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Mn(VII)–Fe(II) pre-treatment for *Microcystis aeruginosa* removal by Al coagulation: Simultaneous enhanced cyanobacterium removal and residual coagulant control

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ABSTRACT

A novel Mn(VII)–Fe(II) pre-treatment was proposed to simultaneously enhance the removal of *Microcystis aeruginosa* by aluminum chloride (AlCl₃) coagulation and enabled lowering the dose of Al as effective coagulation can be achieved only by Al, however, at higher doses. In this process, permanganate [Mn(VII)] and ferrous sulfate [Fe(II)] were dosed sequentially prior to Al. The application of Fe(II) not only avoids the extensive oxidation of *M. aeruginosa* by Mn(VII) but also introduces Fe(III) formed in situ into the system. Results show that, at Al doses of 83.3–108.3 μM, Mn(VII)–Fe(II) pretreatment (Mn(VII) dose: 8.3–16.7 μM; Fe(II) dose: 39.5 μM) is capable of enhancing *M. aeruginosa* removal by 73.4–81.4%. In contrast, only 0–65.4% and 2.7–8.2% increase in *M. aeruginosa* removal is achieved by Mn(VII) and Fe(II) pre-treatment, respectively. The ESI-MS spectrum shows that the freshly formed Fe(III) hydrolyzes much more slowly than pre-formed Fe(III) does, and this effect results in its higher efficiency towards the removal of *M. aeruginosa*. Moreover, in the co-existing system, Fe tends to hydrolyze preferentially and the presence of Fe salts improves the precipitation of Al and vice versa. Thus, the use of Fe and Al as dual-coagulants is practically valuable to control the residual level of coagulant(s) besides its improvement on the removal of *M. aeruginosa*.

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1. Introduction

Algae bloom has received an increasing focus due to the global trend toward eutrophication of drinking water sources, and has various negative effects on water treatment processes (Westerhoff et al., 2005; Fang et al., 2010; Huang et al., 2009).

Common coagulants, either aluminum or iron salts, have difficulty in removing the negatively-charged cells (Henderson et al., 2010; Ma et al., 2012a; Ghernaout et al., 2010) and the algogenic organic matter (AOM) (Pivokonsky et al., 2012; Takaara et al., 2010; Bernhardt and Clasen, 1991). The elevated coagulant doses may improve the removal of algae, but can potentially result in an unacceptably high level of

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coagulant residue. The residual Al at high concentrations is associated with human health risks such as Alzheimer's disease (Kawahara and Kato-Negishi, 2011; Rondeau et al., 2000), while an excessive amount of iron in drinking water contributes to unpleasant color and thus customer complaints.

Application of pre-oxidants such as chlorine, ozone or potassium permanganate has been shown to enhance the algae removal in laboratory- and pilot-scale studies (Chen et al., 2009; Plummer and Edzwald, 2002; Shen et al., 2011). The improved algae removal by pre-oxidation has been mainly attributed to the alteration in external cell membrane (Ma et al., 2012a), the impeded motion of cells (Steynberg et al., 1996) and the release of intracellular organics (Ma et al., 2012a; Chen et al., 2009). However, the oxidation of algae, if extensive, can yield cell lysis, and the subsequent massive release and degradation of intracellular organics might negatively affect the coagulation (Ma et al., 2012a; Paralkar and Edzwald, 1996). Moreover, water quality can be deteriorated by organics such as taste and odor substances, toxins, and precursors of disinfection by-products (DBPs) (Daly et al., 2007; Wert et al., 2014; Li et al., 2014; Zhou et al., 2014). The formation of DBPs is also of concern when the aforementioned oxidants are applied (Fang et al., 2010; Huang et al., 2009; Zhou et al., 2014).

Therefore, in cases where pre-oxidation is used to treat algae-burdened source water, the removal of algae cells without cell rupture is strongly preferred (Drikas et al., 2001). Both the type and dose of pre-oxidant was found to affect the subsequent coagulation of algae (Chen et al., 2009; Steynberg et al., 1996; Ma and Liu, 2002), in which the dissolved organic matter (DOM) also played a significant role (Ma et al., 2012a). The effect that DOM has on the coagulation depends on its concentration and molecular weight (MW). Organics with relatively low level and/or high MW are regarded to enhance the coagulation (Chen et al., 2009; Paralkar and Edzwald, 1996; Bernhardt et al., 1985).

For *Microcystis aeruginosa*-burdened waters, DOM includes natural organic matter (NOM) and AOM. Because AOM consists of organics released from cells naturally and by artificial processes such as oxidation, it is highly valuable to achieve 'moderate pre-oxidation' of algae cells, i.e., to inactivate algae cells but avoid the extensive oxidation of algae that might lead to not only extensive increase in the concentration of DOM but the decrease in the MW of it (Ma et al., 2012a; Paralkar and Edzwald, 1996). Lower MW organics resulted from extensive oxidation were reported to be more easily biodegradable and associated with an increasing risk of DBPs formation (Bose and Reckhow, 2007; Bond et al., 2009). For this consideration, a novel Mn(VII)–Fe(II) process was proposed in our previous study (Ma et al., 2012b), and its high efficiency in terms of algae removal and the mechanism involves in has been well illustrated. Unfortunately, Fe(II) alone should not serve as a coagulant in practice and the doses of *in situ* Fe(III) is highly dependent on the doses of Mn(VII). In the treatment of source water with high density of algae cells, the extremely high doses of Mn(VII) is inevitable to provide sufficient *in situ* Fe(III). However, at high doses of Mn(VII) and Fe(II), this arises another issue that the residual levels of Mn(II), Fe(II), and/or Fe(III) might exceed the maximum contaminant levels (MCLs).

A dual-coagulant approach, i.e., the combined use of different coagulants, has been proposed and demonstrated to

enhance coagulation regardless of that two coagulants were dosed simultaneously or consecutively (Kuusik and Viisimaa, 1999; Wei et al., 2009; Jain et al., 2009; Rong et al., 2013). Dual Al and Fe coagulants showed better improvement in water treatment than each coagulant alone (Cheng et al., 2003). In comparing to the use of a single coagulant, the dual-coagulant application contributed to the hydroxides precipitates with more uniformity and facilitated water clarification (Zapolski and Baran, 1987). Furthermore, the combination of Al and Fe salts showed higher efficiency than that of two kinds of Fe salts in terms of arsenite removal (Jain et al., 2009). However, the contrary result that coagulation efficiency was not necessarily increased by the combined use of Al and Fe salts has also been reported (Johnson and Amirtharajah, 1983).

Currently, rare studies have applied dual coagulants, especially monomer coagulants that was easily available, with respect to algae removal (Cheng et al., 2003). The combined use of different coagulants might be especially desirable in algae coagulation. Aluminum exhibited higher efficiencies in terms of the removal of turbidity, bacteria, and color than iron salts did (Cheng et al., 2003), whereas iron salts were better than aluminum towards the removal dissolved organic carbon (DOC) (Cheng et al., 2003; Knocke et al., 1986). The treatment of algae-burdened water not only involves the removal of suspended algae cells but also that of soluble DOM, the dual-coagulant approach can be advantageous in this case. Meanwhile, the lowered doses of each component may control the residual levels of coagulants.

For the aforementioned concerns, a novel Mn(VII)–Fe(II) pre-treatment prior to Al coagulation was proposed. The objectives of this study are 1) to simultaneously enhance the removal of *M. aeruginosa* and control the level(s) of coagulant residue, and 2) to study the hydrolysis behavior of monomeric Fe and Al salts as dual coagulants. To date, few studies have investigated the hydrolysis mechanisms of Al or Fe in a dual-coagulant system, which might differ from those when each single coagulant was applied alone. This study used the electrospray ionization mass spectrometry (ESI-MS) technique to carefully illustrate the different hydrolysis behaviors in this system. The species transformation during the hydrolysis of pre-formed and freshly-formed Fe(III) was also compared by ESI-MS.

2. Experimental procedures

2.1. Materials and reagents

An axenic strain of *M. aeruginosa* (No. FACHB-905) previously described (Shen and Song, 2007) was used in this study, and was cultured in BG-11 (Rippka et al., 1979) medium. Full details of growth conditions are presented in the [Supplementary Data](#).

Mn(VII) stock solution of 0.5 mM Mn(VII) was prepared every week and stored in darkness. Ferrous sulfate (FeSO_4), ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3$] and aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) (reagent grade) solutions were prepared just before experiments. Source water was collected from the Miyun reservoir located in north China. Its qualities were as follows: turbidity 1.8 NTU, pH 7.7–7.9, temperature 23–25 °C, DOC 2.60 mg/L, Ca 43.2 mg/L.

2.2. Jar tests

M. aeruginosa cultures, harvested at the exponential growth phase, were spiked into source water with a final cell density of 1.0×10^6 cells/mL. The pH of this *M. aeruginosa* suspension was about 8.4. Mn(VII) (if any), Fe salts (if any) and Al salts were successively dosed at 0, 5 (if not specified) and 20 min. Mn(VII) dose of 3.3–16.7 μM , Fe dose of 39.5 μM and Al dose of 33.3–300 μM was applied. The equivalent molar ratio of Mn(VII) to Fe salts is 1:3 (≈ 0.33); while the molar ratios of Mn(VII) to Fe salts in this study ranged from 0.056 to 0.420. Details of jar tests are presented in the [Supplementary Data](#). After settling was complete, samples were collected and divided in two subsamples: the first was measured for residual *M. aeruginosa* by optical density at 680 nm (OD_{680}) with a U-3100 spectrophotometer (Hitachi Co., Japan); and the second was immediately subjected to filtration through a glass fiber filter (0.45 μm , Whatman, British) and then evaluated for K^+ , Fe, Mn and Al. Details of ion measurements are presented in the [Supplementary Data](#).

For some tests, 20 mL of sample was withdrawn at a pre-determined time (as specified in [Fig. 2](#)) and immediately filtered through a glass fiber filter (0.45 μm , Whatman, UK). The filtrate was evaluated for UV_{254} (U-3010, Hitachi Co., Japan) and the levels of metal ions.

For the test investigate the effect that the pre-oxidation time has on the organics, fluorescence excitation-emission matrix (EEM) was used.

2.3. ESI-MS measurements

The ESI time of flight (TOF) mass spectra were applied to study the hydrolysis behavior of Al and Fe separately and in mixed form. The operating parameters are listed in [Supplementary Data](#). ESI mass data was acquired using the MassLynx software 4.0 (Micromass, UK).

3. Result and discussion

3.1. Effect of Fe(II) introduction on *M. aeruginosa* removal by Al

Without any pre-treatments, the coagulation by Al of 83.3–108.3 μM only achieved 0–7% removal of *M. aeruginosa* ([Figure S1](#)). The ratio of [Al dose]:[*M. aeruginosa* removal] significantly increased when the Al dose ranged from 108.3 to 133.3 μM . This indicates an optimum dose range of Al for effective removal of *M. aeruginosa*, due to the possible iso-electric point between Al and algal substances.

Mn(VII) pre-treatment lowered the optimum dose range of Al for effective *M. aeruginosa* removal from 108.3–133.3 μM to 100.0–108.3 μM ([Fig. 1](#)). At Al dose of 83.3 μM , no enhancement in *M. aeruginosa* removal was observed even at Mn(VII) dose as high as 16.7 μM , while the improvement became much more substantial (47%–66%) at Al doses of 100.0 and 108.3 μM . This increase in the efficiency of coagulant is attributed to the pre-oxidation activity of Mn(VII) towards *M. aeruginosa* cells, which benefited the subsequent removal of *M. aeruginosa* by coagulation thereafter ([Chen and Yeh, 2005](#)).

Fig. 1 – *M. aeruginosa* removal by Fe(II)–Al, Mn(VII)–Al, and Mn(VII)–Fe(II)–Al processes. Mn(VII) dose: (A) 3.3 μM (B) 8.3 μM and (C) 16.7 μM . Fe(II) at 39.5 μM (if any) is dosed after the initial 5-min Mn(VII) pre-oxidation. Pre-treatment period: 20 min.

To assess the difference that the introduction of Fe(II) made, *M. aeruginosa* removal was investigated for the Mn(VII)–Fe(II)–Al and Mn(VII)–Al processes as a function of Mn(VII) dose. Mn(VII)–Fe(II) pre-treatment achieved an appreciable

Fig. 2 – Variation of (A) UV_{254} and (B) E_{250}/E_{365} of DOM during Mn(VII)–Al (squares), Mn(VII)–Fe(III)–Al (triangles) and Mn(VII)–Fe(II)–Al (circles) processes. Mn(VII) dose: $6.7 \mu\text{M}$. Fe dose (if any): $39.5 \mu\text{M}$. Al dose: $83.3 \mu\text{M}$. Cyanobacterium density: $1.0 \times 10^6 \text{ cells/mL}$.

improvement in the removal efficiency of cyanobacterium (16.4%–81.5%) (Fig. 1).

As shown in Fig. 1, the introduction of Fe(II) appreciably facilitated this common Mn(VII)-enhanced Al coagulation of *M. aeruginosa*. In general, this enhancement was more significant at lower dose of alum. Thus, the process takes best advantage of the dual-coagulant in cases where the Al dose is lower than the optimum dose range (108.3 – $133.3 \mu\text{M}$) when Al was dosed alone. As compared to the enhancement in *M. aeruginosa* removal achieved by Mn(VII) pre-treatment [$E_{\text{Mn(VII)}}$], the enhancement associated with Mn(VII)–Fe(II) pre-treatment [$E_{\text{Mn(VII)-Fe(II)}}$] (16.0%–72.7%) was considerably higher. For pre-treatment with Fe(II) alone, Fe(II) of $39.5 \mu\text{M}$ slightly improved the *M. aeruginosa* removal by only 3–8% at three Al doses (Figure S2). Clearly, the difference between $E_{\text{Mn(VII)-Fe(II)}}$ and $E_{\text{Mn(VII)}}$ (0.6–70.7%) was more significant than

the enhancement achieved by Fe(II) pre-treatment in the *M. aeruginosa* removal (Fig. 1).

3.2. Moderate pre-oxidation

In the Mn(VII)–Fe(II)–Al process, Fe(II) was mainly oxidized by Mn(VII) that had not reacted with *M. aeruginosa* cells and/or DOM. As a result, further inactivation of *M. aeruginosa* cells by Mn(VII) ceased. This is supported by the lower K^+ levels in the Mn(VII)–Fe(II)–Al process than those in the Mn(VII)–Fe(III)–Al process (Table S1). After absorbed into the vacuole of algae cell, the majority of K^+ stores as enzyme activator (Stewart, 1974) and thus its release can indicate the integrity of cell membrane (Peterson et al., 1995). The lower level of K^+ in Fe(II)-involved processes indicates the less extensive inactivation. In addition, the possibly concomitant release of IOM and its degradation can be alleviated (Ma et al., 2012b). Consequently, effects that DOM has on the coagulation would be beneficial rather than negative.

3.3. Fe(III) formed in situ

Fe(III) formed in situ is introduced into the system in the case of the Fe(II)-associated pre-treatment. This fresh form of Fe(III), deriving from the oxidation of Fe(II), shows more significant efficiency than the pre-formed Fe(III) with regard to the removal of DOM, especially those with unsaturated bonds. First, the addition of Fe coagulant to Al salts further removed DOM. As shown in Fig. 2A, UV_{254} of DOM was decreased by 8.5%–35.2% when Fe compounds were involved. This is attributed to their reaction with organics such as AOM (Pivokonsky et al., 2012, 2006) and/or humic substances (Voelker et al., 1997; Batchelli et al., 2010). In particular, during the coagulation and settling, Mn(VII)–Fe(II)–Al process showed lower UV_{254} values (0.070 – 0.044 cm^{-1}) in comparison to Mn(VII)–Fe(III)–Al process (0.073 – 0.047 cm^{-1}).

Moreover, the addition of Fe(II) coagulant facilitated the removal of organics with lower MW as compared to the pre-formed Fe(III) and alum. E_{250}/E_{365} of DOM associated with the Mn(VII)–Fe(II)–Al, Mn(VII)–Fe(III)–Al and Mn(VII)–Al processes ranged between 5.0 and 6.4, 2.4–3.5 and 2.2–3.2, respectively (Fig. 2B). E_{250}/E_{365} represents the ratio of UV absorption at 250 nm to that at 365 nm, and organics with lower MW correspond to higher E_{250}/E_{365} values (Peuravuori and Pihlaja, 1997). As organics with insufficient MW might interfere with coagulation (Bernhardt et al., 1985), it can be suggested that Fe(III) formed in situ shows much more significant efficiency in terms of DOM (especially that with insufficient MW) removal.

The variation of DOM in the three processes aforementioned reveals the distinct characteristics between freshly formed coagulant and the pre-formed one. To further investigate this difference, the effects of the time interval between the additions of Mn(VII) and Fe [$TIA_{\text{Mn(VII)-Fe}}$] on *M. aeruginosa* removal were compared (Fig. 3A). Firstly, regardless of $TIA_{\text{Mn(VII)-Fe}}$, *M. aeruginosa* removal achieved by the Mn(VII)–Fe(II)–Al process was much higher than that by the Mn(VII)–Fe(III)–Al process. Fe(III) that was freshly derived from Fe(II) oxidation has been shown to facilitate floc growth, compared to pre-formed Fe(III) (Ma et al., 2012b). The difference between

Fig. 3 – Effect of the time interval between the additions of Mn(VII) and Fe(II)/Fe(III) ($TIA_{Mn(VII)-Fe(II)/Fe(III)}$) on (A) *M. aeruginosa* removal and the level of residual (B) Al and (C) Fe, and (D) Mn in Mn(VII)–Fe(II)–Al (triangles) and Mn(VII)–Fe(III)–Al (circles) processes. Mn(VII) dose: 6.7 μ M. Fe dose:

their hydrolysis behaviors was further investigated by ESI-MS. Fig. 4 shows some representative ESI-MS spectra on Fe speciation, with the whole 30-min hydrolysis are presented in Supplementary Data (Figure S3–S5). The main patterns observed in these spectra are designated in Table 1.

Pre-formed Fe(III) rapidly hydrolyzed after being dosed into water (Fig. 4). No new species appeared in the spectra after 2 min, with the relative intensities of each species remaining constant (Table 2). The largest peak at m/z 275 was associated with $[Fe_2^{III}(OH)OSO_4 \cdot (H_2O)_n]^+$, indicating the higher stability of water series (Table 1) than primary species during Fe(III) hydrolysis (Hellman et al., 2006). As suggested by Hellman et al., this term ‘water series’ refers to multinuclear hydrolyzates of Fe those were coordinated water molecule(s).

Fe(III) formed in-situ, derived from the slow oxidation of Fe(II) by dissolved oxygen, hydrolyzed much more gradually in comparison to pre-formed Fe(III) (Figure S3 and S4). There was no notable variation in these spectra in the initial 10 min of hydrolysis (Figure S3). Species of low MW (m/z 73, 91 and 114) dominated the spectra, the intensities of which were significantly higher compared to species at the same m/z in the spectra of Fe(III) hydrolysis, respectively (Figure S4). After hydrolysis of 10 min, the intensities of the aforementioned patterns decreased in a dramatic manner; meanwhile, the pattern characterization introduced new species at m/z 147, 165, and 239 (Table 2). Additionally, the intensity of the species at m/z 239 was 3.2–4.9 times greater than that of the pattern at m/z 257 during 10–30 min hydrolysis (Table 2). No peaks were observed at m/z 275 and 319 in the total recorded spectra (30 min).

Mn(VII) accelerated the transformation of Fe(II) to Fe(III), and thus the apparent hydrolysis of Fe in this system (Figure S5). The ESI-MS spectrum after 2-min hydrolysis was similar to that at 30 min in the Fe(II) system. After 20-min hydrolysis, patterns at m/z 275 could be seen with lower intensity compared to species at m/z 239 in the mass spectra. Patterns at m/z 319 started to appear after 30 min of hydrolysis.

Thus, after the Fe(II) introduction in the Mn(VII)–Fe(II)–Al process, the complicated hydrolysis of in situ-formed Fe(III) occurred in a gradual way. This allowed the positively-charged cation and primary hydrolyzates more opportunity to directly neutralize the negative surface charge of *M. aeruginosa* cells and DOM. Correspondingly, flocs that were formed after destabilization could precipitate slowly. In addition, more fresh reactive surface sites on the in situ-formed Fe(III) that were available for subsequent reactions (Guan et al., 2009) may derive from its slow aging. Furthermore, the continuous provision of freshly formed Fe(III) in the coagulation system outperformed the one-dosage strategy of pre-formed Fe(III) in the removal of *M. aeruginosa* (Ma et al., 2012b).

Secondly, the impact that $T_{Mn(VII)-Fe}$ has on the *M. aeruginosa* removal significantly differed in the Mn(VII)–Fe(II)–Al and Mn(VII)–Fe(III)–Al processes (Fig. 3A). When $T_{Mn(VII)-Fe}$ increased from 0 to 15 min, the difference between the *M.*

118.4 μ M. Al dose: 83.3 μ M. Cyanobacterium density: 1.0×10^6 cells/mL. Pre-treatment period: 20 min.

Fig. 4 – Recorded positive ion mode spectrum of (a) 0.1 mM Fe(III) sulfate solution; (b) 0.1 mM Fe(II) sulfate solution; and (c) 0.1 mM Fe(II) sulfate mixed with 5 μ M Mn(VII), measured as the hydrolysis proceeded.

aeruginosa removal by these two processes narrowed, decreasing from 67% to 6%. Prolonged $\text{TIA}_{\text{Mn(VII)}-\text{Fe(III)}}$ contributed to higher removal in the Mn(VII)–Fe(III)–Al process. Only 15% of *M. aeruginosa* cells were removed with simultaneous addition of Mn(VII) and Fe(III), while a prolonged time interval (15 min) enhanced the removal efficiency to 80%. This can be explained by the aging of preformed Fe(III). The rapid hydrolysis of pre-formed Fe(III) may be completed during the rapid-mixing period, and the aging of the precipitated hydroxides of Fe(III) would inhibit the binding between small floc fragments. As the total pre-treatment period was constant (20 min), a shorter $\text{TIA}_{\text{Mn(VII)}-\text{Fe(III)}}$ indicated a longer aging

time of Fe(III), and thus less active Fe(III) hydrolyzates or precipitates.

In contrast, for the Mn(VII)–Fe(II)–Al process, the time interval between the addition of Mn(VII) and Fe(II) barely affected the removal efficiency of *M. aeruginosa*, which varied between 86% and 91%. The influence that $\text{TIA}_{\text{Mn(VII)}-\text{Fe(II)}}$ had on the aging of freshly formed Fe(III) was probably not that significant, because the gradual oxidation of Fe(II) limited the rate of Fe(III) transformation and thus its hydrolysis. Moreover, longer $\text{TIA}_{\text{Mn(VII)}-\text{Fe(II)}}$ might result in a higher level and/or lower MW of DOM, which can interfere with the coagulation, despite its positive impact on the activity of freshly

Table 1 – Assigned Charged Cationic Iron Complexes in 0.1 mM Fe(III) or Fe(II) Sulfate Solution. Spectra Recorded in Positive Ion Mode.

m/z	Species
73, 91	$[\text{Fe}^{\text{II}}(\text{OH}) \cdot (\text{H}_2\text{O})_n]^+$, $[\text{Fe}^{\text{III}}(\text{OH}) \cdot (\text{H}_2\text{O})_n]^{2+}$
114	$[\text{Fe}_2^{\text{II}}]^{4+}$, $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}]^{5+}$, $[\text{Fe}_2^{\text{III}}]^{6+}$
147, 165, 183	$[\text{Fe}^{\text{II}}(\text{OH}) \cdot (\text{H}_2\text{O})_n]^+$, $[\text{Fe}_2^{\text{III}}(\text{OH})\text{O} \cdot (\text{H}_2\text{O})_n]^{3+}$
239, 257, 275	$[\text{Fe}_2^{\text{III}}(\text{OH})\text{OSO}_4 \cdot (\text{H}_2\text{O})_n]^+$
319	$[\text{Fe}_2^{\text{III}}(\text{OH})(\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_n]^+$, $[\text{Fe}_4^{\text{III}}\text{O}_5(\text{OH})]^+$

Table 2 – Speciation of coagulants and intensities of each species in hydrolysis process. Spectra recorded in positive ion mode.

Solution	Time (min)	Percentage at m/z (%)									
Fe(III)	0	73	94	114	147	165	183	239	257	275	319
	30	3.5	2.3	13.6	12.1	13.4	5.5	13.2	9.0	20.9	6.5
Fe(II)	0	12.7	8.9	78.4	— ^a	—	—	—	—	—	—
	10	4.0	3.0	23.8	14.9	18.7	8.5	23.1	4.0	—	—
Fe(II) + Mn(VII)	30	3.9	2.4	15.7	19.4	21.1	9.2	22.9	5.4	—	—
	2	5.0	3.1	20.8	17.2	20.5	6.1	18.7	8.6	—	—
	30	3.2	2.0	12.6	17.1	20.1	6.3	20.7	5.5	9.1	3.4

^a No peak.

formed Fe(III). Therefore, the *M. aeruginosa* removal was relatively $TIA_{Mn(VII)-Fe(II)}$ -independent due to the factors aforementioned.

Although $TIA_{Mn(VII)-Fe}$ had distinct influence on *M. aeruginosa* removal, the effects of $TIA_{Mn(VII)-Fe}$ on residual Al levels were similar (Fig. 3B). For both processes, the highest level of residual Al was associated with $TIA_{Mn(VII)-Fe}$ of 2 min. Despite that Fe and Al coagulants were not dosed at the same time, the hydrolysis/precipitation of Fe shows influence on that of Al salts. In support of this, the residual Al concentrations in the Mn(VII)–Fe(III)–Al process were observed to be 3–12 $\mu\text{g/L}$, which were higher than those in the Mn(VII)–Fe(II)–Al process when $TIA_{Mn(VII)-Fe}$ ranged between 0 and 15 min. This should be attributed to the different introduction patterns and activity of pre-formed and freshly formed Fe(III), which further influenced the hydrolysis/precipitation of Al salts. This dual-coagulant hydrolysis mechanism will be discussed in detail later.

Residual Fe and Mn showed distinctly different trend from that of residual Al (Fig. 3C and D). For Mn(VII)–Fe(III)–Al process, Fe and Mn precipitated sufficiently with the precipitation ratios of above 0.993 and above 0.977 regardless of

Fig. 6 – Variation of Al precipitation during Mn(VII)–Al (gray cubics) and Mn(VII)–Fe(III)–Al (dark triangles) processes. Mn(VII) dose: 6.7 μM . Fe dose (if any): 39.5 μM . Al dose: 83.3 μM . Cyanobacterium density: 1.0×10^6 cells/mL.

Fig. 5 – Fe precipitation after 30-min settling in Mn(VII)–Fe(II)–Al and Fe(II)–Al processes. Fe(II) dose: 39.5 μM . Mn(VII) dose (if any): 6.7 μM . Pre-treatment period: 20 min. Fe(II) of 39.5 μM (if any) is dosed after the initial 5 min of the pre-treatment.

Fig. 7 – Residual levels of Al after 30-min settling in Mn(VII)–Al, Mn(VII)–Fe(II)–Al and Mn(VII)–Fe(III)–Al processes. *M. aeruginosa* density: 1.0×10^6 cells/mL. Pre-treatment time: 20 min. Fe(II) of 39.5 μM was dosed 5 min after Mn(VII) addition. Alum dose: 83.3 μM .

$TIA_{Mn(VII)-Fe}$. This is attributed to the hydrolysis of pre-formed Fe(III) salts that is more rapid than that of Fe(III) formed *in situ*, as well as the complete transformation of Mn(VII) to its insoluble product, i.e., MnO_2 . Comparatively, in Mn(VII)–Fe(II)–Al process the extent of Fe and Mn precipitation was much lower with the maximum precipitation ratios of 0.993 and 0.130, respectively. Moreover, the lowered time intervals between dosing Mn(VII) and Fe(II) benefited Fe and Mn precipitation, and the highest precipitation ratios of 0.992 for Fe and 0.129 for Mn was associated with $TIA_{Mn(VII)-Fe}$ of 0 min, respectively. The oxidation of *M. aeruginosa* by Mn(VII) mainly occurred in the initial 5–10 min, and its product MnO_2 can also act as an oxidant with Mn^{2+} as reductant (Ma et al., 2012b). This result not only indicates the fast oxidation of Fe(II) by Mn(VII), but infers the possible bridging effect of positively-charged Mn(II) between negative species such as algae and IOM in the subsequent coagulation (Ma et al., 2012b). Furthermore, the difference between Mn and Fe precipitation in Mn(VII)–

Fe(II)–Al process showed similar trends as in Mn(VII)–Fe(III)–Al process, and the precipitation rate of Fe was mainly dependent on the hydrolysis of *in situ* formed Fe(III) rather than the oxidation of Fe(II). It was assumed that *in situ* formed Fe(III) might hydrolyze slower than the pre-formed Fe(III).

In the Mn(VII)–Fe(II)–Al process, the oxidation of Fe(II) resulted in lower ratios of Mn precipitation (Fig. 3D). This arises the concern on unacceptable Mn level that exceeds the National Drinking Water Standard for Mn, i.e., 0.1 mg/L (The ministry of health of the People's Republic of China and China national standardization management committee 2006). It was noted that the concentration of *M. aeruginosa* in this study was as high as 1.0×10^6 cells/mL, which was over 10–100 times higher than those even in case of algae bloom (Ning et al., 2001; Wang et al., 2004; Dai et al., 2008). In practice the Mn(VII) doses may be much lower than that used in this study. In treatment of algae-laden water with lower algae density, i.e., 0.25×10^6 and 0.5×10^6 cells/mL, the decreased Mn(VII) dose (0.45–1.8 μM) may achieve desirable removal of *M. aeruginosa*, and the level of residual Mn can be well controlled to be below 0.1 mg/L accordingly (Figure S6).

3.4. Hydrolysis mechanisms of Fe and Al as dual-coagulant

Beside the high activity of Fe(III) formed *in situ*, the hydrolysis behaviors of Fe and Al as dual-coagulant also contributed to the significant efficiency of the Mn(VII)–Fe(II)–Al process. In support of this suggestion, the improvement of algae removal achieved by Mn(VII)–Fe(III) pre-treatment [$I_{Mn(VII)-Fe(III)}$] was greater than the combined improvement by Mn(VII) and Fe(III) pre-treatments [$I_{Mn(VII)} + I_{Fe(III)}$] (Table S2).

The hydrolysis behaviors of Fe and Al as dual-coagulant were supposed to differ from those when dosed alone, respectively. On one hand, the presence of Al facilitated the hydrolysis of Fe regardless of Mn(VII) application (Fig. 5). Without Mn(VII) pre-oxidation, the concentration of Fe

Fig. 8 – Amount of precipitated Fe salt after 30-min settling in (A) Fe(II)–Al and Fe(III)–Al processes and (B) Mn(VII)–Fe(II)–Al and Mn(VII)–Fe(III)–Al processes. *M. aeruginosa* density: 1.0×10^6 cells/mL. Pre-treatment time: 20 min. Fe(II) of 39.5 μM was dosed 5 min after Mn(VII) addition. Alum dose: 83.3 μM .

Fig. 9 – Precipitation of Al in Mn(VII)–Al and Mn(VII)–Fe(II)–Al process. *M. aeruginosa* density: 1.0×10^6 cells/mL. Pre-treatment time: 20 min. Fe(II) of 39.5 μM was dosed 5 min after Mn(VII) addition. Alum dose: 100 μM .

residue was $0.79 \mu\text{M}$ at the Al dose of $83.3 \mu\text{M}$, which decreased to $0.35 \mu\text{M}$ when a higher dose of Al was applied ($100 \mu\text{M}$). Similar improvement in Fe precipitation by increasing Al dose was observed when Mn(VII) was used to oxidize *M. aeruginosa* cells. This indicated that Al can improve the precipitation of Fe regardless of Mn(VII) oxidation of *M. aeruginosa* cells, which provided additional information to the previous report that claimed an improvement in Fe precipitation by Al salts (Zapolski and Baran, 1987).

On the other hand, the addition of Fe enhanced the precipitation of Al salts in this study. As shown in Fig. 6, the Mn(VII)–Al and Mn(VII)–Fe(III)–Al processes were compared in terms of Al precipitation during the whole coagulation process. The doses of Al and Fe(III) (if any) were 83.3 and $39.5 \mu\text{M}$, respectively. As the coagulation proceeded, the concentration of residual Al decreased from 3.3 to $1.8 \mu\text{M}$ in the Mn(VII)–Al process and from 2.1 to $1.1 \mu\text{M}$ in the Mn(VII)–Fe(III)–Al process. In particular, the precipitation of Al increased more remarkably in the Mn(VII)–Al process, and thus the difference between the Al precipitation narrowed,

decreasing from 0.015 to 0.003 as the coagulation proceeded (Fig. 6). The same results were observed at higher doses of Fe(III) (79 and $118.5 \mu\text{M}$) (Fig. 7). Levels of residual Al were lower than those without the application of Fe(III).

A similar improvement in Al precipitation by Fe(III) occurs in the case of no application of Mn(VII). At Al dose of $100 \mu\text{M}$, Fe(III) pre-treatment of $39.5 \mu\text{M}$ decreased the level of Al residue to $1.4 \mu\text{M}$ from $1.9 \mu\text{M}$ without any pre-treatment (data not shown). Therefore, it can be demonstrated that, regardless of Mn(VII) pre-oxidation, the addition of Fe(III) led to an increased amount of precipitated alum.

Coexisting with Al species, Fe compounds tended to hydrolyze/precipitate preferentially rather than forming AOM-Fe complexes. The positively-charged hydrolyzates of Fe, accordingly, can accelerate/enhance the cross-linking and clustering of AOM-Al complexes and/or Al hydrolyzates. In support of this suggestion, the increase in Fe(II) or Fe(III) dose improved the precipitation of Fe salts (Fig. 8). Higher doses of Fe(II) or Fe(III) enhanced the cross-linking and clustering of Al- and Fe-hydroxide polymers; consequently more significant

Fig. 10 – Recorded positive ion mode spectrum of 0.1 mM Fe(II) sulfate and 0.1 mM AlCl_3 combined and alone. pH: (A) 5.5 and (B) 7.5. All samples were filtered before ESI-MS measurement. Desolvation temperature 120°C , source temperature 150°C .

removal of Fe compounds occurred. On one hand, in respective solution, Al coagulants hydrolyzed in a much slower way as compared to Fe salts (Tang, 1990). On the other hand, Al salts tended to form soluble complexes with AOM rather than flocs or large MW precipitates when co-existing with Fe salts. This differed from the hydrolysis behavior of Al when applied alone (Safarikova et al., 2013). This is attributed to the higher affinity of released proteins to Al species than to iron compounds (Pivokonsky et al., 2006), which might also explain the greater efficiency of iron salts in terms of DOC removal (Knocke et al., 1986).

Similarly, introducing Fe(II) into the pre-treatment improved the precipitation of Al salts (Fig. 9). As compared to the pre-formed Fe(III), Fe(III) freshly formed can further enhance the hydrolysis and thus precipitation of Al (Figs. 2A and 3B). Regardless of Mn(VII) application, lower levels of residual Al were associated with the Mn(VII)–Fe(II)–Al process compared to the Mn(VII)–Fe(III)–Al process. As shown in Fig. 7 and 49%–232% larger amount of Al precipitated in the process involving Fe(II) than in the corresponding Fe(III) process.

This was firstly attributed to the more gradual hydrolysis of freshly formed Fe(III). This kind of Fe(III) consumed OH^- ions in a much slower way as compared to the pre-formed species. In support of this, pre-treatments with Fe(II) did not cause as much pH reduction as Fe(III) pre-treatments (Table S3). Then, the relatively higher pH, achieved by the pre-treatments involving Fe(II) rather than Fe(III), facilitated the subsequent hydrolysis of Al.

Moreover, in the case where Mn(VII) was applied, the reaction between Al and DOM might be another factor in the Fe(II)-derived improvement in Al precipitation. Mn(VII) pre-oxidation of *M. aeruginosa* resulted in the release of intracellular organics including proteins (Table S4), which were apt to form complexes with Al salts (Henderson et al., 2010; Pivokonsky et al., 2006; Gregor et al., 1997). At a low Al:DOM ratio, these soluble Al-protein complexes would interfere with the cross-linking and clustering of Al hydrolyzates (Bernhardt et al., 1985; Jekel and Heinzmann, 1989), resulting in high

levels of residual alum. As compared to Fe(III), Fe(II) could inhibit the extensive pre-oxidation of *M. aeruginosa*. Fe(II) application was associated with lower level of DOM and thus higher Al/DOM ratio, by which the cross-linking and clustering of Al–hydroxide polymers became possible.

To provide further information on the hydrolysis mechanism of Fe and Al as dual-coagulant, ESI-MS was used to compare the hydrolysis behaviors of Fe(III) and Al alone and combined at different pH (Fig. 10). At pH 5.5, the total ion count of Al and Fe(III) in the co-existing system (1050) was 42.8% less than the sum of the TIC values of Al and Fe(III) alone (1836) (Fig. 11). Similarly, 18.7% more Fe(III) and/or Al precipitated when they were present together at pH 7.5. This difference indicates that their coexistence improves the precipitation of coagulant(s) (Fe(III) and/or alum). Therefore, application of dual-coagulation is a practical method to control the coagulant residue.

4. Conclusions

This study has demonstrated that the Mn(VII)–Fe(II)–Al process is an efficient process to enhance the removal of *M. aeruginosa* as well as to control the residual level of coagulant(s). Mn(VII)–Fe(II) pre-treatment achieves an appreciable improvement (16.4%–81.5%), which was even 0.6–70.7% higher than the sum of improvements by Mn(VII) and Fe(II) pre-treatments. Compared to the pre-formed Fe(III), Fe(III) formed in situ shows much more significant efficiency in the removal of *M. aeruginosa*. Additionally, the presence of Al facilitated the precipitation of Fe(III) and vice versa. Therefore, the concomitant application of Al and freshly formed Fe(III) can contribute to lower residual levels of both coagulants. This study mainly focused on the application of dual-coagulant to remove *M. aeruginosa* in the synthesized water matrix and lower the coagulant level in the final effluent. Additional research is needed to assess the feasibility of the Mn(VII)–Fe(II)–Al process in pilot- or full-scale drinking water treatment plants. Considering that *M. aeruginosa* is the dominate cyanobacteria species the cell density applied in this study was much higher than those in practical algae bloom, it is reasonable to presume an effective application of Mn(VII)–Fe(II)–Al process in practical water matrix.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2014.07.011>.

Fig. 11 – Total ion count (TIC) in the spectra of Fe(III) and Al alone and in the form of mixture. Spectra were recorded in positive ion mode. All samples were filtrated before ESI-MS analysis.

REFERENCES

- Batchelli, S., Muller, F.L.L., Chang, K.-C., Lee, C.-L., 2010. Evidence for strong but dynamic iron-humic colloidal associations in humic-rich coastal waters. *Environ. Sci. Technol.* 44 (22), 8485–8490.
- Bernhardt, H., Clasen, J., 1991. Flocculation of microorganisms. *J. Water Supply Res. Technol. AQUA* 40 (2), 76–87.
- Bernhardt, H., Hoyer, O., Schell, H., Lusse, B., 1985. Reaction mechanisms involved in the influence of algogenic matter on flocculation. *Z. Wasser Abwasser Forsch.* 18 (1), 18–30.
- Bond, T., Goslan, E.H., Jefferson, B., Roddick, F., Fan, L., Parsons, S.A., 2009. Chemical and biological oxidation of NOM surrogates and effect on HAA formation. *Water Res.* 43 (10), 2615–2622.
- Bose, P., Reckhow, D.A., 2007. The effect of ozonation on natural organic matter removal by alum coagulation. *Water Res.* 41 (7), 1516–1524.
- Chen, J.-J., Yeh, H.-H., 2005. The mechanisms of potassium permanganate on algae removal. *Water Res.* 39 (18), 4420–4428.
- Chen, J.-J., Yeh, H.-H., Tseng, I.-C., 2009. Effect of ozone and permanganate on algae coagulation removal – pilot and bench scale tests. *Chemosphere* 74 (6), 840–846.
- Cheng, W.P., Yu, R.F., Chen, C.H., Chi, C.H., 2003. Enhanced coagulation on reservoir water by dual inorganic coagulants. *Environ. Eng. Sci.* 20, 229–235.
- Dai, R., Liu, H., Qu, J., 2008. Cyanobacteria and their toxins in Guanting Reservoir of Beijing, China. *J. Hazard. Mater.* 153, 470–477.
- Daly, R.I., Ho, L., Brookes, J.D., 2007. Effect of chlorination on *Microcystis aeruginosa* cell integrity and subsequent microcystin release and degradation. *Environ. Sci. Technol.* 41 (12), 4447–4453.
- Drikas, M., Chow, C.W.K., House, J., Burch, M.D., 2001. Using coagulation, flocculation, and settling to remove toxic cyanobacteria. *J. Am. Water Works Assoc.* 93 (2), 100–111.
- Fang, J., Ma, J., Yang, X., Shang, C., 2010. Formation of carbonaceous and nitrogenous disinfection by-products from the chlorination of *Microcystis aeruginosa*. *Water Res.* 44 (6), 1934–1940.
- Gheraout, B., Gheraout, D., Saiba, A., 2010. Algae and cyanotoxins removal by coagulation/flocculation: a review. *Desalin. Water Treat.* 20 (1–3), 133–143.
- Gregor, J.E., Nokes, C.J., Fenton, E., 1997. Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation. *Water Res.* 31 (12), 2949–2958.
- Guan, X., Ma, J., Dong, H., Jiang, L., 2009. Removal of arsenic from water: effect of calcium ions on As(III) removal in the KMnO_4 -Fe(II) process. *Water Res.* 43 (20), 5119–5128.
- Hellman, H., Laitinen, R.S., Kaila, L., Jalonen, J., Hietapelto, V., Jokela, J., Sarpola, A., Rämö, J., 2006. Identification of hydrolysis products of FeCl_3 - $6\text{H}_2\text{O}$ by ESI-MS. *J. Mass Spectrom.* 41 (11), 1421–1429.
- Henderson, R.K., Parsons, S.A., Jefferson, B., 2010. The impact of differing cell and algogenic organic matter (AOM) characteristics on the coagulation and flotation of algae. *Water Res.* 44 (12), 3617–3624.
- Huang, J., Graham, N., Templeton, M.R., Zhang, Y., Collins, C., Nieuwenhuijsen, M., 2009. A comparison of the role of two blue-green algae in THM and HAA formation. *Water Res.* 43 (12), 3009–3018.
- Jain, A., Sharma, V.K., Mbuya, O.S., 2009. Removal of arsenite by Fe(VI), Fe(VI)/Fe(III), and Fe(VI)/Al(III) salts: effect of pH and anions. *J. Hazard. Mater.* 169 (1–3), 339–344.
- Jekel, M.R., Heinzmann, B., 1989. Residual aluminium in drinking water treatment. *J. Water Supply: Res. Technol. AQUA* 38 (5), 281–288.
- Johnson, P.N., Amirtharajah, A., 1983. Ferric chloride and alum as single and dual coagulants. *J. Am. Water Works Assoc.* 75 (5), 232–239.
- Kawahara, M., Kato-Negishi, M., 2011. Link between aluminum and the Pathogenesis of Alzheimer's disease: the Integration of the aluminum and Amyloid Cascade Hypotheses. *Int. J. Alzheimer's Dis.* 2011, 1–17. <http://dx.doi.org/10.4061/2011/276393>.
- Knocke, W.R., West, S., Hoehn, R.C., 1986. Effects of low temperature on the removal of trihalomethane precursors by coagulation. *J. Am. Water Works Assoc.* 78 (4), 189–195.
- Kuusik, R., Viisimaa, L., 1999. A new dual coagulant for water purification. *Water Res.* 33 (9), 2075–2082.
- Li, L., Shao, C., Lin, T.-F., Shen, J., Yu, S., Shang, R., Yin, D., Zhang, K., Gao, N., 2014. Kinetics of cell inactivation, toxin release, and degradation during Permanganation of *Microcystis aeruginosa*. *Environ. Sci. Technol.* 48 (5), 2885–2892.
- Ma, J., Liu, W., 2002. Effectiveness and mechanism of potassium ferrate(VI) preoxidation for algae removal by coagulation. *Water Res.* 36 (4), 871–878.
- Ma, M., Liu, R.P., Liu, H.J., Qu, J.H., Jefferson, W., 2012a. Effects and mechanisms of pre-chlorination on *Microcystis aeruginosa* removal by alum coagulation: significance of the released intracellular organic matter. *Sep. Purif. Technol.* 86, 19–25.
- Ma, M., Liu, R.P., Liu, H.J., Qu, J.H., 2012b. Effect of moderate pre-oxidation on the removal of *Microcystis aeruginosa* by KMnO_4 -Fe(II) process: significance of the in-situ formed Fe(III). *Water Res.* 46 (1), 73–81.
- Ning, P., Zhu, Y., Xu, X., 2001. Application of ferric chloride in removal of blue algae at algal eruptive period in Dianchi Lake (in Chinese). *Argo Environ. Prot.* 20 (5), 348–350.
- Paralkar, A., Edzwald, J.K., 1996. Effect of ozone on EOM and coagulation. *J. Am. Water Works Assoc.* 88 (4), 143–154.
- Peterson, H.G., Hrudef, S.E., Cantin, I.A., Perley, T.R., Kenefick, S.L., 1995. Physiological toxicity, cell membrane damage and the release of dissolved organic carbon and geosmin by aphanizomenon flos-aquae after exposure to water treatment chemicals. *Water Res.* 29 (6), 1515–1523.
- Peuravuori, J., Pihlaja, K., 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. *Anal. Chim. Acta* 337 (2), 133–149.
- Pivokonsky, M., Kloucek, O., Pivokonska, L., 2006. Evaluation of the production, composition and aluminum and iron complexation of algogenic organic matter. *Water Res.* 40 (16), 3045–3052.
- Pivokonsky, M., Safarikova, J., Bubakova, P., Pivokonska, L., 2012. Coagulation of peptides and proteins produced by *Microcystis aeruginosa*: interaction mechanisms and the effect of Fe-peptide/protein complexes formation. *Water Res.* 46 (17), 5583–5590.
- Plummer, J.D., Edzwald, J.K., 2002. Effects of chlorine and ozone on algal cell properties and removal of algae by coagulation. *J. Water Supply: Res. Technol. AQUA* 51 (6), 307–318.
- Rippka, R., Deruelles, J., Waterbury, J.B., Herdman, M., Stanier, R.Y., 1979. Generic assignments, strain histories and properties of pure cultures of cyanobacteria. *J. Gen. Microbiol.* 111 (1), 1–61.
- Rondeau, V., Commenges, D., Jacqmin-Gadda, H., Dartigues, J.-F., 2000. Relation between aluminum concentrations in drinking water and Alzheimer's disease: an 8-year Follow-up study. *Am. J. Epidemiol.* 152 (1), 59–66.
- Rong, H., Gao, B., Dong, M., Zhao, Y., Sun, S., YanWang, Yue, Q., Li, Q., 2013. Characterization of size, strength and structure of aluminum-polymer dual-coagulant flocs under different pH and hydraulic conditions. *J. Hazard. Mater.* 252–253 (5), 330–337.
- Safarikova, J., Baresova, M., Pivokonsky, M., Kopecka, I., 2013. Influence of peptides and proteins produced by

- cyanobacterium *Microcystis aeruginosa* on the coagulation of turbid waters. *Sep. Purif. Methods* 118, 49–57.
- Shen, H., Song, L., 2007. Comparative studies on physiological responses to phosphorus in two phenotypes of bloom-forming *Microcystis*. *Hydrobiologia* 592, 475–486.
- Shen, Q., Zhu, J., Cheng, L., Zhang, J., Zhang, Z., Xu, X., 2011. Enhanced algae removal by drinking water treatment of chlorination coupled with coagulation. *Desalination* 271 (1–3), 236–240.
- Stewart, W.D.P., 1974. In: Hellebust, J.A. (Ed.), *Algal Physiology and Biochemistry*. University of California Press, Los Angeles.
- Steynberg, M.C., Pieterse, A.J.H., Geldenhuys, J.C., 1996. Improved coagulation and filtration as a result of morphological and behavioural changes due to pre-oxidation. *J. Water Supply: Res. Technol. AQUA* 45 (6), 292–298.
- Takaara, T., Sano, D., Masago, Y., Omura, T., 2010. Surface-retained organic matter of *Microcystis aeruginosa* inhibiting coagulation with polyaluminum chloride in drinking water treatment. *Water Res.* 44 (13), 3781–3786.
- Tang, H., 1990. Basic studies of inorganic polymer flocculants (in Chinese). *Environ. Chem.* 8 (3), 1–12.
- The ministry of health of the People's Republic of China and China national standardization management committee (Ed.), 2006. *Drinking Water Sanitary Standard* (5749-2006).
- Voelker, B.M., Morel, F.M.M., Sulzberger, B., 1997. Iron redox cycling in surface waters: effects of humic substances and light. *Environ. Sci. Technol.* 31 (4), 1004–1011.
- Wang, F., Wang, X., Huang, Y., He, W., Han, H., Wang, L., Jin, P., 2004. Potassium permanganate and chlorine used as coagulation aid for oxidation of high algae-laden water (in Chinese). *China Water Wastewater* 20 (3), 9–11.
- Wei, J., Gao, B., Yue, Q., Wang, Y., Li, W., Zhu, X., 2009. Comparison of coagulation behavior and floc structure characteristic of different polyferric-cationic polymer dual-coagulants in humic acid solution. *Water Res.* 43 (3), 724–732.
- Wert, E.C., Korak, J.A., Trenholm, R.A., Rosario-Ortiz, F.L., 2014. Effect of oxidant exposure on the release of intracellular microcystin, MIB, and geosmin from three cyanobacteria species. *Water Res.* 52, 251–259.
- Westerhoff, P., Rodrigues, M., Baker, L., Sommerfeld, M., 2005. Seasonal occurrence and degradation of 2-methylisoborneol in water supply reservoirs. *Water Res.* 39 (20), 4899–4912.
- Zapolski, A.K., Baran, A.A., 1987. Coagulants and Flocculants in Water Purification Processes (Koagulyaty i flokkulyanty v protsessah ochistki vody). Khimiya, Leningrad.
- Zhou, S., Shao, Y., Gao, N., Deng, Y., Li, L., Deng, J., Tan, C., 2014. Characterization of algal organic matters of *Microcystis aeruginosa*: biodegradability, DBP formation and membrane fouling potential. *Water Res.* 52, 199–207.