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Critical assessment of chitosan as coagulant to remove cyanobacteria

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ABSTRACT

Removal of cyanobacteria from the water column using a coagulant and a ballast compound is a promising technique to mitigate nuisance. As coagulant the organic, biodegradable polymer chitosan has been promoted. Results in this study show that elevated pH, as may be common during cyanobacterial blooms, as well as high alkalinity may hamper the coagulation of chitosan and thus impair its ability to effectively remove positively buoyant cyanobacteria from the water column. The underlying mechanism is likely a shielding of the protonated groups by anions. Inasmuch as there are many chitosan formulations, thorough testing of each chitosan prior to its application is essential. Results obtained in glass tubes were similar to those from standard jar tests demonstrating that glass tube tests can be used for testing effects of coagulants and ballasts in cyanobacteria removal whilst allowing far more replicates. There was no relation between zeta potential and precipitated cyanobacteria. Given the well-known antibacterial activity of chitosan and recent findings of anti-cyanobacterial effects, pre-application tests are needed to decipher if chitosan may cause cell leakage of cyanotoxins. Efficiency- and side-effect testing are crucial for water managers to determine if the selected approach can be used in tailor-made interventions to control cyanobacterial blooms and to mitigate eutrophication.

1. Introduction

Cyanobacterial blooms are still a growing nuisance worldwide (O'Neil et al., 2012; He et al., 2016). These blooms often are symptoms of eutrophication (Smith et al., 1999; Smith and Schindler, 2009), but not always as for instance cyanobacterial blooms and surface scums are also regularly popping up in oligotrophic lakes (Nimptsch et al., 2016). Since many cyanobacterial blooms are comprised of toxin producing species (Carmichael and Boyer, 2016), there is a great need to control these blooms (Bullerjahn et al., 2016). In eutrophic lakes, the first mitigation measure is reducing the external nutrient supply to the water bodies as these nutrients fuel blooms (Smith et al., 1999; Cooke et al., 2005; O'Neil et al., 2012; Paerl et al., 2014, 2016). Only a limited number of lakes, however, will respond rapidly to external load reduction, because internal loading and ongoing diffuse inputs may hamper recovery for decades to centuries (Søndergaard et al., 1999; Carpenter, 2005; Cooke et al., 2005). In addition, external load control is not always economically or practically feasible (Huser et al., 2016), or external load is not the driver of the cyanobacterial nuisance. Thus, in most cases either external load reduction needs to be complemented by in-lake mitigation measures to speed-up recovery, or in-lake curative measures are the only possibility in controlling cyanobacterial nuisance in the short term.

Algaecides are widely used as common curative interventions efficiently eliminating cyanobacterial blooms, but they may come with a major drawback as algaecides induce cyanobacterial cell lysis and consequently release of intracellular toxins (Jones and Orr, 1994; Jančula and Maršálek, 2011; Merel et al., 2013). A promising alternative to algaecides is to flock and sink the cyanobacteria out of the water column while remaining as intact cells (Pan et al., 2006; Lürling and Van Oosterhout, 2013), where after the cyanobacteria and their toxins can be degraded on the

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sediment (e.g., Holst et al., 2003; Grützmacher et al., 2010; Li and Pan, 2015). In this approach, a coagulant and a ballast compound are used to flock and sink the aggregates out of the water column. The ballast compounds may be either modified clays or natural products with phosphate adsorption capacity (e,g., Lürling and van Oosterhout, 2013; Noyma et al., 2016; Waajen et al., 2016) or local soils (e.g., Pan et al., 2006; 2011a; Li and Pan, 2015). Commonly used coagulants are poly-aluminium chloride (PAC) (Pan et al., 2011a; Van Oosterhout and Lürling, 2011; Lürling and Van Oosterhout, 2013), iron(III)chloride (PIX; Waajen et al., 2016), or organic polymers like chitosan (e.g., Pan et al., 2006, 2011b; Noyma et al., 2016).

The organic coagulant chitosan has been promoted in the so-called "modified local soil induced ecological restoration" (MLSIER) technology (Pan et al., 2011b). Chitosan is generally viewed as a non-toxic and eco-friendly coagulant, synthesized by deacetylation of chitin and when protonated in acidic medium behaves as a typical cationic polyelectrolyte (Yang et al., 2016). The protonated free amino groups of chitosan allow electrostatic interactions between these protonated amino groups of chitosan and the negatively charged cyanobacteria (Renault et al., 2009). The long chain polymers can attach to cyanobacteria forming bridges that subsequently can entrap particles when settling (Renault et al., 2009; Tripathy and De, 2006; Chen et al., 2014).

Low concentrations of chitosan (~2 mg L^{-1}) combined with a ballast may be sufficient to flock and sink cyanobacteria (*Microcystis aeruginosa*) effectively in freshwaters (Li and Pan, 2013; Noyma et al., 2016). In a recent study, however, chitosan was totally ineffective in flocking and settling *M. aeruginosa* in water from the brackish lagoon Jacarepaguá, Rio de Janeiro, Brazil (de Magalhães et al., 2017). This was most likely due to relatively large amounts of negative ions gathering around the protonated groups, leading to

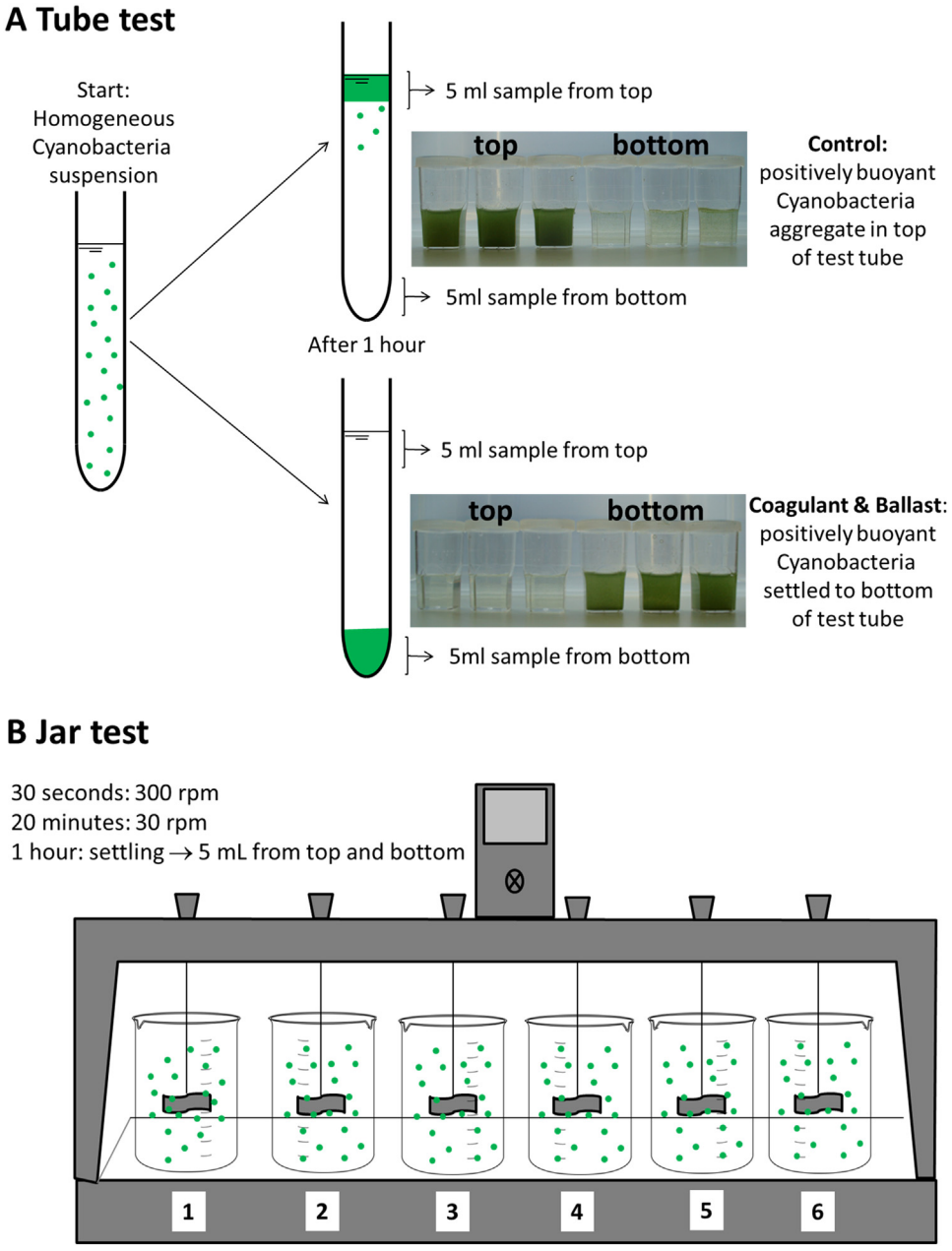

Fig. 1. Schematic design of standard "flock & sink" assays (A Tube test and B Jar test) without or with addition of coagulants, ballast or both in which positively buoyant cyanobacteria will concentrate in the top of test tubes when nothing added, or when solely low dose coagulant is added, while they aggregate at the bottom when a coagulant and ballast are added. Sampling top and bottom 5 mL is used for determining chlorophyll-*a* concentrations and efficiency of PSII.