Journal of Hazardous Materials 189 (2011) 540–545

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Effects of iron and manganese on the formation of HAAs upon chlorinating *Chlorella vulgaris*

Fei Ge*, Xiuzhen Wu, Na Wang, Runliang Zhu, Tong Wang, Yin Xu

Department of Environmental Science and Engineering, Xiangtan University, Egongtang Road, Xiangtan, Hunan 411105, PR China

ARTICLE INFO

Article history:
Received 5 September 2010
Received in revised form 22 February 2011
Accepted 22 February 2011
Available online 1 March 2011

Keywords:
HAAs
Algae
Chlorination
Iron
Manganese

ABSTRACT

The major objective of the present study was to investigate the role of iron and manganese on the formation of haloacetic acids (HAAs) when algae are chlorinated at different pHs. The results showed that both iron and manganese can reduce the yields of dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) on chlorinating green alga *Chlorella vulgaris* (*C. vulgaris*) at a pH range of 6.0–9.0, and the decline of DCAA and TCAA was shown to be more significant at the low pH range. At pH 6.0, DCAA and TCAA yields decreased by 44.5% and 57.3%, respectively with the addition of 0.5 mg L^{-1} iron, and decreased 39.5% and 49.4%, respectively with the addition of 0.5 mg L^{-1} manganese. The main reason for decreasing the yields of HAAs as shown by scanning electron microscope (SEM) is that $Fe(OH)_{3(am)}$ or $MnO_{2(am)}$ coat the algal cells, which then improves their agglomeration of algal cells which is also revealed by the laser particle size analysis (LPSA).

1. Introduction

Algae, which are ubiquitous in rivers, reservoirs and lakes, may cause a series of problems in water treatment in algal blooming seasons. This includes poor settling, clogging filters, breakthrough of small-size algae through sand filters, obnoxious taste and odors and the release of algal toxins [1,2]. In addition, algae can serve as precursors to form disinfection by-products (DBPs) during chlorination. Among these DBPs, trihalomethanes (THMs) and HAAs have drawn particular attention because of their dominant occurrence and potential carcinogenic effects [3,4]. The influences of chlorination condition (including reaction time, chlorine dosage and pH), algal species, algal growth phase, biochemical composition and extracellular organic matter (EOM) on total DBPs formation, specific DBPs yields and DBPs species distribution have been extensively studied in drinking water treatment [5–8].

It is known that some metal compounds (e.g., iron and manganese), which are considered to be indispensable microelements in the growth of algae, are generally detected in source water, especially in eutrophic lakes and reservoirs [9–11]. For example, total iron and manganese concentrations were reported to range from 0.28 to 0.89 mg L^{-1} and from 0.20 to 0.56 mg L^{-1}, respectively in Taihu Lake of China [12]. Furthermore, the water supply pipes are commonly made with metal materials, e.g., iron and copper. The inner surface of metal pipe can be eroded gradually by residual chlorine and thus dissolved metal may increase [13,14]. Therefore, the influence of metal on the formation of DBPs cannot be ignored in drinking water treatment. Blatchley et al. [13] first investigated the effect of copper on chloroform formation during water chlorination and found that copper enhanced $CHCl_3$ formation on chlorination of humic acid. Navalon et al. [15] found that the presence of Mg^{2+} and Ca^{2+} enhanced THM formation in polyols (particularly maltopentaose), citric and humic acids. Li et al. [16] also observed that DCAA formation increased with the increase of dissolved copper concentration, while TCAA formation decreased. Zhu et al. [17] investigated the effect of ferric ions on the formation of THMs during the disinfection of drinking water. They discovered that in the presence of bromide, THM formation was inhibited by the ferric ions in acidic conditions, but was enhanced in basic media. However, the above investigations were conducted by considering humic acid as the model precursor of DBPs, but few studies have focused on the effects of metal on the formation of DBPs from algae in chlorination process.

In the water treatment processes, some metal compounds have been generally used to preoxidize and remove algae. Ma et al. [18] conducted the efficiency and mechanism of potassium ferrate (VI) preoxidation for algae removal by coagulation and observed that $Fe(OH)_{3(am)}$, which was formed after decomposition of potassium ferrate, possibly precipitated on the algal surface. Chen et al. [19,20] investigated the mechanism of algae removal by potassium permanganate and showed that $MnO_{2(am)}$ was adsorbed on the surface of algae, which then promoted the aggregation of algal cells. Hence, the morphology and particle sizes of algal cells could be alternated due to the binding of metal flocculants on the surface of electroneg-

* Corresponding author. Tel.: +86 731 58298290; fax: +86 731 58298172.
E-mail address: gefei@xtu.edu.cn (F. Ge).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.02.076

ative algal cells, which might further lead to the variation of DBPs formation in chlorination.

Based on above background, *C. vulgaris*, a unicellular green alga generally detected in surface water [21], was selected as a representative of alga. HAAs, typical DBPs with high carcinogenic activities to human health [22], were chosen as model DBPs. The effects of iron and manganese on the formation of HAAs from algae in chlorination process were investigated. The main objectives of this work were: (1) to investigate how iron and manganese influence HAAs formation upon the chlorination of *C. vulgaris* at different pHs, and (2) to explore the possible mechanisms for the results in above processes.

2. Materials and methods

2.1. Materials

C. vulgaris (FACHB-6) was obtained from Freshwater Algae Culture Collection of the Institute of Hydrobiology, the Chinese Academy of Sciences. Two HAAs, DCAA with the purity greater than 98% and TCAA with the purity greater than 99%, were both obtained from Acros Organics. 1000 mg L^{-1} DCAA, TCAA stock solutions were prepared in tert-Butyl methyl ether (MtBE, Acros Organics). A stock of free chlorine solution was prepared from commercial sodium hypochlorite (NaClO, 10% active chlorine) and then diluted with Milli-Q pure water (Mill-Q SP VOC, Millipore Co., Bedford, MA). The acute concentration of sodium hypochlorite solution was standardized by sodium thiosulfate titration. Iron and manganese used in the experiments were added in the form of iron (III) nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), and manganese (II) nitrate ($Mn(NO_3)_2$). All solutions were prepared using Milli-Q pure water.

2.2. Cultivation of algae

C. vulgaris was illuminated at the light intensity of 2500 lx from fluorescent lamp for a 14 h light/10 h dark regime at 25 °C according to OECD (The Organisation for Economic Co-operation and Development) [23] and maintained in OECD medium with pH adjusted to 8.0 by NaOH or HCl. The cell concentration of *C. vulgaris* was cultured in the late log growth phase (96 h). Then, the algal cells were collected by centrifuging (4000 rpm, 10 min) twice and prepared for chlorination procedure. Duplicate algae samples were taken for total organic carbon determination under different concentration (TOC 5000, Shimadzu, Japan).

2.3. Chlorination

Chlorination of the model samples in the present study has been carried out at least twice according to the following procedures.

In the experiment of chlorination of algae, sodium hypochlorite was added with the concentration of 10 mg L^{-1} free chlorine (as Cl_2) solution into 500 mL glass bottle, and then pH of the solution were adjusted to 6.0, 7.0, 8.0, 9.0 using HCl and NaOH and buffered with phosphate (50 mL) to maintain the pH. After that, the centrifugated algae solution was quickly added to the glass bottle at initial concentration of 1.75×10^5 cell mL^{-1}, and no significant change of pH value was observed during this process. And the 500 mL sample was kept in oscillation and was quickly subpackaged into 25 mL vials which were placed in air bath with temperature maintained at 25 ± 1 °C with reciprocating rate at 120 rpm. Samples of 25 mL were taken out at 0.083, 0.167, 0.5, 1, 2, 4, 8, 12, 24, 36, 48 h, respectively.

In the experiments of the effects of iron and manganese on the chlorination of algae, 500 mL sample which contained algae and sodium hypochlorite was kept in oscillation incubator and was quickly subpackaged into 25 mL vials. These 25 mL vials were placed in an air bath at 25 ± 1 °C and with a reciprocating rate of 120 rpm. Different concentrations of iron or manganese (0, 0.1, 0.2, 0.3, 0.5, 0.8 and 1.0 mg L^{-1}) were added into the 25 mL glass vials, respectively. Samples of 25 mL were taken out at 24 h.

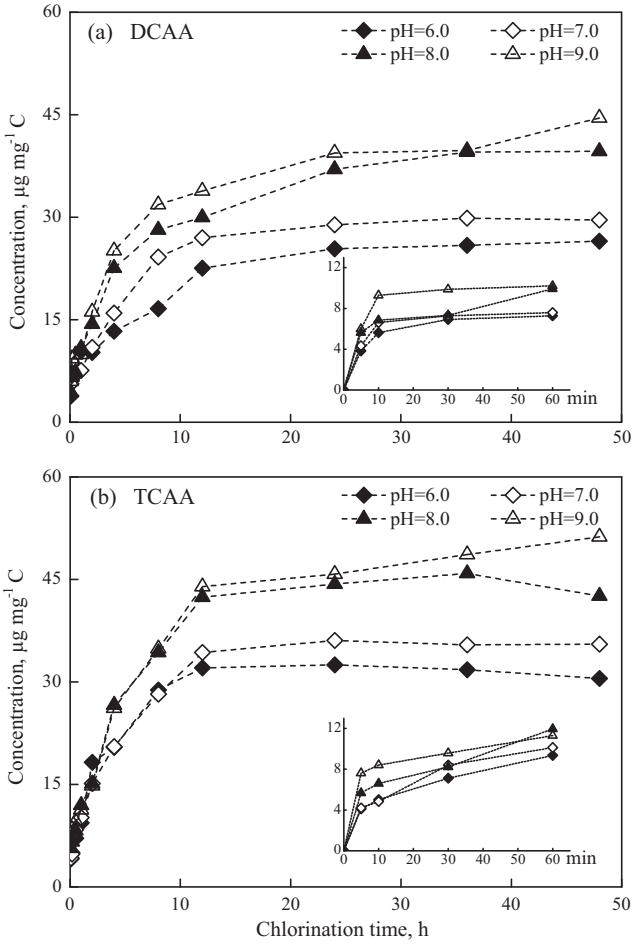

Fig. 1. The yields of HAAs under different pH upon the chlorination of *C. vulgaris*. Initial concentration of algae: 1.75×10^5 cell mL^{-1}, initial concentration of Cl_2: 10 mg L^{-1}.

The residual sodium hypochlorite in samples was decomposed by adding excess sodium thiosulfate, and then the samples were analyzed with USEPA Method 552.3 [24].

2.4. HAAs analysis

HAAs were quantified by liquid/liquid extraction with MtBE, followed by derivatisation with acidic methanol and by GC/ECD analysis (GC-14 C, Shimazu, Japan) in accordance with USEPA Method 552.3. To avoid degradation of HAAs, all samples were processed within 2 days of collection. All analyses were carried out in duplicate. Calibration was made by comparing the HAA concentrations with an external standard commercial kit with known HAAs concentration. The correlation coefficient of calibration curves were greater than 0.99. In addition, the potential impact of the growth medium in terms of HAAs formation can be neglected since the yield of HAA compounds produced by the medium alone was found to be very low compared to those by algae samples.

2.5. Algal cells surface morphology analysis by SEM

Algal samples for SEM analysis were placed in phosphate buffer solution (pH 7.0) and fixed with 2.5% glutaraldehyde at 4 °C over night. After that, samples were washed by phosphate buffer solu-

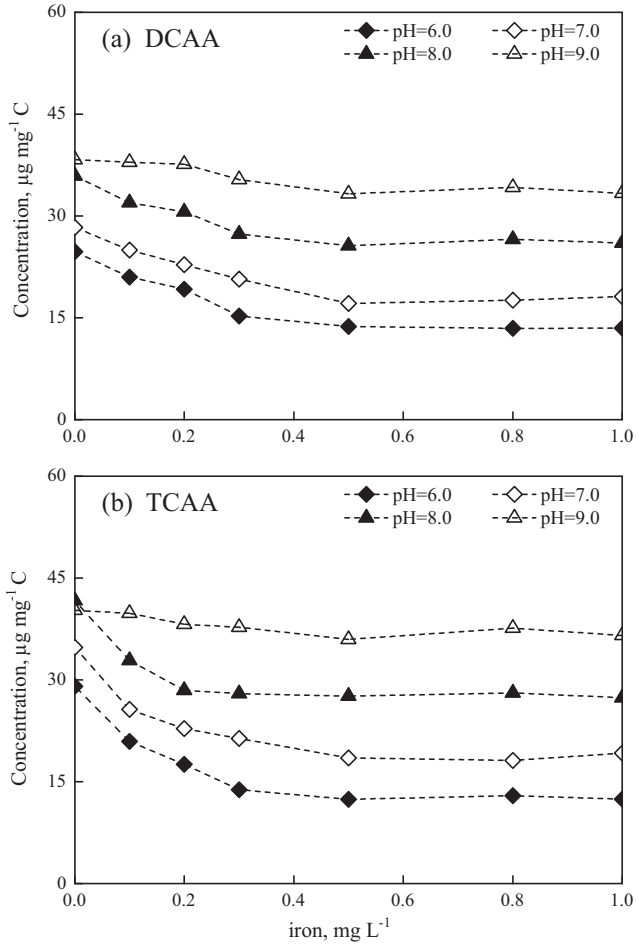

Fig. 2. Effect of iron on the formation of HAAs upon the chlorination of *C. vulgaris*. Initial concentration of algae: 1.75×10^5 cell mL^{-1}, initial concentration of Cl_2: 10 mg L^{-1}, *T*: 24 h.

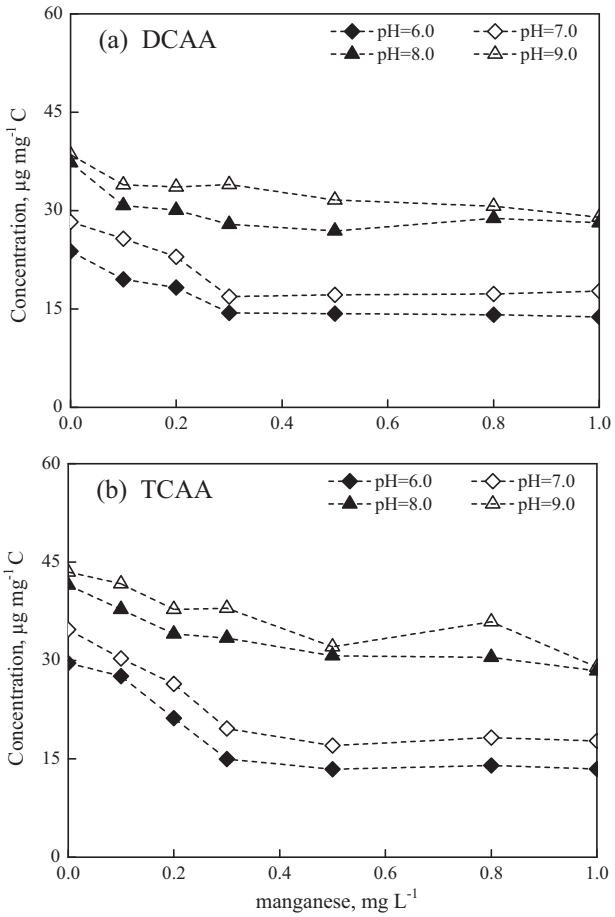

Fig. 3. Effect of manganese on the formation of HAAs upon the chlorination of *C. vulgaris*. Initial concentration of algae: 1.75×10^5 cell mL^{-1}, initial concentration of Cl_2: 10 mg L^{-1}, *T*: 24 h.

tion, and dehydrated successively with different concentrations of ethanol. Then they were dried by critical point drying. Dried samples were mounted on conductive adhesive. The specimens were observed and photographed using a SEM (QUANTA 400, FEI, U.S.A.) at 20 kV.

2.6. Algal particle sizes distribution analysis by LPSA

The particle sizes of the algal samples were measured by LPSA (Malvern Mastersizer 2000®, Malvern Instruments Ltd., U.K.) with the small volume sample presentation unit (capacity of 1000 mL) [25]. Approximately 1000 mL of algal samples were centrifugated into 25 mL after 24 h chlorination, and then were added dropwise into sample cell containing 850 mL of distilled water until an obscuration between 4.5% was obtained. Particle size measurement of each sample was performed using 2000 sweeps and analyzed with the reference refractive index of distilled water. The particle size distribution was calculated by averaging the results of the three samples.

3. Results and discussion

3.1. HAAs yields from C. vulgaris

HAAs yields from *C. vulgaris* under different pH are shown in Fig. 1. Two predominant HAAs, DCAA and TCAA, could be detected upon the chlorination of *C. vulgaris* under experimental conditions, which was in accordance with the results from the chlorination of green alga *Chlamydomonas* sp. [26]. The yields of DCAA were less than those of TCAA under the same conditions, e.g., 25 μg mg^{-1} C for DCAA vs 30 μg mg^{-1} C for TCAA at pH 6.0 after 24 h. This might be ascribed to the different precursor components of DCAA and TCAA in the algal cells. Hong et al. [5] compared model compounds in the formation of HAAs, including bovine serum albumin (BSA), starch and fish oil, as surrogates of algal-derived proteins, carbohydrates and lipids, and the results showed that DCAA yield (28.9 μg mg^{-1} C) was less than TCAA yield (32.9 μg mg^{-1} C). BSA was shown to have higher reactivity (49 μg mg^{-1} C) than fish oil and starch (5 μg mg^{-1} C) in the formation of HAAs.

DCAA and TCAA could be detected in five minutes with the values of 3.84 μg mg^{-1} C and 4.12 μg mg^{-1} C at pH 6.0, respectively. Then, their yields gradually increased with reaction time. In the pH range 6.0–7.0, the yields of DCAA and TCAA could reach a maximum at 12 h. However, in the pH range 8.0–9.0, 24 h was needed to reach the maximum yields. Meanwhile, the yields of HAAs increased with the increase of pH. When pH increased from 6.0 to 9.0, DCAA and TCAA varied from 25.4 μg mg^{-1} C to 39.4 μg mg^{-1} C and from 32.5 μg mg^{-1} C to 45.8 μg mg^{-1} C, respectively at 24 h, which was similar to the results from the chlorination of *Microcystis aeruginosa* reported by Fang and Ma [27].

3.2. HAAs yields from C. vulgaris with iron and manganese

Fig. 2 shows the yields of HAAs upon chlorinating *C. vulgaris* with iron in the pH range of 6.0–9.0 after 24 h. Comparing with

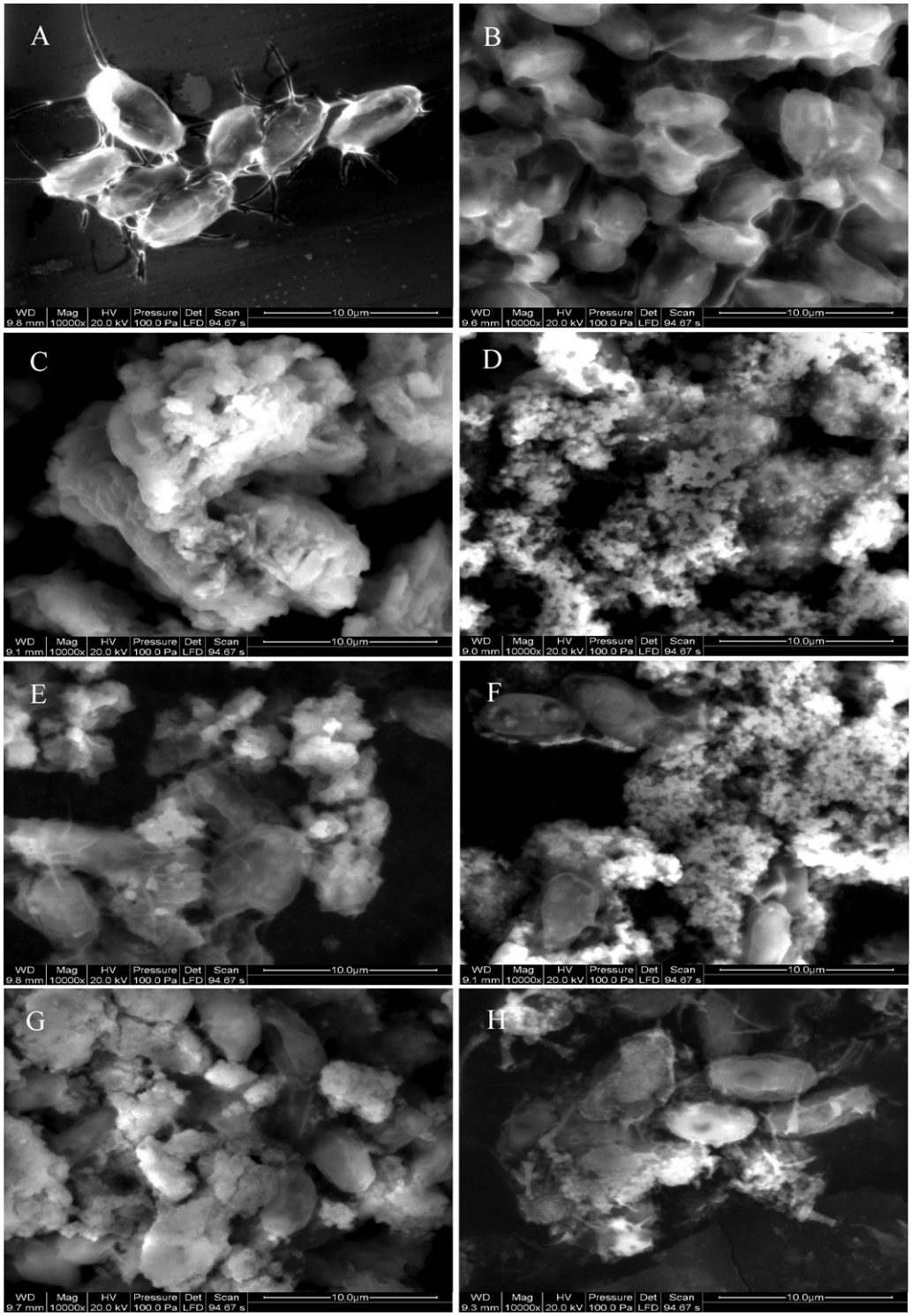

Fig. 4. SEM micrographs of algal cell surface morphology with and without iron or manganese in chlorination. (A) Algae (B) Algae in chlorination (C) $Fe(OH)_{3(am)}$ (D) $MnO_{2(am)}$ (E) Algae with $Fe(OH)_{3(am)}$ (F) Algae with $MnO_{2(am)}$ (G) Algae with iron in chlorination (H) Algae with manganese in chlorination. Initial pH: 6.0, *T*: 24 h.

the control samples (where no iron or manganese was added), the yields of DCAA and TCAA were reduced in the presence of iron (0.1–1.0 mg L^{-1}). With increasing amount of iron, the yields of DCAA and TCAA gradually decreased and then reached minimum values where iron concentrations $\geq$0.5 mg L^{-1}. DCAA and TCAA declined to 21.0 μg mg^{-1} C and 20.9 μg mg^{-1} C with the addition of 0.1 mg L^{-1} iron, and further declined to 13.7 μg mg^{-1} C and 12.4 μg mg^{-1} C with iron $\geq$0.5 mg L^{-1} at pH 6.0, respectively. The decline of HAAs was more significant at a low pH range, and the total amounts of HAAs decreased 27.7 μg mg^{-1} C (11.0 μg mg^{-1} C for DCAA and 16.7 μg mg^{-1} C for TCAA) with the addition of 0.5 mg L^{-1} iron at pH 6.0. In other words, DCAA and TCAA decreased 44.5% and 57.3% compared to the control, respectively. However, the amounts of HAAs decreased by only 9.3 μg mg^{-1} C at pH 9.0.

The yields of HAAs upon chlorinating *C. vulgaris* with the addition of manganese at pH 6.0–9.0 for 24 h are shown in Fig. 3.

When the addition of manganese was ≥0.5 mg L^{-1}, the yields of DCAA and TCAA did not decline continuously with the increase of manganese amount and reached minimum values. The total HAAs produced decreased 24.0 μg mg^{-1} C (9.4 μg mg^{-1} C for DCAA and 14.6 μg mg^{-1} C for TCAA) with the addition of 0.5 mg L^{-1} manganese at pH 6.0, corresponding to 39.5% decrease for DCAA and 49.4% decrease for TCAA at pH 6.0. However, the yield of HAAs only decreased 10.1 μg mg^{-1} C at pH 9.0.

The above results showed that both iron and manganese reduced the yields of DCAA and TCAA in the pH range 6.0–9.0, and the decline of DCAA and TCAA was more significant at the low pH. This indicated that the effects of iron and manganese on HAAs formation were similar.

3.3. Algal cells surface morphology characterization by SEM

Possible mechanisms of the effects of iron and manganese on the chlorination were investigated using SEM to analysis the change of algal cells surface morphology. Fig. 4 shows the SEM micrographs of *C. vulgaris* with and without iron or manganese at pH 6.0 on chlorination after 24 h. Fig. 4A and B shows the image of the algae and algae on chlorination, respectively. Fig. 4C is micrograph of $Fe(OH)_{3(am)}$ and Fig. 4D is micrograph of $MnO_{2(am)}$, which were generated by the hydrolysis of iron (III) and by reacting manganese (II) and chlorine stoichiometrically, respectively. Fig. 4E and F are SEM micrographs of algal cells taken after iron (III) and $MnO_{2\ (am)}$ in algal suspension, respectively. Fig. 4G and H are SEM micrographs of algal cells taken after iron (III) and manganese (II) on chlorination, respectively.

It is known that when sodium hypochlorite is dissolved in water, it hydrolyzes rapidly according to Eq. (1) and combined with H^+ according to Eq. (2).

$$NaClO \rightleftarrows ClO^- + Na^+ \quad (1)$$

$$ClO^- + H^+ \rightleftarrows HClO \quad (2)$$

In the presence of strong oxidants such as ClO^-, manganese (II) will be oxidized to either α -MnO_2 or γ -MnO_2. These conditions provide a porous blackish-brown product which is a mixture of manganese oxides. The principal reaction is given below in the presence of manganese [28]:

$$3Mn^{2+} + 4ClO^- + H_2O \rightarrow MnO_2 + 2H^+ + 2Cl_2 \quad (3)$$

Iron (III) does not have similar reactions as manganese (II) in the presence of ClO^- and exists in different forms under various pH in aqueous solution conditions. The hydrolysis reaction of iron (III) can be depicted as follows:

$$xFe^{3+} + yH_2O \rightleftarrows Fe_x(OH)_y^{(3x-y)+} + yH^+ \quad (4)$$

It is generally considered that Fe^{3+} exists when pH < 4, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ exist in pH 4–6. The main hydrolysis products are $Fe(OH)_{3(am)}$ gel-precipitation in pH 6–8 and $Fe(OH)_4^-$ when pH > 8 [29].

In Fig. 4A, the algal cells were shown to be present in single and/or in agglomerates. In Fig. 4B, the addition of chlorine to the algal suspension caused significant alteration of the algal cell morphology and in some instances induced algal cell lysis. In Fig. 4C, it was observed that $Fe(OH)_{3(am)}$ colloids were generated by the hydrolysis of iron (III), and $MnO_{2(am)}$ was generated by the reaction of manganese (II) with chlorine in Fig. 4D. These phenomena demonstrated that similar reactions would occur with the addition of iron(III) or manganese (II) on chlorination of algae. A significant difference was noticed for the surface of algal cells in Fig. 4E and F in contrast to that in Fig. 4A. With the addition of iron (III) or $MnO_{2(am)}$ to algal suspension, the algal cells retained morphological integrity, however the surface of some algal cells were coated with a thick layer of material. In Fig. 4G and H, some of the algal cells deflated and the inclusion might outflow, which indicated that the strong oxdiation of chlorine caused the damage of algal cells. While other algal cells were still coated with a thick layer of hydrolyzed materials resulting from the formation of $Fe(OH)_{3(am)}$ and $MnO_{2(am)}$ colloids in this process.

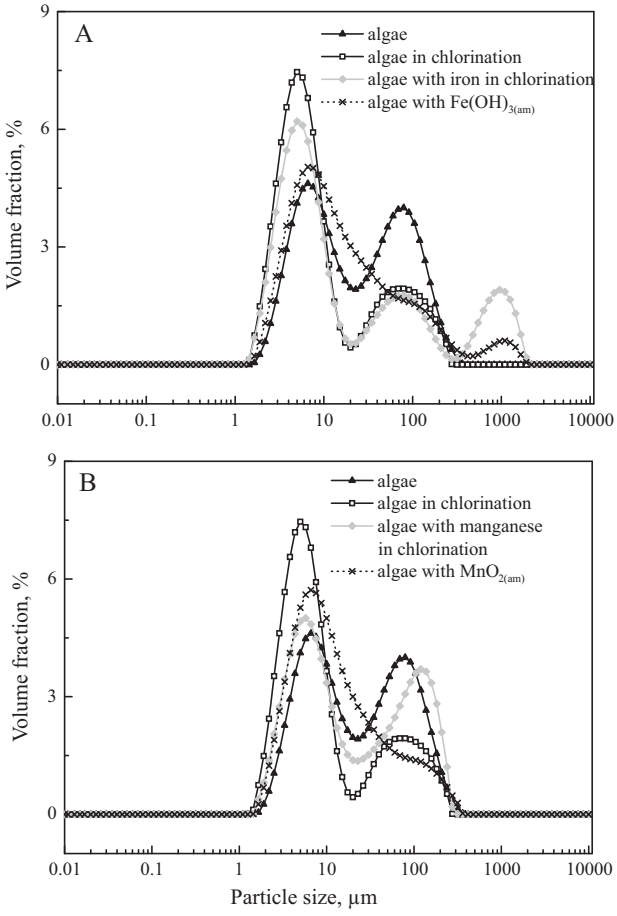

Fig. 5. Effects of iron and manganese on the particle size distribution of algae in chlorination (A) Effect of iron (B) Effect of manganese. Initial pH: 6.0, *T*: 24 h.

The effect of iron and manganese in the chlorination is that the $MnO_{2(am)}$ or $Fe(OH)_{3(am)}$ colloids might attach to the algal surface and obviously change the property of algal surface. In addition, the colloid increases the concentration of particles in water. As a result, the weight of the algal cells increase, and thus the algae settling ability is greatly enhanced [18,19]. The film covering the algal cells reduces contact with chlorine, and hence we propose that this is the reason that in the presence of iron and manganese, $Fe(OH)_{3(am)}$ or $MnO_{2(am)}$ on the surface of *C. vulgaris* decreases the yields of HAAs during the chlorination.

3.4. Algal particle sizes distribution characterization by LPSA

The particle sizes of algal cells after different treatments at pH 6.0 were measured by LPAS, and the results are given in Fig. 5. The coating of $Fe(OH)_{3(am)}$ or $MnO_{2(am)}$ results in the increase of the particle sizes of algal cells after chlorination. Fig. 5A shows two main peaks with a maximum particle size of 6 μm and 100 μm in a bimodal distribution, which ranged from 2 to 20 μm and from 20 to 300 μm, respectively. The former peak corresponds to algal cells in single, and the latter peak corresponds to the algal cells in an agglomeration. In contrast to the control algal suspension, it was observed that the maximum volume fraction of particle size

in 2–20 μm rose from 4.6% to 7.5% with the addition of chlorine, while the maximum volume fraction of particle size in 20–300 μm declined from 3.9% to 1.9%. This could be the destroying of chlorine on the agglomeration of algal cells. When iron was added to algal suspension the particle size distribution changed from a bimodal distribution to a multi-modal distribution. A new distribution peak in the multi-modal distribution occurred in the range of 300–2000 μm, which demonstrated that the addition of iron improved the agglomerate of algal cells. Furthermore, the maximum volume fraction of particle size in 300–2000 μm increased from 0.6% to 1.9% in the presence of iron, due to the enhancement in the agglomeration of algal cells in the chlorination process.

In Fig. 5B, in contrast to the results of the algal suspension in chlorination, it was observed that the addition of manganese improved the agglomeration of algal cells, which could be proved by the decline of the maximum volume fraction of particle size in 2–20 μm (from 7.5% to 4.9%) and the increase of the particle size of maximum volume fraction in range of 20–300 μm (from 80 μm to 120 μm).

The results of Sections 3.3 and 3.4 suggest that the coating of $Fe(OH)_{3(am)}$ or $MnO_{2(am)}$ on the surface of algal cells inhibits the algal cells to contact with chlorine which therefore leads to the decline of HAAs yields in chlorination process.

4. Conclusion

The presence of both iron and manganese significantly reduced the yields of DCAA and TCAA over the pH range of 6.0–9.0 upon chlorination of green alga *C. vulgaris*, and the decline of DCAA and TCAA was more significant in the low pH range. Based on the results of SEM, the surface of algal cells were coated with $Fe(OH)_{3(am)}$ or $MnO_{2(am)}$ on chlorination, which then led to the agglomeration of algal cells on chlorination. This was also supported by the LPAS results. The coating of algal cells by the hydrolysis materials is the main reason for the decline of HAAs yields on chlorination by inhibiting algal cell to contact with chlorine. These results indicate that the effects of metal ions should be concerned on the formation of DBPs in the drinking water disinfection process.

Acknowledgements

We gratefully acknowledge the financial support from Excellent Youth Project of Education Committee of Hunan Province of China (No. 07B077), Research Foundation of National Natural Science Foundation of China (No. 20877065), Program for New Century Excellent Talents in University of China (NECT-10-0148). The author also thanks for Yi Zhu for her assistant in TOC analysis of algae, and Dr. Jianxi Zhu for his help in algal cell surface morphology by SEM and Prof. Stephen C.

Parker for his help in revising the paper.

References

[1] W.P. Cheng, F.H. Chi, Influence of eutrophication on the coagulation efficiency in reservoir water, Chemosphere 53 (2003) 773–778.
[2] S.J. Hoeger, B.C. Hitzfeld, D.R. Dietrich, Occurrence and elimination of cyanobacterial toxins in drinking water treatment plants, Toxicol. Appl. Pharmacol. 203 (2005) 231–242.
[3] C. Chen, X.J. Zhang, L.X. Zhu, J. Liu, W.J. He, H.D. Han, Disinfection by-products and their precursors in a water treatment plant in North China: seasonal changes and fraction analysis, Sci. Total Environ. 397 (2008) 140–147.
[4] N. Ates, S. Sule Kaplan, E. Sahinkaya, M. Kitis, F.B. Dilek, U. Yetis, Occurrence of disinfection by-products in low DOC surface water in Turkey, J. Hazard. Mater. 152 (2007) 526–534.
[5] H.C. Hong, A. Mazumder, M.H. Wong, Y. Liang, Yield of trihalomethanes and haloacetic acids upon chlorinating algal cells, and its prediction via algal cellular biochemical composition, Water Res. 42 (2008) 4941–4948.
[6] J.D. Plummer, J.K. Edzwald, Effect of ozone on algae as precursors for trihalomethane and haloacetic acid production, Environ. Sci. Tech. 35 (2001) 3661–3668.
[7] M.L. Nguyen, P. Westerhoff, L. Baker, Q. Hu, M. Esparza-Soto, M. Sommerfeld, Characteristics and reactivity of algae produced dissolved organic carbon, J. Environ. Eng. 131 (2005) 1574–1582.
[8] J. Huang, N. Graham, M.R. Templeton, Y. Zhang, C. Collins, M. Nieuwenhuijsen, A comparison of the role of two blue-green algae in THM and HAA formation, Water Res. 43 (2009) 3009–3018.
[9] A. Strezov, T. Nonova, Environmental monitoring of heavy metals in Bulgarian Black Sea green algae, Environ. Monit. Assess. 105 (2005) 99–110.
[10] J. de Jong, M. Boye, M.D. Gelado-Caballero, K.R. Timmermans, S.M. Veldhui, R.F. Nolting, C. van den Berg, H. de Baar, Inputs of iron, manganese and aluminium to surface waters of the Northeast Atlantic Ocean and the European continental shelf, Mar. Chem. 107 (2007) 120–142.
[11] Z.H. Liu, X.H. Liu, B. He, J.F. Nie, J.Y. Peng, L. Zhao, Spatiotemporal change of water chemical elements in Lake Dianchi, China, Water Environ. J. 23 (2009) 235–244.
[12] S.Q. Sun, C.W. Wang, J. Ma, X.D. Huang, Research on Mn/Fe removal from the surface water in Taihu Lake area with several preoxidants, Ind. Water Treat. 27 (2007) 42–44, in chinese.
[13] E.R. Blatchley, D. Margetas, R. Duggirala, Copper catalysis in chloroform formation during water chlorination, Water Res. 37 (2003) 4385–4394.
[14] L. Zhang, W.A. Arnold, R.M. Hozalski, Kinetics of haloacetic acid reactions with Fe(0), Environ. Sci. Technol. 38 (2004) 6881–6889.
[15] S. Navalon, M. Alvaro, H. Garcia, Ca^{2+} and Mg^{2+} present in hard waters enhance trihalomethane formation, J. Hazard. Mater. 169 (2009) 901–906.
[16] B. Li, R.P. Liu, H.J. Liu, J.N. Gu, J.H. Qu, The formation and distribution of haloacetic acids 9 in copper pipe during chlorination, J. Hazard. Mater. 152 (2008) 250–258.
[17] Z.Z. Zhu, J. Wang, Y. Ge, H. Ma, J. Zhao, Effects of bromide and ferric ions on formation of tri-halomethanes during disinfection of drinking water by chlorine, Environ. Sci. 28 (2007) 1264–1267, in chinese.
[18] J. Ma, W. Liu, Effectiveness and mechanism of potassium ferrate(VI) preoxidation for algae removal by coagulation, Water Res. 36 (2002) 871–878.
[19] J.J. Chen, H.H. Yeh, The mechanisms of potassium permanganate on algae removal, Water Res. 39 (2005) 4420–4428.
[20] J.J. Chen, H.H. Yeh, I.C. Tseng, Effect of ozone and permanganate on algae coagulation removal-Pilot and bench scale tests, Chemosphere 74 (2009) 840–846.
[21] A. Czaplicka-Kotas, Influence of water quality on the synthesis of photosynthetic dyes in the cells of the algae *Chlorella Vulgaris* for the purpose of surface water biomonitoring, Ochrona Środowiska 29 (2007) 27–33.
[22] Y. Xie, I. Rashid, H. Zhou, L. Gammie, Acidic methanol methylation for HAA analysis-limitations and possible solutions, J. Am. Water Works Assoc. 94 (2002) 115–122.
[23] OECD, OECD Guidelines for the Testing of Chemical, 201: Algal, Growth Inhibition Test, Organization for Economic Co-operation and Development, Paris, 2006, pp. 25–40.
[24] USEPA, Method 552.3: determination of haloacetic acids and dalapon in drinking water by liquid–liquid extraction, in: Derivationand Gas Chromatography with Electron Capture Detection, USEPA Office of Research and Development, Cincinnati, Ohio, 2003, pp. 25–40.
[25] C.L. Schneider, R. Neumann, A.S. Souza, Determination of the distribution of size of irregularly shaped particles from laser diffractometer measurements, Int. J. Miner. Process. 82 (2007) 30–40.
[26] H.C. Hong, M.H. Wong, A. Mazumder, Y. Liang, Trophic state, natural organic matter content, and disinfection by-product formation potential of six drinking water reservoirs in the Pearl River Delta, China, J. Hydrol. 359 (2008) 164–173.
[27] J.Y. Fang, J. Ma, X. Yang, C. Shang, Formation of carbonaceous and nitrogenous disinfection by-products from the chlorination of *Microcystis aeruginosa*, Water Res. 44 (2010) 1934–1940.
[28] Y. Darmane, M. Cherkaoui, S. Kitane, A. Alaoui, A. Sebban, M.E. Touhami, Preparation of chemical manganese dioxide from Moroccan pyrolusite mine waste, Hydrometallurgy 92 (2008) 73–78.
[29] F.J. Millero, W. Yao, J. Aicher, The speciation of Fe(II) and Fe(III) in natural waters, Mar. Chem. 50 (1995) 21–39.