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A coagulation–powdered activated carbon–ultrafiltration – Multiple barrier approach for removing toxins from two Australian cyanobacterial blooms

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ABSTRACT

Cyanobacteria are a major problem for the world wide water industry as they can produce metabolites toxic to humans in addition to taste and odour compounds that make drinking water aesthetically displeasing. Removal of cyanobacterial toxins from drinking water is important to avoid serious illness in consumers. This objective can be confidently achieved through the application of the multiple barrier approach to drinking water quality and safety. In this study the use of a multiple barrier approach incorporating coagulation, powdered activated carbon (PAC) and ultrafiltration (UF) was investigated for the removal of intracellular and extracellular cyanobacterial toxins from two naturally occurring blooms in South Australia. Also investigated was the impact of these treatments on the UF flux. In this multi-barrier approach, coagulation was used to remove the cells and thus the intracellular toxin while PAC was used for extracellular toxin adsorption and finally the UF was used for floc, PAC and cell removal. Cyanobacterial cells were completely removed using the UF membrane alone and when used in conjunction with coagulation. Extracellular toxins were removed to varying degrees by PAC addition. UF flux deteriorated dramatically during a trial with a very high cell concentration; however, the flux was improved by coagulation and PAC addition.

1. Introduction

Cyanobacteria are a major problem for the worldwide water industry as they can produce metabolites toxic to humans in addition to taste and odour compounds that make drinking water aesthetically displeasing [1–4]. It is likely that this problem will be intensified by the effects of climate change through reservoir warming [5–7]. Tropical cyanobacterial species are also becoming more prevalent in temperate climates [8]. Cyanobacteria are even being detected more frequently in colder climates, such as in Canada [9]. The effective removal of cyanobacterial metabolites is therefore an increasingly important priority for the worldwide water industry.

While it is not definitively known why cyanobacteria produce toxins, it has been suggested that toxins are evolutionary carry-overs and may function as protective secretions since researchers have shown some cyanobacterial toxins to be potent inhibitors of aquatic invertebrate grazers [1]. Toxins are formed at all stages of cyanobacterial growth. They generally remain within the cell (intracellular toxin) until stress, damage or cell death and lysis causes their release into surrounding water (extracellular toxin) [10]. Intracellular toxin content is typically highest in the late growth phase and the toxin content has shown a positive correlation with cyanobacteria biomass [11].

Many options for treating water affected by cyanobacterial blooms exist including conventional coagulation and sand filtration, membrane filtration, powdered activated carbon (PAC) addition, granular activated carbon filtration and chemical oxidation by ozone or chlorine. In the absence of any damage to the cells, conventional treatment can be effective for the removal of the intact cells and therefore the majority of the metabolites, for example, microcystin can be up to 98% intracellular [12]. Extracellular metabolites can be effectively removed by PAC [13]. The safest option for water suppliers is to apply a multiple barrier treatment process that is capable of removing both cyanobacteria cells and dissolved metabolites. A multiple barrier process that has the potential to remove both intra- and extracellular metabolites is the combination of coagulation, PAC application and ultrafiltration (UF).

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Two studies have investigated PAC and UF for the removal of microcystin-LR (MCLR) [14,15]. Lee and Walker [14] showed that a PAC–UF system was efficient for MCLR removal using both polyethersulfone (PES) and cellulose acetate (CA) membranes. However, the removal profiles differed for the two membranes. The CA membrane, without PAC addition, did not remove MCLR while the addition of PAC resulted in 70% removal of the toxin. The removal of MCLR by PAC alone was similar to the PAC–UF system indicating that PAC adsorption was the dominant removal mechanism. In the case of the PES membrane, it was shown that this UF membrane alone had adsorptive properties for MCLR with removals similar to that of the combined PAC–UF system. Lee and Walker [14] also studied the effects of natural organic matter (NOM) on MCLR removal. While the CA membrane was not affected by NOM, flux measurements suggested the PES membranes were fouled by NOM. Campinas and Rosa [15] also investigated MCLR removal using a PAC–UF system. The impact of NOM was assessed using model compounds (a mixture of tannic and humic acids) and *Microcystis aeruginosa* culture. Constant flow experiments were performed with a hydrophilic UF hollow-fibre membrane and a mesoporous PAC. In contrast to the findings of [14], NOM had no effect on removal of toxins by their PAC–UF system at 5 mg/L of dissolved organic carbon (DOC) and 15 mg/L PAC.

Gijsbertsen-Abrahamse et al. [16] showed that UF could cause lysis of *Planktothrix agardhii*. They found that a small amount of cell-bound microcystin was released and was measured in the permeate at concentrations equal to or lower than the extracellular microcystin concentrations of the feedwater. Campinas and Rosa [17] observed that *M. aeruginosa* cell lysis occurred at all cell growth phases although greater damage was observed for older cultures. Cell lysis is an issue for a coagulation–PAC–UF system as extracellular toxin would require a higher dose of PAC, making the process more costly.

Optimisation of PAC dosing and selection of the correct UF material is important as various effects of PAC on UF flux have been reported in the literature. Some authors have reported a reduced flux, longer backwash intervals or a reduced frequency of chemical cleaning when using PAC pre-treatment [18–20]. Others have shown little effect [21–23] or increased flux when using PAC [24–26]. Some studies have shown that the membrane hydrophobicity is the key to reduced flux when pre-dosing PAC. Several studies [27–29] observed that PAC reduced flux of hydrophilic membranes and increased the flux of hydrophobic membranes. A multiple barrier approach incorporating coagulation and PAC may improve removal of cyanobacterial toxins and reduce membrane fouling by NOM, as both coagulation and PAC can remove NOM.

Previous studies detailed above have not demonstrated the removal of cyanobacterial cells from natural waters or naturally occurring blooms which may differ from laboratory cultures. No studies to date have used polyvinylidene fluoride (PVDF), a commonly used hollow fibre UF membrane, in a multiple barrier approach to investigate removal of cyanobacteria or to establish removal of both intracellular and extracellular cyanobacterial metabolites.

In this study the use of a multiple barrier approach incorporating coagulation, PAC and a PVDF UF membrane for the removal of intracellular toxin (via cell removal) and extracellular cyanobacterial toxins from naturally occurring blooms in South Australia was investigated. In order to determine the effectiveness of combining coagulation and coagulation–PAC with UF, the efficiency of each treatment barrier was assessed. Also investigated was the impact of these treatments on the UF flux.

2. Methods

2.1. Materials

The PAC used in the laboratory experiments was Acticarb PS1000 (Activated Carbon Technologies, Australia). It is a coal based, steam activated carbon. Aluminium chlorohydrate (ACH) was used as the coagulant for this study as Al_2O_3 (Omega Chemicals, Australia) and was dosed as a 23% solution. Coagulant dose was expressed in terms of Al^{3+} for direct comparison of coagulants with other studies. A commercially available membrane was used for the UF trials (Toray, Japan).

2.2. Feedwater

In November 2009 a bloom of *Anabaena circinalis* occurred in Myponga Reservoir in South Australia at a cell concentration of 460,000 cells/mL. A sample of the bloom material was collected, counted and tested for viability and used in the trial on the following day. Concentrations of cyanobacteria were quantified using gridded a Sedgewick–Rafter chamber. For dense algal populations, a gridded Sedgewick–Rafter chamber allowed for accurate cell identification and concentration without the layering of cells. To quantify *Anabaena*, the number of colonies per chamber, as well as the number of cells in 20 filaments, was determined. This method is accurate to 30%.

In March 2010 a bloom of *Microcystis flos-aquae* occurred in the Torrens Lake, Adelaide, South Australia. The samples taken from this bloom were used as the feedwater to challenge the system. *M. flos-aquae* cell numbers in the sample were 14,800,000 cells/mL which also contained a small number of *Planktothrix mougeotii*, *A. circinalis* and *M. aeruginosa* (<1%). Samples were counted and tested for viability on the same day as the trial.

2.3. Ultrafiltration – integrated membrane tests

A laboratory scale UF unit (Fig. 1) was used which consisted of hollow fibre PVDF membranes with a nominal pore size of 0.02 μm. Ten 10 cm UF fibres were potted using epoxy resin and compacted using ultrapure water (Millipore Pty Ltd, USA). Membranes were operated in an outside-in configuration at a pressure of 160 kPa. Membrane integrity was established using turbidity removal. Each experiment showed removal of turbidity down to 0.1 NTU from raw water values of 12–15 NTU. Each experiment consisted of four operation periods. The first was an ultrapure water flush, the second using only the feedwater, the third using coagulant dosing and the final using both coagulant and PAC at 20 mg/L. Coagulant and PAC were dosed into a flocculation tank agitated at 20 rpm with a detention time of 9 min. A membrane tank prior to the membrane housing ensured a total floc growth time of 11 min. Between each operation period a 2 min backwash involving air scouring and ultrapure water was performed. After each experiment the membrane was cleaned using two protocols: (1) citric acid at pH 2 and (2) NaOH at pH 10. The same membrane was used for each experiment.

2.4. Saxitoxin analysis

Samples analyzed for saxitoxin were undertaken via enzyme linked immunosorbent assay (ELISA) purchased from a commercial supplier (Abraxis LLC, USA). Samples for analyses were diluted in order to bring the samples within the working range of the assay (1:20). These analyses were carried out according to the manufacturer's protocol. The Abraxis ELISA is an antibody-based assay and cross-reactivities for the following saxitoxin analogues are: <0.2% GTX1&4, 1.3% for NEO, 23% for GTX2&3, 29% dcSTX and 100% for STX, as stated by the manufacturer. The lower limit of detec-