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Effect of algal flocculation on dissolved organic matters using cationic starch modified soils

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ABSTRACT

Modified soils (MSs) are being increasingly used as geo-engineering materials for the sedimentation removal of cyanobacterial blooms. Cationic starch (CS) has been tested as an effective soil modifier, but little is known about its potential impacts on the treated water. This study investigated dissolved organic matters in the bloom water after algal removal using cationic starch modified soils (CS-MSs). Results showed that the dissolved organic carbon (DOC) could be decreased by CS-MS flocculation and the use of higher charge density CS yielded a greater DOC reduction. When CS with the charge density of 0.052, 0.102 and 0.293 meq/g were used, DOC was decreased from 3.4 to 3.0, 2.3 and 1.7 mg/L, respectively. The excitation–emission matrix fluorescence spectroscopy and UV_{254} analysis indicated that CS-MS exhibits an ability to remove some soluble organics, which contributed to the DOC reduction. However, the use of low charge density CS posed a potential risk of DOC increase due to the high CS loading for effective algal removal. When CS with the charge density of 0.044 meq/g was used, DOC was increased from 3.4 to 3.9 mg/L. This study suggested, when CS-MS is used for cyanobacterial bloom removal, the content of dissolved organic matters in the treated water can be controlled by optimizing the charge density of CS. For the settled organic matters, other measures (*e.g.*, capping treatments using oxygen loaded materials) should be jointly applied after algal flocculation.

Introduction

When a certain management option is used for the damaged ecosystem restoration, it is essential to consider also any potential unintentional impacts associated with amendment products (Spears et al., 2013). The frequent outbreak of cyanobacterial blooms in eutrophic waters is a global issue, posing serious threats to aquatic ecosystem and human health (Chen et al., 2006; Liu and Le, 2015; Lu et al., 2013; Wang et al., 2013c). Modified soils (MSs) have triggered great interest as geo-engineering materials for cyanobacterial bloom control in recent years (Lürling and van Oosterhout, 2013; Mackay et al., 2014; Spears et al., 2014; Tian et al., 2014). Although many studies on algal removal using MSs have been reported (Li and Pan, 2013; Pan et al., 2011a; Shi et al., 2015; Zou et al., 2005), little is known about its potential impacts on the receiving waters.

In the MS method, modifiers are used to offer soil particles the abilities of charge neutralization and bridging, and make them obtain flocculation potential for cyanobacterial cells (Li and Pan, 2013; Pan et al., 2011a). Several chemical coagulants

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(*e.g.*, aluminum and ferric salts) and organic macromolecular flocculants (*e.g.*, cationic starch, chitosan and *Moringa oleifera*) have been tested as soil modifiers for algal removal (Dai et al., 2015; Li and Pan, 2013; Pan et al., 2006; Shi et al., 2015). Compared with chemical coagulants, organic macromolecular flocculants are often easily biodegradable, eco-friendly and are well accepted by the public (Mukherjee et al., 2014; Ndabigengesere and Narasiah, 1998; Renault et al., 2009). However, when these organic flocculants are sprayed into natural waters, a major concern is the likelihood of dissolved organic matter (DOM) increase in water column. The DOM is a storage pool of nitrogen and phosphorous and an important contributor of biochemical/chemical oxygen demand in eutrophic waters (Bushaw et al., 1996; Qu et al., 2013). The increase of DOM may result in the lost of water quality and the rapid oxygen depletion in the receiving water (Evans et al., 2005; Mermillod-Blondin et al., 2005). However, to date, the use of organic flocculants in MSs has mainly focused on algal removal effect with little consideration of its impacts on DOM in the treated bloom water.

Algae particles are negatively charged, which can stably suspend in water column (Chen et al., 2004). Charge neutralization is a main mechanism operating algal flocculation using MSs, which can reduce the electrostatic repulsion and promote aggregation between MSs and algae particles (Li and Pan, 2013; Shi et al., 2015). To achieve the effective algal removal, desired amount of positive charges are needed to neutralize negative charges on algal cell surface (Li and Pan, 2015; Li et al., 2015). Thus, the charge density may potentially affect the loadings of modifiers, which are directly related to the residual DOM in the treated water. Indentifying and understanding this effect are essential to develop strategies for DOM content control when MS is used for cyanobacterial bloom removal in natural waters.

In this study, a series of cationic starch (CS) with different charge densities were used as soil modifiers (CS-MSs). The flocculation of *Microcystis aeruginosa* (*M. aeruginosa*) using each CS-MSs were conducted by jar tests. Dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254}) and excitation–emission matrix (EEM) fluorescence spectra were used to analyze the DOM after algal removal. The objective of this study is to explore the effect of algal flocculation on DOM in bloom waters using CS-MSs.

1. Materials and methods

1.1. Algal species and culture

M. aeruginosa, a common freshwater bloom-forming cyanobacterium, was used in this study. The *M. aeruginosa* cells (FACHB-905) were obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, and cultivated in BG11 medium. The BG11 medium was composed of 1500 mg/L $NaNO_3$, 75 mg/L $MgSO_4{\cdot}7H_2O$, 40 mg/L K_2HPO_4, 36 mg/L $CaCl_2{\cdot}2H_2O$, 20 mg/L Na_2CO_3, 6 mg/L citric acid monohydrate, 6 mg/L ferric ammonium citrate, 2.86 mg/L H_3BO_3, 1.86 mg/L $MnCl_2{\cdot}4H_2O$, 1 mg/L Na_2EDTA, 0.39 mg/L $Na_2MoO_4{\cdot}2H_2O$, 0.22 mg/L $ZnSO_4{\cdot}7H_2O$, 0.08 mg/L $CuSO_4{\cdot}5H_2O$, and 0.05 mg/L $Co(NO_3)_2{\cdot}6H_2O$. Algal batch cultures were maintained at 25 ± 1°C under continuous cool white fluorescent light of 2000–3000 lx on a 12 hr light and 12 hr darkness regimen in an illuminating incubator (LRH-250-G, Guangdong Medical Apparatus Co. Ltd., China).

1.2. Cationic starch modified soils

CS was prepared by reacting corn starch (Unilever Co. Ltd., China) with cationic monomer, 2,3-epoxypropyl trimethyl ammonium chloride (GTA), using the microwave-assisted method (Lin et al., 2012). The details of the synthesis are as follows: 0.5 g GTA was dissolved in 100 mL of 5.0 g/L NaOH solution with constant stirring for 10 min. Ten grams of starch was added to the above mixture and stirring was continued for another 30 min at a 70°C water-bath. Then, the reaction vessel was placed on the turntable of a domestic microwave oven (Guangdong Galanz Group Co. Ltd., China) and irradiated at the power of 750 W with periodic pause to avoid boiling. This microwave irradiation–cooling cycle was continued until a viscous gel-like mass formed. After being cooled down to room temperature, the gel-like mass was washed with ethanol for three times, dried in a vacuum oven (DZF-6020, Shanghai Yiheng Instrument Co. Ltd., China) at 50°C for 6 hr and then pulverized before use. The obtained product is termed $CS_{0.5:10}$ (0.5:10 is the mass ratio of GTA to starch). Using this method, $CS_{1.0:10}$, $CS_{1.5:10}$ and $CS_{2.5:10}$ were synthesized. As the mass ratio of GTA to starch increased, the charge density and degree of substitution of CS increased, but the intrinsic viscosity and molecular weight showed no significant changes (*t*-test, $p < 0.05$) (Table 1).

The soil used was collected from the bank of Meiliang Bay, Lake Taihu (China). This bay has suffered from severe cyanobacterial blooms over the past years, and MS materials have been tested to settle the blooms (Pan et al., 2006, 2011b). The soil sample was grounded and sieved (180 meshes) before use. For CS-MS preparation, 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. The surface charge of soil and CS-MS particles was characterized using a Zetasizer 2000 (Malvern Co. UK).

Table 1 – The properties of cationic starch.

	Charge density [a] (meq/g)	Degree of substitution [b]	Intrinsic viscosity [c] (dL/g)	Molecular weight [d] ($\times 10^5$)
Native starch	0	0	1.21	4.27
$CS_{0.5:10}$	0.044	0.073	1.31	4.67
$CS_{1.0:10}$	0.052	0.092	1.24	4.39
$CS_{1.5:10}$	0.102	0.166	1.30	4.63
$CS_{2.5:10}$	0.293	0.255	1.08	3.76

[a] Determined using the polyelectrolyte titration method (Kam and Gregory, 1999).
[b] Determined using one point method (Ahmad et al., 1999).
[c] Determined using element analysis method (Lin et al., 2012).
[d] Calculated based on the Mark–Houwink relationship taking '*k*' as 1.18×10^{-3} and '*a*' as 0.89 (Ahmad et al., 1999).