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Cyanobacterium removal and control of algal organic matter (AOM) release by UV/H_2O_2 pre-oxidation enhanced Fe(II) coagulation

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ABSTRACT

Harmful algal blooms in source water are a worldwide issue for drinking water production and safety. UV/H_2O_2, a pre-oxidation process, was firstly applied to enhance Fe(II) coagulation for the removal of *Microcystis aeruginosa* [*M. aeruginosa*, 2.0 (±0.5) × 10^6 cell/mL] in bench scale. It significantly improved both algae cells removal and algal organic matter (AOM) control, compared with UV irradiation alone (254 nm UVC, 5.4 mJ/cm^2). About 94.7% of algae cells were removed after 5 min UV/H_2O_2 pre-treatment with H_2O_2 dose 375 μmol/L, $FeSO_4$ coagulation (dose 125 μmol/L). It was also certified that low residue Fe level and AOM control was simultaneously achieved due to low dose of Fe(II) to settle down the cells as well as the AOM. The result of $L_9(3)^4$ orthogonal experiment demonstrated that H_2O_2 and $FeSO_4$ dose was significantly influenced the algae removal. UV/H_2O_2 induced an increase of intracellular reactive oxidant species (ROS) and a decrease in zeta potential, which might contribute to the algae removal. The total microcystins (MCs) concentration was 1.5 μg/L after UV/H_2O_2 pre-oxidation, however, it could be removed simultaneously with the algae cells and AOM. This study suggested a novel application of UV/H_2O_2-Fe(II) process to promote algae removal and simultaneously control AOM release in source waters, which is a green and promising technology without secondary pollution.

1. Introduction

In 2007, the “green monster” invaded Taihu, China's third largest lake, which provides drinking water for over 2 million people, and turned it into a toxic nightmare while cutting off the normal water supply of Wuxi for 8 days (Guo, 2007). Currently, the “green monster”-cyanobacterial blooms have already become a notorious and serious environmental phenomenon (Paerl and Paul, 2012) and have attracted worldwide concerns, because these blooms are gradually becoming the greatest threat to water quality, public health and aquatic ecosystems (Brooks et al., 2016). *Microcystis aeruginosa* (*M. aeruginosa*), one of the prominent and ubiquitous cyanobacterial species, is the chief culprit of harmful blooms in aquatic environments with eutrophication (Lapointe et al., 2015). During the blooms, *M. aeruginosa* seriously influences water treatment processes by plugging the filtration tanks/membranes. Furthermore, the algal organic matter (AOM) released from algae cells, such as toxins, substances causing taste and odor, and precursors of disinfection by-products (DBPs), can deteriorate water quality and be harmful to humans, animals and aquatic biota (Lui et al., 2011). The effective removal of cyanobacteria is critically important for preventing these issues.

Various methods have been proposed to remove *M. aeruginosa*, such as ultrafiltration (Tan et al., 2008), air flotation (Teixeira and Rosa, 2006), copper sulfate inhibition (Hullebusch et al., 2002), coagulation and sedimentation. Generally, ultrafiltration and air flotation can remove different algae species with high rates of above 90%. However, these methods are usually hindered by the heavy investment and operational cost. Copper sulfate inhibition usually requires large doses, and the residual copper would affect other aquatic biota (Hullebusch et al., 2002). Traditional coagulation and sedimentation is one of the mainstream processes in drinking water plants, but it cannot effectively remove algae due to the low density, high mobility, negatively charged surface and diverse morphology of algae cells (Teixeira and Rosa, 2006). Strategies such as increasing coagulant doses can improve the removal of algae, but may also result in unacceptably high level of coagulant residue, which possibly leads to secondary pollution.

Pre-oxidation is a feasible and popular process to enhance algae removal (Ma et al., 2012a,b). By addition of oxidants, such as Cl_2, O_3,

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$KMnO_4$, ClO_2, persulfate and ferrate, pre-oxidation could assist coagulation by changing zeta potential, destroying the organic coating and inactivating algae cells, resulting in a higher removal efficiency of algae in the subsequent sedimentation (Henderson et al., 2008). For example, ClO_2, Cl_2 and O_3 treatments could increase the removal efficiency of *Chlamydomonas*, *Euglena gracilis* and *Scenedesmus quadricauda*, by 90%, 95% and 99%, respectively (Steynberg et al., 1996; Plummer and Edzwald, 2002). However, most pre-oxidation technologies require a long contact time with algae cells. For instance, to achieve removal efficiencies of 75%, 95.8% and 98.2%, pre-Cl_2, Fe^{2+}-activated persulfate and UV-activated persulfate pre-oxidation methods require 20, 60 and 120 min, respectively (Ma et al., 2012b; Gu et al., 2017; Wang et al., 2016). Moreover, it takes 150 min to settle down 82.3% *M. aeruginosa* cells after pre-oxidation by $KMnO_4$ (Ma et al., 2012a). The longer contact time not only prolongs the treatment process but also increases the risk of releasing undesirable compounds (Lin et al., 2016). Extensive pre-oxidation can cause lysis of algae cells to release the intracellular organic matter (IOM), which can elevate the risk of formation of DBPs and probably inhibit coagulation (Ma et al., 2012a). Therefore, these factors should be carefully considered before applying strong oxidants. Ideal pre-oxidation methods should be moderate to balance the need to avoid extensive pre-oxidation with improving algae removal efficiency. Finally, the addition of some chemical oxidants, such as $KMnO_4$, persulfate and ferrate, could have residual effects, and consequently influence the drinking water quality (Hullebusch et al., 2002). Therefore, developing a new technology aiming to solve the present problems is important and necessary.

Advanced oxidation processes (AOPs) generate strong oxidant-hydroxyl radicals (•OH). They can react rapidly and almost non-selectively with most organic compounds (Liu et al., 2012), therefore have the potential for removing *M. aeruginosa* and AOM at the same time. Combined ultraviolet irradiation (UV, 254 nm UV-C) and H_2O_2 process, as one of AOPs, is widely studied because of its high removal efficiency on contaminants and non-polluting nature (Lee et al., 2017). UV is widely applied in water treatments for its powerful penetration and lethality on cells (Wolfe, 1990). H_2O_2 is a common and widely used chemical for disinfection and water treatment. One of its potential merits compared with other oxidants is environmental friendliness as it degrades to water and oxygen without producing persistent toxic chemicals or byproducts that cause aesthetic odor or color issues. A previous study reported that UV irradiation treatment can effectively impair algae cells and did not involve the addition of any harmful chemicals into water (Tao et al., 2013). It was demonstrated that UV irradiation could inactivate algae by damaging its photosynthesis system, which might exert a positive effect on its removal (Cordi et al., 1997). Alam et al. also found that UV radiation may increase the specific gravity of the cells and thus may adversely affect the ability of the cells to remain in suspension (Alam et al., 2001). Meanwhile, a suitable dose of H_2O_2 could affect the cell integrity of *M. aeruginosa*, cause lipid oxidation and decrease the stability of the cell membrane (Xu et al., 2006; Huo et al., 2015). Therefore, UV/H_2O_2 is expected to be a promising pre-oxidation technology to improve coagulation efficiency for algae removal, due to its strong ability to inactivate algae cells and suppress their growth (Zhang et al., 2017) without any secondary pollution. However, there are no publications investigating UV/H_2O_2 assisted coagulation for algae removal.

In this study, UV/H_2O_2 was firstly used as a pre-oxidation process to assist the subsequent Fe(II)-coagulation-sedimentation process to remove *M. aeruginosa* and AOM. The effects of some critical parameters, including the optimum doses of Fe(II), UV irradiation time, H_2O_2 concentration and reaction time, on the *M. aeruginosa* removal efficiency were investigated. The specific objective is to study the effects of UV/H_2O_2 on the changes in *M. aeruginosa* characteristics including surface properties and the morphology and integrity of cells. The residual Fe concentration after sedimentation was also analyzed to help evaluate the safety of UV/H_2O_2 technology. This study demonstrates that UV/H_2O_2 might be a potential pretreatment process to assist coagulation for the algae removal as well as AOM release control.

2. Materials and methods

2.1. Materials

An axenic strain of *M. aeruginosa* (No. FACHB-905) isolated from Dianchi Lake, China was obtained from the Institute of Hydrobiology, Chinese Academy of Science. All chemicals used in the study were of analytical grade. All solutions were prepared with deionized water. H_2O_2 and ferrous sulfate ($FeSO_4$) solutions were prepared just before experiments.

2.2. Experimental design

2.2.1. Pre-oxidation experiments

The *M. aeruginosa* cells were harvested in the exponential phase and diluted with deionized water to a concentration of 2.0 ($\pm$0.5) $\times$ 10^6 cell/mL. Pre-oxidation experiments were carried out in a cylindrical reactor equipped with a low-pressure UV lamp (254 nm, 8 W, GL Type, XiashiWanhua Co., China) at an average irradiance of 18.0 μW/cm^2 at room temperature (Li et al., 2017).

The UV irradiation time was designed as 0, 1, 4, 5 and 6 min (corresponding to 0, 1.1, 4.3, 5.4 and 6.5 mJ/cm^2) to study the effects of UV doses on algae removal. H_2O_2 pre-oxidation proceeded continuously for 5 min with the different UV irradiation time during the process.

For the contribution of different H_2O_2 concentrations, the H_2O_2 stock solution was added to the reactor containing algae cells to the desired concentrations of 0, 125, 250, 375 and 750 μmol/L, while the pre-treated time of UV/H_2O_2 remained at 5 min.

And for the effects of H_2O_2 pre-oxidation time, 0, 2.5, 5, 10 to 15 min were tested, with the same H_2O_2 dose of 375 μmol/L and UV irradiation for 5 min. For the oxidation time less than 5 min, UV lamp turned on firstly to irradiate 5 min. During the process, H_2O_2 solution stock was dosed to obtain the desired time. On the other hand, H_2O_2 and UV was dosed simultaneously. The UV lamp was turned off after 5 min and H_2O_2 can contact 10 or 15 min.

During all the processes, the solution was homogenized by a magnetic stirrer at a speed of 200 rpm. Samples receiving only stirring but no UV and/or H_2O_2 treatment were set as the control.

2.2.2. Coagulation and sedimentation experiments

After pre-oxidation, 400 mL solution was transferred into a 500 mL beaker immediately. After adding $FeSO_4$ solution into the beaker, coagulation and sedimentation experiments were undertaken using a programmable jar tester (MY3000-6N, Meiyu, China) at room temperature. The reaction solution was rapidly mixed at 250 rpm for 1 min followed by slow mix at 50 rpm for 10 min. After settling for 20 min, clarified supernatant samples were withdrawn from sampling ports 2 cm below the water surface and divided into several subsamples to be analyzed.

2.3. Analytical methods

2.3.1. Density of cells and removal efficiency

M. aeruginosa cell density was determined by optical density at 680 nm (OD_{680}), which was positively correlated to cell number, using a UV–vis spectrophotometer (L6S, Lengguang, China) (Dai