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Decomposition of chloroform and succinic acid by ozonation in a suction-cavitation system: Effects of gas flow

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ABSTRACT

The conductivity of aqueous solutions containing 1 mM chloroform increases upon the chloroform decomposition that is induced by hydrodynamic cavitation in the suction-cavitation system. However, the rate of increase in conductivity (RIC) drops significantly, from 1.314 $\mu\text{S cm}^{-1} \text{min}^{-1}$ without gas flow to 0.552 $\mu\text{S cm}^{-1} \text{min}^{-1}$ with 25 mL min^{-1} of air flow. The RIC decreases further with increasing air flow, until pseudo-zero growth is reached at 200 mL min^{-1} air flow. Introducing O_3 at 33 mL min^{-1} gas flow (effective cavitation) improves RIC, from 0.4193 to 0.5509 $\mu\text{S cm}^{-1} \text{min}^{-1}$, but the enhanced rate (31.4%) is lower than at 200 mL min^{-1} of gas flow (little effective cavitation). The concentrations of dissolved O_2 , O_3 and H_2O_2 , that is formed on-site, increase with increasing gas flow and orifice plate hole diameter. Succinic acid (0.42 mM) is not oxidized by O_3 or H_2O_2 alone, but is rapidly degraded by a combination of $\text{O}_3/\text{H}_2\text{O}_2$ in the suction-cavitation system. The degradation rate of zero-order kinetics increases from 2.604 to 4.788 $\mu\text{M min}^{-1}$ as orifice diameter increases from 5 to 8 mm. Increasing O_3 gas flow and temperature favour SA degradation. Increasing H_2O_2 concentration is more effective in producing OH radicals and promoting the oxidation of succinic acid than increasing O_3 input amount.

Keywords: Chloroform; Succinic acid; Decomposition; Ozonation; Hydrodynamic cavitation.

26 1. Introduction

27 Ozonation is an advanced oxidation process and, as such, is a common process for removing biologically
28 toxic or persistent pollutants from waste water [1,2]. However, only low mineralization levels are achieved
29 since by-products, such as small carboxylic acids, are generated during the process [3]. These by-products
30 lead to COD and TOC reduction levels of less than 50% during the ozonation of dyes for 60-90 min,
31 although decolourization is almost complete [4]. Ozonation is also moderately effective in removing COD
32 from a sanitary landfill leachate [5]. Ozonation is therefore usually used as a pre-treatment to recalcitrance to
33 improve biodegradation via partial oxidation [6,7]. A number of strategies, such as UV irradiation [8],
34 ultrasound [9,10], microbubbles [11,12], specific catalysts [13,14] and H₂O₂ [15], have been combined to
35 improve mineralization during ozonation and to achieve the highest COD and TOC removal efficiency
36 [16,17]. The remarkable ozonation acceleration has been demonstrated in the presence of H₂O₂. TOC is
37 simultaneously decreased because of the enhancement in hydroxyl radical (OH•) formation from the reaction
38 of H₂O₂ with O₃ [18]. The reaction of O₃ with dissociated H₂O₂ is described as follows [19]:



41 A large number of organic contaminants have been efficiently removed using the O₃/H₂O₂ process [20-
42 22]. Moreover, the O₃/H₂O₂ combination leads to important increases in the COD degradation rate in
43 industrial wastewater treatment [23], indicating that OH• formed on-site plays a critical role in the complete
44 mineralization of organic contaminants. In view of OH• formation, the hydrodynamic cavitation (HC)
45 strategy has been regarded as another promising option with which to achieve ozonation process
46 intensification.

47 HC is created during the turbulent flow of liquids and obtained when large pressure drops are generated
48 within a moving liquid [24,25]. It is similar to the effects of ultrasonic cavitation; the thermal cleavage of
49 H₂O and volatile chlorocarbons, as well as the formation of oxidative species, such as Cl₂, OH• and H₂O₂, are
50 induced by numerous hot spots [26,27]. Therefore, the degradation of organic contaminants by the high-
51 energy micro-bubbles and nano-bubbles that are generated by HC have been extensively investigated [28-

52 32]. A HC reactor can be more easily scaled up to industrial scale than an ultrasonic reactor, although its
53 higher energy efficiency has yet to be proven [24,33]. More interestingly, HC can significantly enhance other
54 advanced oxidation processes (AOPs) [34,35], such as photocatalysis [36] and the Fenton process [37,38],
55 allowing nearly complete degradation of organic substrates and a 76% reduction in TOC. Suction-cavitation
56 (SC) is a HC process in which cavitation is generated at the suction side of the pump rather than at the
57 pressure side. In our previous studies, SC exhibited improved energy efficiency over the classic HC on same
58 scale [33].

59 The enhanced effects of HC on the ozonation degradation of organic contaminants and inactivation of
60 microorganisms have been ever more frequently investigated in recent times [39-42]. The complete
61 degradation of triazophos and 96% TOC removal has been achieved using a combination of HC and
62 ozonation (HC/O₃) [42]. In most studies, HC can considerably promote removal efficiency, ozone utilization
63 efficiency and reduce energy consumption and running costs, but little is known about the synergistic
64 mechanisms of the HC/O₃ combination. Chloroform is one of the most frequently used model compounds
65 because of its ultrasonic cavitation induced thermal decomposition. The thermal cleavage of chloroform can
66 also be caused by HC processes, leading to a linear increase in conductivity with the decomposition of
67 chloroform in aqueous solutions [27,33]. The influence of air and ozone/air flow on the HC-induced
68 decomposition of chloroform has been observed in this study in order to reveal the existence of effective HC
69 even under the interference of gas flow.

70 As mentioned above, the formation of refractory carboxylic acids results in lower organic contaminant
71 mineralization with ozonation alone. Succinic acid (SA, HOOC-(CH₂)₂-COOH) is a dicarboxylic acid. It is a
72 food additive, dietary supplement, excipient in pharmaceutical products and relatively stable to oxidants. It is
73 also a common intermediate formed during the oxidative degradation of many organic compounds and
74 cannot be removed by O₃ alone under acidic conditions [43,44]. Catalytic ozonation is therefore usually used
75 to oxidise SA and achieve complete mineralization [13,17]. The OH[•] oxidation rate constant of SA (3.1×10⁸
76 M⁻¹ s⁻¹) is much higher than its ozonation rate constants (less than 0.03 M⁻¹ s⁻¹) at acidic pH [45,46]. SA has
77 therefore been considered a good probe with which to identify oxidative degradation by OH[•] rather than

78 molecular O₃ [13,45,47]. In this study, the degradation of SA is used to reveal the enhanced roles of HC on
79 the formation of OH^{*} in the presence of O₃ or O₃/H₂O₂ in the SC system.

80 **2. Experimental**

81 *2.1. Chemicals*

82 Succinic acid (C₄H₆O₄, Sigma-Aldrich, 99%), hydrogen peroxide (H₂O₂, Sigma-Aldrich, 50 wt. %),
83 phosphoric acid (H₃PO₄, Sigma, 85%), chloroform (CHCl₃, Riedel-de Haen, 99%), potassium
84 indigotrisulfonate (C₁₆H₇K₃N₂O₁₁, Sigma-Aldrich, analytical standard), potassium iodide (KI, Sigma-Aldrich,
85 99.5%), potassium titanium oxalate (K₂TiO(C₂O₄)₂·2H₂O, Sigma-Aldrich, ≥90%) and deionised water (H₂O,
86 conductivity ≤1.5 μS cm⁻¹) were used as received.

87 *2.2. SC/O₃ setup*

88 This device consists of a Fischer ozon-generator 500 (Neckenheim, Germany) with a stabilized voltage
89 supply, and a device for creating HC by suction, as reported previously [40]. The SC device consists of a
90 centrifugal pump, a suction orifice, a heat exchanger, a water tank, a manometer, a flow-meter and some
91 connecting pipes. All of the materials that make contact with reagents are made from stainless steel (SS316).
92 The centrifugal pump (Speck GY-028-2, 2750 rpm, Roth, Germany) is capable of generating a pressure of
93 0.7 MPa and a maximum flow rate of 1980 L h⁻¹. The maximal electrical power was 1.1 kW. The total
94 solution volume was 800 mL. The bulk liquid temperature was maintained by a thermostat. Orifice plates
95 (thickness 1 mm, outer diameter 21 mm) with various single-hole diameters were attached at the suction side
96 of the pump so that the cavitation could be induced by suction. The inner diameter for the connecting pipes
97 was 21 mm. Cavitation events were controlled by orifice diameter. The suction pressure was measured by a
98 manometer and the flow rate through the various orifices was determined using a flow meter. The
99 hydrodynamic parameters of SC device are shown in Table 1.

100
101 **Table 1** Variation of hydrodynamic parameters with orifice plate aperture

102

103 The oxygen flow and pressure were set at 170 mL min⁻¹ and 0.05 MPa, respectively, while the O₃/O₂
104 mixture was passed into the KI solution for 10 min. The O₃ yields were determined with various power
105 settings. 50 or 100 mL min⁻¹ of the O₃/O₂ mixture was typically introduced into the SC system and the rest
106 gas was introduced into the 1 M NaOH solution for the removal of ozone and then was emitted the
107 atmosphere.

108 2.3. *Experimental procedures*

109 Prior to the investigation of SA degradation, the influence of air and ozone/air flow on the decomposition
110 of chloroform and the resulting increase in conductivity induced by SC were studied. The gas flow was
111 sparged with a flow rate in the range of 0-300 mL min⁻¹ into 800 mL of 1 mM chloroform in deionised water
112 (pH 5.8) at the suction side of the pump at 20 °C. Meanwhile, the SC device, with a 5.0 mm-hole orifice
113 plate, was started. The conductivity of the solutions was recorded for 20 min using an online conductivity
114 meter (GMH3430) and the concentration of dissolved oxygen was recorded for 8 min using a dissolved
115 oxygen meter (HACH LANGE HQ10).

116 The influence of gas flow on the concentrations of the dissolved O₃ and H₂O₂ that was formed in water
117 was investigated using the following method; a gas flow containing O₃ was continuously introduced into 800
118 mL of deionised water in the SC system and the concentration of dissolved O₃ in water was periodically
119 measured using the indigo method without interference from other oxidants [48]. The concentration of H₂O₂
120 that was formed on-site was detected using the K₂TiO(C₂O₄)₂ method without interference from other
121 oxidants [49].

122 In a typical SA ozonation run, 800 mL of 0.42 mM SA in deionised water was circulated through the SC
123 reactor for 90 min at 20 °C, while an O₃/O₂ gas flow was introduced into the solution under the suction
124 orifice plate. The pH values were not artificially adjusted during ozonation. The initial pH value was 3.8.
125 Aliquots (1 mL) of the processed solution were periodically extracted from the reaction system and the SA
126 content was analysed using HPLC.

127 *2.4. HPLC analysis*

128 A Jasco LC-2000 Plus HPLC system was used to detect the concentration of SA. The HPLC system
129 contains a DG-2080-53 3-Line Degasser, PU-2080Plus intelligent HPLC-pump, AS-2055Plus intelligent
130 sampler, CO-2060Plus intelligent column thermostat, MD-2010Plus multiwavelength detector, LC-Net
131 II/ADC and Chrompass Chromatography Data System, Vers. 1.8.6.1. A ReproSil-Pur C18-AQ (5 μm , 200 \times
132 4.6 mm) column provided by Dr. Maisch GmbH (Ammerbuch-Entringen, Germany), 200 mM H_3PO_4 mobile
133 phase and UV detection at 210 nm were used. Injection volume was 95 μL . Analyses were performed at a
134 flow rate of 1.0 mL min^{-1} and a temperature of 20 $^\circ\text{C}$.

135 **3. Results and discussion**

136 *3.1. Influence of air flow on SC induced chloroform decomposition*

137 Since it is quite difficult to cause the degradation of hydrophilic compounds such as carboxylic acids
138 using cavitation processes [50], either the decomposition of chloroform and tetrachloromethane or the
139 oxidation of potassium iodide were used to demonstrate the chemical effects of HC [26]. In our previous
140 studies, the 5.0 mm-hole was demonstrated to be the optimal orifice plate aperture for chloroform
141 decomposition in the SC system [33]. HC induced the thermal decomposition and mineralization of
142 chloroform in aqueous solutions, resulting in the release of chloride and hypochlorite ions as well as a
143 subsequent increase in conductivity. The conductivity of the aqueous solution linearly increased with
144 chloroform mineralization, while any agitation weakened the cavitation events and chloroform degradation
145 [51]. It is thus essential to investigate the influence of turbulence, which is induced by the introducing gas
146 flow, on cavitation effects, i.e., chloroform decomposition driven by SC. Various air flows (0-300 mL min^{-1})
147 were sparged into 800 mL of 1 mM chloroform aqueous solutions at the suction side of the pump. The SC
148 system was operated for 20 min to observe the variation in conductivity at 20 $^\circ\text{C}$ and the concentration of
149 dissolved oxygen in the aqueous solutions was first recorded at 8 min. Fig. 1 shows the influence of air flow
150 on conductivity and Fig. 2 presents the variation of dissolved oxygen in the aqueous solutions.

151

152 **Fig. 1.** Influence of introducing air flow on the conductivity of aqueous chloroform solutions in the SC
153 system (800 mL of 1 mM chloroform, pH 5.8, 5.0 mm-hole orifice plate, 20 °C)

154 **Fig. 2.** Influence of introducing air flow on dissolved oxygen in aqueous chloroform solutions in the SC
155 system (800 mL of 1 mM chloroform, pH 5.8, 5.0 mm-hole orifice plate, 20 °C)

156

157 As shown in Fig. 1, the conductivity of the aqueous chloroform solution increased with reaction time in
158 the SC system without air flow, indicating that chloroform suffered decomposition under HC conditions and
159 that chloride ions were released [27,33]. When lower air flow (25 mL min⁻¹) was introduced into the SC
160 system, the rate of increase in conductivity (RIC) significantly dropped from 1.314 to 0.552 $\mu\text{S cm}^{-1} \text{min}^{-1}$.
161 The RIC further declined with increasing air flow rate, until pseudo-zero growth was reached at 200 mLmin⁻¹
162 of air flow rate. There has been some discussion as to the impact of introducing a gas on hydrodynamic
163 cavitation. On the one hand, the stabilized gas nuclei cannot play an essential part in hydrodynamic
164 cavitation, which can readily occur via the generation of nuclei (*ab initio*) by certain forms of mechanical
165 action [52]. On the other hand, gas-filled bubbles grow to visible size and then remain stable while vapour
166 filled bubbles expand and collapse explosively [53]. It would appear that the rising temperature, namely air-
167 nuclei in water, gives rise to cavitation, but attenuates the intensity of collapsing bubbles and reduces the
168 cavitation effectiveness. Overall, the efficiency of SC is gradually attenuated with increasing air flow rate,
169 but efficient SC still exists at lower gas flow rates in the SC system.

170 The amount of dissolved oxygen in the aqueous solutions decreased under suction and the higher air
171 flow relieved the loss of dissolved oxygen (Fig. 2). This implies that increasing air flow and dissolved gases
172 in aqueous solution work against increasing HC efficiency.

173 3.2. Effect of orifice plate on dissolved O₃ and H₂O₂ formation in water

174 Molecular ozone is known for its high selectivity to alkene bonds and unsaturated aromatic compounds.
175 The decomposition of O₃ leads to more reactive and low selectivity species, OH• as well as H₂O₂, in water
176 [1]. Subsequently, the reaction of O₃ with dissociated H₂O₂ produces more OH• [18,19]. Using HC to
177 accelerate O₃ decomposition and form OH• and H₂O₂ is therefore favourable to the oxidative degradation of

178 refractory pollutants in wastewater treatment. The effect of HC on the concentration of the dissolved O₃ and
179 H₂O₂ formed in water was investigated in this study.

180 50 and 100 mL min⁻¹ of gas flow containing 12 mg L⁻¹ O₃ were introduced into 800 mL of deionised
181 water for 20 min at 20 °C in the SC system, and the concentration of dissolved O₃ in water was periodically
182 measured using the indigo method without interference from other oxidants [48]. The results are presented in
183 Fig. 3A and 3B.

184

185 **Fig. 3.** Influence of orifice plate on the concentration of dissolved O₃ in water (800 mL of deionised
186 water, 50 or 100 mL min⁻¹ of gas flows containing 12 mg L⁻¹ O₃, 20 °C).

187 (A: 50 mL min⁻¹ of introducing gas flow)

188 (B: 100 mL min⁻¹ of introducing gas flow)

189

190 As shown in Fig. 3A and 3B, the larger orifice plate aperture favours the dissolution of O₃ in water at the
191 same amount of O₃ introduced. Similarly to the dissolution of O₂, the intensive SC effect induced by the 5
192 mm-hole does not lead to a higher concentration of dissolved O₃ in water. On the one hand, the cycle number
193 is much higher with the larger aperture than with the small aperture, leading to more frequent gas-liquid
194 contact. On the other hand, the higher vacuum degree with smaller apertures results in the degassing effect.
195 Moreover, intensive HC probably accelerates O₃ decomposition, resulting in the formation of more OH[•]
196 radicals and H₂O₂ in water. It is therefore critical to understand the influence of HC on the formation of H₂O₂
197 during aeration with O₃.

198 50 and 100 mL min⁻¹ of 12 mg L⁻¹ O₃-containing gas flow were respectively introduced into 800 mL of
199 deionised water for 120 min at 25 °C with a 5-mm orifice plate or without a restrictor in the SC system, and
200 the H₂O₂ concentration in water was periodically measured using the K₂TiO(C₂O₄)₂ method [49] without
201 interference from other oxidants. Results are shown in Fig. 4.

202

203 **Fig. 4.** Influence of suction-cavitation on the concentration of H₂O₂ formed in water (800 mL of deionised
204 water, pH=5.8, gas flow containing 12 mg L⁻¹ O₃, F1: 50 mL min⁻¹; F2: 100 mL min⁻¹, 25 °C).

205

206 In comparison with the results obtained without a restrictor, the intensive HC induced by the 5 mm-hole
207 orifice plate did not result in more H₂O₂ regardless of gas flow, as shown in Fig.4. It appears that the yields
208 of H₂O₂ and OH• are closely related to the concentration of dissolved ozone in the deionised water (pH 5.8);
209 the higher concentration of dissolved O₃ in water leads to higher H₂O₂ and OH• formation. Effective HC
210 cannot therefore induce additional O₃ decomposition and produce more H₂O₂ and OH• in the SC system.
211 This phenomenon was further demonstrated by the investigation into the ozonation degradation of SA in this
212 study.

213 Moreover, the H₂O₂ yield dropped when the H₂O₂ concentration reached a certain value during the
214 aeration of ozone, indicating that a reaction occurred between O₃ and H₂O₂.

215 3.3. Oxidative degradation of chloroform and SA using O₃, H₂O₂ alone and O₃/H₂O₂ in the SC system

216 As mentioned in a previous discussion, neither chloroform nor SA react with molecular O₃ under acidic
217 conditions [1,43], whereas they can be oxidized by OH• [54], although they are very recalcitrant compounds
218 in comparison to benzene and phenol. The ozonation of chloroform or SA can therefore indirectly reveal the
219 enhanced role that HC plays in the formation of OH• and H₂O₂ in the SC system.

220 Prior to the investigation of SA ozonation, 800 mL of 1 mM chloroform in deionised water was
221 circulated with a 5 mm-hole orifice plate for 20 min at 20 °C in the SC system. Meanwhile, either 33 or 200
222 mLmin⁻¹ of gas flow containing 5 mg L⁻¹ O₃ was introduced into the solutions in order to study the effect of
223 O₃ on the HC induced decomposition of chloroform. The result is shown in Fig. 5.

224

225 **Fig. 5.** Effect of introducing O₃ on the conductivity of aqueous chloroform solutions in the SC system
226 (800 mL of 1 mM chloroform, gas flow containing 5 mg L⁻¹ O₃, 5 mm-hole orifice plate, pH 5.8, 20 °C).

227

228 As shown in Fig. 5, the conductivity of the 1 mM chloroform solution clearly increased under 33 mL
229 min⁻¹ of air flow in the SC system, indicating that chloroform suffered thermal cracking under the effective
230 collapsing cavitation. The RIC with 33 mL min⁻¹ of O₃-containing gas flow reached 0.5509 μS cm⁻¹ min⁻¹,
231 which is 31.4% higher than the value without ozone. By contrast, conductivity increased very slowly under
232 200 mL min⁻¹ of air flow rate, indicating that little chloroform suffered thermal cracking under the weak
233 cavitation effect. Surprisingly, the RIC under 200 mL min⁻¹ of O₃-containing gas flow increased to 0.1169
234 μS cm⁻¹ min⁻¹, which is 3.4 times higher than the value without ozone. It appears that OH radicals were
235 produced to oxidize chloroform during ozonation even in the absence of effective cavitation, while the
236 formation of OH radicals was not enhanced by effective cavitation during ozonation in the SC system. A
237 more detailed investigation was carried out using another refractory substrate, SA.

238 800 mL of 0.42 mM SA in deionised water was circulated via various orifice plates for 120 min at 20 °C
239 in the SC system. Meanwhile, 100 mL min⁻¹ of gas flow containing 19 mg L⁻¹ O₃ was introduced into the
240 aqueous solutions under the effects of various orifice plates with 5, 6, 7 or 8 mm aperture. After 120 min
241 ozonation, the concentration of SA did not significantly decrease regardless of the orifice plate used,
242 indicating that SA is very stable towards O₃ and O₂ molecules, while HC is not capable of promoting the
243 formation of OH• during ozonation. In addition, SA was not degraded under HC alone due to the lower yield
244 of OH• [40].

245 The oxidation potential (1.78 V) of H₂O₂ is lower than that of O₃. Likewise, SA was not considerably
246 oxidized by H₂O₂ alone for 90 min at 20 °C within the SC system, as shown in Fig. 6. Fortunately, SA was
247 rapidly decayed with the combination of O₃ and H₂O₂ in the same system. Obviously, the reaction between
248 O₃ and H₂O₂ exceedingly produces active species, such as OH•, leading to the oxidative degradation of SA.
249 The effect of the orifice plate on SA oxidation using O₃/H₂O₂ should thus be investigated so as to explore the
250 enhanced effects of HC on the formation of OH• in the presence of O₃/H₂O₂.

251

252 **Fig. 6.** Comparison of SA oxidation by introducing O₃, H₂O₂ alone or O₃/H₂O₂ into the SC system (800
253 mL of 0.42 mM SA, 0.40 mmol L⁻¹ O₃ or/and 4 mM H₂O₂, 100 mL min⁻¹ of gas flow rate, 6 mm-hole orifice
254 plate, 20 °C).

255

256 3.4. Effect of HC on the oxidative degradation of SA in the presence of O₃/H₂O₂

257 The aperture of the orifice plate in the SC system remarkably influences cavitation events, the
258 decomposition of chloroform and the ozonation of phenol [33,40]. The 5 mm-hole has proven itself to be the
259 best orifice plate aperture in this SC system, since collapsing cavitation dominates the decomposition of
260 volatile compounds and ozonation of phenol. However, the concentration of dissolved O₃ in the water
261 increases with increasing aperture size, as shown in Fig. 3A and 3B.

262 Fig. 7 presents the effects of orifice plate aperture on the oxidative degradation of SA with reaction time
263 in the presence of O₃/H₂O₂. As shown in Fig. 7, the oxidative degradation of SA follows pseudo zero-order
264 kinetics. The degradation rates (or rate constant) of SA were calculated to be 2.604, 3.024, 3.444, 3.654 and
265 4.788 μM min⁻¹ with gradually increasing orifice diameters (5.0, 5.5, 6.0, 7.0 and 8.0 mm). The correlation
266 coefficients of the integrated pseudo zero-order rate law (see equation 3) were from 0.975 to 0.998.

$$267 \quad \frac{C_t}{C_0} = -\frac{k}{C_0}t + 1 \quad (3)$$

268 where k is the degradation rate constant of SA (μM min⁻¹), C_t represents the concentration of SA at a
269 given time (t), and C_0 represents the initial concentration of SA.

270

271 **Fig. 7.** Effect of orifice plate aperture on oxidative degradation of SA by O₃/H₂O₂ in the SC system (800
272 mL of 0.42 mM SA, 0.40 mmol L⁻¹ O₃ and 4 mM H₂O₂, 100 mL min⁻¹ of gas flow rate, 20 °C).

273

274 The SA degradation rate increased with increasing aperture size, which is consistent with the effect of
275 aperture on dissolved O₃ and O₂ in water. The larger orifice plate aperture induces higher liquid flow leading
276 to improvements in circulation, violent turbulence and the dissolution of O₃ or O₂ in water. The degradation

277 of SA is therefore closely related to the concentration of dissolved O₃ in the aqueous solutions rather than
278 effective HC. In other words, the increasing concentration of dissolved O₃ induced by turbulence and the
279 large orifices favour the formation of OH• during the reaction of O₃ and H₂O₂, while the effective HC
280 induced by small orifices plays little role in either the formation of OH• or the ozonation degradation of SA
281 in the presence of O₃/H₂O₂

282 3.5. Effect of O₃/O₂ gas flow and temperature on the degradation of SA using O₃/H₂O₂

283 In general, gas flow and solution temperature can essentially affect cavitation events. As mentioned
284 above, introducing a gas into the SC system weakens and even eliminates the chemical effects of cavitation,
285 but the concentration of dissolved O₃ increases with increasing gas flow. The higher gas flow is therefore
286 favourable to the oxidative degradation of SA by O₃/H₂O₂ in the SC system. The SA degradation rates
287 increased from 1.81 to 3.95 μM min⁻¹ with increasing gas flow (50 – 200 mL min⁻¹) in the presence of
288 O₃/H₂O₂, (see entries 1-3 in Table 2). In fact, there is little effective cavitation at 200 mL min⁻¹ gas flow in the
289 SC system. This again demonstrates that the increasing concentration of dissolved O₃ rather than effective
290 HC enhances the oxidative degradation of SA by O₃/H₂O₂.

291

292 **Table 2** Effect of gas flow, temperature and O₃ and H₂O₂ concentrations on the degradation of SA by
293 O₃/H₂O₂ in the SC system (800 mL of 0.42 mM SA solutions, 6 mm-hole orifice plate, 90 min of reaction
294 time).

295

296 Solution temperature is another critical factor in the formation and collapse of cavitation bubbles. The
297 optimal temperature for the degradation of chloroform and ozonation of phenol in the SC system is 20 °C
298 [33,40]. When solution temperature is too low, the collapse temperature is also low (see equation (4)).
299 Higher solution temperature leads to a higher vapour pressure, which negatively influences the formation of
300 cavitation and lowers the collapsing temperature (T_{max}) of cavitation.

$$301 \quad T_{max} = \frac{T_0 p_a (\gamma - 1)}{P_v} \quad (4)$$

302 where T_0 is the solution temperature, p_a is the acoustic pressure at the initiation of collapse, γ is the ratio
303 of specific heats of the dissolved gas or vapour, indicating how much heat is released from the gas during the
304 adiabatic compression. p_v is the vapour pressure of the solvent [55].

305 However, SA degradation rates increased from 3.44 to 9.86 $\mu\text{M min}^{-1}$ with rising solution temperature
306 (20 – 30 °C) in the presence of $\text{O}_3/\text{H}_2\text{O}_2$, as shown in entries 2, 4 and 5 of Table 2. This indicates that the
307 oxidation of SA by $\text{O}_3/\text{H}_2\text{O}_2$ is a classical thermal reaction rather than cavitation-driven reaction in the SC
308 system.

309 Overall, factors that are adverse to effective cavitation, such as increasing gas flow and temperature,
310 promoted the oxidative degradation of SA with $\text{O}_3/\text{H}_2\text{O}_2$ in the SC system, indirectly indicating that effective
311 cavitation plays little part in the formation of OH^\bullet in the presence of $\text{O}_3/\text{H}_2\text{O}_2$.

312 3.6. Effect of O_3 and H_2O_2 concentration on SA degradation using $\text{O}_3/\text{H}_2\text{O}_2$

313 The electric power of the O_3 generator varied at constant gas flow (100 mL min^{-1}) and 4 mM H_2O_2 . The
314 degradation rate of SA increased from 2.69 to 5.00 $\mu\text{M min}^{-1}$ with increasing O_3 input concentration (0.25 -
315 1.13 mmol L^{-1}), as shown in entries 2, 6 and 7 of Table 2. It appears that the degradation rate of SA
316 increased by 86% when the O_3 input amount increased 3.5 times.

317 The initial concentration of H_2O_2 was varied while the gas flow (100 mL min^{-1}) and O_3 input (0.40 mmol
318 L^{-1}) were held constant. The SA degradation rate increased from 0.8 $\mu\text{M min}^{-1}$ at 1 mM of H_2O_2
319 concentration to 3.44 $\mu\text{M min}^{-1}$ at 4 mM of H_2O_2 concentration, as shown in entries 2, 8 and 9 of Table 2.
320 This means that the degradation rate increased 3.3 times when H_2O_2 input amount increased 3.0 times.
321 Increasing H_2O_2 concentration is obviously more effective in the formation of OH^\bullet and the oxidative
322 degradation of SA than increasing O_3 input with the O_3 and H_2O_2 combination.

323 4. Conclusions

324 We conclude that introducing a gas flow significantly affects the decomposition of chloroform and the
325 ozonation of SA in the presence of H_2O_2 in the SC system. The larger gas flow decreases the decomposition
326 of chloroform and HC efficiency, but promotes the dissolution of O_3 and O_2 as well as the oxidation of SA
327 under the O_3 and H_2O_2 combination in aqueous solution. Although efficient HC still exists under less than

328 100 mL min⁻¹ air flow in the SC system, it is not capable of increasing the concentration of dissolved O₃ in
329 water and promote the formation of H₂O₂ during ozonation.

330 In summary, the higher gas flow, larger orifice plate aperture, rising temperature, higher O₃ and H₂O₂
331 input amounts favour the ozonation of SA in the presence of H₂O₂ in the SC system. As for the enhanced
332 effects of HC on the degradation of phenol and inactivation of microorganisms observed in previous studies,
333 we speculate that the direct action of molecular O₃ in the numerous micro- or nano-bubbles induced by HC
334 must play a vital role.

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