

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

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Submission to Water Research

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3	Reactivity of chromophoric dissolved organic matter (CDOM) to sulfate
4	radicals: Reaction kinetics and structural transformation
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By Zhang et al

22 Abstract

23 Sulfate radical (SO₄⁻⁻) has been extensively studied as a promising alternative in advanced oxidation processes (AOPs) for water treatment. However, little is known about its reactivity 24 25 to the ubiquitous dissolved organic matter (DOM) in water bodies. SO₄^{•-} would selectively react with electron rich moieties in DOM, known as chromophoric DOM (CDOM), due to its 26 27 light absorbing property. In this study, the reactivity and typical structural transformation of CDOM with SO₄⁻⁻ was investigated. Four well characterized hydrophobic DOM fractions 28 29 extracted from different surface water sources were selected as model CDOM. SO4⁻⁻ was produced through the activation of peroxymonosulfate (PMS) by Co(II) ions at pH 8 in borate 30 31 buffer. The reactivity of CDOM was studied based on the decrease in its ultraviolet 32 absorbance at 254 nm (UVA₂₅₄) as a function of time. The reactivity of CDOM changed with 33 time where fast and slow reacting CDOMs (i.e., CDOM_{fast} and CDOM_{slow}) were clearly distinguished. A second-order rate constant of CDOM_{fast} with SO4^{•-} was calculated by 34 35 plotting UVA₂₅₄ decrease versus PMS exposure; where a R_{ct} value (i.e., ratio of sulfate radical to PMS exposure) was calculated using pCBA as a probe compound. The transformation of 36 37 CDOM was studied through the analysis of the changes in UVA₂₅₄, electron donating capacity, fluorescence intensity, and total organic carbon. A transformation pathway leading to a 38 significant carbon removal was proposed. This new knowledge on the kinetics and 39 transformation of CDOM would ultimately assist in the development and operation of 40 SO₄^{•–}-based water treatment processes. 41

2

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

44 **1. Introduction**

Sulfate radical (SO₄⁻⁻)-based advanced oxidation processes (AOPs) have gained increasing 45 interest in water treatment at both fundamental and applied levels (Siegrist et al. 2011, 46 47 Wacławek et al. 2017). Due to its comparable or even stronger oxidizing capabilities than 'OH. SO4⁻⁻ is also capable of degrading a broad spectrum of trace organic contaminants 48 49 (TOrCs) (e.g., pharmaceuticals, personal care products, and industrial chemicals) which are constantly detected in water bodies (Ghauch et al. 2017, Lutze et al. 2015a). A strong 50 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 SO₄^{•-} a promising alternative for 54 contaminants removal.

Previous studies focusing on the removal of TOrCs by SO₄^{•-} have provided key mechanistic 55 and kinetic insights (Yang et al. 2019, Nihemaiti et al. 2018, Yang et al. 2017). However, little 56 57 is known about the SO4^{•-}-induced reactivity and transformation of dissolved organic matter (i.e., DOM, a highly heterogeneous mixture of organic molecules ubiquitous in aquatic 58 59 environments, and playing multiple key roles in water treatment) (Lutze et al. 2015a, Varanasi et al. 2018, Leenheer and Croué 2003). Briefly, the presence of DOM is known to 60 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 fouling by applying SO₄⁻⁻-based AOPs as a pretreatment strategy (Chu et al. 2015, Xie et al. 63 2015, Cheng et al. 2017, Tian et al. 2018). Therefore, an advanced knowledge on 64

SO4⁻⁻-induced reactivity and transformation of DOM is crucial to different water treatment
processes considering its ubiquitous presence and the promising application of SO4⁻⁻-based
techniques.

The reactivity of DOM with oxidants such as chlorine, ozone, and 'OH has been extensively 68 investigated. The difference in reactivity (i.e., faster reaction rate at the initial oxidation phase 69 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 'OH non-selectively reacts with target substances, SO₄^{•-} mainly reacts with electron rich aromatic or conjugated double bond moieties (Varanasi et al. 2018). 73 74 This reactive DOM fraction has been termed as chromophoric dissolved organic matter (CDOM) due to its light absorbing property (Leenheer and Croué 2003, Lee et al. 2006). 75 Therefore, the degradation rate of CDOM, as measured by ultraviolet absorbance at 254 nm 76 (UVA_{254}) (Westerhoff et al. 2007), could be used to determine its reactivity to SO₄⁻⁻. 77

A detailed study on the transformation of DOM, as a result of its reactivity to SO₄⁻⁻, remains 78 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 SO₄⁻⁻-induced changes of typical DOM characteristics, e.g., electron donating capacity 81 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 transformation of DOM with 'OH was conducted by tracking the changes in chromophoric 84 85 and fluorescent properties (Sarathy and Mohseni 2008). Specifically, the partial oxidation

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 SO4 , 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 SO4 ^{•-} . The reactivity of CDOM was studied by following the
92	decrease of its UVA ₂₅₄ with time. A second order rate constant of fast reacting CDOM was
93	calculated based on an established correlation between UVA254 and radical exposure. By
94	recording the changes in UVA254, 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 SO_4 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.

101 **2. Materials and method**

102 **2.1 Chemical reagents and DOM fractions**

103 Peroxomonosufate (Oxone, $KHSO_5 \cdot 0.5 KHSO_4 \cdot 0.5 K_2 SO_4),$ 2,2'-azinobis 104 (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS; >98%), cobalt(II) sulfate $(\geq 99.0\%)$, sodium tetraborate $(\geq 99.5\%)$, ethanol $(\geq 99.5\%)$, and *tert*-butanol (pure) were 105 106 purchased from Sigma-Aldrich and prepared with Ultrapure water (PURELAB Ultra, ELGA). 107 Sulfuric acid of HPLC grade and sodium thiosulfate (Na₂S₂O₃) were purchased from UNIVAR. p-chlorobenzoic acid (pCBA, Acros Organics) was dissolved in ultrapure water to 108 109 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 of the stock solution was monitored on a daily basis prior to use. 111

Four DOM fractions previously isolated and characterized were selected for this study: Hydrophobic acids (i.e., DOM adsorbed onto XAD-8[®] resin at acid pH and eluted with sodium hydroxide) extracted from Suwannee River water (S-HPOA, USA) and Beaufort Reservoir (B-HPOA, France); hydrophobic DOM (i.e., similar protocol using a mixture of water and acetonitrile for resin elution) isolated from Ribou Reservoir NOM (R-HPO, France) and Colorado River (C-HPO, USA). The characteristics of the DOM isolates were 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 μ M of Co(II) at pH 8. 123 Instead of phosphate buffer, tetraborate was used as a buffer solution due to the reported complexing ability of the former with cobalt. A pH 8 buffer was used due to its improved 124 buffering capacity upon the addition of PMS at high concentrations. 125 The experiments for CDOM reaction kinetics were started by introducing 1 mM PMS. The 126 127 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 tert-butanol at different concentrations (1 or 10 mM) were used as radical quenching agents, 129 130 while pCBA (10 μ 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 of PMS residual and UV absorbance at 254 nm (UVA₂₅₄) without the addition of quenching 132 133 agent. The value of UVA₂₅₄ was further corrected by subtracting the interferences from borate buffer (i.e., including H₂SO₄ for pH adjustment), CoSO₄, and PMS. Also, the contribution of 134 135 PMS at each sampling time was calculated based on the residual PMS concentration and its ϵ_{254nm} measured in this study (12.3 M⁻¹cm⁻¹). For samples subjected to pCBA analysis, the 136 137 reaction was stopped by adding 0.1 mL of ethanol (10 M) to 0.9 mL of sample. Sodium thiosulfate was found inefficient in quenching residual PMS with concentrations as high as 138 139 600 mM.

In order to avoid the interference of quenchers on Electron Donating Capacity (EDC)
measurements, a new set of experiments was performed by using various initial PMS
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 (20°C) in glass bottles installed on a rotary shaker (Ika-Werke GMBH & Co. (KG), 145 Labortechnik KS250 Basic) operated at 500 rpm. 146 147 2.3. Analytical methods 148 2.3.1 Analysis of residual PMS The concentration of PMS was measured by an ABTS*+-based method described elsewhere 149 (Zhang et al. 2016). In this method, ABTS⁺⁺ is generated during the oxidation of ABTS by 150 151 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 $0.2 \text{ mL of CoSO}_4 (20 \text{ mM})$, 10 mL of H₂SO₄ (2%), and 1 mL of water sample was well mixed

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 CoSO₄ (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⁺⁺ was produced by the oxidation of ABTS with sodium

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

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

Fluorescence excitation and emission matrices (EEMs) were obtained using a Fluorescence spectrometer (Cary Eclipse, Varian). The operating parameters were adjusted based on the method from Chen et al (Chen et al. 2003). Briefly, the scan rate and excitation or emission slit bandwidth were set at 600 nm/min and 5nm, respectively. The spectra were recorded by scanning an emission spectra from 290 nm to 550 nm at a 5nm increment with the excitation 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- μ m reverse phase column (AlltimaTM, 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**

The reaction of CDOM with PMS led to an average decrease of 11% in UVA₂₅₄ within 60 188 min (Fig. S2). However, the decrease of UVA254 was remarkably faster in the presence of 189 190 both PMS and Co(II) (Fig. 1). Approximately 55% to 70% decrease in UVA₂₅₄ (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., SO₄⁻) in the Co(II)/PMS system, while the slight UVA254 decrease in the absence of Co(II) catalyst was 193 194 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 throughout the oxidation process (Fig. 1). Specifically, the pseudo-first-order rate constants of 199 200 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_4 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, -NH₃, -OCH₃) exhibited higher reactivity to SO₄^{•-} (Luo et al. 2017); these structures 205 could represent the main contributor to the fast reacting CDOM (i.e., CDOM_{fast}). The slow

reacting CDOM (i.e., CDOM_{slow}) might include lower electron density moieties from the original CDOM constituents as well as the oxidation products of $CDOM_{fast}$ (Xiao et al. 2015, Zhang et al. 2012).

The influence of the aromatic character of the DOM fractions on their reactivity with SO4⁻⁻ 209 was highly expected based on previous findings (Westerhoff et al. 2004, Luo et al. 2017). 210 211 However, the difference in reactivity among the four DOM fractions was more significant during the slow reaction phase. The pseudo-first-order reaction rates of CDOM_{slow} (i.e., 212 $\ln(UVA_{254}/UVA_{254,0})$ versus reaction time) were calculated as 1.20×10^{-2} , 0.84×10^{-2} , 0.63×10^{-2} 213 ², and 0.46×10⁻² min⁻¹ for S-HPOA, B-HPOA, R-HPO and C-HPO, respectively. These 214 215 CDOM_{slow} reactivities linearly increased with the SUVA values as shown in Fig. S3. The 216 CDOM_{fast} reactivity to SO₄^{•-} 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 SO₄⁻⁻ (eq. 1) over 'OH in Co(II)-catalyzed PMS systems at pH 7. Because a pH 8 may 221 promote a higher production of 'OH (eq. 2), the identification of major oxidizing species in the current system was conducted by following the degradation of pCBA as a probe 222 223 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 'OH and SO₄⁻⁻ were summarized in table S3. When 10 mM of radical scavenger (i.e., t-BuOH or EtOH, at a molar 225 226 ratio of 1000:1 versus pCBA) was applied, the pCBA removal efficiency was decreased by

227 approximately 10% in the presence of t-BuOH; while almost no pCBA decrease was observed 228 with the addition of EtOH (Fig. S4). Quantitatively, the ratio of the measured concentration of 'OH to SO₄'-was lower than 3%. These results indicated that SO₄'- was the predominant 229 reactive species at pH 8. This is probably due to the competition for SO₄⁻⁻ by either pCBA 230 $(3.6 \times 10^8 \text{ M}^{-1} \text{s}^{-1})$ or scavengers (i.e., DOM fractions, up to $10^8 \text{ M}^{-1} \text{s}^{-1}$ as discussed below), 231 232 leading to the unfavorable production of 'OH (eq 2). $HSO_{5}^{-} + Co^{2+} = SO_{4}^{\bullet-} + Co^{3+} + OH^{-}$ 233 234 (1) $SO_4^{\bullet-} + OH^- = SO_4^- + {}^{\bullet}OH(k_{SO_4^{\bullet-}, OH^-} = 6.5 \times 10^7 M^{-1} s^{-1})$ 235 236 (2)

237
$$HSO_5^- + Co^{3+} = SO_5^{\bullet-} + Co^{2+} + H^+$$

238 (3)

Therefore, the production of SO4⁻⁻ was investigated following the R_{ct} concept and the 239 analysis of *p*CBA decay. R_{ct} (i.e., the ratio of radical exposure to oxidant exposure) (Elovitz 240 and von Gunten 1999) was used to present the production of SO₄^{•-} with PMS exposure (eq. 241 242 4). According to Elovitz and von Gunten (Elovitz and von Gunten 1999), the consumption of radicals by a probe compound (P) (e.g., pCBA in the current study) is considered 243 insignificant as compared to major radical scavengers (S) (e.g., DOM in current study) if the 244 245 probe compound is present at a considerably low concentration (i.e., $k_{\rm P}[{\rm P}] \leq k_{\rm S}[{\rm S}]$, where $k_{\rm P}$ and $k_{\rm S}$ represents the rate constants of the probe compound and major radical scavengers with 246 247 radicals, respectively). Therefore, a low pCBA concentration (i.e., 1 μ M) was applied to

248	ensure an insignificant radical consumption by p CBA as compared to DOM. Specifically,
249	$k_{pCBA}[pCBA]$ was calculated as approximately 1.4% of $k_{DOM}[DOM]$ under the current
250	experimental condition, where k_{pCBA} and k_{DOM} represent the second order rate constants of
251	pCBA (3.6 × 10 ⁸ M ⁻¹ s ⁻¹) and DOM (6.8 × 10 ³ LmgC ⁻¹ s ⁻¹) with SO ₄ ^{•-} , respectively. The R _{ct}
252	value was only studied for the first 10 min of the reaction. $CDOM_{fast}$ 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 UVA254 or EDC measurements, the rate of catalytic PMS decomposition decreased (Fig. S5) due to the formation of cobalt-DOM 256 257 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-, R-HPO-, and C-HPO-containing system were 41%, 43%, 40%, and 43%, respectively. 259 Specifically, approximately 80% of Co(II) was calculated as forming complexes with DOM 260 261 under the current experimental conditions using the NICA-Donnan model with the constants adapted from Milne et al. (Milne et al. 2003). In DOM-containing solutions with the addition 262 263 of *p*CBA as probe compound, PMS decomposed following a pseudo-first-order reaction (Fig. S6a), as described by (eq. 5), and k (i.e., pseudo-first-order rate constant) was measured as 264 approximately $3.0 \times 10^{-4} \text{s}^{-1}$ independent of DOM origins. The influence of *p*CBA addition (1) 265 266 µM) on PMS decomposition was negligible. For instance, the averaged PMS residual measured in different DOM-containing systems within 10 min was 80% in the absence of 267 268 pCBA (Figure S5) and 79% in the presence of pCBA (Figure S6a). The determined rate

286

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). The degradation of pCBA (Fig. S6b) caused by $SO_4^{\bullet-}$ was described by eq. 6 and 7. By 271 272 combining eq. 4 and 5, *p*CBA degradation could be described using the R_{ct} concept (eq. 8). $R_{ct} = \frac{\int_0^t [SO_4^{\bullet-}] dt}{\int_0^t [PMS] dt}$ 273 274 (4)275 $[PMS] = [PMS]_0 e^{-kt}$ 276 (5) $-\frac{d[pCBA]}{dt} = k_{SO_4^{\bullet}, pCBA}[pCBA][SO_4^{\bullet}]$ 277 278 (6) $\ln \frac{[pCBA]}{[pCBA]_0} = -k_{SO_4^{\bullet}, pCBA} \int_0^t [SO_4^{\bullet}] dt$ 279 280 (7) $\ln \frac{[pCBA]}{[pCBA]_0} = -k_{SO_4, \text{c}, pCBA} R_{ct} [PMS]_0 \int_0^t e^{-kt} dt$ 281 282 (8) By plotting ln (pCBA/pCBA₀) versus PMS exposure, linear correlations were observed as a 283 284 function of PMS exposures (Fig. 2). The R_{ct} value at PMS exposures higher than 0.1 M·s (i.e.

a reaction time of 2–10 min, table S4) for each system was determined from the slope of the

exposures lower than 0.1 M·s (i.e. a reaction time of 0-2 min, table S4) were shown in Fig.

linear regression line (Fig. 2) and listed in Table 1; while the higher R_{ct} values at PMS

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	1.6×10^{-44}), leading to the retardation of the regeneration process and consequently to a
296	slower SO4 production. Moreover, the additional PMS consumption during the regeneration
297	of Co(II) (eq. 3), which inefficiently produced SO ₅ (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**_{fast} to SO₄⁻⁻ and its application

Following the procedures for establishing a relationship between ln ($pCBA/pCBA_0$) and PMS exposure (eq. 8), i.e., obtained by combining eq.(4), eq.(5) and eq.(7)), a similar correlation was also established between ln(UVA₂₅₄/UVA_{254,0}) of CDOM_{fast} and PMS exposure (eq. 9). This correlation was found linear when ln(UVA₂₅₄/UVA_{254,0}) of CDOM_{fast} was plotted against PMS exposure for all DOM fractions (Fig. 3). The good linearity allowed the calculation of the reaction rate constant of CDOM_{fast} with SO₄^{*-} using the R_{ct} value determined in Section 3.2.

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

320 (9)

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

331 Carl Roth) using an indirect kinetic competition method; while Zhou et al. (Zhou et al. 2017) recorded a rate of 1.86×10^3 LmgC⁻¹s⁻¹ for Suwannee River fulvic acid using a direct laser 332 333 flash photolysis method. The difference could be attributed to the fact that the value in this study was only measured for the conceptually isolated fast reacting moieties (i.e., CDOM_{fast}) 334 rather than for the bulk DOM (i.e., a combination of both fast and slow reacting moieties). 335 336 However, the value was one order of magnitude lower than those reported for aromatic compounds ($\sim 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Neta et al. 1977, Fischer and Radom 2001). This difference would 337 be the result of stronger electrosteric repulsion between SO₄^{•-} and structurally complex DOM 338 as compared to simpler organic compounds. The higher reactivity of sulfate radicals to 339 340 $CDOM_{fast}$ than to OH^{-} (~10⁷M⁻¹s⁻¹) was expected to lead to an insignificant production of 'OH (eq. 2) due to its unfavorable formation kinetics. In addition, CDOM_{fast} would be 341 342 preferred to bulk DOM when evaluating the scavenging property of dissolved organic matter in SO4^{•-}-based AOPs under lower PMS exposures, where CDOM_{fast} was the major reactive 343 344 moieties (Fig. 1).

The use of UVA₂₅₄ as a surrogate indicator for the assessment of TOrCs removal efficiency has been extensively studied in ozone- and 'OH-based AOPs (Gerrity et al. 2012, Rosario-Ortiz et al. 2010, Li et al. 2017). This finding could also support its application in SO_4 --based water treatment processes. The study on TOrCs removal efficiency could be achieved using either: i) the kinetics with second order reaction constants of TOrCs and radical exposure (eq. 10), or ii) the correlation established between UVA₂₅₄ decrease and contaminants removal (eq. 11).

352
$$\ln \frac{[TOrCs]}{[TOrCs]_0} = -k_{SO_4^{-}, TOCs} \int_0^t SO_4^{-} dt = -k_{SO_4^{-}, TOCs} \ln \frac{[UVA_{254}]}{[UVA_{254}]_0} / -k_{SO_4^{-}, CDOM}$$
(10)

353
$$\ln \frac{[T \text{OrCs}]}{[T \text{OrCs}]_0} = Slope \times \ln \frac{[U V A_{254}]}{[U V A_{254}]_0} + Intercept$$
(11)

354 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 355 lower capital/operating cost as well as time input. Especially, with the use of an on-line 356 357 spectrophotometer, a quick track of the oxidation efficiency and consequently a rapid 358 adjustment (i.e., oxidant dose or contact time) could also be expected. However, different 359 correlation models should be established for different TOrCs due to the discrepancy in their 360 reactivity. The successful application of this correlation could also be impacted by the 361 fluctuation of water matrices (e.g., HCO₃⁻, NO₃⁻, or Cl⁻) or temperature due to seasonal 362 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 UVA₂₅₄ and fluorescence intensity with increasing PMS concentration (Text S1). Consequently, the UVA₂₅₄ parameter was sufficient as a single process indicator in this SO₄⁻⁻-based oxidation system.

369 **3.4 Sulfate radical-induced CDOM transformation**

- 370 3.4.1 EDC decrease as a function of PMS exposures
- 371

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 ₂₅₄ (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_1), an average of 54% decrease of EDC was
380	recorded when only a 30% decrease of UVA $_{254}$ was observed. For PMS exposures higher
381	than 0.1 M·s (Area b), the averaged normalized UVA $_{254}$ 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 ₂₅₄ at PMS exposure lower than 0.1 M·s in
384	this system indicated that the initial phase of $SO_4^{\bullet-}$ 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 ₂
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 UVA₂₅₄ was observed with a PMS exposure lower than 0.01 M·s (Area a_0 , Fig. 4), which was 394 probably caused by the relatively higher R_{ct} observed under this condition (Fig. S7). 395 Due to a major SO₄⁻⁻consumption by the moieties with EDC at the initial oxidation phase 396 (i.e., PMS exposure < 0.1 M·s), a UVA₂₅₄ decrease was not enhanced even under higher 397 radical exposure (i.e., higher R_{ct}) (Fig. 3). This result supported the selection of lower R_{ct} 398 values (Fig. 2) in the calculation of the second-order rate constants of CDOM_{fast} with SO₄⁻⁻ as
- 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, 64%, 63%, 56%, 49% for S-HPOA, B-HPOA, R-HPO and C-HPO, respectively (i.e., 58% in 404 405 average), was observed under a PMS exposure of 8.04 M·s (Fig. S10). The relationship 406 between UVA₂₅₄ decrease and TOC removal was established and shown in Fig. 5. Interestingly, the TOC removal was minor (i.e., less 10%) during the depletion of the UV 407 408 absorbance of CDOM_{fast} (i.e., UVA₂₅₄ decrease within 50%, as indicated by the red dashed line in Fig. 5). However, the decrease in the chromophoric property of CDOM_{slow} (i.e., 409 observed when UVA₂₅₄ decrease was larger than 50%, right side of the red dashed line in Fig. 410 411 5) led to a considerable TOC removal. These results indicated that the reaction of CDOM_{fast} 412 would mainly lead to the breakdown of complex aromatic structures into small molecular weight fractions with insignificant mineralization. This transformation from larger molecules 413

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

420

Fig. 6.

Interestingly, a good linearity between UVA₂₅₄ decrease and TOC removal during the 421 422 CDOM_{slow} decrease was observed (Fig. 5). These results indicated that the change in 423 CDOM_{slow} could be used in the prediction of TOC removal for surface water during SO4^{•-}-based treatment. This may include water treatment processes targeting the removal of 424 425 organics, e.g., pretreatment for the removal of disinfection byproducts precursors or 426 membranes foulants, membrane cleaning, and the treatment of reverse osmosis concentrates. Nevertheless, under different water matrices this correlation might be affected by pH 427 428 conditions, or the presence of radical scavengers HCO_3^- or Cl^- .

429 3.4.3 Evolution of CDOM transformation with sulfate radical

Based on the findings of this study (i.e., results obtained with the current characterization
techniques), the evolution of the transformation of CDOM by sulfate radicals was
summarized in Fig. 7. The SO4^{•-}-induced reaction of CDOM_{fast}, (i.e., electron donating group
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 ₃ 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 $\text{CDOM}_{\text{slow}}$
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 _{fast} among different organics
455		were minor, while the reactivity $\text{CDOM}_{\text{slow}}$ were observed to increase with SUVA.
456	•	The reactivity of CDOM _{fast} to $SO_4^{\bullet-}$ was calculated at an order of $10^8 \text{ M}^{-1} \text{s}^{-1}$ from the
457		observed linear correlation between CDOM _{fast} decrease and sulfate radical exposure.
458		The correlation also validated the potential application of UVA ₂₅₄ as a surrogate
459		indicator for TOrCs removal efficiency.
460	•	A faster decrease of EDC than UVA ₂₅₄ 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 $CDOM_{fast}$ would proceed with the formation of
463		transient intermediates and ring cleavage products.
464	•	The transformation products of CDOM _{fast} together with the originally less reactive
465		structures, i.e., $CDOM_{slow}$, would undergo slow decarboxylation leading to a
466		significant carbon removal. The linear relationship recorded between CDOM _{slow}

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_4^{-} - based water 469 treatment processes. Specifically, the scavenging capacity of background DOM could be better 470 evaluated using the calculated reactivity of $CDOM_{fast}$ if the applied PMS exposure would 471 mainly cause changes in $CDOM_{fast}$. Also, the correlation established between CDOM and 472 radical exposure would shed light on the applicability of UVA_{254} as an indicator of TOrCs

473	removal efficiency in SO4 ^{•-} -based water treatment processes. However, further site-specific
474	studies on the use of UVA ₂₅₄ as an indicator are highly needed for its successful application.
475	SO4 ^{•-} -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 CDOM _{slow} and consequently increase carbon removal.
481	In addition, carbon removal efficiency could be simply estimated based on the removal of
482	CDOM _{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 Word488 document (Supplementary Information).

489 **References**

- Siegrist, R.L., Crimi, M. and Simpkin, T.J. (2011) In situ chemical oxidation for groundwater
 remediation, Springer Science & Business Media.
- Wacławek, S., Lutze, H.V., Grübel, K., Padil, V.V.T., Černík, M. and Dionysiou, D.D. (2017)
 Chemistry of persulfates in water and wastewater treatment: A review. Chemical
 Engineering Journal 330, 44-62.
- Ghauch, A., Baalbaki, A., Amasha, M., El Asmar, R. and Tantawi, O. (2017) Contribution of
 persulfate in UV-254 nm activated systems for complete degradation of chloramphenicol
 antibiotic in water. Chemical Engineering Journal 317, 1012-1025.
- Lutze, H.V., Bircher, S., Rapp, I., Kerlin, N., Bakkour, R., Geisler, M., von Sonntag, C. and
 Schmidt, T.C. (2015a) Degradation of Chlorotriazine Pesticides by Sulfate Radicals and
 the Influence of Organic Matter. Environmental Science & Technology 49(3), 1673-1680.
- Wang, Y., Le Roux, J., Zhang, T. and Croué, J.-P. (2014) Formation of Brominated
 Disinfection Byproducts from Natural Organic Matter Isolates and Model Compounds in
 a Sulfate Radical-Based Oxidation Process. Environmental Science & Technology 48(24),
 14534-14542.
- Yang, Y., Cao, Y., Jiang, J., Lu, X., Ma, J., Pang, S., Li, J., Liu, Y., Zhou, Y. and Guan, C.
 (2019) Comparative study on degradation of propranolol and formation of oxidation
 products by UV/H2O2 and UV/persulfate (PDS). Water Research 149, 543-552.
- Nihemaiti, M., Miklos, D.B., Hübner, U., Linden, K.G., Drewes, J.E. and Croué, J.-P. (2018)
 Removal of trace organic chemicals in wastewater effluent by UV/H2O2 and UV/PDS.
 Water Research 145, 487-497.
- Yang, Y., Lu, X., Jiang, J., Ma, J., Liu, G., Cao, Y., Liu, W., Li, J., Pang, S., Kong, X. and Luo,
 C. (2017) Degradation of sulfamethoxazole by UV, UV/H2O2 and UV/persulfate (PDS):
 Formation of oxidation products and effect of bicarbonate. Water Research 118, 196-207.
- Varanasi, L., Coscarelli, E., Khaksari, M., Mazzoleni, L.R. and Minakata, D. (2018)
 Transformations of dissolved organic matter induced by UV photolysis, Hydroxyl
 radicals, chlorine radicals, and sulfate radicals in aqueous-phase UV-Based advanced
 oxidation processes. Water Research 135, 22-30.
- Leenheer, J.A. and Croué, J.-P. (2003) Peer Reviewed: Characterizing Aquatic Dissolved
 Organic Matter. Environmental Science & Technology 37(1), 18A-26A.
- 520 Chu, W., Li, D., Gao, N., Templeton, M.R., Tan, C. and Gao, Y. (2015) The control of
 521 emerging haloacetamide DBP precursors with UV/persulfate treatment. Water Research
 522 72, 340-348.
- Xie, P., Ma, J., Liu, W., Zou, J. and Yue, S. (2015) Impact of UV/persulfate pretreatment on
 the formation of disinfection byproducts during subsequent chlorination of natural
 organic matter. Chemical Engineering Journal 269, 203-211.
- 526 Cheng, X., Liang, H., Ding, A., Tang, X., Liu, B., Zhu, X., Gan, Z., Wu, D. and Li, G. (2017)
 527 Ferrous iron/peroxymonosulfate oxidation as a pretreatment for ceramic ultrafiltration
 528 membrane: Control of natural organic matter fouling and degradation of atrazine. Water
 529 Research 113, 32-41.

- Tian, J., Wu, C., Yu, H., Gao, S., Li, G., Cui, F. and Qu, F. (2018) Applying
 ultraviolet/persulfate (UV/PS) pre-oxidation for controlling ultrafiltration membrane
 fouling by natural organic matter (NOM) in surface water. Water Research 132, 190-199.
- 533 Chon, K., Salhi, E. and von Gunten, U. (2015) Combination of UV absorbance and electron
 534 donating capacity to assess degradation of micropollutants and formation of bromate
 535 during ozonation of wastewater effluents. Water Research 81, 388-397.
- Westerhoff, P., Chao, P. and Mash, H. (2004) Reactivity of natural organic matter with
 aqueous chlorine and bromine. Water Research 38(6), 1502-1513.
- Lee, N., Amy, G. and Croue, J.-P. (2006) Low-pressure membrane (MF/UF) fouling
 associated with allochthonous versus autochthonous natural organic matter. Water
 Research 40(12), 2357-2368.
- Westerhoff, P., Mezyk, S.P., Cooper, W.J. and Minakata, D. (2007) Electron Pulse Radiolysis
 Determination of Hydroxyl Radical Rate Constants with Suwannee River Fulvic Acid and
 Other Dissolved Organic Matter Isolates. Environmental Science & Technology 41(13),
 4640-4646.
- Li, T., Jiang, Y., An, X., Liu, H., Hu, C. and Qu, J. (2016) Transformation of humic acid and
 halogenated byproduct formation in UV-chlorine processes. Water Research 102,
 421-427.
- Wang, W.-L., Zhang, X., Wu, Q.-Y., Du, Y. and Hu, H.-Y. (2017) Degradation of natural
 organic matter by UV/chlorine oxidation: Molecular decomposition, formation of
 oxidation byproducts and cytotoxicity. Water Research 124, 251-258.
- Sarathy, S. and Mohseni, M. (2008) The fate of natural organic matter during UV/H2O2
 advanced oxidation of drinking water. Canadian Journal of Civil Engineering 36(1),
 160-169.
- Madhavan, V., Levanon, H. and Neta, P. (1978) Decarboxylation by SO[•]4– Radicals.
 Radiation Research 76(1), 15-22.
- Zhang, T., Chen, Y. and Leiknes, T. (2016) Oxidation of refractory benzothiazoles with
 PMS/CuFe2O4: kinetics and transformation intermediates. Environmental Science &
 Technology 50(11), 5864-5873.
- 559 Chen, W., Westerhoff, P., Leenheer, J.A. and Booksh, K. (2003) Fluorescence
 560 Excitation-Emission Matrix Regional Integration to Quantify Spectra for Dissolved
 561 Organic Matter. Environmental Science & Technology 37(24), 5701-5710.
- Zhou, Y., Jiang, J., Gao, Y., Ma, J., Pang, S.-Y., Li, J., Lu, X.-T. and Yuan, L.-P. (2015)
 Activation of Peroxymonosulfate by Benzoquinone: A Novel Nonradical Oxidation
 Process. Environmental Science & Technology 49(21), 12941-12950.
- 565 Cory, R.M. and McKnight, D.M. (2005) Fluorescence Spectroscopy Reveals Ubiquitous
 566 Presence of Oxidized and Reduced Quinones in Dissolved Organic Matter.
 567 Environmental Science & Technology 39(21), 8142-8149.
- Luo, S., Wei, Z., Dionysiou, D.D., Spinney, R., Hu, W.-P., Chai, L., Yang, Z., Ye, T. and Xiao,
 R. (2017) Mechanistic insight into reactivity of sulfate radical with aromatic contaminants
 through single-electron transfer pathway. Chemical Engineering Journal 327, 1056-1065.

- 571 Xiao, R., Ye, T., Wei, Z., Luo, S., Yang, Z. and Spinney, R. (2015) Quantitative Structure–
 572 Activity Relationship (QSAR) for the Oxidation of Trace Organic Contaminants by
 573 Sulfate Radical. Environmental Science & Technology 49(22), 13394-13402.
- Zhang, H., Zhang, Y., Shi, Q., Ren, S., Yu, J., Ji, F., Luo, W. and Yang, M. (2012)
 Characterization of low molecular weight dissolved natural organic matter along the
 treatment trait of a waterworks using Fourier transform ion cyclotron resonance mass
 spectrometry. Water Research 46(16), 5197-5204.
- Anipsitakis, G.P. and Dionysiou, D.D. (2003) Degradation of Organic Contaminants in Water
 with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt.
 Environmental Science & Technology 37(20), 4790-4797.
- Lutze, H.V., Kerlin, N. and Schmidt, T.C. (2015b) Sulfate radical-based water treatment in
 presence of chloride: Formation of chlorate, inter-conversion of sulfate radicals into
 hydroxyl radicals and influence of bicarbonate. Water Research 72, 349-360.
- Elovitz, M.S. and von Gunten, U. (1999) Hydroxyl Radical/Ozone Ratios During Ozonation
 Processes. I. The Rct Concept. Ozone: Science & Engineering 21(3), 239-260.
- 586 Milne, C.J., Kinniburgh, D.G., Van Riemsdijk, W.H. and Tipping, E. (2003) Generic NICA–
 587 Donnan model parameters for metal-ion binding by humic substances. Environmental
 588 Science & Technology 37(5), 958-971.
- Zhang, Z. and Edwards, J.O. (1992) Chain lengths in the decomposition of
 peroxomonosulfate catalyzed by cobalt and vanadium. Rate law for catalysis by
 vanadium. Inorganic Chemistry 31(17), 3514-3517.
- 592 Neta, P., Huie, R.E. and Ross, A.B. (1988) Rate constants for reactions of inorganic radicals
 593 in aqueous solution. Journal of Physical and Chemical Reference Data 17(3), 1027-1284.
- Anipsitakis, G.P., Stathatos, E. and Dionysiou, D.D. (2005) Heterogeneous activation of
 Oxone using Co 3O 4. Journal of Physical Chemistry B 109(27), 13052-13055.
- Zhou, L., Sleiman, M., Ferronato, C., Chovelon, J.-M. and Richard, C. (2017) Reactivity of
 sulfate radicals with natural organic matters. Environmental Chemistry Letters 15(4),
 733-737.
- Neta, P., Madhavan, V., Zemel, H. and Fessenden, R.W. (1977) Rate constants and
 mechanism of reaction of sulfate radical anion with aromatic compounds. Journal of the
 American Chemical Society 99(1), 163-164.
- Fischer, H. and Radom, L. (2001) Factors Controlling the Addition of Carbon-Centered
 Radicals to Alkenes—An Experimental and Theoretical Perspective. Angewandte Chemie
 International Edition 40(8), 1340-1371.
- 605 Gerrity, D., Gamage, S., Jones, D., Korshin, G.V., Lee, Y., Pisarenko, A., Trenholm, R.A.,
 606 von Gunten, U., Wert, E.C. and Snyder, S.A. (2012) Development of surrogate correlation
 607 models to predict trace organic contaminant oxidation and microbial inactivation during
 608 ozonation. Water Research 46(19), 6257-6272.
- Rosario-Ortiz, F.L., Wert, E.C. and Snyder, S.A. (2010) Evaluation of UV/H2O2 treatment
 for the oxidation of pharmaceuticals in wastewater. Water Research 44(5), 1440-1448.
- 611 Li, W.-T., Cao, M.-J., Young, T., Ruffino, B., Dodd, M., Li, A.-M. and Korshin, G. (2017)
- 612 Application of UV absorbance and fluorescence indicators to assess the formation of

- biodegradable dissolved organic carbon and bromate during ozonation. Water Research111, 154-162.
- Aeschbacher, M., Graf, C., Schwarzenbach, R.P. and Sander, M. (2012) Antioxidant
 properties of humic substances. Environmental Science & Technology 46(9), 4916-4925.
- Ramseier, M.K. and Gunten, U.v. (2009) Mechanisms of phenol ozonation—kinetics of
 formation of primary and secondary reaction products. Ozone: Science & Engineering
 31(3), 201-215.
- Bortolomeazzi, R., Sebastianutto, N., Toniolo, R. and Pizzariello, A. (2007) Comparative
 evaluation of the antioxidant capacity of smoke flavouring phenols by crocin bleaching
 inhibition, DPPH radical scavenging and oxidation potential. Food Chemistry 100(4),
 1481-1489.
- Wenk, J., Aeschbacher, M., Salhi, E., Canonica, S., von Gunten, U. and Sander, M. (2013)
 Chemical Oxidation of Dissolved Organic Matter by Chlorine Dioxide, Chlorine, And
 Ozone: Effects on Its Optical and Antioxidant Properties. Environmental Science &
 Technology 47(19), 11147-11156.
- 628 Chen, J., Gu, B., LeBoeuf, E.J., Pan, H. and Dai, S. (2002) Spectroscopic characterization of
 629 the structural and functional properties of natural organic matter fractions. Chemosphere
 630 48(1), 59-68.
- Anipsitakis, G.P., Dionysiou, D.D. and Gonzalez, M.A. (2006) Cobalt-Mediated Activation of
 Peroxymonosulfate and Sulfate Radical Attack on Phenolic Compounds. Implications of
 Chloride Ions. Environmental Science & Technology 40(3), 1000-1007.

634

Figure captions 635 Fig. 1. UVA₂₅₄ decrease of different DOM fractions in Co(II)/PMS system as a function of 636 637 time. Conditions: $[PMS]_0 = 1.0 \text{ mM}$; Co(II) = 1.0 μ M; DOM = 3.90 \pm 0.11 mgC/L; pH 638 $= 8.00 \pm 0.05$ (10 mM borate buffer); T = 20°C. Fig. 2. Correlation between *p*CBA decay and PMS exposure in Co(II)/PMS system with 639 different DOM fractions. Conditions: $[PMS]_0 = 1.00 \text{ mM}$; Co(II) = 1.00 μ M; $[pCBA]_0$ 640 641 = 1.00 μ M; DOM = 3.90 \pm 0.11 mgC/L; pH = 8.00 \pm 0.05 (10 mM borate buffer); T = 20°C. 642 643 Fig. 3. Correlation between CDOM_{fast} decrease and PMS exposure in Co(II)/PMS system. 644 Conditions: $[PMS]_0 = 1.00 \text{ mM}$; Co(II) = 1.00 μ M; $[pCBA]_0 = 1.00 \mu$ M; DOM = 3.90 645 $\pm 0.11 \text{ mgC/L}$; pH = 8.00 $\pm 0.05(10 \text{ mM borate buffer})$; T = 20°C. 646 Fig. 4. Correlation between normalized UVA₂₅₄ and EDC decrease of different DOM 647 fractions in Co(II)/PMS system. Conditions: PMS exposure = $0.00-8.04 \text{ M} \cdot \text{s}$; Co(II) = 1.00 μ M; DOM = 3.90 \pm 0.11 mgC/L; pH = 8.00 \pm 0.05 (10 mM borate buffer); T = 648 20°C. Areas a₀, a₁, and b illustrated the results obtained with a PMS exposure lower 649 650 than 0.01, lower than 0.1, and larger than 0.1 M·s, respectively. R_E and R_U represented the normalized removal efficiency in EDC and UVA₂₅₄. 651 652 Fig. 5. TOC removal as a function of UVA₂₅₄ decrease. Conditions: PMS exposure = 0.00-8.04 M·s; Co(II) = 1.00 μ M; DOM = 3.90 \pm 0.11 mgC/L; pH = 8.00 \pm 0.05 (10 mM 653 654 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



Fig. 1. UVA₂₅₄ decrease of different DOM fractions in Co(II)/PMS system as a function of time. Conditions: $[PMS]_0 = 1.0 \text{ mM}$; Co(II) = 1.0 μ M; DOM = 3.90 \pm 0.11 mgC/L; pH = 8.00 \pm 0.05 (10 mM borate buffer); T = 20°C.



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



Fig. 4. Correlation between normalized UVA₂₅₄ and EDC decrease of different DOM fractions in Co(II)/PMS reaction system. Conditions: PMS exposure = $0.00-8.04 \text{ M} \cdot \text{s}$; Co(II) = $1.00 \mu \text{M}$; DOM = $3.90 \pm 0.11 \text{ mgC/L}$; pH = 8.00 ± 0.05 (10 mM borate buffer); T = 20° C. Areas a₀, a₁, 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_E and R_U represented the normalized removal efficiency in EDC and UVA₂₅₄.



Fig. 5. TOC removal as a function of UVA₂₅₄ decrease. Conditions: PMS exposure = $0.00-8.04 \text{ M} \cdot \text{s}$; Co(II) = 1.00μ M; DOM = $3.90 \pm 0.11 \text{ mgC/L}$; pH = 8.00 ± 0.05 (10 mM borate buffer); T = 20° C. Red dashed line was drawn to differentiate the correlation between CDOM_{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

DOM fraction	Α	Rct	R ²
S-HPOA	0.588	1.55×10^{-9}	0.935
B-HPOA	0.701	1.95×10^{-9}	0.970
R-HPO	0.670	1.86×10^{-9}	0.990
C-HPO	1.107	3.08×10^{-9}	0.968

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

