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The impact of pre-oxidation with potassium permanganate on cyanobacterial organic matter removal by coagulation

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ABSTRACT

The study investigates the effect of permanganate pre-oxidation on the coagulation of peptides/proteins of *Microcystis aeruginosa* which comprise a major proportion of the organic matter during cyanobacterial bloom decay. Four different permanganate dosages (0.1, 0.2, 0.4 and 0.6 mg $KMnO_4$ mg^{-1} DOC) were applied prior to coagulation by ferric sulphate. Moreover, changes in sample characteristics, such as UV_{254}, DOC content and molecular weight distribution, after pre-oxidation were monitored. The results showed that permanganate pre-oxidation led to a reduction in coagulant dose, increased organic matter removals by coagulation (by 5–12% depending on permanganate dose), microcystin removal (with reductions of 91–96%) and a shift of the optimum pH range from 4.3 to 6 without to 5.5–7.3 with pre-oxidation. Degradation of organic matter into inorganic carbon and adsorption of organic matter onto hydrous MnO_2 are suggested as the main processes responsible for coagulation improvement. Moreover, permanganate prevented the formation of Fe-peptide/protein complexes that inhibit coagulation at pH about 6.2 without pre-oxidation. The study showed that carefully optimized dosing of permanganate improves cyanobacterial peptide/protein removal, with the benefit of microcystin elimination.

1. Introduction

Cyanobacteria are ubiquitous in rivers and reservoirs supplying drinking water treatment facilities. When cyanobacterial populations rise, water treatment technology has to deal not only with increased cell concentration but also with dissolved algal organic matter (AOM) (Zhang et al., 2010). AOM can seriously impair water treatment process efficiency, especially during the decline phase of an algal bloom, when high concentrations of cellular organic matter (COM) are released into source water (Henderson et al., 2008; Zhang et al., 2010; Pivokonsky et al., 2016). The most pronounced adverse effects of AOM on drinking water production and quality are the reduction in coagulation efficiency, shortening filter runs, membrane fouling, decreased adsorption efficiency for micropollutants onto activated carbon, and disinfection by-product formation (Pramanik et al., 2015; Zamyadi et al., 2015; Pivokonsky et al., 2016).

Numerous studies have showed that pre-oxidants such as ozone, chlorine dioxide, chlorine, potassium ferrate (K_2FeO_4) or potassium permanganate ($KMnO_4$) can improve the removal of algal and cyanobacterial cells by coagulation/flocculation (Ma and Liu, 2002; Plummer and Edzwald, 2002; Chen and Yeh, 2005; Henderson et al., 2008; Chen et al., 2009; Ma et al., 2012; Coral et al., 2013; Pranowo et al., 2013; Wang et al., 2013; Xie et al., 2013; Qi et al., 2016). The improvement in cell removal is attributed to cell inactivation, changes in external cell architecture and release of high-molecular weight (MW) extracellular organic matter (EOM) and/or cellular organic matter (COM) that easily combine with coagulants (Pranowo et al., 2013; Wang et al., 2013). However, many studies indicated that pre-oxidants may negatively affect coagulation. Pre-oxidation can lead to cell lysis, releasing undesirable toxins or taste and odour compounds, and to EOM/COM degradation, forming low-MW compounds which may be difficult to coagulate (Hoyer et al., 1987; Paralkar and Edzwald,

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1996; Henderson et al., 2008; Ma et al., 2012; Coral et al., 2013; Pranowo et al., 2013; Wang et al., 2013; Xie et al., 2013). Furthermore, pre-oxidation by chlorine, chlorine dioxide and ozone forms undesirable disinfection by-products (DBPs) (Henderson et al., 2008; Coral et al., 2013; Xie et al., 2013). To avoid the formation of DBPs, permanganate may be used as an alternative pre-oxidant when treating eutrophic source water (Xie et al., 2016).

The effect of permanganate and ozone pre-oxidation on aqueous suspensions of *Microcystis aeruginosa*, subsequent coagulation by aluminium sulphate and the formation of DBPs during downstream chlorination was previously investigated (Xie et al., 2013). Both pre-oxidants increased the removal rate of cells during coagulation (from 56.7% without pre-oxidation) by 15–25% depending on the dose. Pre-ozonation destroyed cell walls and membranes to release COM, and produced more organic nitrogen and lower-MW precursors than permanganate oxidation. This resulted in a dramatic increase in DBP formation during downstream chlorination. Pre-oxidation with permanganate mainly released organic matter adsorbed on the cells' surface without causing any cell damage and led to much lower DBPs formation. Similarly, Chen et al. (2009) demonstrated that both ozone and permanganate, can improve the subsequent algae (*Chlorella* sp.) removal through alum coagulation and sedimentation, increasing algae removal efficiency from 84% to 93% and 98% for optimum doses of ozone and permanganate, respectively. While extensive cell destruction was observed after ozonation, permanganate had the potential to induce the release of EOM from cells. Permanganate also generates manganese dioxides (MnO_2), which may accelerate the flocculation kinetics by increasing particle concentration and promote flocculation by adsorption onto other particles (Petrusevski et al., 1996; Chen and Yeh, 2005; Chen et al., 2009; Xie et al., 2016). However, if $KMnO_4$ is overdosed, increases in residual manganese, colour, turbidity and cell damage can occur (Qi et al., 2016; Xie et al., 2016). Petrusevski et al. (1996) noted that $KMnO_4$ dose and residual manganese were positively correlated, although it was observed that the subsequent application of cationic polymer lowered residual manganese levels. Furthermore, Ma et al. (2012) and Qi et al. (2016) showed that the cellular organic matter (COM) release can be controlled by the subsequent introduction of Fe(II) to quench residual $KMnO_4$.

Studies on the oxidation of AOM in the absence of algal cells are rare and they focus only on the ozonation of algal EOM (Hoyer et al., 1987; Paralkar and Edzwald, 1996; Widrig et al., 1996). Widrig et al. (1996) showed that macromolecular proteins and fatty acids were degraded by ozone into smaller molecules. Similarly, Paralkar and Edzwald (1996) found that ozonation of the EOM showed a consistent trend of decreasing high-MW fractions and increasing medium- and low-MW fractions with increasing ozone dose. Moreover, the charge of the EOM samples was observed to become more negative with ozonation. No attention has been given to the pre-oxidation of COM which has been reported to form the majority of AOM in raw water during algal bloom decay (Zhang et al., 2010).

The aim of this study was to investigate the impact of pre-oxidation on the coagulation of dissolved COM. Potassium permanganate was used as the pre-oxidant to minimize the degradation of COM into smaller molecules which are resistant to coagulation (Pivokonsky et al., 2012). The specific objectives were: (1) to evaluate the changes in COM and MW distribution after permanganate oxidation, and (2) to assess the influence of permanganate oxidation on the coagulation of the COM derived from *Microcystis aeruginosa*. Hence, this paper presents for the first time novel data on the fate of cyanobacterial COM during oxidation using $KMnO_4$. These data demonstrate the operational benefits of selection of optimising the pre-oxidation agent and conditions for successful coagulation of cyanobacterial COM and removal of the associated toxins.

2. Material and methods

2.1. Cultivation of Microcystis aeruginosa and preparation of COM

Microcystis aeruginosa (strain Zap. 2006/2, Department of Culture Collection of Algal Laboratory, Institute of Botany, CAS, Czech Republic) was the species selected for this study, as it is the most abundant and common cyanobacterium occurring in natural water (Pivokonsky et al., 2016). It was cultivated and harvested during the stationary growth phase as described by Pivokonsky et al. (2014). The cells were separated from the culture media by filtering through a 0.22 μm membrane filter (Millipore, USA) and subsequently stirred with ultra-pure water and disrupted in ice bath using an ultrasonic homogeniser (UP400S, Hielscher Ultrasonics, Germany) at 60% amplitude of ultrasonication (240 W) in pulse mode for 5 min. The residual solids were removed by a 0.22 mm membrane filter, and filtrates were concentrated tenfold in a rotary evaporator (Laborota 4000 HB/G1, Germany) at 20 °C. The peptide and protein fraction of COM, which was reported to represent the major portion of *M. aeruginosa* COM (Pivokonsky et al., 2014), was isolated from the cells and used in all subsequent experiments. Peptides and proteins were isolated from the COM by precipitation using $(NH_4)_2SO_4$. The peptide/protein precipitate was separated from the dissolved organic matter by filtration through a 0.22 mm membrane filter (Millipore, USA) and then dissolved in ultra-pure water (Pivokonsky et al., 2012). Peptide/protein concentrations in the subsequent experiments are expressed as concentration of dissolved organic carbon (DOC). The isoelectric points of the isolated peptides and proteins are within a range of 4.8–8.1 (Pivokonsky et al., 2012). In addition, both COM and isolated peptide/protein samples were analyzed for microcystin content (the sum of MC–LR, –RR and –YR). It was found that more than 95% of microcystins contained in COM passed to peptide/protein fraction during its isolation. In the peptide/protein sample with 100 mg L^{-1} of DOC, total MCs concentration was 143.7 μg L^{-1}.

2.2. Pre-oxidation experiments

Solution of 0.02 M $KMnO_4$ (Sigma-Aldrich, USA) was used as pre-oxidant. Solutions of COM peptides/proteins were diluted to the concentration of 8 mg L^{-1} as DOC and adjusted to pH 7 and alkalinity 1.5 mmol L^{-1} (75 mg L^{-1} $CaCO_3$) using 0.1 M HCl and 0.1 M $NaHCO_3$. These were then oxidized with 0.1, 0.2, 0.4 and 0.6 mg $KMnO_4$ per 1 mg DOC. Samples were collected for residual $KMnO_4$ analysis after 1, 3, 5, 10, 20, 30, 40, 50 and 60 min of contact time under mixing at a shear rate of 100 s^{-1} with a magnetic stirrer. This was undertaken to monitor the side effects of extensive oxidation (increased Mn, colour and turbidity levels). In addition, the time needed for the oxidation was determined by measuring the variation of UV absorbance at 254 nm, absorbance at 620 nm, proportional to the amount of phycocyanin, and residual DOC concentrations at each time point, where the time, at which absorbance and DOC stabilised, was taken as the oxidation time required. The changes in the MW distribution of COM peptides/proteins and microcystin concentrations at the time required for complete oxidation, i.e. at 10 min time, were monitored by high-performance size-exclusion chromatography (HPSEC) and by solid phase extraction (SPE) followed by LC/MS/MS, respectively (see section 2.4). The samples were rotary evaporated prior to MW distribution and microcystin analyses (Laborota 4000 HB/G1, Germany) to reach concentrations of 50 mg L^{-1} DOC that are convenient for HPSEC performance and enable microcystin detection.