

Harmful algal blooms mitigation using clay/soil/sand modified with xanthan and calcium hydroxide

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Abstract A method was studied for marine harmful algal blooms (HABs) mitigation using clay, soil, or sand modified with xanthan and calcium hydroxide. Results showed that xanthan could trap and wrap *Amphidinium carterae* cells via bridging and netting interactions due to its superior salt compatibility in seawater. The maximum cell removal efficiency was 55% when xanthan was used alone. The removal effect of xanthan was enhanced by the addition of appropriate calcium hydroxide that decreased the repulsive interaction between anionic xanthan and negatively charged algal cells. Three kinds of minerals (clays, soils, and sands) were ineffective in removing algal cells before treatment. When xanthan and calcium hydroxide were used together as modifiers, the removal efficiency increased to 83–89% within 30 min using 300 mg L⁻¹ clays, soils, or sands modified with 20 mg L⁻¹ xanthan and 100 mg L⁻¹ calcium hydroxide. After several hours, 95–98% cell removal was achieved and there was no significant difference in the removal efficiencies among clays, soils, and sands after being modified with xanthan and calcium hydroxide. Thus, the method would provide an alternative modification approach to suppress and mitigate HABs using local soils/sands and polymers in marine systems.

Keywords Harmful algal blooms mitigation · Flocculation · Xanthan · Sand · Soil · Clay

Introduction

As worldwide aquatic phenomena, harmful algal blooms (HABs) are often marked by the discoloration of surface waters due to the rapid population growth of microscopic algae. One of the challenging and controversial aspects of HAB research relates to methods that directly control or suppress blooms (Anderson 1997). Many approaches such as chemical algicides, flocculants, biological agents, and other physical manipulations have been proposed to reduce impacts (Anderson 1997; Shirota 1989a). With respect to efficiency, cost, and environmental impacts, a promising strategy for HABs mitigation is flocculation and sedimentation of harmful algal cells through clay dispersal (Shirota 1989b; Yu et al. 1994, 2004; Anderson 1997; Pan 1998; Sengco and Anderson 2004; Pan et al. 2006a; Padilla et al. 2010). However, it is still controversial due to the addition of large amounts of exotic materials (Shumway et al. 2003) and the constituents of clays, such as phosphorus, toxic or harmful metals, and radioactive materials (Pan et al. 2011a).

Some reports indicate that algal cell removal effect can be enhanced and clay loading decreased by modifying clays using flocculants or surfactants in the treatment process. For example, after modified with acid or positively charged colloids, the clay loadings have been reduced to 1/5–1/10 of concentrations than previously used (Yu et al. 1999). Sengco et al. (2001) improved algal removal efficiency by modifying clay with commonly inorganic coagulant poly-aluminum chloride (PAC). Sun et al. (2004) tested the effective concentration of yellow loess and sophorolipid; when used together in the combination group, these were reduced to 10% and 25%, respectively, compared with the

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amounts added as individual compounds in the non-combination groups. In these studies, clays are limited to certain types, i.e., montmorillonite, kaolinite, phosphatic clay, and yellow loess, which are not immediately available at some locations that have HABs problems. Chemical reagents and synthetic productions in laboratory (e.g., positively charged colloids and sophorolipid) may not be environment friendly or cost effective when used in large-scale natural blooms.

In recent research, clays, soils, sediments, and sands had higher removal efficiencies against *Microcystis aeruginosa* in freshwater after modification with chitosan, a natural organic flocculant (Pan et al. 2006b, 2011b; Zou et al. 2006). The polymeric bridging and netting function of chitosan was the key mechanism that allowed many local sediment particles to be highly effective in flocculating HAB cells. However, these results had limited direct applicability in seawater, as high ionic strength and alkalinity prevent the unfolding of the polymer chain, thereby weakening chitosan's binding properties (Qun and Ajun 2006; Zou et al. 2006). With further study, it was demonstrated that the cationic hydrolysis products of PAC were beneficial to maintain the netting and bridging properties of chitosan in seawater and a new method was developed for marine HABs mitigation using local beach sand or silica sand modified with chitosan and PAC together (Pan et al. 2011a). In this method, economical and environmental concerns could be reduced through the use of sands and biodegradable chitosan, but the ecological impacts of PAC remain a concern. Therefore, efforts are needed to identify new, environmentally benign and commercially available modifiers in this bloom control strategy, which could turn clays, soils, and sands into effective flocculants to remove HAB cells in marine systems.

Xanthan is an extracellular heteropolysaccharide produced by fermentation of the bacterium *Xanthomonas campestris* (Baumgartner et al. 2008). It has been widely used in a broad range of industries, such as foods, toiletries, oil recovery, cosmetics, pharmacies, etc., due to its superior properties of (1) high viscosity yield even at low concentration, (2) excellent compatibility with salt (up to 150 g L⁻¹ NaCl), (3) low viscosity sensitivity to pH changes (2–11), and (4) stability with respect to temperature (up to 90°C) (García-Ochoa et al. 2000; Rosalam and England 2006). Furthermore, xanthan is of natural origin, relatively cheap to produce, biocompatible and safe as it is assigned with the generally recognized as safe (GRAS) label (Baumgartner et al. 2008). Previous studies showed that xanthan had high flocculating activity in inorganic and organic suspensions (i.e., active carbon, acid clay, cellulose, yeast, and others), which can be enhanced by the presence of Al³⁺, Fe²⁺, or Ca²⁺ ions in solutions (Yokoi et al. 1996;

Tempio and Zatz 1980; Koczo et al. 1998; Mohammed et al. 2007), but no study has been conducted on HABs mitigation using xanthan.

Amphidinium carterae Hulburt is considered a HAB species due to its production of haemolysins, and it has also been linked to fish mortalities (Hulburt 1957; Yasumoto et al. 1987). The motile dinoflagellate species is more difficult to be removed through flocculation compared with non-motile diatoms (Yu et al. 1994). The purpose of the present study was to investigate the removal effects of xanthan alone and in the presence of calcium hydroxide on *A. carterae*, and to propose an alternative modification method using clay/soil/sand modified with xanthan and calcium hydroxide for algal bloom mitigation in marine systems.

Materials and methods

Amphidinium carterae Hulburt culture was obtained from the Oceanography College, Ocean University of China. F/2 medium made with sterile synthetic seawater was used for sub-culturing (Guillard and Hargraves 1993). The synthetic seawater was composed of 23.939 g L⁻¹ NaCl, 5.079 g L⁻¹ MgCl₂·6H₂O, 3.994 g L⁻¹ Na₂SO₄, 1.123 g L⁻¹ CaCl₂, 0.667 g L⁻¹ KCl, 0.196 g L⁻¹ NaHCO₃, 0.098 g L⁻¹ KBr, 0.027 g L⁻¹ H₃BO₃, 0.003 g L⁻¹ NaF and 0.024 g L⁻¹ SrCl₂·6H₂O.

Algal batch cultures were maintained under continuous cool white fluorescent light of about 40–60 μmol photons m⁻² s⁻² in a 12-h light/12-h dark cycle at 25±1°C. The algal removal experiments were conducted during the onset of the mid-exponential growth phase of the algae. The initial cell concentration of *A. carterae* was between 33.3 and 34.0×10⁴ cells mL⁻¹.

Modifier and minerals

Xanthan was purchased from Beijing Qingshengda Chemical Technology Co., Ltd. The xanthan powder was dissolved in deionized water to obtain a solution of 1.0 g L⁻¹ before use. Calcium hydroxide (Ca(OH)₂, often referred as slaked lime, or simply as lime) was obtained from Tianjin Chemical Reagent Factory.

Three kinds of minerals were used. One was clay supplied by the Research Center for Eco-Environmental Sciences, CAS. Another was soil collected from the bank of the Yellow River in Jinan, China. The other was silica sand, analytical grade, obtained from Sinopharm Chemical reagent Co., Ltd. The minerals were dried at 100°C and sieved (<180 μm). Their size distributions were monitored with a laser particle size analyzer Mastersizer 2000 (Malvern Co., United Kingdom). The size fractionation of the tested minerals is shown in Table 1.

Table 1 Size fractionation (percentage of total) of three tested minerals

| Size | <2 μm | 2–8 μm | 8–20 μm | 20–50 μm | 50–80 μm | 80–100 μm | 100–160 μm | >160 μm |
|------|------------------|-------------------|--------------------|---------------------|---------------------|----------------------|-----------------------|--------------------|
| Clay | 8.5 | 18.3 | 25.1 | 29.9 | 11.4 | 3.6 | 3.0 | 0.2 |
| Soil | 3.4 | 4.2 | 5.2 | 55.3 | 26.9 | 5.0 | 0 | 0 |
| Sand | 4.6 | 7.6 | 10.0 | 17.3 | 19.4 | 12.4 | 21.1 | 7.6 |

These minerals and $\text{Ca}(\text{OH})_2$ were prepared as a slurry by adding deionized water to obtain a concentration of 10.0 g L^{-1} , respectively. To modify the minerals, a certain volume of xanthan solution with $\text{Ca}(\text{OH})_2$ suspension at the different ratio were added to a mineral slurry, similar to the clay modification method of Zou et al. (2006). The mixture was well stirred and then ready for use in the algal removal experiments.

Algal removal experiments

The algal removal experiments were conducted using a jar test apparatus (ZR3-6, Zhongrun Water Industry Technology Development Co. Ltd., China). In the experiments, cultures of *A. carterae* were transferred to 250-mL beakers, stirred at 200 rpm for 2 min, followed by 30 rpm for another 5 min, and then, maintained at room temperature without stirring for sedimentation. At the beginning of rapid mixing, xanthan alone, xanthan plus $\text{Ca}(\text{OH})_2$, and minerals modified with xanthan plus $\text{Ca}(\text{OH})_2$ were added to algal cultures in different removal experiments. Without adding any modifier or mineral, the control culture was run including the stirring and sedimentation.

Samples from 2 cm below the surface of the experimental cultures were collected after sedimentation at different times. Residual cells were counted with the 0.1 mL counting chamber under an electromotive microscope (Axioskop 2 mot plus, magnification of $\times 50$, Carl ZEISS, Germany) after being fixed by Lugol solution. Cell removal efficiency of the treatment materials was calculated as $(\text{initial cell concentration} - \text{sample cell concentration}) \times 100\% / \text{initial cell concentration}$ (Pan et al. 2011a). Algal flocs were collected by pipette and observed under the microscope.

All experiments were performed in duplicate and the data were presented as the mean \pm standard deviation. Differences in removal efficiencies between treatments were analyzed using one-way ANOVA (Sengco and Anderson 2004; Padilla et al. 2010), with significant differences implied at $P < 0.05$.

Results

Removal effect of xanthan alone Algal flocs micrographs (Fig. 1) demonstrate that xanthan could wrap and hold *A.*

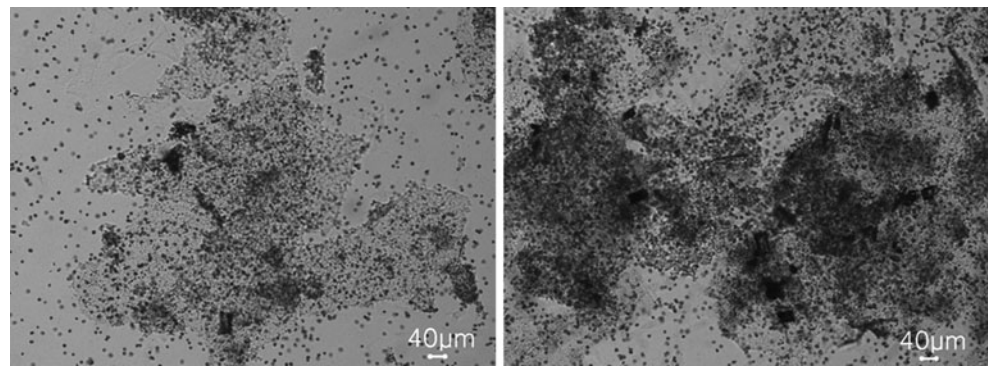
carterae cells as if trapped in network configurations. Algal flocs were fibrous and formed large entangled masses resembling cobwebs by bridging and netting interactions, and they aggregated into large and complex flocs. As shown in the micrographs, there were some algal cells still on the floc surface which could not be captured. When xanthan was used alone, cell removal efficiency increased from 32 to 55% with increasing dosage of xanthan from 1.0 to 10 mg L^{-1} (Fig. 2). However, when xanthan concentration was further increased to 50 mg L^{-1} , algal removal efficiency significantly decreased to 49% ($P < 0.05$). Thus, the maximum cell removal efficiency of xanthan alone was 55% with the residual cell concentration approximating $14.9 \times 10^4 \text{ cells mL}^{-1}$ at 10 mg L^{-1} xanthan.

Removal effect of xanthan and $\text{Ca}(\text{OH})_2$ As shown in Fig. 3, the removal effect of xanthan was influenced by the presence of calcium hydroxide. After the addition of 50 mg L^{-1} $\text{Ca}(\text{OH})_2$ with 5 and 10 mg L^{-1} xanthan, the removal efficiency was 40% and 48%, respectively, which was slightly lower than that when xanthan was used alone. When another 50 mg L^{-1} $\text{Ca}(\text{OH})_2$ was added, the removal efficiency of 5 mg L^{-1} xanthan with 100 mg L^{-1} $\text{Ca}(\text{OH})_2$ significantly increased to 60% ($P < 0.05$) and that of 10 mg L^{-1} xanthan increased to 71% ($P < 0.05$). Cell removal efficiency further increased with increasing $\text{Ca}(\text{OH})_2$ dosage and the removal efficiency of 10 mg L^{-1} xanthan with 200 mg L^{-1} $\text{Ca}(\text{OH})_2$ was over 90%.

Removal effect of clays modified with xanthan and $\text{Ca}(\text{OH})_2$ Considering the addition of clays and pH increased if $\text{Ca}(\text{OH})_2$ used in high concentration, experiments examining the removal effects of clays modified with xanthan and $\text{Ca}(\text{OH})_2$ on *A. carterae* cells included two groups: (a) xanthan and $\text{Ca}(\text{OH})_2$ at a ratio of 1:2, (b) xanthan and $\text{Ca}(\text{OH})_2$ at a ratio of 1:5.

The results shown in Fig. 4a demonstrate that cell removal efficiency of clays modified with xanthan and $\text{Ca}(\text{OH})_2$ at the ratio of 1:2 did not exceed 60% within the concentration range tested. The average removal efficiency of three different ratios (xanthan/ $\text{Ca}(\text{OH})_2$ /clay=1:2:8, 1:2:13, and 1:2:18) was 32% at 5 mg L^{-1} xanthan. Increasing the modified clay dosage did not significantly improve the removal efficiency of *A. carterae* in these group experiments. When xanthan concentration was

Fig. 1 Algal floc micrographs of xanthan and *A. carterae* cells



increased to 20 mg L^{-1} and modified clays also increased by threefold, the average cell removal efficiency was 55%.

In contrast, *A. carterae* removal efficiency by modified clays increased significantly when the ratio of xanthan to $\text{Ca}(\text{OH})_2$ was 1:5. As shown in Fig. 4b, cell removal efficiencies of the ratios (xanthan/ $\text{Ca}(\text{OH})_2$ /clay=1:5:5, 1:5:10, and 1:5:15) were between 36% and 49% at 5 mg L^{-1} xanthan. When xanthan concentration was increased to 15 mg L^{-1} , the average removal efficiency reached 72%. With modified clays further increased, algal removal efficiency reached a maximum of 97% (at the ratio of 1:5:15). In this group experiments, clays also played an important role in enhancing algal cells removal. At 20 mg L^{-1} xanthan with 100 mg L^{-1} $\text{Ca}(\text{OH})_2$, the removal efficiency increased by 21% with increasing the clay dosage from 200 to 300 mg L^{-1} .

Removal effect of clays, soils, and sands modified with xanthan and $\text{Ca}(\text{OH})_2$ Based on the above experimental results, the appropriate ratio among xanthan, $\text{Ca}(\text{OH})_2$, and clays was 20 mg L^{-1} xanthan: 100 mg L^{-1} $\text{Ca}(\text{OH})_2$: 300 mg L^{-1} clays for *A. carterae* removal. Cell removal efficiencies of clays/soils/sands modified with xanthan and $\text{Ca}(\text{OH})_2$ at this ratio, modifiers alone

(20 mg L^{-1} xanthan plus 100 mg L^{-1} $\text{Ca}(\text{OH})_2$) and untreated clays/soils/sands (300 mg L^{-1}), are shown in Fig. 5.

Compared with control experiments, clays, soils, or sands were ineffective in removing algal cells before treatment. When xanthan and $\text{Ca}(\text{OH})_2$ were used together as modifiers, *A. carterae* removal efficiency by modified clays, soils, and sands within 30 min increased to 89, 83, and 88%, respectively, whereas cell removal efficiency of modifiers alone was only 53%. After 2 h of sedimentation, the removal efficiencies of modified clays, soils, and sands were between 92% and 95%, and that of modifiers alone increased to 66%. Using only the minerals, the maximum removal efficiency of clays, soils, and sands after 6 h was 44, 31, and 26%, respectively. This increased to 97–98% when the xanthan and $\text{Ca}(\text{OH})_2$ modifiers were added with clays, soils, or sands. The results in Fig. 5 also demonstrate that there was no significant difference in the removal efficiencies among clays, soils, and sands if the modifiers were present ($P>0.05$).

Discussion

Harmful algal cells tend to float at the water surface because of the negative charged cell surface, low gravity, specific structure, and phototaxis (Zou et al. 2006; Sun and

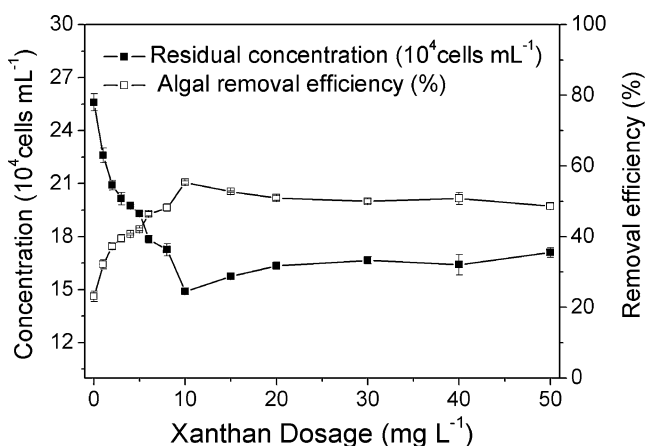


Fig. 2 Algal removal efficiency for xanthan alone (sedimentation time=4 h). The *error bars* represent the standard deviation for the replicate samples

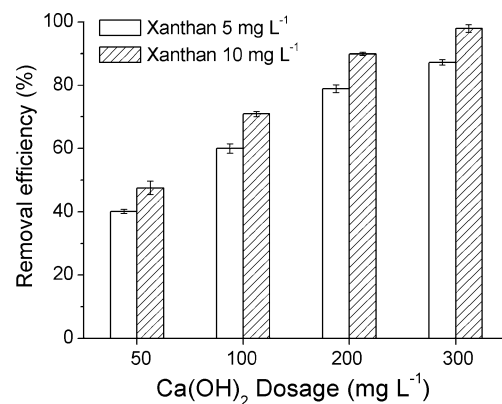


Fig. 3 Algal removal efficiency for xanthan and $\text{Ca}(\text{OH})_2$ (sedimentation time=4 h). The *error bars* represent the standard deviation for the replicate samples

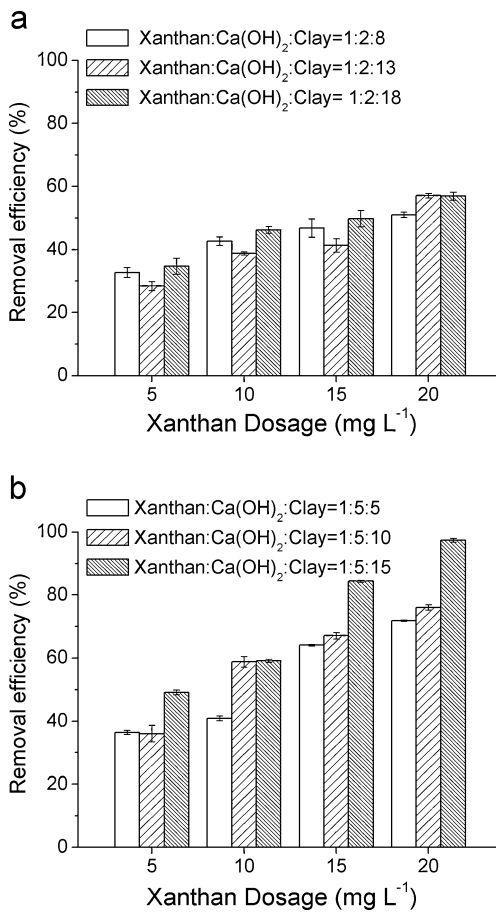


Fig. 4 Algal removal efficiency for clays modified with xanthan and Ca(OH)₂ (sedimentation time=4 h). **a** Xanthan/Ca(OH)₂=1:2 and **b** Xanthan/Ca(OH)₂=1:5. The error bars represent the standard deviation for the replicate samples

Choi 2004). Algal flocculation in waters occurs as a result of attractive anion–cation interactions, as well as hydrophobic or polymer interactions (Divakaran and Pillai 2001; Strand et al. 2002). Clays are also negatively charged in natural waters and hence the electrostatic neutralization

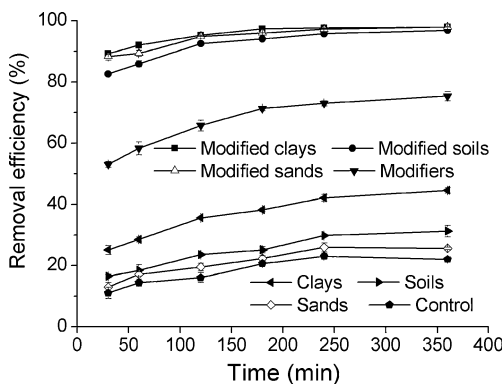


Fig. 5 Algal removal efficiency for clays, soils, and sands modified with xanthan and Ca(OH)₂ at different sedimentation time. The error bars represent the standard deviation for the replicate samples

does not contribute to the aggregation between clay particles and algal cells. Based on the results of this study, the clay itself could not effectively remove *A. carterae* cells through flocculation and sedimentation (Fig. 5). Soil and sand were less efficient in removing the dinoflagellate, likely due to different physical/charge characteristics of the clay. However, these three minerals modified with xanthan and calcium hydroxide were highly efficient in flocculating and sinking *A. carterae* cells.

Xanthan is an anionic polyelectrolyte with a semirigid chain structure. It consists of a β,1-4-D-glucose backbone, as in cellulose (García-Ochoa et al. 2000). Every alternate glucose unit has a three sugar side chain consisting of two mannose residues separated by a glucuronic acid. The mannose closest to the backbone can carry an acetyl group and the terminal mannose a pyruvate group (Rosalam and England 2006; Baumgartner et al. 2008). These acidic residues in the xanthan side chains provide conditions for complexation with cations, such as Na⁺, K⁺, Ca²⁺, and Mg²⁺, leading to intramolecular cross-linking and molecular association (Klaic et al. 2011; Dário et al. 2011). The presence of electrolytes in solutions could stabilize the multi-dimensional network of xanthan and increase interaction between the polymer molecules, with divalent salts more effective (García-Ochoa et al. 2000; Baumgartner et al. 2008; Dário et al. 2011). Due to the superior salt compatibility, xanthan is identified as a potentially useful material for algal removal in marine systems. Floc micrographs in Fig. 1 and algal removal efficiencies in Fig. 2 demonstrate that xanthan, like chitosan in freshwater, could scavenge and remove *A. carterae* cells in seawater by bridging and netting interactions. Due to the negative charge of the xanthan and algal cells in solutions, some cells could not be captured and hence the cell removal efficiency was not very high when xanthan was used alone.

The results in Fig. 3 indicate that the algal removal effect of xanthan was influenced by the addition of calcium hydroxide. When small amounts of Ca(OH)₂ (50 mg L⁻¹) were added, the removal efficiency of xanthan slightly decreased. This effect might be attributed to the reduction in xanthan molecular dimensions resulting from diminished intermolecular electrostatic forces by the acid–base neutralization reaction between acidic xanthan and Ca(OH)₂ (García-Ochoa et al. 2000). However, the algal removal effect of xanthan was significantly enhanced when more Ca(OH)₂ was added. It can be assumed that Ca²⁺ ions supplied by the reaction in solution condense in ionized carboxyl moieties of xanthan and the charge on the trisaccharide side chains of xanthan is partially screened (Baumgartner et al. 2008; Yokoi et al. 1996). With calcium hydroxide concentration increasing, this proposed mechanism would imply that the initially negative net charge on the xanthan helices could drop at around stoichiometric equivalence of Ca²⁺

(Mohammed et al. 2007). Since polyelectrolyte conformations are controlled by the fraction of ionized groups, the presence of calcium hydroxide in solution could increase the inter-polymer interactions and decrease the repulsive interactions between anionic xanthan and negatively charged algal cells. Thus, removal efficiencies of xanthan could be improved by the addition of appropriate calcium hydroxide in solution.

When xanthan and calcium hydroxide were used together as modifiers, cell removal efficiency of the modified clay depended on the ratios and amounts among xanthan, Ca(OH)_2 , and clay (Fig. 4). Higher clay addition to modifiers at the ratio of 1:5 (xanthan/ Ca(OH)_2) improved cell removal efficiency. However, xanthan or the modifiers alone had much lower effect on removing cells from the water column (Figs. 2 and 5). Similar observations were reported by Sengco et al. (2001) who tested aluminum sulfate, PAC, and four organic flocculants against HAB organisms. During the cell removing process, clay particles serve as the frames and weights to the “network” bridged by xanthan and calcium hydroxide among algal cells, which are critical for increasing rates of flocculation and sedimentation of algal flocs. Moreover, the removal effect of three kinds of minerals, clay, soil, and sand, were dramatically improved to a similarly high level after being modified with xanthan and Ca(OH)_2 (Fig. 5). This suggests that the mineral type and degree of purity are less important compared with the density and shape of particles to the aggregations of algal cells, as similar mechanism is noted for using local soils and sediments modified with chitosan for effective HAB cells removal in freshwater (Zou et al. 2006). This would make it possible to use local mineral particles (i.e., clay, soil, sand, and sediment) for treatments, which would reduce transportation costs and environmental concerns in the use of exotic materials.

The method using clay/soil/sand modified with xanthan and calcium hydroxide as well as using local beach sand or silica sand modified with chitosan and PAC (Pan et al. 2011a) for algal cells flocculation and sedimentation in seawater are modifications and developments of the relatively successful approach to suppress freshwater HABs using local soil/sand/sediment and polymers (Pan et al. 2006b, 2011b). In this method, xanthan is non-toxic and environmentally benign. It has been approved by the US Food and Drug Administration in 1969 and the Food and Agriculture Organization (FAO) in 1983 for use a food additive without any specific quantity limitations (García-Ochoa et al. 2000). It does not inhibit growth or cause sensitive irritations. Although calcium could bind with phosphate in waters and the bottom sediments, and helps suppress the growth of HAB organisms (Song et al. 2010), additional experiments examining changes in pH with the treatments should be followed, and impacts on

flocculation, cell viability, and other in water processes measured. When xanthan and Ca(OH)_2 as modifiers were added, the loading of clays, soils, or sands required for effective cell removal was decreased to 300 mg L^{-1} from 500 to $2,500 \text{ mg L}^{-1}$ previously reported (Yu et al. 1994; Sengco et al. 2001; Sun et al. 2004; Padilla et al. 2010). Compared with the lower loading of 120 mg L^{-1} sand modified with 10 mg L^{-1} PAC and 10 mg L^{-1} chitosan reached in recent study (Pan et al. 2011a), the loading of clay/soil/sand and modifiers in this method might be further reduced and still be effective. The removal efficiencies in different conditions, i.e., different cell densities, growth phase, other marine species etc., also need to be tested. Moreover, algal floc formation, sedimentation, and deposition would likely affect other planktonic species and benthonic organisms (Shumway et al. 2003). Further studies are needed to address these issues before large-scale applications can be undertaken. Although more experiments are needed, costs for field use at the concentrations found in this study can be estimated. With the ratios of clay, xanthan, and calcium hydroxide found most effective for removing *A. carterae*, i.e., 20 mg L^{-1} xanthan: 100 mg L^{-1} Ca(OH)_2 : 300 mg L^{-1} clays, approximate costs for a 1-ha area (cleared to a depth of 1 m) would be \$900, based on incremental costs for xanthan and Ca(OH)_2 of \$750 and \$100, respectively. This compares to costs like \$400 and \$1,400 reported for other mitigation techniques (Sun et al. 2004; Pan et al. 2011b).

In conclusion, this study explored a modification of previously detailed flocculation techniques, a method using clay/soil/sand modified with xanthan and calcium hydroxide for algal bloom mitigation in marine systems. The method would reduce potential economical and environmental impacts by using appropriate local soils/sands and xanthan, but further research before large scale application to marine blooms can be considered.

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