=3).

M. aeruginosa can be effectively inactivated while avoiding uncontrolled cell lysis and IOM release.

4. Effect of Ferrate(VI) Pre-oxidation Enhanced Fe(II) Coagulation on the Variation of DOC

To further quantitatively evaluate the extent of IOM release caused by ferrate(VI) enhanced Fe(II) coagulation process, the AOM content characterized by DOC in the settled water was detected. For samples after ferrate(VI) pre-oxidation, since the organics removal efficiency powered by sole ferrate(VI)-induced self-flocculation effect during the pre-oxidation process was proved to be weak (section 2), the evolution of DOC can reflect the damage degree of *M. aeruginosa*. As shown in Fig. 5, the DOC level was taking a turn for the worse, indicating that different degrees of AOM release are accompanied by ferrate(VI) pre-oxidation. Especially, an improper dosage (as high as >30 μM) of ferrate(VI) can impart a high DOC level to the treated water, so that the concentrations of DOC were dramatically increased from 1.78 to 2.91 and 3.59 mg/L with the ferrate(VI) dose increased from 0 to 30 and 50 μM, respectively. While at ferrate(VI) doses of 10 and 20 μM, compared to the control, the DOC values were finitely increased by 21.9% and 25.8%, respectively. These results are in accordance with the changes of the algal surface morphology shown in Fig. 4.

Fig. 5 also shows the variations of DOC after coagulation enhanced by different doses of ferrate(VI). The DOC concentration was reduced with the increase of ferrate(VI) dose from 0 to 20 μM, while increased with the ferrate(VI) dose further increasing to 30 μM and above. It was reported that a large portion of algal released substances could be adsorbed by the Fe(III) flocs [38]. In the present study, the lowest DOC value was obtained at a ferrate(VI) dose of 20 μM, indicating that under this condition, the synergistic effect of AOM adsorption by flocs and AOM degradation by ferrate(VI) oxidation was more dominant than the AOM release caused by pre-oxidation. The mechanism therein can be explained by the fact that during the ferrate(VI)/Fe(II) process, the subsequent addition of Fe(II) stimulated the comproportionation reaction (Eq. (2)), where the residual ferrate(VI) oxidized Fe(II) to form in situ Fe(III) and adsorbed the AOM. Therefore, full attention to the reasonable range of ferrate(VI) dose benefits the effective control of AOM.

5. Effect of Ferrate(VI) Pre-oxidation Enhanced Fe(II) Coagulation on the Control of MC-LR

M. aeruginosa cells release toxic microcystins (MCs) into the bulk liquid in the normal physiological metabolism process or in the case of cell membrane destruction [39]. As one of the most common and important MCs variants, MC-LR, has received the widest attention [40]. The concentration of MC-LR after Fe(II) coagulation enhanced by different doses of ferrate(VI) is illustrated in Fig. 6. Only 9.4% of MC-LR settled down by the adsorption effect of floccules during the sole Fe(II) coagulation-sedimentation process. As expected, ferrate(VI)-based pre-oxidation could substantially improve the Fe(II) coagulation efficiency to enhance the removal of MC-LR. The removal rates of MC-LR ranged from 45.2% to 62.5% when the ferrate(VI) dose was employed within the range of 10-50 μM. Interestingly, the removal performance of MC-LR showed a different trend in comparison to UV_{254} and DOC, with the highest removal rate of 62.5% being obtained at a ferrate(VI) dose of 30 μM instead of 20 μM (Fig. 1 and Fig. 5). One possible reason is that in addition to the adsorption of flocs, the oxidative degradation of ferrate(VI) also plays a vital role in the removal of MC-LR. This speculation is supported by some previous studies [41,42]. As has been noted, pre-oxidation-induced cell destruction was more severe at the ferrate(VI) dose of 30 μM than at 20 μM, thus was bound to cause a higher degree of MC-LR release, but a major part of which could be subsequently removed through oxidative degradation of ferrate(VI) with a higher dose. Besides, the residual MC-LR was further partially removed through adsorption and sedimentation during the formation and growth of the flocs.

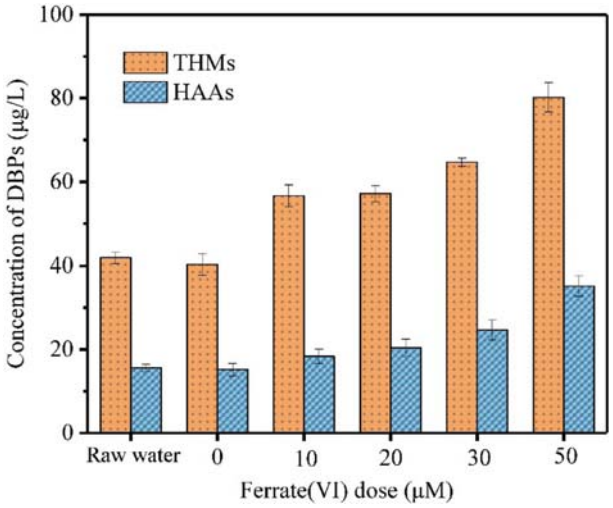

Fig. 7. Effect of ferrate(VI) dose on DBPFP during the chlorination of waters after Fe(II) coagulation-sedimentation. Conditions in jar tests: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.38, temperature 25 °C, Fe(II) dose 80 μM. Conditions in chlorination tests: Sodium hypochlorite dosage according to Cl_2 : TOC mass proportion of 3 : 1, pH 7.0, kept in the dark for 3 d at 25 °C. Error bars represent the standard deviations (n=3).

6. Effect of Ferrate(VI) Pre-oxidation Enhanced Fe(II) Coagulation on DBPFP

Many studies have verified that the released IOM may favor the formation of DBPs during chlorination [8,43,44]. In this work, THMs (TCM) and HAAs (MCAA, DCAA and TCAA) were selected as representative chlorinated DBPs to evaluate the reactivity of AOM to serve as precursors. Fig. 7 shows the variations in the concentrations of THMs and total HAAs after Fe(II) coagulation enhanced by different doses of ferrate(VI). Both THMs and HAAs present a monotonic upward trend. Chen et al. [13] studied *M. aeruginosa*-laden water treatment using UV/persulfate pre-oxidation enhanced PAC coagulation and observed similar results with respect to chlorinated DBPFP. Compared with the raw water, only the sole Fe(II) coagulation did not adversely affect the treated water quality regarding with DBPFP. However, the introductions of pre-oxidation methods like ferrate(VI) and UV/persulfate can apparently increase the DBPFP with increasing oxidant doses. As shown in Fig. 7, as the ferrate(VI) dose increased from 0 to 50 μM, the concentration of THMs increased from 40.31 to 82.21 μg/L, and that of HAAs increased from 15.18 to 35.17 μg/L. Attempts have been made to shed light on this phenomenon. Organic precursors with high reactivity like the phycocyanin (PC) as well as fulvic acids (FA) and carboxylic acids (CA) account for significant portions in the released AOM and were positively correlated with the sharply increased concentration of TCM and TCAA, respectively [45,46]. It was additionally observed that the yield of THMs was apparently larger than that of HAAs, this phenomenon has also been found by Xie et al. [47] when applying pre-ozonization. Unfortunately, although the process of ferrate(VI) enhanced Fe(II) coagulation can achieve high removal efficiencies of *M. aeruginosa* and DOC, it is ineffective or adversely affect the elimination of DBPs precursors. Hence, in the practical applications, it is recommended to control the ferrate(VI) dose below 30 μM to avoid the threat to human health caused by the rapid release of DBPs precursors induced by excessive cell lysis.

CONCLUSION

Ferrate(VI) pre-oxidation process was used to destabilize *M. aeruginosa* and enhance the subsequent coagulation-sedimentation process to effectively remove algae cells and control the released AOM. The closely related algal integrity, flocs characteristics, release and control of AOM involving DOC, MC-LR as well as DBPs precursors were comprehensively evaluated. The following conclusions can be drawn.

Ferrate(VI) proved to be a potential candidate for pre-treatment prior to Fe(II) coagulation when addressing *M. aeruginosa*-laden water, and the oxidative stress powered by ferrate(VI) pre-oxidation contributed to the inactivation of algae cells and the decrease in the absolute value of zeta potential.

The combined ferrate(VI)/Fe(II) process promoted the formation of Fe hydrolyzates, which could further facilitate the aggregation of algae cells and the growth of flocs, resulting in an enhanced coagulation performance in removing OD_{680}, turbidity and UV_{254}.

Ferrate(VI)-induced cell destruction led to varying degrees of increase in DOC, but the concentration of DOC was significantly reduced after the subsequent introduction of Fe(II). AOM release deteriorated with elevated ferrate(VI) dose and could potentially compromise coagulation effect.

Ferrate(VI) at high dose could cause severe cell lysis, accompanied with apparent release of MC-LR and increase of DBPFP. The dosage of ferrate(VI) should be cautiously considered when used as moderate pre-oxidation method to assist in controlling AOM release and to simultaneously avoid the sharp increase of DBPFP.

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