Effects of the interaction between *Microcystis aeruginosa* and nitrobenzene on coagulation-sedimentation performance

Zhiquan Liu, Zhenling Hou, Hua Ma, Zhenqiang Fan, Zhiwei Zhao, Dongmei Liu and Fuyi Cui

ABSTRACT

It is rarely reported that the interaction between xenobiotics and algae may cause potential water quality risks and affect the drinking water treatment process. In the present study, a bench-scale jar test was performed to investigate the effects of the interaction between nitrobenzene (NB) and *Microcystis aeruginosa* on the performance of coagulation-sedimentation by comparing differences in turbidity, optical density at 680 nm (OD_{680}), trihalomethane formation potential (THMFP) and microcystin-LR (MC-LR) in an *M. aeruginosa* solution with or without NB. The results indicated that the quality of *M. aeruginosa*-containing water can be improved significantly by coagulation-sedimentation, and all of the removal rates were more than 80%. The presence of NB did not affect the performance of coagulation-sedimentation directly. However, the interaction between NB and *M. aeruginosa* did change the characteristics of the raw water and affect the performance of coagulation-sedimentation. At a non-lethal concentration, NB did not inhibit the growth of *M. aeruginosa* but weakened the zeta potential of *M. aeruginosa*, which enhanced the removal of turbidity. The products of NB degradation by *M. aeruginosa* cause an increased THMFP in extracellular organic matters, which cannot be removed by coagulation-sedimentation efficiently, increasing the risk of disinfection by-products formation in the following disinfection unit.

Key words | algae, coagulation, sedimentation, THMFP, xenobiotics

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INTRODUCTION

Eutrophication and xenobiotic pollution are two of the most common problems in the aquatic environment. Sometimes, these two problems may occur simultaneously. An official Chinese investigation (Ministry of Environmental Protection of the People's Republic of China 2010) indicates that of the 26 total monitored large lakes and reservoirs, 14 (53.8%) face a eutrophication problem and 16 (61.5%) face a xenobiotic pollution problem. The study also indicates that Taihu Lake, Chaohu Lake and Dianchi Lake are contaminated by a combination of xenobiotics and algae (including cyanobacteria) in the summer. When these lakes are used as drinking water sources, the pollutants can affect the water treatment process and worsen the effluent water quality. The characteristics and effects of individual algal or organic problems on water treatment plants have been well studied (Takaara *et al.* 2010; Tian *et al.* 2010; Shen *et al.* 2011; Zamyadi *et al.* 2012). However, the effects of the interaction between xenobiotics and algae are rarely reported.

Xenobiotics can inhibit the growth and metabolism of algae (Tukaj 1989; Andreozzi *et al.* 2004), while algae and cyanobacteria have the ability to adsorb or degrade xenobiotics (Semple *et al.* 1999). Both interactions depend on the physical and chemical properties of the xenobiotics and the species of algae.

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Due to the interaction between xenobiotics and algae, the characteristics of the raw water may change, hence affecting the performance of water treatment plants. Our previous study (Liu *et al.* 2011) indicated that the presence of nitrobenzene (NB) can enhance the protein productivity of *Microcystis aeruginosa* and result in an increased yield of trihalomethane formation potential (THMFP) by *M. aeruginosa*. However, it is still not clear whether increased THMFP productivity will cause an increased risk of disinfection by-products formation in the effluent of water treatment plants or not.

In the present study, NB, a typical industrial material widely observed in the aquatic environment (Gao *et al.* 2008), and *M. aeruginosa*, a common dominant species of cyanobacteria in eutrophic lakes and reservoirs that can release microcystins (MCs), were selected as the representative pollutants. A bench-scale jar test was conducted to evaluate the effects of the interaction between NB and *M. aeruginosa* on the performance of coagulation-sedimentation.

MATERIALS AND METHODS

M. aeruginosa culturing

Axenic *M. aeruginosa* (FACHB-930) was purchased from the Institute of Hydrobiology at the Chinese Academy of Sciences but was still treated by Semple & Cain's (1996) method to exclude microbial contamination. The stock culture and the experimental culture were incubated under the designed conditions (BG11 medium, 25 °C) as described in our previous publication (Liu *et al.* 2011), and the components of BG11 medium have been listed in supporting information (Tables S1 and S2, available online at http://www.iwaponline.com/jws/063/081.pdf).

Jar test

The bench-scale coagulation-sedimentation experiments were conducted using a standard jar-test unit (ZR2-6, Fuhua Co. Ltd, China) consisting of six 2-L glass jars. The glass jars were used to minimize the adsorption of organic compounds by the containers. Due to the low room temperature (14–18 °C), a water bath was used to maintain the water temperature at 25 ± 1 °C, which is a necessary condition (the lowest temperature) for *M. aeruginosa* blooms. Alkalinity and pH can affect the hydrolysis of coagulants and the performance of coagulation-sedimentation (Gottfried *et al.* 2008). Because the low alkalinity in *M. aeruginosa* solutions limited the coagulation efficiency (less than 70% for the removal of OD_{680}), 106 mg/L sodium carbonate (equivalent to 100 mg/L alkalinity as $CaCO_3$) was added to all the samples before the coagulation-sedimentation experiment. Aluminum sulfate, ferric chloride and polyaluminum chloride (PAC) were used as the coagulants. Following the addition of coagulant, the waters were subjected to rapid mixing for 1 min at 250 rpm, flocculation for 14 min (4 min at 100 rpm and 10 min at 40 rpm), and settling for 30 min.

A pre-experiment (Figure S1, supplementary data, available online at http://www.iwaponline.com/jws/063/081.pdf) showed that at the coagulant dosage optimized for turbidity, other water quality parameters of the settled water also approximated optimal values. Thus, in this study, all of the presented data were obtained at the coagulant dosage optimized for turbidity (the residual turbidity with different coagulant dosages can be found in Figure S2, available online at http://www.iwaponline.com/jws/063/081.pdf). All of the jar tests were conducted in triplicate, and the arithmetic mean (±SD) was used as the final value.

Analytical methods

The algal density was monitored by spectrophotometry at a wavelength of 680 nm (OD_{680}, UV759S, INESA instrument Co. Ltd, China), and cell number counting was performed with a microscope (Olympus BX41, Olympus Optical Co., Ltd, Japan) according to the method adopted by Ma *et al.* (2009). There was a significant linear regression between OD_{680} and cell density (Figure S3, available online at http://www.iwaponline.com/jws/063/081.pdf). We used OD_{680} to study the removal rate of cell density, and checked the initial cell density by microscope analysis before the coagulation-sedimentation experiment to ensure consistent initial conditions in different batch experiments.

THMFP was measured by gas chromatography with an electron capture detector (Agilent 7890N) according to Liu's method (2011). An excess chlorine dosage (1,600 mg/L) was applied to ensure that all the THMFP could be oxidized to form THMs, independent of the actual chlorine dosage

used during disinfection; the results do not reflect the real production of THMs under actual conditions.

The intracellular microcystin-LR (MC-LR) and extracellular MC-LR were extracted and measured according to Meriluoto & Spoof's (2005a, b) method, but the extracellular MC-LR was undetectable (below 1 μg/L) in most instances because of the low death rate of *M. aeruginosa* in the exponential growth phase and the low release rate of MC-LR by the dead cells. Briefly, for the intracellular MC-LR, the algal cells were harvested by filtration (0.45-μm glass fiber filters, Taoyuan Co. Ltd, China), broken by freeze-thawing, and extracted by 75% methanol, while the extracellular MC-LR in the filtrate was extracted by solid phase extraction. Both the intracellular MC-LR and extracellular MC-LR were analyzed by high performance liquid chromatography.

Turbidity was measured using a HACH 2100P turbidimeter. The NB concentration was measured by high performance liquid chromatography (Waters e2695) according to Liu's (2012) method. The UV absorbance at 254 nm (UV_{254}) was measured using a spectrophotometer (UV759S, INESA Instrument Co. Ltd, China) after the samples were filtered through 0.45-μm filters. Dissolved organic carbon (DOC) was measured using a Shimadzu TOC 5000 analyzer (Shimadzu, Kyoto, Japan) after filtration by 0.45-μm filters. Zeta potential (ZP) was measured using a Zetasizer Nano-Z (Malvern Instruments, Worcestershire, UK). Total alkalinity was measured by the Gran titration method.

EXPERIMENT

A mixture of NB and *M. aeruginosa* (NM_5), which was incubated for 5 days with an initial NB concentration of 160 μg/L and an initial cell density of 1.0×10^8 cells/L, was subjected to the jar test. The final density of *M. aeruginosa* in NM_5 was $2.1 \pm 0.1 \times 10^8$ cells/L, and the finial NB concentration was 83.5 ± 2.2 μg/L. An *M. aeruginosa* solution with the same initial cell density (1.0×10^8 cells/L) and an NB solution (without *M. aeruginosa*) with the same initial NB concentration (160 μg/L) were incubated for 5 days and then used as control samples. A fresh mixture of NB and *M. aeruginosa* without incubation (NM_f), which contained the same NB concentration and cell density as the NM_5 samples (i.e. NB concentration of 83.5 μg/L and cell density of 2.1×10^8 cells/L), was also subjected to the jar test. For NM_f, it was assumed that there was no interaction between NB and *M. aeruginosa* in the mixture.

RESULTS AND DISCUSSION

Effect of NB on the performance of coagulation-sedimentation

The removal rates of turbidity, OD_{680}, total THMFP, THMFP in the extracellular organic matter (EOM) and intracellular MC-LR in the *M. aeruginosa* solution and in NM_f were investigated, and the results are presented in Figure 1. The quality of the water containing *M. aeruginosa* was significantly improved by coagulation-sedimentation at an optimized dosage of coagulant. The removal rates of all five parameters (Figure 1) were higher than 80%. In this experiment, there were no other impurities in the *M. aeruginosa* solution except the cyanobacteria cells and their secretions, which caused the turbidity in the water (Divakaran & Pillai 2002). With the good sedimentation of *M. aeruginosa* cells, intracellular MC-LR and turbidity were also removed. Extracellular MC-LR in the settled water was undetectable, which indicated that coagulation-sedimentation would not destroy the *M. aeruginosa* cells

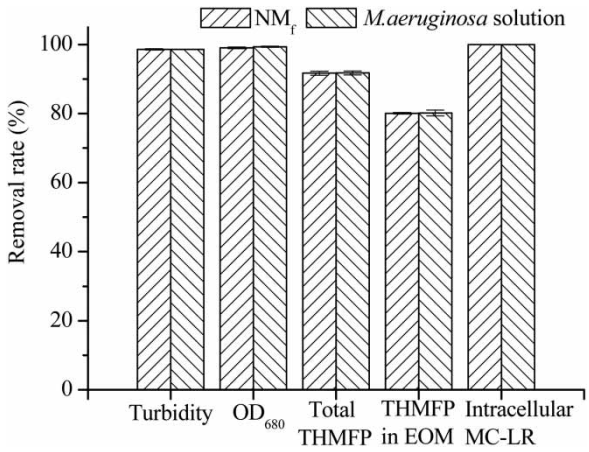

Figure 1 | Results of coagulation-sedimentation of *M. aeruginosa* solution and the fresh mixture of NB and *M. aeruginosa* without incubation (NM_f). Coagulant: $Al_2(SO_4)_3$ at the optimized dosage of 20 mg Al_2O_3/L; 25 ± 1 °C.

and result in a release of intracellular MC-LR into solution as reported by Chow *et al.* (1999). Previous studies (Plummer & Edzwald 2001; Huang *et al.* 2009) show that the majority of THMFP comes from algal cells. Thus, a high removal rate of total THMFP (91.8 ± 0.58%) was obtained.

Surprisingly, a high removal rate of THMFP in EOM (approximately 80%) was also obtained, which is much higher than the removal rate of DOC (31.6%). This phenomenon can be explained by the different removal efficiencies of dissolved organics by coagulation. It is reported that coagulation can remove hydrophobic organics more efficiently than hydrophilic organics, and the former contains considerably more THMFP than the latter (Edzwald 1993). The specific ultraviolet absorbance (SUVA, the ratio of UV_{254} to DOC) is regarded as an indicator of organic composition, and a high value indicates that the water mainly contains hydrophobic, aromatic and high molecular weight compounds, which form THMs more easily during disinfection and can more easily be removed by coagulation (Edzwald 1993). This value also decreased significantly after coagulation, from 2.69 to 1.73 L/mg/m. This change indicated that the organic composition was greatly changed by coagulation with the more efficient removal of hydrophobic organics. Previous studies also indicated that proteins account for 33% of the total DOC in the algal solution, and can be removed completely by coagulation (Henderson *et al.* 2008; Tsai *et al.* 2008). Proteins are also THMFPs, according to the study by Scully *et al.* (1988). Thus, the removal of proteins by coagulation may contribute to the removal of THMFP in EOM. In the settled water, 70.3 ± 9.9% of the total THMFP came from the EOM, which was much higher than that before coagulation-sedimentation (less than 30%).

Neither the performance of coagulation-sedimentation nor the coagulant dosage was affected by the addition of NB. The removal rates of all five parameters in NM_f by coagulation-sedimentation were approximately the same as those in the *M. aeruginosa* solution.

It is predictable that NB does not affect the coagulation-sedimentation of *M. aeruginosa*. NB is a weak hydrophobic material with a solubility of 2.1 g/L at 25 °C (IPCS 2003), and it cannot ionize in the water. These characteristics imply that NB would not disturb coagulant hydrolysis or the coagulation process, including the charge neutralization of colloidal materials and the charge complexation/precipitation of soluble compounds (Randtke 1988; Ye *et al.* 2007). Thus, the presence of NB in the *M. aeruginosa* solution did not affect the coagulation-sedimentation performance directly.

Effect of the interaction of NB and *M. aeruginosa* on the performance of coagulation-sedimentation

The performance of coagulation-sedimentation in treating NM_5 and *M. aeruginosa* solution with three types of coagulant was studied, and the results at the coagulant dosages optimized for turbidity removal are shown in Figure 2. The specific coagulant type did not affect the coagulation-sedimentation performance, and the removal rates of turbidity, OD_{680}, THMFP and MC-LR were similar for different coagulants at their optimized dosages (20 mg Al_2O_3/L for aluminum sulfate, 44.5 mg Fe_2O_3/L for ferric chloride and 39 mg Al_2O_3/L for PAC). The removal rate of THMFP in EOM and residual turbidity in the NM_5 settled water were lower than in *M. aeruginosa* solution, while the removal rates of OD_{680}, total THMFP and intracellular MC-LR were identical. The results of one-way analysis of variance (ANOVA) comparing the removal rates of THMFP in EOM and residual turbidity in the settled water for NM_5 and *M. aeruginosa* solution supported this viewpoint ($p = 0.045$ for turbidity and $p = 3.84 \times 10^{-9}$ for THMFP). After sedimentation, more than 80% of the total THMFP came from the EOM in the settled water of NM_5, which was higher than that observed in the *M. aeruginosa* solution (without NB). Obviously, the interaction between NB and *M. aeruginosa* changed the characteristics of the raw water and affected the coagulation-sedimentation results.

The removal of NB by coagulation-sedimentation is shown in Figure 3. In general, coagulation-sedimentation cannot remove NB efficiently, and the removal rates were always less than 4%. The interaction between NB and *M. aeruginosa* did not affect the removal of NB by coagulation-sedimentation. However, there was a slightly higher removal rate of NB in NM_f than in NM_5, although the difference was not statistically significant (one-way ANOVA, $p = 0.065$). The higher removal rate in NM_f might be attributed to the adsorption of NB by *M. aeruginosa* during the coagulation process.

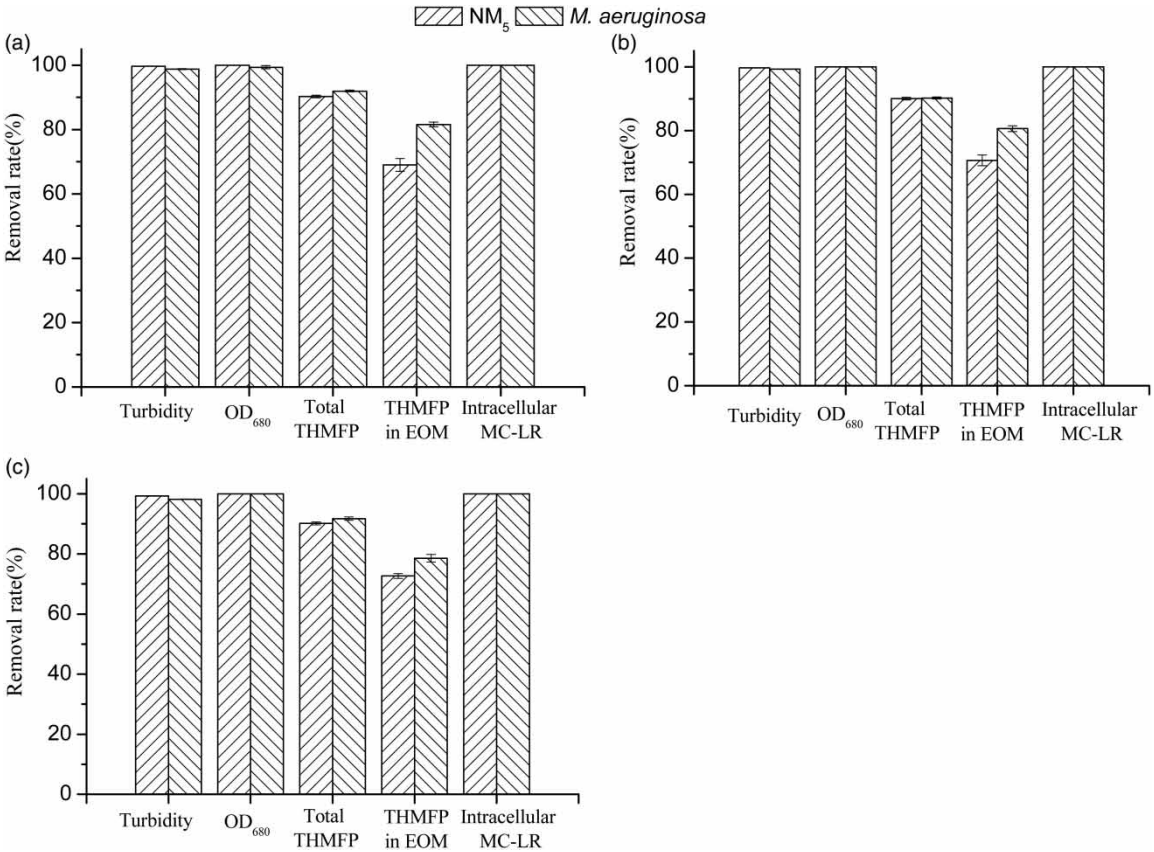

Figure 2 | Results of coagulation-sedimentation of *M. aeruginosa* solution and a mixture of NB and *M. aeruginosa* after a 5-day incubation (NM_5). Coagulant: (a) $Al_2(SO_4)_3$ 20 mg Al_2O_3/L; (b) $FeCl_3$ 44.5 mg Fe_2O_3/L; (c) PAC 39 mg Al_2O_3/L.

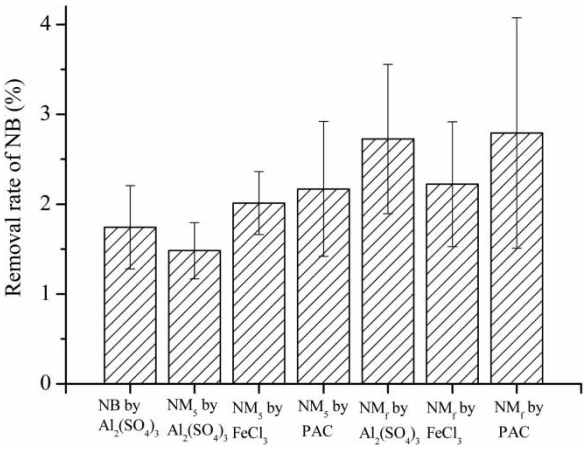

Figure 3 | Removal of NB by coagulation-sedimentation with three types of coagulants. Coagulant dosage: $Al_2(SO_4)_3$ 20 mg Al_2O_3/L; $FeCl_3$ 44.5 mg Fe_2O_3/L; PAC 39 mg Al_2O_3/L. NM_5 – a mixture of NB and *M. aeruginosa* after a 5-day incubation. NM_f – a fresh mixture of NB and *M. aeruginosa* without incubation.

Proposed mechanisms for the effects of the interaction on coagulation-sedimentation

The present study showed that NB did not affect the performance of coagulation-sedimentation directly, and the interaction between NB and *M. aeruginosa* reduced the removal rate of THMFP in EOM and the residual turbidity in the settled water. These variations were independent of coagulant type. In fact, these differences were also observed in the pre-oxidation and coagulation-sedimentation experiments (Figure S4, supplementary data; available online at http://www.iwaponline.com/jws/063/081.pdf). The results indicated that the characteristics of the raw water were changed by the interaction between NB and *M. aeruginosa*, which affected the performance of coagulation-sedimentation.

At a high concentration, NB can inhibit the growth of *M. aeruginosa*. Even at a low concentration, NB can affect cell activities by enhancing the protein productivity and reducing the MC-LR productivity and the photosynthetic rate, among others (Liu *et al.* 2013). *M. aeruginosa* can enhance the elimination of NB by adsorption and biodegradation, and the biodegradation process may produce dissolved compounds, such as aniline, which can be further oxidized to form THMs during chlorination (Liu *et al.* 2012).

The water quality parameters of the *M. aeruginosa* solution and NM_5 are shown in Table 1. With a non-lethal initial NB concentration (160 μg/L), the growth of *M. aeruginosa* was not inhibited by NB, and turbidity and OD_{680} were the same in NM_5 and the *M. aeruginosa* solution after a 5-day incubation. However, other effects of NB on *M. aeruginosa* were evident from differences in water quality parameters.

The pH and alkalinity were changed by the presence of NB after a 5-day incubation, but these variations did not affect the performance of coagulation-sedimentation significantly. Due to photosynthesis, phytoplankton can deplete alkalinity and cause an increase of pH (Talling 1976; Kahara & Vermaat 2003). NB inhibited photosynthesis, resulting in a lower pH and higher alkalinity in NM_5 without growth inhibition. Previous studies (Ye *et al.* 2007; Gottfried *et al.* 2008) have indicated that pH and alkalinity play significant roles in coagulation-sedimentation, which can affect the optimized coagulant dosage and the coagulant efficiency. However, in the present study, alkalinity was adjusted by Na_2CO_3 according to actual values in surface water, which greatly improved the performance of coagulation-sedimentation (turbidity removal rate increased from less than 75% to more than 99%, and OD_{680} removal rate increased from less than 70% to more than 99%). After adjustment, the pH was similar in NM_5 and the *M. aeruginosa* solution (9.34–9.76 for NM_5 and 9.46–9.91 for *M. aeruginosa*). Thus, the initial difference in pH and alkalinity in the present study are negligible.

Interaction with NB changed the surface charges of *M. aeruginosa*, which is responsible for the lower residual turbidity in the settled water. Zeta potential represents the potential stability of the colloidal system, and a weaker zeta potential promotes coagulation (Nachbaur *et al.* 1998; Sharp *et al.* 2006). The negative zeta potential in NM_5

Table 1 | Comparison of water quality parameters in the *M. aeruginosa* solution and the mixture of NB and *M. aeruginosa* after a 5-day incubation (NM_5)

	Turbidity (NTU)	OD_{680} (cm^{-1})	THMFP (μg/L)		MC-LR (μg/L)		pH	ZP (mV)	Alkalinity (mg $CaCO_3$/L)	UV_{254} (cm^{-1})
			The total	In the EOM	Intracellular	Extracellular				
In NM_5	37.96 ± 2.01	0.0820 ± 0.0075	2764 ± 88	796 ± 45	51.7 ± 6.4	–	7.53–8.64	−40.36 ± 3.65	37.20 ± 8.32	0.2729 ± 0.0152
In *M. aeruginosa* solution	37.35 ± 3.23	0.0805 ± 0.0003	2515 ± 112	724 ± 72	68.4 ± 11.2	–	8.76–9.33	−51.16 ± 2.40	27.80 ± 6.51	0.1381 ± 0.0132

increased and therefore enhanced the removal of turbidity by coagulation-sedimentation. Takaara *et al.* (2010) report that *M. aeruginosa* cells can secrete negatively charged hydrophilic substances, which can decrease zeta potential and inhibit their coagulation. The presence of NB may inhibit the secretion of these compounds by *M. aeruginosa*, which would result in increased zeta potential.

NB-enhanced production of THMFP in *M. aeruginosa* EOM may have led to the low removal rate of THMFP in NM_5. Our previous study (Liu *et al.* 2011) indicates that THMFP productivity in EOM can increase up to 50% in the presence of NB, although NB cannot be chlorinated to form THMs directly. These increased THMFP values come from the proteins secreted by *M. aeruginosa* and the degradation products of NB. Figure 1 shows a high removal rate of THMFP in EOM by coagulation, which implies that most of the THMFP secreted by *M. aeruginosa* can be removed by coagulation-sedimentation. Thus, the increased protein content would not affect the removal of THMFP significantly. However, the soluble degradation products of NB cannot be removed efficiently by coagulation-sedimentation, which caused a lower THMFP removal rate than without NB and resulted in a higher proportion of THMFP in the EOM of the settled water (more than 80%, compared with 70.3% without NB). These products increased the initial value of UV_{254} and resulted in a higher residual THMFP concentration in the EOM after coagulation (228 ± 13 μg/L), compared with the *M. aeruginosa* solution without NB (142 ± 12 μg/L). The interaction between NB and *M. aeruginosa* increased the disinfection risk significantly over the non-interactive case, and this risk increased further after coagulation-sedimentation.

Although NB did not inhibit the growth of *M. aeruginosa*, it did negatively affect the performance of coagulation-sedimentation. This effect should be considered when water containing NB and *M. aeruginosa* is used as drinking water resource.

CONCLUSIONS

In the present study, the impacts of the interaction between NB and *M. aeruginosa* on the performance of coagulation-sedimentation were studied by using a bench-scale jar test. The results indicated that coagulation-sedimentation can significantly improve the quality of water containing *M. aeruginosa*. Although NB did not affect the coagulation-sedimentation process directly, the presence of NB did change the performance of coagulation-sedimentation after a 5-day incubation with *M. aeruginosa*, including a reduced removal rate of THMFP in EOM and a lower residual turbidity in the settled water. These effects resulted from the interaction between NB and *M. aeruginosa*. The weak zeta potentials caused by the interaction and the degradation products of NB were responsible for these variations.

The present results imply that the interaction between xenobiotics and algae on water treatment processes should be considered when combined polluted water is used as the drinking water source. However, due to the complexity of xenobiotics and the diversity of algae and cyanobacteria, the present study cannot represent the whole scenario, and further study is necessary.

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REFERENCES

Andreozzi, R., Caprio, V., Ciniglia, C., Champdoré, M., Giudice, R. L., Marotta, R. & Zuccato, E. 2004 Antibiotics in the environment: occurrence in Italian STPs, fate, and preliminary assessment on algal toxicity of amoxicillin. *Environ. Sci. Technol.* **38**, 6832–6838.

Chow, C. W. K., Drikas, M., House, J., Burch, M. D. & Velzeboer, R. M. A. 1999 The impact of conventional water treatment processes on cells of the cyanobacterium *Microcystis aeruginosa*. *Water Res.* **15**, 3253–3262.

Divakaran, R. & Pillai, V. N. S. 2002 Flocculation of algae using chitosan. *J. Appl. Phycol.* **14** (5), 419–422.

Edzwald, J. K. 1993 Coagulation in drinking water treatment: particles, organics and coagulants. *Water Sci. Technol.* **27** (11), 21–35.

Gao, J., Liu, L., Liu, X., Zhou, H., Wang, Z. & Huang, S. 2008 Concentration level and geographical distribution of

nitrobenzene in Chinese surface waters. *J. Environ. Sci.* **20** (7), 803–805.

Gottfried, A., Shepard, A. D., Hardiman, K. & Walsh, M. E. 2008 Impact of recycling filter backwash water on organic removal in coagulation–sedimentation processes. *Water Res.* **42**, 4683–4691.

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

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.

International Programme on Chemical Safety (IPCS) 2003 Nitrobenzene environmental health criteria 230. Geneva: WHO.

Kahara, S. N. & Vermaat, J. E. 2003 The effect of alkalinity on photosynthesis-light curves and inorganic carbon extraction capacity of freshwater macrophytes. *Aquat. Bot.* **75** (3), 217–227.

Liu, Z., Cui, F., Ma, H., Fan, Z. & Zhao, Z. 2011 The role of nitrobenzene on the yield of trihalomethane formation potential in aqueous solutions with *Microcystis aeruginosa*. *Water Res.* **45** (19), 6489–6495.

Liu, Z., Cui, F., Ma, H., Fan, Z., Zhao, Z., Hou, Z. & Liu, D. 2012 Bio-reaction of nitrobenzene with *Microcystis aeruginosa*: characteristics, kinetics and application. *Water Res.* **46** (7), 2290–2298.

Liu, Z., Cui, F., Ma, H., Fan, Z., Zhao, Z., Hou, Z. & Liu, D. 2013 The interaction between nitrobenzene and *Microcystis aeruginosa* and its potential to impact water quality. *Chemosphere* **92** (9), 1201–1206.

Ma, H., Cui, F., Liu, Z. & Fan, Z. 2009 Pilot study on control of phytoplankton by zooplankton coupling with filter-feeding fish in surface water. *Water Sci. Technol.* **60** (3), 737–743.

Meriluoto, J. & Spoof, L. 2005a SOP: extraction of microcystins in biomass filtered on glass-fibre filters or in freeze-dried cyanobacterial biomass. In: *TOXIC: Cyanobacterial Monitoring and Cyanotoxin Analysis* (J. Meriluoto & G. A. Codd, eds). Åbo Akadmi University Press, Turku, Finland, pp. 69–71.

Meriluoto, J. & Spoof, L. 2005b SOP: solid phase extraction of microcystins in water samples. In: *TOXIC: Cyanobacterial Monitoring and Cyanotoxin Analysis* (J. Meriluoto & G. A. Codd, eds). Åbo Akadmi University Press, Turku, Finland, p. 73.

Ministry of Environmental Protection of the People's Republic of China 2010 Report on the state of environment in China, Beijing. Available from: http://jcs.mep.gov.cn/hjzl/zkgb/2010zkgb/201106/t20110602_211577.htm (in Chinese).

Nachbaur, L., Nkinamubanzi, P.-C., Nonat, A. & Mutin, J.-C. 1998 Electrokinetic properties which control the coagulation of silicate cement suspensions during early age hydration. *J. Colloid Interface Sci.* **202** (2), 261–268.

Plummer, J. D. & Edzwald, J. K. 2001 Effect of ozone on algae as precursors for trihalomethane and haloacetic acid production. *Environ. Sci. Technol.* **35** (18), 3661–3668.

Randtke, S. J. 1988 Organic contaminant removal by coagulation and related process combinations. *J. Am. Water Works Assoc.* **80** (5), 40–56.

Scully Jr., F. E., Howell, G. D., Kravitz, R. & Jewell, J. T. 1988 Proteins in natural waters and their relation to the formation of chlorinated organics during water disinfection. *Environ. Sci. Technol.* **22** (5), 537–542.

Semple, K. T. & Cain, R. B. 1996 Biodegradation of phenols by the alga *Ochromonas danica*. *Appl. Environ. Microbiol.* **62** (4), 1265–1273.

Semple, K. T., Cain, R. B. & Schmidt, S. 1999 Biodegradation of aromatic compounds by microalgae. *FEMS Microbiol. Lett.* **170**, 291–300.

Sharp, E. L., Jarvis, P., Parsons, S. A. & Jefferson, B. 2006 The impact of zeta potential on the physical properties of ferric-NOM flocs. *Environ. Sci. Technol.* **40** (12), 3934–3940.

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.

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.

Talling, J. F. 1976 The depletion of carbon dioxide from lake water by phytoplankton. *J. Ecol.* **64** (1), 79–121.

Tian, J., Chen, Z., Nan, J., Liang, H. & Li, G. 2010 Integrative membrane coagulation adsorption bioreactor (MCABR) for enhanced organic matter removal in drinking water treatment. *J. Membr. Sci.* **352** (1–2), 205–212.

Tsai, B.-N., Chang, C.-H. & Lee, D.-J. 2008 Fraction of soluble microbial products (SMP) and soluble extracellular polymeric substances (eps) from wastewater sludge. *Environ. Technol.* **29** (10), 1127–1138.

Tukaj, Z. 1989 The effect of fuel oil on the ultrastructure of the chlorococcal alga *Scenedesmus armatus*. *Protoplasma* **151** (1), 47–56.

Ye, C., Wang, D., Shi, B., Yu, J., Qu, J., Edwards, M. & Tang, H. 2007 Alkalinity effect of coagulation with polyaluminum chlorides: role of electrostatic patch. *Colloids Surf. A Physicochem. Eng. Asp.* **294** (1–3), 163–173.

Zamyadi, A., MacLeod, S. L., Fan, Y., McQuaid, N., Dorner, S., Sauvé, S. & Prévost, M. 2012 Toxic cyanobacterial breakthrough and accumulation in a drinking water plant: a monitoring and treatment challenge. *Water Res.* **46** (5), 1511–1523.

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