Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.1198990

60 (2017) 1–10
January

The performance of several enhanced treatment processes for treatment of algae-containing raw water in typical seasons

Xiaoxiao Li[a,b], Yuejun Zhang[a,*], Xiaolei Zhao[a], Cheng Liu[a]

[a]*School of Chemical Engineering, Nanjing University of Science and Technology, 200 Xiao Ling Wei, Nanjing 210094, China, Tel. +8613605145606; emails: zhyuejun@njust.edu.cn (Y. Zhang), lixiaoxiao33801@sina.com (X. Li), lilyzhao618@163.com (X. Zhao), liuch_1126@yahoo.com.cn (C. Liu)*
[b]*Institute of Applied Technology, Hefei Institutes of Physical Science, CAS, 2221 Changjiang West Road, Hefei 230088, Anhui, China, email: lixiaoxiao33801@sina.com*

Received 19 March 2016; Accepted 29 May 2016

ABSTRACT

The turbidity and algae removal effects of enhanced treatment processes, including the pre-chlorination process and the enhanced coagulation process using composite coagulants composed of poly-aluminum chloride and poly-dimethyldiallyl ammonium chloride (PDMDAAC) for algae-containing raw water in Taihu Lake, were investigated through jar tests in situ in this paper. And the dependence of the treatment effects on both the water quality in the typical seasons and the working mechanism of enhanced processes was analyzed and summarized. The results indicated that the pre-chlorination improved the treatment effect of conventional coagulation process in both the turbidity and algae removal effect for the raw water with the characteristics of high temperature, high algae and organic pollutants content in summer, and it improved also the algae removal effects, but weakened the turbidity removal effects for the raw water with the characteristics of low temperature, low algae content and tiny organic pollutants in winter. However, the enhanced coagulation process using composite coagulants improved even more remarkably the treatment effect of the conventional process using poly-aluminum chloride (PAC) only, for the algae-containing raw water both in summer and in winter. Especially, the improvement extent of the effects of using composite coagulants for algae-containing raw water in summer was more obviously than that in winter due to the characteristics of PDMDAAC and raw water. Besides, the turbidity and algae removal effects of enhanced coagulation process using composite coagulants could not only exceed that of the combined process of pre-chlorination and conventional coagulation using inorganic coagulants, but also indubitably replace the function of pre-chlorination for reducing the risks caused by excessively used chlorine.

Keywords: Algae-containing raw water; Seasonal characteristics; Pre-chlorination; Enhanced coagulation; Composite coagulants; Systemic comparison

1. Introduction

For many years, the problems of eutrophication and algal bloom of freshwater lakes, all over the China and even in some places in the world, have attracted widespread attention and caused great difficulties to the conventional potable water plants [1,2]. There is obvious seasonal variation of algae-containing water quality in freshwater lakes, and the typical seasons are summer and winter in China [3]. The summer is the season for algae bloom; the raw water contains a large amount of suspended particles composed of algae and organic colloids of high electric potential and possesses the characteristics of high temperature and heavy tiny-pollution [4]. In winter, the raw water contains a certain content of algae and organic pollutants and possesses the characteristics of tiny-pollution and low temperature [5]. Both kinds of algae-containing raw water are difficult to treat just relying on the conventional treatment process.

* Corresponding author.

It is well known, the conventional process using inorganic coagulants is no doubt the most economic, safe and effective way applied in both numerous existing and developing potable water plants [6] of using not too serious polluted raw water, and could get satisfactory effect [7]. However, with the more and more serious water pollution, the conventional coagulation process using inorganic coagulants could not meet the requirements of national standards for potable water [8]. To improve the potable water quality, most of the potable water plants located in freshwater lake basin usually employ the enhanced methods, such as selecting high efficient coagulants or combining the pre-chlorination process with the conventional treatment process [9]. Previous studies have showed that for algae-containing raw water, the enhanced coagulation processes using composite coagulants composed of the inorganic coagulants and poly-dimethyldiallyl ammonium chloride (PDMDAAC) with high intrinsic viscosity could demonstrate high turbidity and algae removal effects, and could decrease the inorganic coagulant dose remarkably [10–13]. However, it is very important that the enhanced coagulation processes using composite coagulants should be suitable for the quality of raw water in different or specific season period, in order to obtain satisfactory treatment effect. Unfortunately, there have been few researches discussing the relationship between the raw water quality in the typical seasons and the effects of enhanced treatment processes mentioned above.

Taihu Lake, located in seacoast area of southeastern China, is one of the five largest and most famous freshwater lakes in China. In this paper, the raw water of Taihu Lake was selected as the representative algae-containing raw water, based on annual reports from authorized government agency. And then for the algae-containing raw water of the Taihu Lake in summer and winter, the turbidity and algae removal effects of enhanced treatment methods including the pre-chlorination and the enhanced coagulation using composite coagulants were investigated and compared, systematically, in order to discover some possible relationships between the algae-containing raw water quality in the typical seasons and the effects of enhanced treatment processes and to offer some effectively experiences in practical application.

2. Materials and methods

2.1. Instruments and reagents

Apparatus: Turbidimeter, QZ201, Suzhou Qingan Instruments Co. Ltd., Jiangsu Province, China; six stirring rod combined agitator, TA6-2, Wuhan Henling Technology Co. Ltd., Hubei Province, China; algae count box, Institute of Hydrobiology, Chinese Academy of Sciences, Hubei Province, China; biological microscope, XSP-8C, Shanghai Optical Instruments Factory, Shanghai, China.

Coagulants: PAC with 10.5% Al_2O_3 content (*w*%) and basicity of 75%. PDMDAAC samples were industrial products with 60% content (*w*%) and intrinsic viscosity values $[\eta]$ = 0.55, 1.53, 2.47 and 3.99 dL g^{-1}, respectively.

Preparation of composite coagulants [14]: PDMDAAC samples with different intrinsic viscosity values were dissolved directly in PAC solutions to obtain a series of composite coagulants solutions. The composition of composite coagulants was presented as PAC/PDMDAAC ($[\eta]$ of PDMDAAC/content of PDMDAAC). The content of PDMDAAC in composite coagulants was represented as the mass ratios of PDMDAAC to PAC, which were 5%, 10%, and 20% (*w*/*w*). The composite coagulants were diluted into a certain concentration just before used in jar tests. The doses of PAC and all composite coagulants were calculated based on Al_2O_3 for convenience.

Test raw water: In Wuxi city located in the north coast of the Taihu Lake, the raw water from Meiliang Bay of Taihu Lake was taken as water source polluted by the organic compounds and algae, so it could be seen as a representative of algae-containing raw water. The raw water samples were collected from the water inlet of a potable water plant near Taihu Lake in summer and winter season. The chlorinated raw water for experimental contrast was collected from the pool of chlorinated raw water in the potable water plant during the same period. Chlorine dose for pre-chlorination was about 4.97 mg L^{-1} in summer and 1.44 mg L^{-1} in winter usually used in potable water plant. Table 1 shows the water quality of raw water used in this study.

It could be seen from Table 1 that the raw water and chlorinated raw water samples have the characteristics of high temperature, high algae and organic pollutant content in summer, but have the characteristics of low temperature, contenting algae and tiny-pollution in winter.

2.2. Evaluation of coagulation performance

2.2.1. Jar test and stirring procedures

The standard jar tests were conducted on a program-controlled jar test apparatus. 1.0 L of raw water sample was transferred into each beaker. The predetermined amounts of coagulant were added simultaneously under rapid stirring at 300 rpm for 15 s, and then the following stirring procedures were performed: rapid stirring at 300 rpm for time t_1, middle stirring at 100 rpm for time t_2, slow stirring at 30 rpm for time t_3, and quiescent settling for 30 min. After quiescent settling,

Table 1
Water quality parameters of raw water samples for this study

Season	Pre-chlorination dose (mg·L^{-1})	Temperature (°C)	pH	Turbidity (NTU)	COD_{Mn} (mg·L^{-1})	Algae content (cell·mL^{-1})
Summer	/	28.0–29.0	8.1	32.0–34.0	11.67	3.60–3.70 × 10^4
	4.97	29.0–30.0	7.8	34.0–37.0	10.75	6.20–6.30 × 10^4
Winter	/	5.0–7.0	7.9	30.0–34.0	4.66	1.90–2.10 × 10^4
	1.44	5.0–7.0	7.5	32.0–36.0	5.18	1.70–1.90 × 10^4

the supernatant sample was collected from 2 cm below the water surface for the turbidity and algae content measurements. The stirring time t_1, t_2 and t_3 stimulated the actual production conditions in the potable water plants located in Taihu Lake basin.

The species and content of algae both in raw water and in supernatant were distinguished and counted by using a biology microscope with an algae cell counter. The algae removal rates were calculated according to the Eq. (1).

Algae removal rate (%) = (algae content in raw water – algae content in the supernatant) × 100% / algae content in raw water (1)

2.2.2. Evaluation of treatment effect

Jar tests were carried out by using selected stirring procedures; the residual turbidity and algae removal rate in supernatants using different coagulant doses were measured and compared systematically to investigate their turbidity and algae removal effects.

2.3. Procedures

(1) We collected and analyzed the water quality data of Taihu Lake water samples from the reports issued by Taihu Lake Basin Water Resources Protection Bureau. Then the main characteristics of raw water quality were summarized for further experiments.
(2) PAC was selected for treatment of raw water and chlorinated raw water, in order to investigate the coagulation-aid effect of pre-chlorination. Then the enhanced mechanisms of the pre-chlorination were analyzed and discussed based on the characteristics of pre-chlorination, and the algae species and content in the Taihu Lake raw water in both summer and winter.
(3) The enhanced coagulation effects of using composite coagulants with different content and intrinsic viscosity of PDMDAAC for the Taihu Lake raw water were investigated. Especially, the influence of intrinsic viscosity or content of PDMDAAC in composite coagulants on the enhanced coagulation was analyzed and discussed based on the turbidity and algae removal characteristics of using composite coagulants and the characteristics of raw water quality both in summer and in winter.

The composite coagulants were selected as follows: (1) The PAC/PDMDAAC composite coagulants containing PDMDAAC with the intrinsic viscosity of 2.47 dL g^{-1} and the PDMDAAC content of 5%, 10% and 20% were used for comparison of the content function of PDMDAAC. (2) The PAC/PDMDAAC composite coagulants containing PDMDAAC with the PDMDAAC content of 10% and the intrinsic viscosity of PDMDAAC of 0.55, 1.53, 2.47 and 3.99 dL g^{-1} were used for comparison of the intrinsic viscosity function of PDMDAAC.

Finally, the characteristics of enhanced coagulation process using composite coagulants and pre-chlorination process were investigated and compared systematically, and then the possible relationships between the raw water quality in typical seasons and the effects of enhanced treatment processes could be discovered.

3. Results and discussion

3.1. The Taihu Lake raw water quality in different seasons

The water quality of raw water samples from 33 monitoring points in 9 lake districts of Taihu Lake is monitored monthly by Taihu Lake Basin Water Resources Protection Bureau. Figs. 1 and 2 show the monthly and annual variability of permanganate index (COD_{Mn}) content and *chlorophyll a* content of Taihu Lake raw water from 2006 to 2014 [15].

It could be seen from Fig. 1 that normally, the COD_{Mn} content of Taihu raw water changes a little from January to June, but increases to high level from July to November, and then falls to normal level after November. It could be seen from Figs. 1 and 2 that there is a significant positive correlation between *chlorophyll a* content representing the algae concentration and COD_{Mn} content representing the organic compound content. The *chlorophyll a* content of Taihu Lake raw water in summer is higher than that in winter, and its changing trend is roughly synchronous with the change of temperature. Usually, the *chlorophyll a* content is at low level from January to April and increases in April. From July to October, the algae are thriving in high temperature, so the *chlorophyll a* content of Taihu Lake raw water increases to its peak level [16]. After October, the *chlorophyll a* content of Taihu Lake raw water begins to fall with the decrease of temperature. Therefore, the raw water of Taihu Lake shows the characteristics of high temperature, high algae and organic pollutants content in summer, but the characteristics of tiny-pollution and low temperature in winter.

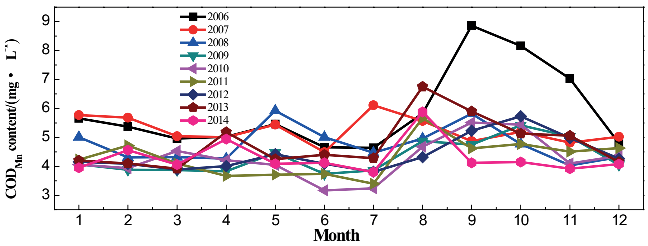

Fig. 1. Variability of average COD_{Mn} content of Taihu Lake raw water.
Note: Demonstrates the monthly variability of average COD_{Mn} content of Taihu Lake raw water during 2006–2014.

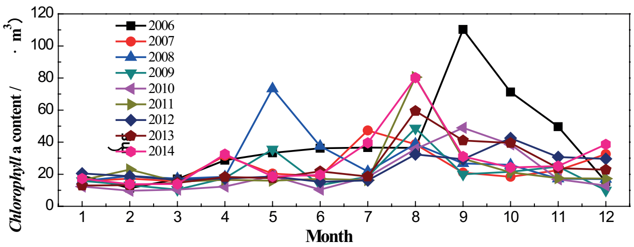

Fig. 2. Variability of average *chlorophyll a* content of Taihu Lake raw water.
Note: Demonstrates the monthly variability of average *chlorophyll a* content of Taihu Lake raw water during 2006–2014.

3.2. The coagulation-aid effect of pre-chlorination

3.2.1. Results

The pre-chlorination process is an enhanced treatment method widely used in the potable water plants located in freshwater lake basin to deal with the situation of water quality deterioration. The function of pre-chlorination is to kill part of algae for the enhancement of the coagulation process. The PAC was selected for treating raw water and chlorinated raw water in order to investigate the coagulation-aid effect of pre-chlorination. The stirring procedure of jar test was obtained according to the actual production conditions of the potable water plants located in Taihu Lake basin. The experimental results are shown in Figs. 3 and 4.

In order to meet the requirement of the national potable water quality standards in China, quite a lot of potable water plants located in Taihu Lake basin set their turbidity standard of supernatant from sedimentation tank as 2 NTU. Based on this, straight lines parallel to the horizontal axis at 2 NTU could be drawn as in Figs. 3 and 4, and then the required doses for reaching residual turbidity of 2 NTU could be obtained from the abscissa values of intersections of the parallel horizontal lines and the curves of dose vs. turbidity. Furthermore, the straight lines parallel to the vertical axis at the required dose for supernatant turbidity of 2 NTU using PAC could be drawn as in Figs. 3 and 4 too, and then the algae removal rate at the same dose for treating raw water and chlorinated raw water could be obtained from the ordinate values of intersections of the parallel vertical lines and the curves of dose vs. algae removal rates. All these obtained information were summarized in Figs. 5 and 6.

From Figs. 3–6, it could be seen that for treating Taihu Lake raw water in summer and using the same kind of coagulants, all curves of the dose vs. residual turbidity for chlorinated raw water were below those for raw water, indicating the higher turbidity removal effect of pre-chlorination, and all curves of the dose vs. algae removal rate for chlorinated raw water were above those for raw water, indicating the higher algae removal effect of pre-chlorination. Therefore, the pre-chlorination process improved the turbidity and algae removal effect for the Taihu Lake raw water in summer. Especially, using the pre-chlorination process could decrease turbidity of supernatant by 9.30% and increase the algae removal rate by 1.12%, compared with conventional coagulation only using PAC, when required turbidity 2.0 NTU of supernatant was achieved. And, when the same dose was used, using the pre-chlorination process could decrease the residual turbidity by 10.28%, and meanwhile increase the algae removal rate by 2.41% comparing with conventional coagulation only using PAC.

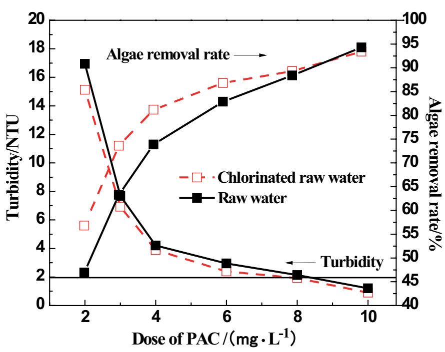

Fig. 3. The influence of pre-chlorination on turbidity and algae removal effect for Taihu raw water in summer.

Note: The curves with empty points and dotted lines are the curves of dose vs. residual turbidity (the descending curves) and the curves of dose vs. algae removal rate (the rising curves) by using PAC and PAC/PDMDAAC (1.53/10%) for chlorinated Taihu Lake raw water in summer, and the curves with solid points and solid lines are the curves of dose vs. residual turbidity (the descending curves) and the curves of dose vs. algae removal rate (the rising curves) by using PAC and PAC/PDMDAAC (1.53/10%) for Taihu Lake raw water in summer.

The composition of composite coagulants was presented as PAC/PDMDAAC ([*η*] of PDMDAAC/PDMDAAC content [*w*/*w*], as shown in section 2.1).

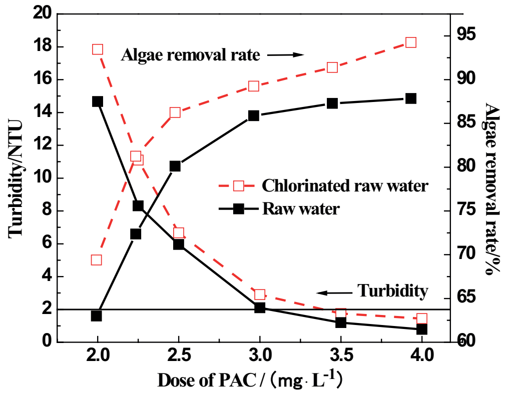

Fig. 4. The influence of pre-chlorination on turbidity and algae removal effect for Taihu raw water in winter.

Note: The curves with empty points and dotted lines are the curves of dose vs. residual turbidity (the descending curves) and the curves of dose vs. algae removal rate (the rising curves) by using PAC and PAC/PDMDAAC (1.53/10%) for chlorinated Taihu Lake raw water in winter, and the curves with solid points and solid lines are the curves of dose vs. residual turbidity (the descending curves) and the curves of dose vs. algae removal rate (the rising curves) by using PAC and PAC/PDMDAAC (1.53/10%) for Taihu Lake raw water in winter.

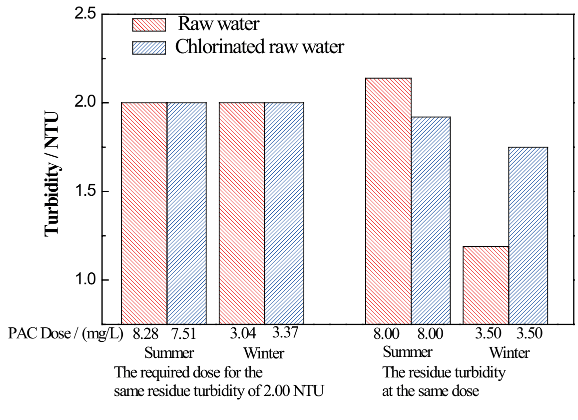

Fig. 5. The influence of pre-chlorination on turbidity removal effect for Taihu raw water.

Note: Demonstrates the influence of pre-chlorination on turbidity removal effect for Taihu raw water, especially the required dose for the same residue turbidity of 2 NTU and the residue turbidity at the same dose.

However, from Figs. 3–6, it could be seen that for treating Taihu Lake raw water in winter and using the same kind of coagulants, all curves of both the dose vs. turbidity and the dose vs. algae removal rate for chlorinated raw water were congruously above those of raw water, indicating lower turbidity removal effect and higher algae removal effect of pre-chlorination, respectively. Therefore, the pre-chlorination process improved the algae removal effect, but decreased the turbidity removal effect for the Taihu Lake raw water in winter. Especially, using the pre-chlorination process could increase the algae removal rate by 4.23%, when required turbidity 2 NTU of supernatant was achieved. And, when the same dose for the residue turbidity of 2 NTU using PAC was used, using the pre-chlorination process could increase the algae removal rate by 4.09% comparing with conventional coagulation only using PAC.

3.2.2. Mechanism analysis

The reason for the results in Figs. 3 and 4 could be explained by the characteristics of pre-chlorination process, and the content and sorts of algae in the raw water. It was reported that one of the important factors, which could influence algae removal rate in coagulation, was the characteristics of algae including the physiological structure, activity, surface charge and metabolites of algae [17]. Meanwhile, chloride as a strong oxidant can seriously damage the physiological structure of algae, kill the algae cells and change the structure of organic compounds. Therefore, pre-chlorination process could demonstrate two different and opposite functions.

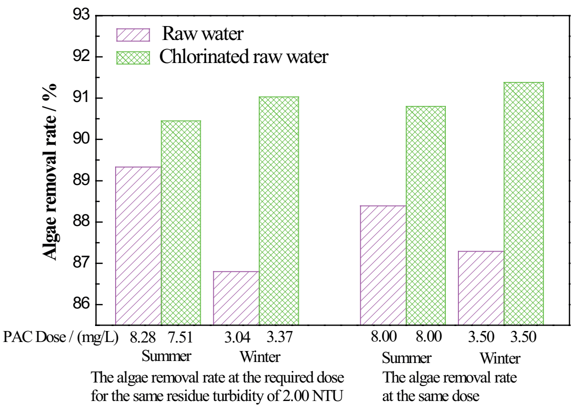

Fig. 6. The influence of pre-chlorination on algae removal effect for Taihu raw water.
Note: Demonstrates the influence of pre-chlorination on algae removal effect for Taihu raw water, especially the algae removal rate at the required dose for the same residue turbidity of 2 NTU and the algae removal rate at the same dose.

On the one hand, the powerful oxidation of chlorine can inhibit the activity of algae, break up the clusters of algae into single algae cells, and damage the surface structures of algae cells, which could result in the improvement of coagulation effect of algae removal [18]. On the other hand, the intracellular organic compounds released into raw water from the damaged algae cells could absorb on the surface of colloidal particles in the raw water, and then increase surface negative charge density of the colloidal particles, leading to the enhancement of colloid stability and resulting in lower coagulation effect of turbidity removal [19,20]. The different effects of pre-chlorination on coagulation in different seasons may be due to the influence of algae content and sorts in the raw water on these two functions. Table 2 shows the algae sorts in Taihu Lake raw water in summer and winter.

It is shown in Table 1 that the algae content in chlorinated raw water was higher than that in raw water, but the COD_{Mn} content in chlorinated raw water was lower than that in raw water, in the case of treating Taihu Lake raw water in summer. The algae contained in the Taihu Lake raw water in summer have the characteristics of complex species, high activity and sharp metabolism due to the high temperature, and especially, there are some clusters of *Microcystis* whose structure could seriously influence coagulation effect [21] (as shown in Table 2). Since a high chloride dose reaching up to about 5 mg L^{-1} for pre-chlorination in summer was used, the positive effects of pre-chlorination including inhibition of algae activity, destruction of algae clusters and decomposition of organic pollutants were enhanced, and then turbidity removal effect in coagulation was improved.

In contrast to the situation in summer, it is shown in Table 1 that algae and COD_{Mn} content in the Taihu Lake raw water in winter were only half of the values in summer. Furthermore, the algae content in chlorinated raw water was lower than that in raw water, but the COD_{Mn} content in chlorinated raw water was higher than that in raw water. However, it was indicated from Fig. 4 that along with the enhancement of algae removal effect in coagulation by pre-chlorination, the turbidity removal effect of coagulation for chlorinated raw water was decreased to lower than that for raw water. The reasons might include the inhibition of algae metabolic activity due to the low temperature, the existing form of single cells presented by the main algae species of *chlorophyta* and *Bacillariophyta* in the raw water

Table 2
The algae sorts contained in the Taihu raw water in summer and winter

Season	Summer			Winter		
Algae division	*Cyonophyta*	*Chlorophyta*	*Bacillariophyta*	*Chlorophyta*	*Bacillariophyta*	Others
Algae genus	*Microcystis*, *Merismopedia*, *Anabaena*, *Spirulina*, *Oscillatoria*, etc.	*Oocystaceae*, *Chlorella*, *Scenedesmus*, etc.	*Melosira*, *Cyclotella*, *Fragilaria*, etc.	*Chlorella*, *Scenedesmus*, etc.	*Cyclotella*, *Melosira*, etc.	*Merismopedia*, *Microcystis*, etc.
Ratio (%)	70–80	20–30		About 80		About 20

(as shown in Table 2), and the relative low organic pollution degree in raw water in winter. Since the relatively low chlorine dose of about 1.5 mg L^{-1} for pre-chlorination was used, the negative effects of pre-chlorination such as prompting release of intracellular compounds of algae cells were kept, and then the turbidity removal effect in coagulation was decreased.

3.3. The coagulation behaviors of composite coagulants

3.3.1. Results

The composite coagulants with the different PDMDAAC content and intrinsic viscosity of PDMDAAC were selected to conduct jar test. The stirring procedure was obtained according to the actual production conditions in the potable water plants located in Taihu Lake basin. The results are shown in Figs. 7 and 8.

It could be seen from Figs. 7 and 8 that the curves of dose vs. residual turbidity for using composite coagulants were below that for using PAC, but the curves of dose vs. algae removal rate for using composite coagulants were above that for using PAC. The higher the content of PDMDAAC or intrinsic viscosity of PDMDAAC was, the lower the curves of dose vs. residual turbidity and the higher the curves of dose vs. algae removal rate for using composite coagulants were.

It was indicated that the turbidity and algae removal effect by using composite coagulants were higher than that

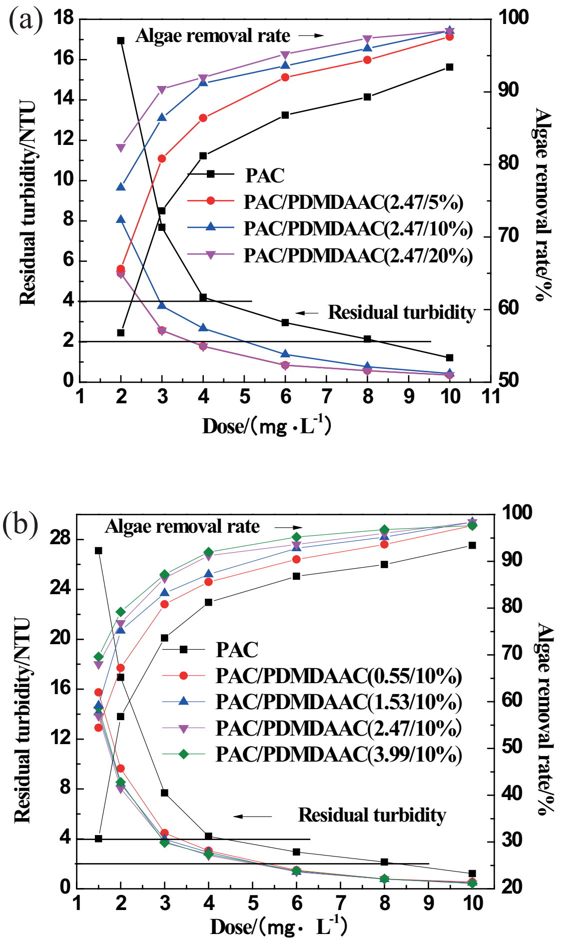

Fig. 7. The turbidity and algae removal effect of PAC/PDMDAAC for Taihu Lake raw water in summer: (a) PAC/PDMDAAC with different PDMDAAC content, (b) PAC/PDMDAAC with different intrinsic viscosity of PDMDAAC.

Note: (a) Demonstrates the curves of dose vs. residual turbidity (the descending curves) and the curves of dose vs. algae removal rate (the rising curves) for using PAC and PAC/PDMDAAC composite coagulants with different PDMDAAC content for Taihu raw water in summer. (b) Demonstrates the curves of dose vs. residual turbidity (the descending curves) and the curves of dose vs. algae removal rate (the rising curves) for using PAC and PAC/PDMDAAC composite coagulants with different intrinsic viscosity of PDMDAAC for Taihu raw water in summer.

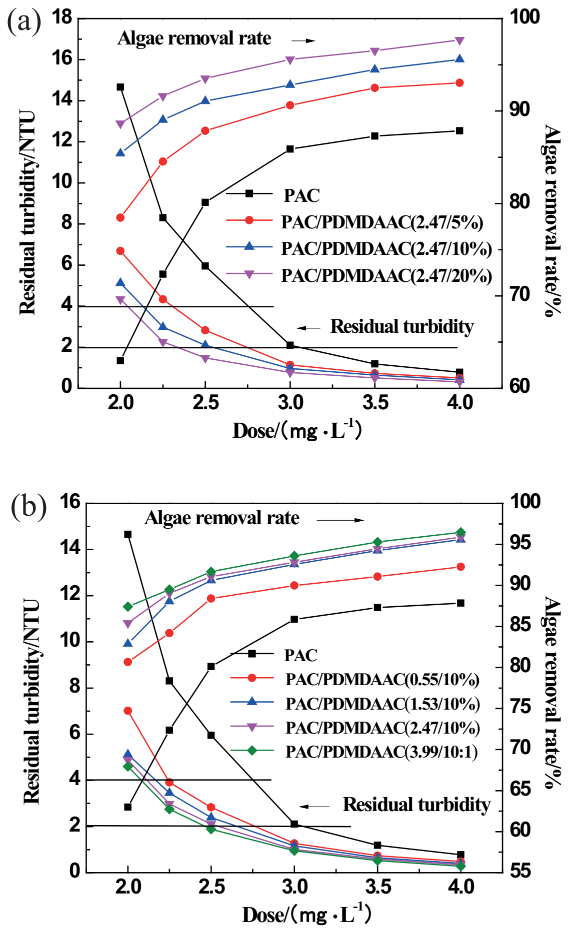

Fig. 8. The turbidity and algae removal effect of PAC/PDMDAAC for Taihu Lake raw water in winter: (a) PAC/PDMDAAC with different PDMDAAC content, (b) PAC/PDMDAAC with different intrinsic viscosity of PDMDAAC.

Note: (a) Demonstrates the curves of dose vs. residual turbidity (the descending curves) and the curves of dose vs. algae removal rate (the rising curves) for using PAC and PAC/PDMDAAC composite coagulants with different PDMDAAC content for Taihu raw water in winter. (b) Demonstrates the curves of dose vs. residual turbidity (the descending curves) and the curves of dose vs. algae removal rate (the rising curves) for using PAC and PAC/PDMDAAC composite coagulants with different intrinsic viscosity of PDMDAAC for Taihu raw water in winter.

by using PAC, and the higher the content of PDMDAAC or intrinsic viscosity of PDMDAAC was, the higher turbidity and algae removal effect of composite coagulants were. When the similar residual turbidity of supernatant was achieved, the enhanced coagulation using composite coagulants could decrease the dose of PAC remarkably and meanwhile increase the algae removal rate compared with the conventional process using PAC only. When the same dose of PAC was used, the process using composite coagulant could decrease the residual turbidity and meanwhile increase the algae removal rate significantly compared with the conventional process of using PAC only.

3.3.2. Mechanism analysis

3.3.2.1. The enhanced coagulation mechanisms of composite coagulants The reason for the higher turbidity and algae removal effect of composite coagulants shown in Figs. 7 and 8 may be that the PDMDAAC is a kind of cationic polymer with a positive charge for each of its structure unit, so that PDMDAAC not only enhanced the charge neutralization ability of PAC, but also changed possibly the species of multinuclear hydroxyl hydrolysates of PAC. Therefore, PDMDAAC could improve the interaction between coagulants and suspended particles in coagulation process, and enhance the specific adsorption of coagulants on the surface of suspended particles and algae cells [22,23].

Meanwhile, as shown in Fig. 9, PDMDAAC with low intrinsic viscosity has short molecular chain, which could easily adsorb on the surface of suspended particles in the "train" type. However, it was difficult to form large flocs through its weak bridging function among suspended particles and algal cells. Therefore, the turbidity and algae removal effect of composite coagulants containing PDMDAAC with low intrinsic viscosity is not so sufficient relatively. PDMDAAC with high intrinsic viscosity has long molecular chain, which could easily adsorb on the surface of suspended particles in both the "loop" and "tail" type, so that the large flocs could be formed through its strong bridging function among suspended particles and algal cells. And then the turbidity and algae removal effect of composite coagulants could be enhanced remarkably [10]. These factors led to the results as follows: The higher the content of PDMDAAC or intrinsic viscosity of PDMDAAC was, the higher turbidity and algae removal effect of composite coagulants were.

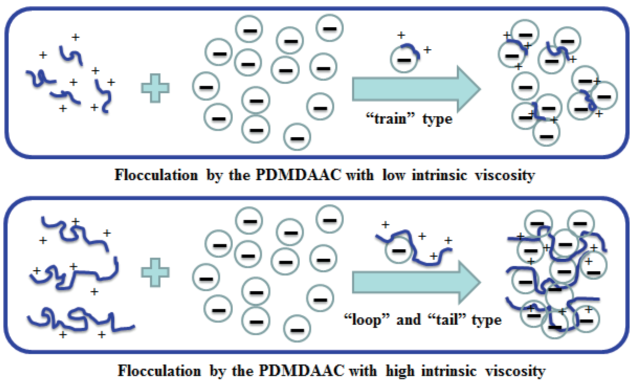

Fig. 9. Flocculation model by PDMDAAC.
Note: Demonstrates the supposed absorption and bridging state of PDMDAAC with low and high molecular weight on the surface of particles in coagulation process.

3.3.2.2. The characteristics of enhanced coagulation processes using composite coagulants In order to meet the requirement of the national potable water quality standards of China, most of potable water plants located in Taihu Lake basin set their turbidity standard of supernatant from sedimentation tank as 2 NTU. But in most situations, the turbidity of supernatant from sedimentation tank can only reach to about 4 NTU due to the deterioration of raw water quality and the limitations of the conventional treatment process. Based on these, straight lines parallel to the horizontal axis at 4 and 2 NTU could be drawn as in Figs. 7 and 8, and then the required doses for reaching residual turbidity of 4 and 2 NTU could be obtained from the abscissa values of intersections of the parallel horizontal lines and the curves of dose vs. turbidity. Furthermore, the straight lines parallel to the vertical axis at the required dose for supernatant turbidity of 2 NTU using PAC could be drawn as in Figs. 7 and 8 too, and then the algae removal rate using different coagulants at the same dose could be obtained from the ordinate values of intersections of the parallel vertical lines and the curves of dose vs. algae removal rates. All these obtained information were summarized in Tables 3 and 4.

It could be seen in Tables 3 and 4 that using composite coagulants could improve the turbidity and algae removal effect in a large extent compared with using PAC. When required residual turbidity of supernatant for treatment process in the local potable water plant along Taihu Lake was achieved in summer or in winter, using composite coagulants could decrease the inorganic coagulants dose by 32.85%–56.28% or 9.67%–24.00%, and meanwhile increase the algae removal rate by 0.69%–5.61% or 3.09%–6.17%, compared with only using inorganic coagulants. And, when the same dose was used in summer or in winter, using composite coagulant could decrease the residual turbidity by more than 45.33%–73.36% or 39.52%–63.33%, and meanwhile increase the algae removal rate by more than 4.47%–7.67% or 4.74%–9.71%, comparing with only using inorganic coagulants, too. In general, the improvement extent of the turbidity and algae removal effect on composite coagulants to PAC for treating Taihu lake raw water in winter is lower than that in summer.

The reasons for the results in Tables 3 and 4 may be that the PDMDAAC not only can change the species of multinuclear hydroxyl hydrolysates of PAC and enhance the charge neutralization ability, but also can intensify the bridge ability of PAC, so that the coagulation effect can be improved [24]. However, the enhanced coagulation effect of composite coagulants is also influenced by other factors including the characteristics of colloidal particles in the raw water, hydrolysis speed and hydrolysate characteristics of PAC and so on.

In summer, the algae and organic pollutants content in Taihu raw water is high; there are more negative charge groups in the surface of colloidal particles in raw water. The PDMDAAC as a kind of polyelectrolyte with strong positive charge could react with particles containing negatively

Table 3
Required doses for supernatants turbidity of 4 and 2 NTU using different coagulants

Item		For supernatant turbidity of 4 NTU		For supernatant turbidity of 2 NTU	
		PAC	PAC/PDMDAAC	PAC	PAC/PDMDAAC
Summer	Dose (mg·L^{-1})	4.24	2.48–3.50	8.28	3.62–5.56
	Decrease range of dose (%)	/	17.45–41.51	/	32.85–56.28
	Algae removal rate (%)	82.28	83.67–86.80	88.06	88.75–93.67
	Increase of algae removal rate (%)	/	1.39–4.52	/	0.69–5.61
Winter	Dose (mg·L^{-1})	2.74	2.03–2.31	3.00	2.28–2.71
	Decrease range of dose (%)	/	15.69–25.91	/	9.67–24.00
	Algae removal rate (%)	83.09	84.26–89.26	85.98	89.07–92.15
	Increase of algae removal rate (%)	/	1.17–6.17	/	3.09–6.17

Table 4
Algae removal rate at the same dose using different coagulants (the dose for residual turbidity of 2 NTU using PAC)

Item	Summer		Winter	
	PAC	PAC/PDMDAAC	PAC	PAC/PDMDAAC
Dose (mg·L^{-1})	8.00	8.00	3.00	3.00
Turbidity (NTU)	2.14	0.57–1.17	2.10	0.77–1.27
Decrease rate of turbidity (%)	/	45.33–73.36	/	39.52–63.33
Algae removal rate (%)	89.93	94.40–97.60	85.87	90.61–95.58
Increase of algae removal rate (%)	/	4.47–7.67	/	4.74–9.71

charged groups easily [25], so the enhanced coagulation effect of PDMDAAC is high in summer. In winter, the algae and organic pollutants content in Taihu raw water is relatively low, and there are less negatively charged groups in the surface of colloidal particles. Then the binding ability of PDMDAAC on the surface of particles in raw water is lower than that in summer, so the improvement extent of the turbidity and algae removal effect on composite coagulants to PAC is lower than that in summer.

3.4. The comparison of enhanced effects of pre-chlorination and composite coagulants

The above experimental results demonstrated that the pre-chlorination and the composite coagulants could improve the turbidity and algae removal effects in Taihu Lake algae-containing raw water. However, it should pay an attention to that the substances released from the broken algae cells can form a series of poisonous and harmful chlorinated by-products under action of chlorine [26]. To compare the enhanced effects of the pre-chlorination and the composite coagulants, the straight lines parallel to the horizontal axis at 2 NTU could be drawn as in Figs. 3, 4, 7 and 8, and then the required doses for reaching residual turbidity of 2 NTU could be obtained from the abscissa values of intersections of the parallel horizontal lines and the curves of dose vs. turbidity. Furthermore, the straight lines parallel to the vertical axis at the required dose for supernatant turbidity of 2 NTU using PAC could be drawn as in Figs. 3, 4, 7 and 8 too, and then the algae removal rate at the same dose could be obtained from the ordinate values of intersections of the parallel vertical lines and the curves of dose vs. algae removal rates. For comparison, just the results of pre-chlorination and the results of composite coagulants whose effects were close to that of pre-chlorination were summarized in Tables 5 and 6.

It could be seen in Tables 5 and 6 that when required residual turbidity of supernatant for treatment process in the local potable water plant along Taihu Lake was achieved in summer or in winter, using PAC/PDMDAAC (1.53/10%) for both seasons could get the lower required dose and the same or more algae removal effects compared with the combined process of conventional coagulation using PAC and pre-chlorination with pre-chlorine dose of 5.0 or 1.5 mg L^{-1}. When the same dose of PAC/PDMDAAC (0.55/10%–1.53/10%) was used in summer or in winter, only using these composite coagulants with lower intrinsic viscosity and content of PDMDAAC could get lower residual turbidity and higher algae removal effects compared with the combined process of conventional coagulation using PAC and pre-chlorination with pre-chlorine dose of 5.0 or 1.5 mg L^{-1}. It means that the turbidity and algae removal effect of enhanced coagulation process using composite coagulant PAC/PDMDAAC (0.55/10%) or PAC/PDMDAAC (1.53/10%) could be higher than that of combination process of conventional coagulation using PAC and pre-chlorination. Furthermore, the higher intrinsic viscosity of the composite coagulants with or the higher content of PDMDAAC in the composite coagulants was, the higher effect of enhanced coagulation process using composite coagulants could be.

Table 5
The comparison of enhanced effects of pre-chlorination and composite coagulants for Taihu Lake raw water in summer

Item		For supernatant turbidity of 2.00 NTU			At the same dose		
		Raw water	Chlorinated raw water	PAC/PDMDAAC (1.53/10%)	Raw water	Chlorinated raw water	PAC/PDMDAAC (0.55/10%)
Summer	PAC dose (mg·L^{-1})	8.28	7.51	5.18	8.00	8.00	8.00
	Turbidity (NTU)	2.00	2.00	2.00	2.14	1.92	0.79
	Change rate of dose or turbidity (%)	/	–9.30	–37.44	/	–10.28	–63.08
	Algae removal rate (%)	89.33	90.45	90.55	88.39	90.80	93.60
	Increase of algae removal rate (%)	/	1.12	1.22	/	2.41	5.21

Table 6
The comparison of enhanced effects of pre-chlorination and composite coagulants for Taihu Lake raw water in winter

Item		Raw water	Chlorinated raw water	PAC/PDMDAAC (1.53/10%)	Raw water	Chlorinated raw water	PAC/PDMDAAC (1.53/10%)
Winter	PAC dose (mg·L^{-1})	3.04	3.37	2.66	3.50	3.50	3.50
	Turbidity (NTU)	2.00	2.00	2.00	1.19	1.75	0.65
	Decrease rate of dose or turbidity (%)	/	+10.86	–12.50	/	+47.06	–45.38
	Algae removal rate (%)	86.80	91.03	91.17	87.29	91.38	94.25
	Increase of algae removal rate (%)	/	4.23	4.37	/	4.09	6.96

In contrast with the conventional coagulation process combined with pre-chlorination, the enhanced coagulation process using composite coagulants do not destroy the structure of algal cells or trigger the release of *microcystins*; rather, the strong absorbing-neutralizing and bridging-netting abilities produced by the composite coagulants can cause algae cells to form bigger floc and settle rapidly without obvious damage of algae cell. As a result, on one hand, the enhanced coagulation process using composite coagulants could replace the function of pre-chlorination, and the chlorine dose both in pre-chlorination and in disinfection also could be decreased because of the enhanced coagulation of composite coagulants and the high water quality of supernatant produced; on the other hand, the risks caused by excessive chlorine could be reduced, and the produced water quality could be improved, spontaneously.

4. Conclusions

Based on the analysis of characteristics of algae-containing Taihu Lake raw water in summer and winter, the turbidity and algae removal effects of enhanced treatment processes including pre-chlorination and enhanced coagulation using composite coagulants were investigated and compared through jar tests. The main conclusions are as follows:

(1) It was discovered that for treating Taihu Lake raw water with the characteristics of high temperature, high algae and organic pollutant content in summer, the pre-chlorination could improve the turbidity and algae removal effect in coagulation. For treating Taihu Lake raw water with the characteristics of low temperature, containing algae and tiny-pollution in winter, the pre-chlorination could improve algae removal effect, but decreased the turbidity removal effect in coagulation.

(2) The results showed that for treating algae-containing raw water, the turbidity and algae removal effect enhanced by using composite coagulants was remarkable. The higher the intrinsic viscosity of PDMDAAC in composite coagulants was, the stronger the enhanced coagulation function was. When required residual turbidity of supernatant for treatment process in the local potable water plant along Taihu Lake was achieved in summer or in winter, using composite coagulants with the PDMDAAC content of 20% and intrinsic viscosity of 3.99 dL g^{-1} could decrease the inorganic coagulants dose by 56.28% or 24.00%, and meanwhile increase the algae removal rate by 8.01% or 6.17%, compared with only using inorganic coagulants. And, when the same dose was used in summer or in winter, using composite coagulant could decrease the residual turbidity by more than 73.36% or 63.33%, and meanwhile increase the algae removal rate by more than

10.13% or 9.71%, comparing with only using inorganic coagulants, too. The improvement extent of the turbidity and algae removal effect on composite coagulants to PAC in summer is stronger than that in winter due to the characteristics of PDMDAAC and the algae-containing raw water.

(3) It was also discovered that the turbidity and algae removal effect of the enhanced coagulation process using composite coagulants could exceed largely that of the combined process of conventional coagulation and pre-chlorination both in summer and in winter. And the enhanced coagulation process using composite coagulants even with a lower intrinsic viscosity and content of PDMDAAC could replace the enhanced coagulation function of pre-chlorination and reduce the risks caused by excessive chlorine, so that the finished water quality could be improved, spontaneously.

Acknowledgments

The kind suggestions from the anonymous reviewers are greatly acknowledged.

This work was supported by the National Natural Science Foundation of China under Grant 21377054; the Science and Technology Support Program of Jiangsu Province for Taihu Lake under Grant BS2007121; and the Natural Science Foundation of Anhui Province under Grant 1508085QE112.

References

[1] T.F. Xu, C.W. Cui, C. Ma, Color composition in a water reservoir and DBPs formation following coagulation and chlorination during its conventional water treatment in northeast of China, Desal. Water Treat., 54 (2015) 1375–1384.

[2] L. Guo, Doing battle with the green monster of Taihu Lake, Science, 317 (2007) 1166.

[3] S. Xu, B. Huang, Z.B. Wei, J. Luo, A.J. Miao, L.Y. Yang, Seasonal variation of phytoplankton nutrient limitation in Lake Taihu, China: a monthly study from year 2011 to 2012, Ecotoxicol. Environ. Saf., 94 (2013) 190–196.

[4] X. Liu, X.H. Lu, Y.W. Chen, The effects of temperature and nutrient ratios on *Microcystis* blooms in Lake Taihu, China: an 11-year investigation, Harmful Algae, 10 (2011) 337–343.

[5] F.Z. Chen, X.L. Song, Y.H. Hu, Z.W. Liu, B.Q. Qin, Water quality improvement and phytoplankton response in the drinking water source in Meiliang Bay of Lake Taihu, China, Ecol. Eng., 35 (2009) 1637–1645.

[6] D.M. Ghaitidak, K.D. Yadav, Effect of coagulant in greywater treatment for reuse: selection of optimal coagulation condition using Analytic Hierarchy Process, Desal. Water Treat., 55 (2015) 913–925.

[7] A. Nowacka, M. Wlodarczyk-Makula, B. Macherzynski, Comparison of effectiveness of coagulation with aluminum sulfate and pre-hydrolyzed aluminum coagulants, Desal. Water Treat., 52 (2014) 3843–3851.

[8] L.P. Wang, L.S. Liu, B.H. Zheng, Eutrophication development and its key regulating factors in a water-supply reservoir in North China, J. Environ. Sci., 25 (2013) 962–970.

[9] Q.H. Shen, J.W. Zhu, L.H. Cheng, J.H. Zhang, Z. Zhang, X.H. Xu, Enhanced algae removal by drinking water treatment of chlorination coupled with coagulation, Desalination, 271 (2011) 236–240.

[10] X.X. Li, Y.J. Zhang, X.L. Zhao, C. Liu, The characteristics of sludge from enhanced coagulation processes using PAC/PDM-DAAC composite coagulants in treatment of micro-polluted raw water, Sep. Purif. Technol., 147 (2015) 125–131.

[11] X.L. Zhao, Y.J. Zhang, X.X. Li, C. Liu, L.L. Zhu, Algae-removal efficiencies of AS/PDM coagulants to Taihu Lake algae-rich water, J. Am. Water Works Assoc., 102 (2010) 119–128.

[12] Y.J. Zhang, X.L. Zhao, X.X. Li, C. Liu, L.L. Zhu, Algae-removal performances of PAC/PDM composite coagulants to Taihu Lake algae-rich raw water in summer, Water Sci. Technol., 62 (2010) 330–339.

[13] X.L. Zhao, Y.J. Zhang, Algae-removing and algicidal efficiencies of polydiallyldimethylammonium chloride composite coagulants in enhanced coagulation treatment of algae-containing raw water, Chem. Eng. J., 173 (2011) 164–170.

[14] Y.J. Zhang, X.L. Zhao, X.X. Li, Preparation and Application Methods of PAC-PDMDAAC Composite Coagulants, CN 101323473 A, China, 2008.

[15] Taihu Lake Basin Water Resources Protection Bureau, Bulletin of Water Resources Quality of Taihu Lake Basin and Southeast Rivers, 163, 2011. [in Chinese]

[16] X. Tan, F.X. Kong, Q.F. Zeng, H.S. Cao, S.Q. Qian, M. Zhang, Seasonal variation of *Microcystis* in Lake Taihu and its relationships with environmental factors, J. Environ. Sci., 21 (2009) 892–899.

[17] R. Henderson, S.A. Parsons, B. Jefferson, The impact of algal properties and pre-oxidation on solid–liquid separation of algae, Water Res., 42 (2008) 1827–1845.

[18] M. Ma, R.P. Liu, H.J. Liu, J.H. Qu, W. Jefferson, Effects and mechanisms of pre-chlorination on *Microcystis aeruginosa* removal by alum coagulation: significance of the released intracellular organic matter, Sep. Purif. Technol., 86 (2012) 19–25.

[19] T. Takaara, D. Sano, H. Konno, T. Omura, Cellular proteins of *Microcystis aeruginosa* inhibiting coagulation with polyaluminum chloride, Water Res., 41 (2007) 1653–1658.

[20] D. Sano, S. Ishifuji, Y. Sato, Y. Imae, T. Takaara, Y. Masago, T. Omura, Identification and characterization of coagulation inhibitor proteins derived from cyanobacterium *Microcystis aeruginosa*, Chemosphere, 82 (2011) 1096–1102.

[21] R.K. Henderson, A. Baker, S.A. Parsons, B. Jefferson, Characterisation of algogenic organic matter extracted from cyanobacteria, green algae and diatoms, Water Res., 42 (2008) 3435–3445.

[22] J.C. Wei, B.Y. Gao, Q.Y. Yue, Y. Wang, W.W. Li, X.B. Zhu, Comparison of coagulation behavior and floc structure characteristic of different polyferric-cationic polymer dual-coagulants in humic acid solution, Water Res., 43 (2009) 724–732.

[23] Z.L. Yang, B.Y. Gao, Y. Wang, X.X. Zhang, Q.Y. Yue, The effect of additional poly-diallyl dimethyl ammonium-chloride on the speciation distribution of residual aluminum (Al) in a low DOC and high alkalinity reservoir water treatment, Chem. Eng. J., 197 (2012) 56–66.

[24] P.A. Moussas, A.I. Zouboulis, Synthesis, characterization and coagulation behavior of a composite coagulation reagent by the combination of polyferric sulfate (PFS) and cationic polyelectrolyte, Sep. Purif. Technol., 96 (2012) 263–273.

[25] Z.L. Yang, B.Y. Gao, Y. Wang, X.X. Zhang, Q.Y. Yue, Relationship between residual Al species, floc operational parameters and coagulation performance during reservoir water treatment by PAC-PDMDAAC, Sep. Purif. Technol., 102 (2013) 147–156.

[26] Q. Zeng, S.H. Zhang, J. Liao, D.Y. Miao, X.Y. Wang, P. Yang, L.J. Yun, A.L. Liu, W.Q. Lu, Evaluation of genotoxic effects caused by extracts of chlorinated drinking water using a combination of three different bioassays, J. Hazard. Mater., 296 (2015) 23–29.