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Chunguang Miao[a], Yi Tang[a], Hong Zhang[a], Zhengyan Wu[a] & Xiangqin Wang[a]
[a] Key Laboratory of Ion Beam Bioengineering, Hefei Institutes of Physical Science, Chinese Academy of Science, Hefei, Anhui 230031, People's Republic of China
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Harmful algae blooms removal from fresh water with modified vermiculite

Chunguang Miao, Yi Tang, Hong Zhang, Zhengyan Wu* and Xiangqin Wang*

Key Laboratory of Ion Beam Bioengineering, Hefei Institutes of Physical Science, Chinese Academy of Science, Hefei, Anhui 230031, People's Republic of China

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Vermiculite and vermiculite modified with hydrochloric acid were investigated to evaluate their flocculation efficiencies in freshwater containing harmful algae blooms (HABs) (*Microcystis aeruginosa*). Scanning electron microscope, Fourier transform infrared spectroscopy, X-ray diffraction, converted fluorescence microscope, plasma-atomic emission spectrometry, and Zetasizer were used to study the flocculation mechanism of modified vermiculite. It was found that the vermiculite modified with hydrochloric acid could coagulate algae cells through charge neutralization, chemical bridging, and netting effect. The experimental results show that the efficiency of flocculation can be notably improved by modified vermiculite. Ninety-eight per cent of algae cells in algae solution could be removed within 10 min after the addition of modified vermiculite clay. The method that removal of HABs with modified vermiculite is economical with high efficiency, and more research is needed to assess their ecological impacts before using in practical application.

Keywords: harmful algal blooms; vermiculite; modified; flocculation; mechanism

1. Introduction

Over the last several decades, harmful algae blooms (HABs) frequently occurred all over the world, causing great damages to aquatic life, human health, local tourism, and coastal aesthetics.[1,2] Algae grow very quickly under high nutrient environment, but the algae cells are short-lived, and the result is a high concentration of dead algae cells which start to decay. The decay process consumes dissolved oxygen in the water body, resulting in hypoxic conditions. Without sufficient dissolved oxygen in the water body, fish and other aquatic animals may die off in large numbers. The species of HABs are very broad, but HABs have one unique characteristic in common, they cause harm to other organisms, either due to their production of toxins or accumulated biomass affecting organisms and food webs. *Microcystis aeruginosa* is a unicellular freshwater cyanobacteria which often forms HABs during warmer months (June–October) in eutrophic lakes. Microcystins, a group of cyclic peptides toxins are produced by *M. aeruginosa*, are potent hepatotoxins for animals and humans. To reduce the impacts of harmful algal blooms in environment, management strategies of harmful algae are needed. Those strategies will reduce the impacts of HABs: (1) prevention: reduce the incidence and extent of HABs before they begin; (2) mitigation: when a bloom is present, minimizing HABs impacts on resources and human health; and (3) control: during an outbreak, directly target and attack the algae blooms.[3] Examples of control strategies might be the direct application of chemical flocculation, biological, ultrasonics, ozonation, and clay flocculation that destroy HAB cells during blooms.[4–7] In this study, vermiculite clay was modified with hydrochloric acid to explore a new algaecide for controlling HABs.

Vermiculite is a magnesium silicate mineral with various amounts of iron and aluminium, which is chemically similar to mica and montmorillonite.[8] Vermiculite has positive charge, which is mainly caused by tetrahedral substitution of Al and Fe(III) for Si, and is generally enhanced by the presence of some interlayer cations. Thus, vermiculite is a great adsorbent.[9,10] Vermiculite is very abundant in China, which has mostly been used for building materials, soil amendments, and adsorbent material.[9,11] but it is seldom used in HABs control in freshwater. The general goal of this study is to evaluate the efficiency of vermiculate clay modification with hydrochloric acid as a new algaecide for controlling HABs. Specifically, we determined the flocculation mechanisms of modified vermiculite on the freshwater cyanobacteria *M. aeruginosa* using scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectrometer, X-ray diffraction (XRD) analysis, converted fluorescence microscope, plasma-atomic emission spectrometry, and Zetasizer.

*Corresponding authors. Emails: zywu@ipp.ac.cn, xqwang@ipp.ac.cn

2. Materials and methods

2.1. M. aeruginosa culture

The microcystin-producing strain *M. aeruginosa* FACHB 905 used in our experiment was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences. *M. aeruginosa* cells are about 2–3 μm in size, which were cultured in BG11 medium at 25 ± 1°C under mechanical illumination of ∼90 mmol photons m^{-2} s^{-1} with a photoperiod cycle of 12 h light and 12 h dark.[12]

2.2. Modified vermiculite preparation

The vermiculite used in this study was obtained from Anhui Mingguang Minerals Co., Ltd., China, with a particle size ≤106 μm (150-mesh) and a purity of above 90%, which was modified by 12 and 6 M hydrochloric acid in a ceramic pot. Vermiculite was mixed with hydrochloric acid in a ceramic pot and exposed to air for 24 h. Then the samples were dried at 70°C to evaporate hydrochloric acid and water thoroughly. The modified vermiculite was designated as 6VE and 12VE for 6 and 12 M HCl-treated, respectively, and the non-treated vermiculite as VE.

2.3. Morphological characterization

SEM (FEI-Sirion 200, USA) was used to observe the morphology of VE, 12VE, and the flocs from the flocculation experiment. VE, 12VE, and acid-soluble material washed from 12VE were placed on glass slides about 1 cm^2 and dried in air. Small amounts of flocs from flocculation were simply placed on glass slides using a pipettor and air dried to avoid damaging the flocs structure at room temperature. The morphology of samples was observed at 5 kV after a 90-s gold spraying.

About 100 μL of algae solution and flocs were placed on the glass slides, and dried in 50°C. Converted fluorescence microscope analysis (Olympus-IX71, Japan) was used to observe the morphology of algae cells and flocs.

2.4. XRD and FTIR analyses

XRD patterns of VE, 12VE, and 6VE were determined with X-ray diffractometer (Philips-X'Pert, the Netherlands). The samples were flattened on a glass pane, and the patterns were recorded in the reflection mode from $2\theta = 0$–$40°$, with a scanning speed and step size of 2/0.05°, respectively.

The FTIR spectrometer (Alpha-T, Bruker) was used to analyse VE, 12VE, and 6VE. The samples were prepared for analysis by mixing 350 mg of KBr approximately with about 1mg of the material and then compressing the mixture to pellets.

2.5. Flocculation experiments

Cells of *M. aeruginosa* used in flocculation experiments were diluted from the original algae solution. Algae solution (400 ml) in a glass beaker (500 ml) with a turbidity of 920 was mixed with 12VE, 6VE, and VE. The doses of 12VE were 50, 75, 100, 125, and 150 mg, and both 6VE and VE were 100 mg. The mixture was stirred at 350 rpm for 2 min, followed by 100rpm for another 1 min at room temperature. Then, the mixture was incubated at room temperature without stirring, which were sampled at 5, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180 min afterwards to measure the turbidity (Tur). The sampling depth was 2 cm under water. Turbidity was measured as absorption spectra using a spectrophotometer (UV-2550, Japan).[13]

2.6. Effective components in the flocculation

Plasma-atomic emission spectrometry (Thermo Fisher Scientific-ICP6300, USA) was used to investigate the effective components in the flocculation process. Algae solution (400 ml) with a turbidity of 920 was mixed with 100 mg 12VE and VE in a glass beaker (500 ml), respectively. The mixture was stirred at 350 rpm for 2 min, followed by 100 rpm for another 1 min. Then, the mixture incubated at room temperature without stirring was sampled at 10, 90, 180 min afterwards to measure the concentration of silica, iron, aluminium, and magnesium. The sampling depth was also 2 cm under water, the following followed this approach.

2.7. Zeta potential analysis

Zetasizer-3000 (Malvern Instruments, UK) was used to study the flocculation mechanism of modified vermiculite. Algae solution (400 ml) with a turbidity of 920 and distilled water (400 ml) were packed in a glass beaker (500 ml) and mixed with 50, 75, 100, 125, and 150 mg 12VE, respectively. The mixture was stirred at 350 rpm for 2 min, followed by 100 rpm for another 1 min. Flocculated after 30 min, sampling for zeta potential test was carried out.[14] All the samples were filtered with a 0.45 μm mixed cellulose esters membrane. Large floc particles were avoided during sampling, which would block the instrument.

3. Results and discussion

3.1. Morphological observations

SEM micrograph of VE is shown in Figure 1(a); vermiculite was distributed in the glass surface with a lamellar structure. As shown in Figure 1(b), the surface of 12VE became rough and the lamellar structure of vermiculite disappeared. As shown in Figure 1(c), some mud-like acid-soluble material washed from the 12VE formed a discontinuous film. As can be seen from Figure 1(d), algae cells were wrapped in a layer of the material. There were some fracture at the edge of algae cells after the flocs dried, and some undissolved vermiculite was present in the upper right corner. Obviously, the film covered on algae cells formed some kind of network structure. The netting was formed due to bridging by the acid-soluble material from 12VE.

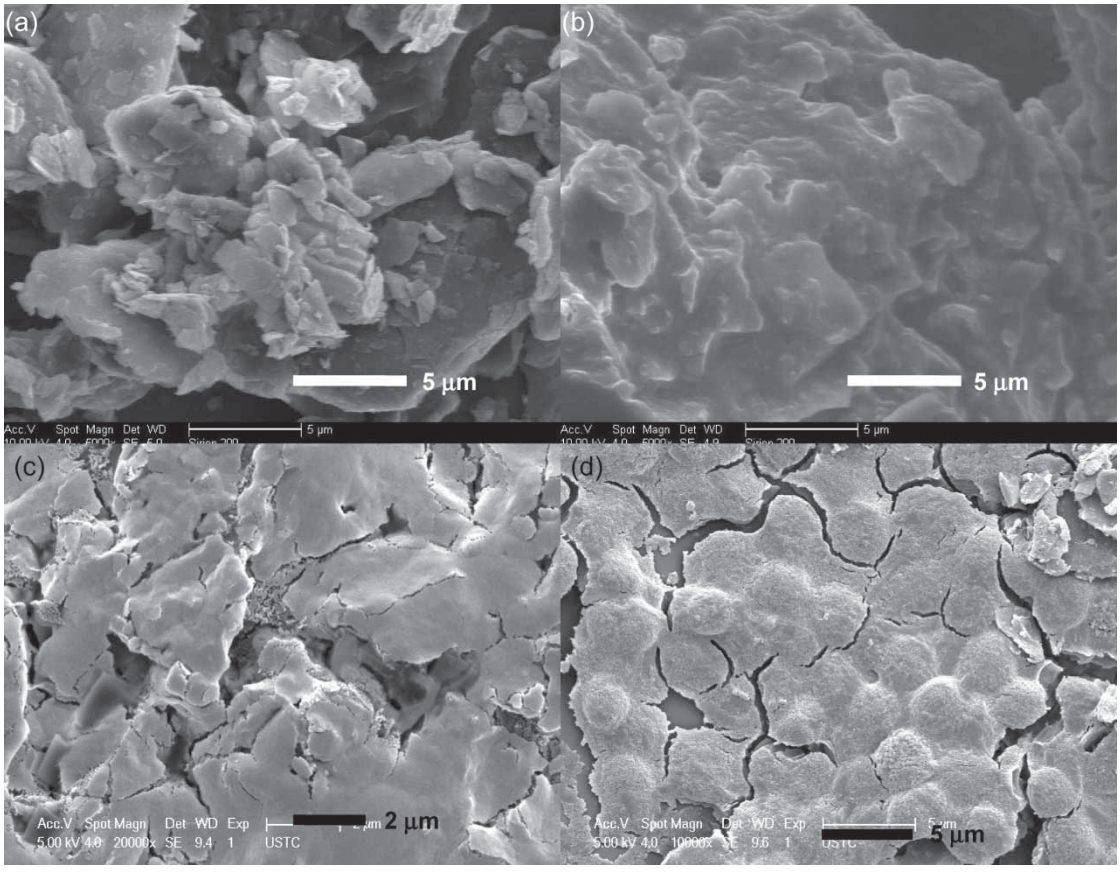

Figure 1. SEM micrographs of VE (5000×) (a); 12VE (5000×) (b); acid-soluble material washed from 12VE (20,000×) (c); and the flocs from flocculation of algae cells and 12VE (10,000×) (d).

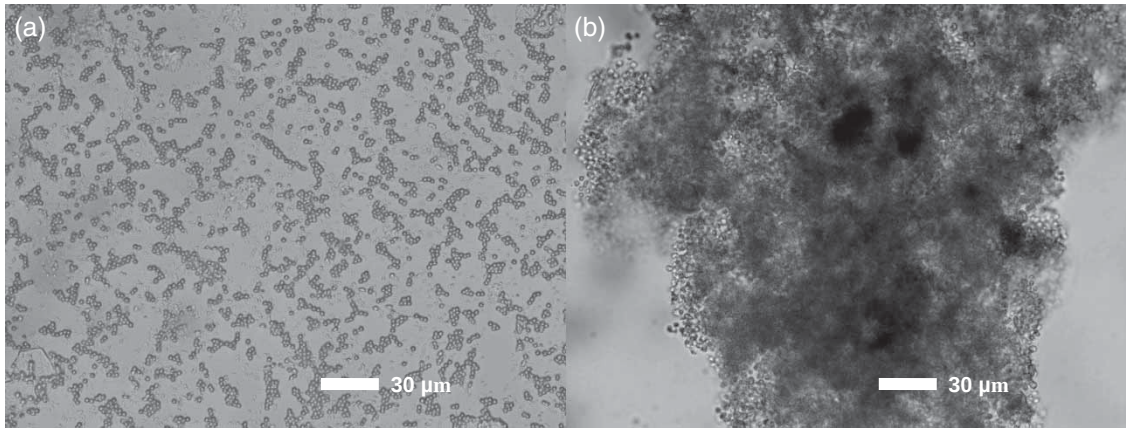

Figure 2. Converted fluorescence microscope images of algae cells (40×) (a) and the flocs (40×) (b) from flocculation of algae cells and 12VE.

The image of algae cells shown in Figure 2(a) was photographed after the sample was dried in air. Flocs was photographed in aqueous solution. As shown in Figure 2(b), cotton-like flocs float in water. The flocculent structure was formed by chemical bridging and netting. Chemical bridging gathered algae cells into groups, then the formation of network structure made the flocs to be steady. Therefore, chemical bridging and netting were the main mechanisms in the flocculation experiment.

3.2. *XRD analyses*

The XRD patterns of vermiculite before and after the acid treatment are shown in Figure 3(a). The peak

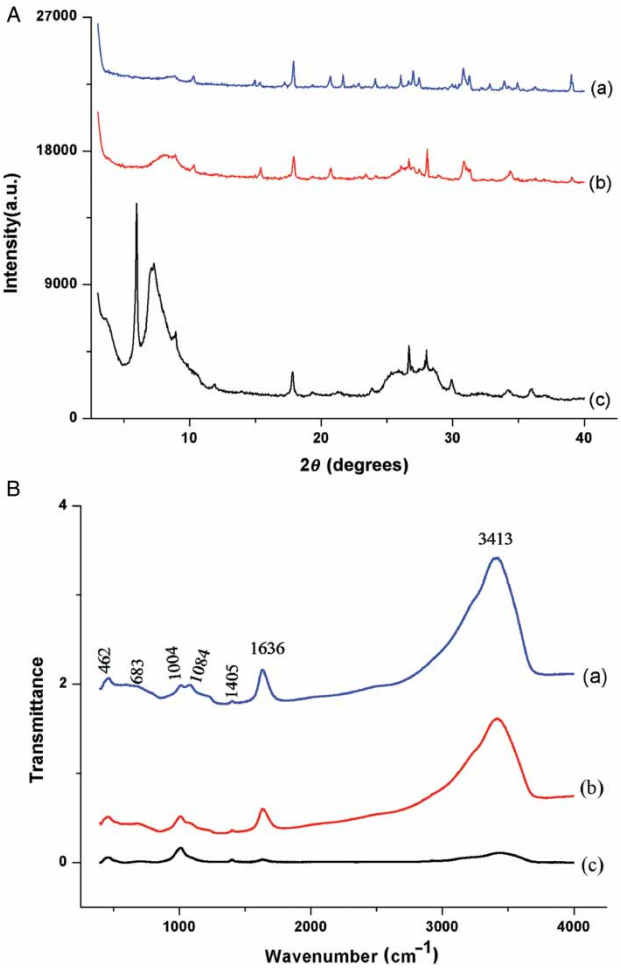

Figure 3. (A) XRD patterns of VE (c), 12M HCl-treated vermiculite (a), and 6M HCl-treated vermiculite (b); (B) FTIR spectra of VE (a), 12VE (c), and 6VE (b).

at $2\theta = 5.95°$ ($d = 1.48$ nm) represented the interlayer spacing of VE. The interlayer spacing of 6VE and 12VE was almost missing after acid treatment. The peaks at 17.8° of VE, 6VE, and 12VE correspond to mica. This suggests that the mica ($AlFeH_2KMgO_2Si$) is more stable to acid treatment than vermiculite. The latter peaks are possibly due to some impurities within vermiculite.[15–17]

3.3. FTIR analysis

As shown in Figure 3(b), the peaks at 462, 683, 1004, and 1084 cm^{-1} were due to Si–O, Al–O, Al–O–H, and Si–O–H vibrations, respectively. The peaks at 1636 and 3413 cm^{-1} were assigned to the –OH stretching vibration of adsorbed water. The peak at 1405 cm^{-1} indicated the existence of N–O in the interlayer of the clay.[17,18] After acid treatment, the FTIR spectrum of vermiculite had some changes as shown in Figure 3(B,b) and 3(B,c), and the intensity of peaks has different reduced ranges, especially in Figure 3(B,c). This indicated that hydrochloric

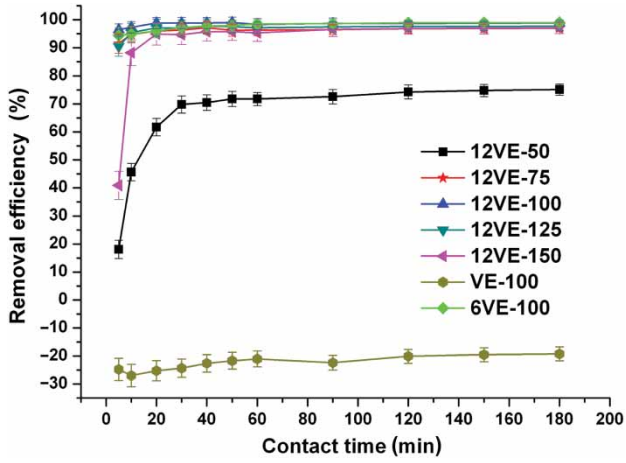

Figure 4. Effect of contact time on removal efficiency of turbidity by VE (100 mg) and 6VE (100 mg), and 12VE (50 mg, 75 mg, 100 mg, 125 mg, and 150 mg, respectively).

acid destroyed the chemical bonds of Si–O, Si–O–Si, and Al–O groups. In addition, the peaks at 1636 and 3413 cm^{-1} were believed to have resulted from the acid treatment process which exposed the hydroxyl groups within the vermiculite. Obviously, high concentrations of acid have more destructive power.

3.4. Flocculation studies

As shown in Figure 4, with the ascending dose from 50 to 150 mg, the removal efficiency of algae cells was enhanced gradually. The dose of 12VE at 100 mg had the optimal removal efficiency. Accordingly, the removal efficiency reached about 90% within 5 min. The removal efficiency of algae cells by 6VE at the dose of 100 mg had a slightly lower removal efficiency than 12VE at 100 mg. Therefore, 6VE might be more cost-effective in practice, because 12VE consumed more acid in the preparation process. As control, the removal efficiency of algae cells by VE (100 mg) was negative. Because the vermiculite in algae solution was suspended after stirring, this could have increase the turbidity of the solution. The pH of the algae solution was 8.3. After the flocculation experiment, the pH of the treated water was 7.3. This change had little effect on water quality. Al ion and Fe ion might form $Al(OH)_3$ and $Fe(OH)_3$ in solution. Cation hydrolysis could cause a decrease in pH.

3.5. Mechanism study

3.5.1. Effective components in the flocculation

The effective components that existed in algae solution before flocculation (a) and effective components in VE and 12VE (b) and the residual content (d) in algae solution after flocculation were measured by plasma-atomic emission spectrometry. The effective components consumed by flocculation (c) at different contact times were calculated

Table 1. The concentration of silica, iron, magnesium, and aluminium existing in the modified vermiculite, treated water after flocculation and consumed by flocculation at 10, 90, and 180 min.

Effective components	Vermiculite	Initial concentration of effective components in algae water (*a*)	Concentration of effective components in vermiculite (*b*)			Concentration of effective components in treated water (*c*)			Concentration of effective components consumed by flocculation (*d*)		
			10 min	90 min	180 min	10 min	90 min	180 min	10 min	90 min	180 min
Fe (mg/L)	12VE	0.0228	10.1200	9.3530	9.6040	0.0175	0.0218	0.0269	10.1253	9.3540	9.5999
	VE	0.0110	0.0739	0.1661	0.0259	0.1482	0.1027	0.1030	−0.0633	0.0744	−0.0661
Al (mg/L)	12VE	0.1142	9.1510	9.6750	10.2100	0.0601	0.0839	0.0936	9.2051	9.7053	10.2306
	VE	0.0673	0.0863	0.2103	0.0354	0.2498	0.2732	0.2977	−0.0962	0.0044	−0.1950
Si (mg/L)	12VE	1.4480	1.3250	1.2790	1.2700	0.1050	0.1630	0.1770	2.6680	2.5640	2.5410
	VE	0.7020	0.1190	0.1560	0.1250	0.8120	0.7600	0.8510	0.0090	0.0980	−0.0240
Mg (mg/L)	12VE	1.2190	5.8020	5.6520	5.5090	6.4920	6.8020	6.7790	0.5290	0.0690	−0.0510
	VE	0.9227	0.1263	0.1503	0.0873	0.7769	0.7569	0.7602	0.2721	0.3161	0.2498

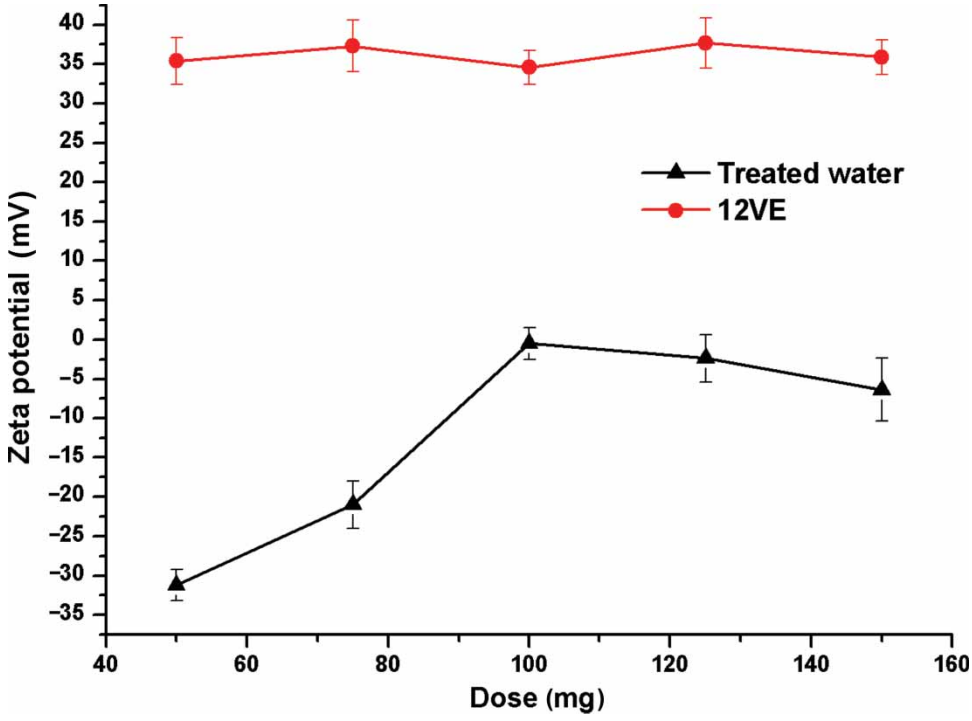

Figure 5. Zeta potential of 12VE and treated water after flocculation.

by the formula: $(c) = (a) + (b) - (d)$.[19] As shown in Table 1, hydrochloric acid dissolved more iron and aluminium, meanwhile less silicon and magnesium from vermiculite. The concentration of iron, silica, and magnesium in 12VE solution reduced over time, but the concentration of aluminium increased gradually. Iron, silica, and magnesium in 12VE were re-adsorbed after being released to the aqueous solution; aluminium was released constantly. Magnesium was effective just 10 min before. As shown in Table 1, as control, the effective components consumed by flocculation experiment used VE almost inappreciably except for magnesium. This agreed well with the results of negative removal efficiency of algae cells by VE. Silica, iron, aluminium, and magnesium were bridges linking algal cells, and coagulating them into flocs.

3.5.2. *Zeta potential analysis*

As shown in Figure 5, the zeta potential of 12VE had a little fluctuation with increased dose. The result indicated that zeta potential of 12VE was fixed at 36 approximately. The initial zeta potential of algae solution without algae cells was −39.7. After flocculation, the zeta potential of treated water increased until the peak at a dose of 100 mg. According to the Derjaguin–Landau–Verwey–Overbeek theory,[20,21] the colloidal system is more stable when the

absolute value of zeta potential is above 30. Colloidal system is unstable when the absolute value of zeta potential is between 10 and 30. If the absolute value dropped to 5 or less, coagulation and flocculation would occur in the colloidal system quickly. Hydrochloric acid dissolved silica, iron, aluminium, and magnesium from vermiculite. The effective components with positive charge mixed with algae solution, which destroyed the electric double layer in the surface of algae cells with negative electricity. Afterwards, the absolute value of zeta potential reduced and the distance between the algal cells diminished. Finally, chemical bridging and netting effect made the algae cells to coagulate. The flocs deposited when the particles were large enough. The bridging and charge neutralization characteristics of effective components were supposed to be the main flocculation mechanism. It made the algal cells to aggregate, and the chemical bridging and netting effect were stronger with the increased dose of 12VE. Finally, the flocculation mechanism of 12VE is summarized, which mainly contains charge neutralization, bridging, and netting mechanisms.

3.6. *Advantages and disadvantages*

The approach that the vermiculite was modified by hydrochloric acid to remove the *M. aeruginosa* cells has several advantages. First, preparation of the modified vermiculite is relatively simple, practically feasible, and cost-effective. Second, after modification with hydrochloric acid, 250 mg/L of modified vermiculite could remove 90% *M. aeruginosa* cells in <5 min. Compared with other algaecide,[19,22–24] it is economical and efficient as previously reported. Last, as a natural component of lake sediments, clay is usually considered as causing fewer environmental impacts than other direct control strategies for HABs, thus this approach is considered to be bio-safe.[19]

However, the flocs settling on lake floor could be one of the main disadvantage in practical application. The sediments are likely to affect other planktonic species in the water body and organisms on the lake floor.[4,5] Some scientists discussed that attack might not be the best form of defense.[25,26] Direct control of HABs through a human-recommended interference might cause more harm to the environment. However, using clay to control HABs may be the best strategy currently when the algae blooms outbreak. Specifically for *M. aeruginosa*, the use of clays could be justified when HABs may contaminate human drinking water sources with toxins, or when the blooms may affect fish farm and kill fish.

4. Conclusions

The addition of modified vermiculite to algae solution was shown to be an effective means for removing HABs. Twelve VE added at a dose of 250 mg/L was observed to remove 98% of algae cells in high concentrations of algae solution while VE had a negative efficiency. The prominent flocculating capacity of 12VE was due to the chemical components such as silica, iron, aluminium, and magnesium released after modification. The studies found that the dominant mechanism was charge neutralization, bridging, and netting, which conferred flocculation process quickly and effectively. These results highlight the effectiveness of the modified vermiculite treatment for decreasing HABs in water body. The clear flocculation mechanism provides a reference for future research. Further work is clearly needed to better understand the impact on aquatic life from flocculant.

Funding

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