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Novel disinfection method for toxic cyanobacteria *(Oscillatoria tenuis)* and simultaneous removal of cyanotoxins aided by recyclable magnetic nanoparticles

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ABSTRACT

An optimized disinfection method with metal ions to address cyanobacteria contamination in freshwater is presented, based on recyclable magnetic nanoparticles. In this study, the disinfection ability of individual metal ions (Ag^+ and Cu^{2+}) and combined ($Ag^+ + Cu^{2+}$) were evaluated with a target cyanobacteria, *Oscillatoria tenuis*, under various environmental conditions. The usage of combined Ag^+ and Cu^{2+} reduces the time and concentration needed to achieve the same disinfection effectiveness compared to individual metal ions. However, the addition of Cu^{2+} and Ag^+ stimulated production of cyanotoxin during disinfection, with an increase of 24.8% for anatoxin-a. To reduce the potential health risk, we evaluated the recovery and reuse of metal ions, and removal of cyanotoxins after disinfection, using magnetic nanoparticles with permanently confined micelle arrays (Mag-PCMA) under various environmental conditions. Recovery efficiency of Ag^+, the most valuable ion, was excellent (99.8%), although it decreased to 74.5% with increasing Cl^- concentration (0–10 mg/L). The regeneration and reuse of Mag-PCMA was studied for 5 cycles. Removal efficiency of Cu^{2+}, anatoxin-a and cylindrospermopsin were minimally changed during the 5 sorption-desorption cycles, and that of Ag^+ remained above 93% by the end of 5th cycle, indicating that this disinfection method may be sustainable for practical use with low energy requirements and minimized environmental impacts.

1. Introduction

Harmful algae blooms (HABs) refer to a rapid increase in toxic algae population in freshwater or marine systems, due to a nutrient overload. HABs threaten aqueous environment by decreasing water quality [4], depleting oxygen [25], accumulating biomass to alter food web dynamics [2], and releasing toxins and secondary metabolites [31]. In particular, some cyanobacteria species produce and release cyanotoxins when the cells rupture or die [41]. Humans and other organisms may be exposed to cyanotoxins either directly via inhalation, ingestion and dermal contact of contaminated water, and indirectly by contacting animals or plants exposed to cyanotoxins, resulting in threats to human and ecological health. People may suffer from acute intoxication and have the symptoms like visual disturbance, nausea, vomiting, acute liver failure, respiratory irritation or even death once exposed to water contaminated with even very low concentrations of cyanotoxins [39–41]. Apart from acute toxicity, cyanotoxins have a close relationship with various diseases through chronic exposure as well. For example, microcystins, a class of cyanotoxins, may cause gastroenteritis, allergic and irritation reactions, and liver diseases after chronic exposure [43]. Thus, seeking efficient ways to deal with HABs caused by cyanobacteria and providing safe drinking water sources is very important for public health.

Generally, particulate cyanobacteria cells can be removed through coagulation, sedimentation, filtration and chlorination in wastewater treatment plants according to the EPA guideline [33]. However, further disinfection is necessary to inactivate residual cyanobacteria, as regrowth during distribution may increase health risks. The use of metal ions as algaecide has been well studied to solve this problem. For example, copper has been shown to be an effective algaecide for various cyanobacteria, including *Microcystis aeruginosa* [27] and *Lyngbya wollei* [3]. Ferrate (VI) can be used for the pre-treatment of two cyanobacteria, *Chlorella* sp. and *Pseudanabaena limnetica* in wastewater treatment plants due to its effective disinfection ability [10]. Compared to other disinfection methods which will produce disinfection by-products (e.g. the use of chlorine [6]) or require high cost of energy or maintenance (e.g.

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ozone or UV radiation [9]), the use of metal ions as algaecides is inexpensive and efficient, thus having great potential for wide application. However, some environmental issues related to metal ions need to be addressed before practical use. First, the residual metal ions in the water after treatment can cause potential environmental risks, as high concentrations of these metal ions are toxic to various aquatic organisms. For example, the 96-h lethal concentration 50% (LC50) of copper ion for 90-day old *Ctenopharyngodon idella* is 5.17 mg/L [19]. *Dentomuricea aff. meteor,* a cold-water gorgonian, is very sensitive to copper ions, with 96 h LC50 of 137 μg/L [24]. Thus, the concentration of residual metal ions needs to be decreased to a safe level after treatment.

Another concern is the release of cyanotoxins during disinfection with metal ions. Some studies have found that the addition of metal ions have a positive effect on the production of cyanotoxin, which will increase the release of cyanotoxin when the cells rupture or die. For example, the addition of Fe will increase the concentration of microcystins produced by *Microcystis aeruginosa* [1]. Traditional technologies such as the use of chemical oxidizing agents, UV radiation and activated carbon adsorption have been shown to be effective for only some types of cyanotoxins. For example, free chlorine is effective for cylindrospermopsin and saxitoxin but not for anatoxin-a [33]. Thus, it is essential to seek an efficient way that can remove a broad range of cyanotoxins before further distribution of the treated water.

To address these issues (i.e, residual metal ions and released cyanotoxins after disinfection), we propose an innovative, more sustainable disinfection method, using magnetic nanoparticles with permanently confined micelle arrays (Mag-PCMA) to achieve simultaneous sorption of both metal ions and cyanotoxins, followed by the regeneration of Mag-PCMA under proper conditions for reuse. A schematic of the process is provided in the graphical abstract. Briefly, cyanobacteria are exposed to metal ions at concentrations needed for disinfection. After sufficient contact time, the treated water is filtered to separate dead algae cells, and Mag-PCMA are added to remove the residual metal ions as well as the cyanotoxins produced during disinfection. Previous studies have shown that Mag-PCMA can achieve simultaneous removal of both organic and inorganic chemicals (e.g. acenaphthene and Cd^{2+}) via hydrophobic interactions and electrostatic attraction [15]. Thus, we hypothesized that the metal ions and cyanotoxins could be effectively removed by Mag-PCMA after disinfection. In the final step, the metal ions adsorbed on Mag-PCMA can be regenerated under proper conditions and reused for several continuous cycles.

The objectives of this study were to: (1) explore the disinfection effectiveness of combined metal ions rather than individual ones to reduce the effective concentration and contact time, and evaluate the influence of different environmental conditions (e.g. pH, nutrient content, water hardness); (2) quantify the production and distribution of extracellular and intracellular cyanotoxins during disinfection; (3) study the simultaneous sorption of metal ions and cyanotoxins with magnetic nanoparticles, and the influence of different environmental conditions on this process; and (4) explore the conditions needed to regenerate the magnetic nanoparticles, and release the metal ions for reuse in continuous cycles.

2. Materials and methods

2.1. Materials

Oscillatoria tenuis (*O. tenuis*) was selected as target cyanobacteria in this study, as it can produce two type of cyanotoxins (i.e. anatoxin-a and cylindrospermopsin) which are of concern in water supply. Both *O. tenuis* and BG-11 medium (used for culturing *O. tenuis*) were purchased from UTEX Culture Collection of Algae at The University of Texas at Austin (USA). Silver nitrate, copper sulfate, nitric acid, sulfuric acid, sodium hydroxide, sodium chloride and calcium carbonate were purchased from Fisher Scientific (USA). Ag^{+} and Cu^{2+} are selected as the metal ions disinfectants as they are commonly used as algaecides in many studies [3,27,29] and have demonstrated effectiveness. Our innovative approach allows the recovery of the metal ions for reuse, making it less expensive and more sustainable. The recipe of BG-11 is presented in Table S1 (Supporting Information). Mag-PCMA was synthesized using the method developed in our previous studies [14–16,34,36,7,8], and the maghemite (iron (III) oxide) nanoparticles (30 nm in diameter) used for synthesis were purchased from Alfa Aesar (USA). Detailed information about synthesizing Mag-PCMA are shown in Supporting Information. All chemicals were used as received without further purification. All solutions were prepared with deionized water (18 MU-cm) from a Barnstead NANOpure Diamond Water Purification System (USA).

2.2. Disinfection of O. tenuis with individual and combined metal ions

The disinfection of *O. tenuis* at exponential phase was performed in 125 mL baffled polycarbonate Erlenmeyer flasks purchased from Corning Inc. (USA), with silver nitrate and copper sulfate as disinfectants. *O. tenuis* culture was exposed to individual metal ions (i.e. Ag^{+}, Cu^{2+}) and combined metal ions (Ag^{+} + Cu^{2+}) at various concentrations (10–200 mg/L) for different contact times (up to 10 h) in BG-11 medium. The concentration of *O. tenuis* was determined by the Trilogy Laboratory Fluorometer (Turner Designs, Inc., USA) and was expressed as total chlorophyll fluorescence (raw fluorescence unit (RFU)/mL). All the chlorophyll fluorescence mentioned in this study refer to the total chlorophyll fluorescence. The chlorophyll fluorescence of *O. tenuis* was 75.91 RFU/mL (1.8 *10^5 cells/mL in cell concentration). The disinfection process was evaluated under various environmental conditions (e.g. initial chlorophyll fluorescence, pH, water hardness, nutrient content, natural organic matter (NOM) and light conditions) within a broad range (Table 1), to simulate the natural environment with complex conditions. The chlorophyll fluorescence of *O. tenuis* for the study with different environmental conditions (except the study about initial chlorophyll fluorescence) was 89.89 RFU/mL (2.1 *10^5 cells/mL in cell concentration).

2.3. Extracellular and intracellular cyanotoxin quantification

To explore how the concentration of extracellular and intracellular cyanotoxin may change over time, *O. tenuis* with initial chlorophyll fluorescence = 111.46 RFU/mL (2.6 *10^5 cells/mL in cell concentration) were exposed to 50 mg/L Ag^{+} and Cu^{2+}, and 5 mL culture samples were collected every 2.5 h. The culture samples were centrifuged at 1500 rpm for 20 min. After centrifugation, 800 μL of supernatant was taken for extracellular toxin quantification, and was transferred into a liquid chromatography glass vial followed by addition of 150 μL of methanol and 50 μL of 1000 ng/mL internal standard mix (^{13}C-labelled anatoxin-a and ^{15}N-labelled cylindrospermopsin). The pellets obtained from centrifugation were used for intracellular toxin extraction by suspending

Table 1
Range of environmental conditions for disinfection with Ag^{+} and Cu^{2+} and the methods for adjustment.

Environmental condition	Range	Method
Initial chlorophyll fluorescence	24.83–143.71 RFU/mL	Addition of different initial concentration of O. tenuis
pH	6–8	Adjusted by 0.1 M nitric acid and 0.1 M NaOH
Water hardness	[$CaCO_3$] = 0–200 mg/L	Addition of $CaCO_3$ from 0 to 200 mg/L
Nutrient content	0% (with no nutrients)– 100% (full strength)	Dilution of the BG-11 medium with deionized water to different percentage
NOM	[Humic acid] = 0–10 mg/L	Addition of humic acid (HA) from 0 to 10 mg/L
Light condition	Light & dark	With/without light irradiation

them in 5 mL of 5% aqueous acetic acid. The suspension was then vortexed for 30 min, sonicated for 30 min and centrifuged for 20 min at 4500 rpm. After centrifugation, 800 μL of supernatant was mixed with 150 μL of methanol and 50 μL of 1000 ng/mL internal standard mix. The toxin quantification was performed on an Agilent 6470 (Agilent Technologies) Triple Quad liquid chromatography/mass spectrometry (LC/MS).

2.4. Simultaneous sorption of metal ions and cyanotoxin with Mag-PCMA

Simultaneous adsorption of Ag^{+}, Cu^{2+} and two cyanotoxins produced by *O. tenuis* (i.e. anatoxin-a and cylindrospermopsin) with Mag-PCMA was evaluated under various conditions. Different amounts of Mag-PCMA particles (20.0–100.0 mg) were added to 20 mL of mixed solution (50 mg/L Ag^{+}, 50 mg/L Cu^{2+}, 20 μg/L anatoxin-a and 20 μg/L cylindrospermopsin) in 20 mL glass vials, and the vials were placed in an end-over-end shaker on a Dayton-6Z412A Parallel Shaft (USA) roller mixer with a speed of 70 rpm at room temperature (22–25 °C) for 24 h to ensure sufficient equilibration time. Adsorption kinetics studies were carried out with the mixture of 50.0 mg Mag-PCMA and 20 mL mixed solution at the same conditions but for a set amount of time, varying from 1 to 8 h. All the studies were done at pH = 7 and room temperature. After mixing well, the Mag-PCMA particles were separated from the aqueous phase with an Eclipse magnet. Samples were collected from the supernatant and diluted with 2% HNO_3 to measure metal ion concentration. The concentration of Ag^{+} and Cu^{2+} was analyzed by an Agilent 7900 (Agilent Technologies) inductively coupled plasma mass spectrometer (ICP-MS). Supernatant samples were also analyzed for the concentrations of anatoxin-a and cylindrospermopsin by LC-MS.

The influence of different environmental conditions on the removal efficiency of Ag^{+}, Cu^{2+}, anatoxin-a and cylindrospermopsin by Mag-PCMA, including pH, concentration of Cl^{-}, water hardness, and NOM were evaluated as well. pH was adjusted to the desired condition (range from 6 to 8) by using 0.1 M NaOH. Different concentrations of Cl^{-} (0, 1 and 10 mg/L) were added into the mixture to explore the possible influence on sorption, as the combinations of Cl^{-} and Ag^{+} may affect the sorption behavior of Mag-PCMA. $CaCO_3$ with a range of concentrations from 50 mg/L to 200 mg/L was used to adjust water hardness. HA with concentration of 1–10 mg/L was introduced to the sorption system, to explore the influence of NOM.

2.5. Regeneration of Mag-PCMA and reuse of metal ions

Regeneration and reuse of Mag-PCMA was investigated in this study. 50 mg/L Ag^{+} and Cu^{2+} and 20 ug/L anatoxin-a and cylindrospermopsin were adsorbed onto the Mag-PCMA particles, followed by magnetic separation of Mag-PCMA from solution. Concentration of Ag^{+}, Cu^{2+}, anatoxin-a and cylindrospermopsin were determined after sorption. The Mag-PCMA collected was first rinsed with methanol to extract sorbed cyanotoxins, then washed with 0.01 M H_2SO_4 (pH=1.70) for 30 min at room temperature to remove sorbed metal ions. The acid-washed Mag-Ligand particles were reused for subsequent sorption experiments and the sorption, extraction, and reuse processes were repeated for five times.

2.6. Data analysis

All tests in this study were performed in triplicate and analysis of variance (ANOVA) was used to test the significance of results. A $p < 0.05$ was considered to be statistically significant. The p values of each test are listed in Table S2.

3. Results and discussions

3.1. Disinfection of O. tenuis with metal ions

3.1.1. Comparison of disinfection effectiveness of various metal ions on O. tenuis

Cu^{2+} and Ag^{+} were selected as disinfectants, and disinfection effectiveness of both individual and combined metal ions at different concentrations were compared. The change in total chlorophyll fluorescence as compared to the initial one was used to determine disinfection effectiveness, since monitoring the level of total chlorophyll is a direct way of tracking algae growth [10]. As shown in Fig. 1 (A) and (B), chlorophyll fluorescence after treatment with low Cu^{2+} or Ag^{+} concentrations (10–20 mg/L) and short contact time (2.5 h for Ag^{+} and 5 h for Cu^{2+}) was higher than that in the control, indicating growth instead of cell death. This might be due to the stimulation of cyanobacteria metabolism at low metal ion concentrations and short exposure times, resulting in increased chlorophyll fluorescence. At longer contact times chlorophyll fluorescence decreased. When exposed to high Cu^{2+} or Ag^{+} concentrations (50–200 mg/L), chlorophyll fluorescence decreased even within a short contact time (2.5 h) and the reduction became more and more significant with longer contact times. Compared to the individual ions, the combination Cu^{2+} + Ag^{+} has better disinfection effectiveness at the same concentration and contact time. As shown in Fig. 1

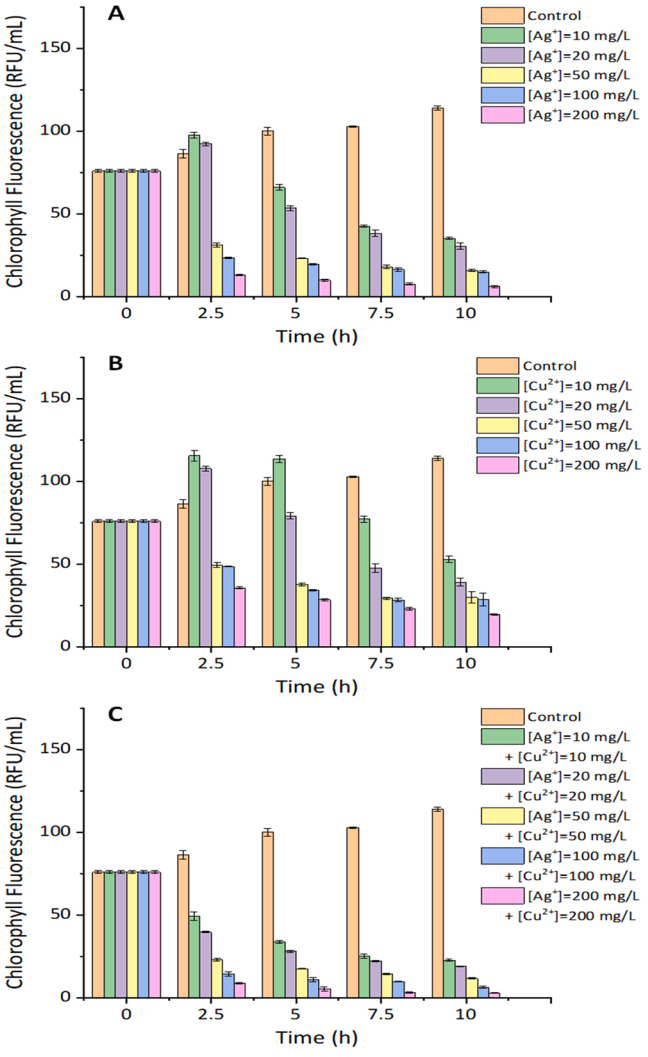

Fig. 1. Disinfection kinetics of *O. tenuis* with different concentrations (10–200 mg/L) of (A) Ag^{+}; (B) Cu^{2+}; and (C) Cu^{2+}+Ag^{+}.

(C), no abnormal increase in chlorophyll fluorescence was observed even at the lower dose and contact time, and the final chlorophyll fluorescence for the combined metal ion treatment was less than that with Cu^{2+} or Ag^{+} at all concentrations and contact times, indicating better disinfection effectiveness with the combined metal ions than the individual ions under same conditions. This is an important finding, since it reduces the use of Ag^{+}, a more expensive ion.

The concentration of disinfectants and contact time are the main factors that determine disinfection effectiveness. To further discuss these factors in a quantitative way, as well as to see if the disinfection effectiveness of combined metal ions is synergetic, the relationship between concentration of disinfectants, contact time and chlorophyll fluorescence can be described with two exponential equations. For a given disinfectant concentration, the relationship between chlorophyll fluorescence and contact time can be described by Eq. (1):

$$\text{Chlorophyll fluorescence} = R_{mc} + R_{dc} e^{-Bc*t} \quad (1)$$

Here, R_{mc} is residual chlorophyll fluorescence after a long time of disinfection at a given disinfectant condition (i.e type of metal ion and concentration); R_{dc} is the decrease in chlorophyll fluorescence compared to the initial chlorophyll fluorescence at $t = 0$. B_c is the rate of disinfection, or the disinfectant ability, under a given condition. A larger value of B_c means it takes a shorter time for the system to reach the same disinfection effectiveness than other conditions. The values of R_{mc}, R_{dc}, and B_c for all systems in this study are shown in Table S3. Due to the metabolic stimulation by individual Ag^{+} and Cu^{2+} treatments at 10 and 20 mg/L, the results of these systems cannot be described by Eq. 1.

The value of B_c follows the order: $Cu^{2+}+Ag^{+} > Ag^{+} > Cu^{2+}$ for the same total concentration of disinfectant. Thus, the combined disinfectant has better disinfection effectiveness than the individual metal ions at the same concentration, and Ag^{+} is better than Cu^{2+} as an individual disinfectant. At low disinfectant concentrations (10 and 20 mg/L), there is clearly a synergistic effect by combining the two metal ions, since the metabolic stimulation is not observed and there is disinfection even at low contact times. To see if the disinfection effectiveness of combined metal ions is additional or synergetic, a comparison of B_c at the higher disinfectant concentration (50, 100 and 200 mg/L) is shown in Fig. 2 (A). Here, the sum of B_c for the individual metal ions is compared to the combination. One can see that B_c ($Cu^{2+}+Ag^{+}$) is less than B_c (Ag^{+}) + B_c (Cu^{2+}) at higher levels of disinfectant concentrations (>50 mg/L). Thus, the disinfection effectiveness of combined disinfectant is not synergetic at high concentrations.

The relationship between disinfectant concentration and chlorophyll fluorescence for a given contact time and type of disinfectant is exponential as well (Eq. 2):

$$\text{Chlorophyll fluorescence} = R_{mt} + R_{dt} e^{-Bt*c} \quad (2)$$

Here, R_{mt} is the residual chlorophyll fluorescence when the concentration of disinfectant is theoretically close to infinity; R_{dt} is the corresponding decrease of chlorophyll fluorescence as compared to the chlorophyll fluorescence with concentration of disinfectants = 0; and B_t indicates the disinfectant ability under specific conditions. A larger value of B_t means lower concentration of disinfectants is required for the system to reach the same disinfection effectiveness. The values of $R_{0\,t}$, R_t, and B_t for all the systems in this study are shown in Table S4.

As shown in Table S4, B_t follows the order: $Cu^{2+}+Ag^{+} > Ag^{+} > Cu^{2+}$ with the same contact time. This means that combined disinfectant has better disinfection effectiveness than individual ions at the same contact time, and Ag^{+} is better than Cu^{2+}. The comparison of B_t ($Ag^{+}+Cu^{2+}$) and B_t (Ag^{+}) +B_t (Cu^{2+}) with different contact times (2.5, 5, 7.5 and 10 h) are shown in Fig. 2 (B). The disinfection effectiveness of the combined metal ions is synergetic when contact time is less than 7.5 h. At t = 10 h, B_t ($Ag^{+}+Cu^{2+}$) is less than B_t (Ag^{+}) +B_t (Cu^{2+}).

The better disinfection ability of the combined $Cu^{2+}+Ag^{+}$ relative to the individual Ag^{+} or Cu^{2+} is mainly due to the differences in disinfection mechanisms for Ag^{+} and Cu^{2+}. Ag^{+} inactivates the algae cells via extracellular binding and precipitating on the cell wall, and intracellular binding with enzymes, DNA or electron donor groups [20]. The disinfection mechanism of Cu^{2+} is mainly the increase in cell wall permeability and destruction of cell walls [21], but does not result in intracellular binding. Thus, the disinfection ability of Cu^{2+} is weaker than Ag^{+}. Both disinfectant concentration and contact time will influence the disinfection effectiveness. At low concentrations, the disinfectant will be attached onto the cell walls and once the concentration increases to a certain level, the cell walls will be damaged. If the concentration of disinfectant continues to increase beyond that level, the additional disinfectant will not accelerate the rate of disinfection, even though it will be attached onto the cell walls as well [21]. Contact time is another important factor in this process since the precipitation and uptake of disinfectant are time-dependent and it will take time for the attached disinfectant to destroy the cell structure [21]. Given enough contact time or disinfectant concentration, the disinfection effectiveness will remain stable at a certain level under those conditions.

When a combination of metal ions ($Cu^{2+}+Ag^{+}$) is applied to the system, synergetic effects appear as it will be easier for Ag^{+} to enter the cell and interact with enzymes or DNA, since the cell wall is damaged by Cu^{2+}. The synergetic effect is significant at low concentrations and short contact times. When the concentration of individual disinfectant is high, or the contact time is long, the disinfection process may reach an equilibrium with individual disinfectants. Thus, no synergetic effect appears under those conditions, but the disinfection effectiveness of combined disinfectant is still better than that with individual metal ions.

In conclusion, disinfection effectiveness of combined metal ions is

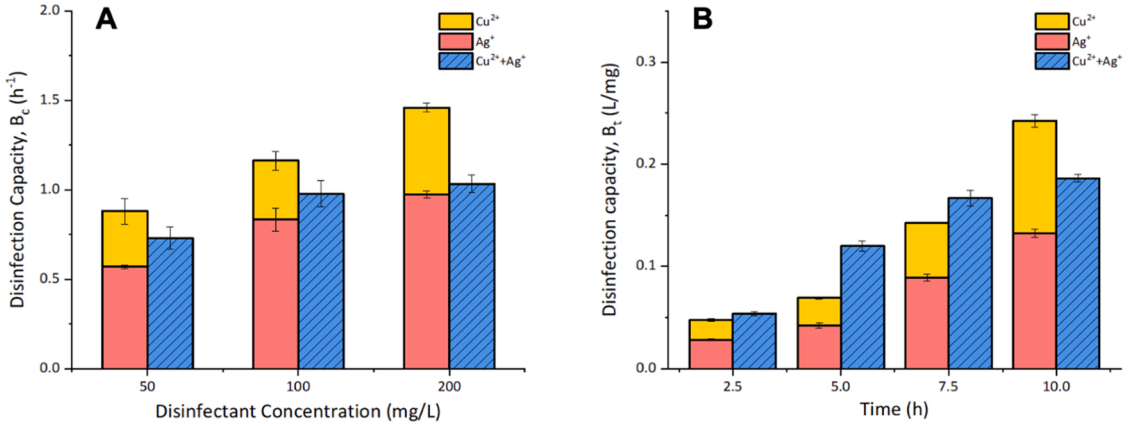

Fig. 2. (A) Comparison of B_c with Ag^{+}, Cu^{2+} and $Ag^{+}+Cu^{2+}$ at different concentrations (p values given in Table S2). (B) Comparison of B_t with Ag^{+}, Cu^{2+} and $Ag^{+}+Cu^{2+}$ at different contact times (p values given in Table S2).

synergetic compared to the addition of individual ones at low concentration and short contact time. At high concentration and long contact time, the disinfection effectiveness of combined ones is weaker than the sum of individual ones but is still stronger than each of them. Thus, treatment with combined metal ions will reach expected disinfection effectiveness with lower concentration and shorter contact time than with individual metal ions. The cell concentration of *O. tenuis* in this study was very high ($1.8 * 10^5$ cells/mL) to be able to simulate an environment with cyanobacteria bloom, which required a high concentration of metal ions and longer contact times, for this proof-of-concept study. One can expect that lower dosages of combined metal ions will be needed to achieve desired disinfection effectiveness for the lower cell concentrations in normal environmental conditions. With further treatment of the residual metal ions in the water after disinfection (i.e. sorption with Mag-PCMA), the concentration of metal ions will be reduced to a safe level which minimizes the potential environmental risk.

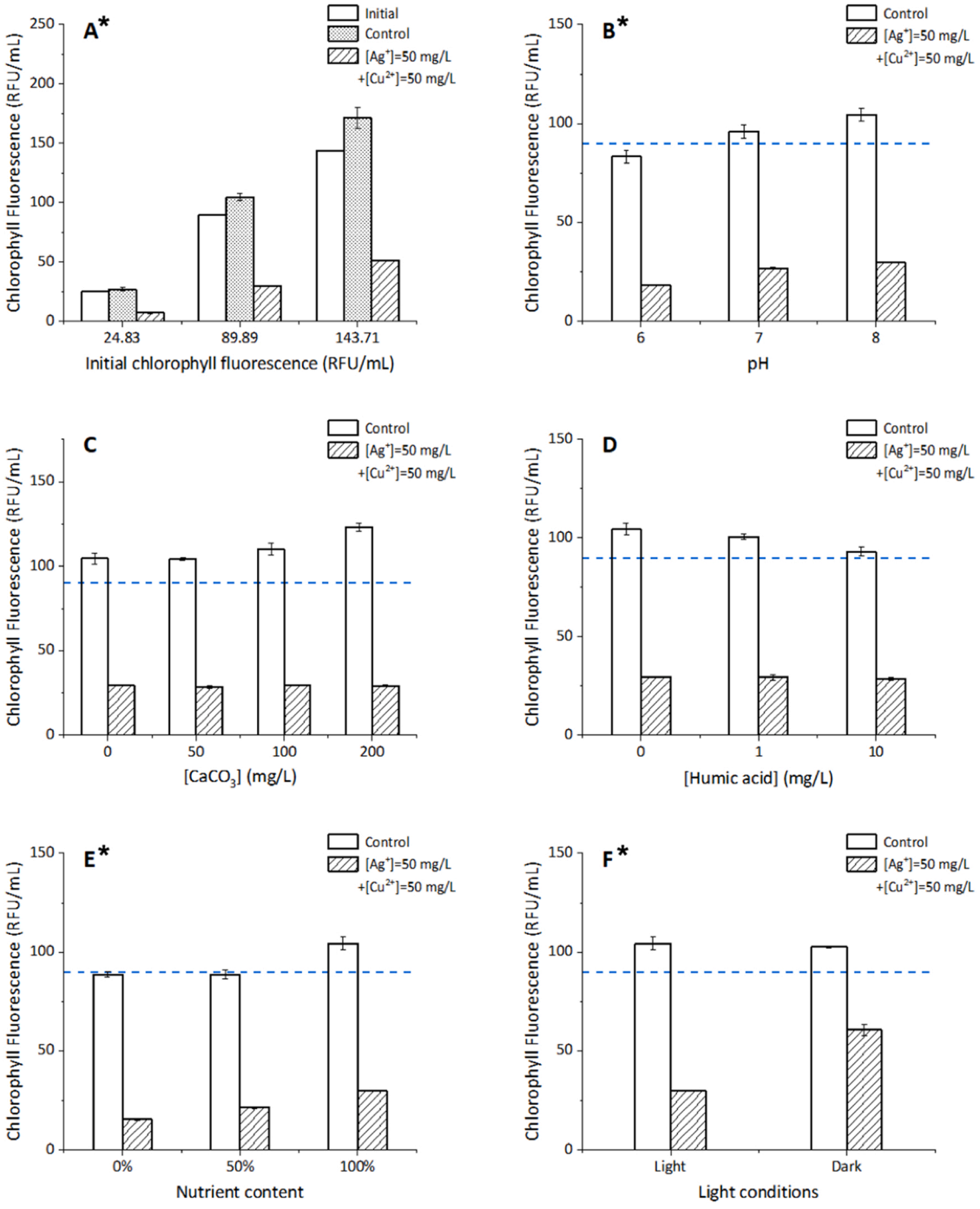

Fig. 3. Disinfection effectiveness as a function of (A) initial chlorophyll fluorescence (24.83, 89.89 and 143.71 RFU/mL respectively); (B) pH; (C) water hardness; (D) NOM; (E) nutrient content; and (F) light condition with $[Cu^{2+}] = 50$ mg/L, $[Ag^{+}] = 50$ mg/L and 2.5 h contact time. The blue dash line refers to the initial chlorophyll fluorescence = 89.89 RFU/mL for (B) to (F), * means there is a statistically significant difference between treated groups under given conditions, p value given in Table S2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.1.2. Influence of various environmental conditions on the effectiveness of disinfection

Various environmental conditions, such as initial cell concentrations, pH, water hardness, NOM, nutrient content and light condition, were considered and their influence on disinfection effectiveness were evaluated. All the experiments were done with exposure to 50 mg/L Cu^{2+} and 50 mg/L Ag^{+} and 2.5 h contact time. Results are shown in Fig. 3 (A)–(F). The initial chlorophyll fluorescence was 89.89 RFU/mL (2.1 *10^5 cells/mL in concentration) for experiments 3B to 3 F. The pH of the BG-11 remained stable at 8 during the studies with different initial cell concentrations, water hardness, NOM, nutrient content and lighting.

3.1.2.1. Effect of initial cyanobacteria concentration on disinfection. Initial cyanobacteria concentration (as determined from chlorophyll fluorescence) of the samples was adjusted to 24.83, 92.58 and 143.71 RFU/mL and then the cyanobacteria were exposed to 50 mg/L Ag^{+} and Cu^{2+} for 2.5 h, to explore the possible influence of cyanobacteria concentration on disinfection effectiveness. As shown in Fig. 3 (A), initial chlorophyll fluorescence is a factor that determines disinfection effectiveness. When exposed to the same concentration of Cu^{2+} and Ag^{+}, the one with lowest initial chlorophyll fluorescence resulted in largest decrease of the final chlorophyll fluorescence (around 71.06% of initial RFU), followed by the medium RFU (66.94%) and the high RFU (64.14% of the initial one). This is supported by previous research stating that the disinfection effect is determined by the initial level of disinfectant per cell [12]. Thus, a higher initial level of disinfectant per cell will accelerate the disinfection process.

3.1.2.2. Effect of pH on disinfection. The pH of the BG-11 medium was adjusted to 6, 7 and 8 respectively with 0.1 M HNO_3 and 0.1 M NaOH to explore the possible influence of pH on disinfection effectiveness. As shown in Fig. 3 (B), the growth and disinfection of *O. tenuis* are sensitive to the change of pH in the environment. Chlorophyll fluorescence decreased the most under an acidic environment (pH = 6), followed by neutral (pH = 7) and alkaline (pH = 8). The possible reason for this phenomenon is due to the speciation of Ag^{+} and Cu^{2+} in the medium under different pH conditions. Although the speciation and concentration of free Ag^{+} remains stable under the environment with pH = 6 to 8, the change of pH will influence the speciation of Cu^{2+} in BG-11 medium, as the constituents include CO_3^{2-} which will combine with Cu^{2+} and form insoluble $CuCO_3$ [13]. Free Cu^{2+} is the dominant species in water under an acidic environment, while $CuCO_3$ dominates at alkaline conditions [13]. Since the free Cu^{2+} ions are the predominant toxic species against microorganisms within short contact time [30], reduction of free Cu^{2+} ions in the medium will weaken the disinfection effectiveness. Thus, the difference of chlorophyll fluorescence in the disinfectant-treated group is due to the change of dominant species of Cu^{2+} at different pH.

3.1.2.3. Effect of water hardness on disinfection. Water hardness, usually expressed as the concentration of $CaCO_3$ in water, is one of the main environmental factors that determine the quality of freshwater. In this study, different concentrations of $CaCO_3$ (50, 100 and 200 mg/L) were added into the system to simulate soft, moderate hard and very hard water. As shown in Fig. 3 (C), the chlorophyll fluorescence increased more with higher concentration of $CaCO_3$ in the control group. However, no significant change of the chlorophyll fluorescence was found in the group treated with Cu^{2+}+Ag^{+} and different concentrations of $CaCO_3$ ($p = 0.165 > 0.05$, Table S2). This is mainly because the speciation of Cu^{2+} and Ag^{+} was not changed substantially with the addition of $CaCO_3$ [5,23]. Thus, water hardness is not a factor that will influence the disinfection process.

3.1.2.4. Effect of NOM on disinfection. NOM, which is derived from decaying plant and animal matter, is one of the main constituents in many environmental and drinking supply water sources, particularly those that harbor cyanobacteria. To evaluate the influence of NOM on the disinfection process, different concentrations of humic acid (HA) (0, 1 and 10 mg/L) were added into the system. As shown in Fig. 3 (D), the growth of *O. tenuis* is influenced by the addition of HA, as the chlorophyll fluorescence decreased with the increasing concentration of HA in the control. However, no significant difference of fluorescence was found between the groups treated with Cu^{2+}+Ag^{+} and different concentrations of HA ($p = 0.423 > 0.05$, Table S2). Although HA could form complexes with Cu^{2+} and Ag^{+}, and the Cu-HA and Ag-HA complex are not so toxic compared to free ions [32,44], the affinity is quite limited under the concentration range of HA considered in this study (0–10 mg/L). Thus, the concentration of effective free Cu^{2+} and Ag^{+} is not influenced noticeably, and no influence on disinfection effectiveness was observed.

3.1.2.5. Effect of nutrient content on disinfection. To explore the influence of different nutrient levels on the disinfection effectiveness, the BG-11 medium for *O. tenuis* was diluted to 0% (i.e. with no nutrient and only deionized water) and 50% of original concentration with deionized water. As shown in Fig. 3 (E), the decrease of nutrients (0% and 50%) did not influence the fluorescence of the control group significantly. This is mainly because the poor nutrient environment will stimulate the metabolism of *O. tenuis* during the short contact time (2.5 h). In the group exposed to Cu^{2+}+Ag^{+}, the fluorescence decreased the most with 0% nutrient, followed by 50% and 100% nutrient. A possible reason for this phenomenon might be that the concentration of free Ag^{+} is affected to the nutrient concentration in the medium, as $CaCl_2$ is one of the ingredients of the medium (Table S1) and Cl^{-} will combine with Ag^{+} thus influencing the disinfection effectiveness. In a low nutrient environment, free Ag^{+} will be present in higher amounts and result in better disinfection effectiveness. Compared to Ag^{+}, the disinfection ability of Cu^{2+} is not influenced by the concentration of nutrients, as the ingredients of the medium do not change the speciation of Cu^{2+} in water.

3.1.2.6. Effect of lighting condition on disinfection. Illumination is essential for the growth of cyanobacteria, thus the influence of lighting conditions on disinfection effectiveness was considered as well. The disinfection process was done under both light and dark conditions for comparison., and the results are shown in Fig. 3 (F). Change of lighting conditions within a short contact time (2.5 h) did not lead to noticeable difference of the chlorophyll fluorescence in the control group. However, the chlorophyll fluorescence decreased more under the lighting condition than that under a dark one in the group exposed to Cu^{2+}+Ag^{+}. As Cu^{2+} is not sensitive to the light, the main reason for this phenomenon is due to one of the disinfection mechanisms by Ag^{+} which is related to the lighting condition. Ag^{+} can combine with the thiol group of proteins and hinder their enzymatic function [20], but the behavior of Ag^{+}-protein complex may be affected by the light irradiation [17]. According to the results from a previous study about disinfection of *E. coli* by Ag^{+}, the inactivation of *E. coli* is enhanced by the photochemical reaction of Ag^{+}-protein complex under UV-A or visible light irradiation [17]. Thus, disinfection is more effective under the illuminated rather than dark conditions.

3.2. Cyanotoxin extraction and quantification

In this study, 5 mL of *O. tenuis* culture was monitored at different times during disinfection to determine the levels of cyanotoxins. After centrifuging the culture, the extracellular toxin was collected from the supernatant, and the intracellular toxin was extracted from the pellet using 5 mL 5% aqueous acetic acid. Samples from both the control and the combined metal ions treatment (50 mg/L each of Cu^{2+} + Ag^{+}) groups were collected and quantified for comparison. Total and extracellular concentration of anatoxin-a increased (Fig. 4 (A)), and the

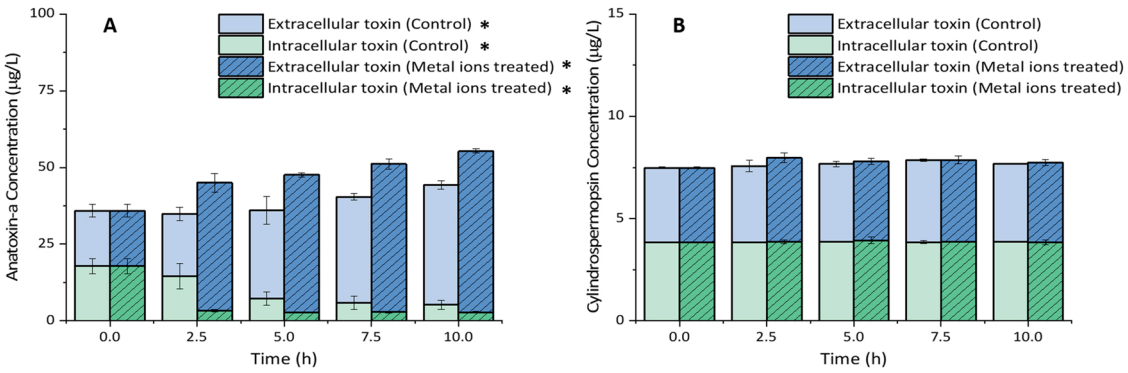

Fig. 4. Concentration of extracellular and intracellular anatoxin-a (A) and cylindrospermopsin (B) versus time during disinfection with $[Cu^{2+}] = 50$ mg/L and $[Ag^{+}] = 50$ mg/L (* means there is a statistically significant difference between treated groups under given conditions, p value given in Table S2).

intracellular concentration decreased overtime in both the control and metal ions treated groups. However, compared to the control group, in the combined metal ion treatment the total, extracellular and intracellular concentrations of anatoxin-a had pronounced changes. Both the increase of total and extracellular concentrations and the decrease of intracellular concentrations were amplified when the *O. tenuis* was treated with Cu^{2+} and Ag^{+}. This indicates that the addition of Cu^{2+} and Ag^{+} will stimulate not only the production of anatoxin-a, but also the release of anatoxin-a through the cell membrane.

In contrast, the addition of disinfectant (combined Cu^{2+} and Ag^{+}) did not lead to a significant change in the total, extracellular and intracellular concentrations of cylindrospermopsin in either the control or treatment groups over time (p values are given in Table S2). Since extracellular cylindrospermopsin concentration increases only in the late exponential or stationary phase [11], and the culture used for this study was at an early exponential phase, both the extracellular and intracellular concentrations of cylindrospermopsin remained stable within 10 h. Although cell lysis during disinfection may lead to the release of cylindrospermopsin, it has been studied that the main reason of increasing extracellular cylindrospermopsin concentration is not due to the release of cylindrospermopsin during cell lysis, but due to the active release or leakage from intact cells [26]. Since the addition of Cu^{2+} and Ag^{+} did not influence the release or leakage of cylindrospermopsin from intact cells, the intracellular and extracellular distribution of cylindrospermopsin remained stable over time.

3.3. Simultaneous sorption of Cu^{2+}, Ag^{+}, anatoxin-a and cylindrospermopsin by Mag-PCMA

3.3.1. Relationship between adsorbent dosage and removal efficiency

Simultaneous sorption of the disinfectants (Cu^{2+} and Ag^{+}, 50 mg/L each) and the cyanotoxins produced by *O. tenuis* (anatoxin-a and cylindrospermopsin, 20 ug/L) at different concentrations of Mag-PCMA (1–5 g/L) were studied at pH = 7 and room temperature. As shown in Fig. 5 (A), Ag^{+} can be efficiently captured by Mag-PCMA, with a removal efficiency reaching 99.5% at 2 g/L of Mag-PCMA. Compared to Ag^{+}, Cu^{2+} cannot be adsorbed by Mag-PCMA with that level of removal efficiency. The removal efficiency of Cu^{2+} increased substantially with higher adsorbent dosage up to 3 g/L, reaching 38.89%. Above 3 g/L the removal efficiency increased asymptotically up to 40.34%, probably due to the challenge of keeping the Mag-PCMA particles suspended at concentrations above 3 g/L.

The main reason for the difference in removal efficiency of Cu^{2+} versus Ag^{+} by Mag-PCMA is due to the sorption mechanism and the core-shell structure of Mag-PCMA. Due to the negatively charged surface, Mag-PCMA can adsorb metal ions through electrostatic interactions. However, since the surface of the magnetite core is coated with cationic surfactant (3-trimethoxysilyl propyl octadecyl dimethyl ammonium chloride), there will be electrostatic repulsion between the coated cationic surfactant and the metal ions, which will cancel out part of the electrostatic interaction. The electrostatic repulsion is determined by the electronegativity of each metal ion (2.00 for Cu^{2+} and 1.93 for Ag^{+}, dimensionless [28]), resulting in the selectivity of sorption among

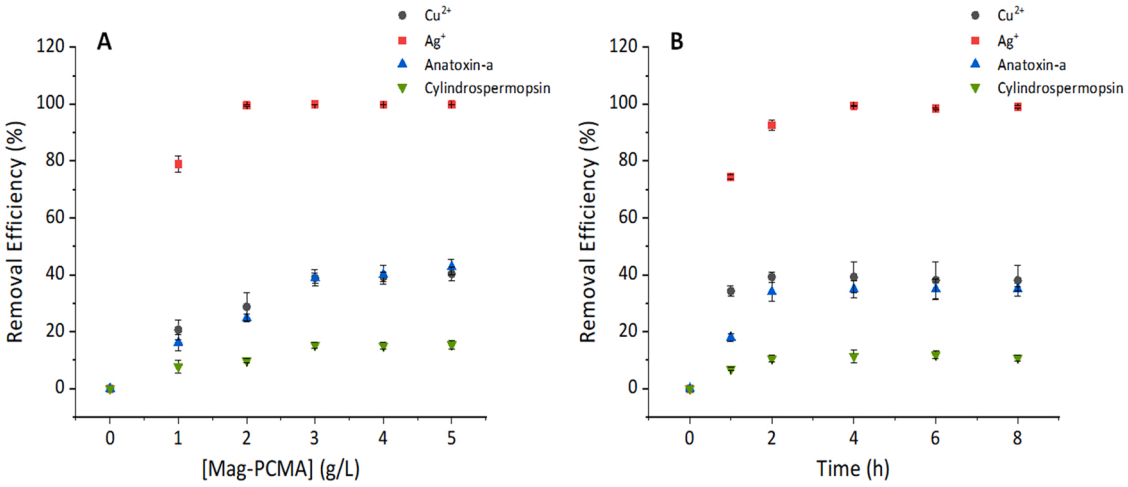

Fig. 5. (A) Adsorption of Cu^{2+}, Ag^{+}, anatoxin-a and cylindrospermopsin onto Mag-PCMA as a function of adsorbent dose with $[Ag^{+}] = 50$ mg/L, $[Cu^{2+}] = 50$ mg/L, [anatoxin-a] = 20 ug/L and [cylindrospermopsin] = 20 ug/L. (B) Sorption uptake of Cu^{2+}, Ag^{+}, anatoxin-a and cylindrospermopsin versus time (with $[Ag^{+}]$ =50 mg/L, $[Cu^{2+}]$ =50 mg/L, [anatoxin-a] =20 ug/L, [cylindrospermopsin] =20 ug/L and [Mag-PCMA] =2.5 g/L).

various metal ions. Stronger repulsion will take place between the cationic surfactant and more positively charged metal ions. Thus, Ag^{+} can be captured by Mag-PCMA with higher efficiency than Cu^{2+}. The concentration of metal ions can be further decreased by additional sorption cycles until reaching a safe level [12].

Simultaneous removal of anatoxin-a and cylindrospermopsin are shown in Fig. 5 (A). Compared to cylindrospermopsin, anatoxin-a can be removed by Mag-PCMA with higher efficiency. 38.91% of anatoxin-a was removed by 3 g/L Mag-PCMA, and the removal efficiency increased slowly up to 42.80% with 5 g/L Mag-PCMA. As comparison, only 15.24% of cylindrospermopsin can be captured by 3 g/L Mag-PCMA, and the removal efficiency remains at this level even with additional dosing of Mag-PCMA up to 5 g/L. The differences in removal efficiency for anatoxin-a and cylindrospermopsin can be explained by considering the sorption mechanism and chemical structure of these two cyanotoxins (Fig. S1). Mag-PCMA can attract anatoxin-a through electrostatic interaction due to its negatively charged surface [15], as anatoxin-a is positively charged in a neutral environment (pKa = 9.4 [38]). Although the same mechanism is valid for sorption between cylindrospermopsin and Mag-PCMA, the anionic sulfur group in cylindrospermopsin (Fig. S1) will weaken the attraction by Mag-PCMA [18]. Thus, the removal efficiency of cylindrospermopsin is lower than that of anatoxin-a at the same dosage of Mag-PCMA. Nevertheless, it is an added value to be able to partially remove these cyanotoxins with the same magnetic nanoparticles used to recover the metal ion disinfectants, thus reducing their concentrations in the treated water. Since in these studies we simulate a cyanobacteria bloom with very high cell concentrations, the concentration of metal ions and cyanotoxins are high. Even so, the simultaneous removal of metal ions and cyanotoxins is considered to be efficient. Less Mag-PCMA would be needed for practical use when the cyanotoxins and metal ions are at a lower level than under the tested conditions, and the removal efficiency of target chemicals will be improved with a reduced initial concentration. Further optimization of the magnetic nanoparticle may result in tailored nanomaterials for this specific application. The high dosage of Mag-PCMA is due to the high concentration of cyanobacteria considered here, and would be optimized for lower concentrations.

3.3.2. Sorption kinetics

Simultaneous sorption kinetics of 50 mg/L Ag^{+}, 50 mg/L Cu^{2+}, 20 ug/L anatoxin-a and 20 ug/L cylindrospermopsin with Mag-PCMA (2.5 g/L) were studied at pH = 7 and room temperature (Fig. 5 (B)). As shown in Fig. 5 (B), rapid sorption occurred within 1 h and the removal efficiency gradually increased until reaching a maximum (99% for Ag^{+} after 4 h, 38.5% for Cu^{2+} after 2 h, 35% for anatoxin-a after 2 h, and 10.5% for cylindrospermopsin after 2 h). The kinetics is mainly influenced by the available sorption sites on the surface of Mag-PCMA. The rapid sorption within 1 h is due to the abundant sorption sites at first. With more and more adsorbates loaded onto the Mag-PCMAs, the available sorption sites decrease, and the sorption rate slows down. Thus, it will take longer time for a system with higher removal efficiency (e.g. Ag^{+}) to reach equilibrium.

3.3.3. Influence of different environmental conditions on adsorption

3.3.3.1. pH. The influence of pH on the adsorption process of the four target chemicals with Mag-PCMA was evaluated with 50 mg/L Ag^{+}, 50 mg/L Cu^{2+}, 20 ug/L anatoxin-a, 20 ug/L cylindrospermopsin and

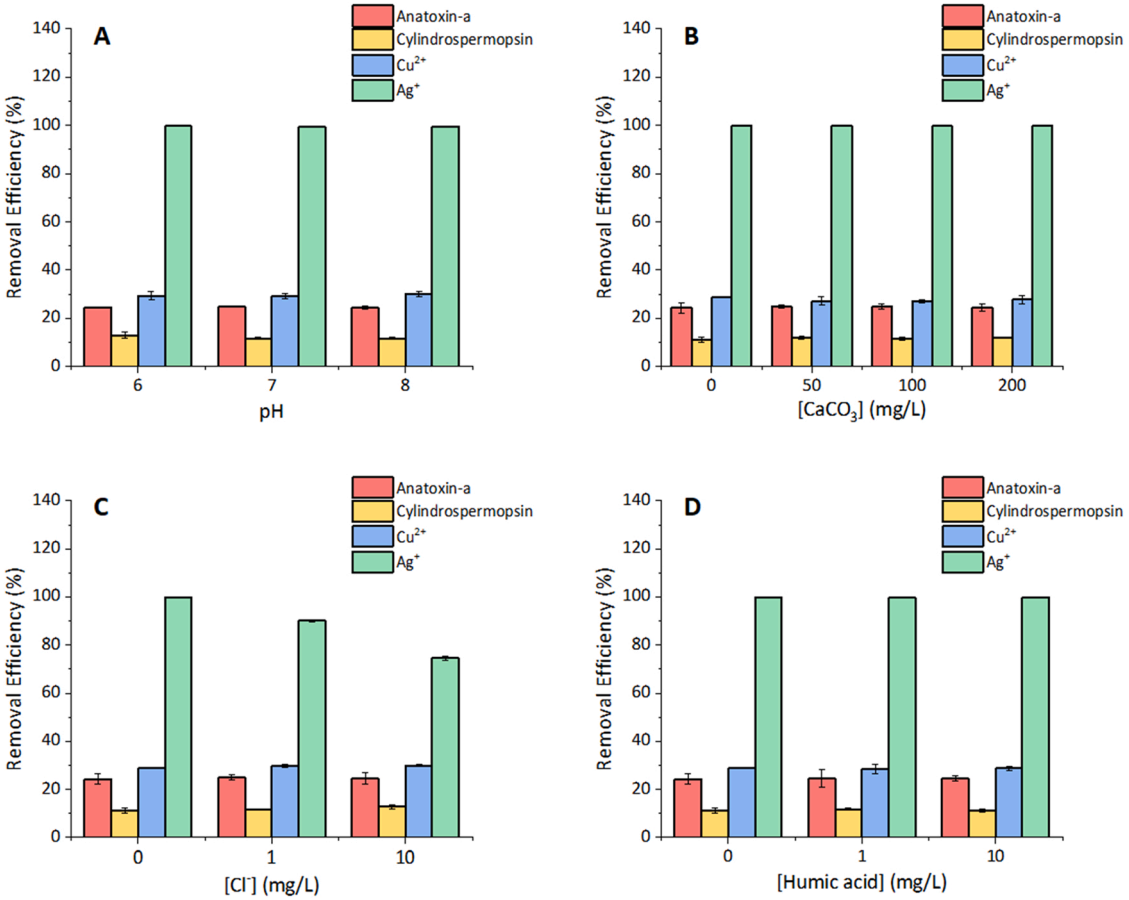

Fig. 6. Influence on sorption for [Ag^{+}] = 50 mg/L, [Cu^{2+}] = 50 mg/L, [cylindrospermopsin] = 20 ug/L, [anatoxin-a] = 20 ug/L and [Mag-PCMA] = 2.5 g/L of different (A) pH; (B) water hardness; (C) Cl^{-} concentration; and (D) NOM concentration.

2.5 g/L Mag-PCMA at room temperature. Removal efficiency of all these four chemicals remained stable when the pH was varied from 6 to 8 (around 99.5% for Ag^+, 28% for Cu^{2+}, 24.5% for anatoxin-a and 11.5% for cylindrospermopsin, Fig. 6 (A)). The p-values for these experiments are given in Table S2. This is mainly due to the sorption mechanism of these four chemicals by Mag-PCMA, which is electrostatic interaction. Since the speciation of Ag^+ and Cu^{2+} remains stable with the change of pH from 6–8 (K_{sp} (AgOH) = 2 * 10^{-8}, K_{sp} ($Cu(OH)_2$) = 2.2 * 10^{-20} at room temperature [35,37]), the removal efficiency was not influenced. Besides, there was no significant change in the surface charge of Mag-PCMA at different pH [15], resulting in stable removal of anatoxin-a and cylindrospermopsin.

3.3.3.2. Water hardness. Different concentrations of $CaCO_3$ were considered to evaluate the possible influence of hardness on the sorption process with Mag-PCMA. As shown in Fig. 6 (B), no significant influence was observed on the removal efficiency (around 99.5% for Ag^+, 28% for Cu^{2+}, 24.5% for anatoxin-a and 11.5% for cylindrospermopsin, p value for these systems are given in Table S2). This is because the addition of $CaCO_3$ did not change the aqueous speciation of Ag^+ and Cu^{2+}, nor did it influence the surface charge of Mag-PCMA. Although a small fraction of Ca^{2+} may be dissolved from $CaCO_3$ and released into the water and be captured by Mag-PCMA, it does not compete significantly with the sorption of Ag^+ and Cu^{2+} (K_{sp} ($CaCO_3$) = 2.8 × 10^{-9} at room temperature [22]). Thus, water hardness is not a major concern for the removal of the target chemicals.

3.3.3.3. Cl^-. The presence of Cl^- may be another factor that could influence the removal of the target chemicals in this study, as Cl^- is able to combine with Ag^+ to form precipitation thus reducing the concentration of free Ag^+ in water. Thus, different concentrations of Cl^- (0, 1 and 10 mg/L) were added. As shown in Fig. 6 (C), no significant change in removal efficiency on Cu^{2+}, anatoxin-a and cylindrospermopsin was observed (around 28% for Cu^{2+}, 24.5% for anatoxin-a and 11.5% for cylindrospermopsin; p values for these systems are given in Table S2), since the presence of Cl^- did not influence the surface charge of Mag-PCMA or the speciation of Cu^{2+} in water. However, the sorption process of Ag^+ was influenced by Cl^-, as the concentration of Cl^- determines the percentage of free Ag^+ in water. With the addition of 1 mg/L Cl^-, free Ag^+ decreased from 100% to 96.74% (K_{sp} (AgCl) = 1.77 * 10^{-10} at room temperature [45]). After sorption, 90.97% of the free Ag^+ was removed by Mag-PCMA, which is less than the removal efficiency without Cl^- (99.5%). When the concentration of Cl^- increased to 10 mg/L, the percentage of free Ag^+ decreased to 41.96%, and the percentage of free Ag^+ adsorbed by Mag-PCMA decreased to 75.64%. Thus, the presence of Cl^- is a factor that needs to be considered when evaluating the disinfection and sorption process with Ag^+. The AgCl complex is likely to precipitate, and Ag can be recovered in the sludges, but it would be a more expensive separation.

3.3.3.4. NOM. Similar to the addition of $CaCO_3$, the presence of humic acid with different concentrations did not influence the removal efficiency of the four chemicals significantly (around 99.5% for Ag^+, 28% for Cu^{2+}, 24.5% for anatoxin-a and 11.5% for cylindrospermopsin in Fig. 6 (D); p values for these systems are given in Table S2). The added HA did not compete with the four target chemicals for sorption sites, as both HA and Mag-PCMA are negatively charged [15,42]. Thus, the surface charge of Mag-PCMA remains stable with the addition of HA. Nor will HA change the speciation of Ag^+ and Cu^{2+}, since the combination between Ag^+ or Cu^{2+} and HA is quite limited at the range of concentrations considered for HA in this study (0–10 mg/L) and is not comparable to that between Ag^+ or Cu^{2+} and Mag-PCMA. This is supported by a previous study of the simultaneous sorption of Cd^{2+}, acenaphthene and NOM. When a large amount of Mag-PCMA (>1 g/L) is added, the difference of sorption capacity of Cd^{2+} and acenaphthene in the absence or presence of NOM is negligible [15].

3.4. Regeneration and reuse of Mag-PCMA

To evaluate the regeneration and reusability of Mag-PCMA, Cu^{2+}, Ag^+, anatoxin-a and cylindrospermopsin adsorbed onto Mag-PCMA were extracted with methanol (for anatoxin-a and cylindrospermopsin) and 0.01 M H_2SO_4 (for Cu^{2+} and Ag^+). After extraction, Mag-PCMA was mixed with 50 mg/L Ag^+, 50 mg/L Cu^{2+}, 20 ug/L anatoxin-a and 20 ug/L cylindrospermopsin immediately to evaluate the simultaneous removal performance of Mag-PCMA after regeneration. The sorption and regeneration processes were repeated for five continuous cycles, and the removal efficiency of Cu^{2+}, Ag^+, anatoxin-a and cylindrospermopsin are shown in Fig. 7 (A) and (B). No significant change in removal efficiencies of Cu^{2+}, anatoxin-a and cylindrospermopsin was observed for the regenerated Mag-PCMA up to 5 cycles (p values are given in Table S2). Although the removal efficiency of Ag^+ decreased gradually during the sorption-desorption cycles, it still remained above 93%, indicating good reusability of Mag-PCMA.

4. Conclusion

In this study, a combination of metal ions (Ag^+ + Cu^{2+}) resulted in better disinfection of *O. tenuis* than the individual ions (Cu^{2+}, Ag^+), since the combination can achieve the same disinfection effectiveness with shorter time and lower concentration. Environmental conditions that will determine the dominant speciation of metal ions (i.e. pH and nutrient content) or will influence the ratio between cyanobacteria cells and free metal ions, will influence disinfection effectiveness, while those that do not influence the metal ions in water (i.e. water hardness and presence of humic acid) will not change the disinfection effectiveness. Although the addition of metal ions will stimulate the production of cyanotoxin during the disinfection process, both the metal ions and cyanotoxins can be effectively removed by Mag-PCMA through simultaneous adsorption later, and the sorption of metal ions and toxins remains stable under various environmental conditions. Thus, the potential environmental risk caused by the use of metal ions as disinfectant and the production of cyanotoxin during disinfection will be substantially reduced. The disinfection method in this study is sustainable, as metal ions and Mag-PCMA can be regenerated with high efficiency and reused for several continuous cycles (removal efficiency above 93% after 5 cycles). Thus, this novel disinfection method is very promising for practical application in the future.

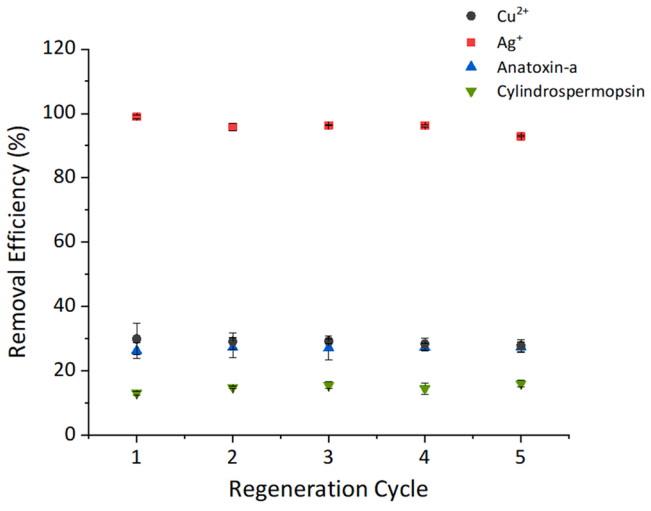

Fig. 7. Sorption and recovery efficiency of Cu^{2+}, Ag^+, anatoxin-a and cylindrospermopsin after five Mag-PCMA regeneration cycles.

CRediT authorship contribution statement

AK contributed with intellectual design of experimental approach, review of experimental methods, editing and revisions of documents, project supervision and funding. **QG** contributed with intellectual design of experimental approach, implementation of experiments and data analysis, primary writing of documents as first author, editing and developing response to revisions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.106589.

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