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1 Oxidation of Refractory Benzothiazoles with PMS/CuFe₂O₄:
2 Kinetics and Transformation Intermediates

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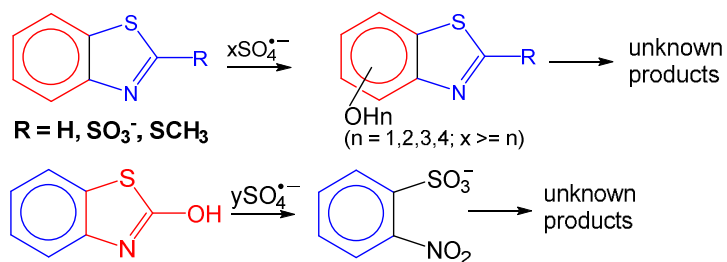
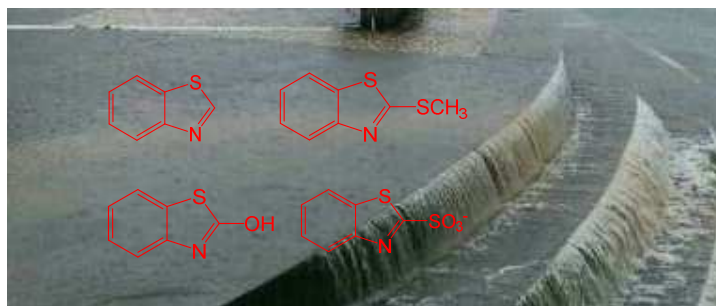
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TOC Art

17



18 ABSTRACT

19 Benzothiazole (BTH) and its derivatives, 2-(methylthio)benzothiazole (MTBT),
20 2-benzothiazolsulfonate (BTSA) and 2-hydroxybenzothiazole (OHBT), are refractory pollutants
21 ubiquitously existing in urban runoff at relatively high concentrations. Here, we report their
22 oxidation by CuFe_2O_4 -activated peroxomonosulfate (PMS/ CuFe_2O_4), focusing on kinetics and
23 transformation intermediates. These benzothiazoles can be efficiently degraded by this oxidation
24 process which is confirmed to generate mainly sulfate radicals (with negligible hydroxyl-radical
25 formation) under slightly acidic to neutral pH conditions. The molar exposure ratio of sulfate radical
26 to residual PMS (i.e. R_{ct}) of this process is a constant which is related to reaction condition and can
27 be easily determined. Reaction rate constants of these benzothiazoles towards sulfate radical are $(3.3$
28 $\pm 0.3) \times 10^9$, $(1.4 \pm 0.3) \times 10^9$, $(1.5 \pm 0.1) \times 10^9$ and $(4.7 \pm 0.5) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively (pH 7 and
29 20°C). Based on R_{ct} and these rate constants, their degradation in the presence of organic matter can
30 be well predicted. A number of transformation products were detected and tentatively identified
31 using triple-quadruple/linear ion trap MS/MS and high-resolution MS. It appears that sulfate radicals
32 attack BTH, MTBT and BTSA on their benzo ring via electron transfer, generating multiple
33 hydroxylated intermediates which are reactive towards common oxidants. For OHBT oxidation, it
34 prefers to break down the thiazole ring. Due to competitions of the transformation intermediates, a
35 minimum PMS/pollutant molar ratio of 10-20 is required for effective degradation. The flexible
36 PMS/ CuFe_2O_4 could be a useful process to remove the benzothiazoles from low DOC waters like
37 urban runoff or polluted groundwater.

38

39 INTRODUCTION

40 Benzothiazole derivatives are used in large volumes as vulcanization accelerators and are present
41 in all kinds of rubber-made products. Because of their wide application and various toxicity effects,
42 release of these compounds is of environmental concern.¹⁻³ The parent molecules initially applied,
43 such as 2-morpholinothiobenzothiazole, however, are usually not detected in water. It is believed
44 they undergo quick transformations in the environment,⁴ and as such only breakdown products of the
45 parent compounds are frequently detected in urban runoff (e.g. stormwater), treated municipal
46 wastewater and surface waters. Typically four breakdown products are frequently detected, i.e.
47 benzothiazole (BTH), 2-(methylthio)benzothiazole (MTBT), 2-benzothiazolsulfonate (BTSA) and
48 2-hydroxybenzothiazole (OHBT).⁴⁻⁷ Concentrations of these compounds are commonly found to
49 be 1 order of magnitude higher in urban runoff (tens of μgL^{-1}) compared to treated municipal
50 wastewater (several μgL^{-1}).⁵ This difference is probably due to the dissolution of tiny rubber
51 particles abraded from automobile tires on roads, making urban runoff a major source of these
52 benzothiazoles in aquatic environments.^{5, 8} These benzothiazoles are relatively resistant toward
53 abiotic transformation.⁵ They are not effectively removed in current wastewater/stormwater
54 treatment practices.^{9, 10} Due to their refractory nature, these compounds have also been found in
55 groundwater and tap water.¹¹ Reports show that BTH and OHBT are frequently detected from
56 human urine at levels of ng L^{-1} ,¹² which possibly is attributed to their existence in drinking water. It
57 is known that BTH, MTBT and OHBT have acute and chronic toxicity effects in the test with
58 *Ceriodaphnia dubia*,¹³ however, there are still no reports on the possible toxicity of BTSA.

59 The presence of these benzothiazoles in drinking water has raised some healthy concerns. Their
60 removal with oxidation techniques has therefore been investigated, where ozonation, UV irradiation,

61 and advanced oxidation processes (AOPs) generating hydroxyl radicals (e.g. photocatalytic
62 oxidation, O_3/H_2O_2 and UV/H_2O_2) have been tested.¹⁴⁻¹⁸ Results of these studies clearly show that
63 hydroxyl radical is the major oxidant species responsible for effective degradation of benzothiazoles.
64 Unfortunately, their transformation products during hydroxyl radical oxidation are rarely reported,
65 making it difficult to comprehensively assess the effects of their oxidative degradation.

66 In recent years, degradation of refractory pollutants by sulfate radicals has attracted many interests
67 in both research and application. Sulfate radical has a reducing potential comparable to or even
68 higher than hydroxyl radical.¹⁹ It reacts with compounds normally via electron transfer, and can be
69 more efficient than hydroxyl radical in the degradation of some contaminants.^{20, 21} Sulfate radicals
70 can be produced from peroxymonosulfate (PMS) or peroxydisulfate (PDS) during activation with
71 metal ions,^{22, 23} metal oxides,²⁴⁻²⁷ alkaline,²⁸ heat,²⁹ UV irradiation,^{21, 30, 31} or phenols and quinones.^{32,}
72 ³³ Magnetically separable $CuFe_2O_4$ was recently developed in our group as well as in several other
73 groups to efficiently activate PMS generating oxidative radicals at neutral pH while requiring no
74 additional chemicals or energy.³⁴⁻³⁶ The $PMS/CuFe_2O_4$ is more flexible than hydroxyl radical-based
75 AOPs which usually require ozone and/or UV, and thus could be preferential in the treatment of
76 urban runoff that occurs periodically. Under these conditions, application of ozone and UV is limited
77 by high equipment costs and low operation frequency.

78 We investigated the stability and the surface catalysis mechanism of $CuFe_2O_4$ for PMS activation
79 in our previous work.³⁴ However, there is still no idea to determine the concentration distribution of
80 radical species for the application of $PMS/CuFe_2O_4$ oxidation, especially the transient concentration
81 of sulfate radicals which are of great interest to remove refractory pollutants. Since the sulfate
82 radical concentration cannot be determined, pollutant removal rates in various water matrices

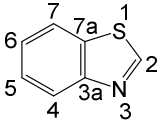
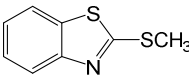
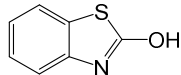
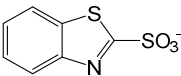
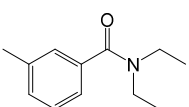
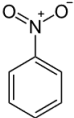
83 consequently cannot be predicted, which probably impedes practical application of this process as
84 well as other sulfate radical-based oxidation processes. Regarding the highly stable benzothiazoles
85 which are of great concern for the reuse of urban runoff for arid and semi-arid regions, they are
86 rarely studied with sulfate radical oxidation for removal efficiency, kinetics and mechanism. In this
87 work, we established a kinetic method to quantify the transient concentrations of sulfate radical
88 during the PMS/CuFe₂O₄ oxidation, determined reaction rate constants of the four benzothiazoles
89 (BTH, MTBT, BTSA and OHBT) with sulfate radical, tentatively identified their transformation
90 intermediates via LC/high-resolution MS and LC/MSⁿ analysis, and proposed their degradation
91 pathway accordingly. The results will shed some light on how to determine transient sulfate radical
92 concentrations and predict pollutant removal rates for the PMS/CuFe₂O₄ process as well as for other
93 sulfate radical-based oxidation processes, and also on the effectiveness and mechanism of sulfate
94 radical reactions with highly stable benzo-heterocyclic compounds.

95 EXPERIMENTAL SECTION

96 **Chemicals and materials.** Benzothiazole (BTH; 96%), 2-(methylthio)benzothiazole
97 (MTBT; 97%), potassium salt of benzothiazolesulfonic acid (BTSA), 2-hydroxybenzothiazole
98 (OHBT; 98%), *N,N*-diethyl-*m*-toluamide (DEET; 97%), nitrobenzene (NB; ≥ 99%),
99 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS; ≥ 98%), peroxomonosulfate (PMS)
100 (Oxone, KHSO₅·0.5KHSO₄·0.5K₂SO₄), and peroxydisulfate (PDS; ≥ 98%) were purchased from
101 Sigma-Aldrich. Nitric acid (64 - 66%), sodium tetraborate (≥ 99.5%), and sodium nitrite (≥ 99%)
102 were purchased from the same company. Methanol (HPLC grade), acetonitrile (HPLC grade), water
103 for LC-MS, formic acid, and ammonium acetate were purchased from Fisher Scientific.
104 6-hydroxybenzothiazole (≥ 96%) and 2-nitrobenzenesulfonic acid (≥ 97%) as authentic references of

105 oxidation products were purchased from TCI America. Information of the benzothiazoles and probe
 106 compounds is given in Table 1. The ultrapure water for HPLC elution and experiments was
 107 produced with a Milli-Q water system.

108 **Table 1.** Benzothiazoles and probe compounds used in this study.

Compound	Abbreviation	Structure	Molecular weight (Da)	$\log K_{ow}$	pK_a
Benzothiazole	BTH		135.18	2.01	1.2 ¹⁶
2-Methylthiobenzothiazole	MTBT		181.27	3.15	1.22 ³⁷
2-Hydroxybenzothiazole	OHBT		151.18	2.12	8.9 ¹⁶
Benzothiazole-2-sulfonic acid	BTSA		214.23	-0.39	2.4-1.0 ⁷
<i>N,N</i> -diethyl- <i>m</i> -toluamide	DEET		191.27	2.18	0.67 ³⁸
Nitrobenzene	-		123.11	1.85	-

109

110 Hydrophobic acid (HPOA) was extracted from Suwanee river water with XAD-8 resin. efOM was
 111 extracted from the effluent of a wastewater treatment plant of Jeddah, Saudi Arabia, also with
 112 XAD-8 resin. A street runoff was collected at November 23rd, 2014, on KAUST campus (University
 113 Boulevard near Harbor Square) during the second precipitation of that month. It was immediately
 114 filtered with 0.45 μm glass-fiber filters (Whatman), characterized ($\text{pH} = 7.7$, $\text{DOC} = 3.1 \text{ mg L}^{-1}$,

7

115 $UV_{254} = 0.13$ (1 cm cell), alkalinity = 22.5 mg L⁻¹ (CaCO₃), chloride = 13 mg L⁻¹, sulfate = 14 mg
116 L⁻¹, and nitrate = 0.9 mg L⁻¹), and stored at 4 °C before using.

117 The preparation of spinel CuFe₂O₄ particles was described in our previous work and showed in
118 detail in Text S1 of Supporting Information (SI).³⁴ The spinel oxide particles have characteristic
119 BET surface area of 20.2 m² g⁻¹, average pore size of 30 nm, average particle size of 0.3 μm, pH_{pzc}
120 (pH at which the surface is zero-charged) of 7.9, and saturated magnetization (M-H) of 24 emu g⁻¹
121 (21 °C).

122 **Experimental procedure.** *Kinetic study.* Experiments were conducted in a glass bottle
123 wrapped with aluminum foil. Pre-determined volumes of stock solutions of the compound and PMS
124 were injected into 200 mL Milli-Q water to get desired initial concentrations. Tetra-borate (10 mM)
125 rather than phosphate was used as a buffer in most of the reactions, because phosphate is a strong
126 ligand for transition metals. The solution was mechanically stirred during the reaction at a rotary
127 speed of 700 rpm (degradation rates of the bezothiazoles were leveled off at rotation speeds over 550
128 rpm under the experimental conditions, meaning that the influence of surface diffusion was
129 minimized) and room temperature (20 °C). The reaction was initiated by introducing CuFe₂O₄
130 particles into the solution. Samples taken at specific time intervals were filtered with 0.45 μm
131 glass-fiber syringe filters (Whatman). The filtration was confirmed to have no impact on the
132 concentrations of the target compounds and PMS. For the analysis of the target compounds, sodium
133 nitrite solution was immediately introduced into the filtrate to quench residual PMS. The nitrite was
134 not added to the samples for the analysis of residual PMS.

135 *Oxidation product study.* Experiments were conducted in 50 mL amber glass bottles with Teflon
136 caps. Twenty mL of the solution containing 0.1 mM of the target compound, various concentrations
137 (0.1-2 mM) of PMS and 1.5 g L^{-1} of CuFe_2O_4 particle were introduced into the reaction bottles and
138 shaken at a rotation speed of 300 rpm. The PMS concentrations were periodically monitored till
139 complete consumption. Then, the suspensions were filtered through $0.45 \text{ }\mu\text{m}$ glass-fiber syringe
140 filters (Whatman) for the analysis of target compounds and oxidation products. No reductant was
141 further applied.

142 **Analysis.** DEET, nitrobenzene, BTH, MTBT, BTSA and OHBT were quantified on a Waters
143 HPLC equipped with a Luna C-18 column ($150 \times 4.6 \text{ mm}$, $5 \text{ }\mu\text{m}$, Phenomenex) at UV wavelengths
144 of 266, 263, 252, 282, 266 and 241 nm, respectively. The column elution condition is shown in
145 Table S1 (SI). The concentration of PMS was analyzed through catalytic transformation of PMS into
146 sulfate radical which reacts instantly with ABTS generating ABTS^+ . In this method, 0.5 mL of
147 ATBS solution (20 mM), 0.2 mL of CoSO_4 solution (20 mM), and 10 mL of diluted H_2SO_4 solution
148 (2%) were mixed with 1 mL of the water sample, and then the absorbance at 734 nm was measured
149 on a spectrometer (DR 500, Hatch). The oxidation of ABTS under this experimental condition was
150 completed within 2 minutes, enabling a kinetic study of PMS decomposition in this work. The
151 calibration curve used for the determination of PMS is shown in Figure S1 (SI).

152 For the kinetic study of benzothiazoles' decomposition in the presence of natural organic
153 matter/effluent organic matter, LC-triple quadrupole/linear ion trap MS/MS (1260 Infinity HPLC,
154 Agilent; Qtrap 5500 mass spectrometer, AB Sciex) operating at multiple reaction monitoring (MRM)
155 mode was applied using the same Luna C-18 column. BTH, MTBT and OHBT were detected at ESI

156 positive mode; BTSA was detected at ESI negative mode. Column elution conditions and MS
157 settings are shown in Table S2 and Text S2 (SI).

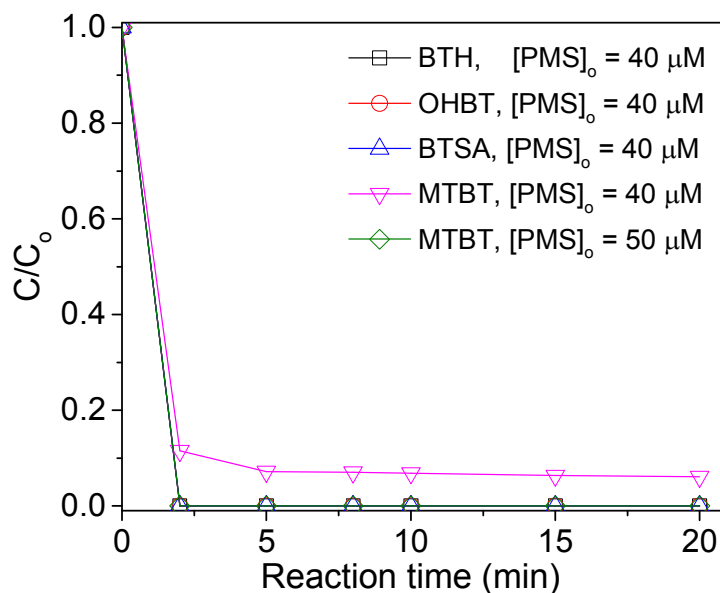
158 Full mass scan and MS^2/MS^3 fragmentation scans for the oxidation products (OPs) were
159 conducted with the same LC-Qtrap MS/MS under the same column elution condition. Accurate
160 masses of the OPs were determined on a LC-high resolution MS system (Surveyor HPLC, Thermal;
161 LTQ Orbitrap Velos mass spectrometer, Thermo) with the same column and elution condition. The
162 empirical formulae of these OPs were proposed with Xcalibur software (Thermo). MS settings are
163 shown in Text S2 (SI).

164 Full mass scan with the LC-Qtrap MS was applied to find potential OP peaks. MS^2 fragmentation
165 of each potential OPs was conducted to find their characteristic fragments that can be applied for
166 MRM detection. Potential OPs in samples oxidized at PMS/compound molar ratios of 1, 2, 5, 8, 10,
167 12, 15 and 20 were detected with the LC-Qtrap MS/MS in MRM mode. OP screening was based on
168 1) peak area (obtained with MRM) variation with the PMS/compound molar ratio (the peak area of a
169 reasonable OP should increase or increase and then decrease with PMS dosage), and 2) whether their
170 empirical formulae as determined with LC-Orbitrap MS are reasonable (e.g. numbers of each
171 elements). For OPs confirmed with the above steps, MS^3 scan of their major MS^2 fragments were
172 conducted with the LC-Qtrap MS/MS to tentatively propose their molecular structures. Because
173 authentic standards are not available to chromatographically confirm most of the proposed structures,
174 Mass Frontier 5.1 software (HighChem), which can predict fragmentation patterns of a given
175 structure based on various known fragmentation mechanisms, was also applied to assist excluding
176 unreasonable isomer structures for the OPs.

177 OP peaks of BTH and MTBT were much more intensive at ESI positive mode than negative mode.
178 Moreover, no new peaks other than those detected in positive mode were detected at negative mode.
179 So, positive mode ionization was applied in the analysis of OPs of BTH and MTBT. OPs of OHBT
180 and BTSA can only be detected at ESI negative mode.

181 RESULTS AND DISCUSSION

182 **Effectiveness of PMS/CuFe₂O₄ for benzothiazoles.** Figure 1 shows decline of the
183 four benzothiazoles during PMS/CuFe₂O₄ oxidation in pure water. The concentration of these
184 compounds declined quickly under this condition, achieving almost complete removal (i.e. below
185 detection limits of 0.01-0.02 μM on the HPLC-UV) within 2 minutes for BTH, OHBT and BTSA at
186 initial PMS/compound molar ratio of 40. For MTBT, its complete removal was also achieved within
187 2 minutes when the initial PMS/MTBT molar ratio was raised to 50. Neither PMS alone nor
188 CuFe₂O₄ alone can remove the benzothiazoles appreciably (not shown here). This result indicates
189 that the PMS/CuFe₂O₄ oxidation is effective for oxidative degradation of these benzothiazoles. A
190 further eight-cycle PMS/CuFe₂O₄ oxidation was conducted by reclaiming the CuFe₂O₄ particles
191 from the reaction solution and reusing them in the next reaction cycle (the experimental and results
192 were shown in Figure S2, SI). The removal of these benzothiazoles in 2 minutes reaction slightly
193 decreased as the CuFe₂O₄ was repeatedly reused, but the removal rates in 10 minutes of each
194 reaction cycle were nearly the same, indicating that the activity of the CuFe₂O₄ was durable for the
195 oxidation of these benzothiazoles.

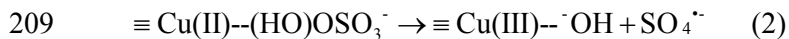
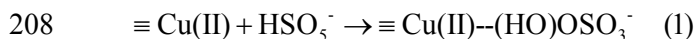


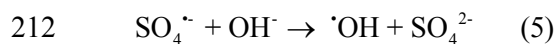
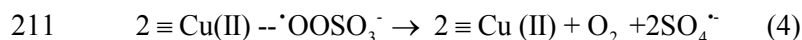
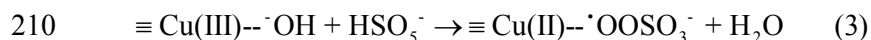
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197 **Figure 1.** PMS/CuFe₂O₄ oxidation of individual benzothiazoles. Conditions: dosage of each
 198 benzothiazoles = 1 μM; CuFe₂O₄ dosage = 200 mg L⁻¹; unbuffered initial pH = 5.6; T = 20 °C.

199 **Evaluation of sulfate radical generation within the PMS/CuFe₂O₄ process.**

200 The PMS/CuFe₂O₄ process produces radicals through surface interactions of the catalyst with PMS
 201 (eq 1-4).³⁴ The sulfate radical reaction with OH⁻ ($k_{\text{SO}_4^{\cdot-}, \text{OH}^-} = 6.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) also produces
 202 hydroxyl radical in water (eq 5), which is more significant at higher pHs.^{31, 39, 40} Presently, we
 203 know that sulfate radical is dominant in this process because pollutant oxidation was scavenged
 204 more by ethanol (reactive towards both hydroxyl radical and sulfate radical) than by *tert*-butanol
 205 (more reactive towards hydroxyl radical than towards sulfate radical).³⁴ However, exact proportions
 206 of these radical species still cannot be quantified. Determination of the concentrations of these
 207 radical species is a prerequisite for kinetic studies.





213 To quantify the radical species (i.e. sulfate radical and hydroxyl radical) generated in the
 214 PMS/CuFe₂O₄ process, nitrobenzene (NB) ($k_{\text{SO}_4^{\cdot-}, \text{NB}} \leq 10^6 \text{ M}^{-1}\text{s}^{-1}$; $k_{\text{OH}^{\cdot}, \text{NB}} = 3.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$)^{41, 42}
 215 and DEET ($k_{\text{SO}_4^{\cdot-}, \text{DEET}} = (1.9 \pm 0.1) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, pH 7; $k_{\text{OH}^{\cdot}, \text{DEET}} = 4.95 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$)^{38, 43} were
 216 applied as probes in the mixture. Decomposition of PMS, DEET, and NB at pHs between 6.0-8.0 are
 217 shown in Figure S3 (SI). The decomposition rates of PMS and DEET were lower at higher pH,
 218 because the repulsion between PMS (mainly in the HSO₅⁻ form) and the slightly negatively charged
 219 CuFe₂O₄ surface ($\text{pH}_{\text{pzc}} = 7.9$) reduces their interaction and the subsequent radical formation. The
 220 decline of NB concentration during PMS/CuFe₂O₄ oxidation was observed to be the same as that of
 221 evaporation caused by stirring (i.e. without PMS and CuFe₂O₄ in Figure S3C, SI), which means that
 222 there was no observable oxidative removal of NB. Based on the reaction rate constants reported in
 223 literature shown above, NB reaction with sulfate radicals is extremely slow compared to its reaction
 224 with hydroxyl radical and the DEET-sulfate radical reaction. The NB degradation result here
 225 indicates clearly that the hydroxyl radical yield is negligible in the PMS/CuFe₂O₄ oxidation, and the
 226 DEET is oxidized by sulfate radicals. Therefore, the decomposition of DEET can be described with
 227 eq 6 (integrated in eq 7). The R_{ct} , a concept developed by Elovitz and von Gunten to correlate
 228 hydroxyl radical generation with ozone decomposition during ozonation,⁴⁴ is adopted here to
 229 describe the exposure ratio of sulfate radical to PMS (eq 8). At a given CuFe₂O₄ dosage, the
 230 decomposition rate of PMS follows a pseudo-first order (Figure S3A, SI), which can be described by

231 eq 9, where k is the pseudo first order decomposition rate which can be obtained by plotting the
 232 logarithm of normalized PMS residual against reaction time. Then, the exposure of sulfate radical
 233 can be expressed as a function of residual PMS during oxidation (eq 10). The DEET residual can
 234 thus be described with eq 11.

$$235 \quad -\frac{d[\text{DEET}]}{dt} = k_{\text{SO}_4^{\bullet-}, \text{DEET}} \cdot [\text{SO}_4^{\bullet-}] \cdot [\text{DEET}] \quad (6)$$

$$236 \quad \ln \frac{[\text{DEET}]}{[\text{DEET}]_0} = -k_{\text{SO}_4^{\bullet-}, \text{DEET}} \cdot \int_0^t [\text{SO}_4^{\bullet-}] dt \quad (7)$$

$$237 \quad R_{\text{ct}} = \frac{\int_0^t [\text{SO}_4^{\bullet-}] dt}{\int_0^t [\text{PMS}] dt} \quad (8)$$

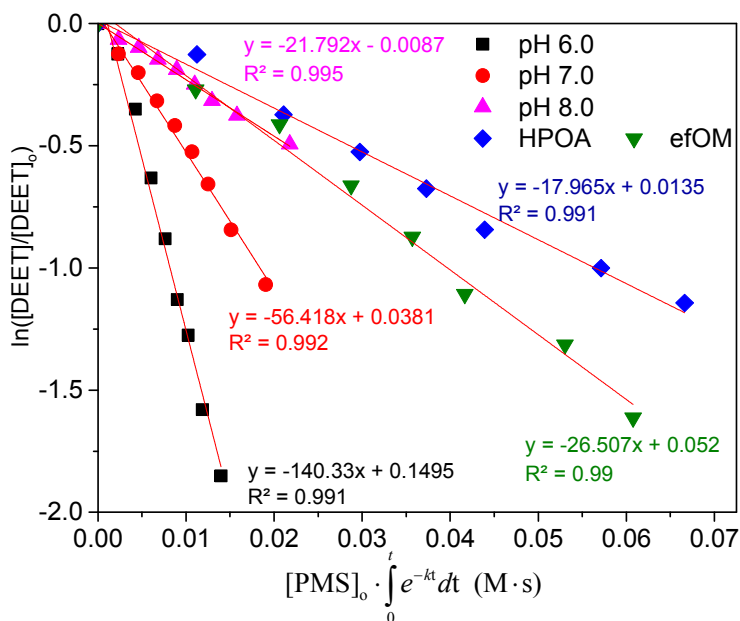
$$238 \quad \ln \frac{[\text{PMS}]}{[\text{PMS}]_0} = -k \cdot t \quad (9)$$

$$239 \quad \int_0^t [\text{SO}_4^{\bullet-}] dt = R_{\text{ct}} \cdot \int_0^t [\text{PMS}] dt = R_{\text{ct}} \cdot [\text{PMS}]_0 \cdot \int_0^t e^{-kt} dt \quad (10)$$

$$240 \quad \ln \frac{[\text{DEET}]}{[\text{DEET}]_0} = -R_{\text{ct}} \cdot k_{\text{SO}_4^{\bullet-}, \text{DEET}} \cdot [\text{PMS}]_0 \cdot \int_0^t e^{-kt} dt \quad (11)$$

241 Based on the decomposition results of PMS and DEET shown in Figure S3A and S3B (SI), linear
 242 relationships were observed between $\ln \frac{[\text{DEET}]}{[\text{DEET}]_0}$ and the exposure of residual PMS,
 243 $[\text{PMS}]_0 \cdot \int_0^t e^{-kt} dt$, at pHs between 6.0-8.0 and also in the presence of the organic matter, HPOA and
 244 efOM (Figure 2 with original data in Figure 3S, SI). Results indicates that, under a given condition
 245 (i.e. specified water matrix, PMS and CuFe_2O_4 dosages), the R_{ct} value is a constant. A constant R_{ct}
 246 value under a specific reaction condition indicates that the transient concentration of sulfate radical

247 is proportional to the residual PMS. This means that sulfate radical cannot be accumulated during the
 248 PMS/CuFe₂O₄ oxidation, it should have been rapidly consumed by the organic/inorganic substances
 249 and its self-combination reactions just like what happens to hydroxyl radical during ozonation.^{31, 45,}
 250 ⁴⁶ As the R_{ct} value can be easily calculated by monitoring PMS and the probe compound, it provides
 251 a simple way to quantify sulfate radical exposure during PMS/CuFe₂O₄ oxidation.



252

253 **Figure 2.** Relationship between DEET degradation and the exposure of residual PMS during
 254 PMS/CuFe₂O₄ oxidation. Conditions in absence of HPOA/efOM: [DEET]₀ = 1 μM; [PMS]₀ = 20
 255 μM; CuFe₂O₄ dosage = 200 mg L⁻¹; 10 mM tetraborate buffered; T = 20 °C. Conditions in presence
 256 of HPOA/efOM: HPOA/efOM = 2 mg DOC L⁻¹; [DEET]₀ = 1 μM; [PMS]₀ = 100 μM; CuFe₂O₄
 257 dosage = 500 mg L⁻¹; 10 mM tetraborate buffered pH = 7; T = 20 °C.

258 **Reaction rate constants of sulfate radical with benzothiazoles.** The
 259 competition kinetic method was applied to determine second-order rate constants of reactions
 260 between sulfate radicals and benzothiazoles using DEET as probe compound. This method of rate
 261 constant determination is applicable for the PMS/CuFe₂O₄ oxidation, because concentrations of
 262 benzothiazoles and DEET even at 20 times lower than those applied in the kinetic study have no

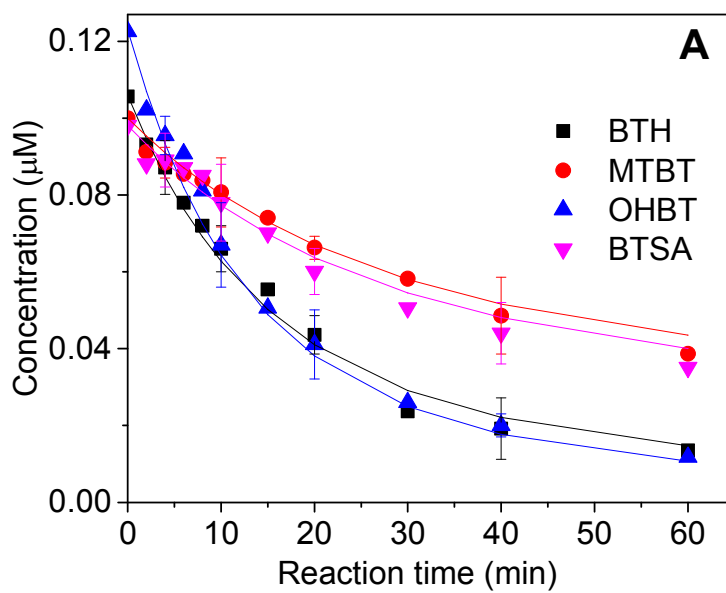
263 appreciable adsorption on the CuFe_2O_4 (Figure S4, SI), meaning these compounds will be degraded
264 in the solution, and surface adsorption-induced degradation can be excluded.

265 Based on the data shown in Figure S5 (SI), second order rate constants of sulfate radicals with
266 BTH, MTBT, BTSA and OHBT were calculated to be $(3.3 \pm 0.3) \times 10^9$, $(1.4 \pm 0.3) \times 10^9$, (1.5 ± 0.1)
267 $\times 10^9$ and $(4.7 \pm 0.5) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively. It was reported that BTH and OHBT react with
268 hydroxyl radicals at rate constants of $(3.9\text{-}8.6) \times 10^9$ and $(4\text{-}5.1) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively.¹⁶ Sulfate
269 radical is thus comparable with hydroxyl radical for BTH and OHBT oxidation. Lutze et al. showed
270 that sulfate radical reacts slower than hydroxyl radical with humic acid and bicarbonate
271 ($k_{\text{SO}_4^{\cdot-}, \text{HA}} = (6.6 \pm 0.4) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$; $k_{\text{OH}^{\cdot}, \text{HA}} = (1.4 \pm 0.2) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; $k_{\text{SO}_4^{\cdot-}, \text{HCO}_3^-} = 2.8\text{-}9.1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$;
272 $k_{\text{OH}^{\cdot}, \text{HCO}_3^-} = 1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$);⁴⁰ therefore, sulfate radicals could be more effective than hydroxyl radicals
273 for the oxidative removal of BTHs for some real water.

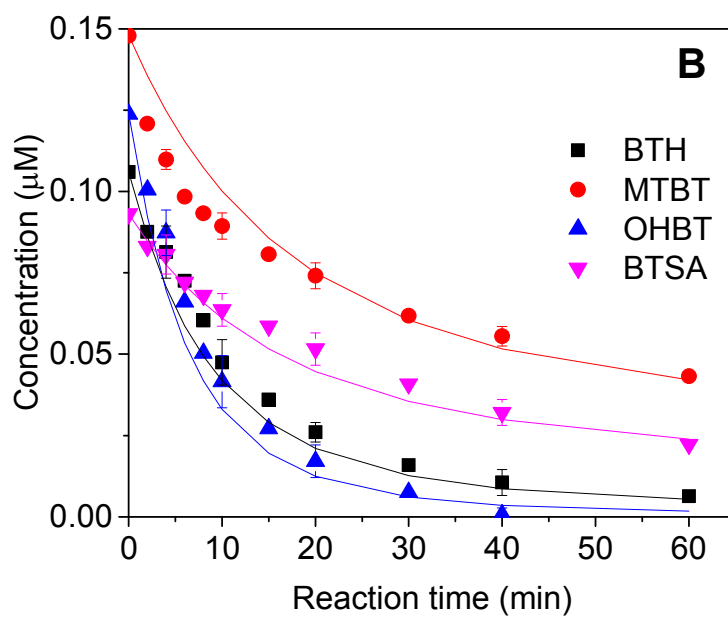
274 **Prediction of BTHs degradation in the presence of organic matter.**

275 Concentrations of residual BTHs during PMS/ CuFe_2O_4 oxidation theoretically can be predicted with
276 eq 12 in the presence of organic matter which ubiquitously exist in water. The evolution of the
277 benzothiazoles in the presence of HPOA/efOM during PMS/ CuFe_2O_4 oxidation is shown in Figure
278 3A and 3B. Based on the measured second-order reaction rate constants and the R_{ct} values calculated
279 from eq. 11 with the decomposition data of PMS and DEET (shown in Figure S6 (SI)), the predicted
280 evolution of the concentrations of the benzothiazoles fit well (Figure 3). The degradation of the
281 benzothiazoles spiked into a real street runoff also fitted well with the model prediction (Figure 3C)
282 (PMS and DEET decomposition in the street runoff were shown in Figure S6 (SI)). The result also
283 indicates that a PMS dosage over 200 μM is needed for a real street runoff if the less reactive MTBT
284 and BTSA are of concern for their concentration.

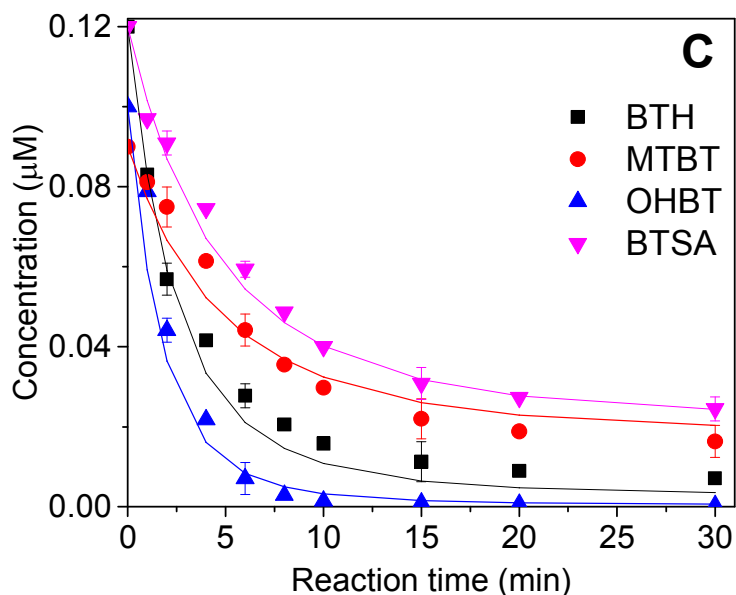
$$285 \quad [\text{BTHs}] = [\text{BTHs}]_0 \cdot e^{-R_{\text{ct}} \cdot k_{\text{SO}_4^{\bullet-}, \text{BTHs}} [\text{PMS}]_0 \cdot \int_0^t e^{-k t} dt} \quad (12)$$



286



287



288

289 **Figure 3.** Degradation of benzothiazoles in HPOA (A) and efOM (B) solutions and in a street runoff
290 (C): symbols represent measured data, and lines are predicted with the kinetic model. Conditions:
291 PMS dose was 100 μM for HPOA and efOM solutions and 200 μM for the street runoff; DOC of
292 HPOA/efOM solutions = 2 mg L^{-1} ; CuFe_2O_4 dosage = 200 mg L^{-1} ; HPOA and efOM solutions were
293 buffered to pH 7.0 with 10 mM tetra-borate; $T = 20^\circ\text{C}$. Error bars represent standard deviation of
294 three replicates.

295 **Transformation products of benzothiazoles formed from PMS/ CuFe_2O_4**

296 **oxidation.** Oxidation products detected for BTH, MTBT, BTSA and OHBT are listed in Table
297 S3-S6 (SI). Evolution of peak areas of these products (detected with MRM mode) and the
298 benzothiazoles with initial PMS/compound molar ratio are presented in Figure S7-S10 (SI). Since
299 authentic standards for most of these oxidation products are not available, their structures were
300 proposed based on their empirical formulae (Table S3-S6, SI) and MS^2/MS^3 fragmentation patterns
301 as summarized in Table S7-S10 (SI). The Mass Frontier 5.1 software was also used to assist in
302 interpreting fragmentation patterns of the parent benzothiazoles and screening possible structures of
303 the oxidation products.

304 1. *Oxidation products of BTH.* The fragmentation pattern of BTH provides a basis to interpret the
305 MS² and MS³ results of the twelve oxidation products. For example, the loss of 27 amu in MS²
306 fragmentation is attributed to the detachment of CHN from the mother molecule (Table S7, SI).
307 Therefore, a 27 amu loss in the fragmentation of an oxidation product signifies that the -CH=N-
308 structure of the thiazole ring is not modified in the oxidation. Consequently, the loss of 44 amu
309 indicates the presence of intact C-S moiety.

310 Four isomers of OP 152 were observed with nearly the same MS²/MS³ fragmentation pattern
311 (Table S7, SI). According to their accurate masses (Table S3, SI), they have one more O atom than
312 the parent BTH. A loss of water (18 amu) was observed during MS² fragmentation of OP 152, which
313 signifies the presence of a hydroxyl group next to an extractable hydrogen.⁴⁷ Since losses of 27
314 (CHN) and 44 (CS) amu were observed respectively in the fragmentation of OP 152 and its
315 fragments, the extra O atom should not be present on the thiazole ring but on the benzo ring. The
316 retention time of 2-hydroxyl benzothiazole (OHBT) which has one O atom attached on 2-C of the
317 thiazole ring (16.2 min) didn't match with those of OP 152 under the same column elution
318 conditions (Figure S11, SI). Moreover, there was no direct loss of 27 amu (CHN) from OHBT in
319 MS² fragmentation (i.e. absence of m/z 125 (Fig S12, SI)), which also confirms that the
320 hydroxy-benzo structure of OP 152 is reasonable. Only one hydroxylated benzothiazole with OH
321 substitution on the benzo ring was commercially available, i.e. 6-hydroxybenzothiazole. It has the
322 same retention time (13.9 min) and MS² fragmentation pattern with OP 152-3, meaning that the
323 structure of this product can be confirmed.

324 OP 168 of BTH has three isomers with two more O atoms than the parent BTH (Table S3, SI).
325 Simultaneous hydroxylation on C atoms of the thiazole ring and the benzo ring seems impossible,

326 because sulfate radical-oxidized OHBT sample had no peaks matching the oxidation products of
327 BTH (Figure S11, SI). Losses of 44 (CS) and 27 (CHN) amu were observed in further fragmentation
328 of its fragments m/z 150 (loss of H_2O) and 140 (loss of CO), respectively (Table S7, SI), indicating
329 that the two O atoms present on the benzo ring but not on 1-S or 3-N of the thiazole ring. A broken
330 benzo ring having two side aldehyde groups is not a possible structure for OP 168, because with
331 fragmentation prediction of Mass Frontier 5.1: 1) this structure has no loss of 18 amu (H_2O) which
332 was observed for OP 168, and 2) it has a loss of 16 amu (O) due to charge remote rearrangement
333 which was not observed for OP 168. OP 184 has three isomers with three more O atoms than the
334 parent BTH. Likewise, the broken benzo ring having olefin alcoholic aldehyde or olefin carboxylic
335 aldehyde groups are not likely structures for OP 184. Purpald test which is sensitive to aldehydes
336 was also applied for the water samples (procedures shown in Text S3, SI), and no aldehyde
337 formation can be noticed. Substitution of three hydroxyl groups on the benzo ring of BTH was thus
338 proposed for OP 184. OP 182 with two H atoms less than OP184 seems to have a quinone moiety.
339 The loss of 44 amu (CS) during MS^2 fragmentation of OP182 as well as the loss of 27 amu (CHN)
340 during MS^3 fragmentation of its fragment m/z 110 indicates that the three O atoms are present on the
341 benzo ring. The losses of 44 and 27 amu were also observed during MS^3 fragmentation of fragments
342 m/z 182 and 110 respectively for OP 200 which has four O atoms more than the parent BTH. The
343 substitution of four hydroxyl groups on the benzene ring of BTH was thus proposed as the structure
344 of OP 200. Further oxidation of these hydroxylated products by sulfate radicals likely leads to
345 opening of the aromatic ring forming small carboxylates (as suggested in sulfate radical oxidation of
346 phenol, chlorophenol, and quinone).^{48, 49} However, these potential small carboxylate products were

347 not detected with LC-MS neither in positive nor in negative mode, possibly because they are very
348 hydrophilic and quickly eluted from the column under the analytical condition.

349 Most of the oxidation products like OP 152, OP 168, OP 182 and OP 200 are still quite reactive
350 towards sulfate radicals (Figure S7, SI). It was confirmed in our previous work that radicals can be
351 generated from PMS at a molar ratio of 1:1 in the PMS/CuFe₂O₄ process.³⁴ Because of competitive
352 consumption of sulfate radicals by these oxidation products, here a PMS/BTH stoichiometry over 12
353 is required to degrade over 90% of BTH under the experimental conditions. Further experiment was
354 conducted to see whether these oxidation products can be oxidized by cheaper oxidants like
355 peroxodisulfate (PDS) (\$0.74 per kg vs. \$2.2 per kg of PMS) and permanganate (PM) (\$1.5 per kg)
356 which readily react with hydroxylated aromatic structures.^{32, 50} PDS and PM were individually
357 introduced into the samples having been oxidized by PMS/CuFe₂O₄ at PMS/BTH = 8 and filtered
358 with 0.45 μm filters (i.e. in the absence of CuFe₂O₄ particles during PDS or PM oxidation). Dosages
359 of PDS and PM were twice of the initial BTH. In this case, the molar ratio of total oxidant to BTH
360 will be comparable with that of PMS/BTH = 10. Figure S13 (SI) shows peak areas of the products
361 obtained from PMS/CuFe₂O₄ oxidation at PMS/BTH = 10 and those further oxidized by PDS and
362 PM after PMS/CuFe₂O₄ oxidation at PMS/BTH = 8. It is clear that PDS and PM can destroy these
363 oxidation products more effectively than sulfate radicals, which means that most of the products can
364 be selectively oxidized by the common oxidants possibly because of their reactive hydroxy-benzo
365 structures. This result also suggests that a combination of sulfate radicals and common oxidants
366 would be able to improve the efficiency and reduce the cost of oxidation. The combination could
367 also possibly be useful to reduce the formation of toxic products when chloride is present at high

368 concentrations in the water, as chlorine radicals (formed by sulfate radical oxidation of chloride)
369 readily react with phenolic structures forming chlorinated products.^{48, 49}

370 **2. Oxidation products of MTBT.** MTBT has losses of 15 (CH₃), 32 (S), 44 (CS), 27 (CHN), and 58
371 (CNS) amu during its MS² and MS³ fragmentation (Table S8, SI). OP 198, having one more O atom
372 than the parent molecule (Table S4, SI), lost 15, 27, 32, and 44 amu during fragmentation, which
373 means that the thiazole ring and its -S-CH₃ side chain were not modified (i.e. hydroxylation occurred
374 on the benzo ring). The same fragmentation losses were observed for OP 214 which has two isomers
375 and two more O atoms than MTBT. Two OH-group substitutions on the benzo ring was thus
376 proposed for OP 214. Opening of the benzo ring with formation of two side aldehyde groups was
377 excluded because of the same reason as mentioned for OP 168 of BTH. OP 230 has three isomers
378 and three more O atoms than MTBT. The losses of 15, 27, 32, and 44 amu were observed during its
379 MS² and MS³ fragmentations, indicating that the thiazole ring is intact. It should have three OH
380 groups substituted on the benzo side. Likewise, OP 246 should have four hydroxyl groups
381 substituted on the benzo ring of MTBT, as it has four more O atoms and losses of 15, 32, 44, and 58
382 amu during MS² and MS³ fragmentation. A stoichiometry of PMS/MTBT higher than 20 is required
383 to achieve over 90% degradation of MTBT (Figure S8, SI). The higher oxidant dose required than
384 BTH oxidation indicates a higher consumption of sulfate radicals by the transformation products of
385 MTBT.

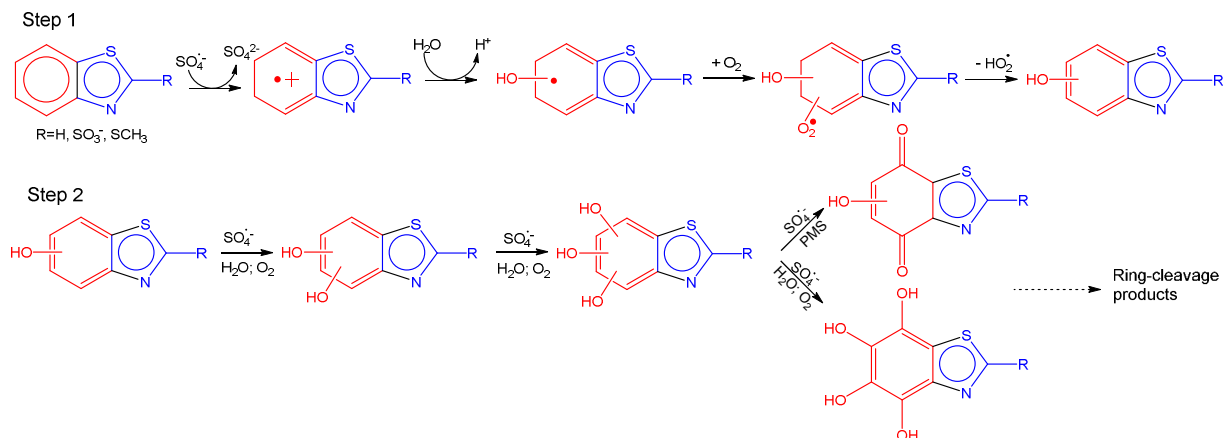
386 **3. Oxidation products of BTSA.** BTSA has losses of 64 (SO₂) and 28 (CO) amu during MS² and
387 MS³ fragmentation respectively at ESI negative mode (Table S9, SI). Successive losses of 80 (SO₃)
388 and 76 (C₆H₄) amu were also observed. The losses of 64, 28 and 80 amu were observed during the
389 fragmentation of OP 230, indicating that the sulfonate group was retained. No loss of 76 amu means

390 that the benzo ring was modified. The extra O atom of OP 230 compared to BTSA (Table S5, SI)
391 should be present on the benzo ring. Accordingly, di- and tri- hydroxyl substitution on the benzo
392 ring were proposed for OP 246 and OP 262, respectively. OP 260, having two H atoms less than OP
393 262, probably has a hydroxylated quinone ring.

394 **4. Oxidation products of OHBT.** Losses of 29 (CHO), 43 (CHON), 60 (COS) and 69 (C₃H₃ON)
395 amu were observed for OHBT during negative mode MS² fragmentation (Table S10, SI). OP 172,
396 which is one C less and two H and two O more than OHBT (Table S6, SI), has a loss of 64 amu
397 which is characteristic for the sulfonate group as shown in the fragmentation of BTSA (Table S9, SI).
398 A loss of 92 amu (C₆H₆N) was observed, which means that the benzene ring is retained. None of the
399 characteristic fragmentation losses of OHBT was observed for OP 172, indicating a breakage of the
400 structure. Therefore, OP 172 should have a sulfonate group attached on the benzene ring, and the
401 thiazole ring is damaged. OP 202 is two H less and two O more than the OP 172. Since losses of 64,
402 80, and 46 (NO₂) amu were observed, the OP 202 should have a sulfonate group and a nitro group
403 attached on the benzene ring, which is reasonable as its retention time and fragmentation pattern
404 matches well with that of 2-nitrobenzenesulfonate. At PMS/OHBT molar ratio of 20, the OHBT
405 dosed (100 μM) as well as the OP 172 were nearly completely degraded. In the meantime, the
406 2-nitrobenzenesulfonate produced was determined to be 6.1 μM, which is much lower than the
407 OHBT dosed, suggesting that this product could be also degradable during the PMS/CuFe₂O₄
408 oxidation. The degradation of 2-nitrobenzenesulfonate by PMS/CuFe₂O₄ was confirmed as shown in
409 Figure S14 (SI). Its degradation rate was lower than that of OHBT, which could be the reason for its
410 accumulation within the PMS dosages applied here.

411 **Proposed reaction mechanism.** According to the structures proposed for the oxidation
412 products, we tentatively conclude that sulfate radicals preferentially attack the benzo ring of BTH,
413 MTBT, and BTSA. For OHBT, sulfate radical attacks more readily the thiazole ring side than the
414 benzo ring.

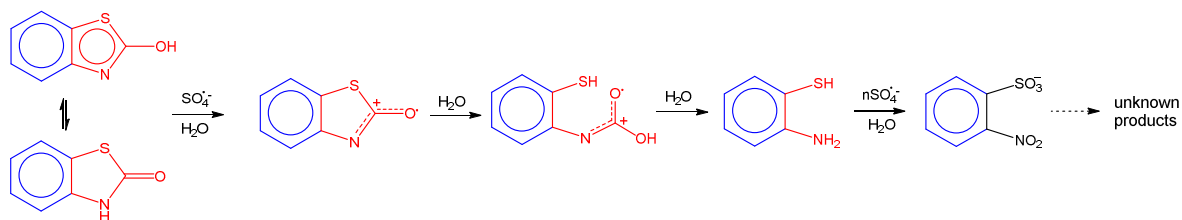
415 Sulfate radical is a strong electrophile. It attacks organic compounds more preferentially via
416 electron transfer than hydrogen abstraction and addition.^{19, 40} Its reaction with benzene via electron
417 transfer is believed to produce hydroxycyclohexadienyl radical through rapid reaction of the benzene
418 radical cation with water.^{19, 51-53} It is known that hydroxycyclohexadienyl radical can efficiently
419 react with oxygen forming peroxy radical which further decomposes giving phenol as product.⁵⁴ The
420 study of Anipsitakis et al. shows that sulfate radical reaction with phenol further produces dihydroxy
421 products (catechol and hydroquinone) following the same mechanism.⁴⁸ It seems that the sulfate
422 radical reaction with BTH, MTBT and BTSA follows a similar pathway with that of benzene and
423 phenol oxidation (Scheme 1). Once the hydroxylated products are formed, further attack on the
424 electron-enriched benzo ring via electron transfer is more favored, which leads to the formation of
425 products with multiple hydroxyl groups on the benzo ring side of these benzothiazoles. This is also
426 supported by the relatively high stoichiometric ratios of PMS required for effective removal of the
427 parent benzothiazoles. Besides hydroxylated products, quinone-like products were also produced,
428 which possibly proceeds through hydrogen abstraction of the hydroxylated products by either sulfate
429 radical or PMS itself.



430

431 **Scheme 1.** Proposed degradation pathway of BTH, MTBT and BTSA during PMS/CuFe₂O₄
 432 oxidation.

433 The sulfate radical oxidation of OHBT follows a different reaction pathway. The OH group on the
 434 thiazole ring is more likely to be attacked by sulfate radicals than the benzo ring via electron transfer
 435 and produces $-O^{\bullet}$ radical cation. The positive charge can shift to the 2-C due to the conjugate
 436 structure. Further hydrolysis in water leads to the detachment of 2-C and the formation of a thiol and
 437 a primary amine group (Scheme 2). The thiol group can be easily oxidized by sulfate radical into
 438 sulfonate group, it can even be oxidized by PMS itself.⁵⁵ The amine group is finally oxidized into a
 439 nitro group. The formation of a nitro derivative from sulfamethoxazole which has an aniline moiety
 440 was also reported in reaction with sulfate radicals generated with PMS/Co²⁺.⁵⁶



441

442 **Scheme 2.** Proposed degradation pathway of OHBT during PMS/CuFe₂O₄ oxidation.

443 **Environmental significance.** In arid and semi-arid regions, urban runoff is considered a
 444 potential water resource for aquifer recharge or nonpotable reuse after proper treatment.⁵⁷
 445 Benzothiazoles usually exist in urban runoff at relatively high concentrations. Effective removal of

446 them is necessary before aquifer recharge to avoid groundwater pollution. The PMS/CuFe₂O₄ could
447 be a useful oxidation process in this case where the application of other advanced oxidation
448 processes (e.g. O₃/H₂O₂ and UV/H₂O₂) has more limitations in adaptation to variable precipitation
449 and infrequent operation. Because of its high stability, the CuFe₂O₄ can also be fabricated into
450 paving bricks or filtration media for in-situ oxidative treatment of street runoff.

451 This study shows that the removal rates of benzothiazoles during PMS/CuFe₂O₄ oxidation can be
452 predicted with predetermined sulfate radical/PMS exposure ratio. This sulfate radical quantification
453 approach will also be useful in investigating the degradation of other refractory pollutants within this
454 process or other sulfate radical-related oxidation processes. Sulfate radical attack produces multiple
455 hydroxylated intermediates for benzothiazoles (except for OHBT). These hydroxylated products
456 seem readily degradable by cheaper oxidants like peroxydisulfate and permanganate. The
457 combination of sulfate radicals with these common oxidants could be practical and useful to reduce
458 treatment costs and improve the degradation of transformation intermediates.

459 ASSOCIATED CONTENT

460 **Supporting Information.** Ten tables, fourteen figures and three texts are included in the
461 supporting information. This information is available free of charge via the Internet at
462 <http://pubs.acs.org>.

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