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.

Keywords

Cationic starch, Modified local soil, Algal flocculation, Cyanobacterial bloom mitigation, Floc breakage

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 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 hr light and 12 hr 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. Afterwards, 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 hr. 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),

$$\log d = \log C - \gamma \log G \quad (1)$$

where d is the median floc diameter ($d_{0.5}$) after breakage (μm); C is the floc strength coefficient; γ is the stable floc exponent which is the main index to quantify the floc stability, and G is the average velocity gradient of shear speed which can be calculated according to Bridgeman et al. (2008).

2.6. Natural bloom water test

Field bloom water was collected from Lake Taihu (China) in Sep. 2014 and flocculated using CS modified soil by jar tests. Algal flocs and *chlorophyll-a* (*chl-a*) content was studied after flocculation. For the floc image study, the flocs were carefully transferred on a glass slide and then photographed by an electromotive microscope (ST-CV320, Chongqing UOP Photoelectric Technology Co., Ltd., China). *Chl-a* was measured after sedimentation for 30 min using the method prescribed in Monitoring Analysis Method of Water and Waste Water (Ministry of Environmental Protection of China, 2002). The flocculation experiments were conducted in triplicate and the results were presented as the mean values.

3. Results

3.1. Surface charge of cationic starch modified soil

The isoeletric point of the native soil was pH 0.5 (Fig. 1). After it was modified by CS, the isoeletric point was remarkably increased to pH 11.8, making the soil possess net positive charge under most natural water conditions (Fig. 1). The zeta potential (ZP) of CS modified soil was relatively stable and kept about +30 mV in the wide pH range of 2.0-10.0, and then decreased to nearly zero at pH 11.8, while the ZP of the native soil gradually decreased from +1.2 to -37.0 in the pH range of 0.4-11.8.

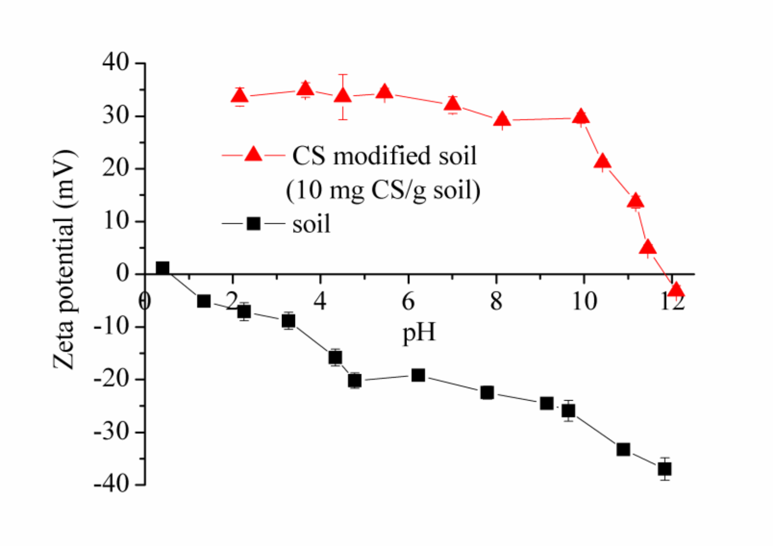

Fig. 1 – Comparison of surface charge between the native soil and cationic starch (CS) modified soil. Error bars indicate standard deviations.

3.2. Dosage effect on algal removal

When the soil concentration was fixed to 100 mg/L, the algal removal efficiency increased from 8% to 86 % as the CS dosage increased from 0 to 10 mg/L, flatted off at 86% in the range of 10-18 mg/L, and then deceased rapidly as the dosage further increased (Fig. 2). When 5, 10 and 80 mg/L of CS was added, 71%, 86% and 45% of the *M. aeruginosa* cells were removed within 30 min, respectively. According to these results, the optimized CS dosage of 10 mg/L was used for subsequent flocculation experiments. After 30 min sedimentation, the ZP of algal cells and algal flocs as a function of CS dosage was measured (Fig. 2). With the increase of CS dosage, the ZP of algal cells increased and charge reversal occurred around the optimal dosage of 10 mg/L. When 5, 10 and 80 mg/L of CS were dosed, the ZP of algal cells was increased to −9.9, −1.0, +20.5 mV, respectively. At the same time, the formed algal flocs became nearly electrically neutral at the low and optimal CS dosage (10 mg/L). The

ZP of algal flocs was +2.5 and +3.4 at 5 and 10 mg/L of CS, respectively. When CS was overdosed, the ZP of the flocs at 80 mg/L reached +33.1 mV.

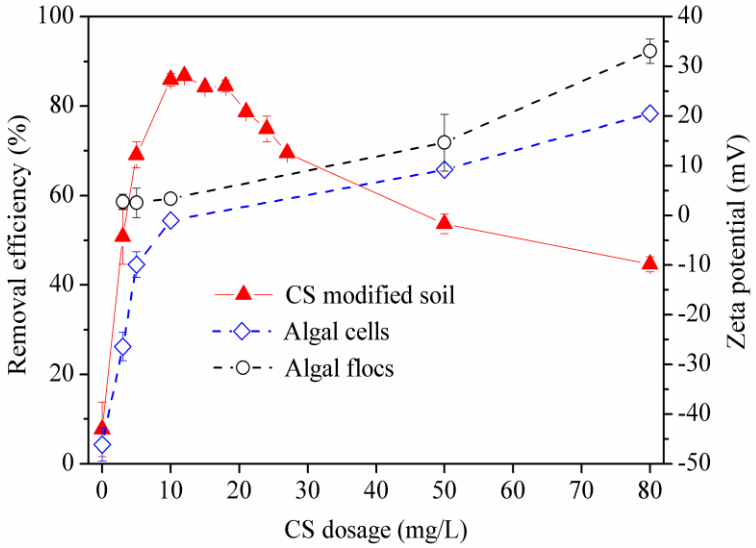

Fig. 2 – Removal efficiency (solid line) and zeta potentials of algal cells and flocs (dotted line) at different dosage of cationic starch (CS). The soil concentration was fixed to 100 mg/L. Error bars indicate standard deviations.

3.3. Floc growth and flocculation kinetics

After CS modified soil was added, algal flocs grew quickly within the initial 2 min. The flocs formed at the CS dosage of 10 mg/L (830 μm) were larger than those formed at 5 mg/L (700 μm) and 80 mg/L (440 μm) (Fig. 3A). After flocculation, the maximum removal efficiency at the CS dosage of 5 and 10 mg/L was quickly achieved within 2 min and stayed relatively stable as time increased. At 30 min, the removal efficiency at 5 and 10 mg/L reached 71% and 86%, respectively. However, the removal efficiency at 80 mg/L increased slowly and reached only 45% at 30 min (Fig. 3B).

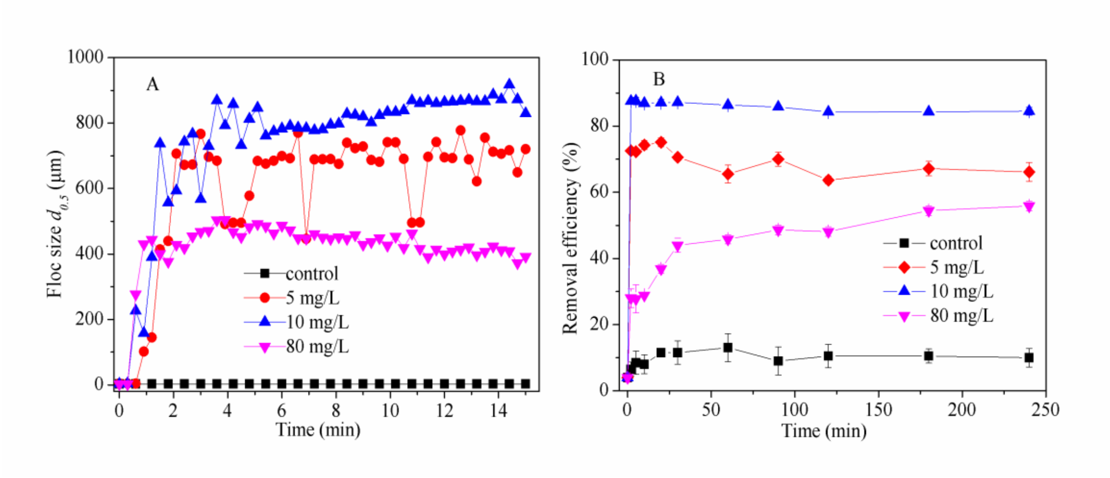

Fig. 3 – The floc growth (A) and flocculation kinetics (B) at different dosage of cationic starch. The soil concentration was fixed to 100 mg/L. Error bars indicate standard deviations.

3.4. Effect of floc breakage

The algal removal using CS modified soil was not significantly influenced by the pH condition in the wide pH range of 4.0-10.0 (Fig. S2). However, the algal floc stability was greatly affected by the pH condition. When the shear speed was 75, 100, 150, 200 and 250 rpm, the floc size at pH 4.0 dropped sharply from 826 μm to 777, 615, 372, 313 and 195 μm, respectively (Fig. 4A); and the floc size at pH 10.0 dropped from 796 μm to 687, 659, 428, 288 and 235 μm, respectively (Fig. 4B). In contrast, the sharp drop of floc size was not observed for the flocs formed at neutral pH. The floc size only reduced slightly from 890 to 823 μm, even when the highest shear speed of 250 rpm was applied (Fig. 4C). The broken floc size was plotted against the G value on a log-log scale according to Eq. (1). The value of floc stability exponent (γ) was obtained from the linearization of the equation, which was 0.82, 0.10 and 0.71 at pH 4.0, 7.0 and 10.0, respectively (Fig. 4D).

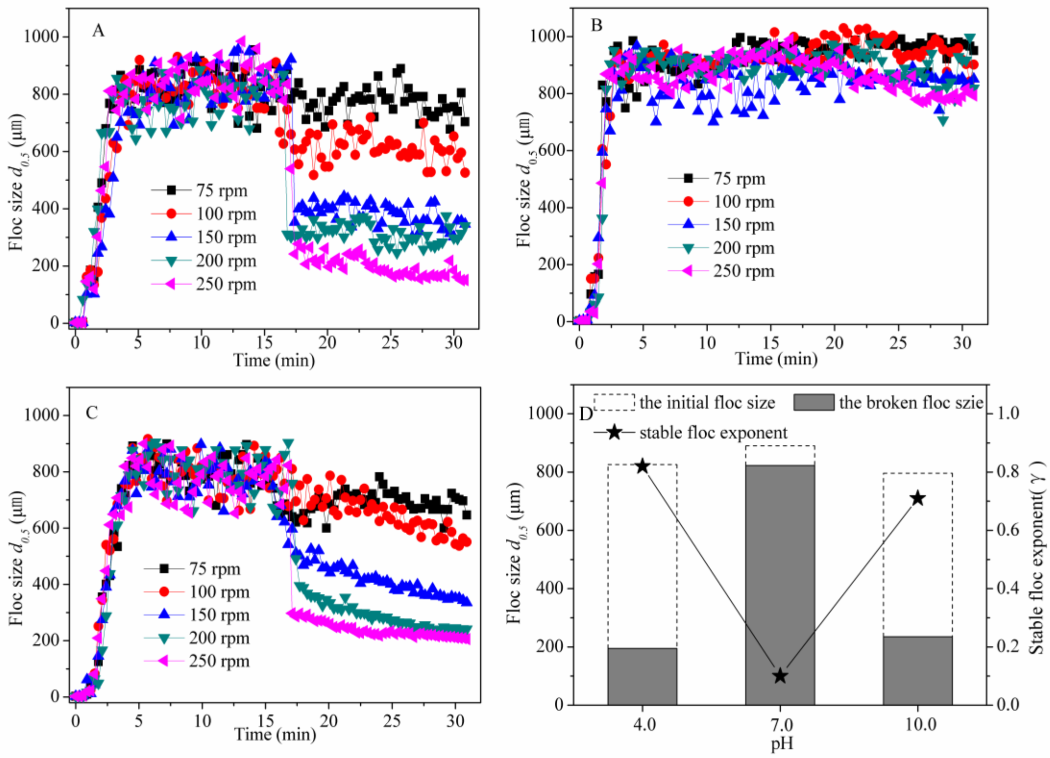

Fig. 4 – Floc breakage profiles at different pH conditions (A, pH = 4.0; B, pH = 7.0; C, pH = 10.0) and the relationship between stable floc exponent and floc breakage (shear speed = 250 rpm) as a function of pH (D). The dosage of the modified soil was 10 mg/L cationic starch - 100 mg/L soil.

3.5 Algal flocculation using lake bloom water

M. aeruginosa in the field is often in colonial form with several hundred micrometers in diameter (Fig 5A). After CS modified soil was added, large flocs of about 4 mm were formed (Fig 5B). With algal cells settled, the *chl-a* concentration in water column was reduced. The optimized dosage of CS was 1.0 mg/L, where the *chl-a* was decreased from 0.8 to 0.03 mg/L (Fig 5C).

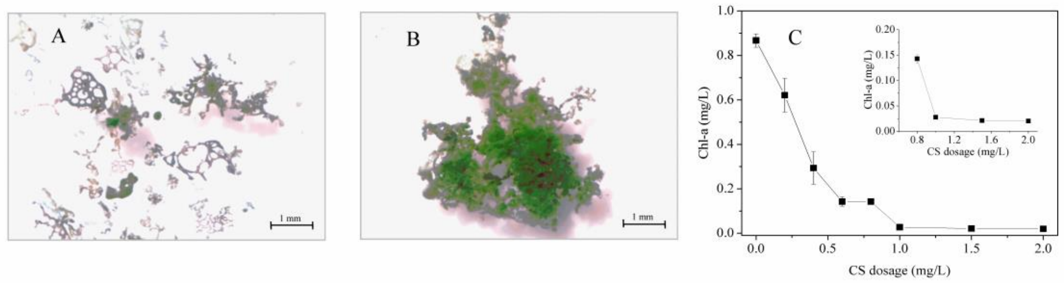

Fig. 5 – Flocculation of lake bloom water using cationic starch modified soil. (A) field colonial *Microcystis aeruginosa* (Lake Taihu, China); (B) the formed flocs; (C) *Chlorophyll-a* (*Chl-a*) concentration at different dosage of cationic starch (CS). The soil concentration was 120 mg/L. Error bars indicate standard deviations.

4. Discussion

4.1. Charge neutralization and algal flocculation

When the soil was modified by CS, the surface charge of CS modified soil was switched from negative to positive under wide pH range less than 11.8 (Fig. 1). This is essential for the modified soil particles to obtain flocculation potential for negatively charged algal cells, since charge neutralization can reduce the electrostatic repulsion between algal cells, and allow aggregation to occur. The long chain of CS is critical for the formation of large flocs through bridging function. Thus, the two-component modifier mechanism of charge and bridging can be realized by CS alone, which is more convenient for practical application.

At the low CS dosage of 5 mg/L, limited algal removal efficiency of 71% yet reasonably large flocs of 700 μm were achieved (Fig. 3A, B). This is because when CS was lowly dosed, only parts of algal cells were combined with the modified soil particle surfaces through charge neutralization. The adsorption of algal cells neutralized the positive charge of the modified soil (+2.5 mV) and reduced electrostatic repulsion between the formed flocs, making the flocs easily bridged into reasonably large ones (700 μm) by the long chains of CS (Fig. 3A). The sedimentation of these large flocs was therefore fast (Fig. 3B). For algal cells left in the overlying water, the ZP was increased from -46.2 to -9.9 mV (Fig. 2), indicating that flocculation is only happened among parts of algal cells. At the CS dosage of 10 mg/L, enough positive charges were provided by CS modified soil to catch up more algal cells, which led to a high removal efficiency of 86%. The charge neutralization reduced electrostatic repulsion between the formed flocs (+3.4 mV) and promoted the flocs into large ones (830 μm) with the bridging of CS chain (Fig. 3A). The flocculation kinetics was therefore fast (Fig. 3B). At the high CS dosage, dispersion re-stabilization was observed. Excess positive charges provided by CS caused the formed flocs positively charged (+33.5 mV, Fig. 2) and re-established electrostatic repulsion between flocs. The flocs were thereby hardly bridged into large ones (440 μm, Fig. 3A), which led to the low removal efficiency at high CS dosage of 80 mg/L (45% in 30 min, Fig. 3B). Thus, the combination of charge neutralization and bridging mechanisms operates the algal flocculation using CS modified soil.

A jar test using the field samples is always necessary to assure the algal removal effect and optimize the material dosage before practical application. Algal flocculation using natural bloom water from Lake Taihu (China) indicated that large flocs could be formed and colonial *M. aeruginosa* could be effectively removed using CS modified soil (Fig. 5). The *chl-a* concentration was decreased from 0.8 to 0.03

mg/L at the optimal CS dosage of 1.0 mg/L (Fig. 5C). Compared with dispersed single *M. aeruginosa* in the lab, colonial ones in the field often have large size and low hydrophilicity, which make them easily flocculated (or need low CS loading).

Soil particles may have great influence on algal flocculation kinetics. In addition to providing the mass or ballast to speed up the floc sedimentation, soil particles not only play as carriers to maintain the modifier concentration on solid surfaces (rather than dissolve large amount of flocculants in the water column), but also enhance the collision frequency between particles, which is crucial to flocculation dynamics (both particle size and concentration). If the modifiers are used alone without soil particles, the formed flocs may still float in the water column with the aid of buoyancy (Fig. S3). Harvesting measures such as air flotation and mechanical collection will be needed to achieve algal removal, which inevitably adds substantial extra work and costs. Although soil particles may consume parts of CS (9% in this study, Fig. S4), it is worthwhile to slightly increase the loadings of cationic starch to achieve the sedimentation removal of algal cells. With algal blooms settled by the modified soil, water transparency can be increased and excess nutrients are transferred from water to sediment under the capping layer with the aid of capping treatment (Pan et al., 2011b; Pan et al., 2012). The enhanced water transparency creates a favorable environment for the growth of submerged vegetation. It is possible for the sealed algal biomass to be turned into fertilizers for the growth of submerged vegetation (Pan et al., 2011b; Zhang et al., 2010).

4.2. Floc stability

The γ value quantitatively describes how the floc size changes when flocs are exposed to a series of shear rates. Generally, a larger γ means the floc stability is lower and the floc is more prone to be broken (Jarvis et al., 2005). The γ value was 0.82 and 0.71 at pH 4.0 and pH 10.0, respectively, which were much higher than the γ (0.10) at pH 7.0 (Fig. 4D). This indicated that the flocs formed at acidic and alkaline conditions are less stable and more prone to be broken into smaller fragments than those formed at the neutral condition. At the shear rate of 250 rpm (G=141.7 s^{-1}), the floc size at pH 4.0 and pH 10.0 dropped sharply from 826 to 195 μm and from 796 to 235 μm, respectively, while the floc size at pH 7.0 only slightly reduced from 890 to 823 μm (Fig. 4). The surface charge of algal cells was affected by pH conditions. The cell surface is less negatively charged at acid conditions and more negatively charged at alkaline conditions (Fig, S5). This may introduce some repulsion in algal flocs and weaken the adsorptive binding in algal flocs, which leads to the low floc stability (Slavik et al., 2012).

Cyanobacterial blooms often elevate water pH and sometimes increase the pH as high as 9.5 (Wang et al., 2013). Since quaternary amine on the polymer does not easily dissociate as pH changes (Wang et al., 2011a), the surface charge of CS modified soil was stable in the pH range from 2.0 to 10.0 (Fig. 1), and algal removal is less affected by the pH condition within this range (Fig. S2). However, the floc breakage might occur when flocs are exposed to high turbulence. The broken flocs are often subject to re-suspension and lead to the lost of algal removal. For practical application, additional measures such as capping might be helpful in solving the re-suspension problem (Pan et al., 2012).

4.3. Cost evaluation

Economic cost is often a limiting factor affecting large scale application of the method in fields, and the cost reduction can be critically dependent on technical breakthrough. Although many modifiers can be used to turn soils into effective algae flocculants (Li and Pan, 2013; Pan et al., 2011a), there may be a great difference in cost. For example, the use of MO would be economically impractical at the places where MO is non-indigenous, since MO can be very expensive when they are exported to some places (Table S1). In this study, the cost of CS is estimated to be 1650 US$/ton, which is more expensive than PAC (650 US$/ton) but much cheaper than chitosan (22,800 US$/ton) and MO (seeds, 96,074 US$/ton) in China (Table S1). The modifier cost of using CS modified soil to achieve algal removal efficiency of ~86% is about 0.02 US$/$m^3$ at the optimal CS dosage of 10 mg/L. The similar algal removal could be achieved by 2 mg/L chitosan-10 mg/L PAC modified soil or 2 mg/L chitosan-3 mg/L MO modified soil, where the modifier cost is 0.05 and 5.72 US$/$m^3$, respectively.

4.4. Environmental implications

In recent years, geo-engineering has triggered much interest as a tool for eutrophication control, which can offer the promise of rapid effects (Lürling and Faassen, 2012; Lürling and van Oosterhout, 2013; Meis et al., 2013). Economic cost and ecological safety are among the major concerns in its application (Spears et al., 2014; Spears et al., 2013). As the raw material, starch is globally distributed, allowing the mass production of cheap CS. The biodegradability and the flocculation effect of CS make it possible to be used at low dosage together with soil particles for natural bloom water treatment. When combined with soil particles, the biotic toxicity of cationic starch can be significantly reduced, which was specifically studied in another study (Wang et al., in this issue). However, the long-term effect on aquatic ecological system even at low dosage is unclear. Further study is needed to evaluate its impacts. Previous studies indicated that, despite the distinct properties, the soil of different origin can often obtain algal flocculation ability after suitable modification (Zou et al., 2006). The local soil collected from lakeside may reduce the transportation cost However, contaminated soil (by heavy metals and fertilizers etc.) is not recommended to be used. In fields, washing and particle fractionation approach can be used to select large amount of fine soil particles, and suitable engineering facilities (such as screw turbine) may be used for mixing.

Although CS is biodegradable, it might be a source of oxygen demand and some settled algal cells may be liberated as it decays in field applications. For these practical problems, it cannot be solved based on flocculation treatment alone. Other measures, such as capping treatments (especially oxygen nanobubble modified one), should be jointly applied after flocculation (Pan et al., 2012; Pan and Yang, 2012). The improved water (by flocculation) and sediment (by capping) environment may create a window period for the restoration of submerged vegetation. The sediment manipulation and submerged vegetation restoration may further affect C, N and P fluxes across the sediment-water and air-water interfaces (CO_2, CH_4, N_2 and N_2O etc.), which may trigger multi-disciplinary studies in the future.

5. Conclusions

Dispersal of CS modified local soils achieved effective removal of cyanobacterial cells with the operation of charge neutralization and bridging mechanisms. Water pH condition did not significantly influence algal removal effect except the floc stability. The flocs formed at acid and alkaline conditions were more prone to be broken than those at the neutral condition. This method greatly reduces the cost and biodegradability concerns by using cheaply available and environmental friendly materials such as local soils and cationic starch. With some additional studies, this approach may be practically useful as a geo-engineering tool for cyanobacterial bloom control.

Acknowledgments

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References

Anderson, D.M., 1997. Turning back the harmful red tide - Commentary. Nature 388 (6642), 513-514.

Anthony, R.J., Ellis, J.T., Sathish, A., Rahman, A., Miller, C.D., Sims, R.C. 2013. Effect of coagulant/flocculants on bioproducts from microalgae. Bioresour. Technol. 149, 65-70.

Atkins, R., Rose, T., Brown, R.S., Robb, M., 2001. The Microcystis cyanobacteria bloom in the Swan River - February 2000. Water Sci. Technol. 43 (9), 107-114.

Baumgartner, S., Pavli, M., Kristl, J., 2008. Effect of calcium ions on the gelling and drug release characteristics of xanthan matrix tablets. Eur. J. Pharm. Biopharm. 69 (2), 698-707.

Bridgeman, J., Jefferson, B., Parsons, S., 2008. Assessing floc strength using CFD to improve organics removal. Chem. Eng. Res. Des. 86 (8A), 941-950.

Carmichael, W.W., 1997. The cyanotoxins. Adv. Bot. Res. 27, 211-256.

Chen, J., Pan, G., 2012. Harmful algal blooms mitigation using clay/soil/sand modified with xanthan and calcium hydroxide. J. Appl. Phycol. 24 (5), 1183-1189.

Chen, W., Jia, Y.L., Li, E.H., Zhao, S., Zhou, Q.C., Liu, L.M., Song, L.R., 2012. Soil-based treatments of mechanically collected cyanobacterial blooms from Lake Taihu: efficiencies and potential risks. Environ. Sci. Technol. 46 (24), 13370-13376.

Edzwald, J.K., 1993. Algae, bubbles, coagulants, and dissolved air flotation. Water Sci. Technol. 27 (10), 67-81.

Ellis, H.A., Utah, S.I., Ogunrinde, A., Ogedengbe, M.O., 1982. Preparation of some cationic starches as flocculants for water. Water Res. 16 (9), 1433-1435.

Everall, N.C., Lees, D.R., 1996. The use of barley-straw to control general and blue-green algal growth in a Derbyshire reservoir. Water Res. 30 (2), 269-276.

Falconer, I.R., 1999. An overview of problems caused by toxic blue-green algae (cyanobacteria) in drinking and recreational waters. Environ. Toxicol. 14 (1), 5-12.

García-Villada, L., Rico, M., Altamirano, M., Sánchez-Martín, L., López-Rodas, V., Costas, E., 2004. Occurrence of copper resistant mutants in the toxic cyanobacteria *Microcystis aeruginosa*: characterisation and future implications in the use of copper sulphate as algaecide. Water Res. 38 (8), 2207-2213.

Grabow, W.O.K., Slabbert, J.L., Morgan, W.S.G., Jahn, S.A.A., 1985. Toxicity and mutagenicity evaluation of water coagulated with *Moringa-oleifera* seed preparations using fish, protozoan, bacterial, coliphage, enzyme and ames salmonella assays. Water SA 11 (1), 9-14.

Guo, L., 2007. Doing battle with the green monster of Taihu Lake. Science 317 (5842), 1166.

Hawkins, P., Runnegar, M., Jackson, A., Falconer, I., 1985. Severe hepatotoxicity caused by the tropical cyanobacterium (blue-green alga) Cylindrospermopsis raciborskii (Woloszynska) Seenaya and SubbaRaju isolated from a domestic water supply reservoir. Appl. Environ. Microbiol. 50 (5), 1292-1295.

Hjorth, M., Jorgensen, B.U., 2012. Polymer flocculation mechanism in animal slurry established by charge neutralization. Water Res. 46 (4), 1045-1051.

Jarvis, P., Jefferson, B., Gregory, J., Parsons, S.A., 2005. A review of floc strength and breakage. Water Res. 39 (14), 3121-3137.

Khalil, M.I., Aly, A.A., 2004. Use of cationic starch derivatives for the removal of anionic dyes from textile effluents. J. Appl. Polym. Sci. 93 (1), 227-234.

Kurniawati, H.A., Ismadji, S., Liu, J.C., 2014. Microalgae harvesting by flotation using natural saponin and chitosan. Bioresour. Technol. 166, 429-434.

Lee, Y.J., Choi, J.K., Kim, E.K., Youn, S.H., Yang, E.J. 2008. Field experiments on mitigation of harmful algal blooms using a Sophorolipid-Yellow clay mixture and effects on marine plankton. Harmful Algae 7 (2), 154-162.

Li, L., Pan, G., 2013. A universal method for flocculating harmful algal blooms in marine and fresh waters using modified sand. Environ. Sci. Technol. 47 (9), 4555-4562.

Lin, Q.T., Qian, S., Li, C.J., Pan, H.P., Wu, Z.Y., Liu, G.G., 2012. Synthesis, flocculation and adsorption performance of amphoteric starch. Carbohyd. Polym. 90 (1), 275-283.

Lürling, M., Faassen, E.J., 2012. Controlling toxic cyanobacteria: Effects of dredging and phosphorus-binding clay on cyanobacteria and microcystins. Water Res. 46 (5), 1447-1459.

Lürling, M., van Oosterhout, F., 2013. Controlling eutrophication by combined bloom precipitation and sediment phosphorus inactivation. Water Res. 47 (17), 6527-6537.

Mackay, E.B., Maberly, S.C., Pan, G., Reitzel, K., Bruere, A., Corker, N., Douglas, G., Egemose, S., Hamilton, D., Hatton-Ellis, T., Huser, B., Li, W., Meis, S., Moss, B., Lürling, M., Phillips, G., Yasseri, S., Spears, B.M., 2014. Geoengineering in lakes: welcome attraction or fatal distraction? Inland Waters 4 (4), 349-356.

Meis, S., Spears, B.M., Maberly, S.C., Perkins, R.G., 2013. Assessing the mode of action of Phoslock® in the control of phosphorus release from the bed sediments in a shallow lake (Loch Flemington, UK). Water Res. 47 (13), 4460-4473.

Ministry of Environmental Protection of China, 2002. The monitoring analysis method of water and waste water (4th, ed.). China Environmental Science Press, Beijing, 241-285.Pal, S., Mal, D., Singh, R.P., 2005. Cationic starch: an effective flocculating agent. Carbohyd. Polym. 59 (4), 417-423.

Pan, G., Zhang, M.M., Chen, H., Zou, H., Yan, H., 2006. Removal of cyanobacterial blooms in Taihu Lake using local soils. I. Equilibrium and kinetic screening on the flocculation of *Microcystis aeruginosa* using commercially available clays and minerals. Environ. Pollut. 141 (2), 195-200.

Pan, G., Chen, J., Anderson, D.M., 2011a. Modified local sands for the mitigation of harmful algal blooms. Harmful Algae 10 (4), 381-387.

Pan, G., Yang, B., Wang, D., Chen, H., Tian, B.H., Zhang, M.L., Yuan, X.Z., Chen, J.A., 2011b. In-lake algal bloom removal and submerged vegetation restoration using modified local soils. Ecol. Eng. 37 (2), 302-308.

Pan, G., Dai, L.C., Li, L., He, L.C., Li, H., Bi, L., Gulati, R.D., 2012. Reducing the recruitment of sedimented algae and nutrient release into the overlying water using modified soil/sand flocculation-capping in eutrophic lakes. Environ. Sci. Technol. 46 (9), 5077-5084.

Pan, G., Yang, B., 2012. Effect of surface hydrophobicity on the formation and stability of oxygen nanobubbles. Chemphyschem. 13 (8), 2205-2212.

Park, T.G., Lim, W.A., Park, Y.T., Lee, C.K., Jeong, H.J., 2013. Economic impact, management and mitigation of red tides in Korea. Harmful Algae 30, S131-S143.

Parker, D.S., Asce, A.M., Kaufman, W.J., Jenkins, D., 1972. Floc breakup in turbulent flocculation processes. J. Sanit. Eng. Div. Asce 98 (Nsa1), 79-&.

Sengupta, M.E., Keraita, B., Olsen, A., Boateng, O.K., Thamsborg, S.M., Palsdottir, G.R., Dalsgaard, A., 2012. Use of Moringa oleifera seed extracts to reduce helminth egg numbers and turbidity in irrigation water. Water Res. 46 (11), 3646-3656.

Shi, Y.L., Ju, B.Z., Zhang, S.F., 2012. Flocculation behavior of a new recyclable flocculant based on pH responsive tertiary amine starch ether. Carbohyd. Polym. 88 (1), 132-138.

Slavik, I., Müller, S., Mokosch, R., Azongbilla, J.A., Uhl, W., 2012. Impact of shear stress and pH changes on floc size and removal of dissolved organic matter (DOM). Water Res. 46 (19), 6543-6553.

Spears, B.M., Dudley, B., Reitzel, K., Rydin, E., 2013. Geo-engineering in lakes-A call for consensus. Environ. Sci. Technol. 47 (9), 3953-3954.

Spears, B.M., Maberly, S.C., Pan, G., Mackay, E., Bruere, A., Corker, N., Douglas, G., Egemose, S., Hamilton, D., Hatton-Ellis, T., Huser, B., Li, W., Meis, S., Moss, B., Lurling, M., Phillips, G., Yasseri, S., Reitzel, K., 2014. Geo-engineering in lakes: A crisis of confidence? Environ. Sci. Technol. 48 (17), 9977-9979.

Vandamme, D., Foubert, I., Meesschaert, B., Muylaert, K., 2010. Flocculation of microalgae using cationic starch. J. Appl. Phycol. 22 (4), 525-530.

Wang, L., Liang, W.Y., Yu, J., Liang, Z.X., Ruan, L.L., Zhang, Y.C., 2013.

Flocculation of *Microcystis aeruginosa* using modified Larch Tannin. Environ. Sci. Technol. 47 (11), 5771-5777.

Wang, S., Liu, C., Li, Q.L., 2011a. Fouling of microfiltration membranes by organic polymer coagulants and flocculants: Controlling factors and mechanisms. Water Res. 45 (1), 357-365.

Wang, S.C., Yang, J.Y., Xu, X.R., 2011b. Effect of the cationic starch on removal of Ni and V from crude oils under microwave irradiation. Fuel 90 (3), 987-991.

Wang, Z.B., Zhang, H.G., Pan, G., Unpublished results. Ecotoxicological assessment of modified soil flocculants for lake restoration using an integrated biotic toxicity index.

Wei, Y.P., Cheng, F., Zheng, H., 2008. Synthesis and flocculating properties of cationic starch derivatives. Carbohyd. Polym. 74 (3), 673-679.

Zhang, L.Y., Li, K.Y., Liu, Z.W., Middelburg, J.J., 2010. Sedimented cyanobacterial detritus as a source of nutrient for submerged macrophytes (*Vallisneria spiralis* and *Elodea nuttallii*): An isotope labeling experiment using ^{15}N. Limnol. Oceanogr. 55 (5), 1912-1917.

Zou, H., Pan, G., Chen, H., Yuan, X.Z., 2006. Removal of cyanobacterial blooms in Taihu Lake using local soils. II. Effective removal of *Microcystis aeruginosa* using local soils and sediments modified by chitosan. Environ. Pollut. 141 (2), 201-205.