



An environmentally friendly approach for mitigating cyanobacterial bloom and their toxins in hypereutrophic ponds: Potentiality of a newly developed granular hydrogen peroxide-based compound

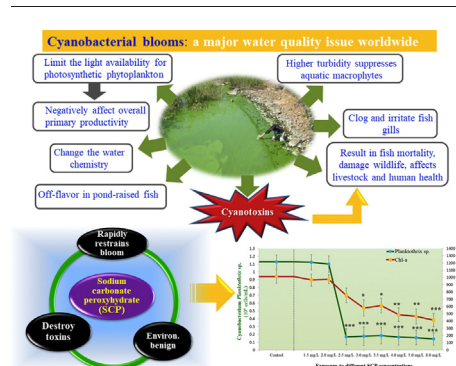
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HIGHLIGHTS

- Cyanobacterial blooms and their toxins are potential threat to aquatic animals.
- Granular H₂O₂ based sodium carbonate peroxyhydrate (SCP) compound was investigated.
- SCP at 2.5 and 4.0 mg/L H₂O₂ effectively suppressed cyanobacterial bloom and toxin.
- SCP left no footprint of H₂O₂ in water; hence, SCP is an eco-friendly compound.

GRAPHICAL ABSTRACT



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ABSTRACT

Cyanobacterial blooms and their associated toxins are growing issues for many aquatic resources, and pose a major threat to human health and ecological welfare. To control cyanobacterial blooms and their toxins, the efficacy of a newly developed granular compound (sodium carbonate peroxyhydrate 'SCP', trade name 'PAK® 27' algaecide) containing hydrogen peroxide (H₂O₂) as the active ingredient was investigated. First, the dose efficacy of the SCP that corresponded to 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0 and 8.0 mg/L H₂O₂ was tested for 10 days in small-scale tanks installed in 0.1-acre experimental hypereutrophic ponds dominated by blooms of the toxic cyanobacterium *Planktothrix* sp. SCP ranging from 2.5–4.0 mg/L H₂O₂ selectively killed *Planktothrix* sp. without major impacts on either eukaryotic phytoplankton (e.g., diatom *Synedra* sp., green algae *Spirogyra* sp. and *Cladophora* sp.) or zooplankton (e.g., rotifers *Brachionus* sp. and cladocerans *Daphnia* sp.). Based on these results, SCP at 2.5 mg/L and 4.0 mg/L H₂O₂ were homogeneously introduced into entire water volume of the experimental ponds in parallel with untreated control ponds. The dynamics of cyanobacterium *Planktothrix* sp., microcystins (commonly occurring cyanotoxins), eukaryotic phytoplankton, zooplankton, and water quality parameters were measured daily for 10 days and followed by a weekly sampling for 6 weeks. Temporal analysis indicated that *Planktothrix* sp. blooms collapsed remarkably in both 2.5 mg/L and 4.0 mg/L H₂O₂ treatments. Both treatments also were accompanied by an overall reduction in the total microcystin concentration. At 2.5 mg/L H₂O₂, the growth of eukaryotic phytoplankton (*Synedra* and *Cladophora* sp.) increased, but these populations along with zooplankton (*Brachionus* and *Daphnia* sp.) were suppressed at 4.0 mg/L H₂O₂. The longevity of 2.5 and 4.0 mg/L H₂O₂ treatment effects were up to 5 weeks. In addition, the added granular algaecide degraded within a few days, thereby leaving no long-term traces of H₂O₂ in the environment.

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1. Introduction

Cyanobacterial blooms have been increasingly reported and are progressively becoming a major water quality issue in pond, lakes, and river ecosystems throughout the world; thus, impacting their fisheries resources (Conley et al., 2009; Paerl and Otten, 2013). These blooms limit light availability for photosynthetic phytoplankton, which negatively affects the overall primary productivity of the ecosystem. High turbidities induced by intense cyanobacterial growth also suppress aquatic macrophytes that serve as habitats for many fishes and invertebrates. Although this phenomenon is more publicized in natural water bodies, aquaculture ponds also are susceptible to these impacts. Cyanobacterial blooms usually comprise both toxin and non-toxin producing species (Baker and Humpage, 1994), though 50% of these blooms can commonly be expected to contain toxic species (Carmichael, 1992). In freshwater systems, the main toxin-producing cyanobacteria genera are *Microcystis*, *Anabaena*, *Planktothrix*, *Lyngbya* and *Cylindrospermopsis* (Chorus and Bartram, 1999). These toxin-forming blooms are often called “harmful algal blooms” or Cyano HABs (Paerl, 2014). Certain species of *Anabaena*, *Microcystis*, *Nodularia* and *Planktothrix* synthesize hepatotoxic peptides while some species of *Aphanizomenon* and *Anabaena* produce neurotoxic alkaloids (Carmichael et al., 1990). Microcystins, however, are the most common group of hepatotoxins. Blooms of microcystin-producing cyanobacteria are frequently reported in water bodies associated with anthropogenic activities (Gobler et al., 2007; Lewitus et al., 2008). Cyanobacteria release toxins upon death or cell lysis, and when discharged into the water column, the toxins can persist for weeks or months (Matthijs et al., 2012). These cyanotoxins account for mass mortality of fishes and can seriously affect wildlife, livestock, and humans (Paerl, 2014; Smith et al., 2008).

Besides toxins, certain cyanobacteria produce secondary metabolites that form “earthy” or “musty” odor compounds (e.g., geosmin and MIB, 2-methyl isoborneol), which produce off-flavors in many pond-raised fishes (Guttman and van Rijn, 2008; Paerl and Tucker, 1995; Smith et al., 2008). The accumulation of off-flavor compounds in fish tissues negatively impacts product quality, reduces palatability, and eventually results in significant economic losses (Engle et al., 1995; Tucker, 2000). In addition, fish producers spend millions of dollars annually to deplete or purge off-flavors from fishes, though this practice severely affects their profit margins (Hanson, 2003). Moreover, cyanobacterial blooms threaten the use and sustainability of many freshwater resources, and are very likely to impact supplies of clean water in the near future, which is an issue of global concern for current fish producers (Heisler et al., 2008; Paerl, 2014; Paerl et al., 2011). Consequently, mitigating cyanobacterial nuisances and their toxins are major challenges to aquaculturists, water quality specialists, and toxicologists.

There are several strategies suggested to remove cyanobacterial blooms. Reducing nutrient loads (typically phosphorus) to prevent eutrophication is probably the best strategy (Barrington et al., 2013a; Bishop and Richardson, 2018; Conley et al., 2009; Dokulil and Teubner, 2000; Lewis Jr. and Wurtsbaugh, 2008; Lewis Jr et al., 2011; Matthijs et al., 2012; Meis et al., 2013; Smith and Schindler, 2009), though it often requires several months to years for the effect to be realized (Gulati and Van Donk, 2002; Matthijs et al., 2012; Søndergaard et al., 2003). Dredging of nutrient-rich sediments from pond bottoms followed by a phosphorus-binding clay treatment is the simplest remedial approach to eliminate phosphorus loads. However, these practices are associated with high operating costs, slow action, and the outcomes are not always predictable or effective (Robb et al., 2003; Van Oosterhout and Lurling, 2011). Additional strategies such as artificial pond mixing also may restrain cyanobacterial populations (Huisman et al., 2004; Visser et al., 1996), but is economically infeasible in most cases. Chemical alternatives including herbicides (e.g., diuron), copper-based compounds (e.g., copper sulfate), and alum have been used for many decades. However, there are concerns with lengthy environmental persistence and risks of ecotoxicity to other non-target aquatic biota,

including green algae, zooplankton, and fishes (Jancula and Marsalek, 2011). High-frequency sonication is a newer method of selectively bursting gas vesicles and vacuoles in cyanobacteria, which disrupts cell membranes and retards photosynthetic activity (Rajasekhar et al., 2012). Although this technique kills the cyanobacterial blooms by lysing their cells, it has no effect on the toxins. Consequently, following mass cell ruptures, large amounts of cyanotoxins are released into surrounding waters, which often deteriorates rather than resolve the water-quality issues.

In light of the well-documented problems associated with cyanobacterial blooms and their toxins, there is a corresponding need for an environmentally-benign treatment that rapidly restrains the cyanobacterial populations while also destroying their toxins. Recently, hydrogen peroxide (H_2O_2) has been proven useful in selectively reducing cyanobacteria in mixed phytoplankton communities (Barrington and Ghadouani, 2008; Barrington et al., 2013a; Bauza et al., 2014; Drabkova et al., 2007; Matthijs et al., 2012; Schrader, 2005; Wang et al., 2012). The algacidal action of H_2O_2 occurs via the formation of free hydroxyl radicals (OH^-) in the solution, which in turn, inhibits electron transport and photosynthetic activity by rendering photosystem II inactive, and thus, causing cellular death (Barrington and Ghadouani, 2008; Barrington et al., 2013a; Samuilov et al., 2004). Nevertheless, adding large volumes of pure H_2O_2 solution directly into water bodies possesses safety concerns, and also is likely to spill during broadcasting, transportation, and storage. An attractive alternative to traditional H_2O_2 solution is sodium carbonate peroxyhydrate (SCP), which is a relatively new, dry granulated H_2O_2 -based algacide (USEPA, 2004). When added to water, SCP decomposes rapidly and liberates H_2O_2 and sodium carbonate.

In the present study, our primary goal was to examine the use of this granulated H_2O_2 -based algacide (SCP) for treating cyanobacterial blooms in ponds. We hypothesized that adding SCP to hypereutrophic experimental ponds would selectively suppress cyanobacterial overgrowth and destroy the associated toxins. We also proposed that SCP added to ponds would degrade within a few days, and that no long-term traces of H_2O_2 would remain. This goal will be met by accomplishing four objectives. The first objective was to investigate the efficacy of a SCP-based algacide to suppress noxious cyanobacteria, and to determine the most appropriate dosage to target cyanobacterial blooms in ponds without negatively affecting non-target biota, including eukaryotic phytoplankton and zooplankton. The second objective was to ascertain whether the application of SCP could destroy microcystins, which is a cyanotoxin. The third objective was to evaluate whether the applied dose of SCP would leave any long-term traces of H_2O_2 in the pond water. The last objective was to gain insights on the longevity of the SCP applications; thus, enabling the formulation of application guidelines to avoid re-establishment of high cyanobacterial biomasses. Findings of this study will provide insights into the current knowledge base of effective, rapid, and safe technologies to successfully control cyanobacterial blooms.

2. Materials and methods

2.1. Experimental site and algal bloom culture

Experimental trials using the granular SCP-based algacide were performed in a series of ponds located at the Aquaculture Research Station on the campus of the University of Arkansas at Pine Bluff (UAPB). The experiments were performed at two different scales: small-scale trials done in outdoor tanks and full-scale trials conducted in experimental ponds.

During May–June 2017, a total of six experimental ponds (0.1-acre each with average depth of 1.2 m) were filled with shallow well water, and fertilized with an inorganic fertilizer and commercially available de-oiled rice bran to stimulate phytoplankton growth. In early July 2017, water from a nearby hypereutrophic pond (i.e., ‘seed stock’) was

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