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UV/persulfate preoxidation to improve coagulation efficiency of *Microcystis aeruginosa*

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Abstract

The performance of UV-activated persulfate (UV/PS) technology as preoxidation process to enhance *Microcystis aeruginosa* removal by subsequent coagulation-sedimentation was firstly evaluated. The results demonstrate that UV/PS preoxidation could successfully promote coagulation of algae cells through the effective neutralization of zeta potential, which was caused by the changes of cell morphology, size distribution and surface properties after simultaneous UV irradiation and formed reactive species (i.e. $SO_4^{\bullet-}$ and $HO^{\bullet}$) oxidation. Since excessive oxidation would cause cell rupture along with the release of organics, which could deteriorate coagulation efficiency, optimal PS dose (60 mg/L) and UV dose (375 mJ/cm^2) were proposed to exist in this study. The concentrations of extracellular algal organic matter

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(AOM) sharply increased by 48.2% during the preoxidation period, while gradually decreased in the following coagulation and sedimentation. Most of the concerned disinfection by-products (DBPs) monotonically decreased or followed fluctuant reduction with increasing PS doses, whereas the trichloromethane, trichloroacetic acid and dichloroacetonitrile persistently increased, which was inferred to be related to the variation of AOM. This study suggests that UV/PS might be a potential pretreatment process to assist coagulation on the removal of algae.

Keywords: *Microcystis aeruginosa*; ultraviolet/persulfate; preoxidation; coagulation; disinfection by-products

1. Introduction

Nowadays the increasing occurrence of harmful algal blooms related to eutrophication in source waters has attracted worldwide concerns for health risk and drinking water production [1-4]. Excessive algae in waters can lead to the vast release of algal organic matter (AOM) including taste- and odor-compounds, neurotoxins, and biotoxins, causing acute or chronic effects on organs and nervous system of aquatic organisms along with biomagnification [5-7]. Moreover, algae cells and AOM have been proven to be precursors for disinfection byproducts (DBPs), which can react with chlorine to form carbonaceous DBPs (C-DBPs) and nitrogenous DBPs (N-DBPs) containing high genotoxicity and carcinogenicity [8-10].

Although many traditional methods such as copper sulfate inhibition [11], sand filtration [12], and flotation [13] and some novel alternative processes such as ultrasonic inactivation [14], gamma-ray irradiation [15], hydrodynamic cavitation [16], and cationic starch modified soils flocculation [17] have been used to remove algae, the conventional coagulation-sedimentation-filtration is still the mainstream treatment process in drinking water treatment plant. However, the coagulation process using aluminum or ferric salts always achieves limited efficiency on the removal of algae and its derived organic matter because of electrostatic repulsion, surface hydrophilicity and steric effects [18-20], subsequently resulting in the deterioration of drinking water quality [21]. As a consequence, to develop assistant technology for improving algae removal by conventional drinking water treatment process is prospected.

Numerous studies have evidenced that preoxidation process can effectively assist

coagulation through the change of zeta potential, destroying the organic coating and inactivation of viable algae, resulting in high removal efficiency of algae and other suspended particles in the following sedimentation or filtration process [22-24]. Common used oxidants for preoxidation include chlorine, chlorine dioxide, ozone, permanganate and ferrate, whereas some drawbacks of using these oxidants, such as production of DBP precursors, release of undesirable compounds and increase of water colority, are also proposed [25-28]. Advanced oxidation processes (AOPs) based on hydroxyl ($HO^{\bullet}$, E^0=1.8–2.7 V) and sulfate radicals ($SO_4^{\bullet-}$, E^0=2.5–3.1 V) have been widely used as novel oxidants to degrade many pollutants [29-31]. The popular used AOPs to generate reactive radicals include ultraviolet/hydrogen dioxide (UV/H_2O_2), ozone/hydrogen dioxide (O_3/H_2O_2), Fenton, ultraviolet/persulfate (UV/PS), and so on [32, 33]. Among these processes, UV/PS is expected to be a promising treatment technology for algae-containing water due to its strong inactivation abilities and growth suppression effects on organisms [34-36]. As inactivated algae cells are easy to be destabilized [22, 24], UV/PS might be a good choice to improve coagulation efficiency of algae. However, there are no publications focusing on the pretreatment of algae-containing water by UV/PS to assist coagulation.

In this study, UV/PS was firstly used as a preoxidation process to enhance *Microcystis aeruginosa* (*M. aeruginosa*) removal by coagulation-sedimentation process. The removal efficiency of algae cells, variation of AOM components and changes of algae characteristics including cell morphology, size distribution and surface properties under different operational conditions were investigated. The DBP formation potential (DBPFP) of settled water was also

analyzed to help evaluate the safety of UV/PS preoxidation technology.

2. Materials and methods

2.1. Materials

M. aeruginosa (No. FACHB-909) was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, and cultured in BG-11 media [37]. The specific algae growth temperature and light-dark cycle were set as 25±1 ℃ and 12 h: 12 h, respectively, in a light growth incubator (250-D, Guohua, China). *M. aeruginosa* in the exponential growth phase were harvested and subsequently diluted by ultrapure water (18.5 MΩ cm, PCDX-J, Pincheng, China) to achieve a cell density of 1×10^6 cell/mL that approaches to the practical cell abundance of *Microcystis* in algae blooms [38]. Thereafter the initial pH of *M. aeruginosa* solution was adjusted to be 7.0 by using 0.1M H_2SO_4 and NaOH.

N,N-diethyl-*p*-phenylenediamine (DPD), nine haloacetic acids (HAAs) mixture standard solution containing bromoacetic acid (MBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chloroacetic acid (MCAA), dibromochloroacetic acid (DBCAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), tribromoacetic acid (TBAA) and trichloroacetic acid (TCAA), seven halogenated volatiles mixture standard solution containing bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), dichloroacetonitrile (DCAN), 1,2-dichloro-2-propanone (DCP), 1,1,1-trichloroacetone (TCP), trichloroacetonitrile (TCAN), and trichloronitromethane (TCNM), and the chloral hydrate (CH) standard solution were purchased from Sigma-Aldrich, USA. A mixture standard

solution containing trichloromethane (TCM), tribromethane (TBM), dibromochloromethane (DBCM), and chlorodibromomethane (CDBM), and the trichloroethylene (TCE) standard solution were obtained from J&K Scientific, China. Polyaluminium chloride (PAC) of analytical grade was purchased from Baishi Chemical, China. Methanol, n-hexane, acetone and methyl tert-butyl ether of HPLC grade were supplied by Tedia, USA. All the other used chemicals of analytical reagent grade at least were obtained from Sinopharm, China. Both PS and PAC stock solutions were freshly prepared each time. A free chlorine stock solution (3000 mg/L as Cl_2) was prepared by diluting NaClO solution with ultrapure water and standardized periodically by using DPD/FAS titration [39].

2.2. Preoxidation-coagulation jar tests

Preoxidation was carried out in a 600 mL cylindrical reactor equipped with a low-pressure UV lamp (254 nm, 23W, GPH 436T5L/4, Philips, The Netherlands) at an average irradiance of 1.25 mW/cm^2 under 25 ℃ following a previous article [40]. PS stock solution was dosed into the reactor containing algae solution to achieve a desired concentration of 60 mg/L and UV dose was set as 375 mJ/cm^2 unless otherwise noted. The solution was homogenized by using a magnetic stirring apparatus at a speed of 200 rpm throughout the preoxidation procedure. Thereafter the *M. aeruginosa* solution was transferred into a 500 mL beaker of a programmable jar tester (TA6-1, Hengling, China) and added 10 mg/L PAC to conduct coagulation experiments under room temperature. The reaction solution was rapidly mixed at 250 rpm for 1 min followed by medium mix at 100 rpm for 3 min and slow mix at 40 rpm for

10 min. After settling for 20 min, supernatant samples were siphoned from 2 cm below the surface for subsequent measurements.

2.3. Chlorination experiments

To evaluate DBPFP of the treated algae solution, chlorination experiments were conducted in 100 mL amber glass bottles capped with Teflon-faced septa which were filled with supernatant solutions at pH 7.0 (10 mM phosphate buffer) following Fang's method [8]. The ratio of chlorine dosages (mg/L as Cl_2) to the total organic carbon (TOC, mg/L) was 3:1. Chlorinated samples were stored in an incubator (BS-1E, Guohua, China) at 25±1 ℃ in dark for 3 days, and then quenched by excess ascorbic acid for the DBPs analysis.

2.4. Analytical methods

The concentration of *M. aeruginosa* solution was measured by optical density at 681 nm (OD_{681}) with a UV-visible spectrophotometer (U-3100, Hitachi, Japan). Chlorophyll-a (Chl-a) was extracted by acetone and subsequently determined using the spectrophotometer according to the method recommend by EPA of China [41]. A turbidimeter (WGZ-2, Ruixin, China), pH meter (Starter-3100, Ohaus, USA) and zeta potential analyzer (ZetaPlus, Brookhaven, USA) were used to measure the turbidity, pH and zeta potential, respectively. The flocs in sedimentary samples were dried by a vacuum freeze dryer (FD-1A-50, Boyikang, China), then sputter coated with gold, and finally observed using a scanning electron microscopy (SEM) (Sirion 200, FEI, USA).

The other parts of samples were centrifuged at 8000 rpm for 15 min and then filtered through a cellulose acetate membrane with pore size of 0.45 μm for the subsequent analysis of dissolved organic carbon (DOC) and fluorescence spectroscopy. The TOC and DOC were determined by using a TOC/TN analyzer (C/N 2100, Analytic Jena, Germany). An F-4600 fluorescence spectrophotometer (Hitachi, Japan) was used to measure the fluorescence excitation-emission matrix (EEM) spectroscopy with the scan ranges of excitation wavelengths (Ex) and emission wavelengths (Em) setting as 200~450 nm at 5 nm intervals and 280~550 nm at 2 nm intervals, respectively. Rayleigh and Raman scatters were eliminated through interpolation method by using MATLAB 2010b (The MathWorks, Inc., USA) [42]. The residual PS concentration was determined according to a rapid spectrophotometric method over measuring the absorbance at 352 nm [43].

A gas chromatography (GC-2014C, Shimadzu, Japan) equipped with an electron capture detector (ECD) and a ZB-5 column (30 m × 0.25 mm, ID 0.25 μm) was used to measure the concentrations of DBPs based on USEPA methods 551.1 and 552.3 [44, 45]. For the volatile DBPs including TCM, TCE, CH, DCAN, TCNM and TCP, the temperature of injector and ECD were set at 200 ℃ and 290 ℃, respectively. The temperature program of oven began at 35 ℃ for 7 min, then ramped to 200 ℃ at 40 ℃/min and held for 2 min. For measuring the three chlorinated acetic acids including MCAA, DCAA and TCAA, the temperature of injector and ECD were set at 210 ℃ and 280 ℃, respectively. The temperature program of oven began at 35 ℃ for 7 min, ramped to 80 ℃ at 8 ℃/min and held for 10 min, then ramped to 200 ℃ at 20 ℃/min and held for 1 min.

3. Results and discussion

3.1. Comparison of UV, PS and UV/PS pretreatment on coagulation

Fig. 1 shows the impacts of three preoxidation processes including PS oxidation, UV irradiation and UV/PS oxidation on the removal of *M. aeruginosa* during the subsequent PAC coagulation-sedimentation process. The sole PAC coagulation-sedimentation without pretreatment was tested as a control, which only achieved limited removal rates of 50.5%, 37.5% and 36.1% for OD_{681}, Chl-a and turbidity, respectively. An approximate removal performance was observed by using a combined process of PS preoxidation and PAC coagulation-sedimentation, indicating little to no promotion on algae removal by PS pretreatment. When the algae solution was pretreated by UV irradiation with a dose of 375 mJ/cm^2, the removal rates of OD_{681}, Chl-a and turbidity were 70.0%, 43.8% and 51.8%, respectively, after coagulation-sedimentation. Among all the chosen treatment processes, the combined process of UV/PS pretreatment and coagulation-sedimentation achieved the highest removal efficiency of algae as that OD_{681}, Chl-a and turbidity were removed by 93.8%, 74.3% and 93.6%, respectively. However, OD_{681}, Chl-a and turbidity only decreased by 16.4%, 28.7% and 15.8%, respectively, after UV/PS oxidation for 5 min (Fig. S1), implying that further removal rates of 77.4%, 45.6% and 77.8% for OD_{681}, Chl-a and turbidity were achieved by the subsequent coagulation-sedimentation (Fig. 1). Consequently, it is easily concluded that algae cells were mainly removed by PAC coagulation-sedimentation when using combined processes of preoxidation and PAC coagulation-sedimentation. Similarly,

higher removal rates of OD_{681}, Chl-a and turbidity when using combined UV irradiation and PAC coagulation-sedimentation could be also achieved in comparison with sole UV treatment. The results demonstrate that pretreatment by both UV and UV/PS, especially for UV/PS, not only can degrade *M. aeruginosa*, but also can improve coagulation efficiency.

It is noteworthy that the variation trend of zeta potential was in accordance with algae removal performance (Fig. 1), which supported that decreasing the absolute value of zeta potential is a vital reason for preoxidation to improve coagulation as reported elsewhere [22, 26]. The surface of untreated algae cell was highly negative-charged with a zeta potential being –31.90 mV, which can be slightly neutralized to –27.31 mV by individual coagulation with 10 mg/L PAC. In comparison with sole PAC coagulation, combination of either PS oxidation or single UV irradiation with PAC coagulation only insignificantly decreased the absolute value of zeta potential. However, UV/PS oxidation without and with PAC coagulation remarkably varied the zeta potential of algae cells to –19.15 mV (Fig. S1) and –11.31 mV (Fig. 1), respectively, suggesting that UV/PS pretreatment could effectively change the surface properties of algae cells.

To further elucidate the short-term impact of UV/PS treatment on *M. aeruginosa*, the size distributions of algae cells before and after preoxidation were explored. As shown in Fig. 2, the size of raw cells mainly distributed among 2~10 μm, which was in agreement with the reported size of *M. aeruginosa* [24]. However, the size distribution range was significantly narrowed with the median particle size (D50) decreasing from 5.520 to 4.393 μm after UV/PS preoxidation for 5 min. The results suggest an acute damage effect on algae cells, which was

inferred to be attributed to the UV light and generated radicals (i.e. $SO_4^{\bullet-}$ and $HO^{\bullet}$) in the system [40]. It is known that a number of organic compounds are always adsorbed on the surface of algae cells in algae-containing water [22], which is supposed to explore the distribution range of algae size. Thus, the changes of algae size after UV/PS preoxidation might be also because of the detached organic matter from the surface of algae cell, which was supported by the study focusing on other preoxidation processes [46].

Furthermore, the surface morphologies of flocs with and without UV/PS preoxidation were observed by using a SEM to visually evidence the possible damage on algae cells and improvement of coagulation performance. The SEM images (Fig. 3) show that although UV/PS pretreatment could induce cell rupture or cytomorphosis to some extent, it could result in the formation of more compact flocs, suggesting that the destabilization and aggregation of algae were enhanced as proposed.

3.2. Effect of PS dose on coagulation

Fig. 4 shows the effect of PS dosages ranging from 20 to 100 mg/L on algae removal in the subsequent PAC coagulation-sedimentation. The removal rate of *M. aeruginosa* was enhanced with the increase of initial PS dosage from 20 to 60 mg/L, while decreased with the initial PS dosage further increasing to 80 mg/L. An optimum PS dose for this experimental condition was advised to be 60 mg/L, at which the removal rates for OD_{681}, Chl-a and turbidity reached up to 95.6%, 92.7% and 94.0%, respectively. As aforementioned, UV/PS oxidation can reduce the absolute value of zeta potential, thus the destabilization and coagulation of algae cells was

expected to be heightened with increasing PS dosage. However, overdose of PS may induce serious cellular damage accompanied with the release of intracellular organic matter (IOM) [40], which was believed to complex with positively-charged aluminum coagulant and impair coagulation efficiency [27]. This speculation was supported by the variation of the zeta potential data (Fig. 4).

It is interesting that when the initial PS concentration varied from 80 to 100 mg/L, the algae removal rate rose by 8.7% along with a sharp decrease of zeta potential from –13.01 to –1.71 mV, which might be connected to solution pH. As displayed in Fig. 5, the pH values after preoxidation gradually reduced with the increase of PS doses, which was attributed to the production of sulfate acid through $S_2O_8^{\bullet-}$ oxidation of water (Eqs. 1~2) [47, 48]. It can be seen that the reaction pH was decreased to around 5.0 at an overdose of 100 mg/L PS. On the one hand, the zeta potential of algae cells could be neutralized by the plentiful positive charged hydrogen ions as well in acid condition [24], which was further supported by the results shown in Fig. S2 that the absolute values of zeta potential of algae cells decreased from 24.32 to 16.03 mV with the solution pH decreased from 9.0 to 5.0. On the other hand, the solution pH would also significantly affect the hydrolysis of PAC, which in return improves the PAC coagulation of algae [49, 50]. However, Fig. S3 shows that the removal rate of algae was the highest at neutral and weak alkaline conditions with reaction pHs ranging from 5.0 to 9.0 when using single PAC coagulation-sedimentation process. As a consequence, the better performance achieved at PS dosage of 100 mg/L than that of 80 mg/L was primarily attributed to the impacts of pH on surface charges of algae cells.

$$SO_4^{\bullet -} + S_2O_8^{2-} \longrightarrow S_2O_8^{\bullet -} + SO_4^{2-} \quad (1)$$

$$S_2O_8^{\bullet -} + \frac{3}{2}H_2O \longrightarrow 2SO_4^{2-} + \frac{3}{4}O_2 + 3H^+ \quad (2)$$

Fig. 5 also shows that the concentration of residual PS in settled water continuously increased from 18.7 mg/L to 48.3 mg/L with increasing the initial PS dosage from 20 mg/L to 100 mg/L. At the experimental optimum PS dose of 60 mg/L, the residual PS concentration was measured to be 35.5 mg/L. Thus, it should be noted that further evaluation of the fate of residual PS in the subsequent drinking water processes and distribution-transportation system should be conducted if applying UV/PS preoxidation in practical project. A fact should be also concerned that a highest concentration of sulfate derived from the decomposition of 60 mg/L PS was 48.4 mg/L, which was much less than the limit value of 250 mg/L in Chinese National Standards for Drinking Water Quality (GB5749-2006), promising the possible application of UV/PS process in drinking water treatment.

3.3. Effect of UV dose on coagulation

The impact of UV dose on the removal of *M. aeruginosa* in subsequent PAC coagulation-sedimentation process was also tested (Fig. 6). The removal rates of algae and turbidity were enhanced with the increase of UV dose within 375 mJ/cm^2, while gradually reduced with further extension of UV dose. Therefore, similar to the influence of PS dosages (Fig. 5), an optimum UV dose at around 375 mJ/cm^2 was proposed, at which dose the highest removal rates of no less than 95% for both OD_{681} and turbidity were achieved. The zeta potential gradually varied from –7.44 mV to 4.31 mV with the increasing of UV dose from

375 to 1050 mJ/cm^2, except for an abrupt decrease at 600 mJ/cm^2.

Fig. S4 shows that the pH of settled water gradually decreased with the increase of UV dose, resulting in a switch to acidic condition when UV dose was over 825 mJ/cm^2. Although the decrease of pH would reduce the absolute value of zeta potential, the excessive extension of UV dose could cause severe cellular damage or large-scale cytolysis, resulting in the complex between IOM and PAC to subsequently decline algae removal [27], which was supported by the continuous increase of DOC and UV_{254} with increasing UV dose from 600 min to 1050 mJ/cm^2 (Fig. S5). It is noteworthy that when the UV dose exceeded825 mJ/cm^2, the charge-reversal of zeta potential occurred, leading to re-stabilization of algae cells which in return induced the sharp decrease of algae and turbidity removal rates aat UV dose of 1050 mJ/cm^2. Moreover, the removal of Chl-a was observed to maintain at high efficiencies (80.3%~90.0%) ranging from 150 to 1050 mJ/cm^2, which was proposed to be attributed to the effective destroy of photosynthetic system of *M. aeruginosa* by UV/PS oxidation [40].

3.4. Characteristics of extracellular AOM

The fluorescence EEM spectra of extracellular AOM in different treatment procedures including preoxidation, coagulation and sedimentation were shown in Fig. S6. According to a previous study [51], the spectra could be delineated into five excitation−emission regions based on fluorescence of model compounds. Regions (I+II), III, IV and V represent aromatic protein-like, fulvic acid-like, soluble microbial by-product-like, and humic acid-like materials, respectively [51]. Fig. S6a shows that in raw algae solution, the extracellular AOM contains

four major broad peaks, corresponding two high intensity protein-like peaks (230/334 nm and 275/332 nm) and two less intensity humic-like peaks (280/438 nm and 340/428 nm) [51, 52]. It can be perceived that these four peaks continuously changed in the following treatment procedures (Figs. S6b to S6d), suggesting a dynamic variation of extracellular AOM.

To further quantitatively analyze the EEM spectra, a fluorescence regional integration (FRI) method was adopted according to Chen's publication [51]. As presented in Fig. 7, the FRI values of regions III, IV and V sharply enhanced by 101.5%, 92.0%, and 178.9%, respectively, after UV/PS preoxidation, while no obvious variation was observed in regions I and II. The results could be explained by the cytoclasis of algae cells and the release of IOM after UV/PS oxidation, which has been proven in our previous study [40]. The insignificant variation of aromatic protein-like materials (regions I and II), similar to the results achieved in the treatment of *M. aeruginosa* by UV irradiation or chlorination [53], might be because of difficult secretion or oxidation of such substances by UV/PS over a short period.

Figs. 7 and S6 also show that PAC coagulation could significantly decrease the intensities of regions I, II, and IV, indicating a removal priority of protein-like and soluble microbial by-product-like substances. This can be explained by the preferential aggregation of compounds with high molecular weights and aromaticity by coagulants [54]. The results supported the aforementioned speculation that the released IOM would complex with aluminum coagulant, resulting in a reduction of algae removal at overdose of PS or overtime of preoxidation (Figs. 4 and 6). Additionally, it is noted that the FRI values of regions III and V slightly decreased by 9.5% and 11.3% after sedimentation, respectively, while regions I, II,

and IV increased again. The results illustrate that fulvic acid-like and humic acid-like materials could be adsorbed on the surface of flocs and then settled down. However, the protein-like and soluble microbial by-product-like substances might be released into the water again due to their high hydrophilicity [51].

Moreover, the DOC in the solution followed a coincident trend with the evolution of summative FRI values of the five regions, reaching a highest concentration of 8.65 mg/L after preoxidation (Fig. 7). However, the concentration of DOC reduced again after coagulation and sedimentation where the DOC value was nearly equal to the control sample. This is to say, although some dissolved organic matter could be released into the solution after preoxidation, a number of them could be further removed in the subsequent coagulation-sedimentation process.

3.5. Impact of UV/PS preoxidation on DBPFP

Fig. 8 shows the impact of UV/PS preoxidation on DBPFP during chlorination of settled waters. The initial TOC of samples for conducting chlorination experiments was displayed in Table S1. The concentrations of TCM, TCAA, and DCAN increased monotonically by 524.7%, 307.7% and 76.9%, respectively, with raising PS dose from 0 to 80 mg/L, which was similar to the variation trends for preozonation of algal suspensions [46]. The results of these three DBPs were supposed to be related to the enhancement of IOM release with increasing PS doses. It is noteworthy that the formation potential of TCM was much higher than other DBPs, might due to the fact that phycocyanin, an important precursor of THMs, was

substantially existed in AOM [55, 56]. Likewise, the increase of TCAA formation can be explained by the release or generation of the active precursors such as fulvic acids and organic carboxylic acids [57]. Actually, this speculation is supported by the results shown in Fig. 7 and S6, illustrating a significant increase of fulvic acid-like (region III) and humic acid-like (region IV) materials after UV/PS preoxidation. According the literatures, DCAN is primarily formed through decarboxylation of amino acids and aldehyde pathways [58, 59]. CH and TCP, following a fluctuant reduction trend different from DCAN, might be due to the oxidation of dissolved aldehyde-precursors to other production such as carboxylic acids at high dosage of PS [46, 60]. Thus, the rise of DCAN formation along with PS dosages was supposed to be firstly attributed to the increase of amino acids through the released IOM (Figs. 7 and S6).

The formation of TCNM and MCAA followed an increasing but then decreasing pattern with the maximum value appeared at a PS dosage of 20 mg/L. As nitro-compounds are important precursors of TCNM [58], the increase of TCNM formation at low PS dosage might be attributed to the formation of nitro-compounds during UV/PS oxidation. The decrease of TCNM with further raising PS dosage was speculated that some formed nitro-compounds were further oxidized to other products by UV/PS oxidation. The variation of MCAA indicates that UV/PS could improve the chlorine substitution for HAAs, contributing to the easy formation of TCAA. However, insignificant variations were observed on the formation of TCE and DCAA, might indicating that UV/PS preoxidation had little impact on the forming or degrading the precursors of these DBPs over a PS dose range of 20 to 80 mg/L.

4. Conclusions

UV/PS preoxidation was demonstrated to be efficient in enhancing *M. aeruginosa* removal by PAC coagulation-sedimentation in laboratory. UV/PS treatment could change the surface properties and ease the negativity of algae cells, subsequently resulting in the promotion of destabilization and aggregation. Optimal PS dosage and UV dose were proposed to exist due to the fact that either overdose of PS or UV could cause cell rupture and IOM release in return to complex coagulants and reduce coagulation efficiency. Although some dissolved organic compounds could be released into the algae solution during UV/PS preoxidation, a great number of them could be further removed in the subsequent coagulation-sedimentation process. Moreover, UV/PS preoxidation played different roles in the formation of various DBPs during chlorination of settled water. For example, UV/PS pretreatment increased the formation of TCM, TCAA, and DCAN, but decreased the formation of CH and TCP to some extent. This study suggests that UV/PS preoxidation is effective in the improvement of coagulation on algae removal, while the extent of preoxidation degree should be seriously concerned as it can remarkably affect both algae removal performance and DBPs formation.

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Appendix A. Supplementary data

Supplementary data (Figs. S1 to S6 and Table S1) associated with this article can be found, in the online version.

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