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Using a novel hydrogen-terminated porous Si wafer to enhance *Microcystis aeruginosa* effective removal by chitosan at a low dosage

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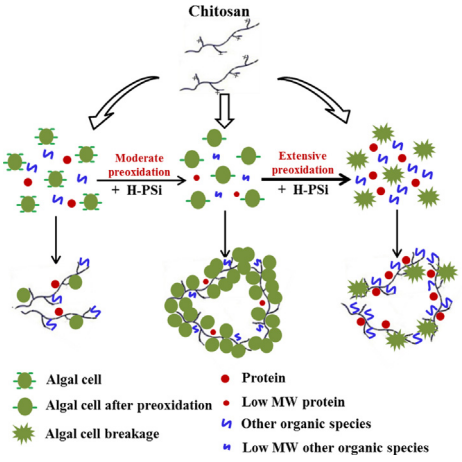
HIGHLIGHTS

- A new method to enhance algae removal by chitosan was put forward.
- H-PSi wafer can efficiently enhance algae removal by chitosan.
- H-PSi wafer has a good reusability.
- Mechanisms of H-PSi wafer for enhancing algae removal by chitosan was expounded.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel hydrogen-terminated porous Si wafer (H-PSi wafer), which could produce active radicals under visible light irradiation and has a good reusability, was proposed to enhance the *Microcystis aeruginosa* removal intactly by chitosan coagulation at a low dosage. The surface charge of *M. aeruginosa*, cell integrity, and release of intracellular organic matter from *M. aeruginosa* were investigated after H-PSi wafer pre-oxidation to reveal the related mechanism. The results show that, the surface charge of *M. aeruginosa* could be decreased after pre-oxidation, which is helpful to coagulation by the charge neutralization. Moderate pre-oxidation with suitable area of H-PSi wafer could avoid the intracellular organic matter released from algal cells and decrease the level of dissolved organic matter, and then the removal rate of *M. aeruginosa* by coagulation could be increased obviously. However, excessive pre-oxidation with larger area of H-PSi wafer will damage the algal cells, with intracellular organic matter releasing and the coagulation efficiency reducing. Furthermore, appropriate pre-oxidation could also effectively decrease the concentration of extracellular microcystins after chitosan coagulation. This study provides a promising technique to remove the toxic algae effectively and prevent the harm of blooms to drinking water production.

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1. Introduction

Algae bloom in water sources such as reservoirs and lakes is a critical issue in drinking water production, because it leads to odor, taste and other severe health issues [1–4]. *Microcystis aeruginosa* (*M. aeruginosa*), a well-known toxin-producing cyanobacterium in fresh water [5], can produce microcystins (MCs), which is hazardous to human health [6]. As a contingency measure for algae removal, coagulation/flocculation is one of the most common methods to treat water bloom. Chen et al. [7] and Ghernaout et al. [8] concluded that coagulation/flocculation is a key step in the water treatment process for algae removal. However, due to the nature of algal cells, including the negatively-charged surface, high motility, low specific density and so forth [9–11], the conventional treatment cannot effectively remove algal cells. To remove algal cells effectively, high dosages of coagulant must be added, which increase the treatment costs and simultaneously form large volumes of sludge that need to be disposed. Furthermore, the sludge produced by the inorganic metallic coagulants (i.e., alum and iron salts) are toxic to the environment [12], and the flocs formed by inorganic metallic coagulants are hard to settle down due to the low density [13].

Considering the above issues, application of natural biopolymers as coagulant may be a more feasible and sustainable alternative. Chitosan, poly-b-(1/4)-2-amino-2-deoxy D-glucose, is a cationic biopolymer which is produced by alkaline deacetylation of chitin, the second most abundant biopolymer in the world [14]. As a non-toxic, non-corrosive and biodegradable flocculant, chitosan has been applied in removing algae [15,16]. Additionally, it can be regenerated in a number of applications [17].

Although chitosan has been proved highly effective in removing algae, chitosan is expensive and the removal efficiency of extracellular MCs by chitosan is only 46.45% even at high dose of 7.31 mg/L [18]. Chemical pre-oxidation can promote the coagulation and sedimentation, increasing the filtration efficiency [10,11,19], and also can degrade the level of extracellular MCs [20,21], is a common method for water treatment plants when the cyanobacterial bloom happens. The common chemical preoxidants are chlorine, chlorine dioxide, ozone and permanganate. However, chlorine will produce trihalomethanes and haloacetic acids, which are harmful by-products [22]. It was also reported that the ozonation of waters containing bromide may lead to the formation of bromate at a high level, which is hazardous to health [10]. In addition, permanganate will cause the increase in the residual Mn, and turbidity [11].

Recently, advanced oxidation processes (AOPs) have become attractive alternatives to conventional chemical oxidation methods for the generation of highly oxidizing and non-selective hydroxyl radical that display higher second-order rate constants (10^8–10^9 M^{-1} s^{-1}) than those of other oxidants [23]. For example, Fast et al. [12] studied the effect of ultrasound on coagulation enhancement for *M. aeruginosa* removal, and found that ultrasound pretreatment could improve the removal efficiency of algal cells obviously. Although ultrasound could promote coagulation process for treating algal turbid water, the high cost of the equipment and its energetic cost restrict its use [24]. Furthermore, titanium dioxide (TiO_2) photocatalysis has been attracting wide attention for inactivation and removal of algae [25]. However, the wide use of TiO_2 is limited by ultraviolet light due to its large band gap (3.2 eV) [26]. To utilize visible light effectively, Huang et al. [27] used the ZnO/γ-Al_2O_3 powder for photocatalytic inactivation and removal of cyanobacteria under solar light. Although ZnO/γ-Al_2O_3 powder was effective in removing cyanobacteria, ZnO/γ-Al_2O_3 powder was difficult to reuse.

Recently, because H-PSi wafer could produce active radicals such as hydroxyl radical and hydrogen radical under visible light irradiation and has a high surface-to-volume (25.43 m^2 g^{-1}) [28,29], it has been widely used in the degradation of contaminants such as methyl orange [28,29], methyl red [30] under visible light irradiation. Moreover, according to our previous studies [28,29], the degradation activity of H-PSi wafer with (100) oriented crystal planes for methyl orange was highly stable within 8 recycle times, which means that it exhibits a good reusability. However, to our best knowledge, the enhanced coagulation by H-PSi wafer pre-oxidation for algae removal has not been studied. Furthermore, extensive pre-oxidation will cause the lysis of algal cells and the release of intracellular organic matter (IOM). In addition to the risk of MCs released from algal cells, the released IOM also inhibited coagulation when they were of high concentrations or insufficient molecular weight [31]. Therefore, an ideal pre-oxidation should be taken to achieve the balance between the two aspects of improving the algae removal and avoiding extensive pre-oxidation of algal cells.

This study aimed to: (1) investigate the removal efficiencies of *M. aeruginosa* and extracellular MCs by chitosan coagulation after H-PSi wafer pre-oxidation, (2) test the effects of H-PSi wafer pre-oxidation on algal cells and dissolved organic matter (DOM), and (3) explore the possible mechanisms of pre-oxidation enhancing algae removal by chitosan flocculation at a low dosage.

2. Materials and methods

2.1. Materials and reagents

M. aeruginosa (FACHB-905) was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, and grown in BG-11 medium (pH 7.5) [32]. The cultures were cultivated in a constant temperature incubator at 25 °C under 2000 lx with a light-dark cycle of 12 h/12 h *M. aeruginosa* cultures were harvested at the exponential growth phase at a concentration of 2×10^6 cells/mL, to simulate an algae bloom [33]. The pH of the *M. aeruginosa* suspension was about 8.6.

Chitosan (Mw = 50000, D.D = 95%) was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). As reported in our previous, chitosan was dissolved in a 1.0% dilute aqueous acetic acid solution and mixed with a magnetic stirrer at 100 rpm for over 24 h to obtain 1.0% (w/w) stock solution [18].

H-PSi wafer was prepared by photo-electrochemical (PEC) porosification experiments, which was conducted in a two-electrode cell at room temperature with *p*-type Si (100) wafers (the resistivity of 0.5–1 Ω cm, 510 μm thick) as the anode and a platinum wire as the counter electrode (cathode) in 49% HF/ethanol solution (V:V = 1:1) under room light. The anodization process was performed in a constant voltage of 15 V controlled by a (GWINSTEK, GPD-3303S) source meter for 10 min [29]. After etching, the samples were rinsed with ethanol and dried in N_2. Then the H-PSi wafer was used to oxidize *M. aeruginosa* immediately under visible light irradiation.

2.2. Pre-oxidation and coagulation experiments

Jar tests were carried out with 300 mL sample in 500 mL beaker and conducted on a jar test apparatus (ZR4-6; Zhongrun Water Industry Technology Development Co., Ltd., China) at the room temperature of 25 ± 1 °C.

For pre-oxidation experiments, several sterilized glass beakers, containing 300 mL algae suspension and a specified area of H-PSi

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