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Removal of *Microcystis aeruginosa* using cationic starch modified soils

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ABSTRACT

A cheap and biodegradable modifier, cationic starch (CS), was used to turn local soils into effective flocculants for *Microcystis aeruginosa* (*M. aeruginosa*) removal. The isoelectric point of soil particles was remarkably increased from pH 0.5 to 11.8 after modification with CS, which made CS modified soil particles positively charged and obtain algal flocculation ability. At the soil concentration of 100 mg/L, when the CS modifier was 10 mg/L, 86% of *M. aeruginosa* cells were removed within 30 min. Lower or higher CS dosage led to limited algal removal. About 71% and 45% of *M. aeruginosa* cells were removed within 30 min when CS was 5 mg/L and 80 mg/L, respectively. This is because only part of algal cells combined with CS modified soil particles through charge neutralization at low dosage, while flocs formed at high CS dosage were positively charged which prevents further aggregation among the flocs. The floc stability was quantified by a floc breakage index under applied shear force. Algal flocs formed at acid and alkaline conditions were more prone to be broken than those at the neutral condition. The cost and biodegradability concerns may be largely reduced through the use of CS modified local soils. For field applications, other practical issues (e.g., re-suspension) should be further studied by jointly using other methods.

1. Introduction

The frequent outbreak of cyanobacterial blooms in eutrophic freshwaters is a global issue, posing serious threats to aquatic life, human health, water quality, commercial fisheries, and coastal aesthetics (Falconer, 1999; Guo, 2007; Hawkins et al., 1985). Over the past several decades, great efforts have been made to develop bloom mitigation strategies around the world (Chen et al., 2012; Edzwald, 1993; Everall and Lees, 1996; Garcia-Villada et al., 2004). The use of natural clays as a means to remove algal blooms through flocculation and sedimentation has received increasing attention in recent decades (Anderson, 1997; Atkins et al., 2001; Lee et al., 2008; Pan et al., 2006). However, the low flocculation efficiency and the high clay loading (0.25–2.5 g/L) limit its wide application in fields (Lee et al., 2008; Pan et al., 2006). Coagulant/flocculent modified clays/sands/soils could largely enhance the flocculation efficiency and reduce the material loading, and are considered as potential geo-engineering materials for cyanobacterial bloom mitigation (Mackay et al., 2014; Park et al., 2013; Spears et al., 2014).

Several modifiers including chitosan, *Moringa oleifera* (MO), xanthan and polyaluminum chloride (PAC) have been tested to modify clay/sand/soil for algal flocculation (Chen and Pan, 2012; Li and Pan, 2013; Pan et al., 2011a). Chitosan, xanthan and MO, biodegradable natural polymers, are potentially environmental friendly (Baumgartner et al., 2008; Grabow et al., 1985; Kurniawati et al., 2014). However, economic concern may largely limit the application of the methods at large scale due to the high cost of these materials. MO is extracted from MO seeds which are not easily available in many parts of the world, and it is still lack of commercial products as coagulants (Sengupta et al., 2012). For commercially available PAC, it cannot be biodegraded although it is relatively cheap, which may be a concern for the ecological sustainability. Previous studies suggest that high algal removal efficiency using local clay/sand/soil can be achieved through the two-component modifier mechanism (e.g., chitosan-PAC or chitosan-MO) (Li and Pan, 2013; Pan et al., 2011a). In this mechanism, one modifier is responsible for charge modification that makes solid particles possess net positive charge in natural waters and obtain algal flocculation ability. The other is to enhance the bridging function that aggregates small, light, and fluffy flocs into large and dense ones. It remains a challenge to find cheap and safe modifier

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materials that can make the two-component mechanism working. So far, there are few both cost-effective and biodegradable modifiers that can make clay/sand/soil particles obtain both charge neutralization and bridging functions for cyanobacterial bloom removal.

Cationic starch (CS), a commonly used organic coagulant, has been used to flocculate negatively charged pollutants in wastewater treatment (Ellis et al., 1982; Khalil and Aly, 2004; Pal et al., 2005). The coagulant property is attributed to the positive charge and bridging function of CS polymer chain (Wang et al., 2011b), which may potentially make it qualify as a clay/sand/soil modifier for algal removal. CS is both cheap and biodegradable (Pal et al., 2005; Wei et al., 2008). If CS is used as the clay/sand/soil modifier, the cost and biodegradability concerns may be potentially reduced. Although studies on algal biomass harvesting using CS have been reported (Anthony et al., 2013; Vandamme et al., 2010), the flocculation dynamics and floc stability were not well understood before, and there are no studies on the use of CS modified solid particles for sedimentation removal of cyanobacterial blooms.

Algal floc stability is an important property for effective algal removal. The formed flocs are often exposed to a range of stresses such as current and wind induced turbulence in fields, which may result in floc breakage and the lost of algal removal. Descriptive methods are currently used to quantify algal floc stability (e.g., floppy, fragile, dense), which have hindered further studies and applications of the technology. Flocs can be broken under an increased shear force, and the reduction of floc size and the shear force applied can be used to quantify its stability (Parker et al., 1972). So far, few studies have been seen on the characterization of algal floc stability in the area of cyanobacterial bloom mitigation.

In this study, CS was used to modify lakeside soil to flocculate and settle *Microcystis aeruginosa* (*M. aeruginosa*). Dosage effect on removal efficiency, surface charge and floc size was studied and the associated flocculation mechanism was investigated. Floc breakage experiments were conducted and a method was studied to quantify the stability of algal flocs. Field lake water was also collected and flocculated to test the algal removal effect of CS modified soil. The objective of this study is to develop a cheap and environmental friendly local soil modification method for the mitigation of cyanobacterial blooms.

2. Materials and methods

2.1. Algal species and culture

M. aeruginosa, a common freshwater bloom-forming cyanobacterium, was used in this study. The inoculum of *M. aeruginosa* (FACHB-905) was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, and cultivated in BG11 medium in the laboratory. Algal batch cultures were performed in an illuminating incubator (LRH-250-G, Guangdong Medical Apparatus Co., Ltd., China) with continuous cool white fluorescent light of 2000–3000 lux on a 12 h light and 12 h darkness regimen, and the temperature was maintained at 25 ± 1 °C.

2.2. Cationic starch preparation

Corn starch with a moisture content of 11.4% was purchased from Unilever Co., Ltd., China. CS was prepared using microwave-assisted method (Lin et al., 2012). Briefly, 2.0 g 2,3-epoxypropyl trimethyl ammonium chloride (GTA) was dissolved in 100 mL of 5.0 g/L NaOH solution. The mixture was stirred thoroughly for 10 min. Then, 10.0 g corn starch was added into the above mixture. Stirring was continued for another 30 min at a 70 °C water-bath. The reaction vessel was placed on the turntable of a microwave oven (WD750S, Guangdong Galanz Group Co. Ltd., China) and irradiated at the power of 750 W. Periodically, the microwave irradiation was paused at 65 °C to avoid boiling, with the aim to prevent unwanted vapors formation. The microwave irradiation-cooling cycle was repeated for five times. Afterward, the reaction vessel and its contents were cooled down to the room temperature. The gel-like mass left in the reaction vessel was washed with ethanol for three times, and the targeted precipitate was collected and dried in a vacuum oven (DZF-6020, Shanghai Yiheng Instrument Co., Ltd., China) at 50 °C for 6 h. The obtained CS was pulverized before use. The degree of substitution of cationic starch is 0.18, which was determined using elemental analysis (Shi et al., 2012).

2.3. Modified local soil

The soil used was collected from the Lake Taihu north offshore (China). The soil sample was washed with deionized water, dried at 90 °C for 10 h, and then grounded and sieved (74 μm) before use. The prepared CS was dissolved in deionized water to obtain a solution of 2 g/L. A certain amount of CS was used to modify the soil suspension according to the dose conditions tested. The soil concentration used in all the flocculation experiments was fixed to 100 mg/L (Fig. S1).

2.4. Algal flocculation

Flocculation experiments were performed in a jar test apparatus (ZR3-6, Zhongrun Water Industry Technology Development Co. Ltd., China) with a series of 300-ml beakers containing 200 ml of *M. aeruginosa* cultures in mid-to late-exponential growth phase. The initial *M. aeruginosa* concentration was $3.15-3.25 \times 10^9$ cells/L. The temperature was 22 ± 1 °C during the flocculation experiment. After CS modified soil was added, the solution was stirred at 200 rpm for 1 min and 40 rpm for another 15 min. The control was run in the above mentioned algal media without adding any soil or CS. The flocculation experiments were conducted at raw algal solution pH of 8.60. The pH was relatively stable after the addition of CS modified soil and kept at 8.60 ± 0.1. After sedimentation for 2, 5, 10, 20, 30, 60, 90, 120, 180 and 240 min, samples were collected from 2 cm below the surface to enumerate cell numbers with an electromotive microscope (Axioskop 2 mot plus, Carl ZEISS, Germany), respectively. All the flocculation experiments were conducted in triplicate and the results were presented as the mean values and standard deviations. Cell removal efficiency was calculated as: (initial cell concentration − sample cell concentration) × 100%/initial cell concentration.

The zeta potential of soil, CS modified soil, algal cell and algal floc was characterized using a Zetasizer 2000 (Malvern Co. United Kingdom). Dynamic size growth of algal flocs during the flocculation reaction (15 min) was analyzed using a laser particle size analyzer Mastersizer 2000 (Malvern Co. United Kingdom). The set up of the apparatus was described previously (Li and Pan, 2013), and the mean diameter, $d_{0.5}$, was used to measure the floc size.

2.5. Floc breakage

This experiment was conducted to study the stability of algal flocs under different pH conditions (pH = 4.0, 7.0 and 10.0). After algal flocculation was completed, the formed flocs were stirred at a shear speed of 75, 100, 150, 200, and 250 rpm, respectively, for 15 min, and the dynamic size change of algal flocs was monitored. The floc stability was evaluated by the γ value in the empirical relationship (Parker et al., 1972),

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