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Controlling harmful algae blooms using aluminum-modified clay

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ABSTRACT

The performances of aluminum chloride modified clay (AC-MC), aluminum sulfate modified clay (AS-MC) and polyaluminum chloride modified clay (PAC-MC) in the removal of *Aureococcus anophagefferens* were compared, and the potential mechanisms were analyzed according to the dispersion medium, suspension pH and clay surface charges. The results showed that AC-MC and AS-MC had better efficiencies in removing *A. anophagefferens* than PAC-MC. The removal mechanisms of the three modified clays varied. At optimal coagulation conditions, the hydrolysates of AC and AS were mainly monomers, and they transformed into $Al(OH)_{3(am)}$ upon their addition to algae culture, with the primary mechanism being sweep flocculation. The PAC mainly hydrolyzed to the polyaluminum compounds, which remained stable when added to the algae culture, and the flocculation mainly occurred through polyaluminum compounds. The suspension pH significantly influenced the aluminum hydrolysate and affected the flocculation between the modified clay and algae cells.

1. Introduction

The frequency, intensity, and geographic extent of harmful algae blooms (HABs) have increased worldwide in recent years and caused profound and deleterious effects on aquatic ecosystems, aquaculture, tourism and public health (e.g., Anderson et al., 2012; Liu et al., 2013; Al Shehhi et al., 2014), which has increased the focus on developing effective, environmentally friendly and relatively inexpensive methods of controlling HABs. The control of HABs and the mitigation of their effects using clay is a promising method worldwide (e.g., Shirota, 1989; Yu et al., 1994a; Anderson, 1997; Sengco and Anderson, 2004; Kim, 2006), and it has been fully implemented in the field, with good results reported in Japan, South Korea and China (Shirota, 1989; Sengco and Anderson, 2004; Lee et al., 2008; Song et al., 2010). However, unmodified clay was inefficient in the removal of algae cells, and such processes require a large amount of clay (Sengco et al., 2001; Yu et al., 2004), which complicates field applications; in addition, the high loads of clay may cause ecological concerns (Lee et al., 2008; Orizar et al., 2013). Thus, research has been conducted to increase the removal efficiency and reduce the amount of clay required for removal. Maruyama et al. (1987) found that inorganic acid-treated clay improved the removal efficiency, and Yu et al. (1994c) used polyaluminum chloride (PAC) to modify the clay surface and subsequently proposed the clay surface modification theory (Yu et al., 1994a, 1994b, 1994c, 1995). A number of materials and methods used to modify clay surfaces have improved the HAB removal efficiency (e.g., Yu et al., 1994c, 1999; Sengco et al., 2001; Sun et al., 2004a; Sun et al., 2004b; Pierce et al., 2004; Lee et al., 2008; Liu et al., 2010), and researches related to HAB control have focused on screening for more cost-effective clay modification materials and methods and exploring the corresponding removal mechanisms (e.g., Sun et al., 2004a).

Aluminum chloride (AC), aluminum sulfate (AS) and PAC (e.g., Yu et al., 1994c; Sengco et al., 2001; Pierce et al., 2004; Sengco et al., 2005; Hagström and Granéli, 2005; Pan et al., 2011) can be used to increase HAB removal efficiency. The differences in the molecular structure and properties of these compounds could lead to significant differences in the modified clay suspension, which would influence the removal efficiency. Previous studies have shown that the removal efficiency of PAC-MC prepared with seawater (SW) was substantially lower than that with deionized water (DW) (Sengco et al., 2001; Yu et al., 2004), and the sulfate in the suspension was found to be an important factor. However, the difference between the removal efficiencies of AC-MC or AS-MC prepared by DW and SW is still unclear. In addition, few studies have compared the removal efficiencies of the three aluminum-modified clays. Comparisons of the removal efficiency of each modified clay suspension prepared using different dispersion mediums may contribute to a better understanding of the flocculation mechanisms and optimum application conditions in the field.

Brown tide is a type of HAB caused by the picophytoplankton *Aureococcus anophagefferens*, and such phenomena have occurred in the United States (1985) (Sieburth et al., 1988), South Africa (1997) (Probyn et al., 2001) and China (2009) (Zhang et al., 2012). Since the first report of brown tide, this algae has continuously bloomed in

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Hebei Province coastal waters and caused significant ecological and economic losses. In 2011, a southward trend in brown tide was observed, and HABs were observed in Yantai coastal waters, Shandong Province. Previous studies indicated that clay showed little removal efficiency because of its small size and high density (Sengco et al., 2001; Yu et al., 2004). The wide distribution of *A. anophagefferens* from the surface to the bottom also increased the difficulty in controlling brown tide. Therefore, studies seeking more effective control methods have received great attention.

Based on the results of the cited studies, we compared the ability of three types of aluminum-modified clay to remove *A. anophagefferens* and drew contour diagrams of the modified clay surface charge and removal efficiency (alum dosage versus suspension pH). The potential mechanisms underlying the efficiency of each modified clay were analyzed from the suspension pH, clay particle surface charge and alum hydrolysis products. A uniform algae flocculation mechanism model was developed for the three modified clays, and the relationships among the alum dosage; modified clay surface charge in the clay suspension, algae culture and clay-algae flocs; and the removal efficiency (%) were established. The differences in the ability of each modified clay to remove freshwater and seawater HABs and the practical implications of increasing the removal efficiency were also discussed.

2. Materials and methods

2.1. Algae culture and clay preparation

An *A. anophagefferens* (CCMP 1984) culture was bought from the US National Center for Marine Algae and Microbiota (East Boothbay, ME, USA). Each *A. anophagefferens* cell was approximately 2 μm to 3 μm in diameter and unable to move freely. The algae was cultured in L1 culture medium (Guillard and Hargraves, 1993) at 20 ± 1 °C under a light intensity of approximately 60–65 μmol photons m^{-2} S^{-1} and a 14:10 light:dark cycle. The growth of the cultured algae was monitored by measuring the fluorescence using a TD-700 fluorometer (Turner Designs, Sunnyvale, CA, USA), and the measurement method was calibrated by counting cells in a blood cell counting chamber. The algae removal experiments were performed using cultures in the mid-to-late exponential growth phase, with cell densities of 8.0×10^9 cells/L to 11.0×10^9 cells/L.

The clay used in this experiment was collected from Jiangsu Province, China, and it showed a relatively high removal efficiency for *A. anophagefferens* in a previous study (Zhang et al., 2013). The reagents used in this experiment were all of analytical grade. The AC and AS were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China), and the PAC was obtained from Guangfu Fine Chemical (Tianjin, China), and the Al_2O_3 contents were 20.42%, 15.22% and 28.59%, respectively, as measured by the zinc chloride standard solution titration method. The modified clay was prepared as described by Yu et al. (1994c). The DW was obtained from a Milli-Q water purification system (Millipore, Billerica, MA, USA). The SW was collected offshore at Qingdao, China and then passed through 0.45 μm membrane filter (Whatman, Buckinghamshire, UK) to remove the particulate matter.

2.2. Comparison of the removal efficiencies of the three types of aluminum-modified clay

The removal efficiency of the three aluminum-modified clays at the same alum dosage was determined. The modified clay suspension was prepared using DW and SW, with the clay concentration in suspension at 25 g/L and the alum concentration at 2.85×10^{-2} mol/L. A predetermined clay dosage was added to the algae culture, and the removal efficiency was determined at 0.10 g/L clay, 0.25 g/L clay, 0.50 g/L clay, 1.0 g/L clay, 1.5 g/L clay and 2.0 g/L clay. The removal experiments were run in triplicate. The zeta charges (Zetasizer Nano ZS, Malvern Instruments, Malvern, UK) of the clay particles and the pH values of the clay suspensions were also determined.

2.3. Effects of dispersion medium and suspension pH on the removal efficiency of the three types of aluminum-modified clay

The effects of the pH of the three modified clay suspensions (prepared with DW or SW) on the efficiency at which *A. anophagefferens* was removed was determined. Modified clay suspensions containing the same alum dosage were prepared with DW and SW. The clay concentration in the suspension was 25 g/L, and the total alum was 2.85×10^{-2} mol/L. The pH of the clay suspension was adjusted to 3, 5, 7, 9, or 11 by adding aqueous HCl or NaOH. The pH obtained at this stage was within ±0.05 of the target pH. The clay particles continued exchanging ions with the dispersion medium; therefore, the pH values were measured and recorded before the removal experiments. The pH adjustment was repeated if the final pH was far from the target pH, and 0.10 g/L clay and 0.20 g/L clay were added to the algae culture to test its removal efficiency. The removal experiments were run in triplicate. The zeta potentials of the clay particles at various pH conditions were also measured (Zetasizer Nano ZS, Malvern Instruments).

2.4. Removal efficiencies of the three modified clay at different alum dosages

Removal efficiency diagrams at different pH values and alum dosages of the three aluminum-modified clays were drawn. The clay concentration in the suspensions was 25 g/L, and the tested concentrations of Al were 7.14×10^{-3} mol/L, 1.43×10^{-2} mol/L, 2.85×10^{-2} mol/L, 4.28×10^{-2} mol/L and 5.71×10^{-2} mol/L. The target pH values in this experiment were 3, 5, 7, 9 and 11, and the pH adjustment method was as described in Section 1.3. pH adjustments were repeated if the final pH was far from the target pH. The removal experiments were conducted at a clay concentration of 0.25 g/L and run in triplicate. The zeta potentials of the clay particles at different pH conditions were also measured (Zetasizer Nano ZS, Malvern Instruments).

2.5. Measurements of the removal efficiency, clay surface potential and pH

Each removal experiment was conducted in a 50 mL test tube at 20 ± 1 °C. A 50 mL aliquot of the algae culture in the mid-to-late exponential growth phase was placed in the tube, and the required amount of the modified clay suspension was added, with the mixture briefly shaken by hand until the clay was thoroughly dispersed. The tubes were placed in racks and allowed to stand for 3 h under the culture conditions described above. A 45 mL aliquot of the upper layer of the algae culture was then transferred to another tube to measure the fluorescence of the culture (TD-700 fluorometer, Turner Designs). Each experiment was performed in triplicate. The removal efficiencies were later presented as the mean ± standard deviation. The differences between the mean removal efficiencies were tested for statistical significance using the unpaired Student's t-test. The statistical analysis was performed using SPSS 13.0 software (IBM, Armonk, NY, USA).

The cell removal efficiency was calculated using the following equation:

$$\text{Removal efficiency }(\%) = [1-(\text{final fluorescence of treatment} \div \text{final fluorescence of control})] \times 100\%,$$

where the final fluorescence of the control was used to account for cell sinkage.

The pH values were measured using a LEICI PHS-3C digital pH meter (INESA Scientific Instrument Co., Ltd., Shanghai, China). The unit was calibrated at the beginning of each testing day using a commercially prepared buffer.