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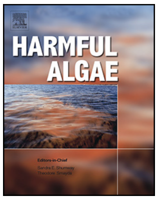

Mitigation of harmful algal blooms using modified clays: Theory, mechanisms, and applications

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ABSTRACT

Clay dispersal is one of only a few mitigation methods for harmful algal blooms (HABs) ever applied in the field; however, low flocculation efficiency has always been the most significant drawback associated with natural unmodified clays. This review discusses key factors affecting the flocculation efficiency, based on results obtained in studies of the mechanisms underlying interactions between clay particles and HAB organisms. It further elaborates clay surface modification theory and methods for improving removal efficiency of HAB cells, followed by descriptions of various modified clays successfully prepared with removal efficiencies of HAB cells that are up to hundreds of times greater than natural clays and have lower dosing requirements of 4–10 t/km^2. Presently, modified clays are the most widely used method for the mitigation of HAB in the field in China. This review also evaluates potential ecological effects of modified clay disposal on water quality, typical aquatic organisms, benthic environments, and ecosystems. Both laboratory and field results have demonstrated that modified clays markedly can actually improve water quality after treatment and pose no negative effects on aquatic ecosystems.

1. Introduction

Harmful algal blooms (HABs) are a global marine disaster and their prevalence is increasing worldwide with the intensification of human activities. These HAB are not only capable of destroying marine ecosystems and impacting human health, but also threatening the safety of many industries using ambient seawaters (e.g. coastal nuclear power plants). Anderson (1997) proposed that one day the disaster would be stopped. Indeed, there is need to develop effective methods and technologies to control HAB in order to deal with their unexpected and extensive impacts that may compromise the safety of marine ecosystems, human health, and nuclear power plants.

Technically, many methods can be used to control HAB as long as they are capable of killing the HAB organisms and inhibiting bloom formation. These methods can be classified as chemical (Cao and Yu, 2003; Divakaran and Sivasankara Pillai, 2002; Li et al., 2014; Ma and Liu, 2002; Marvin, 1964; Rounsefell and Evans, 1958; Sun et al., 2004a, 2004b; Yu et al., 1993), physical (Kim, 2006; Shirota, 1989),or biological methods (Doucette, 1995; Kodama et al., 2006; Marcoval et al., 2013; Tang et al., 2015; Wang et al., 2006; Wang and Yu, 2005; Yang et al., 2015; Zhang et al., 2008). Most methods, however, have limited application due to negative ecological impacts, high costs, or poor maneuverability in the field. As a result, very few methods can be applied on a large scale in the field.

In the late 1970s, mitigation of HAB using clays was studied and applied to Kagoshima coastal waters, Japan (Imai et al., 2006; Shirota, 1989; Yu et al., 1993). As the basic component of soil, clays have several advantages, they do not cause pollution, involve low cost, and are convenient to use in the field. As such, the clay disposal method immediately garnered widespread interest (Anderson, 1997; Beaulieu et al., 2005; Kim, 2006; Park et al., 2013; Sengco and Anderson, 2004; Sengco et al., 2001; Yu et al., 1994a). Currently, it has been one of only a few HAB mitigation methods applied in the field (Anderson et al., 2001; Kim, 2006; Yu et al., 1993; Getchis and Shumway, 2017). Nevertheless, natural clays have low flocculating efficiency, which is the most serious drawback that often leads to the requirement of an exorbitant

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amount of clays to achieve an effective efficiency in the field. As a result, this leads to increased ecological impact, higher cost and greater logistic challenges. For instance, it was reported that the clay dosage in aquaculture sites in Japan was 110–400 t/km^2 (Shirota, 1989), and the loess dosage used in the control of *Cochlodinium polykrikoides* blooms in Korea was 384 t/km^2 (Anderson et al., 2001). Thus, low removal efficiency, high dosage, and large deposition loads on the sediments serve as the bottleneck of the clay method when applied in the field (Sengco et al., 2001; Yu et al., 2004; Getchis and Shumway, 2017).

Numerous studies on improving the removal efficiency of clays have been performed (Lee et al., 2008; Liu et al., 2010; Maruyama et al., 1987; Miao et al., 2014; Sengco et al., 2001; Sun et al., 2004a, b; Yu et al., 1994c, 1999). In the 1990s, the interaction between clay particles and HAB organisms was intensely studied by Yu and coworkers (see Yu and Zou, 1994; Yu et al., 1994a,b,c, 1995b) who determined the key factors controlling the flocculation efficiency of clays. Clay surface modification theory and methods for improving removal efficiency of HAB cells have been proposed. Various modified clays have been prepared with the removal efficiencies that are dozens to hundreds of times greater than unmodified natural clays, and the resulting dosing requirement decreased to 4–10 t/km^2. Presently, modified clays are the most widely used method for the mitigation of HAB in China.

Table 1
Zeta potentials of some kinds of marine phytoplankton (Sengco, 2001).

Class	Organism	Zeta Potential (mV)
Bacillariophyceae	*Skeletonema costatum*	−7.6
	Thalassiosira weisflogii	−3.0
	Chaetoceros simplex	−2.5
Chrysophyceae	*Aureococcus anophagefferens*	−5.6
	Pavlova lutheri	−16.5
Chlorophyceae	*Tetraselmis chui*	−7.5
	Chlamydomonas sp.	−13.6
	Dunaliella salina	−11.0
	Prasinocladus marinus	−24.1
Coccolithophyceae	*Cricosphaera carterae*	−13.8
Oyptophyceae	*Rhodomonas lens*	−13.9
	Rhodomonas salina	−13.2
Dinophyceae	*Heterocapsa triquetra*	−5.3
	Prorocentrum micans	−7.7
	Prorocentrum minimum	−12.4
	Alexandrium tamarensis	−4.5
	Karenia brevis	−5.8
	Karenia mikimotoi	−3.6

2. Theory and methods of clay surface modification

2.1. Theory

The clay modification theory originated from HAB flocculation experiments by Yu et al. (Yu and Zou 1994; Yu et al., 1994a, 1995b), who found that the HAB organism removal efficiencies of clays depended on clay structure and type. The authors reported that certain types of kaolinites had better removal efficiencies, which did not agree with the traditionally believed notion that montmorillonite has the best removal efficiency. To prove this new experimental result theoretically, Yu et al. (1994a,b, 1995c) applied the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin et al., 1987) to the control of HAB using clay for the first time, and studied the interaction between HAB cells and clay particles, which could be described as electrostatic repulsion (V_R) and Van der Waals attraction (V_A) as follows:

$$V = V_R + V_A \tag{1}$$

$$V_R = \frac{\varepsilon r_a r_b(\psi_a^2 + \psi_b^2)}{4(r_a + r_b)}\left[\frac{2\psi_a\psi_b}{\psi_a^2 + \psi_b^2}\ln\left(\frac{1 + \exp(-\kappa H_0)}{1 - \exp(-\kappa H_0)}\right)\right.$$
$$\left. + \ln(1 - \exp(-2\kappa H_0))\right]$$

$$V_A = A\iint\frac{d\nu_1 d\nu_2}{L^6} \tag{3}$$

V denotes the flocculation interaction between HAB cells and clay particles, which can be divided into V_R and V_A; a and b denote the clay particles and HAB cells, respectively; r_i and ψ_i denote the radius and surface potential of particle "i"; ε denotes dielectric permittivity; κ denotes the reciprocal of Debye–Hückal length; H_0 denotes the distance between the interacting particles; L denotes the distance between particles; A denotes Hamaker constant; and ν denotes the volume of clay particles or HAB cells.

Kaolinites and montmorillonites are both layer-structured; kaolinites have two layers (-Al-Si-) while montmorillonites have three layers (-Si-Al-Si-). Natural clay minerals are electronegative due to surface hydration and lattice defects in seawater, and the surface negative charges of montmorillonites are stronger than those of kaolinites. The surface charges of HAB cells in seawater are also electronegative as shown in Table 1 (Sengco, 2001; Rosa et al., 2017). The repulsive forces between clay particles and HAB cells reduce the flocculation efficiencies of natural clays, and to an even greater extent for montmorillonites (Yu and Zou, 1994) compared with kaolinites. Furthermore, the analysis of V_A also suggested that flocculation efficiencies were related to factors such as particle size, shape, and distance and kaolinites have stronger V_A than montmorillonites (Yu et al., 1994b, 1995b).

The aforementioned theory not only explained the experimental result that flocculation of kaolinites is stronger than that of montmorillonites, but also revealed that the surface properties of clay particles are critical factors controlling flocculation efficiencies. Based on this theory, suppose that the surface of clay particles is modified using the positively charged modifier M^{Z+}, the clay surface potential would be altered as follows (Yu et al., 1994c):

$$\psi_a = \frac{F}{A\times C}\left[\{\equiv S - OH_2^+\} - \{\equiv S - O^-\} + \sum_{i=1}^{Z}(Z-i)\left\{(\equiv S - O)_i M^{Z-i}\right\}\right] \tag{4}$$

where ψ_a denotes the surface potential of the modified clay particles, F denotes faraday constant, A denotes the total surface area of clay particles (m^2/L), C denotes surface capacitance, $\{\equiv S-\}$ denotes concentrations of surface functional groups, and Z denotes the chemical valence of modifier M.

According to Eq. (4), the surface charge of clay particles changes from negative to positive with increasing M^{Z+} concentration, and the interaction (V_R) gradually converts from electrostatic repulsion to electrostatic attraction (Fig. 1). This indicates, in theory, that surface modification of clay particles can improve flocculation between HAB cells and the clay particles. Further, the length of the modifier molecular chain can also affect the V_A, and an appropriate chain length will reduce the distance between the clay particles and HAB cells (i.e. bridge effect), contributing to an improvement in flocculation efficiencies according to Eq. (3). The validity of the theory has been proved by a series of additional studies from Yu et al. (1994c) that used the polyaluminum chlorides (PACS) to