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Potent removal of cyanobacteria with controlled release of toxic secondary metabolites by a titanium xerogel coagulant

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ABSTRACT

Cyanobacteria blooming is a serious environmental issue throughout the world. Removal of cyanobacterial cells from surface water with controlled release of cyanobacterial organic matter (COM), especially toxic microcystins (MCs), would potentially reduce the processing burden in follow-up water treatment. Coagulation is a key technique in water treatment. Herein, the potential application of a novel titanium xerogel coagulant (TXC) was evaluated for the treatment of cyanobacteria-laden water in terms of cyanobacteria removal efficiency, variation of cell viability, the release and evolution of COM in the floc accumulation and storage process. Under acidic to neutral conditions, TXC showed a higher removal efficiency of approximately 99% for cyanobacteria and a lower residual Ti concentration than the widely-used commercial polyferric sulfate (PFS) and polyaluminum chloride (PAC). Another advantage of TXC was the reduced MCs concentration caused by the released acetylacetone (AcAc) from the hydrolysis of TXC. Under solar irradiation, AcAc degraded the extracellular MCs from an initial concentration of 40 μg/L to a residual concentration of 7 μg/L during a 16-day floc storage process. The low residual Ti concentration (< 0.04 mg/L) and the efficient removal of COM/MCs following TXC coagulation reduced the toxicity to photobacteria. The results demonstrate that TXC is a promising dual-effect coagulant for treatment of cyanobacteria-laden water.

1. Introduction

Cyanobacteria (blue-green algae, cyanophyceae) are highly adaptable prokaryotes, which are able to cause extensive and striking blooms, especially in freshwater ponds or lakes (Briand et al., 2002). They have become a growing concern for drinking water utilities, because they can interfere with treatment in various ways, primarily by plugging filters and by producing secondary metabolites and taste and odor-causing substances (Graham et al., 2010; Carmichael, 1992). Microcystins (MCs) are a class of toxins produced by certain freshwater cyanobacteria, such as *Microcystis* (primarily *M. aeruginosa*), *Anabaena*, *Oscillatoria*, and *Nostoc* (Sangolkar et al., 2006). MC-LR is one of the most common MCs and is toxic to both humans and animals (Dawson, 1998). The World Health Organization (WHO) has set a guideline value of 1.0 μg/L for MC-LR (WHO, 1998). Therefore, cyanobacteria and cyanobacterial organic matter (COM, including both intracellular and extracellular organic matter) are critical concerns in drinking water treatment.

Chemical coagulation has been a basic process in cyanobacteria-laden drinking water treatment due to its low price and high removal efficiency (Teixeira et al., 2010; Pan et al., 2012). Traditional coagulants, such as ferric or aluminum salts, have been extensively studied for their use in the removal of cyanobacteria (Chen et al., 2013; Chow et al., 1998; Ho et al., 2012; Peterson et al., 1995; Sun et al., 2012; Velzeboer et al., 1995). However, the residual Al/Fe in the treated water sometimes exceeds the upper limit of water standards (0.2 mg/L for Al and 0.3 mg/L for Fe), which would be a severe threat to human health. As alternatives to metal salts, biodegradable and human-safe natural materials, such as clays (Pan et al., 2012), chitosan (Ahmad et al., 2011), cationic starch (Vandamme et al., 2010), and tannin (Wang et al., 2013), have been proposed as promising coagulants for cyanobacteria removal. However, due to the negative surface charge, high motility, diverse morphology, and low specific density of the cyanobacterial cells as well as the extracellular organic matter (EOM), the traditional coagulation treatment can hardly achieve satisfactory removal (Takaara et al., 2010; Ma et al., 2007). Several pretreatment strategies have been attempted, such as complicated pre-modification of natural coagulants with aldehydes, amines, and cationic reagents for enhanced entrapment of cyanobacteria cells (Beltrán-Heredia

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et al., 2010) or $KMnO_4$ preoxidation (Ma et al., 2012), prechlorination (Chen et al., 2009; Lin et al., 2016), UV irradiation (Alam et al., 2001), and ozonation (Chen et al., 2009; Schneider and Tobiason, 2000) in Al/Fe coagulation to reduce the content of EOM. However, the oxidation of cyanobacteria may lead to cell lysis. The subsequent massive release of intracellular organic matter (IOM) might deteriorate the water quality (Peterson et al., 1995). Therefore, the chemical stress introduced to the cell membranes during coagulation process is an issue of concern.

The effects of coagulants on cell integrity critically depended on the type and dose of coagulants, as well as the coagulation conditions, which were all key parameters to guarantee an efficient removal of intact cyanobacterial cells without causing additional release of intracellular toxins (Chow et al., 1998; Li et al., 2015; Sun et al., 2012, 2013). After coagulation, the cyanobacteria cells are transferred into the accumulated flocs, in which the cyanobacteria are prone to losing viability because of the cell damage (Li et al., 2015). Once toxic MCs were released into water, they are hard to be removed by the subsequent clarification/filtration treatment (Chow et al., 1998; Teixeira and Rosa, 2005). Therefore, controlling the release of MCs is important in the coagulation process. Otherwise, we need effective ways to degrade the MCs that are released during the floc accumulation process.

A gelation approach was developed to prepare titanium-based coagulants in our previous work (Wang et al., 2016). The resultant titanium xerogel coagulant (TXC) showed distinct advantages over titanium tetrachloride (TC) and polytitanium tetrachloride (PTC) in water/wastewater treatment by overcoming the shortcomings of TC and PTC, including the low effluent pH, the narrow workable dose and solution pH (Wang et al., 2016). Furthermore, the TXC overshadowed the commercial polyferric sulfate (PFS) on several industrial wastewaters with larger floc size and higher removal capacity (Wang et al., 2016). The TXC was prepared with a sol-gel process using acetylacetone (AcAc) as the hydrolysis inhibitor. In recent years, AcAc has been reported as a potent photoactivator, which could effectively degrade various organic pollutants (Zhang et al., 2014a, 2017). Even being anchored in titanium xerogel, AcAc also showed an interesting photo-activity, which led to a repeatable and reversible sorption of dyes to the xerogel (Zhang et al., 2014b). Therefore, it is reasonable to expect that TXC could be bifunctional in the treatment of cyanobacteria-laden water: removing the cyanobacterial cells and simultaneously reducing the concentration of MCs.

To the best of our knowledge, the application of Ti-salt coagulants in cyanobacteria-laden water has not yet been studied. The optimal coagulation condition and the effects on cyanobacterial cell integrity during Ti-salts coagulation are totally unknown. In the present work, the application potential of TXC in cyanobacteria-laden water treatment was systematically investigated in terms of cyanobacteria removal efficiency, variation of cell viability, the release and evolution of COM (especially MCs) in the floc accumulation and storage process. Two commercial inorganic coagulants, PFS and poly aluminum chloride (PAC), which are widely used in most drinking water treatment plants in China, were selected for comparison under controlled laboratory conditions.

2. Materials and methods

2.1. Materials

2.1.1. Cyanobacteria culturing

A freshwater cyanobacteria culture, *M. aeruginosa* (strain FACHB-905), was purchased from Institute of Hydrobiology, Chinese Academy Science (Wuhan, China) and cultivated in sterile BG11 medium (Stanier et al., 1971). The cultures grew in a chamber incubator subjected to a 16 h/8 h light/dark cycle, where temperature was controlled at 25/15 °C. The cultivation of cyanobacteria was conducted in an open erlenmeyer flask. The cultures were mixed three times a day and were harvested at the late exponential phase of growth. The cyanobacteria solution at 28-day cultivation was frozen at −28 °C for 24 h, followed by ultrasonication (200 W) for 10 min. After centrifugation at 10000 rpm for 10 min, the resultant supernatant was filtrated with a 0.22 μm membrane. The filtrate was denoted as COM.

2.1.2. Cyanobacteria-laden water

A simulated cyanobacteria-laden water was prepared by mixing *M. aeruginosa* culture (10^7 cells/mL) with a 0.9% NaCl solution to achieve a final cell density of approximately 3×10^6 cells/mL according to the WHO guidance for the high probability of adverse health effects (WHO, 1999). The initial extracellular and intracellular MCs concentration in the simulated cyanobacteria-laden water were 1.3 and 40.3 μg/L, respectively. A natural cyanobacteria-laden water was collected from Lake Taihu (the third largest inland freshwater lake and a drinking water source in China) at the high cyanobacteria outbreak period in October with a cell density of 8.5×10^6 cells/mL.

2.1.3. Reagents

PFS (Fe content: 19%, basicity: 11%) and PAC (Al_2O_3 content: 30%, alkalinity degree: 40%) were commercially available product purchased from Lvliao Industry Co. Ltd. (China). TXC (Ti content: 25%) was synthesized with a molar ratio of 1: 1/8: 4 ($TiCl_4$/AcAc/H_2O), following the reported procedures (Wang et al., 2016). MC-LR (≥ 95% by HPLC) with a molecular weight of 995 was purchased from Taiwan Algal Science Inc. and was used directly without any pretreatment. The chemical structure of MC-LR is presented in Fig. S1 (in the Supplementary Data-SD). Bioluminescence *V. fischeri* was purchased from Institute of Soil Science, Chinese Academy Sciences, Nanjing, China. Unless otherwise specified, the other chemicals used in this study were purchased from the Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Experimental section

2.2.1. Coagulation experiments

Coagulation experiments were carried out with a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China). Initially, the cyanobacteria samples were rapidly mixed at 200 revolutions per minute (rpm) for 1 min, followed with a slow stirring phase at 40 rpm for 15 min to promote the collision of particles and hence floc growth, and finally a 20 min settling period. The solution pH was adjusted to 5–10 with 0.1 M HCl or NaOH solution, whenever needed.

2.2.2. Floc storage experiments

Coagulation was conducted under the optimal dose (12 mg Ti/L (TXC), 12 mg Fe/L (PFS), and 2 mg Al/L (PAC)) and solution pH (7.0) for the floc storage experiments. Coagulation system (stirring with coagulant) and blank control system (stirring-only) were built to evaluate the cell integrity and viability in flocs after stocking for 0, 2, 4, 6, 8, 10, 12, 14 and 16 days. Flocs and supernatants were sampled every two days from initially 1 L of cyanobacteria-laden solutions to measure the physicochemical parameters following coagulation.

2.2.3. Photoirradiation experiments

Photoirradiation experiments under simulated sunlight were conducted with a 250 W Xenon (Xe) lamp in a rotating disk photoreactor (Nanjing Xujiang, China) (Wang et al., 2014). Sample