

# **The Role of Ferrate (VI) in the Pretreatment of Algal Cells and Algal Organic Matters: A Review**

Saige Wang <sup>1,2</sup>, Shuyi Yang <sup>3</sup>, Huan Chen <sup>4</sup> and Qiufeng Lin <sup>5,\*</sup>

- <sup>1</sup> Faculty of Geographical Science, Beijing Normal University, Beijing 100875, China; wsgbnu@163.com
- <sup>2</sup> Advancing Systems Analysis (ASA) Program International Institute for Applied Systems Analysis, 2361 Laxenburg, Austria
- <sup>3</sup> College of Environment, Zhejiang University of Technology, Hangzhou 310014, China; 202005090225@zjut.edu.cn
- <sup>4</sup> CECEP DADI (Hangzhou) Environmental Remediation Co., Ltd., Hangzhou 310014, China; kelly\_chenhuan@163.com
- <sup>5</sup> Department of Earth and Environmental Studies, Montclair State University, Montclair, NJ 07043, USA
- \* Correspondence: linq1@montclair.edu

**Abstract:** Algal blooms are caused by excessive levels of nitrogen, phosphorus, and other plant nutrients in water. Algae and algal organic matter (AOM) pose a great threat to the quality of drinking water. This manuscript offers a systematic review of algal removal by ferrate (Fe(VI)) oxidation, including the conditions for the removal of different algae by Fe(VI) and the factors affecting the removal efficiency. On this basis, the oxidation and coagulation mechanisms of algae removal by Fe(VI) are discussed. Then, the review introduces the process combining Fe(VI) pre-oxidation with aluminum sulfate action. The addition of aluminum sulfate can further enhance the coagulation effect and reduce the formation of disinfection byproducts (DBPs) in the subsequent chlorination process by effectively removing AOM, which is recognized as a precursor of DBPs. In addition, recent studies on the combined application of Fe(VI) and Fe(II) are also reviewed. In a reasonable dose range, the synergistic effect of Fe(VI) and Fe(II) can significantly improve the removal of algae and algal toxins. Finally, this review provides a comprehensive evaluation of the applicability of Fe(VI) in removing algal material, offers guidance for the harmless treatment of algae with Fe(VI), and identifies future research questions.

Keywords: ferrate; algal removal; AOM; algal toxins; Fe(VI) combined methods

## 1. Introduction

In recent years, the addition of nutrients to aquatic ecosystems by human activities (e.g., agricultural runoff, wastewater discharges, and land use changes) has increased the frequency and geographic distribution of harmful algal blooms (HABs), posing a potential threat to aquatic ecosystems and human health [1,2]. Thus, surface water eutrophication, an emerging ecological phenomenon, has become a major concern in many countries [3]. Although algae utilize carbon dioxide as their primary substrate for photosynthesis, initiating the flow of energy into living organisms and playing a crucial role in the global carbon cycle, they produce a wide array of secondary metabolites, including toxins and volatile compounds [4]. These secondary metabolites not only affect the quality of drinking water and aquatic products, but also further endanger human health and the ecological environment [5]. Meanwhile, algae also produce unpleasant tastes and odors and clog filters, further damaging water treatment systems and reducing the quality of drinking water [6]. However, algal cells are stable in water due to their unique physiological characteristics, such as high hydrophilicity [7], low specific gravity, negative surface charge, and high migration rate; so, the efficient removal of algae has been a primary challenge in water treatment processes [3].



Citation: Wang, S.; Yang, S.; Chen, H.; Lin, Q. The Role of Ferrate (VI) in the Pretreatment of Algal Cells and Algal Organic Matters: A Review. *Water* 2024, *16*, 1361. https://doi.org/ 10.3390/w16101361

Academic Editor: Hassimi Abu Hasan

Received: 6 March 2024 Revised: 29 April 2024 Accepted: 2 May 2024 Published: 11 May 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The commonly used algal removal treatment in practical applications includes ozone, potassium permanganate, and sodium hypochlorite [8]. Ozone could effectively diminish algal blooms and associated toxins [9] but may form byproducts such as aldehydes and phthalates, presenting a toxicological hazard to the endocrine system [10]. Other strong oxidant agents (e.g., potassium permanganate, free chlorine, and copper sulfate) face similar dilemmas [11]. Free chlorine derived from sodium hypochlorite is another disinfectant, but its use increases the formation of disinfection byproducts (DBPs) [12]. Copper sulfate also has a relatively good inhibition effect on algal damage, but the release of copper has a negative effect on other aquatic microorganisms [13]. Although traditional aluminum-based coagulants effectively remove algae from drinking water sources, an excessive intake of aluminum salts is easily linked to an increased risk of Alzheimer's disease [14]. Therefore, there is an urgent demand to create an innovative, reliable, environmentally friendly, and low-cost technology for dealing with the drinking water safety crisis caused by algal blooms.

Ferrate (i.e., Fe(VI)), a highly efficient and eco-friendly oxidant, is capable of mitigating targeted contaminants by multiple mechanisms, such as chemical oxidation, disinfection, in situ coagulation, precipitation, and adsorption. Thus, Fe(VI) is recognized as a promising tool in future algal control. Fe(VI) has high standard redox potentials of 2.2 V NHE and 0.72 V NHE in acidic and alkaline solutions, respectively [15], endowing its capacity for algal removal. Figure 1 shows the general scheme of multistage algal removal using Fe(VI)based technology. Of note, the weak alkalinity of water bodies during seasonal algal blooms causes Fe(VI) to exhibit relatively low oxidation capabilities, effectively preventing the excessive oxidation of algal cells and the potential release of undesired organic matter [8,16]. Moreover, the in situ formation of ferric hydroxide was proven to significantly accelerate the removal of contaminants by the combination of oxidation and coagulation [17,18]. For example, Zhou et al. demonstrated that the significant enhancement of algal removal by Fe(VI) could be ascribed to oxidization-based algal inactivation and to self-coagulation induced by Fe (III) formed in situ. Therefore, Fe(VI) oxidation is suspected to be an effective treatment for eliminating algal pollution. However, there are still some shortfalls in the application of Fe(VI) to remove algae, such as the low utilization of Fe(VI) and the unsatisfactory coagulation by in situ formed Fe(III) [19]. Some scholars carried out a targeted optimization, including the development of Fe(VI)-mediated pre-oxidation combined with subsequent chlorination or the application of aluminum sulfate and Fe(II). Although some researchers have studied Fe(VI) and Fe(VI) combination technologies to a certain extent, a comprehensive understanding of these technologies, including their efficacy in algal removal, the factors influencing their performance, and the underlying degradation mechanisms, has not been achieved, as shown in the existing literature.



Figure 1. Scheme of multistage algal removal using Fe(VI) treatment.

Therefore, this review aims to thoroughly evaluate the efficiency of algal cell removal by Fe(VI) and investigate the impact of different solutions, water matrix constituents, and operating conditions on algal removal. The specific mechanism of algal removal by Fe(VI) is explored deeply. The removal efficiency of algal organic matter (AOM) and various algal toxins by Fe(VI) is summarized. The advantages of methods combining Fe(VI) with other chemicals and their influence on the reduction of algal toxins are further compared. Finally, this review offers a reference for the treatment of seasonal algae-rich water and points out future development directions of algal removal technologies to reduce eutrophication.

# 2. Damage of Algal Cells by Fe(VI)

2.1. The Destruction of Different Algae

Planktonic algae and their metabolites in water sources significantly affect effluent water quality. Fe(VI) demonstrated effective inactivation of C. aegagropila, M. aeruginosa, and *Chaetoceros affinis*. Table 1 reports the removal conditions and efficiency of algae by Fe(VI) oxidation. Under appropriate Fe(VI) concentration, pH, temperature, and hydraulic conditions, the algal removal rates were above 40%, proving that different algae could be inactivated by Fe(VI). For the same species of algae (e.g., M. aeruginosa), the removal efficiency changed with the reaction parameters. Fe(VI) showed different removal efficiencies for different algae under the corresponding reaction conditions, probably due to differences in surface characteristics of the cells [20]. The oxidation of Fe(VI) had significant effects on the behavior and cell structure of algae, and the extensive destruction of algal cells was obviously observed, as shown in Figure 2. At the same time, intracellular components and algal toxins were released into the surrounding medium, which might have been caused by Fe(VI) stimulation of algal cells or the cleavage of the algal sheath caused by Fe(VI) oxidation. In addition, Fe(III) produced by Fe(VI) reduction reduced the negative charge on the surface of algal cells through charge neutralization, promoting the aggregation of algal cells. Furthermore, cyanobacterial blooms in China eutrophic waters are primarily composed of Microcystis, Oscillatoria, and Anabaena species [21,22]. Current research predominantly focuses on the removal of *Microcystis aeruginosa*, with other algal species receiving less attention. Future studies should broaden their scope to include species such as Oscillatoria tenuisa and more comprehensively assess the effectiveness of Fe(VI) in treating algal blooms.



**Figure 2.** Digital photos of algae-laden water (**A**) and water pre-oxidized with 0.01 mM (**C**), 0.02 mM (**E**), and 0.03 mM (**G**) Fe(VI) and coagulated with 0.5 mM FeCl<sub>3</sub>. Corresponding scanning electron microscope (SEM) photos of algae in beakers (**B**,**D**,**F**,**H**). (Adapted from He et al. [21]).

## 2.2. Factors Affecting Fe(VI) Removal Efficiency

*pH*. The stability and reactivity of Fe(VI) are highly dependent on pH [23]. In weakly acidic environments, Fe(VI) has a redox potential of up to 2.2 V [24,25]. Fe(VI) is decom-

posed rapidly at an acidic pH, but has the greatest stability at pH~10.0, as reported in studies that showed a half-life of 102 s at pH 6.0 and of 105 s at pH 10.0 [26]. At suitable pH conditions, cell density and turbidity are dramatically reduced once Fe(VI) dose exceeds their respective threshold levels (defined as the minimum effective iron dose (MEID)) [27]. Alshahri et al. showed that the removal percentages of *P. limnetica* and *Chlorella* spp. were highest at pH 8.0 and 9.0 [28,29], respectively. The removal of algal cells may be limited by the weak oxidation capacity of Fe(VI) at higher pH and by the undesired rapid self-decomposition of Fe(VI) at lower pH. Furthermore, pH also affects the surface charge distribution of algal cells. When the pH value is as high as 10.0, Fe(OH)<sub>3</sub> and the cell surface will have the same charge, and coagulation will be hindered by electric repulsion forces, thus reducing the removal rate of algae.

*Agitation*. Agitation is one of the factors affecting Fe(VI)-mediated oxidation of algae in practical applications. According to previous research, taking *Cladophora aegagropila* as the research object, the removal efficiency of algal cells with a low Fe(VI) concentration (0.78 mM) under static conditions was only 16% after 300 min [27], while the removal efficiency in a stirred (dynamic) system was 30%. When Fe(VI) concentration was increased to 1.55 mM, about 60% of algal cells were damaged [30,31]. Agitation increased the probability of collision between algal cells and Fe(VI) particles [32], increasing the oxidation rate and enhancing the coagulation effect [33,34]. In the actual treatment process of algae-rich water, a rotary mixer is set up to enhance the contact between algae and the algaecide [35]. This approach has a good effect on flocculation and sedimentation to remove algae. However, the stirring intensity should be increased with the increase of algal cell density, which often leads to high energy consumption.

*Temperature*. Temperature also has a noticeable effect on algal removal by Fe(VI) oxidation. Kubinakova [24] added 2 mL of a 8.93 M Fe(VI) solution to water containing *Cladophora aegagropila* at 38 °C and found that the removal rate reached 89%. In contrast, the removal rate of the control group at 25 °C was only 24%. In addition, for other algal cells treated with a relatively low Fe(VI) concentration (in 0.5 mL and 1.0 mL) the removal rate increased with the increase in temperature. Interestingly, when algae were immersed in water at the temperature of 38 °C for 30 min, damage to the algal cells (almost 40%) was evident even when the temperature was raised without Fe(VI) as an algaecide. The increase in the algal removal rate at high temperatures might be attributed to increased particle transport and collision rates through the reduction of viscosity [2]. In addition, temperature affects the physiological responses and metabolic rates of algae and the utilized coefficient of nutrients [36]. A high temperature will reduce the activity of enzymes in algal cells and inhibit the growth of algae [10].

| Species of Algae | Parameters   | <b>Removal Efficiency</b> | Ref.      |
|------------------|--|---------------------------|-----------|
| C. aegagropila   | Fe(VI) concentration = 3.57 mM, pH 9.0, application time 120 min | 98%                       | Ref. [24] |
| M. aeruginosa    | Fe(VI) concentration = 0.27 mM, pH 7.2, application time 16 d    | 64%                       | Ref. [7]  |
| M. aeruginosa    | Fe(VI) concentration = 0.54 mM,<br>pH 7.2, application time 16 d | 70%                       | Ref. [7]  |
| M. aeruginosa    | Fe(VI) concentration = 0.13 mM, pH 5.5, application time 90 min  | 95.3%                     | Ref. [6]  |
| M. aeruginosa    | Fe(VI) concentration = 0.02 mM, pH 7.5, application time 90 min  | 40.4%                     | Ref. [6]  |
| Chlorella sp.    | Fe(VI) concentration = 0.29 mM, pH 7.0, application time 30 min  | 46.2%                     | Ref. [35] |

Table 1. The removal conditions and efficiency of algae removal by Fe(VI) oxidation.

| Species of Algae    | Parameters   | Removal Efficiency | Ref.      |
|---------------------|--|--------------------|-----------|
| P. limnetica        | Fe(VI) concentration = 0.29 mM,<br>pH 7.0, application time 30 min | 58.1%              | Ref. [35] |
| Chaetoceros affinis | Fe(VI) concentration = 0.05 mM,<br>pH 9.0 application time 80 min  | 94–100%            | Ref. [29] |

Table 1. Cont.

## 2.3. Mechanism of Algal Damage

Fe(VI) in water exists in four protonated forms (e.g.,  $H_3FeO_4^+$ ,  $H_2FeO_4$ ,  $HFeO_4^-$ , and  $FeO_4^{2-}$ ) with  $pK_1 = 1.6$ ,  $pK_2 = 3.5$ , and  $pK_3 = 7.3$  [37]. Within the typical pH range of water treatment,  $HFeO_4^-$  and/or  $FeO_4^{2-}$  are the predominant high-valence iron species [6]. Figure 3 shows the possible steps of ferrate oxidation of AOM. The mechanism of Fe(VI) oxidation is generally divided into two stages. First, Fe(VI) affects the structure and properties of organic matter in microalgal cells, causing algal cell inactivation and toxin decomposition. Oxidative stress by Fe(VI) leads to the desorption of the organic protective layer on the algal cell surface [38], reducing the surface's positive and negative charges. Fe(VI) destroys the algal cell wall and membrane components (such as amino acids) through oxidation [39]. After damaging the cell wall and membrane, Fe(VI) further enters the cell and destroys its internal contents [40]. Second, Fe(III) generated from the reduction of Fe(VI) and intracellular biopolymers released from damaged algal cells trigger in situ coagulation and cell aggregation [41].



Figure 3. Possible reaction steps of ferrate oxidation of AOM(x). (Adapted from Yu et al. [20]).

Electrostatic forces are one of the factors affecting Fe(VI) coagulation. Zhou et al. observed the decomposition products of Fe(VI) on the surface of algae (e.g., colloidal iron hydroxide [Fe(OH)<sub>3</sub>]) through scanning electron microscopy. These precipitates can significantly change the surface properties of cells, promoting the aggregation of algal cells. In situ generated Fe(III) reduces the negative charge on the surface of algal cells through charge neutralization. After increasing the Fe(VI) dosage, the zeta potential tends to zero, which is favorable for particle aggregation [18,42]. When the amount of Fe(VI) exceeds the MEID value, the repulsive electrostatic force between suspended particles is sufficiently reduced, leading to their rapid condensation, eventually stabilizing under the action of gravity [43]. Meanwhile, the extracellular organic matter (EOM) from algal cells induced by Fe(VI) is also an essential factor in the coagulation of the algae–Fe(VI) system [44]. EOM is mainly composed of proteins, polysaccharides, and lipids and exhibits anionic and non-ionic polyelectrolyte behaviors [45]. The amount and properties of EOM produced vary with algal species, oxidant type, and oxidant dose [13]. Depending on its concentration and molecular weight, EOM can enhance or hinder flocculation [46].

## 3. Degradation of Algae-Derived Organic Matters by Fe(VI)

## 3.1. Degradation of AOM by Fe(VI)

AOM is an important protoplasmic organic derivative produced by algae, mainly composed of extracellular polysaccharides and proteins [41,47], which includes EOM and intracellular organic matter (IOM) [48]. IOM is internal material or organelles that are released from cell lysis due to the aging of algal populations and aggressive physico-chemical processes [49]. Algae produce a large amount of viscous extracellular polysaccharides, which enhance the hydrophilicity and viscosity of algal cells. Therefore, dissolved AOM is challenging to be removed by traditional methods, causing severe pollution in water. However, the removal rate of AOM by Fe(VI) is between 88 and 93%. Especially, the removal rate of low-molecular-weight (LMW) acids is between 98 and 100% [50]. Thus, Fe(VI) effectively removes organic matter derived from algae. Through oxidation, Fe(VI) can transform organic compounds into more easily precipitated or removed forms, thereby reducing the concentration of organic matter derived from algae. In addition, the main component of AOM are biopolymers (BPs), which mainly consist of surface-active polysaccharides with carboxyl and hydroxyl groups. BPs may have a strong affinity for trivalent metal Fe(III), forming large-size colloidal Fe-BP complexes, and the complex particles are large enough to easily settle after coalescing, which results in a removal efficiency of AOM of up to 97–100%. Therefore, Fe(VI) effectively removes AOM derived from algae through mechanisms such as oxidation, adsorption, and precipitation, thereby improving water quality.

#### 3.2. Degradation of Algal Toxins by Fe(VI)

Among the HAB-associated pollutants, algal toxins are of particular concern, as these traceable compounds have been linked to various health effects and can cause a range of serious liver, digestive, nervous, and skin diseases in humans [51,52]. Of note, 25–30% of the existing 50 genera of freshwater cyanobacteria can produce toxins, such as *Microcystis, Anabaena, Aphanizomenon, Oscillatoria, Cylindrosperomopsis,* and *Lyngbya*. Toxins produced by cyanobacteria include anatoxin-a, anatoxin-as, aplysiatoxin, cylindrospermopsin, microcystin LR, nodotoxin R, and saxitoxin [53]. The United States has not yet established the maximum pollution level for cyanotoxins but included them in the U.S. Environmental Protection Agency (EPA) Final Contaminant Candidate List 4 (CCL4) [6].

Algal toxins are not considered a defense mechanism of algal cells but are released during oxidative stress and nutrient deprivation [54]. These toxins are mainly composed of seven-amino acid rings, which are stable, non-volatile, and water-soluble [55]. These properties make algal toxins persistent in the environment and difficult to be degraded by conventional treatment methods. As a strong oxidizing agent, Fe(VI) could inactivate algal cells and decompose the released algal toxins. Subsequently, these macromolecular toxins are captured by Fe(VI)-induced iron flocs through coagulation and then settle down by gravity. Furthermore, the oxidation efficiency of algal toxins depends on the pH. At pH 5.5, the toxin removal rate was 90% with 0.05 mM Fe (VI). In contrast, at pH 7.5, the toxin removal rate was only 78% with a Fe(VI) dose of 0.16 mM. The effects of Fe(VI) pre-oxidation on M. aeruginosa viability and the fate of microcystins in different waters were analyzed. It was found that although Fe(VI) induced cell lysis, the concentration of extracellular microcystins did not increase significantly. The results showed that the toxin was easily oxidized and decomposed, but its removal efficiency depended on the dosage of Fe(VI), the pH, and the contact time [56,57]. Fe(VI) has a satisfactory degradation effect on various algal toxins produced by various algae. Compared with other conventional algal removal agents, Fe(VI) does not generate harmful byproducts in the removal process, avoiding secondary pollution. However, when using Fe(VI) to oxidize algal toxins, it is indispensable to strictly control the dosage of Fe(VI) and the solution pH.

When treating algae-rich water with Fe(VI), the toxicity towards algae exhibits variability, influenced by factors such as Fe(VI) concentration, algal species, algal physiological state, and treatment duration. Fe(VI) functions as a potent oxidizing agent, initiating reactions with organic compounds on the surface of algal cells, thereby inducing membrane rupture and damage. This process leads to cell death and the subsequent release of toxic intracellular substances, including algal toxins [58]. Furthermore, Fe(VI) can interfere with algal photosynthesis and respiration processes, thereby disrupting their physiological functions. The toxicity effects are concentration-dependent, with higher Fe(VI) concentrations exerting more pronounced toxic effects, potentially resulting in acute cell death [59]. It should be noted that different algae species may display varying sensitivities to Fe(VI), with some exhibiting greater susceptibility, and others possessing inherent resistance. Thorough evaluation of Fe(VI) reaction conditions and concentration and diligent monitoring and control measures are essential when treating algae-rich water, thereby mitigating potential adverse effects, including the presence of algal toxins.

## 4. Fe(VI) Combined with Aluminum Sulfate for Algal Removal

Aluminum sulfate, known for its low cost, simple operation conditions, and efficacy in large-scale water purification, remains the most widely used chemical for algal removal [60]. The concentration of the particles formed by Fe(VI) reduction is usually too low to cause effective coagulation, and flocculation achieved by adding aluminum sulfate after Fe(VI) pretreatment can significantly improve the removal of algae. When Fe(VI) and aluminum sulfate are combined, the synergistic effect of pre-oxidation by Fe(VI) and subsequent flocculation by aluminum sulfate can achieve a remarkable algal removal efficiency in a very short time [20]. On the one hand, Fe(VI)-dependent pre-oxidation inactivates part of the algae and induces the formation of coagulants. On the other hand, the formation of intermediate forms of precipitant iron species during pre-oxidation improves coagulation by increasing the particle concentration in water. In addition, aluminum sulfate reduces the stabilization of algae through charge neutralization or algal aggregation, thereby improving flocculation and solid–liquid separation in a later stage [61]. It was observed that the ferric hydroxide colloid derived from Fe(VI) decomposition caused the conglomeration of algal cells during prolonged pre-oxidation and the damaged algal cells changed the zeta potential on their surface, while aluminum sulfate continually enhanced the subsequent coagulation by inducing the sedimentation of the remaining algal cells [62,63]. Moreover, the concentration of AOM in water samples decreased within a short contact time when using this combined technique for algal removal. Besides the oxidation of AOM by Fe(VI), also the addition of aluminum sulfate can promote the removal of AOM. The aluminum hydroxide colloids formed by aluminum sulfate strengthened the adsorption of AOM [64]. Therefore, Fe(VI) combined with aluminum sulfate further increases the removal rate of residual algae and reduces the cost of water purification. However, the potential toxicity increase due to high residual aluminum levels calls for the careful management and further optimization of this technique in future research and applications [61,65].

#### 5. Fe(VI) Combined with Fe(II) for Algal Removal

When Fe(VI) is used for algal removal, Fe(VI) oxidation is affected by environmental pH and Fe(VI) dose. Fe(II), serving as a pre-oxidation agent, was applied to enhance conventional Fe(VI)-dependent oxidation and coagulation in algae-laden water treatment. The oxidative stress powered by the pre-oxidation of Fe(VI) led to the deactivation of algal cells and a decrease in the zeta potential. The coupling of Fe(VI) and Fe(II) produces a large amount of Fe(OH)<sub>3</sub>. The in situ formed Fe(OH)<sub>3</sub> in the presence of abundant reactive surfaces promoted floc growth by facilitating the clustering and cross-linking of AOM and algal cells, simultaneously leading to satisfactory reductions in OD<sub>680</sub>, turbidity, and UV<sub>254</sub> of the analyzed samples [43,66]. In contrast, an overdose of Fe(VI) would result in severe cell destruction along with the release of IOM. Previous results showed that the zeta potential decreased from -5.39 mV to -11.26 mV and -21.85 mV when Fe(VI) dose increased from 1.78 to 2.91 and 3.59 mg/L, respectively [14]. On the one hand, excessive oxidation by Fe(VI) endowed the algal cell surface with a powerful capacity to consume

positively charged Fe(II) coagulants [67]. On the other hand, the adverse effects of IOM release outweighed the removal ability of the flocculant to adsorb organic matter.

Also the algal toxin removal ability of the combination of Fe(VI) and Fe(II) should not be neglected. The MC-LR released following pre-oxidation-induced cell destruction was first degraded by Fe(VI)-dependent oxidation [60]. During the formation and growth of flocs, the residual MC-LR was further removed by adsorption and precipitation [59]. Fe(II)-based solidification significantly improved the oxidation and flocculation efficiency of Fe(VI); so, the removal rate of MC-LR was also substantially improved [37,68]. In summary, although the combination of Fe(VI) and Fe(II) can dramatically promote the removal of algal cells, AOM, and algal toxins, the selection of Fe(VI) and Fe(II) doses should be carefully considered to avoid excessive pre-oxidation leading to severe cell lysis, IOM leakage, and severe impairment of coagulation.

#### 6. Perspectives

In recent years, water blooms caused by eutrophication have frequently erupted, posing serious challenges to drinking water treatment and a threat to its safety. Consequently, comprehensive research on algaecides, particularly Fe(VI), has become crucial. Fe(VI) is recognized as a promising agent in drinking water treatment systems due to its dual primary treatment mechanisms: chemical oxidation and coagulation. Used commonly in liquid form, Fe(VI) is highly effective at removing algae at a relatively low cost. The efficacy of Fe(VI) is influenced by factors such as pH, hydrodynamic conditions, and temperature. Excessive algal growth releases AOM and toxins, degrading water quality and posing health and environmental risks. Fe(VI) is particularly effective at removing AOM, which underscores its advantages as an algal removal agent. Detailed studies on the characteristics of AOM and their correlation with DBP formation during chlorination are essential to fully understand the oxidation mechanisms of Fe(VI) and to optimize the treatment of algae-rich waters.

Moreover, addressing the end-chain processing of algae biomass after treatment is critical. Once settled by algaecides like Fe(VI), the biomass often retains a substantial water amount. Fe(VI) not only reduces this intercellular water, enhancing dehydration and increasing the solid content in the resultant sludge, but also offers opportunities for resource recovery. Properly processed, this biomass could be converted into biofuels, agricultural fertilizers, or other valuable bioproducts, thus supporting a circular economy and promoting a sustainable algal management. This prospect encourages further research into harmless dehydration processes and the exploration of Fe(VI) broader application potential to achieve effective coagulation, oxidation, and dehydration in algae removal.

Fe(VI) is versatile and capable of being used alone or in combination with other reagents. When combined with chlorine, it significantly reduces the subsequent DBP formation compared to chlorination alone. Fe(VI) also enhances conventional Fe(II)-dependent coagulation when used for pre-oxidation, although it requires a careful dosage management to prevent excessive pre-oxidation. However, the preparation and stabilization of Fe(VI) present notable challenges, as its decomposition rate heavily depends on its purity and initial state, the method of preparation, and environmental conditions such as temperature and pH. Therefore, reducing Fe(VI) environmental dependency and expanding its application scope remain a primary focus for future research.

## 7. Conclusions

In conclusion, algal blooms and AOM pose a significant risk to drinking water quality. This review highlights the effectiveness of Fe(VI) oxidation in algae removal. Factors affecting Fe(VI) efficiency, oxidation and coagulation mechanisms, and the combined use of Fe(VI) and aluminum sulfate are discussed. This combined approach enhances coagulation, reduces DBP formation, and effectively removes AOM. Furthermore, the synergistic effect of Fe(VI) and Fe(II) improves algae and algal toxin removal. This evaluation provides

valuable insights for the safe and efficient treatment of algal material, thereby guiding future research in this area.

**Author Contributions:** S.W.: conceptualization, methodology, data analysis, and original draft preparation. S.Y.: data analysis and original draft preparation. H.C.: data analysis and original draft preparation. Q.L.: review, editing, and supervision. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the National Natural Science Foundations of China (72103022) and the China Postdoctoral Science Foundation (2020TQ0048, 2021M700460).

Data Availability Statement: The authors do not have permission to share the data.

**Conflicts of Interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### References

- 1. Zhao, G.Q. Enhanced algae removal by Ti-based coagulant: Comparison with conventional Al- and Fe-based coagulants. *Environ. Sci. Pollut. Res.* **2018**, 25, 13147–13158.
- 2. Wurtsbaugh, W.A.; Paerl, H.W.; Dodds, W.K. Nutrients, eutrophication and harmful algal blooms along the freshwater to marine continuum. *Wires Water* **2019**, *6*, e1373. [CrossRef]
- Ma, J.; Liu, W. Effectiveness and mechanism of potassium ferrate(VI) preoxidation for algae removal by coagulation. *Water Res.* 2002, 36, 871–878. [CrossRef] [PubMed]
- 4. Singh, S.K.; Sundaram, S.; Sinha, S.; Rahman, M.A.; Kapur, S. Recent advances in CO<sub>2</sub> uptake and fixation mechanism of cyanobacteria and microalgae. *Crit. Rev. Environ. Sci. Technol.* **2016**, *46*, 1297–1323. [CrossRef]
- 5. Dong, F.; Fu, C.; Feng, M.; Wang, D.; Song, S.; Li, C.; Sharma, V.K. Simultaneous generation of free radicals, Fe (IV) and Fe (V) by ferrate activation: A review. *Chem. Eng. J.* 2024, 481, 148669. [CrossRef]
- 6. Deng, Y.; Wu, M.; Zhang, H.; Zheng, L.; Acosta, Y.; Hsu, T.T.D. Addressing harmful algal blooms (HABs) impacts with ferrate(VI): Simultaneous removal of algal cells and toxins for drinking water treatment. *Chemosphere* **2017**, *186*, 757–761. [CrossRef]
- Liu, S.Y.; Xu, J.; Chen, W.L.; David, B.E.; Wu, M.; Ma, F. Impacts of potassium ferrate(VI) on the growth and organic matter accumulation, production, and structural changes in the cyanobacterium *Microcystis aeruginosa*. *Environ. Sci. Pollut. Res.* 2017, 24, 11299–11308. [CrossRef] [PubMed]
- 8. Pieterse, A.; Cloot, A. Algal cells and coagulation, flocculation and sedimentation processes. *Water Sci. Technol.* **1997**, *36*, 111–118. [CrossRef]
- 9. Sharma, V.K.; Zboril, R.; Varma, R.S. Ferrates: Greener Oxidants with Multimodal Action in Water Treatment Technologies. *Acc. Chem. Res.* 2015, *48*, 182–191. [CrossRef]
- 10. Wu, Z.; Shen, H.; Ondruschka, B.; Zhang, Y.; Wang, W.; Bremner, D.H. Removal of blue-green algae using the hybrid method of hydrodynamic cavitation and ozonation. *J. Hazard. Mater.* **2012**, *235–236*, 152–158. [CrossRef]
- 11. Dong, F.; Li, J.; Lin, Q.; Wang, D.; Li, C.; Shen, Y.; Song, S. Oxidation of chloroquine drug by ferrate: Kinetics, reaction mechanism and antibacterial activity. *Chem. Eng. J.* 2022, 428, 131408. [CrossRef] [PubMed]
- 12. Zhang, J.; Chen, Y.; Liao, Y.; Wang, Q.; Yu, J. Studies on the degradation of trace phenol and indole odorants by chlorine and permanganate in drinking water treatment. *Chemosphere* **2021**, *286*, 131551. [CrossRef] [PubMed]
- 13. Spellman, C.; Goodwill, J.E.; Addison, E.L. Physicochemical implications of cyanobacteria oxidation with Fe(VI). *Chemosphere* **2020**, *266*, 128956.
- 14. Zhou, J.; Zhao, Z.; Liu, J.; Peng, W.; Xiao, P. Removal of *Microcystis aeruginosa* and control of algal organic matters by potassium ferrate(VI) pre-oxidation enhanced Fe(II) coagulation. *Korean J. Chem. Eng.* **2019**, *36*, 1587–1594. [CrossRef]
- 15. Dong, F.; Fu, C.; Meng, Z.; Lin, Q.; Li, J.; Zeng, T.; Song, S. A two-stage Fe (VI) oxidation process enhances the removal of bisphenol A for potential application. *Sci. Total Environ.* **2024**, *907*, 167879. [CrossRef] [PubMed]
- Zhang, H.; Zheng, L.; Li, Z.; Pi, K.; Deng, Y. One-step ferrate(VI) treatment as a core process for alternative drinking water treatment. *Chemosphere* 2019, 242, 125134. [CrossRef] [PubMed]
- 17. Henderson, R.K.; Parsons, S.A.; Jefferson, B. The impact of differing cell and algogenic organic matter (AOM) characteristics on the coagulation and flotation of algae. *Water Res.* **2010**, *44*, 3617–3624. [CrossRef]
- Dong, F.; Lin, Q.; Li, C.; He, G.; Deng, Y. Impacts of pre-oxidation on the formation of disinfection byproducts from algal organic matter in subsequent chlor (am) ination: A review. *Sci. Total Environ.* 2021, 754, 141955. [CrossRef] [PubMed]
- 19. Yang, X.; Yao, L.; Wang, Y. Simultaneous removal of algae, microcystins and disinfection byproduct precursors by peroxymonosulfate(PMS)-enhanced Fe(III) coagulation. *Chem. Eng. J.* **2022**, 445, 136689. [CrossRef]
- 20. Yu, J.; Zhang, K.; Zhu, Q.; Wu, C.; Huang, S.; Zhang, Y.; Yao, S.; Pang, W. A Review of Research Progress in the Preparation and Application of Ferrate (VI). *Water* **2023**, *15*, 699. [CrossRef]
- 21. He, H.Y.; Qiu, W.; Liu, Y.L. Effect of ferrate pre-oxidation on algae-laden water ultrafiltration: Attenuating membrane fouling and decreasing formation potential of disinfection byproducts. *Water Res.* **2021**, *190*, 116690. [CrossRef] [PubMed]

- 22. Lee, T.H.; Chen, Y.M.; Chou, H.N. First report of microcystins in Taiwan. Toxicon 1998, 36, 247–255. [CrossRef] [PubMed]
- 23. Huang, W.J.; Lu, Y.M.; Yu, W.L. Toxicity and bioaccumulation of monomethylmercury in freshwater cyanobacteria: Oscillatoria tenuisa and *Microcystis aeruginosa*. *Environ. Forensics* **2012**, *13*, 255–261. [CrossRef]
- 24. Kubinakova, M. Effect of ferrate on green algae removal. Environ. Sci. Pollut. Res. 2017, 24, 21894–21901. [CrossRef] [PubMed]
- 25. Zhang, S.; Jiang, J.Q. Comparative removal of imidacloprid, bisphenol-S, and azithromycin with ferrate and FeCl<sub>3</sub> and assessment of the resulting toxicity. *J. Chem. Technol. Biotechnol.* **2021**, *96*, 99–112. [CrossRef]
- 26. Kareema, B.Y.; Tameemi, H.M.A. The effectiveness and kinetics of petrolim refinery wastewater treatment using potassim ferrate as an oxidant and coagulant. *AIP Conf. Proc.* 2022, *1*, 2450.
- 27. Lee, Y.; Kissner, R.; Von Gunten, U. Reaction of Ferrate(VI) with ABTS and Self-Decay of Ferrate(VI): Kinetics and Mechanisms. *Environ. Sci. Technol.* **2014**, *48*, 5154–5162. [CrossRef] [PubMed]
- 28. Lv, D.; Zheng, L.; Zhang, H.; Deng, Y. Coagulation of colloidal particles with ferrate (VI). *Environ. Sci. Water Res. Technol.* **2018**, *4*, 701–710. [CrossRef]
- Alshahri, A.H.; Fortunato, L.; Zaouri, N.; Ghaffour, N.; Leiknes, T.O. Role of dissolved air flotation (DAF) and liquid ferrate on mitigation of algal organic matter (AOM) during algal bloom events in RO desalination. *Sep. Purif. Technol.* 2020, 256, 117795. [CrossRef]
- Dubrawski, K.L.; Cataldo, M.; Dubrawski, Z.; Mazumder, A.; Wilkinson, D.P.; Mohseni, M. In-situ electrochemical Fe(VI) for removal of microcystin-LR from drinking water: Comparing dosing of the ferrate ion by electrochemical and chemical means. *J. Water Health* 2018, 16, 414. [CrossRef]
- 31. Vadasarukkai, Y.S.; Gagnon, G.A. Influence of the Mixing Energy Consumption Affecting Coagulation and Floc Aggregation. *Environ. Sci. Technol.* **2017**, *51*, 3480–3489. [CrossRef]
- 32. Rossini, M.; Garrido, J.G.; Galluzzo, M. Optimization of the Coagulation–Flocculation Treatment: Influence of Rapid Mix Parameters. *Water Res.* **1999**, *33*, 1817–1826. [CrossRef]
- 33. Edzwald, J.K. Coagulant mixing revisited: Theory and practice. J. Water Supply Res. Technol. 2013, 62, 67–77. [CrossRef]
- Lin, Y.; Lou, Y.; Li, A.; Wei, Y.; Li, H.; Zhou, M.; Li, Y. Effects of pre-oxidation by ozone, permanganate and ferrate on generation and toxicities of disinfection byproducts. *Int. J. Environ. Sci. Technol.* 2021, 16, 5969–5984. [CrossRef]
- Dong, F.; Liu, J.; Li, C.; Lin, Q.; Zhang, T.; Zhang, K.; Sharma, V.K. Ferrate (VI) pre-treatment and subsequent chlorination of blue-green algae: Quantification of disinfection byproducts. *Environ. Int.* 2019, 133, 105195. [CrossRef] [PubMed]
- Shen, Q.; Zhu, J.; Cheng, L.; Zhang, J.; Zhang, Z.; Xu, X. Enhanced algae removal by drinking water treatment of chlorination coupled with coagulation. *Desalination* 2011, 271, 236–240. [CrossRef]
- Wu, C.-D.; Xu, X.-J.; Liang, J.-L.; Wang, Q.; Dong, Q.; Liang, W.-L. Enhanced coagulation for treating slightly polluted algaecontaining surface water combining polyaluminum chloride (PAC) with diatomite. *Desalination* 2011, 279, 140–145. [CrossRef]
- 38. Rush, J.D.; Zhao, Z.; Bielski, B.H. Reaction of ferrate (VI)/ferrate (V) with hydrogen peroxide and superoxide anion—A stopped-flow and premix pulse radiolysis study. *Free Radic. Res.* **1996**, *24*, 187–198. [CrossRef]
- Liu, L.; Li, L.; Wu, Z.; Song, L. Physiological responses to ferrate (VI) stress in *Microcystis aeruginosa*. In Proceedings of the 2011 International Conference on Remote Sensing, Environment and Transportation Engineering, Nanjing, China, 24–26 June 2011; IEEE: Piscataway, NJ, USA, 2011; pp. 5153–5156.
- Liu, S. Impacts of Potassium Ferrate (VI) on the Growth, Protein, and Enzyme of the *Microcystis aeruginosa*. Water Air Soil. Pollut. 2019, 230, 173. [CrossRef]
- 41. Wu, Q.-Y.; Lu, X.-S.; Feng, M.-B.; Wang, W.-L.; Du, Y.; Yang, L.-L.; Hu, H.-Y. Reduction of cytotoxicity and DNA double-strand break effects of wastewater by ferrate (VI): Roles of oxidation and coagulation. *Water Res.* **2021**, 205, 117667. [CrossRef]
- 42. Henderson, R.K.; Baker, A.; Parsons, S.A.; Jefferson, B. Characterisation of algogenic organic matter extracted from cyanobacteria, green algae and diatoms. *Water Res.* **2008**, *42*, 3435–3445. [CrossRef] [PubMed]
- 43. Clasen, J.; Mischke, U.; Drikas, M. An improved method for detecting electrophoretic mobility of algae during the destabilisation process of flocculation: Flocculant demand of different species and the impact of DOC. J. Water Supply 2000, 49, 89–101. [CrossRef]
- Lian, J.; Cheng, X.; Zhu, X.; Luo, X.; Xu, J.; Tan, F.; Wu, D.; Liang, H. Mutual activation between ferrate and calcium sulfite for surface water pre-treatment and ultrafiltration membrane fouling control. *Sci. Total Environ.* 2023, *858*, 159893. [CrossRef] [PubMed]
- 45. Ma, X.-Y.; Zhang, Z.-H.; Li, Q.-S.; Hu, S.-F.; Wang, H.-Y.; Li, J.; Chen, J.-M. Simultaneous removal of algae and its odor metabolites in raw water by potassium ferrate. *Desalin Water Treat.* **2014**, *52*, 357–364. [CrossRef]
- Pivokonsky, M.; Kloucek, O.; Pivokonska, L. Evaluation of the production, composition and aluminum and iron complexation of algogenic organic matter. *Water Res.* 2006, 40, 3045–3052. [CrossRef] [PubMed]
- 47. Li, T.; Dong, B.; Liu, Z.; Chu, W. Characteristic of algogenic organic matter and its effect on UF membrane fouling. *Water Sci. Technol.* **2011**, *64*, 1685–1691. [CrossRef] [PubMed]
- Villacorte, L.O.; Ekowati, Y.; Neu, T.R.; Kleijn, J.M.; Winters, H.; Amy, G.; Schippers, J.C.; Kennedy, M.D. Characterisation of algal organic matter produced by bloom-forming marine and freshwater algae. *Water Res.* 2015, 73, 216–230. [CrossRef] [PubMed]
- 49. Wang, X.; Wang, X.; Mi, J.; Du, Q.; Wang, Y.; Chen, W.; Sun, D.; Song, W.; Shao, M.; Jia, R. UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> removal efficiency and characterization of algae-derived organic matter and odorous substances. *J. Environ. Chem. Eng.* **2023**, *11*, 109128. [CrossRef]

- Li, L.; Gao, N.; Deng, Y.; Yao, J.; Zhang, K. Characterization of intracellular & extracellular algae organic matters (AOM) of *Microcystic aeruginosa* and formation of AOM-associated disinfection byproducts and odor & taste compounds. *Water Res.* 2012, 46, 1233–1240.
- Alshahri, A.H.; Fortunato, L.; Ghaffour, N.E.; Leiknes, T.O. Advanced coagulation using in-situ generated liquid ferrate, Fe (VI), for enhanced pretreatment in seawater RO desalination during algal blooms. *Sci. Total Environ.* 2019, 685, 1193–1200. [CrossRef]
- Dai, G.; Quan, C.; Zhang, X.; Liu, J.; Song, L.; Gan, N. Fast removal of cyanobacterial toxin microcystin-LR by a low-cytotoxic microgel-Fe(III) complex. *Water Res.* 2012, 46, 1482–1489. [CrossRef] [PubMed]
- Massey, I.Y.; Yang, F.; Ding, Z.; Yang, S.; Guo, J.; Al-Osman, M.; Kamegni, R.B.; Zeng, W.M. Exposure routes and health effects of microcystins on animals and humans: A mini-review. *Toxicon Int. J. Devoted Exch. Knowl. Poisons Deriv. Anim. Plants Microorg.* 2018, 151, 156–162. [CrossRef] [PubMed]
- 54. Antoniou, M.G.; Boraei, I.; Solakidou, M.; Deligiannakis, Y.; Abhishek, M.; Lawton, L.A.; Edwards, C. Enhancing photocatalytic degradation of the cyanotoxin microcystin-LR with the addition of sulfate-radical generating oxidants. *J. Hazard. Mater.* **2018**, 360, 461–470. [CrossRef] [PubMed]
- 55. Pimentel, J.; Giani, A. Microcystin production and regulation under nutrient stress conditions in toxic microcystis strains. *Am. Soc. Microbiol.* **2014**, *80*, 5836–5843. [CrossRef]
- 56. He, X.; Liu, Y.L.; Conklin, A.; Westrick, J.; Weavers, L.K.; Dionysiou, D.D.; Lenhart, J.J.; Mouser, P.J.; Szlag, D.; Walker, H.W. Toxic cyanobacteria and drinking water: Impacts, detection, and treatment. *Harmful Algae* **2016**, *54*, 174–193. [CrossRef] [PubMed]
- 57. Ross, C.; Santiago-Vázquez, L.; Paul, V. Toxin release in response to oxidative stress and programmed cell death in the cyanobacterium *Microcystis aeruginosa*. *Aquat. Toxicol.* **2006**, *78*, 66–73. [CrossRef]
- 58. Valdiglesias, V.; Kiliç, G.; Costa, C.; Fernández-Bertólez, N.; Pásaro, E.; Teixeira, J.P.; Laffon, B. Effects of iron oxide nanoparticles: Cytotoxicity, genotoxicity, developmental toxicity, and neurotoxicity. *Environ. Mol. Mutagen.* 2015, 56, 125–148. [CrossRef] [PubMed]
- Jiang, W.; Chen, L.; Batchu, S.R.; Gardinali, P.R.; Jasa, L.; Marsalek, B.; Zboril, R.; Dionysiou, D.D.; O'Shea, K.E.; Sharma, V.K. Oxidation of Microcystin-LR by Ferrate(VI): Kinetics, Degradation Pathways, and Toxicity Assessments. *Environ. Sci. Technol.* 2014, 48, 12164–12172. [CrossRef]
- 60. Islam, A.; Jeon, D.; Ra, J.; Shin, J.; Kim, T.Y.; Lee, Y. Transformation of microcystin-LR and olefinic compounds by ferrate(VI): Oxidative cleavage of olefinic double bonds as the primary reaction pathway. *Water Res.* **2018**, *141*, 268–278. [CrossRef]
- 61. Botté, A.; Zaidi, M.; Guery, J.; Fichet, D.; Leignel, V. Aluminium in aquatic environments: Abundance and ecotoxicological impacts. *Aquat. Ecol.* 2022, *56*, 751–773. [CrossRef]
- Mahmoud, E.A.; Gad Mohamed, A.M.; Farrag, A.E.H.A.; Aboeldahb, S.A. Evaluation of the most promising techniques overcoming the algal problems takes place during the purification of drinking water. *Environ. Sci. Pollut. Res.* 2021, 28, 44239–44248. [CrossRef] [PubMed]
- 63. Liang, Y.; Jun, M.; Liu, W. Enhanced removal of lead (II) and cadmium (II) from water in alum coagulation by ferrate (VI) pretreatment. *Water Environ. Res.* 2007, *79*, 2420–2426. [CrossRef] [PubMed]
- 64. Tien, K.T.; Graham, N.; Jiang, J.-Q. Evaluating the coagulation performance of ferrate: A preliminary study. In Proceedings of the ACS Symposium Series, San Francisco, CA, USA, 19 September 2008.
- Alshahri, A.H.; Giagnorio, M.; Dehwah, A.H.; Obaid, M.; Missimer, T.M.; Leiknes, T.; Ghaffour, N.; Fortunato, L. Advanced coagulation with liquid ferrate as SWRO desalination pretreatment during severe algal bloom. Process performance, environmental impact, and cost analysis. *Desalination* 2022, 537, 115864. [CrossRef]
- 66. Yuan, B.-L.; Qu, J.-H.; Fu, M.-L. Removal of cyanobacterial microcystin-LR by ferrate oxidation–coagulation. *Toxicon* 2002, 40, 1129–1134. [CrossRef]
- 67. Jin, Y.; Chen, F.; Xu, B.; Ma, G.; Zhang, L.; Yang, Z.; Liu, R.; Sun, C.; Cheng, X.; Guo, N. Iron-based technology coupling moderate preoxidation with hybrid coagulation for highly effective removal and moderate growth inhibition of Oscillatoria in drinking water treatment plants. *J. Environ. Chem. Eng.* **2022**, *10*, 107723. [CrossRef]
- Darko, B.; Jiang, J.-Q.; Kim, H.; Machala, L.; Zboril, R.; Sharma, V.K. Advances made in understanding the interaction of ferrate (VI) with natural organic matter in water. In *Water Reclamation and Sustainability*; Elsevier: Amsterdam, The Netherlands, 2014; pp. 183–197.

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.