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$TiCl_3$ coagulation for algae-laden water treatment: Performance, control of algal organic matters release and mechanism

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Abstract−Efficient elimination of algal cells with simultaneous inhibition of algal organic matters release is vital for the safety of drinking water. $TiCl_3$ as a coagulant was first applied for *Microcystis aeruginosa* removal in the present study. At the same dosage of 130 μM, higher removal efficiency of 98.1% for algae cells was obtained in $TiCl_3$ coagulation than 64.5% for $TiCl_4$, and the same trend was observed in turbidity and dissolved organic compound removal. Owing to the low reduction capacity of $TiCl_3$, a low damage cell ratio was achieved. While charge neutralization plays a crucial role in the $TiCl_3$ coagulation, the reduction capacity of $TiCl_3$ appears to be decisive for improving the algae removal efficiency. This study suggests that $TiCl_3$ could be a promising coagulant for efficient removal of algae and inhibition of algal organic matter release.

Keywords: *Microcystis aeruginosa*, $TiCl_3$, Coagulation, Reduction Capacity, Cell

INTRODUCTION

Algae bloom resulting from eutrophication in surface water is becoming one of the greatest threats to the water safety, receiving worldwide critical concern [1]. The high cell concentration and the released algal organic matters (AOMs) during algal blooms can seriously decrease the efficiency of drinking water treatment plants (DWTPs) via inhibiting coagulation [2], shortening the filtration cycle and eliminating the residual chlorine [3]. As the precursors of disinfection by-product (DBPs), AOMs including microcystins (MCs) and taste and odor compounds are deleterious to human and aquatic biota [4]. Obviously, it is essential to develop new strategies to enhance the removal efficiency of algae cells while simultaneously diminishing the adverse influence.

Coagulation-sedimentation-filtration is the most common treatment process in DWTPs [5]. Coagulation has been projected to be the most economic process for algae removal [6]. However, algae cells are recalcitrant to coagulation due to electrostatic repulsion, diverse morphology, and high motility [7,8]. To attain effective removal of algae, high dosage of coagulant is frequently applied, which could result a high residue concentration of metal ions in the effluent of sedimentation and produce massive chemical sludge [9].

The chemical oxidants introduced before coagulation process could change the surface charge of algae, inactivate the algae cells, mineralize the intracellular organic matters, and improve the algae removal. Oxidants (e.g., Cl_2, ClO_2, O_3, persulfate, ferrate and $KMnO_4$) could increase algae removal efficiency of the coagulation with less coagulant dosage [10-12]. Nevertheless, lysis of algae caused by excessive dosage of oxidants could emit intercellular organic matters, which are the typical precursors of DBPs.

Ti salts were used as coagulants in the beginning of the 20th century (Block, 1916). Due to the complete hydrolysis of Ti salts, the concentration of Ti ion residues in the effluent of sedimentation is far lower than other transition metal coagulants [13]. Furthermore, TiO_2, a value added photocatalyst, could be generated during the coagulation process [14]. Highly charged Ti salts, including $TiCl_4$, $Ti(SO_4)_2$ and $TiOSO_4$, can remove organic matters, heavy metals, turbidity and fluoride ions more efficiently than Al and Fe flocculants [15-17]. $TiCl_4$ exhibited more productive removal of algae than $FeCl_3$, especially at low dosage [18].

In comparison with $TiCl_4$, which can form cloudy TiO_2 and HCl in humid air, $TiCl_3$ is frequently applied as reduction agent for organic molecular synthesis and organic matter measurements due to its stability and safety [19]. With greater size of floc, dissolved organic matter was more efficiently removed by $TiCl_3$ than $AlCl_3$ [20]. Additionally, the reaction between $TiCl_3$ and AOMs on the surface of algae could change the charge of algae cells, which might promote the removal of algae [21]. According to the results from these previous studies, $TiCl_3$ might be a promising coagulant for efficient removal of algae. However, a study on the application of $TiCl_3$ as coagulant for algae removal is still absent.

In this study, $TiCl_3$ was first applied as reduction agent and coagulant for removal of *Microcystis aeruginosa* (*M. aeruginosa*), which is the chief culprit of algal blooms in the aquatic environment. The removal efficiency and control of AOMs release were evaluated. The safety of $TiCl_3$ coagulation process was assessed by means of investigating the change of surface property, integrity of algal cells, MCs release and DBPs formation potential (DBPFP). Finally, the mechanism of coagulation removal of algal cells in the presence of $TiCl_3$ was supposed.

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MATERIALS AND METHODS

1. Materials and Reagents

M. aeruginosa was purchased from the Institute of Aquatic Biology (Wuhan, China) and was cultured in BG-11 medium with a light intensity of 2,000 lux and a light-dark cycle of 12 hours : 12 hours at 25 °C. *M. aeruginosa* used in the experiment was taken from the late stage of its exponential growth cycle and diluted with Milli-Q water to obtain a cell density of 2.0 (±0.5)×10^6 cells/mL, which is approximately equal to the cell density during the outbreak period of *M. aeruginosa* in practical water.

The reagents used in BG-11 medium, $TiCl_3$ solution, $TiCl_4$ were obtained from Macklin Inc, China. Microcystin-LR (MC-LR) ELISA kit was purchased from Shanghai Yubo Biotechnology Co., Ltd. (China). The standard solutions of DBPs, such as trichloromethane (TCM), chloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA), were purchased from Sigma-Aldrich (USA). The other chemical reagents used in the study were analytical or chromatographic grade and purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (China). The free chlorine (HClO) stock solution was prepared through diluting sodium hypochlorite solution (5 wt%) followed by a standardization according to American Public Health Association (APHA) standard method [22]. The $TiCl_4$ solution was added into the frozen cubes slowly with hydrochloric acid and diluted to obtain the same molar concentration as the purchased $TiCl_3$ solution. SYTOX Green nucleic acid stain was purchased from Invitrogen (USA).

2. Experimental Protocols

2-1. $TiCl_3$ and $TiCl_4$ Coagulation-sedimentation Experiments

All the coagulation experiments were carried out on a programmable jar tester (ZR4-6, ZhongRun, China) at 25 °C. Initially, an aliquot of 200 mL of simulated suspension with *M. aeruginosa* was transferred into a 250 mL glass beaker. The suspension was then stirred at 250 rpm for 30 s to make it homogeneously mixed. The coagulation-sedimentation experiment was started by rapidly introducing $TiCl_3$ or $TiCl_4$ solution. The reaction solution was stirred at a speed of 250 rpm for 30 s, which was kept at 100 rpm for 1.5 min in the following and finally at 40 rpm for 15 min. The reaction solution was settled for 15 min. Following sedimentation, the supernatant was collected from 1 cm under the liquid surface for subsequent experiments and related analysis. The sediment was separated by centrifuge at 4,000 rpm for 10 min and dried at 40 °C prior to the following characterization. Control experiments without added $TiCl_3$ or $TiCl_4$ were conducted under the same conditions.

2-2. Chlorination Experiment

DBPFP of the supernatant was determined by chlorination experiments conducted in 20 mL amber bottles. The pH of the supernatant was adjusted to 7 with KH_2PO_4 buffer and NaOH (0.05 M) solution. After pH adjusting, the ratio of chlorine to dissolved organic compound (DOC) of the supernatant was set at 3 : 1 (based on the weight). The supernatant was kept in the dark condition at 25 °C for 72 h. Finally, the chlorination reactions were quenched with ascorbic acid.

3 Analytical Method

3-1. Analysis of OD_{680} and Turbidity

The OD_{680} of the algae supernatant, an indicator for cell density of *M. aeruginosa*, was determined by an ultraviolet-visible spectrophotometer (DR6000, HACH Co.). The turbidity of the algae supernatant was determined by a portable turbidity meter (2100Q, HACH Co.).

3-2. Analysis of K^+ Release and DOC

The algae samples were centrifuged at 6,000 rpm for 10 minutes to remove flocs, and then the supernatant was transferred to a glass storage bottle. In the following, two aliquots of supernatant were filtered by a 0.22 μm polyethersulfone (PES) membrane and a 0.45 μm PES Membrane for K^+ analysis and DOC analysis, respectively. K^+ release is an auxiliary indicator to evaluate the cell damage caused by the coagulation process, referring to Jia et al. [23], who established the following expression for cell damage calculation:

$$\text{cell breakage} = \frac{C - C_0}{C_t - C_0} \times 100\%$$

In this expression, C represents K^+ concentration after coagulation, C_0 is the K^+ concentration before coagulation, and C_t is the K^+ concentration of the sample with 30 minutes of ultrasonic treatment. K^+ was determined by an inductively coupled plasma emission spectrometer (ICP-OES, 700 Series, Agilent Technologies), and DOC was determined by a total organic carbon (TOC) analyzer (Multi N/C 2100S, Jena).

3-3. Flow Cytometry

Flow cytometry (FACS Aria III, BD Biosciences) was applied to determine the integrity of algal cells according to the method reported in the previous study [24]. The damaged cells were marked by SYTOX. The green fluorescence of SYTOX green stain was collected in channel FL1 (530 nm), while the red fluorescence of chlorophyll-a in channel FL3 (630 nm). Data were further processed by CellQuest software.

3-4. Analysis of DBPFP

Analysis of DBPFP followed the methods of the US Environmental Protection Agency 551.1 and 552.3, DBPFP in the present study. Methyl tert-butyl ether was applied as a solvent for liquid/liquid extraction. The quantitative analysis was completed by a gas chromatograph (GC,7890N, Agilent Technologies) equipped with an electron capture detector and HP-5 column (30×0.32 mm, ID× 0.25 μm, J & W Scientific).

3-5. Characterization of Flocs

The separated flocs were dried at 38 °C for 72 hours in an electric blast drying oven (HD-E804-45A, HaiDa International). Prior to platinum spraying, the sample was evenly spread on the conductive glue and slightly pressed with flat metal. Finally, the prepared sample was analyzed with a field emission electron microscope (FESEM, JSM-7800F, JEOL).

3-6. FTIR Spectroscopy

The dried algae floc mixed with KBr was characterized by Fourier transform infrared spectrometer (FTIR, Nicolet iS50, Thermo Fisher Scientific).

3-7. Analysis of XPS and Zeta Potential

An X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, Thermo Fisher Scientific) was used to complete the photoelectron spectroscopy measurement scan of the algae flocs. The analysis scan started from 0 to 1,200 eV, and the measurement interval was 1 eV. A high-resolution XPS scan on Ti and C elements for each sample

was performed to facilitate the following analysis. Zetasizer (Nano ZS90, Malvern Panalytical) was used to measure zeta potential.

RESULTS AND DISCUSSION

1. Effect of Various Coagulants on *M. aeruginosa* Removal

The performance of $TiCl_3$ was significantly higher than $TiCl_4$ in experiments with 130 μM coagulant dosage for algal removal (Fig. 1(a)). The removal efficiency of OD_{680}, turbidity, and DOC was 64.5%, 70.4% and 53.2% for $TiCl_4$, which was 98.1%, 93.0%, and 68.3% for $TiCl_3$, respectively.

During coagulation, charge neutralization is the critical factor in reducing the zeta potential and subsequently decreasing net charge repulsion between algae cells. The zeta potential of flocs from $TiCl_3$ coagulation was −1.125 mV, whereas $TiCl_4$ was 13.260 mV at a dosage of 130 μM (Fig. 1(a)). According to the results, excess $TiCl_4$ changed the surface charge from negative to positive, preventing the agglomeration of algae cells. The dosage of $TiCl_4$ was decreased to 90 μM in the succeeding experiment. Although the removal efficiency of OD_{680}, turbidity and DOC increased to 68.8%, 74.6%, and 50.5%, respectively, the removal efficiency was still significantly lower than $TiCl_3$.

The hydrolysis product of $TiCl_3$ and $TiCl_4$ is $Ti(OH)_4$ [25,26], though the surface-absorbing algae organic matters (S-AOMs) could be reduced by $TiCl_3$ in the coagulation process. The reduction reaction increased the magnitude of surface negative charge, which requires more Ti^{4+} to neutralize. With more Ti^{4+} combined on the surface of algae cells, more algae cells agglomerated together during flocculation, resulting in larger flocs (Fig. 1(b)). The enlarged algae flocs increased the sedimentation rate and the algal cell removal efficiency. Therefore, $TiCl_3$ may be an excellent coagulant for removing *M. aeruginosa* because of its reduction ability.

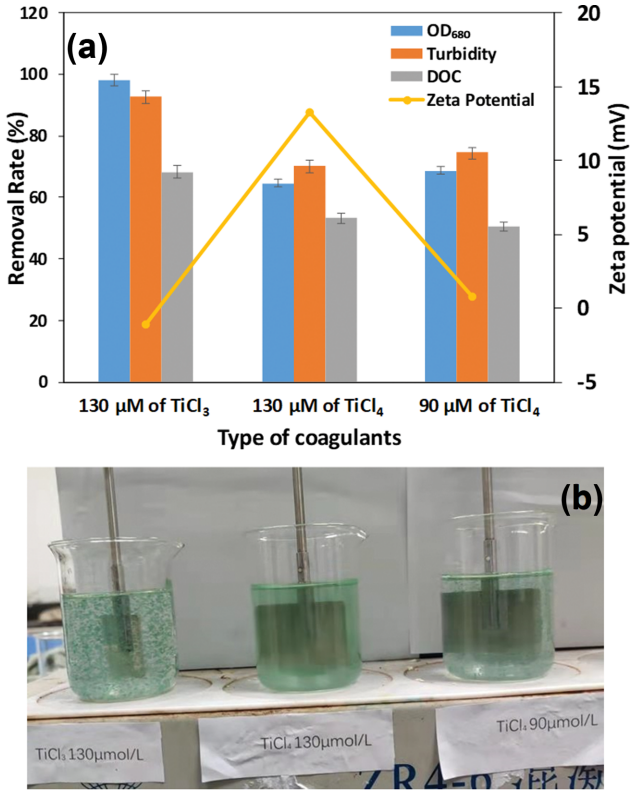

Fig. 1. (a) Comparison of *M. aeruginosa* removal between $TiCl_3$ and $TiCl_4$ ($TiCl_3$ dosage: 130 μM, $TiCl_4$ dosage: 90 μM and 130 μM); (b) Comparison of floc size in various coagulation processes. Conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.16, initial zeta potential −45.64 mV, temperature 25 °C. Error bars represent the standard deviations (n=3).

2. Effects of $TiCl_3$ Concentration on the Removal of *M. aeruginosa*

Experiments were conducted at a concentration between 40 to 240 μM to investigate the effect of $TiCl_3$ concentration on *M. aeruginosa* removal (Fig. 2). The removal efficiency of OD_{680} and turbidity was close to zero with the absence of flocs at 40 μM dosage, indicating that a low concentration of $TiCl_3$ could not neutralize the negative surface charge to form flocs. The removal efficiency of OD_{680} and turbidity rose from 1.9% and 1.7% to 98.1% and 93.0% as the $TiCl_3$ concentration increased from 40 μM to 130 μM. The higher concentration of $TiCl_3$ can neutralize the surface charge and initiate the flocculation of algae. By increasing $TiCl_3$ dosage to 240 μM, the removal of OD_{680} and turbidity decreased from 98.1% and 93.0% to 96.5% and 52.6%. Note that the change of the removal efficiency of OD_{680} and turbidity changed significantly at this time. The zeta potential for the removal rate of algal cells was 10.3 mV, which was not far from the 0 mV, indicating that the removal effect of coagulation was still excellent. However, for turbidity, the excessive $TiCl_3$ may produce a significant number of colloids composed of the water-insoluble $Ti(OH)_4$ [27], which can increase the turbidity of the solution system rapidly.

As previously reported, algae cells are resistant to most conventional coagulation processes because of S-AOMs, which can protect algae from damage and instability [8]. To improve algae removal, S-AOMs must be destroyed to make the algae unstable, which will inevitably increase the DOC concentration in the solution. Therefore, DOC is also an important indicator to evaluate the removal of *M. aeruginosa*. As the concentration of $TiCl_3$ increased from 40

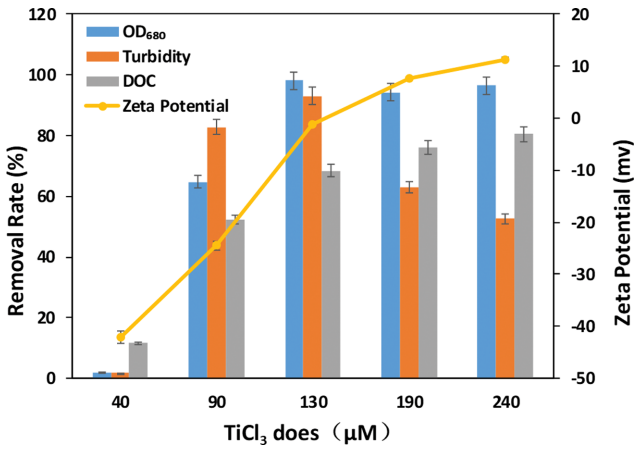

Fig. 2. Effects of $TiCl_3$ on *M. aeruginosa* removal. Conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.16, temperature 25 °C. Error bars represent the standard deviations (n=3).

to 240 μM, the removal efficiency of DOC increased from 11.3% to 80.2% (Fig. 2). Although the S-AOMs were destroyed and released into the solution during the $TiCl_3$ coagulation process, in-situ formed $Ti(OH)_4$ had a high affinity with organic matters, maintaining the high removal efficiency of DOC [28]. However, the removal efficiency of DOC increased much faster at the concentration of 40 and130 μM, when the zeta potential gradually decreased to 0 mV and the electrostatic repulsion diminished. The DOC removal efficiency still increased after 0 mV zeta potential, which may be attributed to physical entrapment and flocs adsorption [29].

On the other hand, the addition of $TiCl_3$ dosage increased the zeta potential of flocs and improved algal removal, indicating that charge neutralization is important in the $TiCl_3$ coagulation process. According to previous studies, the only dominant effect under acidic conditions was the charge neutralization of titanium coagulant [13], and the removal of pollutants by titanium salt under alkaline conditions was mainly achieved through sweep flocculation. During coagulation, the pH of the algae solution was maintained at weakly alkaline (pH 8.16) in this study. However, in the $TiCl_3$ coagulation process, charge neutralization was critical than sweeping flocculation in the. The possible explanation was that the strong reducibility of $TiCl_3$ destructed the S-AOMs, and in-situ formed $Ti(OH)_4$ adhering to the surface of algal cells, which could increase the zeta potential of the surface of the algae and make algae unstable.

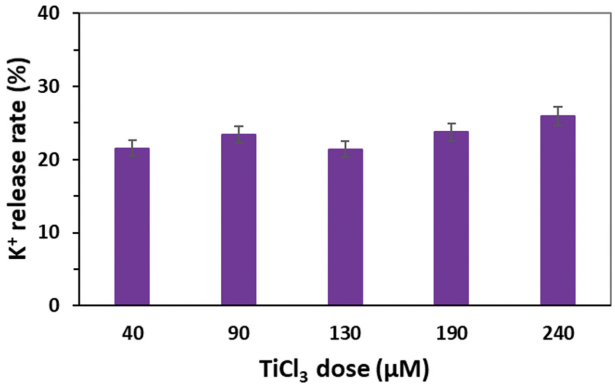

Fig. 3. K^+ release efficiency during $TiCl_3$ coagulation process. Conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.16, temperature 25 °C. Error bars represent the standard deviations (n=3).

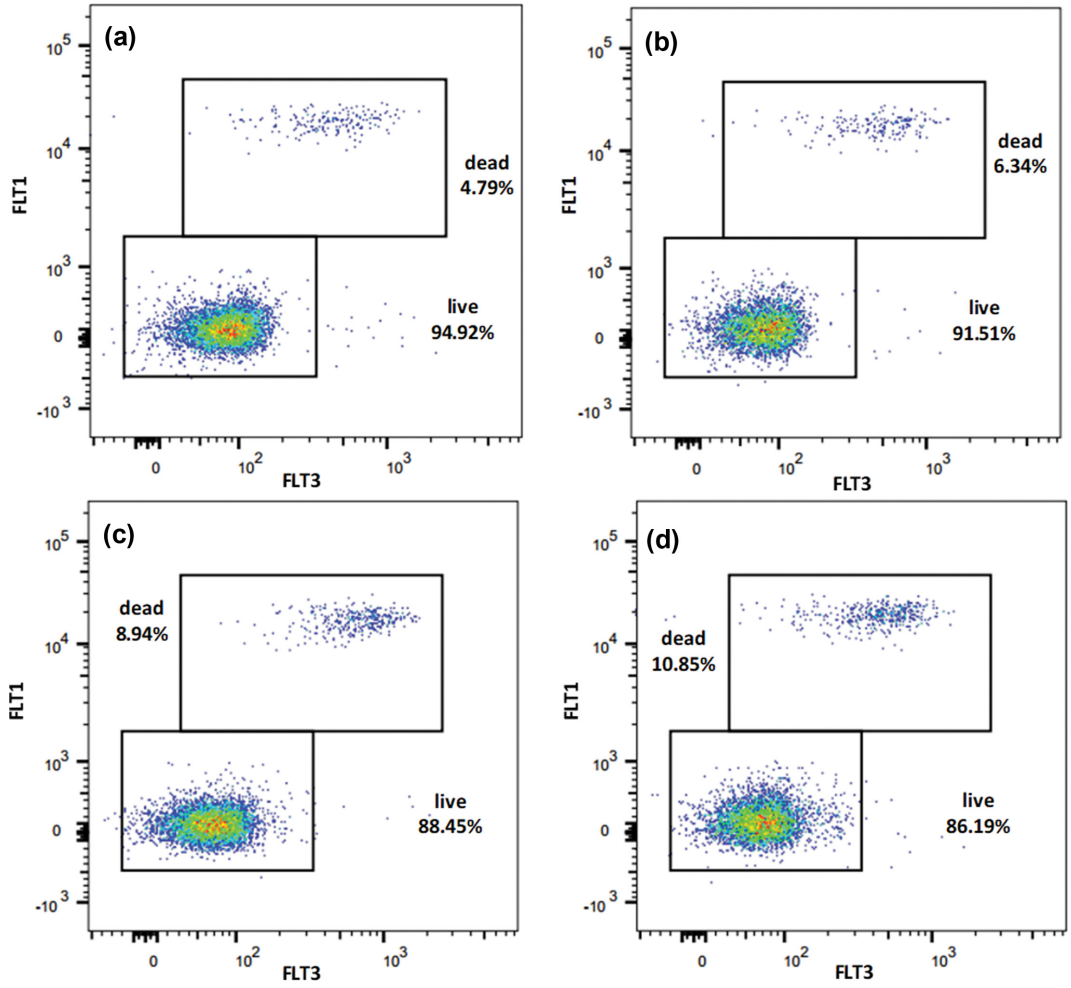

Fig. 4. Ratio of algal cells detected by flow cytometry in coagulation process with various dosage of $TiCl_3$: (a) 0 μM, (b) 90 μM, (c) 130 μM and (d) 240 μM.

3. Evaluation of Cell Integrity, MC-LR, AOMs Release and DBPFP

Fig. 3 shows the variation of K^+ release rate at various $TiCl_3$ concentration. Although the K^+ release rate reached 21.4% when the $TiCl_3$ dosage was 40 μM, as the dosage continued to increase, the K^+ release rate remained constant in the figure. The K^+ release efficiency was still 21.4% at the optimal dosage (130 μM). The results show that $TiCl_3$ can only cause a slight release of K^+, indicating only a small amount of cell damaged, which is milder than other potent oxidizing agents. For example, ClO_2 could cause severe cell damage [30], and the PS/Fe(II) oxidation process could result in a 62.6% cell destruction efficiency in 60 min [31]. The competitive advantage of $TiCl_3$ is that even if it is in excess, it will not result in a high cell destruction rate, which exhibited the addition of $TiCl_3$ creating a relatively mild environment and removing algae without destroying the algae cells.

Flow cytometry was used to assess the effects of $TiCl_3$ coagulation on algal cells. SYTOX could permeate the damaged cell membrane and stain nuclear acid, increasing the fluorescence intensities in channel FL1. Meanwhile, in channel FL3, the red fluorescence intensity corresponding to living cells was collected. Therefore, the fluorescence intensity of algal cells could be exhibited in a series of pseudo-color plots (Fig. 4). The plot with stronger red fluorescence intensity was attributed for living cells and stronger green fluorescence intensity for damaged cells. It could be seen from Fig. 4 that the ratio of damaged cells was only 10.9% at the highest dosage of $TiCl_3$, which revealed the reduction effect was mild. The results demonstrated that the $TiCl_3$ coagulation process is suitable for algal removal and AOM release control.

As previously stated, the addition of $TiCl_3$ can maintain an excellent *M. aeruginosa* removal effect with inevitable algal cell rupture. Therefore, evaluating the effect of $TiCl_3$ on the removal of MC-LR in the process of *M. aeruginosa* and DBPFP, which has been proven have a great relationship with AOMs, is critical to the safety of the method in the actual application process. Fig. 5 shows how the removal rate of DOC and the concentration of MC-LR varied with the $TiCl_3$ dosage during the *M. aeruginosa* coagulation removal. Generally, the DOC removal rate is increasing, whereas the concentration of MC-LR is decreasing, but it remains relatively high. Previous studies found that conventional water treatment processes could remove MC-LR in cells by removing algae cells, but were ineffective for treating extracellular toxins [32,33]. When the addition of $TiCl_3$ was up to 240 μM $TiCl_3$, the concentration of MC-LR remained at 5.73 μg/L. Obviously, the strong reducibility of $TiCl_3$ could not destroy MC-LR, and only a small part of MC-LR could be removed by adsorption. Since in the molecular weight, most DOC is much larger than MC-LR, the DOC removed by adsorption is significantly more. In terms of removing MC-LR, although titanium-based coagulants are at a disadvantage compared with oxidants, compared with other commonly used metal coagulants (such as aluminum-based, iron-based coagulants), titanium-based coagulants have an advantage, and can achieve a higher MC-LR removal rate at a significantly high dosage [34-37]. Compared with most of the methods of pre-oxidation and enhanced coagulation and algae removal, adding excess $TiCl_3$ will not cause large-scale algae cell rupture, resulting in severe AOMs release and significantly reduced DOC removal rate. Therefore, in the actual project, the $TiCl_3$ dosage can be increased to enhance the removal effect of MC-LR to meet the actual requirements.

Fig. 6 shows the changes of DBPFP concentration in the chlorination process of raw water and water after $TiCl_3$ coagulation treatment. Two chlorinated DBPs were selected, including trihalomethanes (THMs) represented by TCM and haloacetic acids (HAAs) represented by MCAA, DCAA, and TCAA. It can be seen from the figure that with the increase of $TiCl_3$ dosage, the concentration of the generated THMs and HAAs was continuously decreasing. For TCM, at the optimal $TiCl_3$ dosage, the concentration decreased to 42.1% of raw algae solution, and at the highest $TiCl_3$ dosage, the concentration further decreased to 34.4%. The results reveal that $TiCl_3$ could effectively remove the TCM precursor, which can be

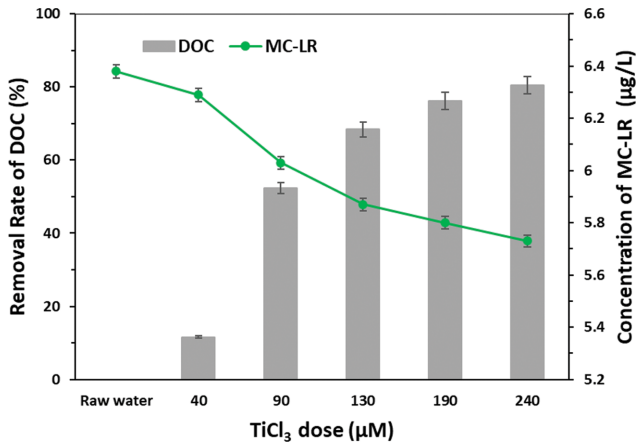

Fig. 5. Removal efficiencies of MC-LR and DOC during $TiCl_3$ coagulation process. Conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.16, temperature 25 °C. Error bars represent the standard deviations (n=3).

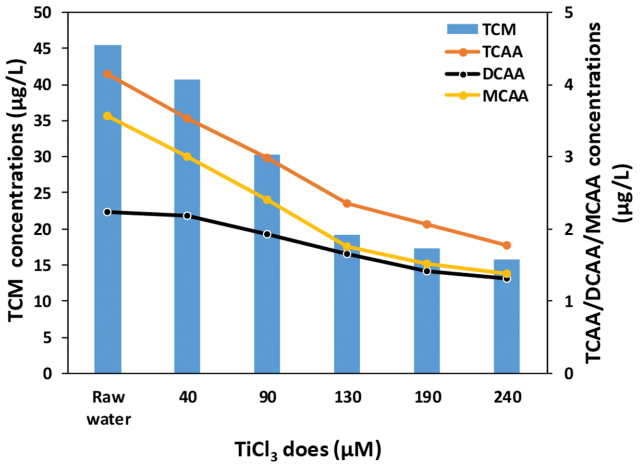

Fig. 6. Effects of $TiCl_3$ coagulation process on DBPFP during chlorination of settled waters. Coagulation conditions: Initial algal cell density: 2.0×10^6 cells/mL, initial pH 8.16, temperature 25 °C. Conditions in chlorination tests: Chlorine dosage (as Cl_2)/TOC (as C) 3 : 1 (mass ratio), pH 7.0, temperature 25 °C, reaction time 72 h (in dark).

attributed to the fact that $TiCl_3$ can effectively remove humic-like and protein-like matters to achieve a high DOC removal rate [20], and humic-like and protein-like matters have stronger THMs generating activity [38]. Furthermore, the generation of HAAs in $TiCl_3$ coagulation process is lower than THMs. Generally, humic-like acids are their main precursors of HAAs [39]. Hence, it is likely that $TiCl_3$ will reduce the concentration of HAAs by effectively removing humic-like acids [20]. Therefore, when $TiCl_3$ is used to treat water containing *M. aeruginosa*, part of the DBPFP can be effectively controlled compared to other pre-oxidation treatments [40].

4. Mechanism of $TiCl_3$ Removal of *M. aeruginosa*

To better explain the mechanism of the reaction, XPS broad spectrum scanning was performed on the algae flocs without and after $TiCl_3$ coagulation to determine the changes of element valence and functional group content before and after the reaction. The C 1s XPS signal of the algae flocs without and after coagulation can be decomposed into four peaks (Fig. 7(a)-(b)). The binding energies of the four peaks of fresh algae flocs are 284.2, 284.8, and 285.73, as well as 288.0 eV, corresponding to C=C, C-C/C-H, C-N, and C=O bonds [41,42]. The four peaks in the spectra of post-coagulation flocs shifted to lower binding energies, demonstrating the electron from in-situ formed $Ti(OH)_3$ transferred to the surface organic matters of algae. Then, the electron density of the extracellular organic matters of algae was enhanced by $Ti(OH)_3$ [43].

Fig. 7(c)-(d) exhibits the high-resolution XPS spectra of N 1s for algae flocs before and after coagulation. Compared with algae flocs without coagulation, a new peak appeared in the N 1s signal of the algae flocs after coagulation, which may reveal that the reduced organic matters anchored on the surface spectra of the $Ti(OH)_4$,

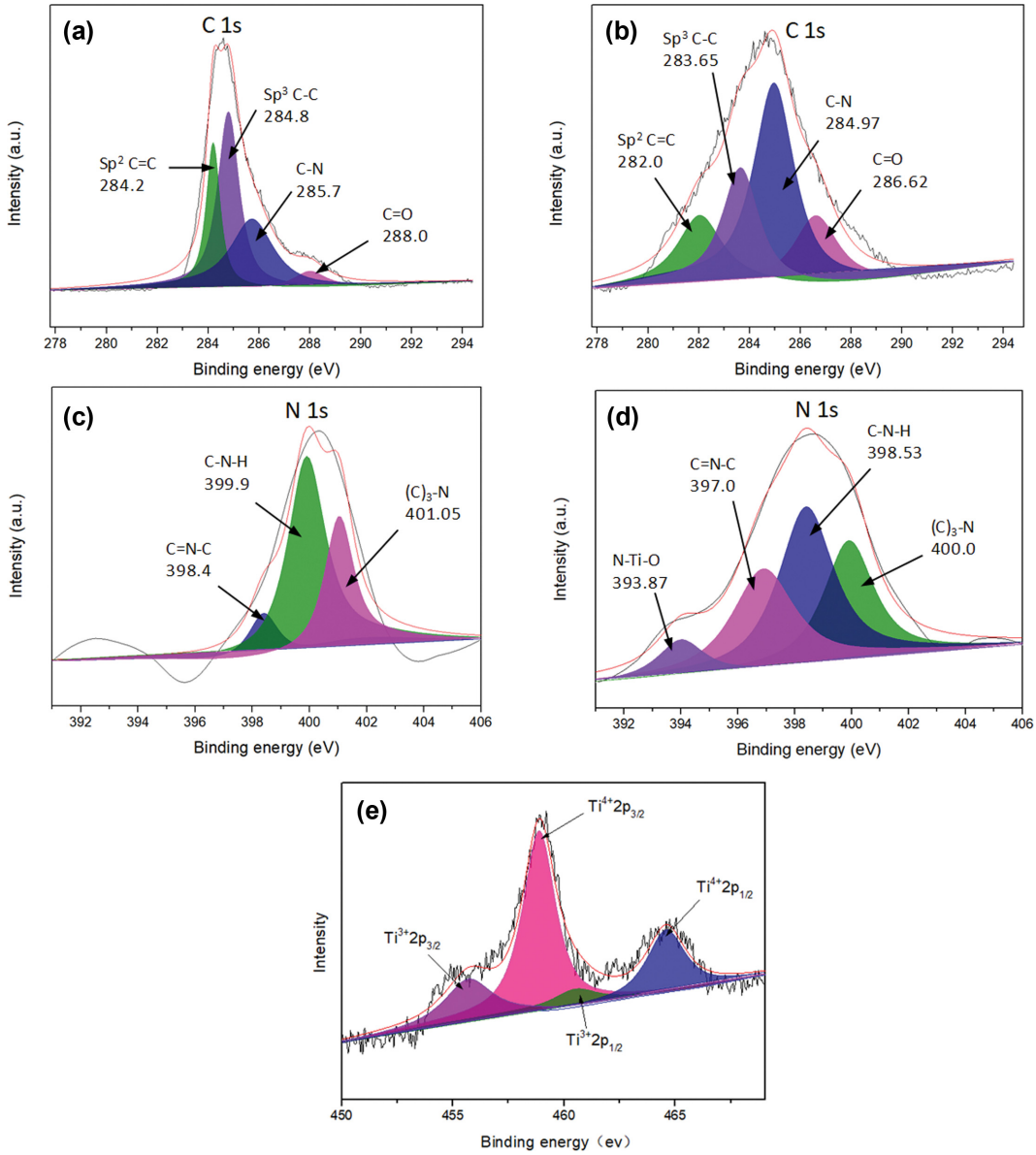

Fig. 7. XPS characterization of algae flocs. C 1s spectrum of algae flocs before coagulation (a) and after coagulation (b); N 1s spectrum of algae flocs before coagulation (c) and after coagulation (d); (e) Ti 2p spectrum of algae flocs after coagulation.

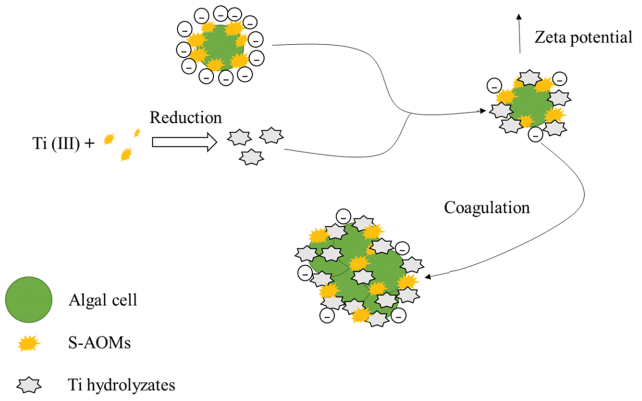

Fig. 8. Graphical abstract of the possible mechanisms of *M. aeruginosa* removal by $TiCl_3$ coagulation process.

forming the O-Ti-N bonds [44]. Furthermore, all the peaks in the spectra of post-coagulation flocs shifted to lower binding energies, which were consistent with the changing trend of C 1s peaks, further confirming the existence of redox reaction between algal organic matters and in-situ formed $Ti(OH)_3$.

Fig. 7(e) shows the Ti 2p XPS signal of the algae flocs after coagulation. This area can be divided into four peaks. The peaks at the binding energies of 458.89 and 464.6 eV belonged to Ti $2p_{1/2}$ and Ti $2p_{3/2}$ spin-orbital splitting photoelectrons in Ti^{4+}, respectively [45]. The other two peaks belong to the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ spin-orbital splitting photoelectrons in Ti^{3+} [46]. Fig. 7(e) exhibits that the main titanium element on the surface of the algae was Ti^{4+}. Furthermore, the distance between the two peaks of Ti^{4+} is 5.71 eV, which is also the same as the state of Ti^{4+} in the stable TiO_2 [47].

Combined with the above results, the mechanism of $TiCl_3$ coagulation process toward algal removal revealed based on Fig. 8: Ti^{3+} had undergone a redox reaction with organic matter on the surface of the algae, which changed the structural properties and of the organic matter and decreased the charge of algal cells. Therefore, more $Ti(OH)_4$ was required to neutralize the negative zeta-potential of the cells, which were beneficial for formatting large flocs and removal of *M. aeruginosa*.

5. Economic Evaluation

Compared with traditional metal coagulants such as Fe and Al salts, titanium salt coagulants are at a disadvantage in production costs. Still, they are at an advantage in terms of operation cost and disposal cost. In terms of production cost, according to the data of the world's largest trade website (Table 1), $TiCl_3$ is higher than aluminum and iron coagulants, and the cost is similar to low-quality chitosan but far lower than better-quality chitosan.

The flocs formed by the titanium salt coagulant are large in terms of operating cost, the sedimentation speed is fast, and the residence time in the water is short [48]. This requires the use of less space when constructing the need for less area when constructing flocculation and sedimentation tanks, thereby reducing construction costs [13].

However, traditional Fe and Al salt coagulants will produce a large amount of sludge, causing soil pollution and rising costs inevitably [13]. The advantage of titanium salt coagulants regarding disposal cost is that the sludge produced can be recycled and reused. It was achieved by being calcined at high temperature to form higher activity TiO_2 than commercial TiO_2 [49], which can make up for disposal costs and even create revenue.

To sum up, $TiCl_3$ based coagulation process may be a promising technology for efficient algal removal in surface water treatment.

CONCLUSIONS

This study demonstrates that the $TiCl_3$ coagulation process has a good removal efficiency on *M. aeruginosa* cells, and the addition process is simple and easy to operate. Under optimal dosage, the removal rate of OD_{680}, turbidity, and DOC reached 98.1%, 93.0%, and 68.3%, respectively. As the dosage continued to increase, the K^+ release rate did not increase significantly, indicating that the reduction effect of $TiCl_3$ is moderate and will not cause a large amount of damage to algal cells. $TiCl_3$ can reduce S-AOMs, change their structural properties, destroy the stability of algal cells, reduce their surface potential, and effectively remove *M. aeruginosa* cells. Because the $TiCl_3$ coagulation process can effectively remove *M. aeruginosa* cells, this process may be applied to actual projects. However, further verification is needed to extend the process to other algae species to realize its application in natural water bodies and engineering.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Table 1. Price of raw materials for preparation of coagulants or flocculants (obtained from https://www.alibaba.com on July 5, 2021)

Raw material	Price ($/ton)	Raw material	Price ($/ton)
$AlCl_3$	900-1,220	$Al_2(SO_4)_3 \cdot 18H_2O$	700-2,000
$FeCl_3$	500-1,000	$Fe_2(SO_4)_3 \cdot 7H_2O$	200-600
Chitosan	10,000-100,000	$TiCl_3$	11,500

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Supporting Information

$TiCl_3$ coagulation for algae-laden water treatment: Performance, control of algal organic matters release and mechanism

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1. FESEM Characterization of Algae Flocs

In order to further explore the effect of $TiCl_3$ coagulation on the water containing *M. aeruginosa*, the changes of algae flocs were studied, and the surface morphology of the algae flocs with various dosage after coagulation was observed, as shown in Fig. 1. Fig. 7(a) shows the case where the dosage of $TiCl_3$ is 90 μM. It can be seen from the figure that there is small amount of titanium oxides crystals on the surface of the algae cells, and the flocs were still relatively loose. The results are consistent with the insufficient coagulation efficiency at this dose. When the dosage is increased to 130 μM, it can be seen from Fig. 7(b) that the algae cells are clustered together by titanium oxides crystals, and the flocs are quite dense. When the dosage continued to increase to 240 μM, it can be seen from Fig. 7(c) that the surface of the algae cells was covered by titanium oxides, and the morphology of the algae cells is not easy to be observed, revealing the excessive dosage of coagulant. Moreover, it can be seen from Fig. 7 that the algal cells remained relatively intact regardless of the dosage, and the structure was not significantly damaged, which is consistent with the previous conclusions.

2. FTIR Spectroscopy Analysis of Algae Flocs

FTIR spectroscopy analysis was performed on the algae flocs without coagulation and after coagulation with $TiCl_3$ to determine the composition and functional group changes of the algae flocs before and after coagulation (Fig. 2). For both of the samples, two bands appeared at wavenumber of 3,300 cm^{-1} and 2,927.9 cm^{-1}, which may be assigned to the stretching vibration of O-H [1] and C-H of organic polysaccharides on the surface of algae [2]. Meanwhile, three adsorption peaks located at 1,656.07 cm^{-1}, 1,383.68 cm^{-1}, and 1,241.93 cm^{-1} were attributed to C=O in the protein, COO^- in the atty acids and phosphodiesters in DNA, respectively [3]. In

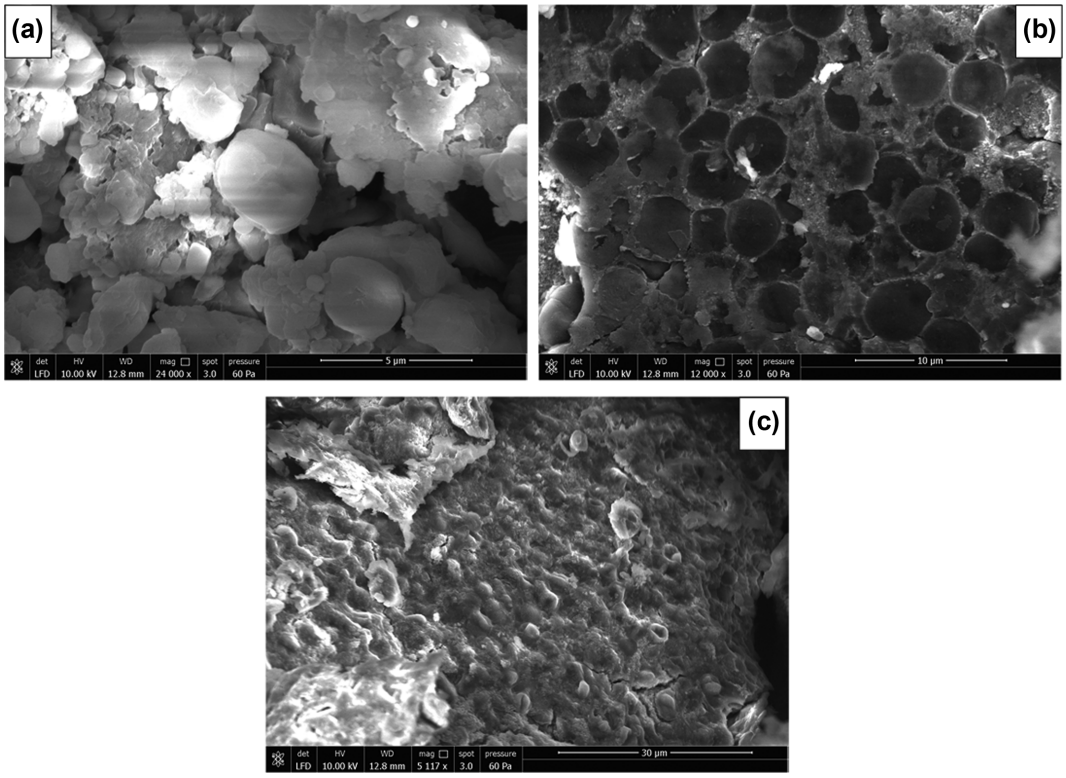

Fig. S1. FESEM images of algae flocs with various dose of $TiCl_3$: (a) 90 μM; (b) 130 μM and (c) 240 μM.

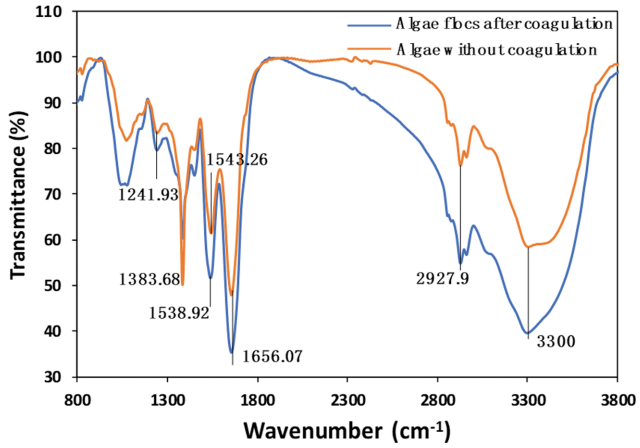

Fig. S2. FTIR spectra of algae flocs and algae cells.

addition, absorption peaks were also observed at 1,543.6 cm^{-1} for the algae cells, which was considered to be related to the C-N stretching vibration of protein-like organics [4]. In the FTIR spectrum of algae flocs after coagulation, a red-shift of 4.58 cm^{-1} of 1,543.6 cm^{-1} band appeared in comparison with pure algae cells. The results demonstrated that almost no significant changes were observed in the FT-IR spectra.

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