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Removal of cyanobacteria and cyanotoxins from lake water by composites of bentonite with micelles of the cation octadecyltrimethyl ammonium (ODTMA)

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ABSTRACT

Cyanobacteria and their toxins present potential hazard to consumers of water from lakes, reservoirs and rivers, thus their removal via water treatment is essential. The capacity of nano-composites of Octadecyltrimethyl-ammonium (ODTMA) complexed with clay to remove cyanobacterial and their toxins from laboratory cultures and from lake water, was evaluated. Column filters packed with micelles of ODTMA complexed with bentonite and granulated were shown to significantly reduce the number of cyanobacteria cells or filaments and their corresponding toxins from laboratory cultures. Fluorescence measurements demonstrated that cyanobacteria cells lost their metabolic activity (photosynthesis) upon exposure to the micelle (ODTMA)–bentonite complex, or ODTMA monomers. The complex efficiently removed cyanobacteria toxins with an exceptional high removal rate of microcystins. The effectiveness of the complex in elimination of cyanobacteria was further demonstrated with lake water containing cyanobacteria and other phytoplankton species. These results and model calculations suggest that filters packed with granulated composites can secure the safety of drinking water in case of a temporary bloom event of toxic cyanobacteria.

1. Introduction

Due to eutrophication and climatic changes, cyanobacterial blooms are increasing in freshwater ecosystems all around the world (Markensten et al., 2010; Paerl and Huisman, 2009; Paerl and Paul, 2012; Visser et al., 2016; Scholz et al., 2017). These blooms severely disrupt the functioning of aquatic ecosystems and potential water use because many cyanobacterial species are able to produce a variety of toxic metabolites, which are harmful to both humans (Kuiper-Goodman et al., 1999) and animals (Codd et al., 2005). During late summer of 2104, a large toxic cyanobacterial bloom shut down the drinking water supply for Toledo, OH, USA, causing massive disruption in this city of over a half million inhabitants (Tanber 2 August 2014). Over the last two decades, more than 60% of the lakes in China have undergone harmful cyanobacteria blooms (HCBs), in which the toxin producer, *M. aeruginosa*, is one of the dominant cyanobacteria species (Song et al., 2007). The three largest shallow freshwater lakes, Taihu, Chaohu and Dianchi, have experienced eutrophication problems and frequently suffer from toxic cyanobacteria blooms (Liu et al., 2011). In early summer of 2007, a massive accumulation of *Microcystis* biomass in Lake Taihu overwhelmed the drinking water plant and caused a drinking water crisis in Wuxi city, which affected more than 4 million people (Guo, 2007; Qin et al., 2007, 2010).

Elimination of cyanobacteria and their toxins from freshwater sources during the water treatment process is essential in order to meet water supply standards for cyanotoxins (Westrick et al., 2010). Chlorination has been the main strategy for disinfecting drinking water but it has minor effect on the removal of cyanotoxins of the microcystin contingent. Adsorption technology based on granulated activated carbon and advanced oxidation processes (AOP) are currently the preferred processes to remove cyanotoxins from water (Szlag et al., 2015; Westrick et al., 2010). However, this process targets only soluble toxins but not the toxic cells of the cyanobacteria.

Abbreviations: ODTMA, octadecyltrimethyl-ammonium; MC, microcystin; CYN, cylindrospermopsin; F_t, chlorophyll fluorescence intensity; Q_y, photosynthetic quantum yield.

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In a search for an efficient technology that may rapidly and reliably remove cells of cyanobacteria and other phytoplankton species from water, we examined micelle-clay complexes that were previously reported efficient in removal of microorganisms from water (Shtarker-Sasi et al., 2013; Nir et al., 2015; Rakovitsky et al., 2016). Micelle-clay complexes are formed by an interaction of an organic cation with a large alkyl chain, such as ODTMA with sodium bentonite. The micelles, which include several tens to about several hundred molecules, are in the nanometer range, whereas the clay platelets have a thickness of around 1 nm and a typical area of around 1 μm^2 (Mishael et al., 2002). The micelle-clay complex ODTMA-bentonite is constructed to have an excess of positive charges of half of the cation-exchange capacity (CEC) of the clay mineral. The focus in the current study has been on removal of cyanobacteria and their corresponding toxins from lake water by filtration. The study demonstrates adsorption and inactivation of cyanobacteria from laboratory cultures and lake water upon exposure to granulated (ODTMA) micelle-clay complex, and inactivation of cyanobacteria by ODTMA cations as monomers.

2. Materials and methods

2.1. Organisms and culture conditions

Two species of cyanobacteria were used. The filamentous *Aphanizomenon ovalisporum* (Nostocales) and the single cells *Microcystis aeruginosa* (Chroococcales). Single species cultures were cultivated in a BG11 medium (Stanier et al., 1971) at 20 °C and continuous light of 15 μmol quant m^{-2} s^{-1}, to obtain cell density of ca $1{\cdot}10^7$ cells mL^{-1} (*M. aeruginosa*) or $1.5{\cdot}10^4$ filaments mL^{-1} (*A. ovalisporum*) with chlorophyll concentration of ca 3000 μg L^{-1}. Cultures were diluted to the desired cell density prior to each experiment.

2.2. Materials

Bentonite was purchased from Tolsa – Steetley, UK. The bromide salt of the organic cation ODTMA was purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO). Quartz sand (0.8–1.5 mm particle size) was provided by Negev Minerals LTD, Israel. Non-woven, polypropylene geotextile filter was manufactured by Markham Culverts Ltd, Papua- New Guinea.

2.3. Micelle–clay complex preparation

Granulated complexes of ODTMA-clay were prepared as described in (Nir et al., 2015). Sieving of the granules was applied for particle sizes between 0.3 and 2 mm.

2.4. Batch experiments

Stock solution of the bromide salt of the ODTMA adsorbate was 15 mM. Diluted cultures with a predefined cell/filament concentrations of *A. ovalisporum* or *M. aeruginosa* were exposed to different concentrations of ODTMA for 5 min or longer, with occasional mixing. Cultures were sampled prior and at time intervals post exposure to ODTMA and analyzed for instantaneous chlorophyll fluorescence (Ft) and for photosynthetic activity using the rapid fluorescence induction kinetics protocol of a portable fluorimeter (see below). Similarly, the effect of ODTMA-clay granulated complex on both cyanobacteria cultures was studied. Granulated complex was added to cultures with a predefined cell/filament concentrations of *A. ovalisporum,* or *M. aeruginosa* at final granule concentration ranged between 0 and 50 mg L^{-1} in 15 mL test tubes. Tubes were agitated for 10 min followed by a settling period of 5 min. The upper water layer was sampled and analyzed for instantaneous chlorophyll fluorescence (Ft) and for photosynthetic activity.

The capacity of ODTMA-clay granulated complex to sorb cyanobacteria toxins, microcystin-LR and cylindrospermopsin, was studied in batch experiments. Granulated complex (1 g L^{-1}) was added to a 50 mL tube containing a toxin solution. Tubes containing toxins at concentrations ranging between 0 and 400 μg L^{-1} were continuously agitated for 20 h. At the end of the incubation period the granules were removed by filtration and the concentration of the residual soluble toxins was determined.

2.5. Filtration experiments

Filtration columns (20 or 40 cm length, 5 cm diameter, and 20 cm length, 1.6 cm diameter) were prepared, with geotextile coverings at the inlet and outlet. Measured weights of complex (ODTMA-clay), 10 g (or 40 g) were mixed with 650 g (or 1200 g) of washed quartz sand, and included in 20 (or 40) cm length columns. Approximately, a 2 cm layer of sand was added to the upper and lower ends of the column in order to fill it completely. The columns were connected to a peristaltic pump (Cole-Palmer Masterflex L/S, Vernon Hills, Illinois, USA) with Tygon tubes. The filtration flow rate was 25 or 40 mL min^{-1} for filters of 5 cm diameter and 4.25 or 10.0 mL min^{-1} for filters of 1.6 cm diameter. Prior to each experimental run, tap water was added to the columns at a slow rate in an upward direction in order to eliminate air pockets and channeling. Each experiment was conducted in duplicate.

2.6. Column regeneration

Regeneration was conducted for a 20 × 5 cm filter (10 g of complex) by washing with 2 L of a 0.5% Na-hypochlorite solution at a flow rate of 2 mL min^{-1} followed by 2 L of tap water. At this stage, only one regeneration step was executed.

2.7. Lake sampling

Water samples were collected at a fixed pelagic station located at the center of the lake with an Aberg-Rhode 51 sampler from 1 m depth. Three batches of lake water, 30 L each, were collected during three consecutive days and shipped to the lab for the filtration experiment.

2.8. Analytical procedures

2.8.1. Cyanobacteria and phytoplankton count

Lake water samples were monitored for phytoplankton assemblage and algal biomass composition. The taxonomic composition of the phytoplankton and the biomass were determined under inverted light microscope on samples treated with Lugol's solution and settled as described by (Utermöhl, 1958). The determination of biomass bio-volume per liter was based on microscopic counts of species, and measurements of the species dimensions and estimation of their volume (Hillebrand et al., 1999). Similar procedure was used to count filaments of *A. ovalisporum* in cultures. The concentrations of *M. aeruginosa* cells were measured under light microscope using Neubauer hemocytometer cell counting chamber (Baxter Scientific, Deerfield, Il, USA). The relationships between chlorophyll concentrations and the cell or filament concentrations are presented in Fig. S1 for both cyanobacteria species.

2.8.2. Chlorophyll determination

Water samples were filtered on Whatman GF/F glass fiber filters. Filters were grinded in 90% acetone and the chlorophyll