Enhanced coagulation for algae removal through the control of zeta potential with diatomite
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ABSTRACT

Advanced technology for more efficient treatment of algae-containing water is always needed. The feasibility of using diatomite for advanced treatment of algae-containing surface water and controlling algae removal process through zeta potential was investigated in this study. Results demonstrated that the addition of diatomite is advantageous due to reduction of the polyaluminium chloride (PAC) dose required for satisfactory treatment of *Microcystis aeruginosa* (MA) and zeta potential which can well reflect the MA removal efficiency. The zeta potential at optimum removal was measured and it was observed that when the zeta potential was reduced to the range of $\pm 14.4$ mV and $\pm 3.53$ mV, removal of MA and associated organic material was optimized. Process control using zeta potential is therefore a viable tool for algae removal by enhanced coagulation combining PAC with diatomite.

Key words | diatomite, *Microcystis aeruginosa*, PAC, zeta potential

INTRODUCTION

*Microcystis aeruginosa* (MA) as one of the dominant species in eutrophic natural water, has been identified a worldwide, significant risk to water supplies when it occur in reservoirs, lakes and rivers used as water sources (Pan et al. 2006). The presence of algae can cause a series of problems for drinking water treatment due to its ability to produce toxins as well as taste and odor compounds, which have greatly deteriorated the water quality and damaged surface waters’ natural functions (Yan et al. 2004, 2005). Furthermore, algae is known to interrupt the drinking water treatment process, causing short filter runs, increases in coagulant demand, and microbial regrowth in distribution systems (Boller & Blaser 1998; Schmidt et al. 1998; Plummer & Edzwald 2001; Chen et al. 2009). Thus it has become one of the top priorities to develop water-bloom control techniques that are safe, highly efficient, cost effective which can remove algae during the initial stages to ensure minimal impact on subsequent processes of drinking water treatment.

Previous studies have used PAC and clay coagulation respectively to remove algae (Beaulieu et al. 2005; Jiang & Kim 2008). However PAC and other chemical reagents may not be environmental friendly or cost effective when used in large quantities, while clay requires a large dosage and a long time for sedimentation. Additionally the flocs formed by traditional coagulation are hard to settle down due to the low density (Henderson et al. 2008a, b). It would be better if harmful algal blooms (HABs)-control technique could be friendly to the ecosystem (Sengco et al. 2001). A very promising way to do this is to use natural, nontoxic and inexpensive clays as coagulant aid so as to reduce the coagulant dose. Diatomite ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) is a siliceous rock available in large deposits around the world (Khraisheh et al. 2004). It has a unique combination of physical and chemical properties, which make it applicable as an adsorbent and a flocculant for pollutants encountered in wastewater (Erdem et al. 2005; Wu et al. 2005). However, such an enhanced coagulation process with PAC, combining diatomite as coagulant aid and adsorbent, has received little prior attention for the removal of algae.

Knowledge of the zeta potential is of importance in evaluating the stability of particle dispersions undergoing particle aggregation and adjusting coagulant dosage levels periodically in order to minimize the cost of chemicals for water purification (Kim & Sansalone 2008). Zeta potential gives a measurement of the apparent surface charge. Reduction in the magnitude of the negative zeta potential
signifies a reduction in the repulsive electrostatic forces and a critical zeta potential can be reached where the attractive van der Waals forces overcome these electrostatic forces and thus particles agglomerate. Given that the coagulation of algae is predominately charge related then the electrical character of the algae is likely to be a key parameter in describing the process. The use of zeta potential for monitoring and controlling the traditional coagulation of algae combining dissolved air flotation has been well researched and found to be of great benefit (Henderson et al. 2008a, b). Yet there have been fewer studies investigating the use of zeta potential for controlling the enhanced coagulation and sedimentation of MA combining PAC and diatomite. In addition, the effects of PAC and diatomite dose, pH, and adding sequence on the removal of MA have not been identified.

The main objective in this study is to evaluate the feasibility of the application of diatomite to enhance the algae removal and assess the applicability of zeta potential for investigating the colloidal stability of MA suspensions and controlling the coagulation when combined with sedimentation.

MATERIALS AND METHODS

Test water

Model water treatment experiments were performed with tap water spiked with Microcystis aeruginosa (MA) cells until a specific concentration of chlorophyll-α (chl-α) was achieved, as already reported by Margarida Ribau Teixeira (Teixeira & Rosa 2006). The chl-α concentration of the culture was determined, a proper volume was added to tap water (the volume rate of the culture to tap water is about 1.1:10) and the resulting suspension was analyzed to verify the chl-α concentration. The model water had following characteristics: pH, 7.5–7.5, turbidity, 20 ± 0.5 NTU, OD_{680} 0.097, and chl-α concentration, 211.1 μg/L.

Reagents

Diatomite was obtained from the Ningbo Daily Chemical Factory of Zhejiang province.

Stock solution of PAC (polyaluminium chloride with containing 29% Al₂O₃, stock solution with 1,200 mg/L Al₂O₃) was prepared in distilled water. In jar-test experiments the coagulant dose varied between 10 and 80 mg/L.

Algae culture

MA was obtained from the FACHB, Institute of Hydrobiology, Chinese Academy of Sciences, and cultivated in axenic BG-11 medium at 24 ± 1 °C under fluorescent light (1,000 lx, 12-h light/12-h dark). The BG-11 medium was composed of 1.5 g/L NaNO₃, 40 mg/L KH₂PO₄, 75 mg/L MgSO₄·7H₂O, 56 mg/L CaCl₂·2H₂O, 6.0 mg/L Citric acid, 6.0 mg/L Ferric ammonium citrate, 1.0 mg/L EDTANa₂, 20 mg/L NaCO₃, 2.86 mg/L H₃BO₃, 1.86 mg/L MnCl₂·4H₂O, 0.22 mg/L ZnSO₄·7H₂O, 0.39 mg/L Na₂MoO₄·2H₂O, 0.08 mg/L CuSO₄·5H₂O and 0.05 mg/L Co(NO₃)₂·6H₂O. It was controlled to pH 7.0 before autoclaving by adding either 0.1 M NaOH or 0.1 M HCl solutions.

Analytical methods

The MA cell concentration was presented by the optical density of the cell suspension at 680 nm (OD_{680}) using a UNIC 2100 spectrophotometer.

For chl-α analysis, samples were filtered through 0.45 μm filter and the chlorophylls were extracted using 10 ml acetone (90%). The optical densities of the extracts were measured at 665 and 750 nm using a UNIC 2100 spectrophotometer and chl-α concentration was computed from Lorenzen equations (Lorenzen 1967).

Turbidity was measured in a 2100P TURBIDIMETER. pH values were measured at 25 °C using a PHS-3C meter.

The zeta potential measurements in this study utilized a zeta meter (Zetasizer Nano ZS90, Malvern Instruments, UK), which measures the zeta potential using a combination of the measurement techniques: Electrophoresis and Laser Doppler Velocimetry. Samples were injected slowly into the zeta meter and all zeta potential results were obtained in triplicate to calculate an average value. The zeta potentials of algae flocs were measured at the end of the rapid mix section.

Dissolved organic carbon (DOC) was analyzed by a TOC Analyzer (Liqui TOC, GER) after filtration through 0.45 μm membrane, and the filtration was carried out immediately after the sample was taken.

Jar-test experiments

Jar tests were performed on algal suspensions at room temperature (about 20 °C), using a six-paddle stirrer (ZR4-6, CHN). Each 0.4 L sample was dosed with a predetermined concentration of diatomite and alum from a diatomite and
a PAC stock solution. It was slowly mixed for 2 min at 50 rpm, then rapidly mixed for 2 min at 200 rpm, followed by a slow mixing for 10 min at 50 rpm, and at last a quiet settling of 30 min. Diatomite was added before PAC besides the addition sequence experiment. At the end of the settling period, the supernatant was taken at 3 cm below the water surface to determine the residual algae concentration. The algae suspensions pH was adjusted to 7.5 approximately by adding predetermined amount of either 1 M HCl or 1 M NaOH. The base of the selection of coagulation pH at 7.5 is to simulate the coagulation of natural algae-laden water.

RESULTS AND DISCUSSION

Algae growth phase

The growth of MA generally goes through several stages. During the distinct stages, algae growth capacities are also different. Figure 1 shows the chl-α concentration and zeta potential variation of MA during the culture period.

The chl-α concentration increases according to a standard growth curve, as shown in Figure 1. There were totally four stages of the growth, adaptive phase, exponential phase, stationary phase and death phase. After about 8 days, the exponential phase began, and the chl-α concentration was about $2.2 \times 10^3 \mu g/L$; 16 days later, the stationary phase started, and the death phase came to the end.

The zeta potentials of MA during the four growth phases were also investigated (Figure 1). The values were all negative, which indicated MA cells are negatively charged in ground surface waters. During the cultivation time, the zeta potential almost remained level, fluctuating between $-25.5 \text{ mV}$ and $-37.3 \text{ mV}$. But at the exponential phase, the zeta potential values (absolute value) were relatively larger. It has been postulated that this phenomenon is due to variations in quantity and composition of extracellular organic matter (EOM) attached to the cell surface (Henderson et al. 2008a, b). It is the organic matter present that controls the surface charge as opposed to the cell surface itself.

Owing to previous observations and this study suggesting that growth cycle can affect system zeta potential, attributed to varying concentration and character of algae cells. It was ensured that MA was always harvested at the same stage of growth, selected at the late exponential phase growth. All model water experiments were carried out with cells in the exponential growth stage.

Zeta potential of MA cells and diatomite particles

A zeta potential value on its own without a quoted pH is a virtually meaningless number. The effect of pH on the zeta potential of MA and diatomite samples is presented in Figure 2. When more alkali was added to their suspensions, both algae cells and diatomite particles tended to acquire a more negative charge. For diatomite, when acid was added, a point was reached where the negative charge is neutralized near pH 4.0. Any further addition of acid can cause a build up of positive charge. It shows that both MA cells and diatomite particles are negatively charged in natural surface water so that their interaction mechanism cannot be explained through electrostatic neutralization. Over most of this pH range, the zeta potential of MA was found to be more negative than that of diatomite. The zeta potential of diatomite was found to be a strong function of pH, ranging from $+0.42 \text{ mV}$ at pH $= 4.0$ to $-31.2 \text{ mV}$ at pH $= 10.0$.
Algae removal with PAC

PAC as a pre-polymerized inorganic coagulant contains high positive charge than conventional ones such as aluminium chloride, and strong charge-neutralization and electro-patch coagulation are thought to be the dominant mechanisms for PAC, which explains the better performance of PAC achieved (Wu et al. 2009). Figure 3 shows the variation of chl-a removal and zeta potential as a function of PAC dose. The zeta potential of original suspension was about $-29.4$ mV and the chl-a concentration was 211.1 $\mu$g/L. When the PAC dose was less than 20 mg/L, the zeta potential increased remarkably with the PAC dose, and the chl-a concentration dramatically decreased. However, as the PAC dose was more than 20 mg/L, the zeta potential grew up slightly, but the chl-a removal remained approximately constant attributed to a change in dominating the coagulation mechanism from charge neutralization to sweep flocculation. The point where the plot passes through zero zeta potential is called the isoelectric point and is very important from a practical consideration. It is normally the point where the colloidal system is least stable (Mouchet 1998). When coagulant dose increased to 50 mg/L, zeta potential of flocs formed after coagulation moved from the negative side into the positive side, and it achieved the isoelectric point at the PAC dose between 40 and 50 mg/L. After zeta potential changed to be positive, the chl-a removal started to decrease, thus inferred that there was a potential for utilizing zeta potential for process control. The onset of optimum removal was observed as the zeta potential approached more neutral values. To achieve a good chl-a reduction above 95%, the zeta potential should be controlled between $-1.72$ and $0.993$ mV, with a PAC dose between 30 and 50 mg/L.

Algae treatment combining PAC with diatomite

In order to determine whether diatomite can enhance PAC coagulation, the 10 mg/L, 15 mg/L, and 20 mg/L dose were used at the following research. Figure 4 compares the coagulation performance of combining PAC with different doses of diatomite. It can be observed that flocs produced from coagulation with PAC only were not very dense and showed a tendency to float, giving rise to some final turbidity. MA contains gas vacuoles to aid buoyancy to make its density lower, therefore it is difficult to achieve such large, compact flocs (Henderson et al. 2008a, b). When diatomite was used as a coagulant aid for its high density, the flocs obtained were very coarse and almost completely settled in a short time. For the enhanced coagulation combining PAC with diatomite, greater chl-a reduction was achieved; more than 96% chl-a can be removed at a PAC dose of 15 mg/L and diatomite dose of 40 mg/L, which saves almost 50% of PAC dose. This also demonstrates improved performance than that achieved at a PAC dose of 20 mg/L and diatomite dose of 40 mg/L. Thus the PAC dose of 15 mg/L and diatomite dose of 40 mg/L were used at the following research.

Although difficulties exist in distinguishing the mechanism throughout the aggregation process, some insight can be expected in examining the zeta potential variation and algae removal as a function of coagulants dosage. After diatomite was added, zeta potential showed a slightly decline (Figure 4). With the increase of the dose of diatomite, zeta potential dropped from $-16.3$ mV, $-12.4$ mV and $-5.54$ mV to $-20.2$ mV, $-14.4$ mV and $-12.0$ mV, respectively. It could be seen that the zeta potential was not getting closer to the isoelectric point, while chl-a removal rate gradually

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**Figure 3 |** Effect of PAC dose on chl-a removal and zeta potential. Chl-a initial concentration is 211.1 $\mu$g/L. PAC dose is 10 to 80 mg/L.

**Figure 4 |** Effect of diatomite dose on chl-a removal and zeta potential. Chl-a initial concentration is 211.1 $\mu$g/L. PAC dose is 10, 15, 20 mg/L respectively and diatomite dose is 0–80 mg/L.
increased. Generally, colloidal particles are thought to be coagulated and aggregated through the actions of charge neutralization, patch aggregation, bridge connection and sweep flocculation in series or synchronously (Wu et al. 2009). The variation of zeta potential indicated that by strengthening adsorption-bridge and sweep flocculation, diatomite incorporated the cells into flocs more efficiently, producing settleable flocs of great density, size and strength.

Certain coagulation experiments have taken surface charge into account by measuring the zeta potential when examining conditions for optimal removal. It had been observed that on adjusting the zeta potential of an algal suspension with a specific operational range, removal of algae was significantly improved (Mouchet 1998; Henderson et al. 2008a, b). The range was noted to alter depending on the clarification procedure.

The proper zeta potential interval also changed (Figure 5). To illustrate, optimum removal for MA was observed at zeta potential values less negative than −14.4 mV. Good removal of MA observed at all dosages for which zeta potential values ranged from −14.4 mV to 3.53 mV. It was noted that no decrease in removal efficiency was observed at positive zeta potentials. It is obvious that zeta potential operational ranges may become wider when combining PAC and diatomite as opposed to coagulation with PAC alone.

Effect of pH on enhanced coagulation

The most important factor that affects zeta potential is pH. Adjusting the quantity of acid and alkali to change pH values, which means adding electrolyte into the colloidal solution, will affect the nature of colloidal charged, compressing the electrical double layer, and changing the shape and nature of algae cells in the water, thus affects the zeta potential. Figure 6 showed that the zeta potential kept decreasing when pH values were between 5 and 9. The isoelectric point of this enhanced coagulation was found to occur at pH between 7 and 8. After that, the zeta potential continued to decrease and chl-a removal could keep a very high value. When pH value increased to 8, the chl-a removal increased to 98%, which was the optimum. At that time, the zeta potential was −2.49 mV, not the isoelectric point. This indicated that charge neutralization is an important mechanism for flocculation, but not the only coagulation mechanism; sweep flocculation had also played a great role during the coagulation process.

Overall, optimum removal was obtained irrespective of pH if the zeta potential was maintained between −14.4 mV and 3.53 mV. Secondly, coagulation experiments conducted at pH 5 achieved more positive zeta potential and coincided with a decrease in cell removal. This was attributed to restabilization of the system as a result of the extremes of positive charge which caused electrostatic repulsion (Duan & Gregory 2005).

Effect of addition sequence

The effect of addition sequence of PAC and diatomite was investigated (Figure 7). The addition sequence was found to have a great effect on the algae removal. The better algae removal of the coagulation system was achieved when diatomite was added prior to or at the same time as PAC, giving OD680 residuals of only 0.002 and 0.003, respectively. When diatomite was added after PAC, algae removal was low, due to the loosely flocs. Therefore diatomite should not be added after PAC. The zeta potentials

Figure 5 | Zeta potential operation window for MA removal.

Figure 6 | Effect of pH on enhanced coagulation by PAC and diatomite. CHL-a initial concentration is 211.1 μg/L. PAC dose is 15 mg/L and diatomite dose is 40 mg/L.
with different addition sequence were also measured. The result shows that the algae removal is closely related to the zeta potential. When diatomite was added previously or at the same time with PAC, the zeta potential were $-6.65 \text{ mV}$ and $-9.05 \text{ mV}$, respectively, which were all close to the isoelectric point. However, the zeta potential was $-27.4 \text{ mV}$, far away from the isoelectric point when diatomite was added after PAC. This phenomenon indicates that zeta potential can well reflect the algae removal efficiency and is a good way for process control.

**EOM removal**

Algae systems comprise two major components: cells and EOM (Henderson et al. 2008a, b). EOM is the organic matter present that controls the surface charge as opposed to the cell surface itself (Henderson et al. 2008a, b). Therefore the relationship between EOM residual and zeta potential was studied in this research. By centrifuging the MA suspension for 15 min at 10,000 G, EOM samples were prepared. Initial DOC was adjusted to about 8 mg/L and the residual DOC and zeta potential of each system were analyzed. Diatomite dose adopted was 40 mg/L and differ the PAC addition.

Zeta potential operational window for the EOM of MA is shown in Figure 8. When the DOC values came to zero, zeta potential was in the range of $-14.6 \text{ mV}$ and $+3.98 \text{ mV}$, with DOC values of 0.92 mg/L and 0, respectively. Therefore, while the zeta potential was between $-14.6$ and $+3.98 \text{ mV}$, EOM (measured as DOC) can also be well removed.

A further benefit of using zeta potential as a control method for removal is that it takes into account removal of both components of the algae system: algae cells and EOM. In brief, optimum algae removal was observed between $-14.4 \text{ mV}$ and $+3.53 \text{ mV}$.

**CONCLUSIONS**

The present study confirms that enhanced coagulation combining PAC and diatomite possesses the capacity for removal of MA in surface water. The following are concluded from this study.

Although the total dose of PAC and clay is relatively high in comparison with the doses of PAC coagulation alone, the abundant availability, lower cost, greater algae removal efficiency, together with reduced harmful chemical residuals in the treated water by combining diatomite have demonstrated advantages, and this could provide water industries with an alternative treatment reagent in coping with the problems related to algae.

The result indicated combination of PAC and diatomite is more feasible. They are capable of removing algae over a wider zeta potential range. It was determined that, provided the zeta potential range was kept between $-14.4 \text{ mV}$ and $+3.53 \text{ mV}$, through a combination of coagulant dose and/or pH adjustment as preferred, optimum removal efficiency of both cells and EOM occurred. The zeta potential could also well reflect the algae removal efficiency of different adding sequence of PAC and diatomite. Adding diatomite at the same time or prior to PAC can enhance algae removal.

In brief, the use of zeta potential for process control is a viable tool for enhanced coagulation of algae removal combining PAC and diatomite.
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