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## Rapid oxidation of paracetamol by Cobalt(II) catalyzed sulfite at alkaline pH

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31 promising strategy by using sulfite and transition metal such as Co(II) to promote  
32 organic compounds degradation in water under neutral and alkaline pH conditions.

33

#### 34 **Keywords**

35 Sulfate radical, sulfite ion, cobalt ion, advanced oxidation processes, paracetamol.

36

#### 37 **1. Introduction**

38 Advanced oxidation processes based on sulfate radical (SR-AOPs) have emerged  
39 as a promising method in the field of oxidative decontamination of polluted water and  
40 soil [1-3]. Sulfate radical ( $\text{SO}_4^{\bullet-}$ ), a strong one-electron oxidant, has relatively high  
41 standard redox potential ( $E^0 = 2.6 \text{ V vs NHE}$ ) with an oxidation potential comparable to  
42 or even higher than that of hydroxyl radical [4]. Moreover,  $\text{SO}_4^{\bullet-}$  can react *via* electron  
43 transfer, by addition to C-C double bonds and H-abstraction [5, 6], thus, it is able to  
44 oxidize a large number of pollutants such as phenol derivatives and aniline in water  
45 [7-9].  $\text{SO}_4^{\bullet-}$  can be generated in homogeneous or heterogeneous systems *via* photolysis,  
46 thermolysis and radiolysis [10, 11] or *via* transition metal activation of persulfate  
47 ( $\text{S}_2\text{O}_8^{2-}$ , PS) [7, 12-15] and peroxymonosulfate ( $\text{SO}_5^{2-}$ , PMS) [16, 17].

48 In fact, PMS can be activated by various transition metals such as Fe, Mn, Ni and Co  
49 in the homogenous systems [1, 18]. Among them, Co and Fe are the most commonly  
50 used metal to promote radical formation due to their occurrence in natural media and  
51 low cost. Huang and Huang investigated the ability of Co(II) and PMS system to  
52 degrade Bisphenol A at pH 7, and achieved an efficient detoxification and  
53 mineralization method [19]. A process based on the sulfate radicals generation through  
54 iron (Fe(II), Fe(III)) activation of PMS or PS was studied for polychlorinated biphenyls  
55 degradation in aqueous system [20]. The high oxidation efficiency and slow rate of  
56 consumption of the oxidants make metal-mediated activation system a feasible strategy  
57 for degradation of recalcitrant organic compounds. Furthermore, PMS activation using  
58 cobalt oxide or cobalt-metal oxide as heterogeneous catalysts also gains significant  
59 relevance in water treatment applications [21]. The cobalt oxides such as CoO, CoO<sub>2</sub>,  
60 CoO(OH), Co<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>, Fe-Co mixed oxide nanocatalysts, cobalt oxide

61 supported on MgO (Co/MgO), on TiO<sub>2</sub> (Co/TiO<sub>2</sub>) and Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> and combined with  
62 other metals were used as efficient heterogeneous catalysts for activation of PMS  
63 [22-25]. The most advantage of heterogeneous catalyst is that solid particles can be  
64 easily removed from liquid phase and, in some cases, reused.

65 Recently, sulfite ions were found to react with transition metals such as Fe(II),  
66 Fe(III) and Cr(VI) to generate SO<sub>4</sub><sup>•-</sup> and application for the azo dyes and amine  
67 compounds decontamination was tested [17, 26-30].

68 In our previous work, we reported some novel AOPs using Fe(II)-sulfite,  
69 Fe(III)-sulfite, photo-Fe(II)-sulfite system able to produce oxysulfur radicals  
70 (including SO<sub>3</sub><sup>•-</sup>, SO<sub>4</sub><sup>•-</sup> and SO<sub>5</sub><sup>•-</sup>). Combined with the work conducted by other  
71 researchers [31-33], the basic chain oxidation mechanisms of oxysulfur radicals  
72 generation has been investigated.

73 In this work, Co(II)-sulfite ions (S(IV)) system has been investigated to promote  
74 the paracetamol degradation in water. Paracetamol (PARA) is a widely used analgesic  
75 and antipyretic drug and an important material for the manufacturing of azo dyes.  
76 PARA was chosen as a target contaminant in this work due to its presence in the  
77 environment from several emissions from manufacturing facilities, consumer use and  
78 disposal, and hospital waste [34, 35]. The effect of pH, initial PARA concentration,  
79 Co(II)/S(IV) molar ratio, the presence of oxygen were investigated. Moreover, the  
80 activation mechanism and contribution of reactive oxygen and sulfur species were  
81 elucidated by using different kinds of radical scavengers and transient absorption  
82 spectroscopy.

83

84

## 85 **2. Materials and Methods**

### 86 *2.1 Chemicals*

87 Cobalt(II) sulfate (CoSO<sub>4</sub>·7H<sub>2</sub>O, analytical reagent grade), Cobalt(II) oxide (CoO)  
88 and Paracetamol (C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>), were purchased from Sinopharm Chemical Reagent Co.,  
89 Ltd. Sulfite solutions (from Na<sub>2</sub>SO<sub>3</sub>, Sinopharm Chemical Reagent Co., Ltd) were  
90 prepared just prior to measurements. The radical scavengers tert-butyl alcohol (TBA),

91 ethanol (EtOH) as well as NaOH and H<sub>2</sub>SO<sub>4</sub> which were used to adjust the pH of the  
92 solutions, were obtained from Sinopharm Chemical Reagent Co., Ltd. Methanol was  
93 HPLC grade and purchased from Fisher Corporation. Ammonium thiocyanate  
94 (NH<sub>4</sub>SCN) and Methyl isobutyl ketone (MIK) used to determine the concentration of  
95 Co(II), were obtained from Sigma, France. All chemicals were used without further  
96 purification. Ultrapure water with 18.2 MΩ cm resistivity used in this work was  
97 obtained through a water purification system.

98

### 99 *2.2 Degradation experiments*

100 All experiments were conducted in a 250 mL open cylindrical reactor cooled by an  
101 external jacket water circulation at a constant temperature of 25°C. Appropriate  
102 amounts of the PARA, scavengers and Na<sub>2</sub>SO<sub>3</sub> were mixed in the solution and the pH  
103 was adjusted using a pHS-3C pH meter by adding dilute NaOH and H<sub>2</sub>SO<sub>4</sub> until desired  
104 value. Each solution was constantly stirred with a Polytetrafluoroethylene  
105 (PTFE)-coated magnetic stirrer and purged with air with a fixed flow of 0.8 L min<sup>-1</sup>.

106 Each experiment was initiated spiking with Co(II) or CoO into the solution.  
107 Samples were withdrawn at fixed interval times and analyzed immediately to determine  
108 the remaining concentration of PARA and Co(II). For radical-scavenging experiments,  
109 specific concentrations of TBA or EtOH were added to the solutions before Co(II)  
110 addition. In order to assess the role of oxygen during Co(II)-sulfite solution were  
111 purged by bubbling N<sub>2</sub> (99.99%) or O<sub>2</sub> (99.99%) for 30 min before and throughout the  
112 experiment. A dissolved oxygen (DO) meter (8403, AZ Instrument Co. Ltd.) was used  
113 to determine the oxygen concentration in solution. During anoxic reaction, the DO  
114 was 0.01 mg L<sup>-1</sup> while for O<sub>2</sub> saturated solution a concentration of 20 mg L<sup>-1</sup> was  
115 determined. All experiments were carried at least two times.

116

### 117 *2.3 Chemical analysis*

118 The concentration of PARA was determined using a high-performance liquid  
119 chromatography (HPLC) Shimadzu LC-10A system equipped with UV-vis detector  
120 (SPD-10AV; Shimadzu) and an ODS-C18 column (25 cm × 4.6 mm, 5 μm; Shimadzu,  
121 Kyoto, Japan). The separation was carried out using methanol:water (25:75 v/v) as

122 isocratic mobile phase at a flow rate of  $1.0 \text{ mL min}^{-1}$ . The detector was set at 241 nm.  
123 The concentration of Co(II) in solution was determined by Methyl isobutyl ketone and  
124 Ammonium thiocyanate (see Supplementary material for the method description and  
125 Fig. S1) [36]. An optical-fiber coupled to a spectrophotometer (UV-1601 Shimadzu,  
126 Japan) was used to scan the UV–vis absorption spectra of Co(II)- $\text{SO}_3^{2-}$  complex.

127 For  $\text{SO}_4^{\bullet-}$  reactivity a laser flash photolysis (LFP) system was used with 266 nm  
128 excitation following the procedure reported by Wu et al. [15]. Analysis of transient  
129 decay and second order rate constant determination (using PARA concentrations from  
130 0 to 0.1 mM) were determined at 470 nm corresponding to the maximum absorption  
131 of  $\text{SO}_4^{\bullet-}$ . The second order rate constants were determined at pH 5.0 and 11.0  
132 corresponding to the molecular and deprotonated forms respectively of PARA ( $\text{pK}_a =$   
133 9.5).

134

### 135 **3. Results and discussion**

136

#### 137 *3.1 Effect of initial pH on paracetamol degradation*

138 The effect of the initial pH on the Co(II)+S(IV) system oxidation of PARA was  
139 investigated from 3.0 to 11.0. The initial concentrations of Co(II) and  $\text{SO}_3^{2-}$  were 0.1  
140 mM and 1.0 mM, respectively and during the reaction, air (otherwise stated) was  
141 constantly bubbled at a flow rate of  $0.8 \text{ L min}^{-1}$ . The PARA degradation shows a strong  
142 pH-dependence as illustrated in Fig. 1A. Despite a negligible degradation at relatively  
143 acidic values (pH 3.0 – 5.0), PARA degradation is enhanced from pH 5.0 to pH 10.0  
144 while a decrease is observed at pH 11.0. It is interesting to observe that degradation  
145 efficiency between pH 3.0 and 10 is strongly correlated to the  $\text{HSO}_3^-/\text{SO}_3^{2-}$  speciation  
146 in solution ( $\text{pK}_a = 7.2$ ) as shown in Fig. 1B in which degradation of PARA after 30 min  
147 at different pH values is correlated to the concentration of  $\text{SO}_3^{2-}$  in solution. However,  
148 at pH 11, the inhibition of PARA degradation can be attributed to the formation of  
149 insoluble Cobalt-hydroxide ( $\text{Co(OH)}_2$ ) complex that is expected to precipitate in  
150 solution [37].

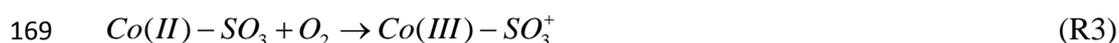
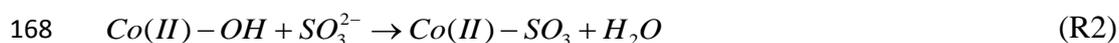
151 Moreover, it has been reported that deprotonated complexes ( $\text{Co(II)-OH}$ ), which

152 is more reactive toward  $\text{SO}_3^{2-}$  compared to  $\text{HSO}_3^-$  would be formed at alkaline pH  
 153 values (R1) leading to the formation of a  $\text{Co(II)-SO}_3$  complex [27].  $\text{Co(II)-SO}_3$  could  
 154 be oxidized to  $\text{Co(III)-SO}_3^+$  complex in the presence of dissolved oxygen as reported in  
 155 different works (R2 and R3) [38].  $\text{SO}_3^{\bullet-}$  could be generated during the redox reaction  
 156 between the  $\text{Co(III)-SO}_3^+$  complex and  $\text{SO}_3^{2-}$  (R4).

157 UV-vis absorption spectra of  $\text{Co(II)}$ ,  $\text{S(IV)}$ ,  $\text{Co(II)}$  and  $\text{S(IV)}$  during the reaction  
 158 (Fig. S1) were acquired to investigate the complexation between  $\text{Co(II)}$  and  $\text{S(IV)}$ . The  
 159 result showed that: only  $\text{Co(II)}$  or  $\text{S(IV)}$  at pH 9.0 did not show absorption in the range  
 160 250-600 nm. However, when  $\text{S(IV)}$  was added to the solution containing 0.1 mM  $\text{Co(II)}$   
 161 an absorption band absorbing up to  $\sim 600$  nm is present. The presence of this new  
 162 absorption band demonstrates that the  $\text{Co(II)-S(IV)}$  complex could be formed and  
 163 decreasing in the absorption during time proved the reaction between  $\text{Co(II)}$  and  $\text{S(IV)}$ ,  
 164 and corresponding depletion of  $\text{S(IV)}$ .

165

166



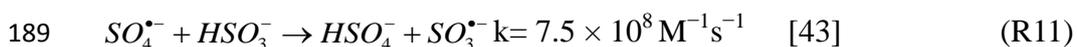
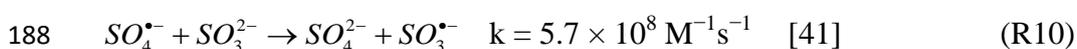
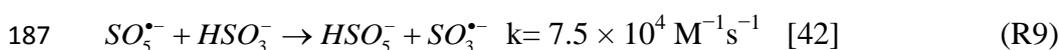
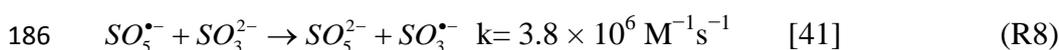
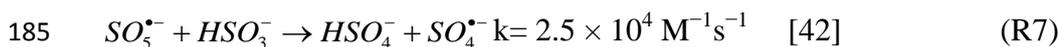
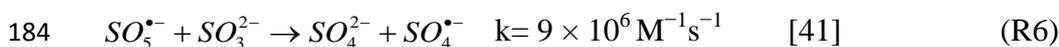
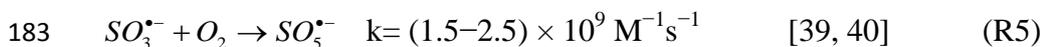
171

172 The pH represents also a key factor influencing the  $\text{SO}_3^{\bullet-}$  reactivity in water. In  
 173 fact, the primary step is the oxygen-mediated oxidation of  $\text{SO}_3^{\bullet-}$  to  $\text{SO}_5^{\bullet-}$  (R5), this  
 174 latter can react with  $\text{HSO}_3^-/\text{SO}_3^{2-}$  leading to the formation of  $\text{SO}_3^{\bullet-}$  and  $\text{SO}_4^{\bullet-}$  (R6-R9).

175 As reported in R6 and R8,  $\text{SO}_5^{\bullet-}$  could react with  $\text{SO}_3^{2-}$  to generate  $\text{SO}_3^{\bullet-}$  and  
 176  $\text{SO}_4^{\bullet-}$  at a rate constant around  $10^5$ - $10^6$ .  $\text{SO}_4^{\bullet-}$  could react with PARA or with  $\text{SO}_3^{2-}$   
 177 leading to the generation  $\text{SO}_3^{\bullet-}$  (R10), then a  $\text{SO}_x^{\bullet-}$  ( $\text{SO}_3^{\bullet-}$ ,  $\text{SO}_4^{\bullet-}$  and  $\text{SO}_5^{\bullet-}$ ) cycle can  
 178 be achieved. However, in the presence of  $\text{HSO}_3^-$  (acidic conditions),  $\text{SO}_5^{\bullet-}$  reacts with  
 179  $\text{HSO}_3^-$  to generate  $\text{SO}_4^{\bullet-}/\text{SO}_3^{\bullet-}$  with a relatively shower rate constants (R7 and R9)

180 compared to the reactivity with  $SO_3^{2-}$ . The overall reaction rate between  $SO_5^{\bullet-}$  and  
181  $SO_3^{2-}$  is ~1–2 orders of magnitude higher than between  $SO_5^{\bullet-}$  and  $HSO_3^-$ .

182



190

### 191 3.2 S(IV) and Co(II) effect on the PARA degradation

192 Different amounts of Co(II) were used to investigate the effect of Co(II)  
193 concentration on the PARA removal at pH 9.0 (Fig. 2A). When experiments were  
194 conducted using a Co(II) concentration between 0.05 and 0.15 mM and a fixed sulfite  
195 concentration of 1.0 mM, no significant differences were observed on the PARA  
196 degradation profile. One of reasons explaining the slightly effect of Co(II)  
197 concentration may be the fast recycle of Co(II) and Co(III) in the presence of a  
198 stoichiometry excess of S(IV) concentrations in aerated solution (R3-R4). Moreover,  
199 when the concentration of Co(II) was monitored during the reaction (see the  
200 Supplementary material for the method description), it was found that its concentration  
201 was nearly stable (Fig. S3). Such results suggest that in the presence of enough sulfite  
202 in solution, the cobalt recycle could achieved very fast leading to the generation of  
203  $SO_3^{\bullet-}$  at the same time. Even the addition of Co(II) didn't play a relevant role on the  
204 paracetamol degradation, but for the sake of feasibility and accuracy, 0.1 mM Co(II)  
205 was employed during all experiments, as when the experiments were conducted under  
206 low concentration of Co(II) such as 0.05 mM, the repeatability could not be ensured

207 every time.

208 The dependence of the PARA degradation on the initial concentration of S(IV)  
209 was also investigated (Fig. 2B). An increase in S(IV) concentration (between 0.5 to 1  
210 mM) accelerate the PARA degradation being , through Co(II) reactivity, a source of  
211  $\text{SO}_3^{\bullet-}$ . However, at higher sulfite ions concentrations (2 mM) there is no more  
212 enhancement of PARA degradation and this effect could be attributed to the reactivity  
213 competition of  $\text{SO}_4^{\bullet-}/\text{SO}_5^{\bullet-}$  between PARA and  $\text{SO}_3^{2-}$  (R8 and R10). Hence, the  
214 balance between S(IV) concentration and its catalytic character is a key factor for the  
215 oxidative system efficiency.

216 In all these experiments (Fig. 2) it is impossible to obtain more than 90% of PARA  
217 degradation. This observation is certainly due to a competition reaction of the sulfate  
218 radicals on PARA, the excess of sulfite and the degradation products of PARA. After a  
219 short period of time sulfate radicals react no more on paracetamol due to its low  
220 concentration.

221

### 222 *3.3 Effect of O<sub>2</sub>*

223 The effect of oxygen concentration on the PARA degradation using 0.1 mM of  
224 Co(II) and 1 mM of S(IV) was investigated comparing results from aerated and  
225 nitrogen-purged solutions. When experiment was conducted in aerated solution (under  
226 air bubbling), a PARA degradation plateau was reached after first 10 min corresponding  
227 to ~82% of degradation (Fig. 3). However, under nitrogen-saturated solution, the  
228 efficiency dropped to less than 8% confirming that oxygen is a crucial parameter.  
229 Oxygen strongly favors the degradation of pollutant through  $\text{SO}_3^{\bullet-}$  oxidation into  $\text{SO}_5^{\bullet-}$   
230 that undergo further reaction to form  $\text{SO}_4^{\bullet-}$  in the solution (R5-R7).

231

### 232 *3.4 Radical species involvement*

233 The second order rate constants of sulfate radical with molecular and deprotonated  
234 PARA (at pH 9.0, pH used in our experiments, about 25 % of PARA is under  
235 deprotonated form) were determined from the linear fit of pseudo-first order decay  
236 monitored at 470 nm (corresponding to the maximum absorption of sulfate radical) vs

237 concentration of PARA in solution (Fig. S4). The second order rate constant was  
238 estimated to be  $1.33 \pm 0.79 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (at pH 5) and  $6.14 \pm 0.99 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (at pH  
239 11.0) corresponding respectively to the molecular and deprotonated form, on the phenol  
240 group, of PARA.

241 To shed light onto radical mechanism involved in such system, EtOH and TBA  
242 were used as radical scavengers. This competition kinetic approach is based on the  
243 different second-order rate constant with  $\text{HO}^\bullet$  and  $\text{SO}_4^{\bullet-}$  ( $k_{\text{TBA},\text{HO}^\bullet} = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$   
244 [44] which is nearly three orders of magnitude higher than  $k_{\text{TBA},\text{SO}_4^{\bullet-}} = 8.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$   
245 [45] and  $k_{\text{EtOH},\text{HO}^\bullet} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [44],  $k_{\text{EtOH},\text{SO}_4^{\bullet-}} = 5.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [41]). In the  
246 presence of TBA (up to 6 mM) no effect was observed on the PARA degradation [Fig.  
247 S5] indicating that hydroxyl radical are not generated using Co(II) 0.1 mM and  $\text{SO}_3^{2-}$   
248 1 mM at pH 9.0. Indeed, if hydroxyl radical were produced in the system, addition of 1  
249 mM TBA should be scavenged about 98 %  $\text{HO}^\bullet$  reducing drastically the PARA  
250 degradation. However, when EtOH was used as radical scavenger in solution (Fig. 4)  
251 PARA degradation rate and efficiency (after 30 min) were modified. In the presence  
252 of 500 mM of EtOH, a complete inhibition of PARA degradation should be expected  
253 on the basis of second order rate constant reported before. But, PARA is still degraded  
254 with ~ 29% of disappearance after 30 min. Such trend could be explained considering  
255 the possible involvement of  $\text{SO}_5^{\bullet-}$  during PARA degradation. In fact, EtOH is not able  
256 to scavenge strongly  $\text{SO}_5^{\bullet-}$  due to the very low rate constant ( $k_{\text{EtOH},\text{SO}_5^{\bullet-}} < 10^3 \text{ M}^{-1} \text{ s}^{-1}$   
257 [46]).

258 Such results suggest that  $\text{SO}_4^{\bullet-}$  represent the main radical leading to the degradation,  
259 but also possible implication of  $\text{SO}_5^{\bullet-}$  during degradation of PARA is possible.

260

### 261 3.5 Heterogeneous reaction between CoO and $\text{SO}_3^{2-}$

262 Cobalt oxide such as CoO,  $\text{CoO}_2$ ,  $\text{CoO}(\text{OH})$ ,  $\text{Co}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  were usually used  
263 to react with PMS to oxidize different kinds of organic pollutants [24]. Experiments to  
264 prove the efficiency of sulfite activation by CoO were conducted at pH 9.0 with the

265 paracetamol concentration of 10  $\mu\text{M}$  and  $\text{SO}_3^{2-}$  at 1.0 mM. As shown in Fig. 5, when  
266 0.1 mM and 1.0 mM CoO were added to the solution, the degradation efficiency were  
267 32.9% and 71.7%, after 30 min respectively, which indicates that CoO exhibit a good  
268 catalytic activity. One of heterogeneous catalysts advantages belong to their stability  
269 and their reusability as catalyst. However, oxide can easily agglomerate during catalytic  
270 reaction, resulting in the reduction of catalytic performance [47], also cobalt ion  
271 leaching and dissolving problem can cause the same potential environmental and health  
272 problem as homogeneous catalysts do. As reported in Fig. 5 and Fig. 2A, the initial  
273 degradation rate is completely different in the two systems, very fast with soluble Co(II)  
274 and much slower with CoO. This observation shows that the reactivity of sulfite with  
275 cobalt is efficient in homogeneous phase and so with cobalt oxide a first process of  
276 solubilisation seems necessary.

277

### 278 *3.6 Sequential experiments for high concentration paracetamol*

279 Sequential experiments were performed with multiple additions of S(IV) to  
280 enhance the degradation of high concentration of paracetamol in this Co(II)-S(IV)  
281 system. In the experiment, the concentration of paracetamol was 500  $\mu\text{M}$ , Co(II) was  
282 0.5 mM, and the initial pH value of solution was adjusted to 9.0 and then controlled  
283 during the whole reaction. 5 mM S(IV) was added to the solution at the beginning,  
284 while 0.5 mM were spiked every 20 min. After 200 min of reaction, (Fig. S6) nearly  
285 complete PARA degradation was archived. Compared to Co(II), which is recycled  
286 during the reaction, sulfite is consumed as transforms into  $\text{SO}_3^{\bullet-}$  and subsequently into  
287  $\text{SO}_4^{2-}$ . So due to the depletion of S(IV), multiple additional sulfite is necessary to  
288 promote sequential treatment.

289

## 290 **4. Conclusion**

291 Our results showed the high efficiency of this Co(II)-S(IV) system using PARA as  
292 organic pollutant model in aqueous solution at alkaline pH. In this system, the  
293 degradation of paracetamol depend on initial concentrations of S(IV) and strongly the  
294 pH. In fact, it is clear that dissolved oxygen plays a crucial role allowing the oxysulfure

295 radicals oxidation to initiate the reaction. The results of radical scavenger experiments  
296 demonstrate that  $\text{SO}_4^{\bullet-}$  and also  $\text{SO}_5^{\bullet-}$  (to a lesser extent) are involved during the  
297 paracetamol degradation. Furthermore, heterogeneous catalyst CoO also could react  
298 with sulfite to degrade paracetamol to a large extent. In general, this research work  
299 provides a new promising strategy by using sulfite and transition metal Co(II) to  
300 degrade organic compounds in wastewater under alkaline environment. One of the  
301 perspectives of this work is to perform same experiments with other metals in order to  
302 assess their ability to promote the radical generation from sulfite under dark and light  
303 conditions.

304

305

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315

## 316 **References**

- 317 [1] G.P. Anipsitakis, D.D. Dionysiou, *Environ. Sci. Technol.* 37 (2003) 4790-4797.  
318 [2] P. Shukla, H. Sun, S. Wang, H.M. Ang, M.O. Tadé, *Catal. Today* 175 (2011) 380-385.  
319 [3] Y. Zuo, J. Zhan, T. Wu, *J. Atmos. Chem.* 50 (2005) 195-210.  
320 [4] P. Neta, R.E. Huie, A.B. Ross, *J. Phys. Chem. Ref. Data* 17 (1988) 1027-1284.  
321 [5] H.V. Lutze, S. Bircher, I. Rapp, N. Kerlin, R. Bakkour, M. Geisler, C. von Sonntag, T.C. Schmidt,  
322 *Environ. Sci. Technol.* 49 (2015) 1673-1680.  
323 [6] Y. Ren, L. Lin, J. Ma, J. Yang, J. Feng, Z. Fan, *Appl. Catal., B* 165 (2015) 572-578.  
324 [7] G.P. Anipsitakis, D.D. Dionysiou, M.A. Gonzalez, *Environ. Sci. Technol.* 40 (2006) 1000-1007.  
325 [8] Y.-T. Lin, C. Liang, J.-H. Chen, *Chemosphere* 82 (2011) 1168-1172.  
326 [9] X. Xie, Y. Zhang, W. Huang, S. Huang, *J. Environ. Sci.* 24 (2012) 821-826.  
327 [10] M.G. Antoniou, A.A. de la Cruz, D.D. Dionysiou, *Appl. Catal., B* 96 (2010) 290-298.  
328 [11] J. Criquet, N. Karpel Vel Leitner, *Chem. Eng. J.* 169 (2011) 258-262.  
329 [12] H. Guo, N. Gao, Y. Yang, Y. Zhang, *Chem. Eng. J.* 292 (2016) 82-91.  
330 [13] L.W. Matzek, K.E. Carter, *Chemosphere* 151 (2016) 178-188.  
331 [14] Y. Wu, R. Prulho, M. Brigante, W. Dong, K. Hanna, G. Mailhot, *J. Hazard. Mater.* 322, Part B  
332 (2017) 380-386.  
333 [15] Y. Wu, A. Bianco, M. Brigante, W. Dong, P. de Sainte-Claire, K. Hanna, G. Mailhot, *Environ. Sci.*  
334 *Technol.* 49 (2015) 14343-14349.  
335 [16] C. Qi, X. Liu, J. Ma, C. Lin, X. Li, H. Zhang, *Chemosphere* 151 (2016) 280-288.  
336 [17] T. Zhang, H. Zhu, J.-P. Croué, *Environ. Sci. Technol.* 47 (2013) 2784-2791.  
337 [18] A.B. Kurukutla, P.S.S. Kumar, S. Anandan, T. Sivasankar, *Environ. Eng. Sci.* 32 (2014) 129-140.  
338 [19] Y.-F. Huang, Y.-H. Huang, *J. Hazard. Mater.* 167 (2009) 418-426.  
339 [20] A. Rastogi, S.R. Al-Abed, D.D. Dionysiou, *Appl. Catal., B* 85 (2009) 171-179.  
340 [21] F. Ghanbari, M. Moradi, *Chem. Eng. J.* 310, Part 1 (2017) 41-62.  
341 [22] H. Liang, H. Sun, A. Patel, P. Shukla, Z.H. Zhu, S. Wang, *Appl. Catal., B* 127 (2012) 330-335.  
342 [23] M. Stoyanova, I. Slavova, S. Christoskova, V. Ivanova, *Appl. Catal. A* 476 (2014) 121-132.  
343 [24] Y. Wang, L. Zhou, X. Duan, H. Sun, E.L. Tin, W. Jin, S. Wang, *Catal. Today* 258 (2015) 576-584.  
344 [25] Y. Zhu, S. Chen, X. Quan, Y. Zhang, *RSC Adv.* 3 (2013) 520-525.  
345 [26] L. Chen, X. Peng, J. Liu, J. Li, F. Wu, *Ind. Eng. Chem. Res.* 51 (2012) 13632-13638.

346 [27] Z. Liu, S. Yang, Y. Yuan, J. Xu, Y. Zhu, J. Li, F. Wu, *J. Hazard. Mater.* 324, Part B (2017) 583-592.  
347 [28] Y. Yuan, S. Yang, D. Zhou, F. Wu, *J. Hazard. Mater.* 307 (2016) 294-301.  
348 [29] D. Zhou, L. Chen, C. Zhang, Y. Yu, L. Zhang, F. Wu, *Water Res.* 57 (2014) 87-95.  
349 [30] D. Zhou, Y. Yuan, S. Yang, H. Gao, L. Chen, *J. Sulfur Chem.* 36 (2015) 373-384.  
350 [31] D.T.F. Kuo, D.W. Kirk, C.Q. Jia, *J. Sulfur Chem.* 27 (2006) 461-530.  
351 [32] Y. Zuo, *Geochim. Cosmochim. Acta* 59 (1995) 3123-3130.  
352 [33] Y. Zuo, J. Zhan, *Atmos. Environ.* 39 (2005) 27-37.  
353 [34] M.J. Benotti, R.A. Trenholm, B.J. Vanderford, J.C. Holady, B.D. Stanford, S.A. Snyder, *Environ.*  
354 *Sci. Technol.* 43 (2009) 597-603.  
355 [35] L. Zhang, J. Hu, R. Zhu, Q. Zhou, J. Chen, *Appl. Microbiol. Biotechnol.* 97 (2013) 3687-3698.  
356 [36] D. Katakis, A.O. Allen, *J. Phys. Chem.* 68 (1964) 1359-1362.  
357 [37] K.H. Chan, W. Chu, *Water Res.* 43 (2009) 2513-2521.  
358 [38] W. Pasiuk-Bronikowska, T. Bronikowski, M. Ulejczyk, *Environ. Sci. Technol.* 26 (1992)  
359 1976-1981.  
360 [39] R.E. Huie, P. Neta, *J. Phys. Chem.* 88 (1984) 5665-5669.  
361 [40] G.V. Buxton, S. McGowan, G.A. Salmon, J.E. Williams, N.D. Wood, *Atmos. Environ.* 30 (1996)  
362 2483-2493.  
363 [41] U. Deister, P. Warneck, *J. Phys. Chem.* 94 (1990) 2191-2198.  
364 [42] R.E. Huie, P. Neta, *Atmos. Environ.* 21 (1987) 1743-1747.  
365 [43] P.H. Wine, Y. Tang, R.P. Thorn, J.R. Wells, D.D. Davis, *J. Geophys. Res.* 94 (1989) 1085-1094.  
366 [44] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, *J. Phys. Chem. Ref. Data* 17 (1988)  
367 513-886.  
368 [45] C.L. Clifton, R.E. Huie, *Int. J. Chem. Kinet.* 21 (1989) 677-687.  
369 [46] E. Hayon, A. Treinin, J. Wilf, *J. Am. Chem. Soc.* 94 (1972) 47-57.  
370 [47] J. Deng, S. Feng, K. Zhang, J. Li, H. Wang, T. Zhang, X. Ma, *Chem. Eng. J.* 308 (2017) 505-515.  
371

372 **Figures Captions**

373

374 **Fig. 1:** Effect of initial pH values on PARA degradation. Condition:  $[\text{PARA}]_0 = 10 \mu\text{M}$ ,  
375  $[\text{Co(II)}]_0 = 0.1 \text{ mM}$ ,  $[\text{Na}_2\text{SO}_3]_0 = 1.0 \text{ mM}$ ,  $T = 25^\circ\text{C}$ ,  $F_{\text{air}} = 0.8 \text{ L min}^{-1}$ .

376

377 **Fig. 2:** Effect of (A) Co(II) and (B) S(IV) concentrations on PARA degradation.  
378 Condition:  $[\text{PARA}]_0 = 10\mu\text{M}$ ,  $\text{pH}_0 = 9.0$ ,  $T = 25^\circ\text{C}$ ,  $F_{\text{air}} = 0.8 \text{ L min}^{-1}$ .

379

380 **Fig. 3:** Effect of oxygen on PARA degradation. Condition:  $[\text{PARA}]_0 = 10\mu\text{M}$ ,  $[\text{Co(II)}]_0$   
381  $= 0.1 \text{ mM}$ ,  $[\text{Na}_2\text{SO}_3]_0 = 1.0 \text{ mM}$ ,  $\text{pH}_0 = 9.0$ ,  $T = 25^\circ\text{C}$ ,  $F_{\text{air}} = 0.8 \text{ L min}^{-1}$ .

382

383

384 **Fig.4:** Effect of radical scavenger of EtOH on PARA degradation.

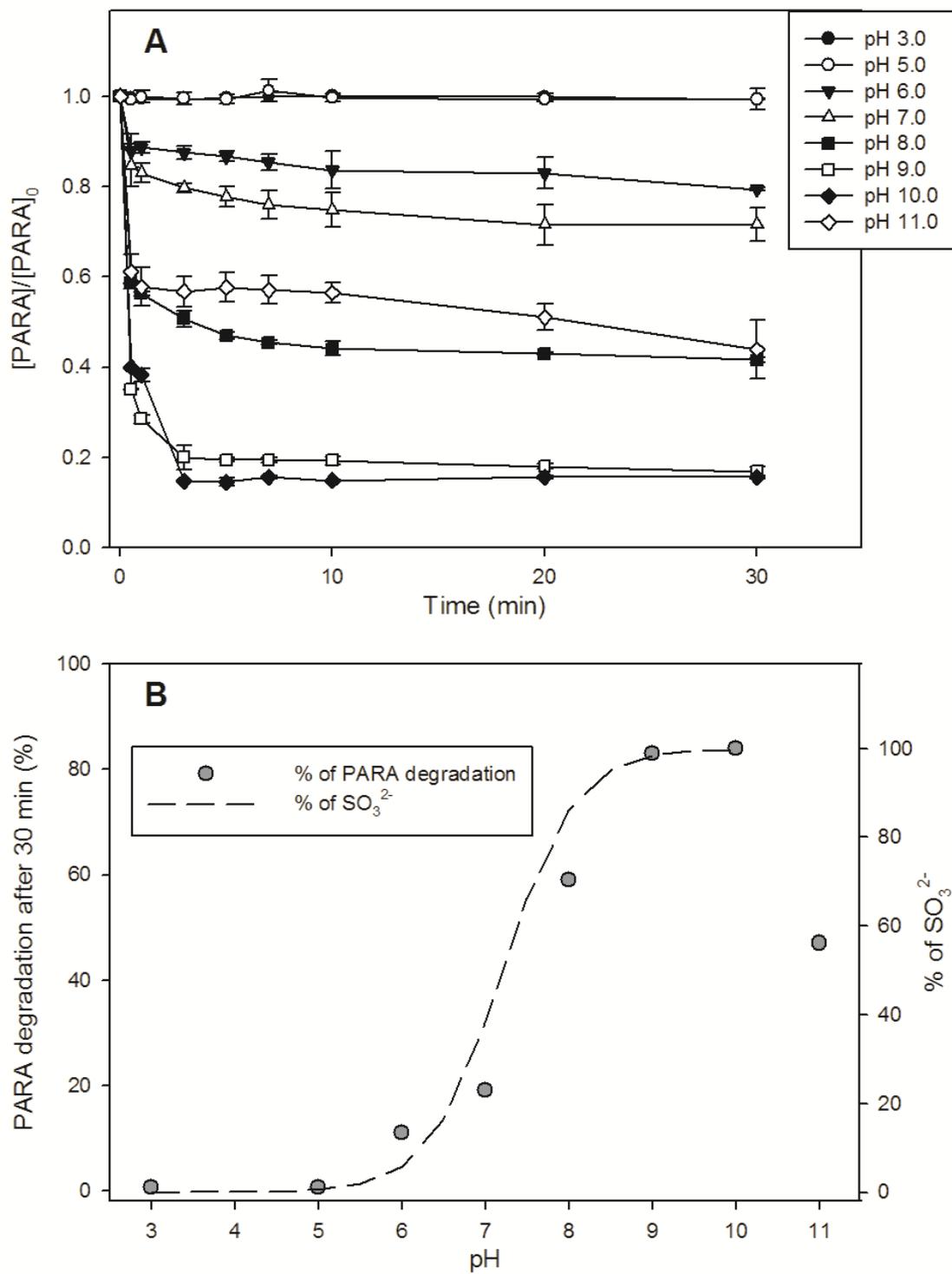
385 Condition:  $[\text{PARA}]_0 = 10\mu\text{M}$ ,  $[\text{Co(II)}]_0 = 0.1 \text{ mM}$ ,  $[\text{Na}_2\text{SO}_3]_0 = 1.0 \text{ mM}$ ,  $\text{pH}_0 = 9.0$ ,  $T =$   
386  $25^\circ\text{C}$ ,  $F_{\text{air}} = 0.8 \text{ L min}^{-1}$ .

387

388 **Fig. 5:** Effect of heterogeneous catalyst CoO react with S(IV) to degrade PARA.

389 Condition:  $[\text{PARA}]_0 = 10\mu\text{M}$ ,  $[\text{Na}_2\text{SO}_3]_0 = 1.0 \text{ mM}$ ,  $\text{pH}_0 = 9.0$ ,  $T = 25^\circ\text{C}$ ,  $F_{\text{air}} = 0.8 \text{ L}$   
390  $\text{min}^{-1}$ .

391



**Fig. 1**

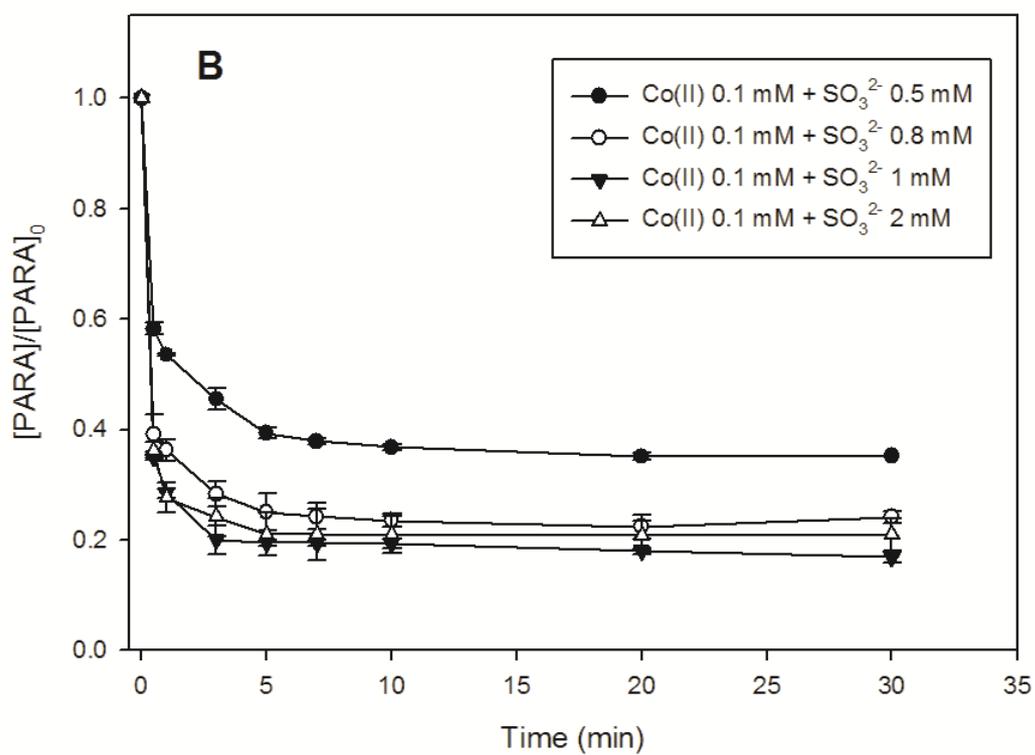
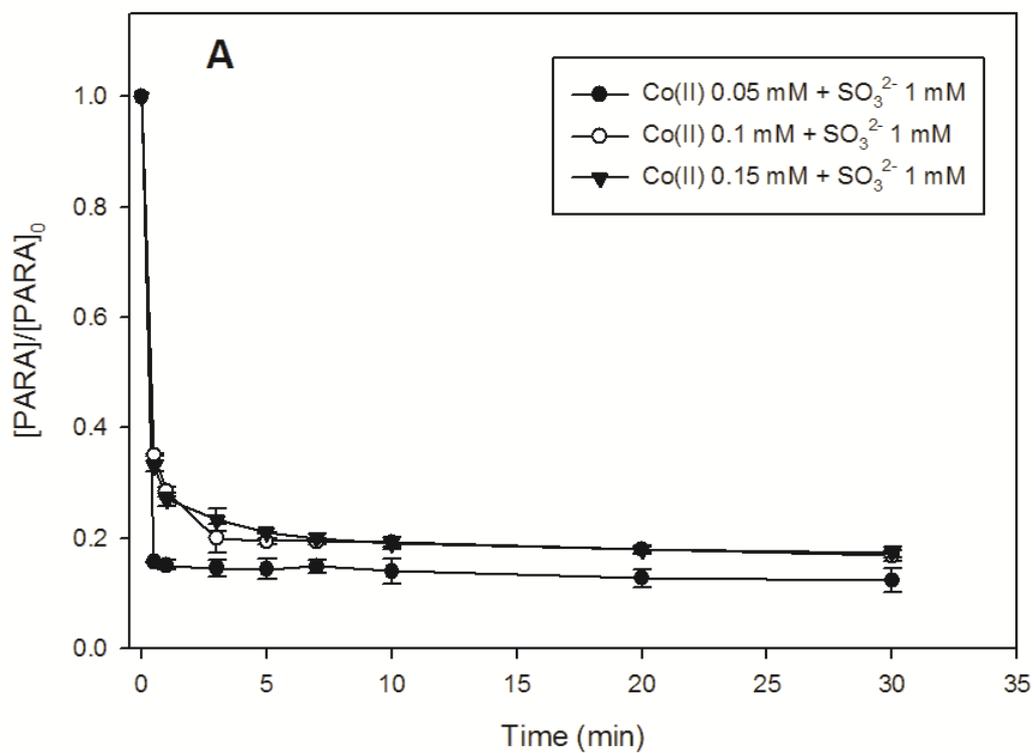
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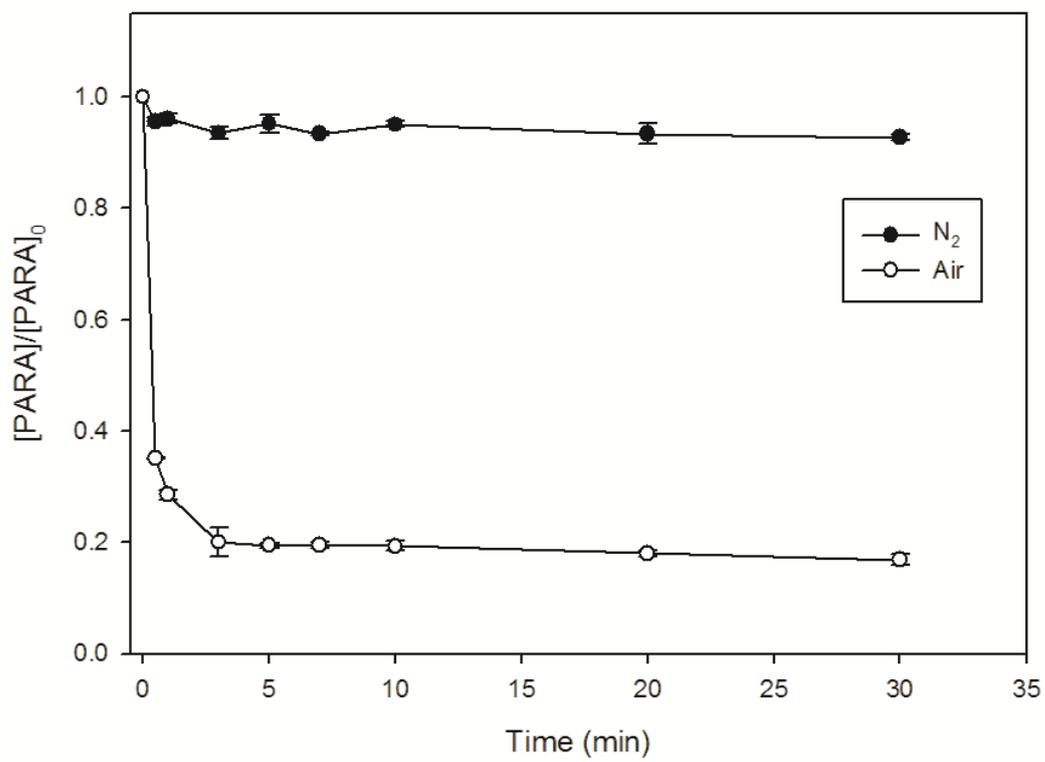
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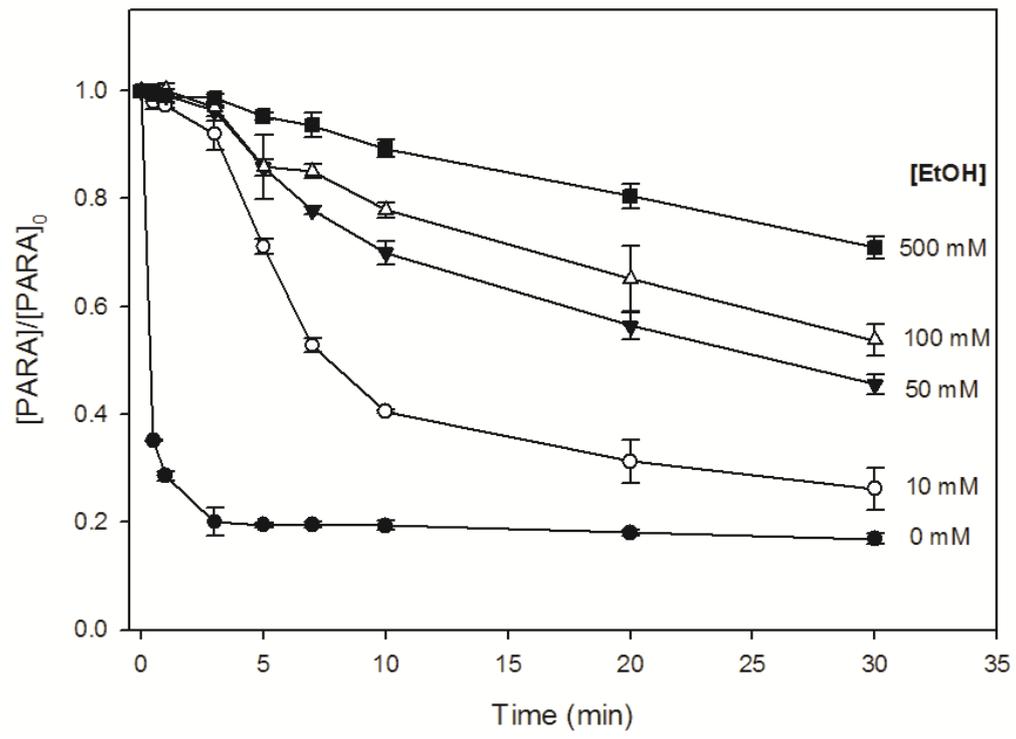
398 **Fig. 2**



399

400 **Fig. 3.**

401

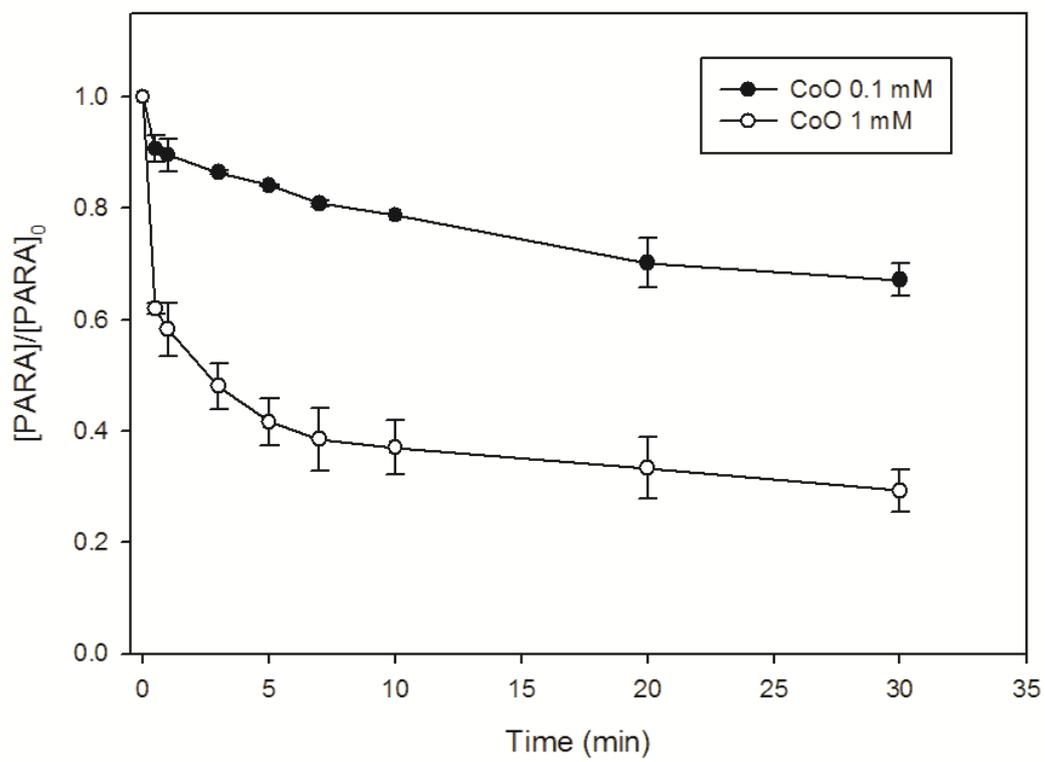


402

403

**Fig.4.**

404



405

406 **Fig. 5**

407

408

## Supplementary material

### **Rapid Oxidation of Organic Contaminants by Cobalt(II) Catalyzed Sulfite at Alkaline pH**

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Mailhot<sup>2\*</sup>

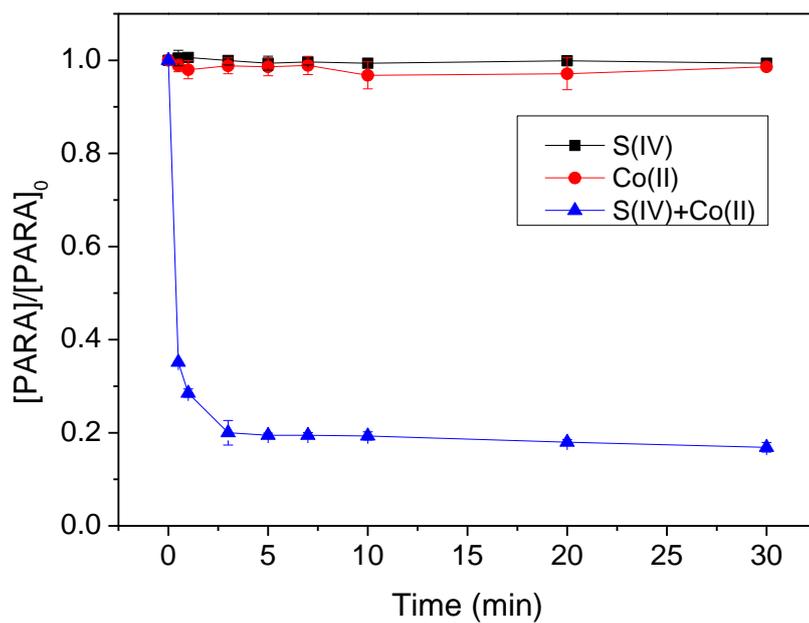
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#### **Preliminary experiment using Co(II)-S(IV)**

A typical degradation of Paracetamol by three different kinds of system (only Co(II), only sulfite(S(IV)), Co(II)+S(IV)) is presented in Fig.S0. The result showed that when the experiment conducted in the presence of S(IV) without any catalyst, negligible change in paracetamol concentration was observed. A similar trend was also achieved in the experiment by only using Co(II) even after being centrifuged for 15 min at 9000 rpm. There was no precipitation occurred, which illustrated that there is no adsorption in this system and neither S(IV) nor Co(II) added to the reagent had an effect on Paracetamol. However, when both S(IV) and Co(II) were in solution, Paracetamol can be degraded to more than 80% in 10 min. These results suggest that Paracetamol degradation depends heavily on the reaction between S(IV) and Co(II), it proceeded only when S(IV) and Co(II) were present.



436

437 **Fig.S0** The effect of control experiments under various conditions on paracetamol

438 degradation. Condition:  $[\text{PARA}]_0 = 10\mu\text{M}$ ,  $[\text{Co(II)}]_0 = 0.1\text{ mM}$ ,  $[\text{Na}_2\text{SO}_3]_0 = 1.0$

439  $\text{mM}$ ,  $\text{pH}_0 = 9.0$ ,  $T = 25^\circ\text{C}$ ,  $F_{\text{air}} = 0.8\text{ L min}^{-1}$ .

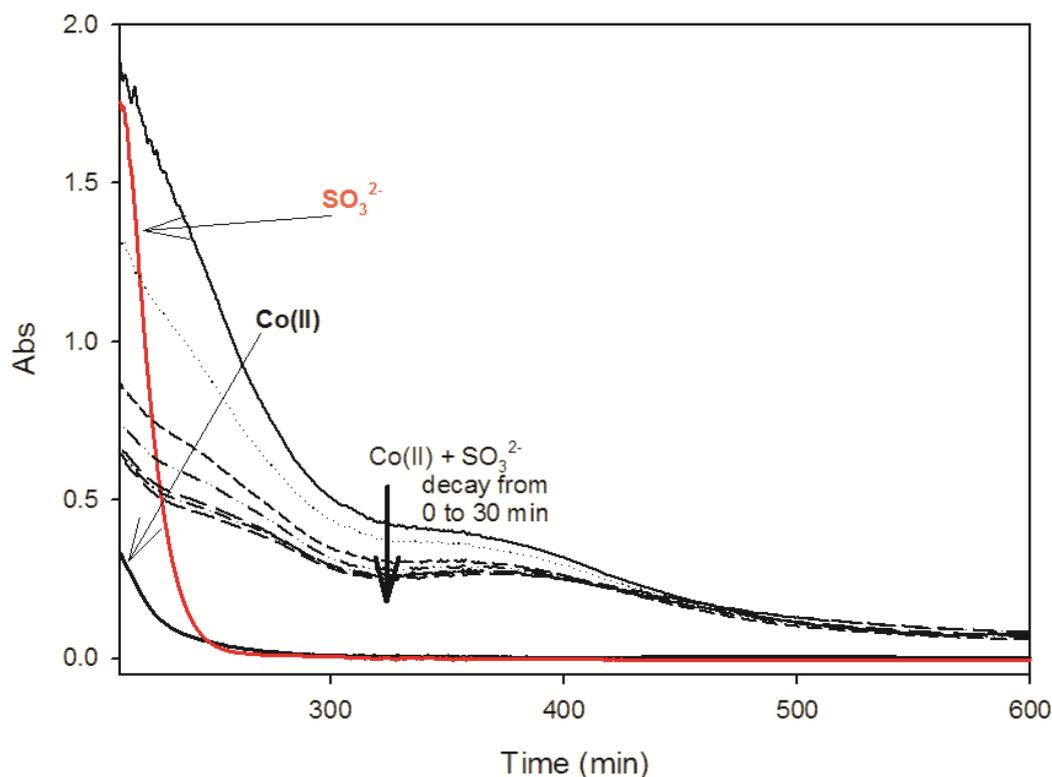
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441

442

### 443 UV spectra of the reaction solution

444



445

446 **Fig. S1.** UV-vis spectra of reaction solution at specific time intervals during the  
447 reaction. Conditions:  $[\text{Co(II)}]_0 = 0.1 \text{ mM}$ ,  $[\text{Na}_2\text{SO}_3]_0 = 1.0 \text{ mM}$ ,  $\text{pH}_0 = 9.0$ ,  $T$   
448  $= 25^\circ\text{C}$ ,  $F_{\text{air}} = 0.8 \text{ L min}^{-1}$ .

449

450

451

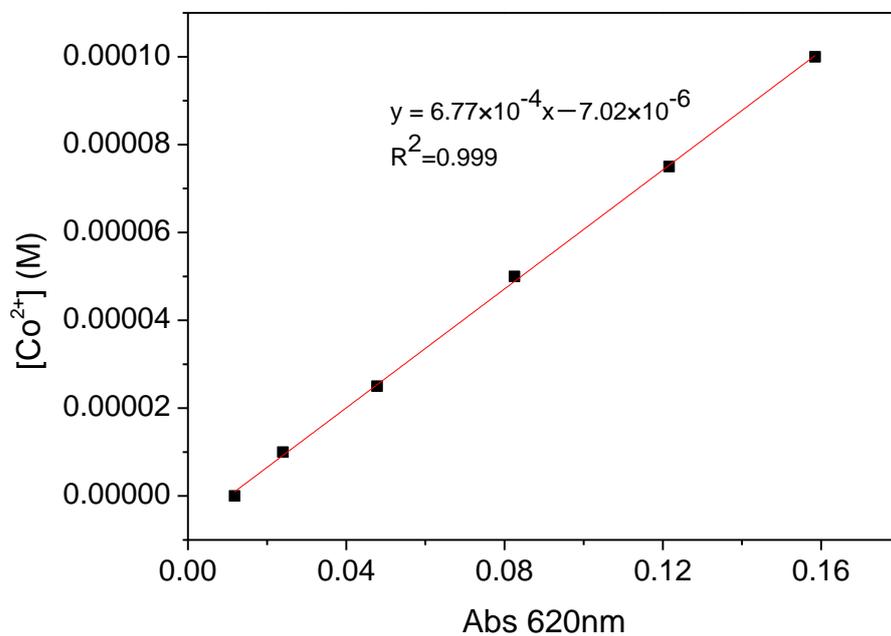
### 452 Cobalt(II) quantification

453 The calibration of Cobalt(II) was measured by preparing a series of standard solutions,  
454 firstly, 5 mL cobalt(II) and 1 mL  $\text{NH}_4\text{SCN}$  (566g/L) was added to a 10 mL centrifuge  
455 tube and hand shaken for 1 min, then another 4 mL pure MIK was added to the mixture,  
456 and ultrasonic shaking for 1 min and equilibrating until stratification occurred. Using the  
457 UV-Vis spectrophotometer for the absorbance at 620 nm for the upper layer complex  
458 which containing Cobalt(II). The calibration curve is presented in Fig. S2a.

459 The calibration equation is:

460

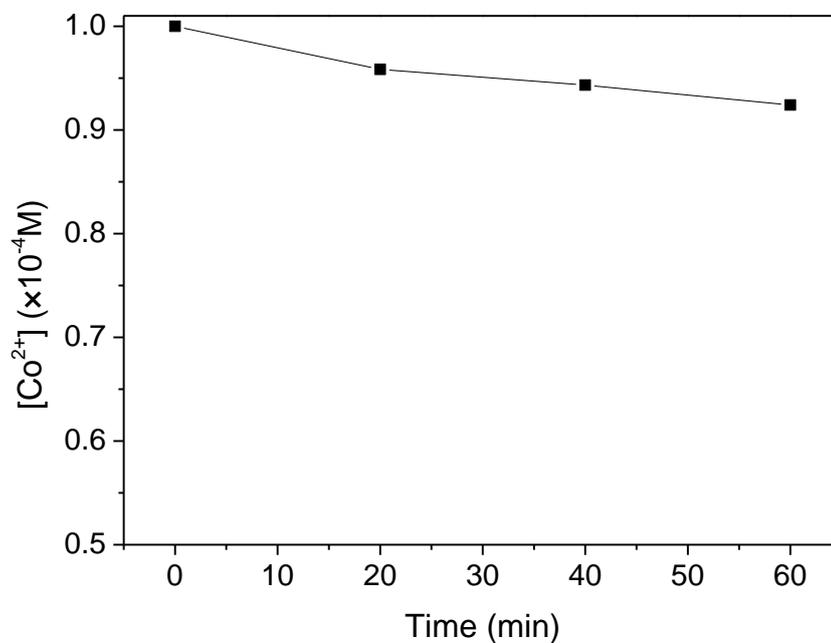
461  $[\text{Co}^{2+}] \text{ (M)} = (6.77 \times 10^{-4} \times \text{Abs}_{620 \text{ nm}}) - 7.02 \times 10^{-6}$



462

463 **Fig.S2. Co(II) concentration vs Abs at 620 nm using described method**

464



465

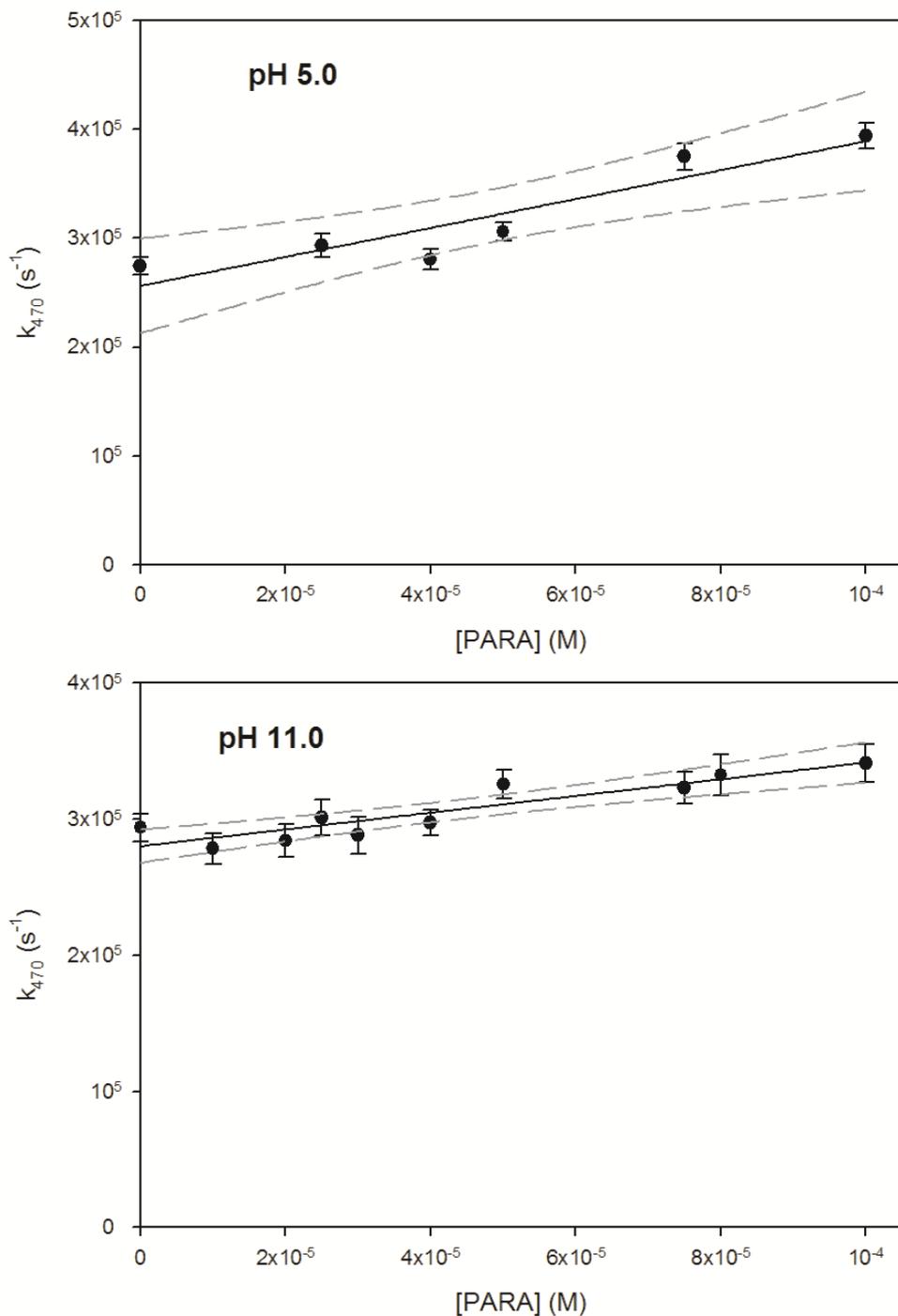
466 **Fig. S3. Co(II) concentration during the reaction.**

467

Condition:  $[\text{PARA}]_0 = 10 \mu\text{M}$ ,  $[\text{Co(II)}]_0 = 0.1 \text{ mM}$ ,  $[\text{Na}_2\text{SO}_3]_0 = 1.0 \text{ mM}$ ,  $\text{pH}_0 =$

468

9.0,  $T = 25^{\circ}\text{C}$ ,  $F_{\text{air}} = 0.8 \text{ L min}^{-1}$ .



470

471

472 Fig. S4 : Pseudo-first order decay of sulfate radical monitored at 470 nm vs PARA

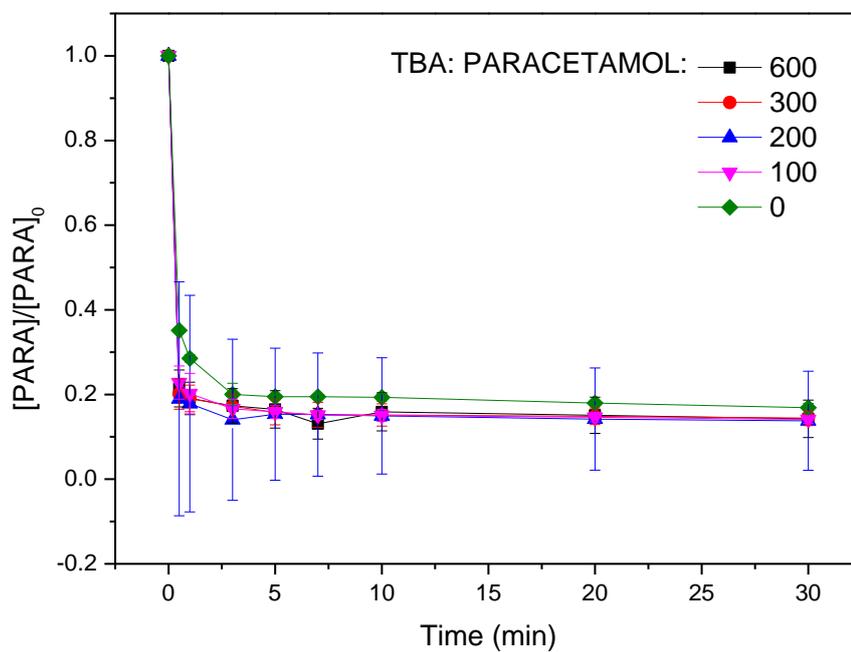
473 concentration for molecular (pH 5.0) and deprotonated form (pH 11.0).solid

474 line represents the linear fit of the experimental data and the dashed lines

475 denote the 95% confidence interval of this fit.

476

477 **The radical scavenger of TBA**



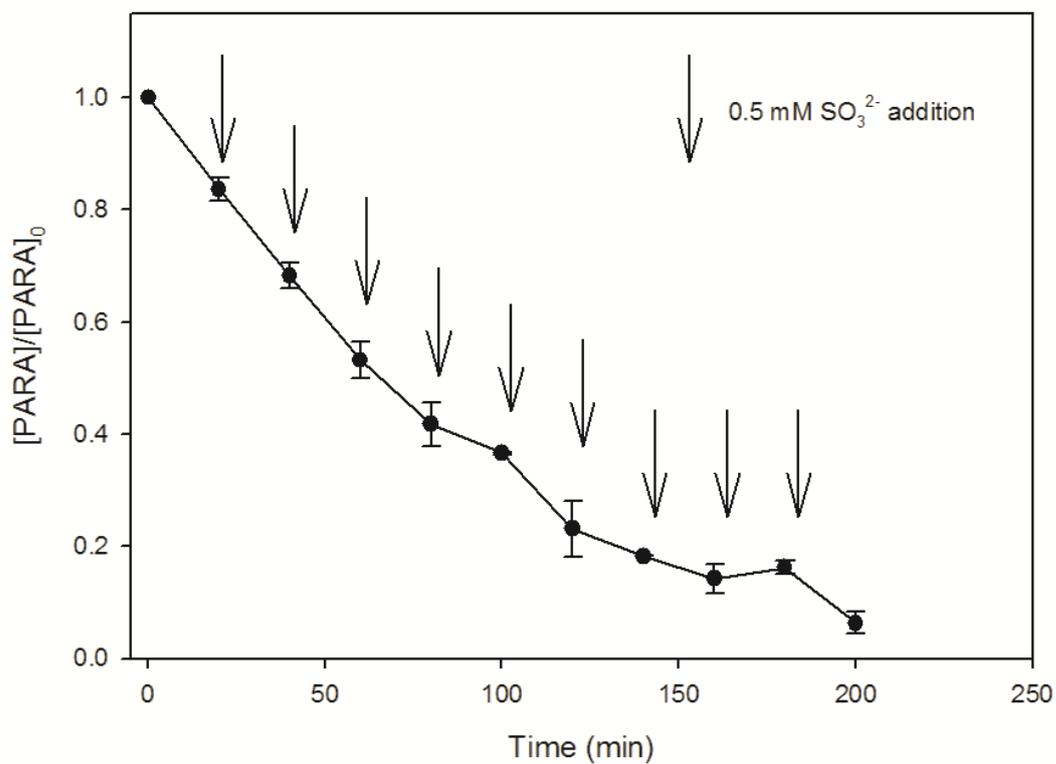
478

479 **Fig. S5.** Effect of TBA on paracetamol degradation.

480 Condition:  $[\text{PARA}]_0 = 10\mu\text{M}$ ,  $[\text{Co(II)}]_0 = 0.1\text{ mM}$ ,  $[\text{Na}_2\text{SO}_3]_0 = 1.0\text{ mM}$ ,  $\text{pH}_0 =$

481 9.0,  $T = 25^\circ\text{C}$ ,  $F_{\text{air}} = 0.8\text{ L min}^{-1}$ .

482



483

484 **Fig. S6.** Changes in paracetamol concentration over time in sequential experiments for  
 485 the oxidation of paracetamol at high concentration. Initial conditions:  $[\text{PARA}]_0 = 500$   
 486  $\mu\text{M}$ ,  $[\text{Co(II)}]_0 = 0.5 \text{ mM}$ ,  $[\text{Na}_2\text{SO}_3]_0 = 5.0 \text{ mM}$ ,  $\text{pH}_0 = 9.0$ ,  $T = 25^\circ\text{C}$ ,  $F_{\text{air}} = 0.8 \text{ L min}^{-1}$ .  
 487 Multiple additions of  $0.5 \text{ mM S(IV)}$  every 20 min.

488