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Performance and characteristics**

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1 **Removal of *Microcystis aeruginosa* by UV-activated persulfate: Performance and**
2 **characteristics**

3
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13 **Abstract**

14 Cyanobacteria blooms in source waters have become a worldwide issue for drinking
15 water production. UV-activated persulfate (UV/PS) technology was firstly applied to
16 remove cultivated *Microcystis aeruginosa* in bench scale. The presence of persulfate
17 significantly enhanced both cytolysis and algal organic matter mineralization
18 compared with UV-C inactivation alone. Around 98.2% of algal cells were removed
19 after UV/PS process treatment for 2 h at a dosage of PS being 1500 mg/L
20 (approximately 6 mM). Both sulfate and hydroxyl radicals were proven to contribute

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21 to the removal of algae and the loss of cell integrity. The cultivated *Microcystis*
22 *aeruginosa* in death growth phase were found to be more vulnerable to UV/PS
23 treatment than those growing in log phase, thus a significant lower dosage of PS is
24 needed to achieve the desired removal efficiency. This study suggested a novel
25 application of UV/PS process in the removal of algae in source waters due to the high
26 degradation efficiency of both algal cells and their derived organic matter.

27

28 *Keywords:* *Microcystis aeruginosa*; Ultraviolet; Persulfate; Cell integrity; Algal
29 organic matter

30

31

32 **1. Introduction**

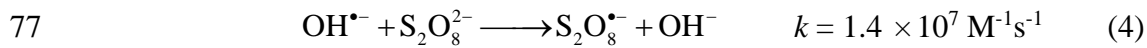
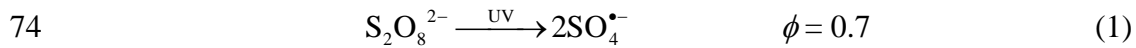
33 In recent decades, harmful algal blooms have frequently occurred in source waters
34 such as lakes, rivers and reservoirs associated with eutrophication throughout the
35 world [1-4]. *Cyanobacteria*, a prominent and ubiquitous issue, has attracted
36 worldwide attention among the harmful algal blooms. Along with excessive algal cells,
37 the algal organic matter (AOM) including extracellular organic matter (EOM) and
38 intracellular organic matter (IOM) generated via metabolic excretion always cause
39 serious water problems [5]. The AOM produced by some specific *Cyanobacteria*
40 genera including *anabaena*, *microcystis*, *planktothrix*, etc. has been proven to
41 comprise taste- and odor- substances, such as 2-methylisoborneol and geosmin [6],
42 and a wide range of toxic intracellular metabolites being suggested to cause both acute
43 and chronic effects on hepatocyte and central nervous system of aquatic organisms
44 and biomagnify [7-10]. Moreover, algal cells and AOM have been reported to be
45 important precursors of vast disinfection by-products (DBPs) including traditional
46 trihalomethanes (THMs), haloacetic acids (HAAs) and emerging nitrogenous DBPs
47 (N-DBPs) containing high genotoxicity and carcinogenicity [11-13].

48 However, the conventional drinking water treatment plant only shows limited
49 removal efficiency on algal cells due to electrostatic repulsion, surface hydrophilicity
50 and steric effects [14-16]. The residual cells after sedimentation could adhere to the
51 filter material surface subsequently causing filter clogging, penetrate into the water
52 supply pipe network, and finally impair the drinking water quality [17]. It should be

53 noted that the dissolved AOM generated via metabolic excretion are even more
54 different than algal cells to be removed by using traditional
55 coagulation-sedimentation-filtration process [18], which may adversely affect
56 conventional water production via inhibition of coagulation [19, 20].

57 Activated persulfate (PS) oxidation has been studied as an alternative conventional
58 advanced oxidation process (AOP) in water treatment [21-23]. The AOP using PS is
59 mainly achieved by the formation of reactive sulfate radical ($\text{SO}_4^{\bullet-}$, $E^0=2.65\text{--}3.1\text{ V}$)
60 through the decomposition of PS by heat, transit metals, light, microwave or
61 ultrasound [24-26]. Similar to hydroxyl radical (HO^{\bullet} , $E^0=1.8\text{--}2.7\text{ V}$), electron-transfer
62 is expected to be a vital reaction when $\text{SO}_4^{\bullet-}$ is used to degrade organic pollutants [27].
63 However, $\text{SO}_4^{\bullet-}$ is more selective in comparison with hydroxyl radical in general, thus
64 might be more effective in the degradation of some organic pollutants in the presence
65 of radical scavengers [27]. Particularly, PS activated by zerovalent iron was recently
66 used for disinfection of ballast water and achieved a result that the species of marine
67 phytoplankton could be inactivated by such a process without generating harmful
68 byproducts [28]. However, to our knowledge, activated PS technology has not been
69 utilized for algae removal in source waters.

70 Among the known PS-activation processes, ultraviolet (UV) radiation at 254 nm
71 can activate the PS to generate $\text{SO}_4^{\bullet-}$ through Eq. 1 with a quantum yield of 0.7 mol
72 E/s [29], and the other main chemical interactions subsequently take place were
73 summarized in Eqs. 2 ~ 5 [30].



79 Furthermore, UV process has been applied to suppress algae growth in many cases
 80 accompanied by chlorophyll bleaching and inhibition of metabolic activity [31-35].
 81 Therefore, the UV radiation can be regarded as one of the feasible techniques to
 82 activate the PS for drinking water treatment applications.

83 In the present study, the performance of UV-activated PS (UV/PS) process on algae
 84 removal has been investigated using *Microcystis aeruginosa* (*M. aeruginosa*), a most
 85 abundant and common occurring cyanobacteria specie [36]. Additionally, variations in
 86 the characteristics of AOM during the UV/PS treatment were identified to further
 87 recognize the plausible by-products within the oxidation process.

88

89 **2. Materials and methods**

90 **2.1. Materials**

91 The *M. aeruginosa* (No. FACHB-909) was purchased from the Institute of
 92 Hydrobiology, Chinese Academy of Sciences, and laboratorial cultivated in a light
 93 growth incubator (Guohua Electric Co., Ltd., China). The *M. aeruginosa* was
 94 incubated under the specific growth conditions (25 ± 1 °C with a light-dark cycle of

95 12 h: 12 h) in BG-11 media [37]. The algae solutions in log phase were harvested and
96 diluted using ultrapure water (18.5 MΩ cm) produced from a water purifier (PCDX-J,
97 Pincheng Co. Ltd, China). Then a final cell density of 1×10^6 cell/mL was achieved
98 for the experiments, which mimics to the practical density in harmful algal blooms
99 [38].

100 All chemicals used in the experiments were of analytical reagent grade at least.
101 Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), sodium hydroxide, hydrochloric acid, methanol (MeOH)
102 and tert-butyl-alcohol (TBA) were obtained from Sinopharm Chemical Reagent Co.,
103 Ltd., China. Powdered $\text{Na}_2\text{S}_2\text{O}_8$ was added to the prepared *M. aeruginosa* solutions to
104 achieve designated concentrations of PS each time. Solution pH was subsequently
105 adjusted to be 7.0 which is around the pH of natural water by using HCl and NaOH at
106 a concentration of 0.1 M.

107

108 **2.2. Experimental reactor and procedures**

109 Algae removal experiments were carried out in a cylindrical pyrex reactor (600 mL
110 effective volume) with a low-pressure UV lamp (254 nm, 23W, GPH 436T5L/4,
111 Philips Electronics Ltd., The Netherlands) (Fig. S1). An immersion well made of high
112 purity quartz was placed inside the glass reactor. The UV lamp was fixed inside the
113 immersion well. Cooling water was pumped through the thin annular zone of the
114 immersion well to prevent overheating of the reaction solutions. In order to achieve a
115 stabilized radiation intensity (measured to be 1.25 mW/cm^2 in average by the reported

116 method [39]), the lamp was always switched on for 15 min before being placed into
117 the reactor. A magnetic stirring apparatus at a speed of 200 rpm was used to
118 homogenize the solutions throughout the experiments. Samples were collected via the
119 sampling port at specific time intervals. To evaluate the reaction mechanisms in the
120 UV/PS system, MeOH and TBA were added as scavengers for hydroxyl and sulfate
121 radicals. Each batch of experiment was carried out in triplicate. As the formed $\text{SO}_4^{\cdot-}$
122 could be scavenged by high concentrations of $\text{S}_2\text{O}_8^{2-}$ and Cl^- from BG-11 media and
123 HCl solution (section 3.2), the presence of anions including NO_3^- and HCO_3^- at
124 concentrations as usual in natural waters was expected to play little role in the
125 removal of algal cells (Fig. S2). Thus, the impacts of co-existing anions would not be
126 further discussed in the following sections.

127

128 **2.3. Analytical methods**

129 The cell concentration of *M. aeruginosa* was measured using an UV-visible
130 spectrophotometer (U-3100, Hitachi, Japan) at a wavelength of 681 nm since the
131 optical density at 681 nm (OD_{681}) is linearly correlated with counted cell number by
132 microscope within the experimental range [40, 41]. Thus, the removal efficiency of
133 algal cells (ρ , %) can be calculated using Eq. 6.

$$134 \quad \rho = \frac{(\text{OD}_{681_0} - \text{OD}_{681_t})}{\text{OD}_{681_0}} \times 100\% \quad (6)$$

135 where OD_{681_0} and OD_{681_t} were the optical density values at 0 min and t min.

136 Chlorophyll-a (Chl-a) was extracted using acetone solution and then measured

137 using the spectrophotometer at wavelengths of 663 nm, 645 nm and 630 nm according
138 to the reported method [42].

139 The algal cell integrity before and after treatment was monitored by a flow
140 cytometer (Accuri C6, BD Biosciences, USA) equipped with an argon laser emitting
141 (wavelength fixed at 488 nm) for fluorescence measurement. Algal cells were stained
142 using SYTOX green nucleic acid stain (Invitrogen, Life Technologies, USA) [43].
143 Fluorescent filters and detectors were equipped to collect green fluorescence in
144 channel FL1 (530 nm) and red fluorescence in channel FL3 (630 nm), which
145 represents damaged and integrated cells, respectively, since SYTOX could penetrate
146 damaged cells and stain the nucleic acid to emit green fluorescence.

147 Extracellular AOM was extracted from reaction solution by centrifuging the cell
148 suspension at 8000 rpm for 15 min and subsequently filtering the supernatant through
149 0.45 μm cellulose acetate membranes [5]. The extracellular AOM was characterized
150 on fluorescence spectroscopy, UV-Vis spectrum scan, and total organic carbon (TOC).
151 A fluorescence spectrophotometer (F-4600, Hitachi, Japan) was used to measure the
152 fluorescence excitation–emission matrix (EEM) spectroscopy of AOM. Excitation
153 wavelengths (Ex) were scanned from 200 to 450 nm with 5 nm intervals and emission
154 wavelengths (Em) from 280 to 550 nm with 2 nm intervals. The scanning speed was
155 set at 1200 nm/min. Background signals were minimized by subtracting the signals of
156 the blank (i.e. ultrapure water). The EEM data were analyzed by MATLAB 2010b
157 (The MathWorks, Inc., USA). The UV-Vis spectrum scan of AOM ranging from 200

158 to 700 nm was measured using the U-3100 spectrophotometer. The concentration of
159 dissolved organic carbon (DOC) in the prepared sample was measured using a
160 TOC/TN analyzer (C/N 2100, Analytic Jena, Germany).

161 The persulfate concentration was measured by universal iodometric titration
162 method [44]. The procedure was conducted by mixing 2 mL samples and 10 mL KI
163 stock solution (10% mass fraction) in 40 mL ultrapure water. Then the resulting
164 solutions were equilibrated for 3 h in dark, and subsequently titrated by calibrated
165 Na₂S₂O₃ solution (0.1 M). A turbidimeter (Ruixin WGZ-2, China) was used to
166 measure the turbidity of algal solution before and after treatment. The *M. aeruginosa*
167 cells in suspension for morphology observation were firstly centrifuged at 6000 rpm
168 to collect the precipitate, and then dried by a vacuum freeze dryer (model FD-1A-50,
169 Shanghai Boyikang Instrument Co., Ltd., China). Thereafter, the dried algae samples
170 were sputter coated with gold by the sputter coater, and then photographed using a
171 scanning electron microscopy (SEM) (Sirion 200, FEI, USA) at 10 kV.

172

173 **3. Results and discussion**

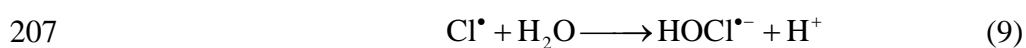
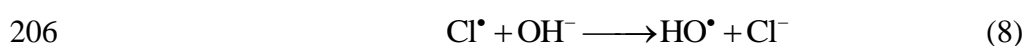
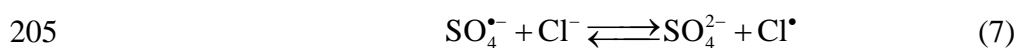
174 ***3.1. Comparison of UV, PS and UV/PS processes on algae removal***

175 Fig. 1 shows the removal of *M. aeruginosa* based on the changes of OD₆₈₁ (Fig. 1a)
176 and Chl-a (Fig. 1b) by using three different oxidation processes, UV irradiation, PS
177 oxidation and combined UV/PS oxidation, at 25 °C with the initial reaction pH being
178 7.0. Negligible decrease of OD₆₈₁ and Chl-a was observed using PS oxidation alone at

179 a concentration of 1500 mg/L (about 6 mM) over a period of 120 min, indicating little
180 to no oxidation of algal cells by PS directly. In contrast, UV irradiation could degrade
181 algal cells to some extent with OD₆₈₁ and Chl-a being removed by 21.8% and 87.9%,
182 respectively, after 120 min of radiation. The results corroborate that UV at 254 nm can
183 effectively destroy the photosynthesis system of *M. aeruginosa*, but hardly cause
184 large-scale cell cytolysis, which was also reported in other publications [32, 45].
185 UV/PS process showed the highest levels of removal efficiency for both OD₆₈₁
186 (98.2%) and Chl-a (99.8%) among the three oxidation processes.

187 As PS oxidation and UV irradiation had limited degradation efficiency on algal
188 cells, it could be expected that the reactive radicals, i.e. SO₄^{•-} and HO[•], produced in
189 UV/PS system were responsible for the observed degradation of algal cells. The
190 conclusion was further proved by the results shown in Fig. S3 that the presence of
191 MeOH and TBA inhibited the removal of OD₆₈₁ significantly when using UV/PS
192 process. MeOH is usually considered as an effective quencher for both the SO₄^{•-} and
193 HO[•] [46]. However, TBA is an effective quencher for HO[•], but not for SO₄^{•-} [29].
194 Thus, they could be used to distinguish SO₄^{•-} and HO[•] based on the difference of the
195 degradation rate of target compounds. Fig. S3 shows that co-existence of either
196 MeOH or TBA inhibited the removal of OD₆₈₁, while the inhibiting ability of MeOH
197 is stronger than that of TBA. It proved that both SO₄^{•-} and HO[•] contributed to the
198 oxidation of algal cells in the experiment. It is known that activation of PS by UV
199 only generate SO₄^{•-} (Eq. 1) without the production of HO[•] [29]. However, HO[•] was

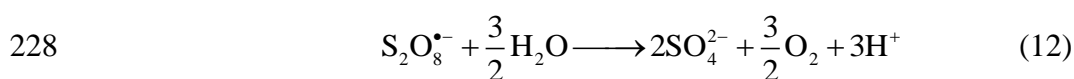
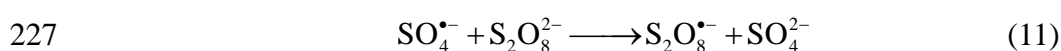
200 proposed to be generated when $\text{SO}_4^{\bullet-}$ reacts with OH^- at a rate constant of 6.5×10^7
 201 $\text{M}^{-1} \text{S}^{-1}$ through Eq. 4 [30], or with water at a rate constant of $8.3 \text{ M}^{-1} \text{S}^{-1}$ through Eq.
 202 3 [47]. Besides, the presence of chloride could convert $\text{SO}_4^{\bullet-}$ to HO^\bullet through reactions
 203 shown in Eqs. 7 ~ 10 [48], especially when the reaction pH was higher than 5.0,
 204 which make sure the presence of HO^\bullet in the experiment [49].



209 **3.2. Effect of initial PS dose on algae removal**

210 The effect of initial PS dose ranging from 0 mg/L to 1500 mg/L on the removal of *M.*
 211 *aeruginosa* by focusing on the changes of OD_{681} and Chl-a was investigated (Fig. 2).
 212 The removal rates of OD_{681} and Chl-a increased with the increase of initial PS dosage.
 213 When the dosage of PS increased from 0 mg/L to 1500 mg/L (about 6 mM), the
 214 removal rates of OD_{681} and Chl-a increased from 21.8% and 87.9% to 98.2% and
 215 99.8%, respectively, after treatment for 120 min. It should be noted that, the rapid
 216 decrease of Chl-a was observed in the initial 60 min treatment (including the only UV
 217 irradiation case), but not for the removal of OD_{681} . The result suggested that the
 218 photosynthetic system of *M. aeruginosa* was damaged immediately through
 219 synergetic irradiation and oxidation in UV/PS system, possibly due to the rapid
 220 destruction in gene expression of both *psbA* (for D1) and *cpc* (for phycocyanin) [50].

221 The variation of pHs over time under different initial PS doses was displayed in Fig.
 222 S4. Negligible change of pHs was observed under UV irradiation alone over a period
 223 of 120 min. However, solution pHs gradually reduced in UV/PS system during the
 224 oxidation, which was enhanced with the increase of PS doses. The results can be
 225 explained by the production of sulfate acid through $S_2O_8^{\bullet-}$ oxidation of water (Eqs. 11
 226 and 12) [30, 51]:



229 Fig. S5 shows that the dissolved oxygen (DO) in the experimental solution
 230 significantly increased in the initial 30 min when using UV/PS process to treat algae,
 231 supporting the speculation on oxidation of water by $S_2O_8^{\bullet-}$. Then the gradually
 232 reduction of DO in the subsequent 90 min might due to the release into air, reacting
 233 with HO^{\bullet} adducts to produce peroxy transients [52], and being converted to
 234 oxygen-centered radicals which could be consumed by algae and its derived organic
 235 matter [53].

236 If the dosed persulfate was completely decomposed, formed sulfate at
 237 concentrations of 800 mg/L and 1200 mg/L would be achieved when the dosages of
 238 persulfate were 1000 mg/L and 1500 mg/L, respectively. A sulfate concentration that
 239 is higher than 600 mg/L in drinking water might cause taste alteration and diarrhea
 240 [54]. However, it should be noted that the concentrations of *M. aeruginosa* in most
 241 source waters were always lower than 10^6 cells/mL. When the initial cell density was

242 reduced to 2.3×10^5 cells/mL, the residual OD₆₈₁ and turbidity decreased by 57.9%
243 and 62.3%, respectively, after UV/PS process treatment for 120 min with an initial PS
244 dosage of 200 mg/L (Fig. S6).

245

246 ***3.3. Effect of growth phase on algae removal***

247 The growth of *M. aeruginosa* can be modeled with four different phases: lag phase,
248 log phase, stationary phase, and death phase. The removal of algae in their log phase
249 and death phase were investigated due to the large variation of cell population and
250 dissolved organic substances [55]. The effect of growth phase on the removal of *M.*
251 *aeruginosa* was studied under different PS doses (Fig. 3). The removal of OD₆₈₁ in
252 death phase kept high efficiencies (>92.8%) for all the initial concentrations of PS
253 ranging from 0 mg/L to 1000 mg/L over an oxidation period of 120 min. However, for
254 the cells in log phase, the removal of OD₆₈₁ only increased from 21.8% to 83.7% with
255 the initial dosage of PS increasing from 0 mg/L to 1500 mg/L after reaction for 120
256 min, which was much lower than the removal efficiencies for the algal cells in death
257 phase. Similarly, the removal efficiency of Chl-a ranging from 90.7% to 98.5% in
258 death phase by using UV/PS was also higher than that ranging from 87.9% to 97.6%
259 in log phase.

260 The easier removal of *M. aeruginosa* in death phase than that in log phase by using
261 UV/PS process was supposed to be connected to the disparity of biological activity,
262 EOM component, and morphologies of algal cells in different growth phases [56].

263 Besides, the autolysis of cells largely occurred in death phase [19], which might also
264 contribute to the high removal efficiency.

265

266 **3.4. Mineralization of AOM**

267 Fig. 4 shows the residual TOC and extracellular DOC of *M. aeruginosa* suspension at
268 different PS doses. Negligible changes of TOC and extracellular DOC were observed
269 after single UV irradiation over a period of 120 min, indicating that limited
270 UV-induced mineralization of AOM occurred, which was in accordance with the
271 previous report [57]. On the other hand, the results reveal that the UV irradiation only
272 had limited damage on the structure of algal cell and did not cause large-scale
273 cytolysis [58], since an increase in DOC concentration would be found due to the
274 release of IOM from damaged algal cells [25, 48].

275 With the dosage of PS increasing from 0 mg/L to 1500 mg/L (about 6 mM), the
276 TOC and extracellular DOC were decreased from 12.50 and 7.59 mg/L to 1.63 and
277 1.61 mg/L, respectively, over a reaction period of 120 min. The significant removal of
278 extracellular DOC (decreased by 79.6% at 1500 mg/L PS dosage) indicates that
279 UV/PS process can effectively mineralize AOM in the reaction solution. Moreover,
280 the result of higher reduced concentration of TOC than extracellular DOC in the
281 presence of PS can be explained by the fact that released dissolved IOM could make
282 up parts of mineralized DOC, reflecting that UV/PS oxidation can induce destruction
283 of algal cell structures. This speculation was supported by the result that residual TOC

284 (1.63 mg/L) and extracellular DOC (1.61 mg/L) were extremely approximate at an
285 initial PS dosage of 1500 mg/L.

286 The UV-Vis spectra of *M. aeruginosa* solution before and after UV/PS treatment
287 were also studied (insert graph in Fig. 4). The absorbance of solution ranging from
288 200 to 700 nm was significantly decreased after UV/PS treatment, which was in
289 accordance with the changes of TOC and DOC. It is noteworthy that, the peak at 681
290 nm was disappeared after treatment, suggesting the effective removal of algal cells in
291 UV/PS system.

292

293 ***3.5. Evolution in fluorescence EEM spectra of extracellular AOM***

294 The effects of UV/PS process treatment on fluorescence EEM spectra of extracellular
295 AOM are shown in Fig. 5 and Table S1. There were four fluorescence peaks at Ex/Em
296 wavelengths of 270/442 nm (peak A), 350/432 nm (peak C), 230/330 nm (peak T₂),
297 and 280/330 nm (peak T₁) in the control sample (Fig. 5a), which represented
298 fulvic-like, humic-like and protein-like substances, and dissolved microbial
299 metabolites, respectively [59, 60]. The strong signal at peak T₁ suggested high
300 concentration of protein-like substances contained in EOM, which was similar to
301 other reports [61, 62].

302 However, after UV/PS process treatment for 5 min, peaks A and C were observed to
303 be significantly enhanced, accompanied with the disappearance of peaks T₁ and T₂ in
304 contrast (Fig. 5b). This can be explained that UV/PS process was supposed to cause

305 cell secretion and decomposition which was expected to produce fulvic-like and
306 humic-like substances [63, 64].

307 When the treatment time was over 30 min, all the four peaks were disappeared
308 (Figs. 5c and 5d), whose possible reasons were proposed as below: 1) UV/PS process
309 could further oxidize and even mineralize the formed humic-like and fulvic-like
310 substances (Fig. 4); and 2) the large-scale cell cytolysis and metabolites release
311 mainly occurred in the initial reaction period under UV/PS oxidation, which was
312 similar to the ozonation of *cyanobacteria* [65].

313 Additionally, comparative experiments of single UV irradiation, PS alone and
314 UV/PS process treatment on the changes of the fluorescence EEM spectra of
315 extracellular AOM were conducted (Fig. S7). After treatment for 30 min, UV
316 irradiation caused significant decrease of peak T₁, but slight enhancement of peak C.
317 While the treatment of algae by PS alone had negligible impact on the fluorescence
318 EEM spectra of the extracellular AOM. In comparison with UV irradiation or PS
319 oxidation alone, UV/PS treatment caused the most significant decline of all the peaks
320 on the fluorescence EEM spectra. Thus, it is reasonable to conclude that the formed
321 reactive species, such as hydroxyl and sulfate radicals, in UV/PS process contribute to
322 the degradation of organic matter.

323

324 ***3.6. Cell integrity and cellular morphology***

325 Fig. 6 shows the impacts of PS oxidation, UV irradiation, and UV/PS treatment on

326 cell integrity by using a flow cytometer to measure changes in cell permeability and
327 chlorophyll auto-fluorescence. P1 and P2 regions represent damaged and integrated
328 cell population, respectively. In Fig. 6a, the proportion of live cells was 96.1%,
329 reflecting that the vast majority of *M. aeruginosa* cells without any treatment were
330 intact. Compared with the control sample, the damaged cells shown in P1 region was
331 found to be only slightly increased by 1.8% after 2 days reaction with PS alone (Fig.
332 6b), indicating that individual PS oxidation played little to no roles in destruction of
333 *M. aeruginosa* cells . In contrast, UV was observed to be more effective in decreasing
334 the live algal cells as shown in regional P2 of Fig. 6c that the amount of live algal
335 cells was reduced. However, the amount of algal cells shown in regional P1 was also
336 decreased. Since the green fluorescence in channel FL1 (Regional P1) was from the
337 stained nucleic acid by SYTOX [43], the results can be explained by the fact that UV
338 irradiation could damage nucleic acid [66, 67]. Among the four treatment processes,
339 UV/PS process had the strongest ability to damage algal cells (Fig. 6d). After
340 treatment for 30 min, the integrated cell population was significantly reduced,
341 indicating that the reactive substances in UV/PS system, such as $\text{SO}_4^{\bullet-}$ and HO^{\bullet} , can
342 strongly damage the cell integrity. No signals were found in regional P1 suggested
343 that UV/PS could further oxidize nucleic acid effectively due to the synergetic effect
344 of UV irradiation and the generated reactive radicals.

345 The surface morphologies of *M. aeruginosa* cells before and after UV/PS treatment
346 were observed using the SEM. Compared to the algal cells without any treatments

347 (Fig. 7a), the surface morphologies of cells were deformed and the cellular structure
348 was completely lost after the UV/PS treatment (Fig. 7b). Some apparent materials
349 were found to be released from the cells, which were probable to be amino acids and
350 carbohydrates [28].

351

352 **3.7. Persulfate decomposition**

353 Fig. 8a shows the persulfate decay under different initial PS doses ranging from 500
354 to 1500 mg/L. In each case, residual persulfate was less than 2% over a reaction
355 period of 120 min. The decomposition of persulfate followed the first-order kinetics
356 model (Fig. 8b), suggesting that the presence of algal cells and AOM had little impact
357 on the self-decomposition of persulfate, which was supported by the insignificant
358 oxidation potential of PS on algal cells and AOM compared to UV/PS process (Figs. 1
359 and S7). The added PS was almost completely decomposed ($\geq 99.9\%$) during the
360 reaction when the initial concentration of PS was less than 1000 mg/L. Even at initial
361 dosages of 1250 mg/L and 1500 mg/L, the average residual PS concentrations were
362 only 2.14 mg/L (about 0.2%) and 23.6 mg/L (about 1.6%) after treatment for 120 min,
363 respectively. Thus, it is concluded that application of UV/PS process in the removal of
364 algae in natural water had little potential to cause undesired risk from the residual PS.

365

366 **4. Conclusions**

367 UV/PS process is demonstrated to be an effective technology for the removal of *M.*

368 *aeruginosa* in laboratory. The formed reactive species including $\text{SO}_4^{\bullet-}$ and HO^\bullet were
369 proven to be the most important reasons for the removal of algal cells. Increasing PS
370 dosage could improve the removal of algal cells and the mineralization of AOM. With
371 the addition of 1500 mg/L (about 6 mM) PS, removal rates up to 98.2% and 99.8% of
372 algal cells and Chl-a, respectively, were achieved in UV/PS system over a reaction
373 period of 120 min. *M. aeruginosa* in death phase was easier to be removed by using
374 UV/PS treatment than that in log phase. Although the UV/PS process significantly
375 damaged the structures of algal cell and caused the release of IOM, these derived
376 organic compounds along with the dissolved EOM could be further mineralized in the
377 subsequent reaction period. The fast decomposition of persulfate might insure the
378 safety of using UV/PS to remove algal cells to some extent.

379

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384

385 **Appendix A. Supplementary data**

386 Supplementary data (Figs. S1 to S7 and Tab. S1) associated with this article can be
387 found, in the online version.

388

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