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**Reactivity of chromophoric dissolved organic matter (CDOM) to sulfate radicals: Reaction kinetics and structural transformation**

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**22 Abstract**

23 Sulfate radical ( $\text{SO}_4^{\bullet-}$ ) has been extensively studied as a promising alternative in advanced  
24 oxidation processes (AOPs) for water treatment. However, little is known about its reactivity  
25 to the ubiquitous dissolved organic matter (DOM) in water bodies.  $\text{SO}_4^{\bullet-}$  would selectively  
26 react with electron rich moieties in DOM, known as chromophoric DOM (CDOM), due to its  
27 light absorbing property. In this study, the reactivity and typical structural transformation of  
28 CDOM with  $\text{SO}_4^{\bullet-}$  was investigated. Four well characterized hydrophobic DOM fractions  
29 extracted from different surface water sources were selected as model CDOM.  $\text{SO}_4^{\bullet-}$  was  
30 produced through the activation of peroxymonosulfate (PMS) by Co(II) ions at pH 8 in borate  
31 buffer. The reactivity of CDOM was studied based on the decrease in its ultraviolet  
32 absorbance at 254 nm ( $\text{UVA}_{254}$ ) as a function of time. The reactivity of CDOM changed with  
33 time where fast and slow reacting CDOMs (i.e.,  $\text{CDOM}_{\text{fast}}$  and  $\text{CDOM}_{\text{slow}}$ ) were clearly  
34 distinguished. A second-order rate constant of  $\text{CDOM}_{\text{fast}}$  with  $\text{SO}_4^{\bullet-}$  was calculated by  
35 plotting  $\text{UVA}_{254}$  decrease versus PMS exposure; where a  $R_{\text{ct}}$  value (i.e., ratio of sulfate radical  
36 to PMS exposure) was calculated using pCBA as a probe compound. The transformation of  
37 CDOM was studied through the analysis of the changes in  $\text{UVA}_{254}$ , electron donating capacity,  
38 fluorescence intensity, and total organic carbon. A transformation pathway leading to a  
39 significant carbon removal was proposed. This new knowledge on the kinetics and  
40 transformation of CDOM would ultimately assist in the development and operation of  
41  $\text{SO}_4^{\bullet-}$ -based water treatment processes.

42 **Keywords:** Sulfate radical, CDOM, reaction kinetics, structural transformation, carbon  
43 removal

## 44 **1. Introduction**

45 Sulfate radical ( $\text{SO}_4^{\bullet-}$ )-based advanced oxidation processes (AOPs) have gained increasing  
46 interest in water treatment at both fundamental and applied levels (Siegrist et al. 2011,  
47 Waclawek et al. 2017). Due to its comparable or even stronger oxidizing capabilities than  
48  $\cdot\text{OH}$ ,  $\text{SO}_4^{\bullet-}$  is also capable of degrading a broad spectrum of trace organic contaminants  
49 (TOrcs) (e.g., pharmaceuticals, personal care products, and industrial chemicals) which are  
50 constantly detected in water bodies (Ghauch et al. 2017, Lutze et al. 2015a). A strong  
51 oxidation capacity, together with a high selectivity (i.e., lower scavenging of background  
52 organics) (Lutze et al. 2015a), multiple means of radical generation (Wang et al. 2014), and a  
53 favored storage/transport of stable solid precursors, make  $\text{SO}_4^{\bullet-}$  a promising alternative for  
54 contaminants removal.

55 Previous studies focusing on the removal of TOrcs by  $\text{SO}_4^{\bullet-}$  have provided key mechanistic  
56 and kinetic insights (Yang et al. 2019, Nihemaiti et al. 2018, Yang et al. 2017). However, little  
57 is known about the  $\text{SO}_4^{\bullet-}$ -induced reactivity and transformation of dissolved organic matter  
58 (i.e., DOM, a highly heterogeneous mixture of organic molecules ubiquitous in aquatic  
59 environments, and playing multiple key roles in water treatment) (Lutze et al. 2015a,  
60 Varanasi et al. 2018, Leenheer and Croué 2003). Briefly, the presence of DOM is known to  
61 decrease the removal efficiency of TOrcs due to its radical scavenging effect. Also, DOM  
62 transformation or removal can control disinfection byproducts formation or membrane  
63 fouling by applying  $\text{SO}_4^{\bullet-}$ -based AOPs as a pretreatment strategy (Chu et al. 2015, Xie et al.  
64 2015, Cheng et al. 2017, Tian et al. 2018). Therefore, an advanced knowledge on

65  $\text{SO}_4^{\bullet-}$ -induced reactivity and transformation of DOM is crucial to different water treatment  
66 processes considering its ubiquitous presence and the promising application of  $\text{SO}_4^{\bullet-}$ -based  
67 techniques.

68 The reactivity of DOM with oxidants such as chlorine, ozone, and  $\cdot\text{OH}$  has been extensively  
69 investigated. The difference in reactivity (i.e., faster reaction rate at the initial oxidation phase  
70 as compared to subsequent reaction phases) of different DOM isolates has been previously  
71 correlated with their structural variability and complexity (Chon et al. 2015, Westerhoff et al.  
72 2004). Interestingly, while  $\cdot\text{OH}$  non-selectively reacts with target substances,  $\text{SO}_4^{\bullet-}$  mainly  
73 reacts with electron rich aromatic or conjugated double bond moieties (Varanasi et al. 2018).  
74 This reactive DOM fraction has been termed as chromophoric dissolved organic matter  
75 (CDOM) due to its light absorbing property (Leenheer and Croué 2003, Lee et al. 2006).  
76 Therefore, the degradation rate of CDOM, as measured by ultraviolet absorbance at 254 nm  
77 ( $\text{UVA}_{254}$ ) (Westerhoff et al. 2007), could be used to determine its reactivity to  $\text{SO}_4^{\bullet-}$ .

78 A detailed study on the transformation of DOM, as a result of its reactivity to  $\text{SO}_4^{\bullet-}$ , remains  
79 challenging due to its structural complexity and a lack of analytical techniques. Alternatively,  
80 traditional DOM characterization techniques could be applied to provide some insights into  
81  $\text{SO}_4^{\bullet-}$ -induced changes of typical DOM characteristics, e.g., electron donating capacity  
82 (EDC), optical property (chromophoric or fluorescent property), molecular weight, or organic  
83 content (Li et al. 2016, Wang et al. 2017). For instance, an investigation on the  
84 transformation of DOM with  $\cdot\text{OH}$  was conducted by tracking the changes in chromophoric  
85 and fluorescent properties (Sarathy and Mohseni 2008). Specifically, the partial oxidation

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86 (i.e., no significant carbon removal) of DOM led to the breakdown of larger molecules, ring  
87 open of aromatic structures and the formation of small organics. Interestingly, due to the  
88 favorable decarboxylation mechanism driven by  $\text{SO}_4^{\bullet-}$ , a higher DOM mineralization would  
89 be expected (Varanasi et al. 2018, Madhavan et al. 1978).

90 To fill this knowledge gap, the objective of this study was to investigate the reactivity and  
91 transformation of CDOM with  $\text{SO}_4^{\bullet-}$ . The reactivity of CDOM was studied by following the  
92 decrease of its  $\text{UVA}_{254}$  with time. A second order rate constant of fast reacting CDOM was  
93 calculated based on an established correlation between  $\text{UVA}_{254}$  and radical exposure. By  
94 recording the changes in  $\text{UVA}_{254}$ , electron donating capacity (EDC), fluorescence intensity  
95 (FI), and total organic carbon (TOC), information on CDOM transformation was obtained. A  
96 Co(II)-activated peroxymonosulfate (PMS) process was used for the production of  $\text{SO}_4^{\bullet-}$  due  
97 to its high efficiency and simplicity. Four well characterized hydrophobic DOM fractions of  
98 different origins and characteristics were selected as model CDOM. This selection of organic  
99 isolates obtained from various sources shaping different characters represents a significant  
100 advance compared to model organics used in previous investigations.

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## 101 2. Materials and method

### 102 2.1 Chemical reagents and DOM fractions

103 Peroxomonosulfate (Oxone,  $\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$ ), 2,2'-azinobis  
104 (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS;  $\geq 98\%$ ), cobalt(II) sulfate  
105 ( $\geq 99.0\%$ ), sodium tetraborate ( $\geq 99.5\%$ ), ethanol ( $\geq 99.5\%$ ), and *tert*-butanol (pure) were  
106 purchased from Sigma-Aldrich and prepared with Ultrapure water (PURELAB Ultra, ELGA).  
107 Sulfuric acid of HPLC grade and sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) were purchased from  
108 UNIVAR. *p*-chlorobenzoic acid (pCBA, Acros Organics) was dissolved in ultrapure water to  
109 a concentration of 0.2 mM and used as a stock solution. A PMS stock solution of a high  
110 concentration (10 mM) was prepared and kept at 4°C due to its instability. The concentration  
111 of the stock solution was monitored on a daily basis prior to use.

112 Four DOM fractions previously isolated and characterized were selected for this study:  
113 Hydrophobic acids (i.e., DOM adsorbed onto XAD-8<sup>®</sup> resin at acid pH and eluted with  
114 sodium hydroxide) extracted from Suwannee River water (S-HPOA, USA) and Beaufort  
115 Reservoir (B-HPOA, France); hydrophobic DOM (i.e., similar protocol using a mixture of  
116 water and acetonitrile for resin elution) isolated from Ribou Reservoir NOM (R-HPO, France)  
117 and Colorado River (C-HPO, USA). The characteristics of the DOM isolates were  
118 summarized in [table S1](#).

### 119 2.2 Experimental setup and procedures

120 Experiments were conducted in 40-mL amber glass vials with Teflon caps. A pre-determined  
121 amount of Co(II) as well as DOM stock solution were added into the 10 mM borate buffer to



122 obtain a final composition of  $3.90 \pm 0.11$  mg C/L of DOM and 1  $\mu$ M of Co(II) at pH 8.  
123 Instead of phosphate buffer, tetraborate was used as a buffer solution due to the reported  
124 complexing ability of the former with cobalt. A pH 8 buffer was used due to its improved  
125 buffering capacity upon the addition of PMS at high concentrations.

126 The experiments for CDOM reaction kinetics were started by introducing 1 mM PMS. The  
127 use of a high initial PMS concentration would allow for a study under both low and high  
128 PMS exposure conditions, representative of different water treatment processes. Ethanol and  
129 *tert*-butanol at different concentrations (1 or 10 mM) were used as radical quenching agents,  
130 while *p*CBA (10  $\mu$ M) was used as a model compound to quantify primary reactive species.  
131 Samples were collected at specified time intervals and subjected to immediate measurement  
132 of PMS residual and UV absorbance at 254 nm (UVA<sub>254</sub>) without the addition of quenching  
133 agent. The value of UVA<sub>254</sub> was further corrected by subtracting the interferences from borate  
134 buffer (i.e., including H<sub>2</sub>SO<sub>4</sub> for pH adjustment), CoSO<sub>4</sub>, and PMS. Also, the contribution of  
135 PMS at each sampling time was calculated based on the residual PMS concentration and its  
136  $\epsilon_{254\text{nm}}$  measured in this study ( $12.3 \text{ M}^{-1}\text{cm}^{-1}$ ). For samples subjected to *p*CBA analysis, the  
137 reaction was stopped by adding 0.1 mL of ethanol (10 M) to 0.9 mL of sample. Sodium  
138 thiosulfate was found inefficient in quenching residual PMS with concentrations as high as  
139 600 mM.

140 In order to avoid the interference of quenchers on Electron Donating Capacity (EDC)  
141 measurements, a new set of experiments was performed by using various initial PMS  
142 concentrations (i.e., from 0.00 to 1.00 mM) to achieve experimental conditions with different

143 PMS exposures. PMS residual was periodically monitored, and all samples were analyzed  
144 after complete PMS consumption. All experiments were performed at room temperature  
145 (20°C) in glass bottles installed on a rotary shaker (Ika-Werke GMBH & Co. (KG),  
146 Labortechnik KS250 Basic) operated at 500 rpm.

## 147 **2.3. Analytical methods**

### 148 ***2.3.1 Analysis of residual PMS***

149 The concentration of PMS was measured by an ABTS<sup>•+</sup>-based method described elsewhere  
150 (Zhang et al. 2016). In this method, ABTS<sup>•+</sup> is generated during the oxidation of ABTS by  
151 sulfate radical produced through the catalytic transformation of PMS, and then it was  
152 spectrophotometrically measured. Briefly, a solution containing 0.5 mL of ABTS (20 mM),  
153 0.2 mL of CoSO<sub>4</sub> (20 mM), 10 mL of H<sub>2</sub>SO<sub>4</sub> (2%), and 1 mL of water sample was well mixed  
154 and measured at a 734 nm wavelength with a spectrophotometer (Cary 60, Agilent). The  
155 calibration curve for PMS determination was shown in Fig. S1. A high concentration of  
156 CoSO<sub>4</sub> (20 mM) was applied to accelerate the catalytic decomposition of PMS. However, this  
157 interference has been taken into consideration with the measurement of a blank sample with  
158 no PMS addition, as suggested by the calibration curve in Figure S1. Also, a background  
159 DOM would not be influential due to a measurement recorded at 734nm.

### 160 ***2.3.2 Characterization of DOM transformation***

161 The EDC of DOM samples was analysed based on a method developed by Chon et al (Chon  
162 et al. 2015). Briefly, a size exclusion chromatography (SEC) coupled with post column  
163 reaction was used, where ABTS<sup>•+</sup> was produced by the oxidation of ABTS with sodium

164 persulfate in acidic environment. A TOYOPEARL HW-50S column (8mm×30cm) was  
165 selected for SEC using a 50 mM borate eluent (pH 7.8) at a flow rate of 0.2 mL/min. The  
166 post-column injection of ABTS<sup>•+</sup> solution was operated at 0.05 mL/min from the helium  
167 pressurised generator. The reaction coil was connected to two UV detectors positioned in  
168 series (Agilent 1100 series, USA): the first one recording UV absorbance of DOM at 254 nm,  
169 and the second one recording the signal for ABTS/ABTS<sup>•+</sup> at 405 nm.

170 A Cary 60 spectrophotometer (Agilent, USA) was used to collect absorbance data or to  
171 record the UV-vis spectra from 200 nm to 800 nm in 1cm path length quartz cell. The TOC  
172 concentration of each sample was measured with a Shimadzu TOC-L analyser (SHIDMAZU,  
173 Japan).

174 Fluorescence excitation and emission matrices (EEMs) were obtained using a Fluorescence  
175 spectrometer (Cary Eclipse, Varian). The operating parameters were adjusted based on the  
176 method from Chen et al ([Chen et al. 2003](#)). Briefly, the scan rate and excitation or emission  
177 slit bandwidth were set at 600 nm/min and 5nm, respectively. The spectra were recorded by  
178 scanning an emission spectra from 290 nm to 550 nm at a 5nm increment with the excitation  
179 wavelength ranging from 220 nm to 400 nm at a 5 nm increment.

180 The concentration of *p*CBA was measured with a HPLC unit equipped with a UV detector  
181 (Agilent 1100 series, USA) recording absorbance at 238 nm and with a 250 mm\*4.6mm C18  
182 5- $\mu$ m reverse phase column (Alltima<sup>TM</sup>, GRACE). The mobile phase consisted of 60%  
183 methanol and 40% phosphoric acid (0.1%, V/V). The *p*CBA calibration curve was built using  
184 gradually diluted stock solution.

185

### 186 3. Results and Discussion

#### 187 3.1 Biphasic decrease of CDOM in Co(II)/PMS system

188 The reaction of CDOM with PMS led to an average decrease of 11% in UVA<sub>254</sub> within 60  
189 min (Fig. S2). However, the decrease of UVA<sub>254</sub> was remarkably faster in the presence of  
190 both PMS and Co(II) (Fig. 1). Approximately 55% to 70% decrease in UVA<sub>254</sub> (depending on  
191 the DOM fraction) was observed in Co(II)-catalyzed PMS system within 60 min. This  
192 enhanced reaction was caused by the generation of reactive species (e.g., SO<sub>4</sub><sup>•-</sup>) in the  
193 Co(II)/PMS system, while the slight UVA<sub>254</sub> decrease in the absence of Co(II) catalyst was  
194 probably due to the reaction of quinones with PMS as previously reported (Zhou et al. 2015).  
195 The occurrence of quinones within humic substances has been widely acknowledged (Cory  
196 and McKnight 2005).

197

#### Fig. 1.

198 Noticeably, a fast and slow reaction phase could be distinguished for all DOM fractions  
199 throughout the oxidation process (Fig. 1). Specifically, the pseudo-first-order rate constants of  
200 the fast reaction phase were 4.2 to 6.9 times higher than the rate constants of the slower  
201 reaction phase. These results showed a significant difference in the reactivity of CDOM with  
202 SO<sub>4</sub><sup>•-</sup> due to the heterogeneous structural property of the organic matter isolates. It has been  
203 previously reported that aromatic structures substituted with electron donating groups (i.e., –  
204 OH, –NH<sub>2</sub>, –OCH<sub>3</sub>) exhibited higher reactivity to SO<sub>4</sub><sup>•-</sup> (Luo et al. 2017); these structures  
205 could represent the main contributor to the fast reacting CDOM (i.e., CDOM<sub>fast</sub>). The slow

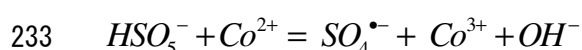
206 reacting CDOM (i.e., CDOM<sub>slow</sub>) might include lower electron density moieties from the  
207 original CDOM constituents as well as the oxidation products of CDOM<sub>fast</sub> (Xiao et al. 2015,  
208 Zhang et al. 2012).

209 The influence of the aromatic character of the DOM fractions on their reactivity with SO<sub>4</sub><sup>•-</sup>  
210 was highly expected based on previous findings (Westerhoff et al. 2004, Luo et al. 2017).  
211 However, the difference in reactivity among the four DOM fractions was more significant  
212 during the slow reaction phase. The pseudo-first-order reaction rates of CDOM<sub>slow</sub> (i.e.,  
213 ln(UVA<sub>254</sub>/UVA<sub>254,0</sub>) versus reaction time) were calculated as 1.20×10<sup>-2</sup>, 0.84×10<sup>-2</sup>, 0.63×10<sup>-</sup>  
214 <sup>2</sup>, and 0.46×10<sup>-2</sup> min<sup>-1</sup> for S-HPOA, B-HPOA, R-HPO and C-HPO, respectively. These  
215 CDOM<sub>slow</sub> reactivities linearly increased with the SUVA values as shown in Fig. S3. The  
216 CDOM<sub>fast</sub> reactivity to SO<sub>4</sub><sup>•-</sup> of the four DOM fractions was further discussed in the  
217 following sections.

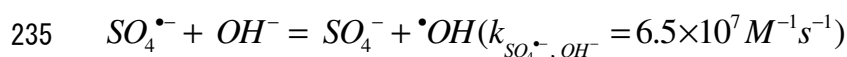
### 218 3.2 Evaluation of sulfate radical production

219 Anipsitakis and Dionysiou (Anipsitakis and Dionysiou 2003) reported the predominant role  
220 of SO<sub>4</sub><sup>•-</sup> (eq. 1) over <sup>•</sup>OH in Co(II)-catalyzed PMS systems at pH 7. Because a pH 8 may  
221 promote a higher production of <sup>•</sup>OH (eq. 2), the identification of major oxidizing species in  
222 the current system was conducted by following the degradation of *p*CBA as a probe  
223 compound under different scavenging conditions (Lutze et al. 2015b). The second-order rate  
224 constants of *p*CBA and radical scavengers (i.e., *t*-BuOH and EtOH) with <sup>•</sup>OH and SO<sub>4</sub><sup>•-</sup> were  
225 summarized in table S3. When 10 mM of radical scavenger (i.e., *t*-BuOH or EtOH, at a molar  
226 ratio of 1000:1 versus *p*CBA) was applied, the *p*CBA removal efficiency was decreased by

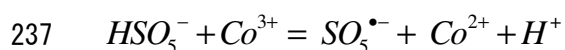
227 approximately 10% in the presence of *t*-BuOH; while almost no *p*CBA decrease was observed  
228 with the addition of EtOH (Fig. S4). Quantitatively, the ratio of the measured concentration  
229 of  $\cdot\text{OH}$  to  $\text{SO}_4^{\bullet-}$  was lower than 3%. These results indicated that  $\text{SO}_4^{\bullet-}$  was the predominant  
230 reactive species at pH 8. This is probably due to the competition for  $\text{SO}_4^{\bullet-}$  by either *p*CBA  
231 ( $3.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ) or scavengers (i.e., DOM fractions, up to  $10^8 \text{ M}^{-1}\text{s}^{-1}$  as discussed below),  
232 leading to the unfavorable production of  $\cdot\text{OH}$  (eq 2).



234 (1)



236 (2)



238 (3)

239 Therefore, the production of  $\text{SO}_4^{\bullet-}$  was investigated following the  $R_{\text{ct}}$  concept and the  
240 analysis of *p*CBA decay.  $R_{\text{ct}}$  (i.e., the ratio of radical exposure to oxidant exposure) (Elovitz  
241 and von Gunten 1999) was used to present the production of  $\text{SO}_4^{\bullet-}$  with PMS exposure (eq.  
242 4). According to Elovitz and von Gunten (Elovitz and von Gunten 1999), the consumption of  
243 radicals by a probe compound (P) (e.g., *p*CBA in the current study) is considered  
244 insignificant as compared to major radical scavengers (S) (e.g., DOM in current study) if the  
245 probe compound is present at a considerably low concentration (i.e.,  $k_{\text{P}}[\text{P}] \ll k_{\text{S}}[\text{S}]$ , where  $k_{\text{P}}$   
246 and  $k_{\text{S}}$  represents the rate constants of the probe compound and major radical scavengers with  
247 radicals, respectively). Therefore, a low *p*CBA concentration (i.e., 1  $\mu\text{M}$ ) was applied to

248 ensure an insignificant radical consumption by *p*CBA as compared to DOM. Specifically,  
249  $k_{p\text{CBA}}[p\text{CBA}]$  was calculated as approximately 1.4% of  $k_{\text{DOM}}[\text{DOM}]$  under the current  
250 experimental condition, where  $k_{p\text{CBA}}$  and  $k_{\text{DOM}}$  represent the second order rate constants of  
251 *p*CBA ( $3.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ) and DOM ( $6.8 \times 10^3 \text{ LmgC}^{-1}\text{s}^{-1}$ ) with  $\text{SO}_4^{\bullet-}$ , respectively. The  $R_{\text{ct}}$   
252 value was only studied for the first 10 min of the reaction.  $\text{CDOM}_{\text{fast}}$  was observed reactive  
253 within this timeframe (Fig. 1). The conversion from reaction time to PMS exposure was  
254 illustrated in Table S4.

255 Although no noticeable interference was observed with  $\text{UVA}_{254}$  or EDC measurements, the  
256 rate of catalytic PMS decomposition decreased (Fig. S5) due to the formation of cobalt-DOM  
257 complex. For instance, a 57% PMS decomposition was observed within 60 min in the  
258 DOM-free system. However, the PMS decomposition values for S-HPOA-, B-HPOA-,  
259 R-HPO-, and C-HPO-containing system were 41%, 43%, 40%, and 43%, respectively.  
260 Specifically, approximately 80% of Co(II) was calculated as forming complexes with DOM  
261 under the current experimental conditions using the NICA-Donnan model with the constants  
262 adapted from Milne et al (Milne et al. 2003). In DOM-containing solutions with the addition  
263 of *p*CBA as probe compound, PMS decomposed following a pseudo-first-order reaction (Fig.  
264 S6a), as described by (eq. 5), and  $k$  (i.e., pseudo-first-order rate constant) was measured as  
265 approximately  $3.0 \times 10^{-4} \text{ s}^{-1}$  independent of DOM origins. The influence of *p*CBA addition (1  
266  $\mu\text{M}$ ) on PMS decomposition was negligible. For instance, the averaged PMS residual  
267 measured in different DOM-containing systems within 10 min was 80% in the absence of  
268 *p*CBA (Figure S5) and 79% in the presence of *p*CBA (Figure S6a). The determined rate

269 (within 10 min) was predominantly contributed by a catalytic decomposition since  
 270 self-decomposition of PMS was found negligible within 2 hr at room temperature (20°C).  
 271 The degradation of *p*CBA (Fig. S6b) caused by  $SO_4^{\bullet-}$  was described by eq. 6 and 7. By  
 272 combining eq. 4 and 5, *p*CBA degradation could be described using the  $R_{ct}$  concept (eq. 8).

$$273 \quad R_{ct} = \frac{\int_0^t [SO_4^{\bullet-}] dt}{\int_0^t [PMS] dt}$$

$$274 \quad (4)$$

$$275 \quad [PMS] = [PMS]_0 e^{-kt}$$

$$276 \quad (5)$$

$$277 \quad -\frac{d[pCBA]}{dt} = k_{SO_4^{\bullet-}, pCBA} [pCBA] [SO_4^{\bullet-}]$$

$$278 \quad (6)$$

$$279 \quad \ln \frac{[pCBA]}{[pCBA]_0} = -k_{SO_4^{\bullet-}, pCBA} \int_0^t [SO_4^{\bullet-}] dt$$

$$280 \quad (7)$$

$$281 \quad \ln \frac{[pCBA]}{[pCBA]_0} = -k_{SO_4^{\bullet-}, pCBA} R_{ct} [PMS]_0 \int_0^t e^{-kt} dt$$

$$282 \quad (8)$$

283 By plotting  $\ln(pCBA/pCBA_0)$  versus PMS exposure, linear correlations were observed as a  
 284 function of PMS exposures (Fig. 2). The  $R_{ct}$  value at PMS exposures higher than 0.1 M·s (i.e.  
 285 a reaction time of 2–10 min, table S4) for each system was determined from the slope of the  
 286 linear regression line (Fig. 2) and listed in Table 1; while the higher  $R_{ct}$  values at PMS  
 287 exposures lower than 0.1 M·s (i.e. a reaction time of 0–2 min, table S4) were shown in Fig.



288 **S7.** Higher  $R_{ct}$  values at the initial oxidation stage (PMS exposure < 0.1 M·s, results  
289 discussed in section 3.4.1) have also been reported during the ozonation of surface waters  
290 (Elovitz and von Gunten 1999). The change of  $R_{ct}$  in the current study was likely due to the  
291 Co(II) regeneration process. Specifically, the conversion of Co(II) to Co(III) with a  
292 precipitate formation of the latter has been considered as a probable explanation for the  
293 slowing down of the catalytic rate with time at pH above 5.9 (Zhang and Edwards 1992).  
294 With a pH of 8 used in this study, Co(III) might have also precipitated out as  $Co(OH)_3$  ( $K_{sp} =$   
295  $1.6 \times 10^{-44}$ ), leading to the retardation of the regeneration process and consequently to a  
296 slower  $SO_4^{\cdot-}$  production. Moreover, the additional PMS consumption during the regeneration  
297 of Co(II) (eq. 3), which inefficiently produced  $SO_5^{\cdot-}$  (Neta et al. 1988), would also lead to a  
298 decreased  $R_{ct}$ . A change in Co(II) catalytic behavior at different pH probably associated with  
299 Co(III) precipitation at higher pH has also been observed in previous studies. For instance,  
300 the degradation rate of 2,4-DCP in Co(II)/PMS system slowed down with reaction time at pH  
301 7 (Anipsitakis et al. 2005), while it remained unaffected at pH 2 (Anipsitakis and Dionysiou  
302 2003). Considering that no enhanced  $UVA_{254}$  decrease (explained in Section 3.4.1) was  
303 observed (Fig. 1) in contrast to the significantly higher *p*CBA degradation (Fig. S6b) at the  
304 initial oxidation stage (i.e., PMS exposure lower than 0.1 M·s), the relatively lower  $R_{ct}$  values  
305 (Table 1) determined after the initial short stage were used in the analysis of the following  
306 section.

307 **Fig. 2.**

308  
309 **Table 1.**

### 310 3.3 Reactivity of CDOM<sub>fast</sub> to SO<sub>4</sub><sup>•-</sup> and its application

311 **Fig. 3.**

312 Following the procedures for establishing a relationship between  $\ln(pCBA/pCBA_0)$  and PMS  
 313 exposure (eq. 8), i.e., obtained by combining eq.(4), eq.(5) and eq.(7)), a similar correlation  
 314 was also established between  $\ln(UVA_{254}/UVA_{254,0})$  of CDOM<sub>fast</sub> and PMS exposure (eq. 9).  
 315 This correlation was found linear when  $\ln(UVA_{254}/UVA_{254,0})$  of CDOM<sub>fast</sub> was plotted against  
 316 PMS exposure for all DOM fractions (Fig. 3). The good linearity allowed the calculation of  
 317 the reaction rate constant of CDOM<sub>fast</sub> with SO<sub>4</sub><sup>•-</sup> using the R<sub>ct</sub> value determined in Section  
 318 3.2.

$$319 \ln \frac{[UVA_{254}]}{[UVA_{254}]_0} = -k_{SO_4^{\bullet-}, CDOM} R_{ct} [PMS]_0 \int_0^t e^{-kt} dt$$

320 (9)

321 Interestingly, the reaction rate constants of CDOM<sub>fast</sub> for all DOM fractions were at the same  
 322 order of magnitude. The highest CDOM<sub>fast</sub> value was recorded for S-HPOA ( $4.59 \times 10^8$   
 323  $M^{-1}s^{-1}$ ), also exhibiting the highest SUVA (4.78). The lowest CDOM<sub>fast</sub> value was observed  
 324 for C-HPO ( $1.99 \times 10^8 M^{-1}s^{-1}$ ), also showing lowest SUVA (2.14). However, B-HPOA  
 325 (SUVA: 4.06) showed a lower  $k$  value than R-HPO (SUVA: 3.22), i.e.,  $3.04 \times 10^8 M^{-1}s^{-1}$   
 326 versus  $3.48 \times 10^8 M^{-1}s^{-1}$ , respectively. Therefore, the correlation between the reactivity of  
 327 CDOM<sub>fast</sub> and SUVA of the corresponding DOM fraction would need additional investigation  
 328 by including a larger pool of DOM fractions. These reaction rate constants were one order of  
 329 magnitude higher than the data previously reported (i.e.,  $\sim 10^7 M_C^{-1}s^{-1}$ ). For instance, Lutz et  
 330 al (Lutze et al. 2015a) observed a rate of  $6.8 \times 10^3 LmgC^{-1}s^{-1}$  for humic acid (Depur from

331 Carl Roth) using an indirect kinetic competition method; while Zhou et al (Zhou et al. 2017)  
332 recorded a rate of  $1.86 \times 10^3 \text{ LmgC}^{-1}\text{s}^{-1}$  for Suwannee River fulvic acid using a direct laser  
333 flash photolysis method. The difference could be attributed to the fact that the value in this  
334 study was only measured for the conceptually isolated fast reacting moieties (i.e.,  $\text{CDOM}_{\text{fast}}$ )  
335 rather than for the bulk DOM (i.e., a combination of both fast and slow reacting moieties).  
336 However, the value was one order of magnitude lower than those reported for aromatic  
337 compounds ( $\sim 10^9 \text{ M}^{-1}\text{s}^{-1}$ ) (Neta et al. 1977, Fischer and Radom 2001). This difference would  
338 be the result of stronger electrosteric repulsion between  $\text{SO}_4^{\bullet-}$  and structurally complex DOM  
339 as compared to simpler organic compounds. The higher reactivity of sulfate radicals to  
340  $\text{CDOM}_{\text{fast}}$  than to  $\text{OH}^-$  ( $\sim 10^7 \text{ M}^{-1}\text{s}^{-1}$ ) was expected to lead to an insignificant production of  
341  $\bullet\text{OH}$  (eq. 2) due to its unfavorable formation kinetics. In addition,  $\text{CDOM}_{\text{fast}}$  would be  
342 preferred to bulk DOM when evaluating the scavenging property of dissolved organic matter  
343 in  $\text{SO}_4^{\bullet-}$ -based AOPs under lower PMS exposures, where  $\text{CDOM}_{\text{fast}}$  was the major reactive  
344 moieties (Fig. 1).

345 The use of  $\text{UVA}_{254}$  as a surrogate indicator for the assessment of TOrCs removal efficiency  
346 has been extensively studied in ozone- and  $\bullet\text{OH}$ -based AOPs (Gerrity et al. 2012,  
347 Rosario-Ortiz et al. 2010, Li et al. 2017). This finding could also support its application in  
348  $\text{SO}_4^{\bullet-}$ -based water treatment processes. The study on TOrCs removal efficiency could be  
349 achieved using either: i) the kinetics with second order reaction constants of TOrCs and  
350 radical exposure (eq. 10), or ii) the correlation established between  $\text{UVA}_{254}$  decrease and  
351 contaminants removal (eq. 11).

$$\ln \frac{[\text{TOrCs}]}{[\text{TOrCs}]_0} = -k_{\text{SO}_4^{\bullet-}, \text{TOrCs}} \int_0^t \text{SO}_4^{\bullet-} dt = -k_{\text{SO}_4^{\bullet-}, \text{TOrCs}} \ln \frac{[\text{UVA}_{254}]}{[\text{UVA}_{254}]_0} / -k_{\text{SO}_4^{\bullet-}, \text{CDOM}} \quad (10)$$

$$\ln \frac{[\text{TOrCs}]}{[\text{TOrCs}]_0} = \text{Slope} \times \ln \frac{[\text{UVA}_{254}]}{[\text{UVA}_{254}]_0} + \text{Intercept} \quad (11)$$

As compared to the direct measurement of TOrCs in a full-scale water treatment plant, the indirect monitoring of UV absorbing parameters using spectrophotometer would require lower capital/operating cost as well as time input. Especially, with the use of an on-line spectrophotometer, a quick track of the oxidation efficiency and consequently a rapid adjustment (i.e., oxidant dose or contact time) could also be expected. However, different correlation models should be established for different TOrCs due to the discrepancy in their reactivity. The successful application of this correlation could also be impacted by the fluctuation of water matrices (e.g.,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ , or  $\text{Cl}^-$ ) or temperature due to seasonal changes.

The use of UV absorbing indices of humic substances in combination with their fluorescence properties has also been suggested as indicators in ozone-based water treatment processes (Li et al. 2017). However, similar decreasing trend was observed in the current study between  $\text{UVA}_{254}$  and fluorescence intensity with increasing PMS concentration (Text S1). Consequently, the  $\text{UVA}_{254}$  parameter was sufficient as a single process indicator in this  $\text{SO}_4^{\bullet-}$ -based oxidation system.

### 3.4 Sulfate radical-induced CDOM transformation

#### 3.4.1 EDC decrease as a function of PMS exposures

**Fig. 4.**

372 Electron donating capacity (EDC) associated with the presence of phenolic structures with  
373 different degree of substitution has been previously reported for aquatic humic substances  
374 (Aeschbacher et al. 2012). The change in EDC (Fig. S8) was studied for each DOM fraction  
375 under various PMS exposures. The different PMS exposures were obtained by applying  
376 varying initial PMS concentrations for the same contact time (i.e., 20 h) and the calculation of  
377 the PMS exposures was detailed in Text S2, SI. In addition, the changes in normalized EDC  
378 and UVA<sub>254</sub> (Fig. S9) of the four DOM fractions were plotted in Fig. 4. This figure shows that  
379 for PMS exposures lower than 0.1 M·s (Area a<sub>1</sub>), an average of 54% decrease of EDC was  
380 recorded when only a 30% decrease of UVA<sub>254</sub> was observed. For PMS exposures higher  
381 than 0.1 M·s (Area b), the averaged normalized UVA<sub>254</sub> decreased from 70% to 13% (i.e., a  
382 57% decrease), whereas the averaged normalized EDC decreased from 46% to 7% (i.e., a 39%  
383 decrease). The larger decrease of EDC than UVA<sub>254</sub> at PMS exposure lower than 0.1 M·s in  
384 this system indicated that the initial phase of SO<sub>4</sub><sup>•-</sup> reaction was the oxidation of phenolics  
385 into quinone-type structures with similar chromophoric properties (Ramseier and Gunten  
386 2009). This reaction is thermodynamically favourable considering the very low oxidation  
387 potential of phenolic structures (0.153–0.620 V) (Bortolomeazzi et al. 2007) and the strong  
388 reduction potential of sulfate radicals (2.5–3.1V) (Anipsitakis and Dionysiou 2003). A similar  
389 observation has been previously reported during the treatment of humic substances by ClO<sub>2</sub>  
390 or HClO, where hydroquinone or catechol moieties (i.e., major EDC contributors (Chon et al.  
391 2015)) were proposed as oxidized by HClO through electron transfer rather than electrophilic  
392 substitution (Wenk et al. 2013). Interestingly, a more pronounced decrease in EDC than in

393 UVA<sub>254</sub> was observed with a PMS exposure lower than 0.01 M·s (Area a<sub>0</sub>, Fig. 4), which was  
394 probably caused by the relatively higher R<sub>ct</sub> observed under this condition (Fig. S7).

395 Due to a major SO<sub>4</sub><sup>•-</sup> consumption by the moieties with EDC at the initial oxidation phase  
396 (i.e., PMS exposure < 0.1 M·s), a UVA<sub>254</sub> decrease was not enhanced even under higher  
397 radical exposure (i.e., higher R<sub>ct</sub>) (Fig. 3). This result supported the selection of lower R<sub>ct</sub>  
398 values (Fig. 2) in the calculation of the second-order rate constants of CDOM<sub>fast</sub> with SO<sub>4</sub><sup>•-</sup> as  
399 described in section 3.3.

#### 400 **3.4.2 TOC removal efficiency at various PMS exposures**

401 **Fig. 5.**

402 In order to further explore the transformation of CDOM by sulfate radicals, the TOC content  
403 of the solution under different PMS exposures was measured. A significant TOC removal,  
404 64%, 63%, 56%, 49% for S-HPOA, B-HPOA, R-HPO and C-HPO, respectively (i.e., 58% in  
405 average), was observed under a PMS exposure of 8.04 M·s (Fig. S10). The relationship  
406 between UVA<sub>254</sub> decrease and TOC removal was established and shown in Fig. 5.  
407 Interestingly, the TOC removal was minor (i.e., less 10%) during the depletion of the UV  
408 absorbance of CDOM<sub>fast</sub> (i.e., UVA<sub>254</sub> decrease within 50%, as indicated by the red dashed  
409 line in Fig. 5). However, the decrease in the chromophoric property of CDOM<sub>slow</sub> (i.e.,  
410 observed when UVA<sub>254</sub> decrease was larger than 50%, right side of the red dashed line in Fig.  
411 5) led to a considerable TOC removal. These results indicated that the reaction of CDOM<sub>fast</sub>  
412 would mainly lead to the breakdown of complex aromatic structures into small molecular  
413 weight fractions with insignificant mineralization. This transformation from larger molecules

414 to smaller ones was evidenced by the blue shift or band contraction (Chen et al. 2002) in  
415 fluorescence emission spectra (Fig. 6). Specifically, the decrease in the band width at 1/2  
416 maximum fluorescence intensity was calculated as 24 nm, 24 nm, 33 nm, and 88 nm for  
417 S-HPOA, B-HPOA, R-HPO, and C-HPO, respectively. In contrast, the reaction of CDOM<sub>slow</sub>  
418 would mainly undergo through decarboxylation, which directly led to the observed carbon  
419 removal.

### 420 Fig. 6.

421 Interestingly, a good linearity between UVA<sub>254</sub> decrease and TOC removal during the  
422 CDOM<sub>slow</sub> decrease was observed (Fig. 5). These results indicated that the change in  
423 CDOM<sub>slow</sub> could be used in the prediction of TOC removal for surface water during  
424 SO<sub>4</sub><sup>•-</sup>-based treatment. This may include water treatment processes targeting the removal of  
425 organics, e.g., pretreatment for the removal of disinfection byproducts precursors or  
426 membranes foulants, membrane cleaning, and the treatment of reverse osmosis concentrates.  
427 Nevertheless, under different water matrices this correlation might be affected by pH  
428 conditions, or the presence of radical scavengers HCO<sub>3</sub><sup>-</sup> or Cl<sup>-</sup>.

### 429 3.4.3 Evolution of CDOM transformation with sulfate radical

430 Based on the findings of this study (i.e., results obtained with the current characterization  
431 techniques), the evolution of the transformation of CDOM by sulfate radicals was  
432 summarized in Fig. 7. The SO<sub>4</sub><sup>•-</sup>-induced reaction of CDOM<sub>fast</sub>, (i.e., electron donating group  
433 substituted aromatic structures) was mainly initiated through single electron transfer or

434 addition. The depletion of EDC would initially take place through the electron transfer from  
435 phenolic hydroxyl groups to sulfate radical as suggested by Reaction 1. Reaction 2 would  
436 produce hydroxylated C-centered radical cations and consequently lead to the formation of  
437 ring cleavage products (Anipsitakis et al. 2006). Remarkably, Reaction 4 would take place  
438 due to the high electron density at R<sub>3</sub> site leading to the formation of smaller fluorescent  
439 molecules, as suggested by the blue shift of fluorescence emission spectra (Fig. 6). The  
440 production of smaller molecules from complex structures could also be evidenced by the  
441 increased fluorescence signal (Figure S13) at lower PMS exposure, as the smaller aromatic  
442 moieties would be more fluorescent due to weaker intramolecular quenching effect. The  
443 decarboxylation of carboxyl groups (Reaction 3), i.e., newly formed or originally  
444 incorporated within DOM structures, would be the main reaction mechanism of CDOM<sub>slow</sub>  
445 transformation (Madhavan et al. 1978) leading to a significant removal of TOC. However, a  
446 more detailed study would be highly recommended for the optimization of process conditions  
447 for maximum carbon removal.

448 **Fig. 7.**

#### 449 **4. Conclusions**

450 The current study provided systematic information on both the reactivity and fate of CDOM  
451 with sulfate radical. DOM fractions with different origins and characteristics were used in this  
452 investigation. The main conclusions included:



- 
- 453 • Fast and slow reacting CDOM could be distinguished within all DOM fractions.  
454 Interestingly, the difference in the reactivity of CDOM<sub>fast</sub> among different organics  
455 were minor, while the reactivity CDOM<sub>slow</sub> were observed to increase with SUVA.
- 456 • The reactivity of CDOM<sub>fast</sub> to SO<sub>4</sub><sup>•-</sup> was calculated at an order of 10<sup>8</sup> M<sup>-1</sup>s<sup>-1</sup> from the  
457 observed linear correlation between CDOM<sub>fast</sub> decrease and sulfate radical exposure.  
458 The correlation also validated the potential application of UVA<sub>254</sub> as a surrogate  
459 indicator for TO<sub>r</sub>Cs removal efficiency.
- 460 • A faster decrease of EDC than UVA<sub>254</sub> at lower PMS exposure indicated a preferred  
461 oxidation of phenolic structures (i.e., preferential decrease of Electron Donating  
462 Capacity). Afterwards, the oxidation of CDOM<sub>fast</sub> would proceed with the formation of  
463 transient intermediates and ring cleavage products.
- 464 • The transformation products of CDOM<sub>fast</sub> together with the originally less reactive  
465 structures, i.e., CDOM<sub>slow</sub>, would undergo slow decarboxylation leading to a  
466 significant carbon removal. The linear relationship recorded between CDOM<sub>slow</sub>  
467 reduction and TOC removal could be used to predict carbon removal.
- 468 The findings in this work would highly assist in the design and operation of SO<sub>4</sub><sup>•-</sup>- based water  
469 treatment processes. Specifically, the scavenging capacity of background DOM could be better  
470 evaluated using the calculated reactivity of CDOM<sub>fast</sub> if the applied PMS exposure would  
471 mainly cause changes in CDOM<sub>fast</sub>. Also, the correlation established between CDOM and  
472 radical exposure would shed light on the applicability of UVA<sub>254</sub> as an indicator of TO<sub>r</sub>Cs

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473 removal efficiency in  $\text{SO}_4^{\bullet-}$ -based water treatment processes. However, further site-specific  
474 studies on the use of  $\text{UVA}_{254}$  as an indicator are highly needed for its successful application.  
475  $\text{SO}_4^{\bullet-}$ -based advanced oxidation technique could be developed to address the need for DOM  
476 removal in varying water treatment scenarios, e.g., pretreatment for the removal of disinfection  
477 by-products precursors or membrane foulants, application of catalytic membrane for organic  
478 fouling mitigation, membrane cleaning, or the treatment of reverse osmosis concentrate  
479 produced from reclaimed water treatment plants. Also, an increased PMS dose could be  
480 applied to increase the reaction rate of  $\text{CDOM}_{\text{slow}}$  and consequently increase carbon removal.  
481 In addition, carbon removal efficiency could be simply estimated based on the removal of  
482  $\text{CDOM}_{\text{slow}}$  due to the observed good correlation.

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### 486 **Appendix A. Supplementary information**

487 Supplementary information related to this article could be found in a separate Microsoft Word  
488 document (Supplementary Information).

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**Figure captions**

**Fig. 1.** UVA<sub>254</sub> decrease of different DOM fractions in Co(II)/PMS system as a function of time. Conditions: [PMS]<sub>0</sub> = 1.0 mM; Co(II) = 1.0 μM; DOM = 3.90 ± 0.11 mgC/L; pH = 8.00 ± 0.05 (10 mM borate buffer); T = 20°C.

**Fig. 2.** Correlation between pCBA decay and PMS exposure in Co(II)/PMS system with different DOM fractions. Conditions: [PMS]<sub>0</sub> = 1.00 mM; Co(II) = 1.00 μM; [pCBA]<sub>0</sub> = 1.00 μM; DOM = 3.90 ± 0.11 mgC/L; pH = 8.00 ± 0.05 (10 mM borate buffer); T = 20°C.

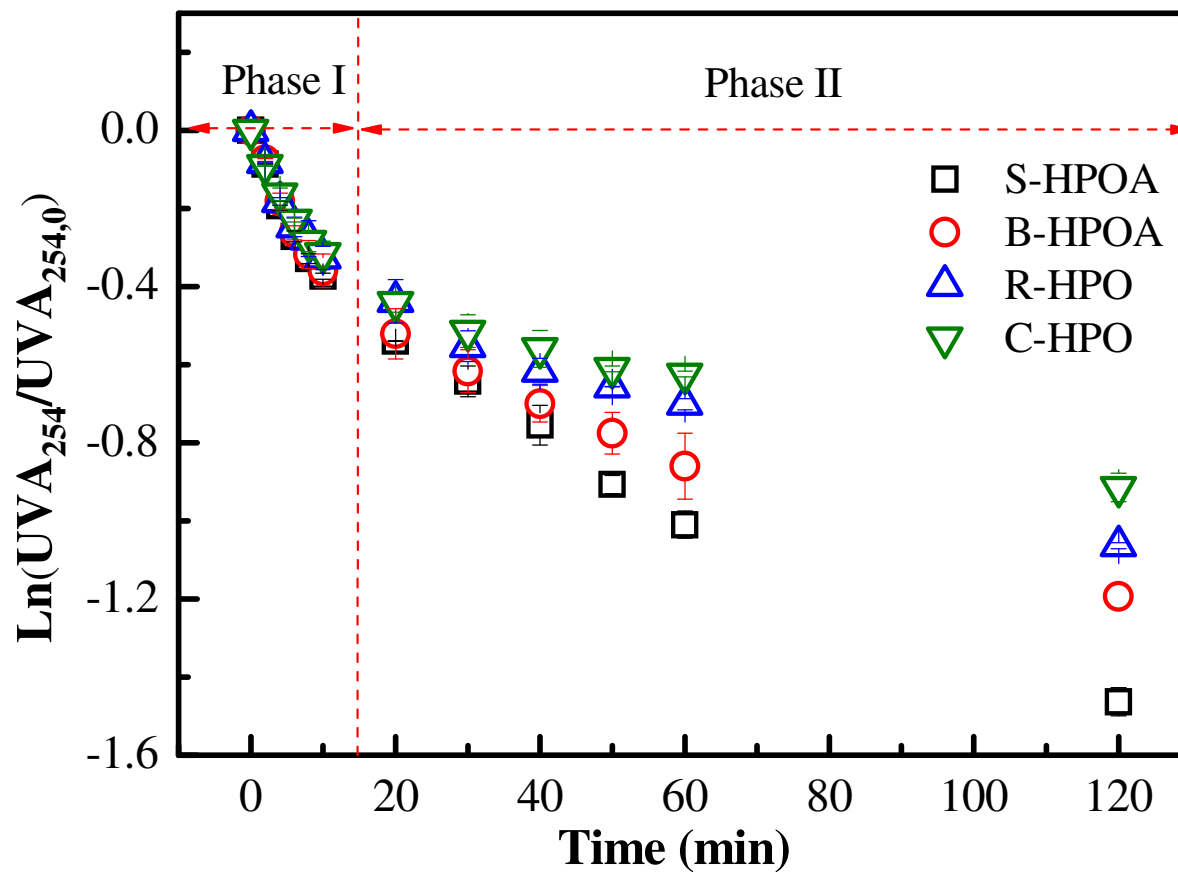
**Fig. 3.** Correlation between CDOM<sub>fast</sub> decrease and PMS exposure in Co(II)/PMS system. Conditions: [PMS]<sub>0</sub> = 1.00 mM; Co(II) = 1.00 μM; [pCBA]<sub>0</sub> = 1.00 μM; DOM = 3.90 ± 0.11 mgC/L; pH = 8.00 ± 0.05(10 mM borate buffer); T = 20°C.

**Fig. 4.** Correlation between normalized UVA<sub>254</sub> and EDC decrease of different DOM fractions in Co(II)/PMS system. Conditions: PMS exposure = 0.00–8.04 M·s; Co(II) = 1.00 μM; DOM = 3.90 ± 0.11 mgC/L; pH = 8.00 ± 0.05 (10 mM borate buffer); T = 20°C. Areas a<sub>0</sub>, a<sub>1</sub>, and b illustrated the results obtained with a PMS exposure lower than 0.01, lower than 0.1, and larger than 0.1 M·s, respectively. R<sub>E</sub> and R<sub>U</sub> represented the normalized removal efficiency in EDC and UVA<sub>254</sub>.

**Fig. 5.** TOC removal as a function of UVA<sub>254</sub> decrease. Conditions: PMS exposure = 0.00–8.04 M·s; Co(II) = 1.00 μM; DOM = 3.90 ± 0.11 mgC/L; pH = 8.00 ± 0.05 (10 mM borate buffer); T = 20°C. Red dashed line was drawn to differentiate the correlation between CDOM<sub>fast</sub> and CDOM<sub>slow</sub> with TOC removal.

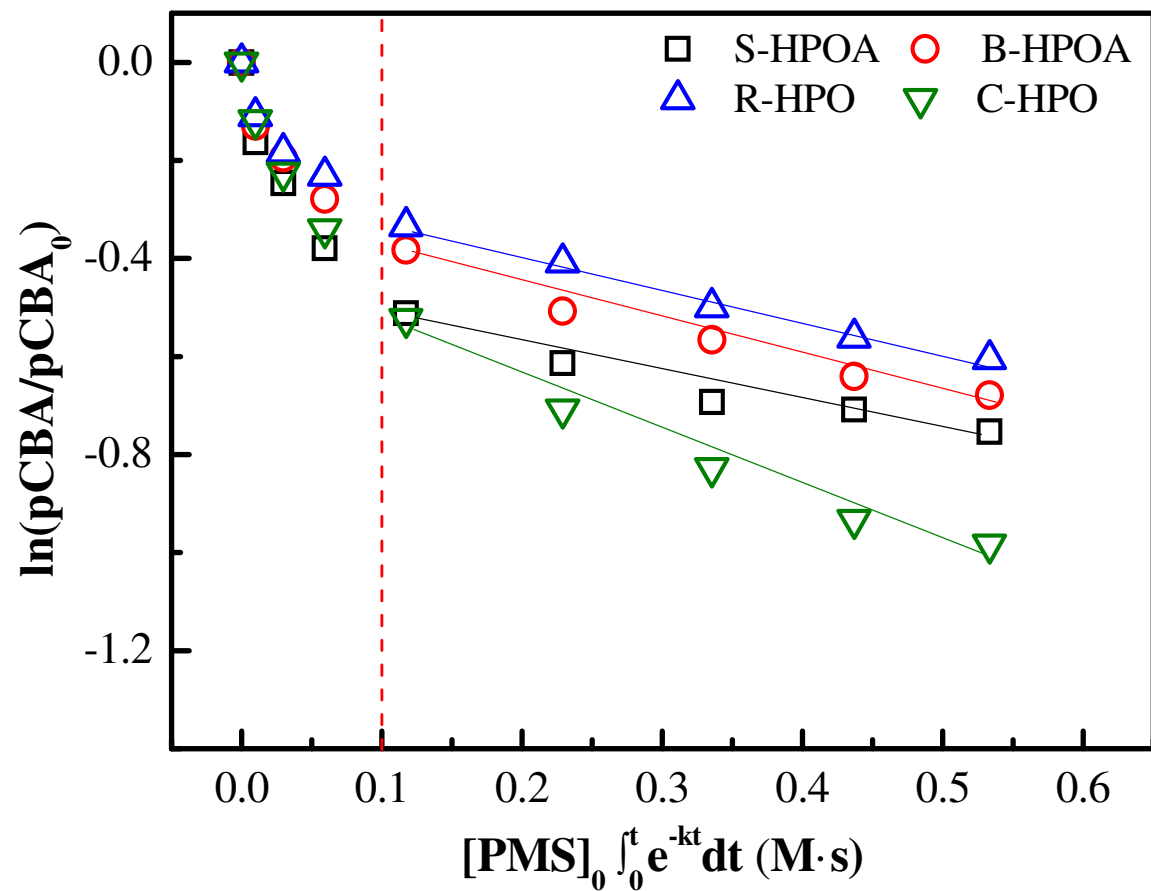
**Fig. 6.** Normalized emission spectra by its respective maximum fluorescence intensity of (a) S-HPOA, (b) B-HPOA, (d) R-HPO, and (d) C-HPO at an excitation wavelength of 230nm. The legend in each figure represented various PMS exposures.

**Fig. 7.** Proposed pathway of sulfate radical-induced DOM transformation

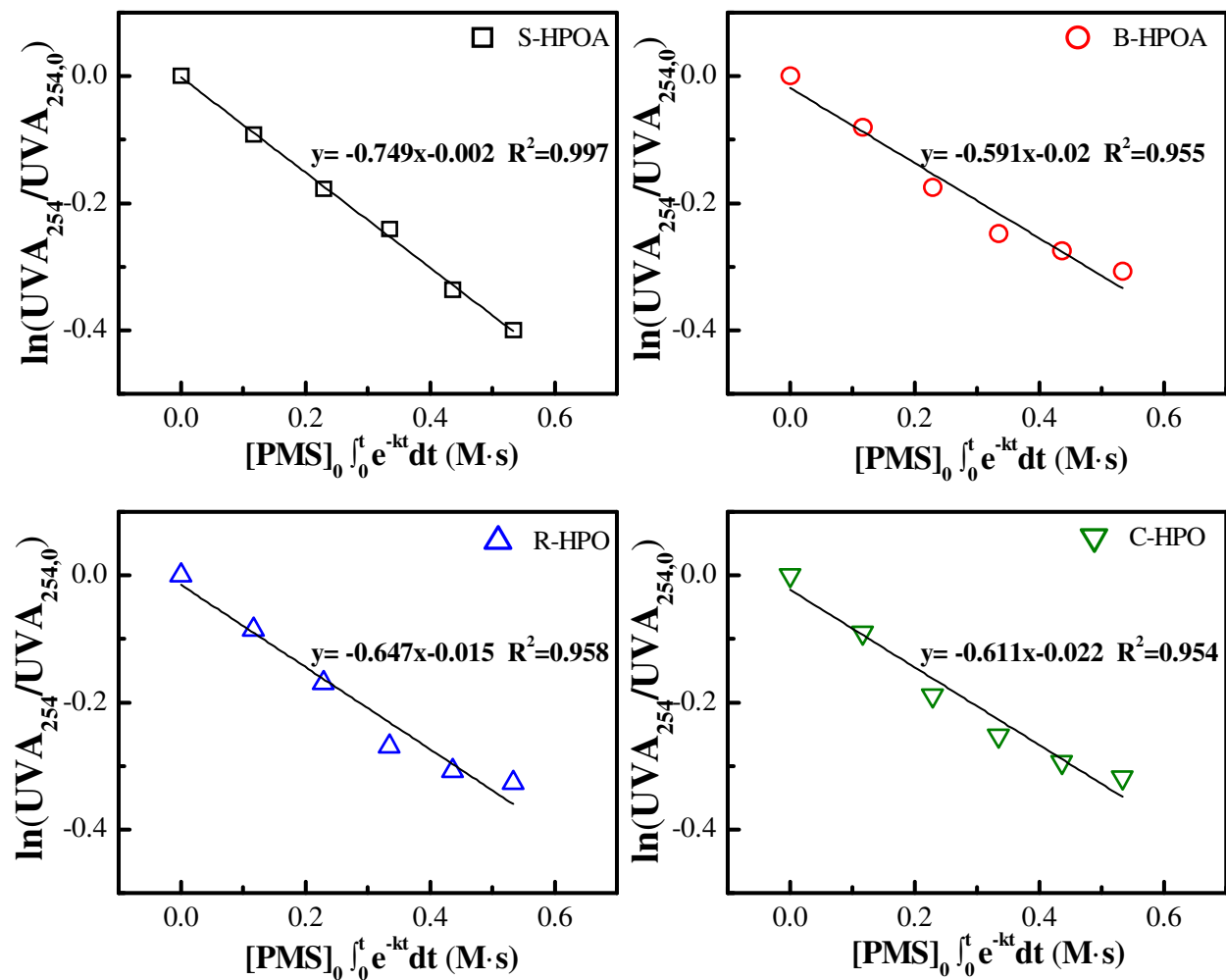


**Fig. 1.** UVA<sub>254</sub> decrease of different DOM fractions in Co(II)/PMS system as a function of time. Conditions: [PMS]<sub>0</sub> = 1.0 mM; Co(II) = 1.0 μM; DOM = 3.90 ± 0.11 mgC/L; pH = 8.00 ± 0.05 (10 mM borate buffer); T = 20°C.

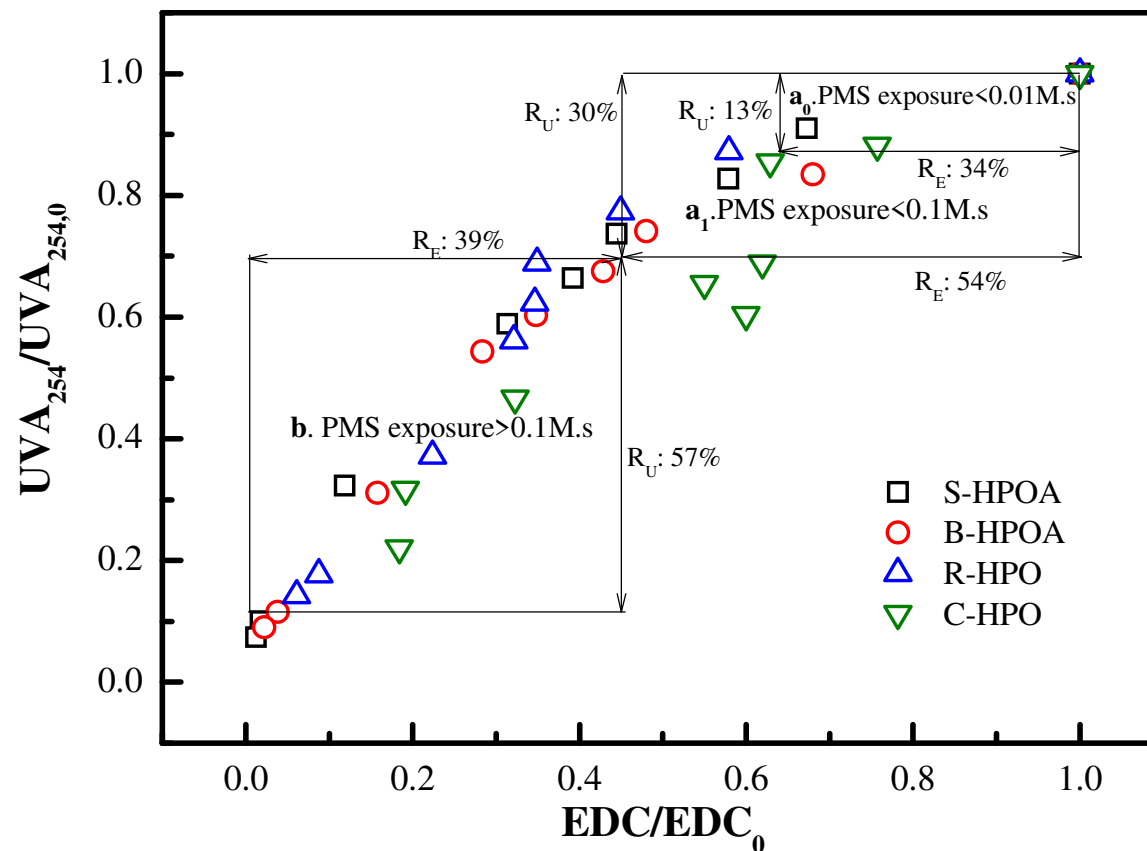




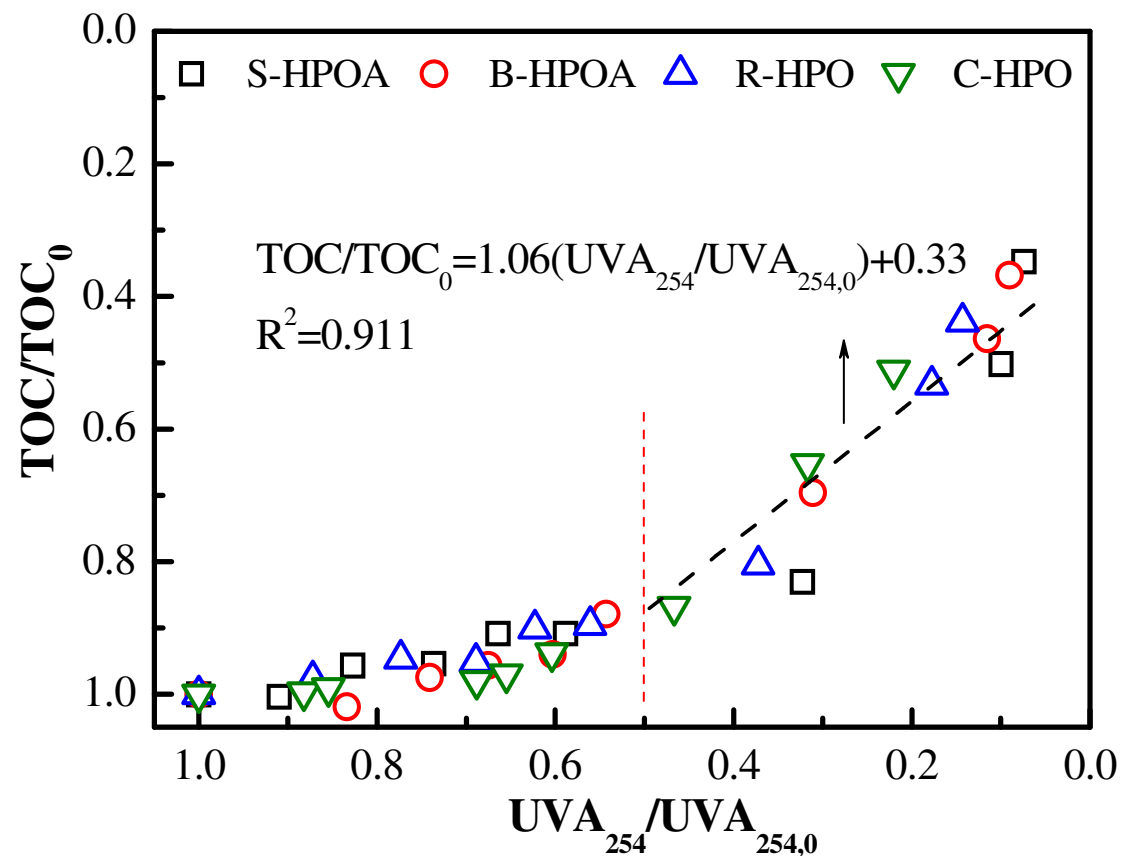
**Fig. 2.** Correlation between *pCBA* decay and PMS exposure in Co(II)/PMS system with different DOM fractions. Conditions:  $[PMS]_0 = 1.00$  mM;  $Co(II) = 1.00$   $\mu$ M;  $[pCBA]_0 = 1.00$   $\mu$ M; DOM =  $3.90 \pm 0.11$  mgC/L; pH =  $8.00 \pm 0.05$  (10 mM borate buffer); T = 20°C.



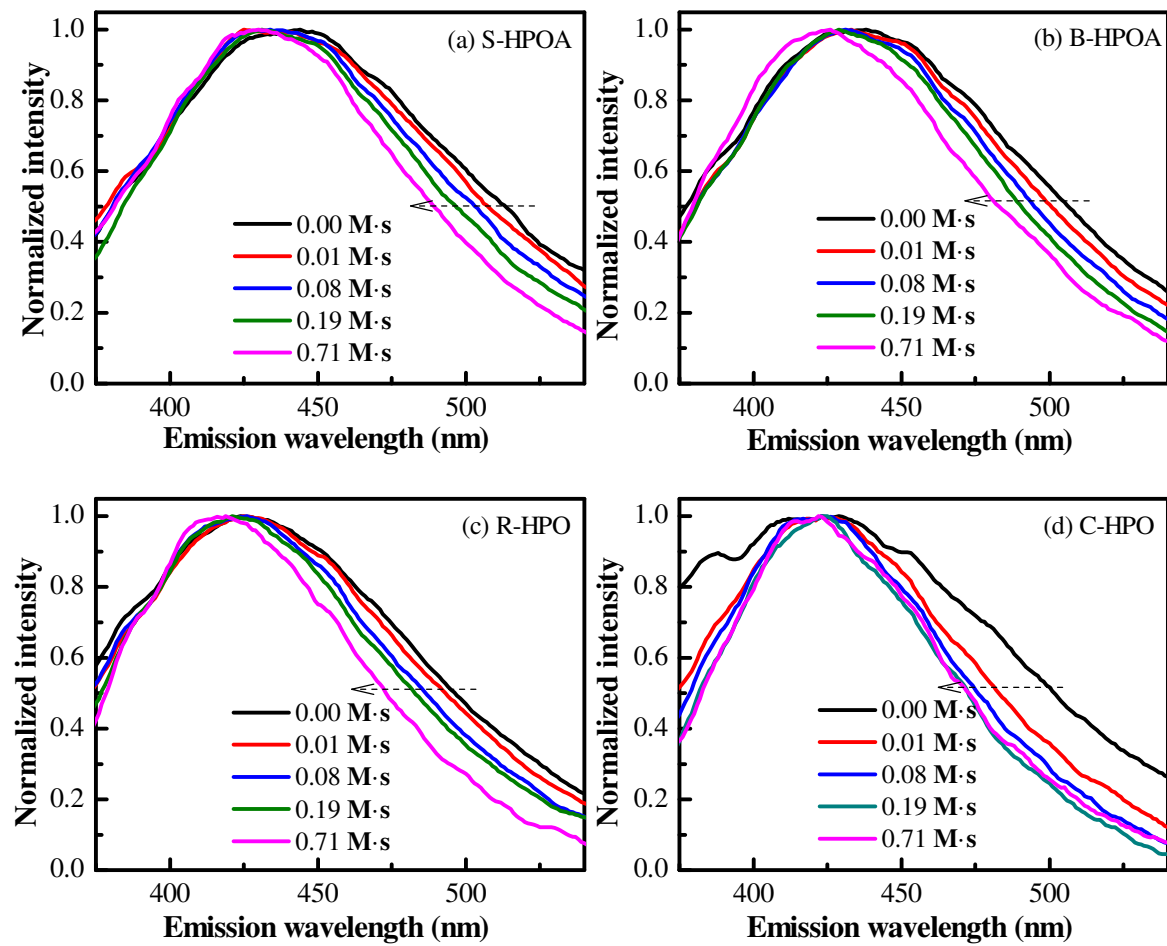
**Fig. 3.** Correlation between  $CDOM_{fast}$  decrease and PMS exposure in Co(II)/PMS system. Conditions:  $[PMS]_0 = 1.00$  mM;  $Co(II) = 1.00$   $\mu$ M;  $[pCBA]_0 = 1.00$   $\mu$ M;  $DOM = 3.90 \pm 0.11$  mgC/L;  $pH = 8.00 \pm 0.05$  (10 mM borate buffer);  $T = 20^\circ C$ .



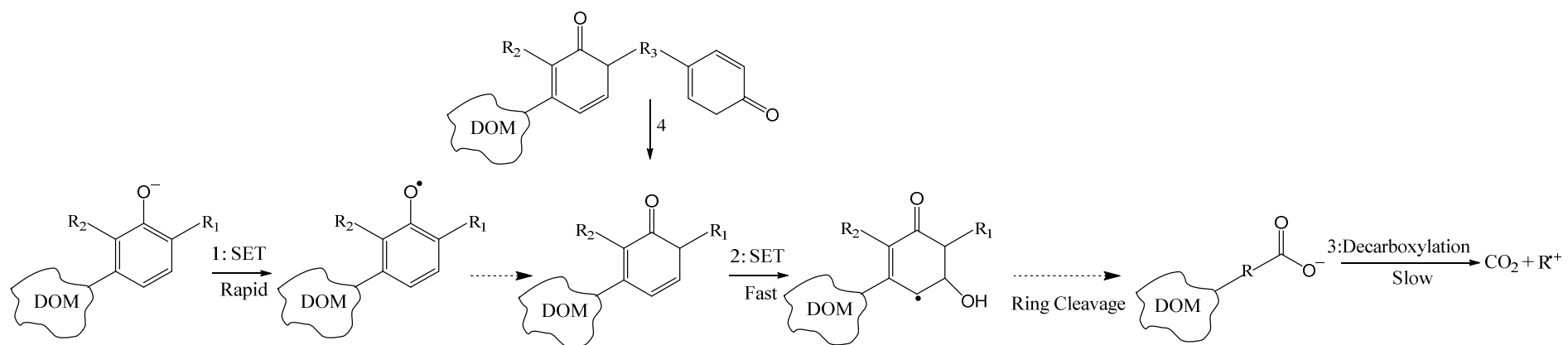
**Fig. 4.** Correlation between normalized UVA<sub>254</sub> and EDC decrease of different DOM fractions in Co(II)/PMS reaction system. Conditions: PMS exposure = 0.00–8.04 M·s; Co(II) = 1.00 μM; DOM = 3.90 ± 0.11 mgC/L; pH = 8.00 ± 0.05 (10 mM borate buffer); T = 20°C. Areas a<sub>0</sub>, a<sub>1</sub>, and b illustrated the results obtained with a PMS exposure lower than 0.01, lower than 0.1, and larger than 0.1 M·s, respectively. R<sub>E</sub> and R<sub>U</sub> represented the normalized removal efficiency in EDC and UVA<sub>254</sub>.



**Fig. 5.** TOC removal as a function of  $UVA_{254}$  decrease. Conditions: PMS exposure = 0.00–8.04 M·s;  $Co(II) = 1.00 \mu M$ ;  $DOM = 3.90 \pm 0.11 \text{ mgC/L}$ ;  $pH = 8.00 \pm 0.05$  (10 mM borate buffer);  $T = 20^\circ C$ . Red dashed line was drawn to differentiate the correlation between  $CDOM_{fast}$  and  $CDOM_{slow}$  with TOC removal.



**Fig. 6.** Normalized emission spectra by its respective maximum fluorescence intensity of (a) S-HPOA, (b) B-HPOA, (d) R-HPO, and (d) C-HPO at an excitation wavelength of 230nm. The legend in each figure represented various PMS exposures.



**Fig. 7.** Proposed pathway of sulfate radical-induced DOM transformation

**Table 1.**  $R_{ct}$  values in different DOM-containing systems under PMS exposure higher than 0.1 M·s ( $\ln(pCBA/pCBA_0) = -A([PMS]_0 \int_0^t e^{-kt} dt) + B$ ,  $R^2; R_{ct} = A/k_{SO_4^{\cdot-}, pCBA}$ )

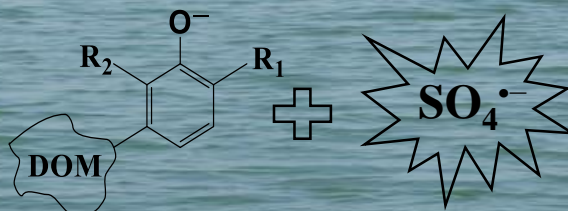
DOM fraction	A	$R_{ct}$	$R^2$
S-HPOA	0.588	$1.55 \times 10^{-9}$	0.935
B-HPOA	0.701	$1.95 \times 10^{-9}$	0.970
R-HPO	0.670	$1.86 \times 10^{-9}$	0.990
C-HPO	1.107	$3.08 \times 10^{-9}$	0.968

Suwannee River, USA

SUVA: 4.78

Beaufort Reservoir, France

SUVA: 4.06

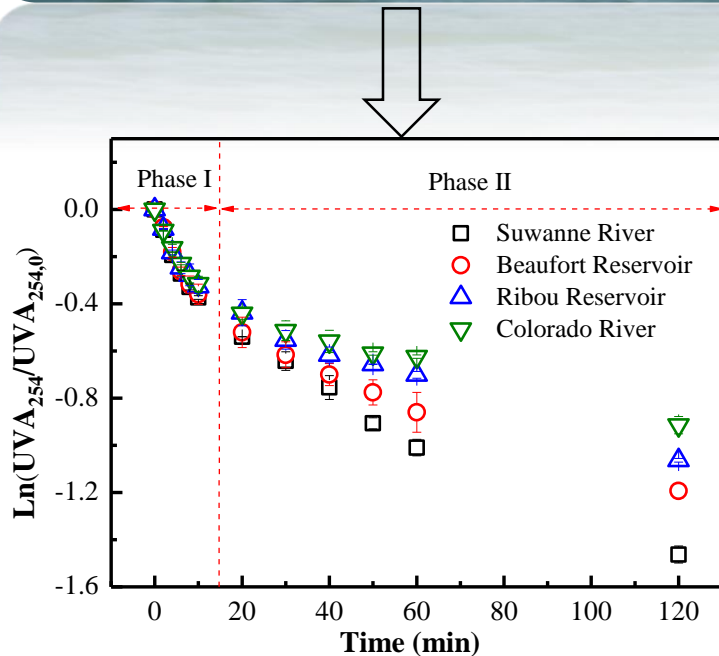


Ribou Reservoir, France

SUVA: 3.22

Colorado River, USA

SUVA: 2.14



Phase I: CDOM<sub>fast</sub>

$$k_{CDOM_{fast}, SO_4^{\bullet-}} \sim 10^8 M^{-1} s^{-1}$$

Phase II: CDOM<sub>slow</sub>

*Carbon removal*