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 ClO₂ 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 ClO₂ 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.

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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...
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 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 (DBFP) 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 OCI– 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 Cyclotella sp. (Lin et al., 2016). Furthermore, DWTPs in the outside islands of Taiwan often face to the dramatic increase in the cell population (105–107 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, ClO2 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 ClO2 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 + ClO2) 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 + ClO2) on coagulation flotation for the removal of algal cells from two natural cyanobacteria-rich waters containing M. aeruginosa (MA) and Cylindropermopsis 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...
Nephelometric Turbidity Units
Turbidity (NTU) 25.57 ± 1.03 22.43 ± 0.94 21.07 ± 1.22 21.65 ± 1.08

removed by microbubbles at a pressure of 3.8 kg/cm². A f t e r
of 0.4 L/min. The remained algal cells and AOM were further
1 min, followed by a slow mixing at 30 r/min (G = 350 sec⁻¹). The total
oxidant dosage of 1 mg/L was conducted following the practical
dosing in DWTP. Preoxidation with dual dosing was conducted with NaOCl
and ClO₂ in the ratios of 1:1 (0.5 mg/L/0.5 mg/L as Cl) and 1:2
(0.33 mg/L/0.67 mg/L as Cl), respectively. After chlorination,
coagulation at different dosages of alum (Al₂(SO₄)₃·18H₂O) was
carried out at a rapid mixing at 200 r/min (G = 350 sec⁻¹) for
1 min, followed by a slow mixing at 30 r/min (G = 25 sec⁻¹) for
15 min. The suspension flowed to a flotation tank at a flow rate
of 0.4 L/min. The remained algal cells and AOM were further
removed by microbubbles at a pressure of 3.8 kg/cm². After
cogulation–flotation, suspensions were immediately
withlained to determine their residual cell count, turbidity, and
DOC. Fluorescence excitation–emission matrix (EEM) and
high-performance size-exclusion chromatography (HP-SEC)
were also used to determine the variation of chemical compo-
nents and molecular weight distribution of suspension of each
step. Furthermore, the concentrations of THMs were deter-
mined by gas chromatograph–mass spectrometry (GC–MS) to
quantify the DBFP of the supernatants.

1.3. Fluorescence EEM

Water samples were analyzed after preoxidation and flotation
by the EEM to determine the chemical composition of the
organic matter. Three millimeter water samples were
measured with a Cary Eclipse fluorescence spectrophotome-
ter (Varian Inc., Palo Alto, USA). All water samples were
adjusted to pH 7.0 ± 0.1 and then filtered through 0.45 μm
Polytetrafluoroethylene (PTFE) membranes before each EEM
scan. EEM spectra were collected by increasing the scanning
emission range from 250 to 600 nm with 2 nm increments.
The excitation wavelength ranged from 200 to 500 nm with
10 nm increments. The fluorescence of water samples was
determined at a scanning rate of 1200 nm/min by using excitation
and emission slit bandwidths of 5 nm. The voltage of the photomultiplier tube was set to 800 V for low-level light
detection. For each test, the EEM spectra of water samples
were subjected to four fluorescent regions with excitation/
emission wavelengths (Ex/Em) of 350/435–450, 250–280/425,
humic-like (region II), fulvic-like (region III), protein-like
(region I), and aromatic protein-like substances (region IV)
(Chen et al., 2003). According to these four regions, the average
fluorescent intensities (AFIs, a.u) were calculated for each
substance category.

1.4. HP-SEC

HP-SEC system was used to compare the molecular weight
differences in the organic matter of water samples after
preoxidation and after flotation. HP-SEC was carried out using
a degasser (DEGASYS DG-1310, Uniflows Co. Ltd., Japan), a feed
pump (BETA 10 Gradient pump, Ecom spol. s.r.o., Czech
Republic), a chromatography column (TSK G2000SWx1, TOSOH
Co., Tokyo, Japan), and two on-line detectors, a
ultraviolet-visible (UV-vis) variable wavelength detector (SAP-
PHIRE 600, Ecom spol. s.r.o., Czech) and a refractive index
detector (JOTA 2, Precision Instruments, France). The two
detectors were connected in series and controlled by software
Peak-ABC. The feed pump was set at a flow rate of 1 mL/min.
Water samples were adjusted to pH 7.0 ± 0.1 and then filtered
with 0.45 μm PTFE membranes before HP-SEC analysis. Poly-
ethylene glycols (PEG, 200, 1000, 4000, 8000 and 20,000 Da) were
used to calibrate the apparent molecular weight. The absorp-
tion wavelength of the UV detector was set at 254 nm.

Table 1 – Characteristics of Microcystis aeruginosa (MA) and Cylindrospermopsis raciborskii (CR)-rich waters with and without
oxidation.

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Parameter</th>
<th>Without oxidation</th>
<th>NaOCl</th>
<th>NaOCl + ClO₂ (1:1)</th>
<th>NaOCl + ClO₂ (1:2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA-rich water</td>
<td>Nephelometric</td>
<td>7.89 ± 0.15</td>
<td>7.38 ± 0.13</td>
<td>6.84 ± 0.22</td>
<td>7.03 ± 0.41</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>DOC (mg/L)</td>
<td>5300 ± 990</td>
<td>3700 ± 250</td>
<td>3900 ± 310</td>
<td>3100 ± 420</td>
</tr>
<tr>
<td></td>
<td>TOC (mg/L)</td>
<td>9.12 ± 0.16</td>
<td>10.03 ± 0.21</td>
<td>11.47 ± 0.19</td>
<td>11.43 ± 0.51</td>
</tr>
<tr>
<td></td>
<td>Specific POC (μg/L)</td>
<td>12.39 ± 0.06</td>
<td>12.04 ± 0.08</td>
<td>12.23 ± 0.26</td>
<td>12.06 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>(μg/L)</td>
<td>0.617</td>
<td>0.543</td>
<td>0.195</td>
<td>0.203</td>
</tr>
<tr>
<td>CR-rich water</td>
<td>Turbidity (NTU)</td>
<td>25.57 ± 1.03</td>
<td>22.43 ± 0.94</td>
<td>21.07 ± 1.22</td>
<td>21.65 ± 1.08</td>
</tr>
<tr>
<td></td>
<td>DOC (mg/L)</td>
<td>5800 ± 770</td>
<td>74,000 ± 5500</td>
<td>65,700 ± 4200</td>
<td>36,250±5800</td>
</tr>
<tr>
<td></td>
<td>TOC (mg/L)</td>
<td>17.45 ± 0.25</td>
<td>17.51 ± 0.15</td>
<td>17.96 ± 0.31</td>
<td>17.92 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>Specific POC (μg/L)</td>
<td>21.09 ± 0.12</td>
<td>20.89 ± 0.08</td>
<td>20.83 ± 0.15</td>
<td>20.60 ± 0.06</td>
</tr>
</tbody>
</table>

Specific POC (μg/L) = (TOC – DOC) / cell count; all data was determined in the triplicate analysis.
Table 2 – AFI EEM spectra for MA- and CR-rich waters with and without oxidation.

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Fluorescence region</th>
<th>Without oxidation</th>
<th>NaOCl</th>
<th>NaOCl + ClO₂ (1:1)</th>
<th>NaOCl + ClO₂ (1:2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA-rich water</td>
<td>SMP-like</td>
<td>34.43</td>
<td>31.88</td>
<td>38.26</td>
<td>33.00</td>
</tr>
<tr>
<td></td>
<td>Humic-like</td>
<td>40.39</td>
<td>41.31</td>
<td>40.62</td>
<td>41.28</td>
</tr>
<tr>
<td></td>
<td>Fulvic-like</td>
<td>72.42</td>
<td>24.01</td>
<td>33.83</td>
<td>37.86</td>
</tr>
<tr>
<td></td>
<td>Aromatic protein-like</td>
<td>42.04</td>
<td>11.49</td>
<td>19.72</td>
<td>17.18</td>
</tr>
<tr>
<td>CR-rich water</td>
<td>SMP-like</td>
<td>31.93</td>
<td>22.06</td>
<td>25.81</td>
<td>18.91</td>
</tr>
<tr>
<td></td>
<td>Humic-like</td>
<td>34.92</td>
<td>31.16</td>
<td>33.77</td>
<td>25.75</td>
</tr>
<tr>
<td></td>
<td>Fulvic-like</td>
<td>51.79</td>
<td>48.37</td>
<td>50.86</td>
<td>38.05</td>
</tr>
<tr>
<td></td>
<td>Aromatic protein-like</td>
<td>27.53</td>
<td>21.06</td>
<td>23.55</td>
<td>17.29</td>
</tr>
</tbody>
</table>

AFI: average fluorescent intensity (au.); EEM: excitation-emission matrix; SMP: soluble microbial products.

Fig. 1 – Variation of residual turbidity, cell count, and DOC with alum dosage in oxidation-assisted coagulation–flotation for *Microcystis aeruginosa* (MA) and *Cylindrospermopsis raciborskii* (CR)-rich waters.
1.5. GC–MS for THM analysis

The formation potentials of four major THMs (e.g., chloroform (TCM), bromoform (TBM), bromodichloromethane (BDCM), and dibromochloromethane (DBCM)) were determined using GC–MS (Agilent 6890GC/5970MSD, Cary, NC), following Environmental Protection Agency (EPA) method 524.2. The chlorine of each sample was spiked to 5 times DOC with sodium hypochlorite. All samples were adjusted to pH 7.0 ± 0.1 and stored in headspace-free amber glass bottles at room temperature. After 7 days the water samples were acidified and quenched with ammonium chloride to obtain THMFP.

2. Result and discussion

2.1. Effect of preoxidation on the algal cell degradation and AOM release

The deterioration of algal cells and the release of AOM by preoxidation directly influence coagulation (Chen et al., 2009; Henderson et al., 2010). The effects of preoxidation with single dosing (NaOCl) and dual dosing (NaOCl + ClO2) on the cell removal and DOC release were first investigated. Table 1 shows that preoxidation with single and dual dosing markedly reduced the turbidity and cell count in the supernatant in both MA and CR-rich waters.

In this study, CR cells are generally elongated (40–130 μm in length) with a thick cell-wall (2–5 μm in width), while MA cells are spherical, 3–7 μm in diameter. It is likely that most CR cells were split into fragments by the preoxidation, while MA cells were attacked, accompanied by the release of AOM. The reduction of turbidity and cell count by dual dosing preoxidation (NaOCl:ClO2 = 1:2) was more pronounced compared to single dosing (NaOCl), especially in the case of CR-rich water. It is attributed to the stronger oxidative ability of ClO2 to attack the intact algal cells compared to NaOCl (Lin et al., 2015, 2016). Thus, the dual dosing resulted in greater decreased in algal cell counts.

Although the number of affected cells in CR-rich water was remarkably higher than in MA-rich water, the residual DOC in CR-rich water changed negligibly after preoxidation with either single or dual dosing, whereas the residual DOC increased in the case of MA-rich water, as shown in Table 1. The content of specific particulate organic carbon (POC) (i.e., (the amount of TOC – the amount of DOC) / total algal cell counts) for each cell in the MA-rich water (0.617 μg/L per cell) was markedly higher compared to CR-rich water (0.041 μg/L per cell) before preoxidation. With preoxidation, even though single or dual dosing significantly reduced the number of algal cells in CR-rich water from approximately 88,000 to 36,250 cells/mL, only a trace amount of DOC was released. By contrast, it destroyed the
algal cells in MA-rich water to release more amount of DOC compared to CR-rich water.

To further understand the characteristics of the released AOM in water after preoxidation, EEM fluorescence spectra of the organic substances in MA-rich and CR-rich waters before and after preoxidation were investigated. Table 2 gives EEM spectra for four fluorescent regions. After preoxidation, the dissolved organic matter (DOM) in two cyanobacteria-rich waters contained a large amount of protein-like and fulvic-like substances along with a few humic-like substances, similar to that reported in a previous study (Lin et al., 2015). Detailed examination of DOM fluorophores showed that all fractionated intensities for CR-rich water had been slightly reduced, while only the intensities of fulvic-like and protein-like substances for MA-rich water had been substantially reduced. In the case of MA-rich water, preoxidation with single dosing (NaOCl) or dual dosing (NaOCl + ClO₂) markedly degraded the protein-like substances because NaOCl preferentially reacts with organic nitrogenous substances and degrades their structure (Deborde and von Gunten, 2008). Moreover, because most of the fulvic-like substances were in the MA-rich water, they reacted with oxidants during preoxidation with either single or dual dosing. The decreased intensity of both fulvic-like and protein-like substances was more significant during preoxidation with single dosing than that with dual dosing. However, only the intensity of humic-like substances did not decrease after preoxidation of MA-rich water. These results are in agreement with a previous study (Ou et al., 2011), where a rapid increase of humic-like substances was accompanied by the gradual decrease in protein-like fluorescent during the chlorination of MA cells. It could be concluded that the algal cells in MA-rich water would tremendously contribute fluorescent matter that affects coagulation–flotation performance for algae removal.

2.2. Effect of preoxidation on algae and DOC removal by coagulation–flotation

Although algal cells can be amenable to coagulation, coagulation is always constrained by AOM in water (Henderson et al., 2010; Pivokonsky et al., 2016). After preoxidation the behavior of released AOM in MA-rich and CR-rich waters would indirectly influence the coagulant consumption and AOM destabilization. Consequently, the effects of the release of AOM after perpreoxidation on coagulation–flotation was further investigated. Fig. 1 shows that, at an optimum Alum dosage (7.4 × 10⁻⁵ mol/L as Al), preoxidation with dual dosing prior to alum coagulation–flotation effectively enhanced the destabilization of algal cells compared to single dosing (NaOCl), leading to a sufficient reduction of turbidity and removal of algal by flotation. For instance, approximately 95% of cells was removed from CR-rich water, while only 75% of cells was removed from MA-rich water by pretreatment of dual dosing preoxidation (NaOCl:ClO₂ = 1:2). However, the residual DOC in treated MA-rich water was higher than before

![Fig. 3 - Molecular weight distribution of MA- and CR-rich waters before and after coagulation-flootation at the optimum dosage with and without preoxidation. Dosage: 7.4 × 10⁻⁵ mol/L as Al.](image-url)
coagulation, even though higher alum dosage had been applied. By contrast, the residual DOC in treated CR-rich water was reduced significantly. Because of the AOM released from the ruptured MA cells, this inhibited the destabilization of DOM. The fewer DOM released after preoxidation, the smaller the increase in DOC in treated CR-water. The preoxidation reaction between algal species and oxidants thus significantly influences the performance of coagulation–flotation for algae removal.

Fig. 2 shows that the coagulation–flotation of MA-rich and CR-rich waters enhanced reducing the intensities of humic-like, fulvic-like, and SMP-like substances, while the intensity of aromatic protein-like substances was scarcely changed in the EEM spectra. It has been reported that large DOM with more than 10 kDa is easily destabilized by coagulation, while the small DOM with less than 1 kDa, mostly nitrogenous organic matter, inhibits coagulation (Takaara et al., 2007; Pivokonsky et al., 2016). Furthermore, DOM with aromatic or aliphatic functional groups preferentially reacts with Al species in coagulation and then destabilizes DOM by complexation or co-precipitation (Lin et al., 2014). The large carbonaceous organic substances (humic-like and fulvic-like) and nitrogenous substances (SMP-like) in MA-rich and CR-rich waters were therefore effectively removed by preoxidation-assisted coagulation–flotation, while small aromatic protein-like substances remained unchanged.

The distribution of molecular weight of DOM before and after preoxidation-assisted coagulation–flotation was also analyzed using an HP-SEC coupled with a UV254 detector to verify the effect of preoxidation on the release of AOM and the

Fig. 4 – The corresponding trihalomethane (THM) formation potential (THMFP) of supernatant after coagulation–flotation with different peroxidation strategies for MA- and CR-rich waters.
DOM removal by coagulation–flotation, as shown in Fig. 3. In the case of MA-rich water, preoxidation with single and dual dosing significantly caused the release of large molecular weight (MW) AOM from algal cells, resulting in an increase in DOM molecules of more than 5 kDa. This released DOM was then partially removed by coagulation–flotation (Fig. 3a). For CR-rich water, the larger DOM molecules of more than 1 kDa were effectively removed after coagulation–flotation, but smaller DOM molecules (<1 kDa) were still remained (Fig. 3b). It is likely that the remained DOM predominantly comprised humic-like substances, as shown in Table 2. Furthermore, the molecular weight distribution of DOM implies that dual dosing was more effective in removing DOM molecules of more than 10 kDa than single dosing. In summary, the reduction of DOM and algal cells in cyanobacteria-rich waters strongly depends on the quantities and component of AOM release during preoxidation.

2.3. Effect of preoxidation on THMFP of cyanobacteria-rich waters

The algae-derived organic matter is recognized as one of the important THM precursors of DBP (Huang et al., 2009). THMFP of algae-rich water can be effectively reduced by coagulation–flotation (Chu et al., 2011). However, the characteristics of AOM released from algal cells during preoxidation strongly affect the performance of coagulation–flotation for algae and DOC removal, and which directly regulate the variation in THMFP of algae-rich water after treatment. The variation in THMFP of MA-rich and CR-rich waters after preoxidation-assisted coagulation–flotation was determined and is shown in Fig. 4. The THMFP of MA-rich supernatant by preoxidation with single dosing (NaOCl) or dual dosing (NaOCl + ClO2) was insensitive to alum dosage (Fig. 4a). By contrast, the THMFP of CR-rich supernatant rapidly declined with increasing alum dosage (Fig. 4b). Furthermore, the reduction in THMFP in the preoxidation of MA-rich water was independent of single or dual dosing, while THMFP was significantly reduced by preoxidation with dual dosing (NaOCl + ClO2) in the case of CR-rich water. The discrepancies in THMFP between MA- and CR-rich waters are primarily caused by the content and characteristics of AOM released during preoxidation. The more AOM releases by preoxidation, the more THM precursors are ineffectively removed by coagulation–flotation processes. The appropriate preoxidation for suitable algae-laden waters is thus crucial in controlling THMs. These results also suggested that the integration of dual dosing preoxidation coupled with coagulation–flotation might further minimize the THMFP of treated water.

Two cyanobacteria-rich water samples were collected near the coastal area, where a certain amount of Br ions (up to 0.1 mg/L) is present in the raw water. In this instance, the precursors of Br-THM (i.e., BDCM, DBCM, and TBM) in MA-rich and CR-rich waters were ineffectively reduced by preoxidation-assisted coagulation–flotation, even at high alum dosage. Because these precursors are hydrophilic molecules with low molecular weight, alum coagulation is not able to effectively destabilize them (Pivokonsky et al., 2016; Zhao et al., 2016). Small DOM molecules thus cannot be effectively removed by coagulation–flotation, and supernatant still contains the bromine-carried THM precursors.

3. Conclusions

Preoxidation with single dosing (NaOCl) and dual dosing (NaOCl + ClO2) is effective in reducing the algal cells from both cyanobacterial-rich waters, but ruptures the cells at different levels, causing the differential release of AOM from algal cells in MA-rich and CR-rich waters. Preoxidation deforms the algal cells and increases the residual DOC in MA-rich water, while the DOC in CR-rich water is insensitive to preoxidation. After preoxidation the quantities and composition of the released AOM strongly affect the performance of coagulation–flotation. The released AOM from algal cells in MA-rich water cause poor DOC removal by coagulation–flotation as well as increased THMFP. On the other hand, the corresponding THMFP derived from coagulated CR-rich water can be controlled by high alum dosages. Compared to single dosing, dual dosing is more effective in assisting algal destabilization by coagulation–flotation, lowering the residual THMFP, especially for CR-rich water. It is concluded that the oxidant-species interaction greatly influences the performance of preoxidation-assisted coagulation–flotation for algae, and that released AOM removal that directly controls the corresponding THMFP.

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REFERENCES


