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Algal removal from cyanobacteria-rich waters by preoxidation-assisted coagulation–flotation: Effect of algogenic organic matter release on algal removal and trihalomethane formation

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ABSTRACT

The cyanobacteria-bloom in raw waters frequently causes an unpredictable chemical dosing of preoxidation and coagulation for an effective removal of algal cells in water treatment plants. This study investigated the effects of preoxidation with NaOCl and ClO_2 on the coagulation–flotation effectiveness in the removal of two commonly blooming cyanobacteria species, *Microcystis aeruginosa* (MA) and *Cylindrospermopsis raciborskii* (CR), and their corresponding trihalomethane (THM) formation potential. The results showed that dual dosing with NaOCl plus ClO_2 was more effective in enhancing the deformation of cyanobacterial cells compared to single dosing with NaOCl, especially for CR-rich water. Both preoxidation approaches for CR-rich water effectively reduced the CR cell count with less remained dissolved organic carbon (DOC), which benefited subsequent coagulation–flotation. However, preoxidation led to an adverse release of algogenic organic matter (AOM) in the case of MA-rich water. The release of AOM resulted in a poor removal in MA cells and a large amount of THM formation after oxidation-assisted coagulation–flotation process. The reduction in THM formation potential of CR-rich waters is responsible for effective algae and DOC removal by alum coagulation. It is concluded that the species-specific characteristic of cyanobacteria and their AOM released during chlorination significantly influences the performance of coagulation–flotation for AOM removal and corresponding THM formation.

Introduction

Algae proliferation in reservoirs frequently constrains the unit operation in drinking water treatment plants (DWTPs) because of their vast increase in not only cell population but also algogenic organic matter (AOM) as a byproduct during algal photosynthesis and the lysis of senescent algal cells (Pivokonsky et al., 2016). The sudden excessive growth of algae in reservoirs excessively burdens water purification units, with subsequent deterioration of water quality. Algal proliferation causes drastic changes in turbidity, pH, taste and odor, and the amount of organic matter in treated water (Coral et al., 2013). For instance, when strip or needle algae, such as the diatom *Syendra acus*, appears in the raw water, it frequently challenges the operation

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of coagulation–sedimentation unit because of its very poor settling rate (Henderson et al., 2008). Consequently, the deep-bed filter is easily blocked by the algae, leading to an increase in the frequency of backwashing (Joh et al., 2011). Furthermore, because of some algae and cyanobacteria release neurotoxins and biotoxins during metabolism, they are of concern about the safety of drinking water (Landsberg, 2002; Wang et al., 2013). An effective approach to the pretreatment of algae-rich waters is thus crucial in overcoming the challenges posed by algae proliferation at DWTPs.

Coagulation is a traditional process to destabilize algae and enhance the algal removal with Al-based coagulant or chitosan-based flocculants (Lin et al., 2015, 2016; Shi et al., 2016). In practice, the coupling process of coagulation and dissolved air flotation (DAF) has been widely employed to remove algae from algae-rich waters (Edzwald, 1993; Teixeira and Rosa, 2006; Henderson et al., 2009, 2010). In this coupling process, coagulated particles are attached by microbubbles, then removed by turbulent flotation (Rulyov, 2001). It is an essential process to destabilize algal cells that are then removed by the attachment of microbubbles to algal flocs (Edzwald, 1993). Compared to sedimentation, DAF is a more powerful process for the removal of blue-green and green algae from raw waters (Teixeira and Rosa, 2006; Henderson et al., 2010). Even in the presence of natural organic matter (NOM), DAF still accounted for more than 90% of the removal of *Microcystis aeruginosa* with optimum coagulant dosing (Teixeira and Rosa, 2007).

However, when algae bloom, preoxidation with sodium hypochlorite, chlorine dioxide, or ozone is often required as a further pretreatment step prior to coagulation for the effective removal of algae by either flotation or sedimentation. Preoxidation enhances the destabilization of algal cells, resulting in the reduction of the coagulant dosage required (Henderson et al., 2008). Unfortunately, this may also induce the release of AOM from the ruptured cells (*i.e.*, intracellular organic matter (IOM)) (Ma et al., 2012a), which results in negative impacts on subsequent treatment units and worsens the quality of finished drinking water (Ma et al., 2012b; Zhou et al., 2014; Lin et al., 2015). For instance, in the case of algae destabilization by coagulation, the released AOM with a high ratio of proteins favors forming the protein–alum complex that substantially inhibits the destabilization of algal cells (Takaara et al., 2010). This phenomenon results in increasing coagulant consumption and impairs the performance of subsequent solid–liquid separation units (Takaara et al., 2007; Ma et al., 2012b). Importantly, AOM comprises of various substances, such as amino acids, polysaccharides, and other small molecular acids, which is highly hydrophilic (Leloup et al., 2013) and not amendable to coagulation (Pivokonsky et al., 2016). AOM has been well proved as a potential precursor to disinfection byproducts (DBPs) (Nguyen et al., 2005). The rapid release of AOM by excessive preoxidation would elevate severe DBP formation potential (DBPFP) in drinking water. Furthermore, because the physical and chemical properties of algal species vary widely between species (Henderson et al., 2008), it is difficult to control chemical dosing for preoxidation and coagulation in DWTPs so as to control such algae-derived DBP formation. Hence, an appropriate dosing approach of preoxidation and coagulation for various algae-rich waters is pivotal for the performance of DWTPs.

In Taiwan, sodium hypochlorite (NaOCl) is commonly used among chlorine-based disinfectants for the preoxidation because preoxidation with NaOCl is a simple and cost-effective approach as well as has a strong ability to deactivate algae (Lin et al., 2016). NaOCl preoxidation destroys algal cells by the diffusion of HOCl and OCl^- at neutral pH to rupture the cells (Peterson et al., 1995). Although preoxidation with NaOCl can impair cell viability and deteriorate the chemosphere of cyanobacteria *M. aeruginosa* (Ma et al., 2012b) or of green algae *Pediastrum simplex* cells, it may fail to rupture the thick cell-wall of algae such as diatom *Cylotella* sp. (Lin et al., 2016). Furthermore, DWTPs in the outside islands of Taiwan often face to the dramatic increase in the cell population (10^6–10^7 cells/mL) with a high concentration of dissolved organic matter (>20 mg/L) during summer times; NaOCl preoxidation might be insufficient to pretreat such a great number of algal cells. Consequently, the extra dosing of NaOCl is required, but it would cause a severe formation of DBPs, where trihalomethanes (THMs) concentration in finished water in DWTPs easily exceeds the regulated concentration. On the other hand, ClO_2 preoxidation does not induce the THM formation (Kim et al., 2015), and it has stronger oxidative ability than NaOCl to lyse most of the algal cells of various species (Zhou et al., 2014; Lin et al., 2015, 2016). However, because ClO_2 is an explosive gas and unstable chemicals, it is only used as an additional dosage along with NaOCl when severe algal eutrophication occurs.

To date, a few studies have highlighted the impact of preoxidation-assisted coagulation–flotation on the removal of algal cells from various algae-rich waters (Edzwald, 1993; Teixeira and Rosa, 2006; Henderson et al., 2009, 2010). However, there is very limited information about the fate of the released AOM during preoxidation with dual dosing (NaOCl + ClO_2) for natural algal-rich water treatment, and its impacts on algae removal by coagulation–flotation and the corresponding THM formation potential (THMFP). This study aimed to investigate the effects of preoxidation with dual dosing (NaOCl + ClO_2) on coagulation–flotation for the removal of algal cells from two natural cyanobacteria-rich waters containing *M. aeruginosa* (MA) and *Cylindrospermopsis raciborskii* (CR). The effect of AOM release during preoxidation on the corresponding THMFP was also evaluated.

1. Materials and methods

1.1. *Characteristics of algae-rich waters*

Natural cyanobacteria-rich waters predominantly containing MA and CR (90% cell population) were collected from Tai-Hu and Tian-Pu reservoirs in Kimmen, Taiwan with initial pH values of 7.15 and 7.52, respectively. To identify algal species and cell counts, water samples were placed in a hemocytometer (Neubauer-improved, Marienfeld, Germany). The number of cells was then determined by a light microscope (ExwaveHAD, Sony, Japan). Only intact cells were counted in this study; cell fragments after treatment were not considered in the count. The turbidity of the water was determined using a turbidity meter (2100P, Hach, USA) and the pH with a pH meter (InoLab Multi Level, WTW, Germany). The total organic carbon (TOC) and dissolved organic carbon (DOC) of water samples were