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Multiple roles of UV/$KMnO_4$ in cyanobacteria containing water treatment: Cell inactivation & removal, and microcystin degradation

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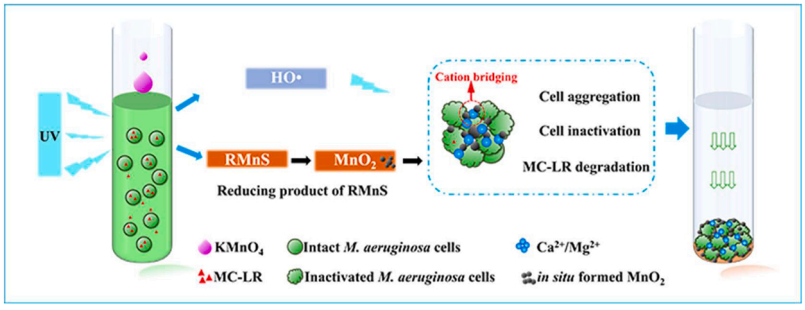
HIGHLIGHTS

- Significant synergy of UV/$KMnO_4$ on cyanobacteria treatment was observed.
- UV/$KMnO_4$ achieved efficient inactivation of cyanobacterial cells.
- Effective degradation of microcystins was simultaneously achieved.
- The cells were removed efficiently via self-settling after UV/$KMnO_4$ treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Cyanobacterial blooms present great challenges to drinking water treatment and human health. The novel combination of potassium permanganate ($KMnO_4$) and ultraviolet (UV) radiation is engaged as a promising advanced oxidation process in water purification. This study investigated the treatment of a typical cyanobacteria, *Microcystis aeruginosa* by UV/$KMnO_4$. Cell inactivation was significantly improved by UV/$KMnO_4$ treatment, compared to UV alone or $KMnO_4$ alone, and cells were completely inactivated within 35 min by UV/$KMnO_4$ in natural water. Moreover, effective degradation of associated microcystins was simultaneously achieved at UV fluence rate of 0.88 mW cm^{-2} and $KMnO_4$ dosages of 3–5 mg L^{-1}. The significant synergistic effect is possibly attributable to the highly oxidative species produced during UV photolysis of $KMnO_4$. In addition, the cell removal efficiency via self-settling reached 87.9 % after UV/$KMnO_4$ treatment, without additional coagulants. The fast in situ generated manganese dioxide was responsible for the enhancement of *M. aeruginosa* cell removal. This study firstly reports multiple roles of UV/$KMnO_4$ process in cyanobacterial cell inactivation and removal, as well as simultaneous microcystin degradation under practical conditions.

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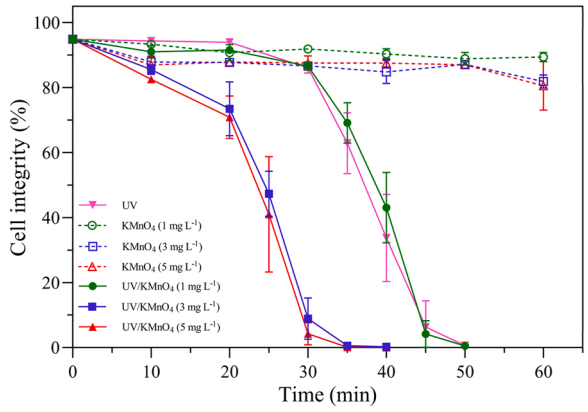

Fig. 1. Alternation of cell integrity of *M. aeruginosa* during $KMnO_4$, UV, and UV/$KMnO_4$ treatments in YHTR water. Conditions: UV fluence rate = 0.88 mW cm^{-2}, pH = 7.5, the initial cell density of *M. aeruginosa* = ~7.5 × 10^5 cells mL^{-1}.

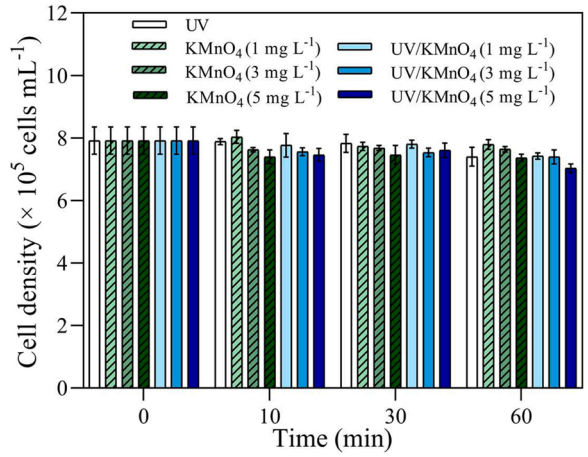

Fig. 2. The change in the cell density of *M. aeruginosa* during $KMnO_4$, UV, and UV/$KMnO_4$ treatments in YHTR water. Conditions: UV fluence rate = 0.88 mW cm^{-2}, pH = 7.5, the initial cell density of *M. aeruginosa* = ~7.5 × 10^5 cells mL^{-1}.

1. Introduction

The frequent occurrence of cyanobacterial blooms has become a global concern, which can severely impair aquatic ecosystems and drinking water quality [41,46]. In particular, cyanotoxins such as microcystins (MCs) produced by cyanobacteria, have been reported to induce serious harm to human health [1,12,70]. Besides, the associated algal organic matters (AOM) may cause membrane fouling, and serve as precursors of disinfection by-products (DBPs) during water treatment processes [18,29,52]. Unfortunately, conventional water treatments including coagulation, sedimentation and filtration generally show poor efficiency in cyanobacterial removal. Also, they are unable to eliminate cyanotoxins [10,60].

Pre-oxidation using potassium permanganate ($KMnO_4$), chlorine, or ozone has been applied to facilitate the subsequent coagulation for overall cyanobacterial removal [64]. However, in addition to their inherent complexity in the operation of water treatment plants (WTPs), it is likely difficult for those multiple steps to achieve efficient cyanobacterial inactivation & removal [38,68]. The breakthrough of cyanobacterial cells and toxins still can be frequently observed in the treated water [21,49,67,69]. Furthermore, although pre-oxidation can inactivate cyanobacteria and thus inhibit their growth, chlorine and ozone may induce the leakage of cyanotoxins and intracellular organic matter (IOM) [17,26,58], and the formation of DBPs [13,18,33].

$KMnO_4$ has been considered as an environmentally friendly barrier for cyanobacteria treatment, without producing undesirable DBPs [11,56,71]. It has been widely applied in WTPs because of its low cost, stability, and simple operation [14,57]. However, $KMnO_4$ is a selective oxidant and its efficiency in purifying cyanobacteria-laden water is relatively limited [30,31,45]. For instance, most of cyanobacterial cells remained healthy after 5 mg L^{-1} $KMnO_4$ treatment for 5 h, and the residual MCs are considerably higher than the guideline value (1.0 μg L^{-1}) by the World Health Organization [15]. Moreover, the reaction between $KMnO_4$ and cyanobacteria is relatively slow, thus there could be a high concentration of residual $KMnO_4$ after several hours [15,31], which will cause a pink taint to drinking water [62].

Recent studies reported that the activation of $KMnO_4$ via ultraviolet (UV) radiation is a promising way to enhance its efficiency [20,61]. Highly reactive species including hydroxyl radicals (HO•) and reactive manganese species (RMnS), and adsorptive species of in situ formed manganese dioxide (MnO_2) can be generated in UV/$KMnO_4$ process [19,61]. HO• is a highly reactive oxidant for cyanobacteria inactivation and MC reduction [3]. The role of RMnS including Mn(VI) and Mn(V) in MC degradation has not been reported, but they have high reactivity toward organic contaminants with electron-rich moieties, such as benzene rings, conjugated double bonds, and sulphinyl [7]. Hence, RMnS may likely contribute to MC degradation, due to the structure of MCs containing benzene rings and conjugated double bonds [4,7]. Moreover, the in situ formed MnO_2 may promote the aggregation of algal cells, and then profit the cell removal from water [8]. Therefore, the cooperation of oxidation and adsorption in UV/$KMnO_4$ system may potentially mitigate cyanobacteria and their metabolites in one-step treatment. However, to date, the related information of UV/$KMnO_4$ on the treatment of harmful microorganisms (e.g., cyanobacteria) remains unknown and deserves investigation.

Consequently, the main objective of this study was to explore the multiple functions of UV/$KMnO_4$ for the control of cyanobacteria-laden water. The specific aims were to (1) evaluate the efficiency of UV/$KMnO_4$ process in the inactivation of cyanobacterial cells; (2) assess the potential impacts of UV/$KMnO_4$ treatment on cyanobacteria, such as the fate of MCs and the release of IOM; and (3) investigate the subsequent cyanobacterial cell removal via self-settling, after UV/$KMnO_4$ treatment.

2. Materials and methods

2.1. Water source and quality

Raw water was obtained from Yuhangtang River (YHTR, Hangzhou, China). The sampled water was filtered through 1.2 μm glass fiber filter (GF/C, Whatman, England), 0.45 μm and then 0.2 μm cellulose acetate filters (Xinya, China). The water quality of the filtered water is shown in Table S1. The filtered YHTR water was then stored in a refrigerator at 4 °C, prior to the followed experiments.

2.2. Materials and reagents

A toxin-producing strain of *Microcystis aeruginosa* (FACHB-905) was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, China. The strain was verified as producing MCs, mainly MC-LR. *M. aeruginosa* was grown in sterilized basal glucose (BG-11) media [55], and sub-cultured routinely to maintain logarithmic growth. Cultures were incubated under a cool fluorescent light flux (12 h:12 h light-dark cycle, 25 μmol photos m^{-2} s^{-1}) at a constant temperature of 25 ± 1 °C, to achieve healthy cultures with high cell density. *M. aeruginosa* cultures with an initial cell density of around 7.5 × 10^5 cells mL^{-1} were used in the subsequent experiments, diluting with BG-11 media or YHTR water. Prior to the UV/$KMnO_4$ oxidation experiments, the cultures were adjusted to pH 7.5 ± 0.1 either using 0.1 M filtered hydrochloride or

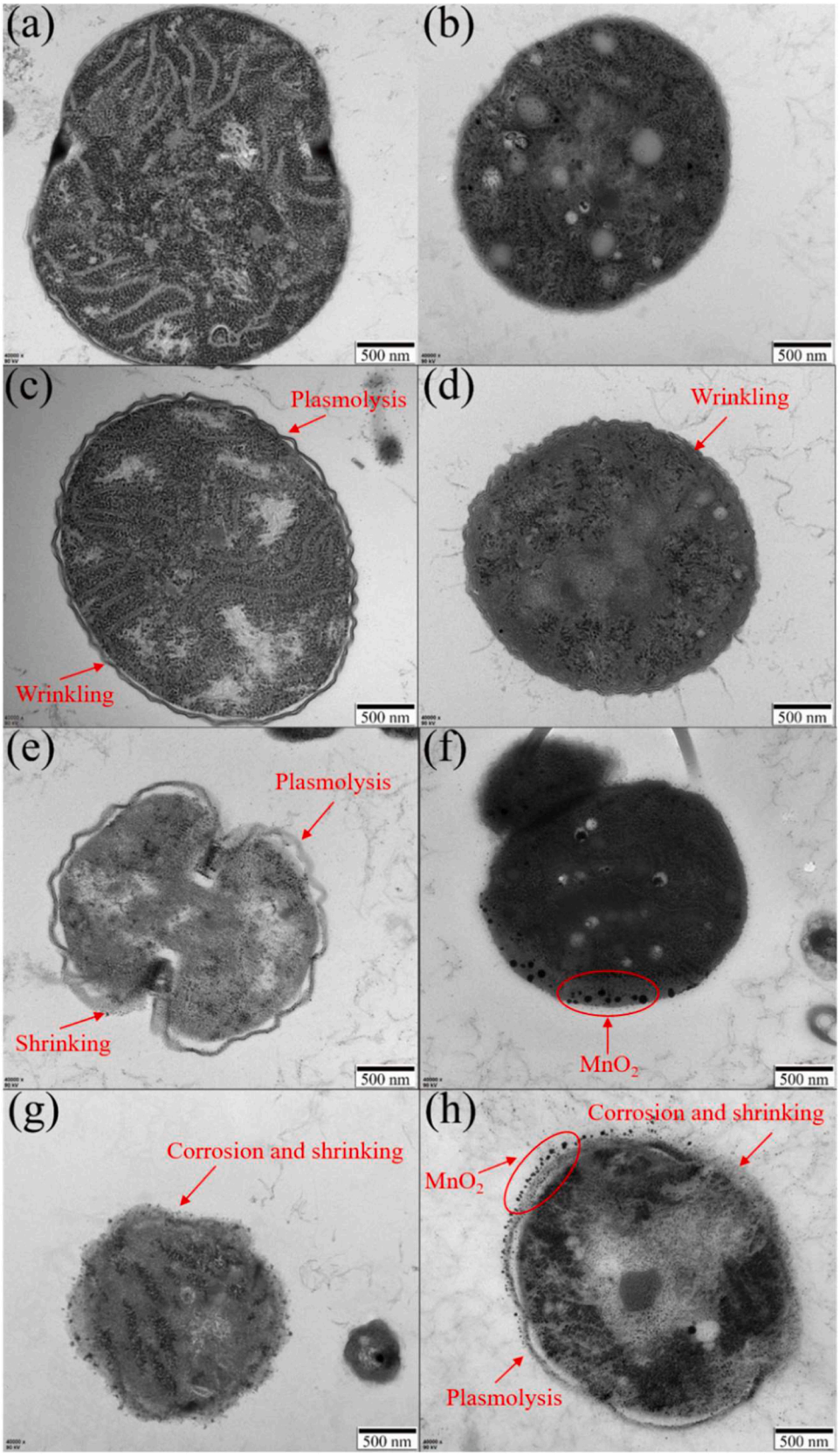

Fig. 3. TEM images of *M. aeruginosa* cell structure after $KMnO_4$, UV, and UV/$KMnO_4$ treatments in the YHTR water, (a) blank control, (b) $KMnO_4$ ($KMnO_4$ dosage of 5 mg L^{-1}, exposure time = 60 min), (c, d) UV (exposure time = 60 min), (e, f) UV/$KMnO_4$ ($KMnO_4$ dosage of 5 mg L^{-1}, exposure time = 10 min), and (g, h) UV/$KMnO_4$ ($KMnO_4$ dosage of 5 mg L^{-1}, exposure time = 60 min). Conditions: UV fluence rate = 0.88 mW cm^{-2}, pH = 7.5, the initial cell density of *M. aeruginosa* = ~7.5×10^5 cells mL^{-1}.

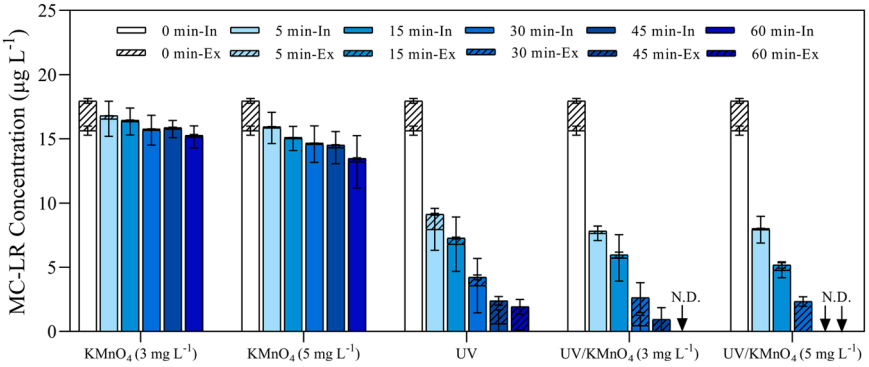

Fig. 4. Concentrations of intracellular (In) and extracellular (Ex) MC-LR during $KMnO_4$, UV, and UV/$KMnO_4$ treatments in the YHTR water. Conditions: UV fluence rate = 0.88 mW cm^{-2}, pH = 7.5, the initial cell density of *M. aeruginosa* = ~7.5 × 10^5 cells mL^{-1}. N.D. means the concentrations of MC-LR were below the detection limit.

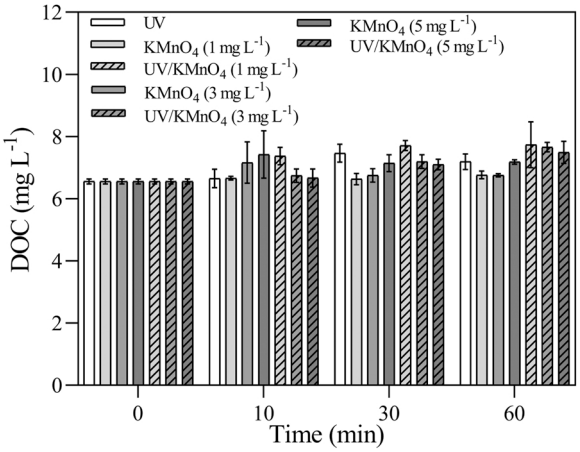

Fig. 5. The DOC of EOM in *M. aeruginosa* samples during $KMnO_4$, UV, and UV/$KMnO_4$ treatments in the YHTR water. Conditions: UV fluence rate = 0.88 mW cm^{-2}, pH = 7.5, the initial cell density of *M. aeruginosa* = ~7.5 × 10^5 cells mL^{-1}.

sodium hydroxide. All chemicals and reagents were analytical grade or chromatographic grade. All solutions were made using ultra-pure water (18.2 MΩ•cm, Synergy, Merck Millipore, Germany).

2.3. Experimental reactor and procedures

The irradiation experiments were conducted in a photoreactor (JT-GHX-A, Jutong, China) with a quartz sleeve in the center, where a low-pressure mercury lamp (GPH 212T5L/4, Heraeus, Germany) at a wavelength of 254 nm was placed (Fig. S1). Compared with the reactor that place the UV light in the water, this reactor would be better to conduct parallel samples like microorganisms at the same time, reducing the errors between samples. The experimental temperature was maintained at 25 ± 1 °C using a continuous recirculation water system and one cooling fan. The *M. aeruginosa* sample was continuously stirred at a low speed with a magnetic stirrer. The average UV fluence rate was determined to be about 0.88 mW cm^{-2} by using iodide/iodate chemical actinometry [53]. The cyanobacterial samples were dosed with the $KMnO_4$ stock solution (2.0 g L^{-1}) to achieve the desired $KMnO_4$ concentrations, and were simultaneously exposed to UV irradiation. Samples were collected by taking one quartz tube from the photoreactor at predetermined contact time. Control tests of cyanobacterial treatment by UV photolysis alone or $KMnO_4$ oxidation alone were performed in a similar manner. At each time interval, the cyanobacterial samples were quenched immediately with sodium thiosulfate at a stoichiometric ratio, and used for analyses of cell density, cell integrity, MC-LR, and extracellular organic matters (EOM), except for the determination of $KMnO_4$ residual, cell structure, and cell settling.

2.4. M. aeruginosa settling test

The UV/$KMnO_4$ pre-treated (5 mg L^{-1} $KMnO_4$, reaction time of 30 min) cyanobacterial suspensions were subsequently placed in the quartz tubes without mixing for the settling tests. Tests of blank control, UV photolysis alone (reaction time of 30 min), pre-synthesized MnO_2 alone (5 mg L^{-1} MnO_2, reaction time of 30 min), or $KMnO_4$ oxidation alone (5 mg L^{-1} $KMnO_4$, reaction time of 30 min) were conducted simultaneously in a similar manner. The pre-synthesized MnO_2 was prepared by mixing MnO_4^- and Mn^{2+} with a ratio of 2:3 ($2\ MnO_4^- + 3\ Mn^{2+} + 2\ H_2O \rightarrow 5\ MnO^2 + 4\ H^+$). In addition, influence of exposure time (10, 30, and 60 min) and pH values (4.0, 7.5, and 10.0) on the performance of UV/$KMnO_4$ pre-treatment were assessed to explore their impacts on the followed cell settling. During the tests, samples were collected from the suspensions at the depth of 2 cm below the water surface, at time intervals of 1, 2, 4, and 6 h. The removal efficiency (Re) during self-settling was calculated by Eq. (1).

$$Re = (N_0 - N_t)/N_0 \times 100\% \quad (1)$$

where N_0 is the initial cell concentration of cyanobacteria in the suspension, and N_t is the cell concentration of cyanobacteria at a settling time t.

2.5. Analytical methods

Cyanobacterial samples for analysis of cell density were treated with Lugol's iodine and counted by a microscope (ECLIPSE E100, Nikon, Japan) at × 100 magnification [32]. The cyanobacterial cell integrity was evaluated immediately upon sampling using flow cytometry (CytoFLEX, Beckman Culter, USA) combined with SYTOX Green nucleic acid stain (Invitrogen, USA). SYTOX positive and SYTOX negative cells represent inactivated and viable cells, respectively. The measurement parameters were detailed in a previous study [32]. The cyanobacterial suspensions were pretreated referred to previous studies [8,43], with slight modification, and then the morphology and structure of cells were observed by a scanning electron microscope (SEM, Zeiss Sigma 500, Germany) and a transmission electron microscope (TEM, Hitachi Model H-7650, Japan), respectively.

Cyanobacterial suspension (200 mL) was sampled at each time interval for MC-LR analysis. A 100 mL sample was filtered with a 0.45 μm and then a 0.22 μm glass-fiber membrane (Xinya, China) for extracellular MC-LR analysis. Another 100 mL sample was filtered after frozen and thawed 3 times, for total (intracellular + extracellular) MC-LR

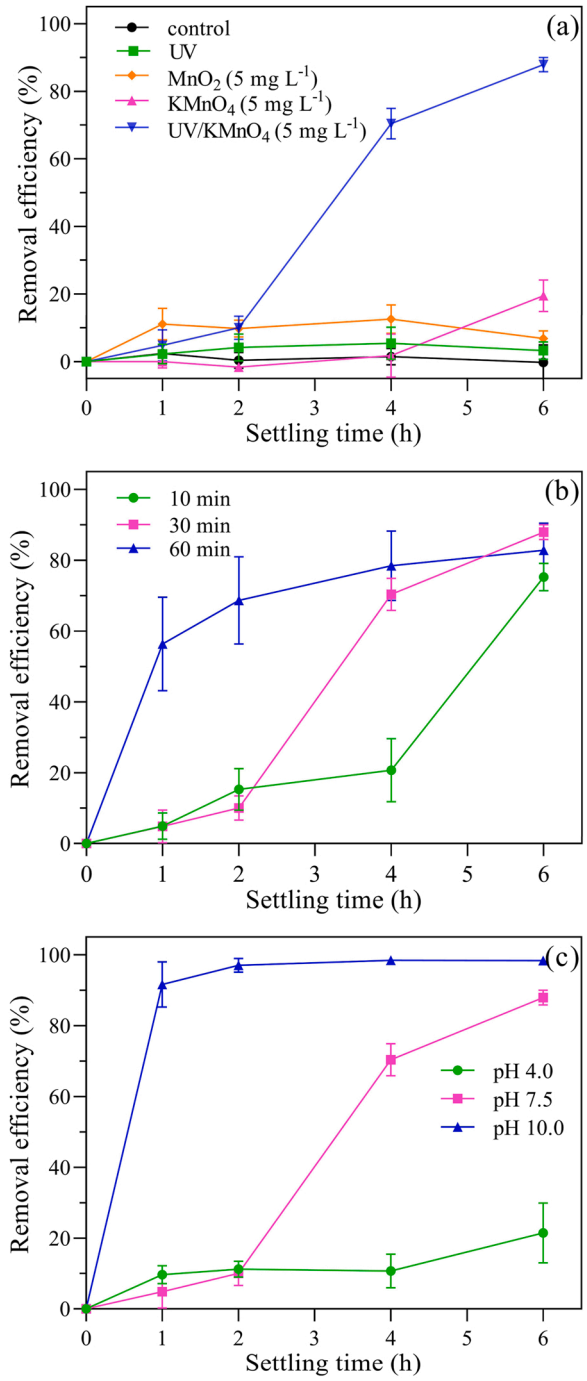

Fig. 6. Effects of (a) UV, pre-synthesized MnO_2, $KMnO_4$, and UV/$KMnO_4$ treatments on cell settling of *M. aeruginosa*. Effects of (b) exposure time and (c) pH by UV/$KMnO_4$ treatment on cell settling of *M. aeruginosa*. The initial cell density of *M. aeruginosa* ~7.5×10^5 cells mL^{-1}, $KMnO_4$ dosage of 5 mg L^{-1}, UV fluence rate of 0.88 mW cm^{-2}, and YHTR water was applied. Conditions: (a) exposure time = 30 min, pH = 7.5; (b) exposure time = 10, 30 and 60 min, pH= 7.5; and (c) exposure time = 30 min, pH = 4.0, 7.5 and 10.0.

analysis. The filtrates were concentrated by C18 solid-phase (Waters, USA) extraction according to Nicholson et al. [40]. The concentration of MC-LR was detected by a high-performance liquid chromatography (HPLC, 1260 infinity II, Agilent, USA). The HPLC was equipped a C18 column (125 mm × 4.6 mm × 5 μm, Waters, USA). The mobile phase condition was prepared as described by Lin et al. [32], with a slight modification.

The cyanobacterial suspension (40 mL for each sample) was filtered through 0.45 μm glass-fiber membrane (Xinya, China) to obtain the EOM. A volume of 30 mL filtrate was used to determine the dissolved organic carbon (DOC) by a TOC analyzer (TOC–V CPH, Shimadzu, Japan). The absorbance of cyanobacterial filtrate (with a volume of 10 mL) was measured at 254 nm (UV_{254}). The specific UV_{254} absorbance (SUVA) was obtained by calculating the ratio of the UV_{254} and the DOC concentration. The concentrations of residual $KMnO_4$ in the samples were monitored by measuring the absorbance at 525 nm using a UV/VIS spectrometer (Evolution 300, Thermo Scientific, USA) [16]. The formaiton of MnO_2 particles in cyanobacterial samples were determined through the absorbance at 200–800 nm [23]. In addition, the absorbance in the cyanobacterial filtrate (filtered with 0.22 μm nylon filter) at 418 nm was applied to estimate the possible interference caused by MnO_2 collodials in the analysis of $KMnO_4$ concentration (Table S2) [28]. The negligible absorbance indicated that there was no interference in the determination of $KMnO_4$ concentration by colloidal MnO_2 (Table S2).

3. Results and discussion

3.1. Inactivation of *M. aeruginosa* cells in $KMnO_4$, UV, and UV/$KMnO_4$ treatments

The inactivation of *M. aeruginosa* by various processes were assessed, as shown in Fig. 1 and Fig. S2. $KMnO_4$ (1–10 mg L^{-1}) was ineffective to inactive cyanobacterial cells within 1 h in BG-11 media (Fig. S2), as agreed with previous studies [15,32]. Under UV irradiaiton, the cells kept healthy during the first 30 min (~1.58 J cm^{-2}), after which the inactivation of cells increased rapidly. However, there were still 12.0 % of the cells undamaged after 60 min. Literature also indicated that UV alone could inactivate *M. aeruginosa* cells via attacking their protein, chlorophyll-a, and phycocyanin. The inactivation effects increased with UV dose [43]. In comparison, the change of cell inactivation after UV/$KMnO_4$ (1 mg L^{-1}) treatment was similar with UV alone. However, UV/$KMnO_4$ with higher $KMnO_4$ dosages had considerablely larger impacts on *M. aeruginosa* cells, which damaged all of the cells after 60 min. Furthermore, the cell inactivation increased with increasing $KMnO_4$ dosage, and about 17.7 %, 33.4 %, 58.4 %, 66.0 %, and 95.6 % of the cells were inactivated after 30 min of UV/$KMnO_4$ treatments, with $KMnO_4$ dosages of 1.5, 2, 3, 5, and 10 mg L^{-1}, respectively. The high efficiency of UV/$KMnO_4$ in cyanobacteria inactivation may be owing to the formation of HO• and RMnS [20,61]. HO• can cause damage to most constituent of cyanobacterial cells, including proteins, lipids, and DNA [48], and the effectiveness on cell inactivation is significantly higher than other oxidants (e.g., hydrogen peroxide) [3]. RMnS may also contribute to destruct cell membrane, by attacking the membrane components (e.g., peptidoglycan and proteins) with electron-rich moieties [27,39,6].

Generally, a similar tendency was observed for the change in cell inactivation in real water (YHTR water) compared to those in BG-11 media, while the cells were more susceptible to all the treatments (Fig. 1). It was found that the integrity of cyanobacterial cells remained unchanged in YHTR water (Fig. S3), indicating that there was no osmotic shock and cell death caused by the natural water. UV/$KMnO_4$ (3 and 5 mg L^{-1}) achieved completely inactivation of cyanobacterial cells after 35 min treatment. The relatively lower efficiency in BG-11 media may be caused by the existence of various components. For instance, it has been reported that ions like citrate and Manganese (II) in BG-11 media may compete for the oxidants [2,42]. This study also showed that $KMnO_4$ decreased more rapidly in BG-11 media than YHTR water, without cyanobacterial cells (Fig. S4a & 4b). Besides, the nitrate in the media may have an "inner filter" effect that could reduce the fraction of incident UV-flux [35,44]. Similar to that in BG-11 media, the trends of cell inactivation by UV alone and UV/$KMnO_4$ (1 mg L^{-1}) are almost the same. This indicates there may be a threshold concentration of $KMnO_4$ (1 mg L^{-1}) in the UV/$KMnO_4$ system, that is required to enhance its

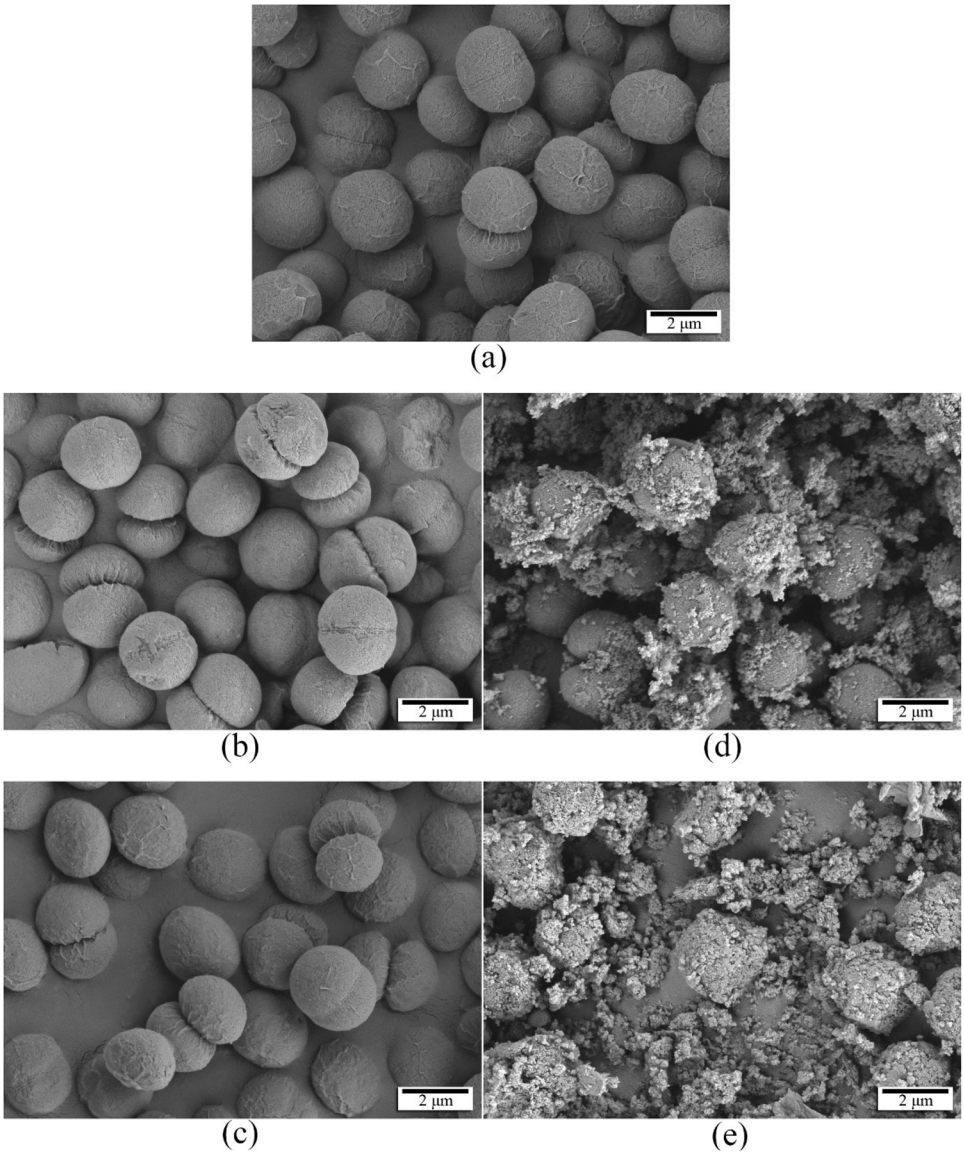

Fig. 7. SEM images (×8000) of *M. aeruginosa* cell morphology after $KMnO_4$, UV, and UV/$KMnO_4$ treatments, (a) blank control (pH = 7.5), (b) UV (exposure time = 30 min, pH = 7.5), (c) $KMnO_4$ ($KMnO_4$ dosage of 5 mg L^{-1}, exposure time = 30 min, pH = 7.5), (d) UV/$KMnO_4$ ($KMnO_4$ dosage of 5 mg L^{-1}, exposure time = 30 min, pH=7.5), and (e) UV/$KMnO_4$ ($KMnO_4$ dosage of 5 mg L^{-1}, exposure time = 30 min, pH = 10.0). Conditions: UV fluence rate = 0.88 mW cm^{-2}, the initial cell density of *M. aeruginosa* = ~7.5 × 10^5 cells mL^{-1}.

effectiveness. It may be attributed to that the background water and extracellular cyanobacterial metabolites had priority to consume $KMnO_4$. In the UV/$KMnO_4$ system (1 mg L^{-1}), $KMnO_4$ was completely depleted in 30 min (Fig. S4c & 4d). Thus, for UV/$KMnO_4$ with $KMnO_4$ concentration $\leq$ 1 mg L^{-1}, inadequate oxidant was available to attack the membrane of cyanobacterial cells.

Although *M. aeruginosa* cells could be inactivated by UV and UV/$KMnO_4$ treatments (Fig. 1; Fig. S2), most of the cells had clear structure and were countable by microscopy (images not shown), in both BG-11 media and natural water. This agrees with previous studies that showing *M. aeruginosa* cells were inactivated while their densities remained fairly constant by UV or $KMnO_4$ [32,43]. There were no significant differences ($P > 0.05$) observed in cell densities of cyanobacterial samples during the UV treatment for 60 min in BG-11 media (Fig. S5). Similarly, the cell density remained almost constant after 60 min of $KMnO_4$ treatment with initial dosages of 1 and 3 mg L^{-1}, while about 8.2 % decrease in cell density was observed at 5 mg L^{-1} $KMnO_4$ ($P < 0.05$). Declines of 6.1 %, 4.5 %, and 13.4 % in cell density were observed for *M. aeruginosa* samples exposure to UV/$KMnO_4$, at $KMnO_4$ dosages of 1, 3, and 5 mg L^{-1}, respectively. The results of *M. aeruginosa* cell densities in YHTR water were generally consistent with those in BG-11 media. Reductions of 6.3 %, 6.7 %, and 11.2 % were observed in cell densities of *M. aeruginosa* samples after UV/$KMnO_4$ treatments, at $KMnO_4$ dosages of 1, 3 and 5 mg L^{-1}, respectively (Fig. 2). As the phenomena were similar between BG-11 and YHTR water, the tests hereafter was investigated in YHTR water, which presents a more practical situation.

TEM graphs were taken to compare the ultrastructure of *M. aeruginosa* cells (Fig. 3). The images further showed that *M. aeruginosa* remaining as whole cells rather than fragmentation, after various treatments. The cell was smooth and intact in the control group, with regular structures and distributions of thylakoids and other cytoplasmic inclusion bodies (Fig. 3a) [44]. After exposure to 5 mg L^{-1} $KMnO_4$ for 60 min, the cell was still intact and smooth; however, some cytoplasmic inclusion bodies became less clear (Fig. 3b). For UV irradiation, obvious cell changes were observed, including wrinkling of cell membrane, plasmolysis, and indistinct cytoplasmic inclusion bodies (Fig. 3c & d). Apparently, UV/$KMnO_4$ (5 mg L^{-1}) induced more drastic distortion on *M. aeruginosa* cells (Figs. 3e–h), significant plasmolysis, shrinking, and wrinkling occurred in the cells, after 10 min (Fig. 3e & f). After 60 min treatment, in addition to corrosion and shrinking, a large loss of inclusions and distortional cellularity in the *M. aeruginosa* cells were observed, suggesting a complete cell necrosis (Fig. 3g & h). This further indicates UV/$KMnO_4$ has strong ability in cyanobacterial

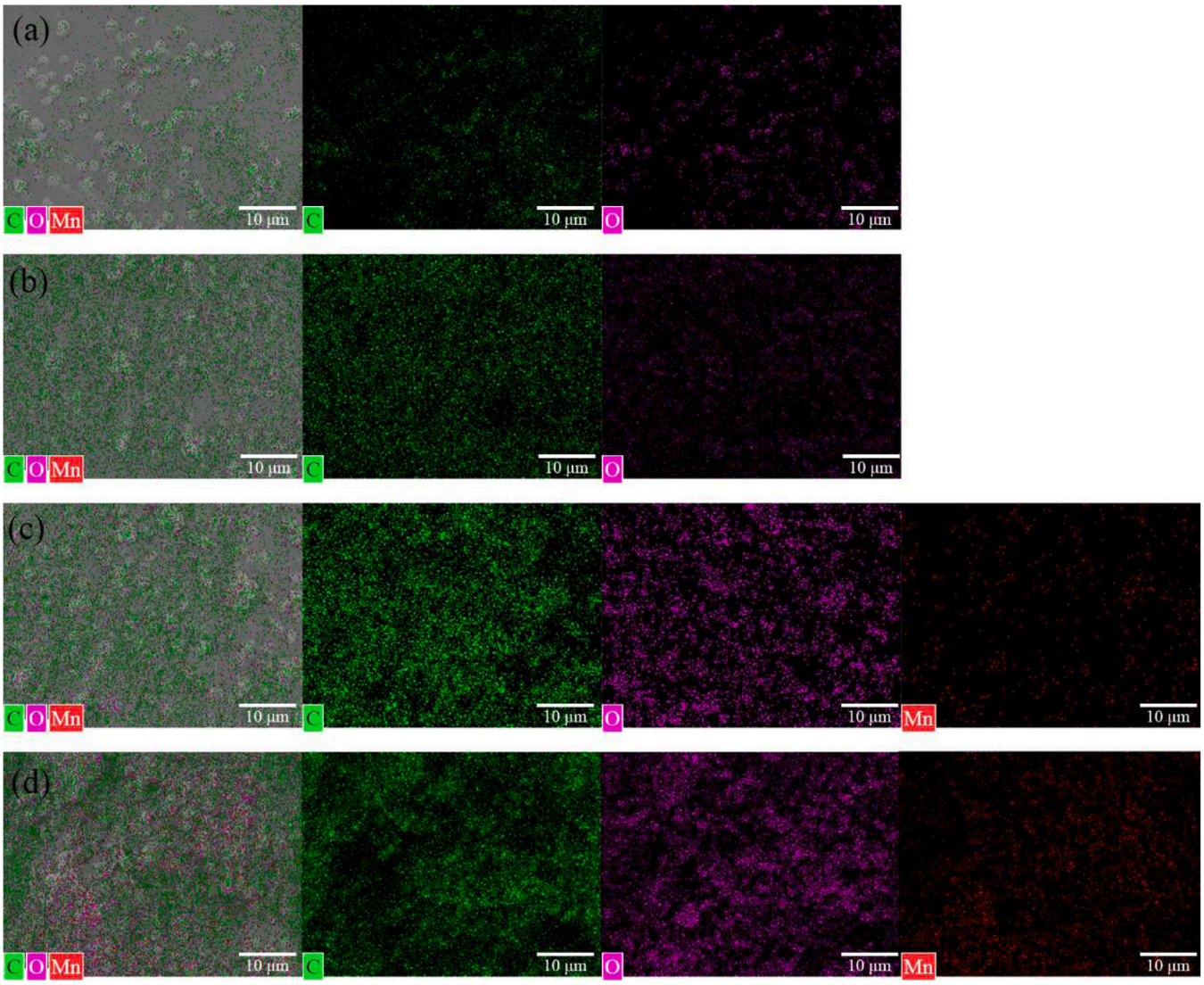

Fig. 8. SEM-EDS mapping images of *M. aeruginosa* after $KMnO_4$ and UV/$KMnO_4$ treatments, (a) blank control (pH = 7.5), (b) $KMnO_4$ ($KMnO_4$ dosage of 5 mg L^{-1}, exposure time = 30 min, pH = 7.5), (c) UV/$KMnO_4$ ($KMnO_4$ dosage of 5 mg L^{-1}, exposure time = 30 min, pH=7.5), and (d) UV/$KMnO_4$ ($KMnO_4$ dosage of 5 mg L^{-1}, exposure time = 30 min, pH = 10.0). Conditions: UV fluence rate = 0.88 mW cm^{-2}, the initial cell density of *M. aeruginosa* = ~7.5 × 10^5 cells mL^{-1}.

inactivation.

3.2. The fate of MC-LR and EOM during $KMnO_4$, UV and UV/$KMnO_4$ treatments

Concentrations of MC-LR were analyzed during UV, $KMnO_4$, and UV/$KMnO_4$ treatments (with $KMnO_4$ doses of 3 and 5 mg L^{-1}) in the natural water (Fig. 4). The initial concentrations of the intracellular and dissolved MC-LR were 15.64 and 2.32 μg L^{-1} in the *M. aeruginosa* samples. The total MC-LR were oxidized gradually during 3 and 5 mg L^{-1} $KMnO_4$ treatments, respectively. The concentrations of dissolved MC-LR were below the initial concentration at all sampling times, with 0.13 and 0.26 μg L^{-1} remaining after 60 min, respectively. However, only small amounts of intracellular MC-LR were degraded, the reduction rates were 3.1 % and 15.5 % after 3 and 5 mg L^{-1} $KMnO_4$ oxidation for 60 min, respectively. Compared to $KMnO_4$, UV and UV/$KMnO_4$ were more effective in MC-LR destruction (Table S3). The MC-LR decreased rapidly within the first 5 min, followed by a relatively slow decline. However, UV alone cannot achieve complete toxin removal, with 0.04 μg L^{-1} of intracellular MC-LR and 1.88 μg L^{-1} of extracellular MC-LR remaining at 60 min, respectively. Those findings agreed with previous studies, as a common water treatment process, $KMnO_4$ or UV alone was able to degrade MC-LR to varying degrees, while it is difficult to completely remove MC-LR, especially within a short time (< 1 h) [30,43]. Contrarily, there were no MC-LR detectable at 60 and 45 min by UV/$KMnO_4$ treatment, at $KMnO_4$ doses of 3 and 5 mg L^{-1}, respectively. The enhanced effectiveness in MC-LR degradation may be owing to the intermediates such as HO• and RMnS during UV/$KMnO_4$ process [20]. The result implies that UV/$KMnO_4$ can achieve efficient removal of MC-LR under applicable conditions (e.g., UV fluence of about 3.2 J cm^{-2}, $KMnO_4$ of 3 mg L^{-1}).

We also measured DOC for the cyanobacterial samples treated by UV/$KMnO_4$, to evaluate the released amounts of IOM (Fig. 5). The concentrations of DOC in the cyanobacterial samples dosed with 1 and 3 mg L^{-1} $KMnO_4$ were similar to the initial value of 6.56 mg L^{-1} ($P > 0.05$), at all sampling time. However, 5 mg L^{-1} $KMnO_4$ caused an increase of DOC, with the amount of 7.18 mg L^{-1} ($P < 0.05$) at 60 min. Similarly, only slightly increases in DOC were observed in the cyanobacterial samples, after exposure to UV and UV/$KMnO_4$ ($P < 0.05$). The concentrations of DOC were 7.19 and 7.49 mg L^{-1} after UV and UV/$KMnO_4$ (5 mg L^{-1}) treatments for 60 min, respectively. The amounts of released DOC by UV/$KMnO_4$ treatments were relatively smaller than

other oxidation such as ozone, chlorine, and UV/chlorine [9,65]. For instance, UV/chorine increased the concentration of DOC from 9.0 mg L^{-1} to 13.2 mg L^{-1} within 60 min in *M. aeruginosa* samples [9]. The exuded IOM will greatly reduce water quality and increase the formation of DBPs in post-chlorination [18,65]. UV_{254} and SUVA can be used to characterize the aromatic or double-bond content of organic compounds in water [36], which are precursors of DBPs [22,24,54]. The values of UV_{254} and SUVA decreased in all treatments, and largest decreases were observed in UV/$KMnO_4$ treatment (Table S4 & S5). Hence, this phenomenon suggests that UV/$KMnO_4$ is superior to other oxidation processes for cyanobacteria treatment, without increasing the DOC level and DBPs formation potential [47,66].

3.3. *M. aeruginosa* cell removal via self-settling after UV/$KMnO_4$ treatment

There was almost no change of cell removal in the control samples via self-settling, similar phenomenon was observed after UV irradiation (Fig. 6a). The removal efficiency of cyanobacterial cells was less than 15 % during the self-settling process, after treatment with pre-synthesized MnO_2 alone. Cell removal was not observed during the first 4 h settling time in the *M. aeruginosa* sample that pre-treated with 5 mg L^{-1} $KMnO_4$ alone for 30 min, while the removal efficiency increased to 19.5 % after settling for 6 h. UV/$KMnO_4$ (5 mg L^{-1}) pre-treatment exhibited considerably better ability in removing cyanobacterial cells via settling, with the removal efficiency of 87.9 % after 6 h. Hence, self-settling after UV/$KMnO_4$ treatment probably can simplify operations and reduce chemical usage for cyanobacterial removal, in comparison to coagulation and sedimentation.

According to the SEM images, the morphologies of cyanobacterial samples after UV or $KMnO_4$ treatment were similar to those in the untreated control samples (Fig. 7a–c). In contrast, visible alterations in the surface of *M. aeruginosa* cells were observed apparently after exposure to UV/$KMnO_4$ (5 mg L^{-1}), coating with a thick layer of particles and forming as flocs (Fig. 7d & e). TEM analysis also showed there were large number of particles surrounding *M. aeruginosa* cells after UV/$KMnO_4$ treatment (Fig. 3f & h). The elemental mapping results revealed that the cells were covered with abundant O and Mn (Fig. 8), suggesting there might be large amounts of MnO_2 colloids produced from $KMnO_4$ (Fig. 7d & e). Hence, the in situ formed MnO_2 probably could facilitate conglomeration of cyanobacterial cells and potentially remove the cells from water column [8,51]. Furthermore, as the inactivated cyanobacteria remain as whole cells, rather than fragmentation, it may benefit the floc growth (Fig. 3). In addition, the released IOM induced by oxidation may enhance the incorporation of MnO_2 into cyanobacterial flocs, thus increasing cell aggregation and removal from aqueous phase (Fig. 5) [8].

The decay of $KMnO_4$ and generation of MnO_2 are shown in Fig. S4d and Fig. S6, to further investigate the mechanisms of significant differentiation of cyanobacterial cell removal by $KMnO_4$ alone and UV/$KMnO_4$. For $KMnO_4$ alone, its degradation in cyanobacterial samples was considerably slower than UV/$KMnO_4$ (Fig. S4). The UV−vis spectra at the wavelengths of 200–800 nm during $KMnO_4$ and UV/$KMnO_4$ processes were also analyzed (Fig. S6). The absorbance at feature peak at 525 nm of [Mn(VII)] was 0.107 cm^{-1} initially, and obviously, it decreased more rapidly under UV irradiation. The absorbance increased from 0.049 cm^{-1} to 0.062 and 0.114 cm^{-1}, respectively for $KMnO_4$ and UV/$KMnO_4$ after 30 min at 418 nm (referred to MnO_2) [28]. Those phenomena revealed that larger amounts of in situ formed MnO_2 was generated in UV/$KMnO_4$ treatment, compared to that in $KMnO_4$ alone. It may be owning to that UV irradiation stimulates MnO_4^- from the ground state to the excited state, thus reducing the activation energy for MnO_4^- decomposition to MnO_2 [23]. Meanwhile, the in situ formed MnO_2 by UV irradiation may have the auto-catalytic effect, which further advantaged the decomposition of MnO_4^- [23,50]. Consequently, the in situ formed MnO_2 in UV/$KMnO_4$ were proposed as the main species for followed cyanobacterial floc growth and cell settling, while $KMnO_4$ alone lacked such capability.

The impact of different exposure time (10, 30, and 60 min) by UV/$KMnO_4$ (5 mg L^{-1}) pre-treatment on the followed *M. aeruginosa* cell settling was investigated (Fig. 6b). All the pre-treatments caused progressive cell removal via subsequent settling, probably due to the considerable amounts of in situ formed MnO_2 (Fig. S6). The cell removal during the first 4 h settling was enhanced with increasing exposure time of UV/$KMnO_4$ pre-treatment. For instance, the removal efficiency improved from 4.9 % to 56.3 % after settling for 1 h, with UV/$KMnO_4$ pre-treatment increasing from 10 min to 60 min. This might be due to the higher formation of MnO_2 during extensive UV/$KMnO_4$ pre-treatment (Fig. S6), which resulted in greater settleability of *M. aeruginosa* samples. However, the removal efficiency of the samples pre-treated with different time could achieve a similar value (around 80 %) thereafter, at the settling time of 6 h (Fig. 6b). It was possible that the in situ formed MnO_2 during UV/$KMnO_4$ pre-treatment further catalyzed the residue $KMnO_4$ reducing to MnO_2 [23], thus facilitating the removal of cyanobacterial cells subsequently.

Fig. 6c shows the settling rate of *M. aeruginosa* cells after UV/$KMnO_4$ (5 mg L^{-1}) pre-oxidation of 30 min, at pH of 4.0, 7.5, and 10.0. Only 21.4 % of the cells were removed from the suspension via settling within 6 h, under pre-exposure condition of pH 4.0. The effectiveness of cyanobacterial removal via settling was greatly enhanced at higher pH values of 7.5 and 10.0 . The cell removal efficiency reached 91.6 % after only 1 h settling, with UV/$KMnO_4$ pre-treatment under pH 10.0. The SEM micrograph of the cyanobacterial flocs treated with UV/$KMnO_4$ under pH 7.5 showed less coverage by particles, as compared to that under pH 10.0. The weight percent of Mn covered on cyanobacterial cells was 3.3 % and 8.9 % under pH of 7.5 and 10.0, respectively (Table S6), which implied larger amounts of MnO_2 was formed under pH 10.0. However, it should be noted that both cyanobacterial cells and MnO_2 have negatively charged surface under neutral and alkaline conditions, and MnO_2 is more negatively charged with increased pH values. This suggests the attachment between cyanobacteria and MnO_2 would be hindered by electric repulsion [34,52]. Therefore, the enhancing settleability of cyanobacterial samples should not be solely attributed to MnO_2. Alternatively, the existence of cations such as calcium ions (Ca^{2+}) (24.31 mg L^{-1}) in the background water may serve as a cation bridge between two negatively charged surfaces (Table S1). Firstly, as reported, the aggregation of MnO_2 particles could be significantly promoted at a Ca^{2+} concentration as low as 8 mg L^{-1}, and the more negatively charged MnO_2 with increasing pH is beneficial for Ca^{2+} adsorption and its aggregation [34,59]. Moreover, Ca^{2+} may have a bridging effect to enhance the adsorption of MnO_2 onto cyanobacterial cells under alkaline condition [34]. Consequently, the specific gravity of cyanobacterial flocs was increased under pH 10.0, which resulted in the enhancement of cell settleability. Therefore, the generation of in situ formed MnO_2 was essential, and the enhanced removal efficiency of cyanobacteria may result from the joint effects of MnO_2 and existence of Ca^{2+}. The cyanobacteria contaminated water is generally alkaline and the presence of $\geq$ 24 mg L^{-1} Ca^{2+} is ubiquitous in natural waters [37,5,63]; other cations like magnesium ions (Mg^{2+}) may have the same bridging effect [25]. Therefore, the results in this study imply that cyanobacterial cells can be efficiently removed by UV/$KMnO_4$ under real conditions.

4. Conclusions

UV radiation combined with $KMnO_4$ was evident to have a significant synergistic effect on cyanobacteria treatment in natural water. Compared to UV alone or $KMnO_4$ alone, the inactivation of *M. aeruginosa* cells was greatly improved in UV/$KMnO_4$ process. Meanwhile, both intracellular and extracellular MC-LR were effectively degraded during UV/$KMnO_4$ treatment. The generation of highly reactive species may account for the high efficiency in UV/$KMnO_4$ process. Interestingly, efficient removal of *M. aeruginosa* cells was achieved via self-settling after UV/$KMnO_4$ treatment, which was likely attributable to the rapid

accumulation of in situ formed MnO_2. The typical cations in real water such as Ca^{2+} and Mg^{2+} can further improve the aggregation and settleability of cyanobacterial cells, showing good significance for the efficient and safe removal of cyanobacteria under practical conditions.

Environmental implication

This study shows UV/$KMnO_4$ process moderately damages cyanobacterial cells, i.e., cell densities keep constant and IOM is slightly released after UV/$KMnO_4$ treatment. This is superior to other oxidation processes, since UV/$KMnO_4$ treatment can achieve efficient inactivation & removal of cyanobacterial cells, and effective removal of cyanotoxins, without increasing the DOC level and DBP formation potential. The settling time for cyanobacterial removal can be shortened by adding coagulants, based on particular water conditions. According to its outstanding capacity and multiple functions, the UV/$KMnO_4$ process is promising in the purification of cyanobacteria contaminated waters.

CRediT authorship contribution statement

Jiajia Fan: Writing - Original Draft, Writing - review & editing, Project Administration, Conceptualization, Resources, Supervision. **Jianwei Zeng:** Data curation, Visualization, Formal analysis, Investigation, Writing - review. **Xuchun Li:** Conceptualization, Writing - editing. **Kaiheng Guo**: Writing - editing. **Wang Liu:** Data curation. **Jingyun Fang:** Conceptualization, Methodology, Supervision, Writing - editing.

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.

Data availability

Data will be made available on request.

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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.jhazmat.2023.131772.

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