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Activated sodium percarbonate-ozone (SPC/O₃) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1,4-dioxane in water.

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Corresponding Author:	Grzegorz Boczkaj, PhD.Sc.Eng. Gdansk University of Technology: Politechnika Gdanska Gdansk, POLAND
First Author:	Kirill Fedorov
Order of Authors:	Kirill Fedorov Manoj P. Rayaroth Noor S. Shah Grzegorz Boczkaj, PhD.Sc.Eng.
Abstract:	<p>Hydrodynamic cavitation (HC) was employed to activate sodium percarbonate (SPC) and ozone (O₃) to degrade recalcitrant 1,4-dioxane. The degradation efficiency >99% with a rate constant of $4.04 \times 10^{-2} \text{ min}^{-1}$ was achieved in 120 min under the optimal conditions of cavitation number (Cv) 0.27, pH 5, molar ratio of oxidant to pollutant (rox) 8, ozone dose of 0.86 g h⁻¹ under 25±2 °C with initial concentration of 1,4-dioxane 100 ppm. The application of HC with SPC/O₃ increased the degradation efficiency by 43.32% in 120 min, confirming a synergistic effect between the coupled processes. In addition, the degradation efficiency of 1,4-dioxane in HC/SPC/O₃ was superior as compared to HC/H₂O₂/O₃, suggesting that the presence of SPC has a significant role in degradation of 1,4-dioxane. Radical quenching experiment revealed highest contribution of hydroxyl (HO•) radicals in the degradation of 1,4-dioxane among carbonate (CO₃⁻) and superoxide (O₂⁻) radicals. The presence of co-existing anions resulted in an inhibitory effect in the following order: SO₄²⁻ > NO₃⁻ > Cl⁻. Based on GC-MS analysis, ethylene glycol diformate (EGDF) was detected as the main degradation product of 1,4-dioxane. The observed intermediate supports the radical route of 1,4-dioxane oxidation, which involves H-abstraction, ΔC-C splitting at the α-C position, subsequent dimerization, fragmentation and mineralization. Electric energy per order (EEO) for best process was 102.65 kWh-m³-order⁻¹. Total cost of treatment was estimated as approx. 24 USD/m³. These findings confirmed the SPC as an efficient, environmentally-friendly alternative to H₂O₂ and broadened the scope of HC-based AOPs for water and wastewater treatment.</p>
Response to Reviewers:	<p>Reviewer #2</p> <p>1. The authors have tried to address some problems raised in the previous comments. Nevertheless, one issue remains to be clarified before the manuscript can be considered for publication. The energy consumption (EEO) reported in Table 9 needs to be carefully checked. EEO refers to the energy demand for abating the concentration of a compound, not TOC, by 1 order in 1 m³ water. The EEO for E-peroxone and photoelectron-peroxone reported in Table 9 is about 3-5 orders of magnitude higher than the values reported for these processes in literature, for example, Li et al., 2021; Yao et al., 2018; Yao et al., 2016. There must be something wrong in the calculations, which should be clarified. Therefore, a minor revision is required for the present manuscript.:</p> <p>Response: Thank you for pointing this out and literature provided. We apologize that our previously presented data were incorrect and we agree with your suggestion. We tried to estimate EEO values for processes available in the literature, however in some cases there were limited data.</p> <p>Therefore, we have revised the data presented in Table 9. The EEO values of electro-peroxone and photo-electro-peroxone were calculated in accordance with the equation</p>

provided by Wang et. al., [1] using rate constant of 1,4-dioxane degradation and assuming the average cell voltage as 7.8 V [2]. Obtained values along with corresponding references were indicated in discussion and the calculation was shown in Supplementary data.
Corresponding comments on this aspect were provided in revised version of manuscript.

References:

[1]H. Wang, J. Zhan, L. Gao, G. Yu, S. Komarneni, Y. Wang, Kinetics and mechanism of thiamethoxam abatement by ozonation and ozone-based advanced oxidation processes, *J. Hazard. Mater.* 390 (2020) 122180.
doi:10.1016/J.JHAZMAT.2020.122180.

[2]H. Wang, S. Yuan, J. Zhan, Y. Wang, G. Yu, S. Deng, J. Huang, B. Wang, Mechanisms of enhanced total organic carbon elimination from oxalic acid solutions by electro-peroxone process, *Water Res.* 80 (2015) 20–29.
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COVER LETTER FOR SUBMISSION OF REVISED MANUSCRIPT
**Activated sodium percarbonate-ozone (SPC/O₃) hybrid hydrodynamic cavitation system
for advanced oxidation processes (AOPs) of 1,4-dioxane in water**

Subject: **SUBMISSION OF A REVISED MANUSCRIPT FOR EVALUATION**

Dear prof. Kusic,

We are enclosing herewith a revised manuscript entitled "*Activated sodium percarbonate-ozone (SPC/O₃) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1,4-dioxane in water*".

All of the suggestions raised by the Editor and Reviewer were thoroughly considered and adapted in the paper. We hope that the Reviewer will be satisfied.

With the submission of this manuscript we certify that the above-mentioned manuscript has not been published elsewhere, accepted for publication elsewhere or under editorial review for publication elsewhere

Sincerely yours,



Corresponding author

Prof. Grzegorz Boczkaj, PhD. Sc. Eng.

Gdansk University of Technology

Title: Activated sodium percarbonate-ozone (SPC/O₃) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1,4-dioxane in water
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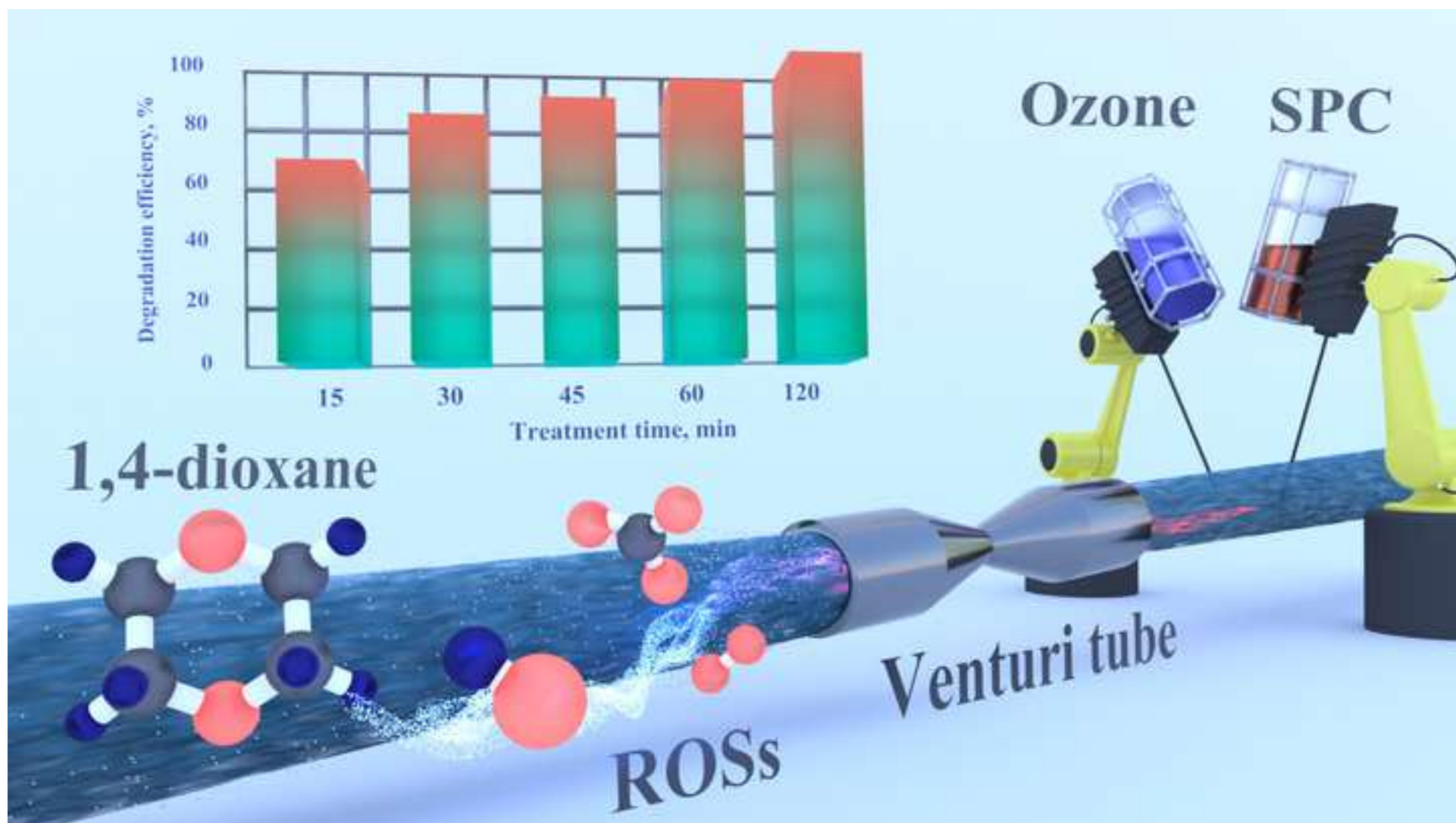
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Highlights

- Synergistic HC/SPC/O₃ process for degradation of emerging environmental pollutants
- Superior performance of HC/SPC/O₃ comparing to HC/H₂O₂/O₃
- Improvement of sustainability and process safety of AOPs by percarbonate oxidant
- Green advanced oxidation based on cavitation phenomenon
- Importance of hydrodynamic cavitation in activation of oxidants

Activated sodium percarbonate-ozone (SPC/O₃) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1,4-dioxane in water.

Kirill Fedorov¹, Manoj P. Rayaroth², Noor S. Shah³, Grzegorz Boczkaj^{1,4,*}

¹*Gdańsk University of Technology, Faculty of Civil and Environmental Engineering, Department of Sanitary Engineering, 80-233 Gdańsk, G. Narutowicza 11/12 Str, Poland.*

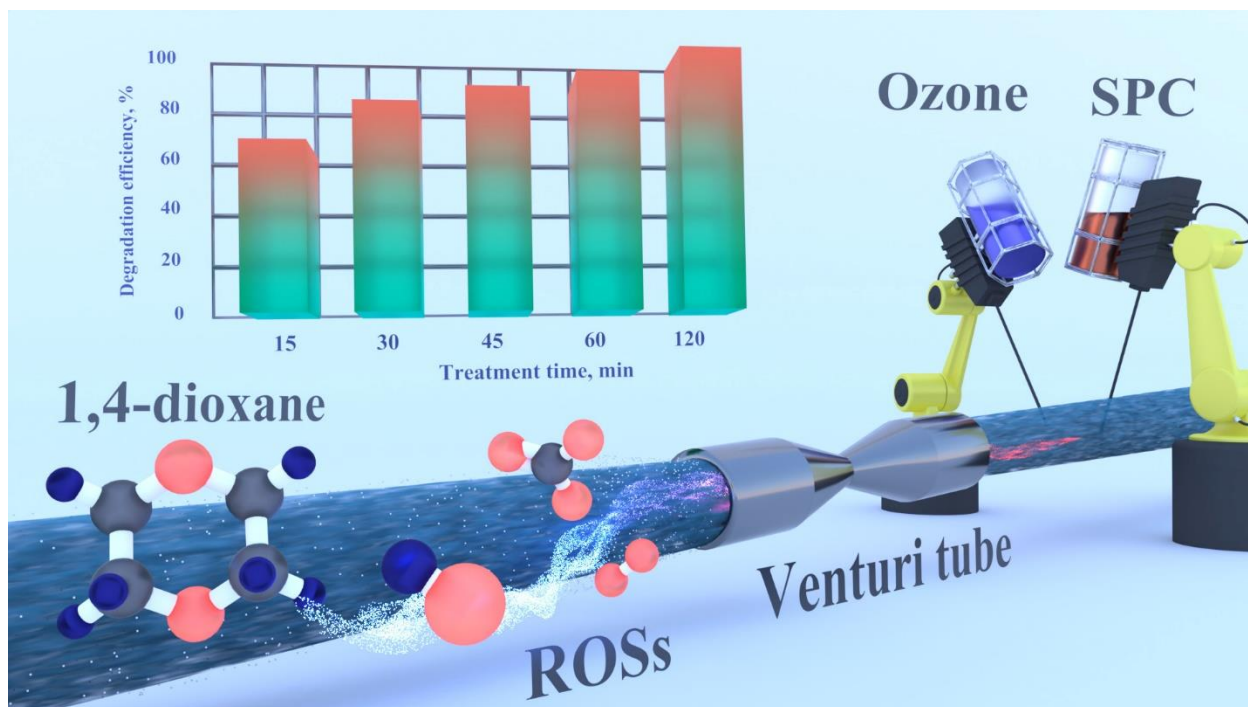
²*GREMI, UMR 7344, Université d'Orléans, CNRS, 45067 Orléans, France.*

³*Department of Environmental Sciences, COMSATS University Islamabad, Vehari Campus 61100, Pakistan.*

⁴*EkoTech Center, Gdansk University of Technology, G. Narutowicza St. 11/12, 80-233 Gdansk, Poland.*

** Corresponding author: Dr Grzegorz Boczkaj, Assoc. Prof., PhD. Sc. Eng. Gdansk University of Technology, Faculty of Civil and Environmental Engineering, Department of Sanitary Engineering, 80 – 233 Gdansk, G. Narutowicza St. 11/12, Poland. Fax: (+48 58) 347-26-94; Tel: (+48) 697970303; E-mail: grzegorz.boczkaj@pg.edu.pl or grzegorz.boczkaj@gmail.com*

Graphical abstract



1 Abstract

2 Hydrodynamic cavitation (HC) was employed to activate sodium percarbonate (SPC) and ozone (O₃) to
3 degrade recalcitrant 1,4-dioxane. The degradation efficiency >99% with a rate constant of $4.04 \times 10^{-2} \text{ min}^{-1}$
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16 per order (E_{EO}) for best process was $176,79 \text{ kWh} \cdot \text{m}^{-3} \cdot \text{order}^{-1}$. Total cost of treatment was estimated as
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18 alternative to H₂O₂ and broadened the scope of HC-based AOPs for water and wastewater treatment.

19 Keywords: percarbonate; wastewater treatment; ozonation; reactive oxygen species; process
20 intensification; Emerging organic pollutants EOCs.

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25 1. Introduction

26

27 1,4-dioxane also named as 1,4-diethylene oxide, an important stabilizer of chlorinated solvents has found
28 a wide variety of industrial applications such as aerosol additive, wetting and dispersing agent. It is also
29 formed during the production of surfactants and synthesis of poly(ethylene) terephthalate [1]. The
30 occurrence of 1,4-dioxane has been detected in municipal water supply, landfill leachate and
31 groundwaters [2,3]. Such widespread occurrence of 1,4-dioxane is mainly originated due to the improper
32 disposal of the effluents, resistance of 1,4-dioxane to biodegradation and merely complete miscibility
33 with water. In terms of toxicity, 1,4-dioxane has been shown carcinogenic to animals and classified as
34 potentially (Class B2) carcinogenic to human by the United States Environmental Protection Agency
35 [1,4]. In connection with this, stringent water quality standards regulating the concentration of 1,4-
36 dioxane in water have been adopted to reduce the health risk. However, the conventional water treatment
37 methods based on biodegradation were found ineffective towards 1,4-dioxane [5–7]. Therefore,
38 tremendous efforts have been devoted for the development of technologies to degrade 1,4-dioxane in
39 water. Among the tested technologies, advanced oxidation processes (AOPs) based on the generation of
40 highly reactive radical species appeared to be promising green technologies for remediation of 1,4-
41 dioxane from aqueous environment [5,8–11].

42 As a part of AOPs, H_2O_2 produces hydroxyl (HO^\bullet) radicals with an extremely strong oxidation capacity
43 (E^0 2.8 V), which can allow to achieve complete mineralization of treated organic pollutants [12]. The
44 production of HO^\bullet radicals is generally proceeded through the combination of H_2O_2 with oxidants (PS,
45 PMS), catalysts (Fe^{2+} , TiO_2) or energy input (ultrasound, UV-irradiation). Among the combined
46 processes, $\text{H}_2\text{O}_2/\text{O}_3$ is a well-known and powerful method denominated as peroxone, which involves
47 direct and indirect oxidation of pollutants. The effectiveness of $\text{H}_2\text{O}_2/\text{O}_3$ has been proven towards the
48 degradation of 1,4-dioxane [6,13], dyes [14], pharmaceuticals [15,16], volatile organic compounds
49 (VOCs) [17] and wastewaters [18,19]. In peroxone process, HO^\bullet radicals are generated *via* the accelerated
50 decomposition of O_3 initiated by H_2O_2 and alternative activation of H_2O_2 by O_3 . Nevertheless, the use of
51 H_2O_2 is associated with serious safety concerns related with a risk of explosion during the transportation
52 and corrosion of equipment. Moreover, the application of H_2O_2 in AOPs is commonly related with self-

53 scavenging or radical recombination reactions raising the issue of H₂O₂ dosage and introduction mode
54 optimization.

55 Recently, studies on H₂O₂-based AOPs are focused on sodium percarbonate (SPC), namely Na₂CO₃ ×
56 1.5H₂O₂ as a safe and cheap alternative to H₂O₂. Besides, this trend is reasoned with a number of
57 advantages such as prevention of acidification of treated media and wide operating pH range [20,21].
58 Attempts on SPC activation have been made using Fe²⁺ [22–24], graphene oxide [25], protonated g-C₃N₄
59 [26], zero valent iron (ZVI) [27], vanadium (IV) [28], UV [29] and ultrasound [21]. Unlike H₂O₂, the
60 oxidation capacity of SPC-based AOPs is conditioned by a variety of ROS, including superoxide (O₂^{•-})
61 and carbonate (CO₃^{•-}) radicals. The latter is generated through the consumption of HO[•] radicals and
62 exhibit lower oxidation potential of 1.78 V at pH 7 [30]. In spite of this, CO₃^{•-} radicals selectively react
63 with organic pollutants containing electron rich functional groups. For instance, as an electron acceptor
64 CO₃^{•-} radical rapidly reacts with *p*-substituted phenols and anilines with a rate constant of 10⁷-10⁸ M⁻¹ s⁻¹
65 and 10⁵-10⁷ M⁻¹ s⁻¹, respectively [31–33]. Moreover, the concentration of CO₃^{•-} radicals in sunlit surface
66 water appeared to be two orders of magnitude higher than HO[•] radicals under the same conditions [34].
67 Therefore, SPC-based AOPs are seemed to be a preferable option for the degradation of organic
68 pollutants bearing electron rich moieties and, particularly, 1,4-dioxane.

69 Although, AOPs are considered as effective and environmentally friendly techniques for the degradation
70 organic contaminants, the industrial implementation of AOPs in water treatment schemes is hindered. To
71 achieve a satisfactory level of degradation, the application of traditional AOPs require high operational
72 cost due to large consumption of oxidants and energy [35]. In the light of this, a recent trend on
73 integration of AOPs with cavitation is a promising route for the improvement of AOPs. The development
74 of hybrid processes based on cavitation and AOPs showed encouraging results anticipating the
75 implementation of novel technologies in water/wastewater treatment [36–39]. Cavitation is an emerging
76 technique which is often employed to improve the effectiveness of AOPs. The key mechanism relying
77 behind the cavitation phenomenon relate to the formation, growth and violent collapse of cavitation
78 bubbles. Since, the collapse of bubbles releases a large magnitude of energy in a short time interval,
79 regions of extreme conditions or so-called “hot spots” are created. Such conditions are capable to form
80 radical species through to the pyrolytic disassociation of water or proceed the activation of H₂O₂, O₃ and
81 other peroxides. Owing to the continuous flow operation, high cavitation yield and effectiveness

82 towards the degradation of pollutants, hydrodynamic cavitation has a great potential for scale up and
83 application in real wastewater treatment systems [40–42]. Herein, this study was performed with the
84 following objectives: i). to investigate the degradation of 1,4-dioxane in SPC/O₃ process under
85 hydrodynamic cavitation (HC); ii). to understand the synergy in HC/SPC/O₃ the degradation kinetics of
86 1,4-dioxane in sole and coupled processes; iii). to identify the reactive species in HC/SPC/O₃ by
87 quenching experiments using specific radical scavengers; iv). to perform the degradation under
88 environmental relevant conditions varying pH and in the presence of inorganic anions; and finally, v). to
89 identify the transformation products and elucidate the mechanism of 1,4-dioxane degradation in
90 HC/SPC/O₃.

91

92 **2. Materials and methods**

93

94 *2.1 Chemicals*

95

96 1,4-dioxane (reagent grade, p.a., 99%), sodium nitrate (pure), sodium hydroxide (pure p.a., 98.8%),
97 chloroform (pure p.a.), acetone, dichloromethane, 2-propanol (pure p.a.), hydrogen peroxide (pure p.a.,
98 30%), potassium iodide (pure p.a.) and sodium thiosulfate pentahydrate (acs pure p.a.) were purchased
99 from POCH (Poland). Sodium percarbonate (avail. H₂O₂ 20-30%), cyclohexanone and phenol were
100 purchased from Sigma-Aldrich (Germany). Sodium sulfate (anhydrous, pure, p.a.), sodium carbonate
101 (anhydrous, pure p.a.), sodium azide (pure p.a.) and sulfuric acid (pure p.a., 95%) were purchased from
102 Chempur (Poland). Sodium chloride (pure) was purchased from Stanlab (Poland) and 1,4-benzoquinone
103 (99%) was purchased from Acros Organics (Belgium). All chemicals and solvents were of analytical
104 grade and were used as received without purification. Ultrapure quality water (18.2 MΩcm⁻¹) from
105 Millipore® system (Direct-Q UV-R model) was used for preparation of reaction solution.

106

107 *2.2 Experimental procedure*

108

109 The degradation experiments of 1,4-dioxane were conducted in a hydrodynamic cavitation reactor with
110 close-circuit system (Supplementary data, **Fig. S1**). The reactor was composed of feed tank equipped with

111 a mechanical stirrer, temperature indicator and water condenser to maintain the reaction temperature.
112 Sequential pumping system (MS 801-4, 1360 min⁻¹, TECHTOP® MOTOR, Shanghai, China) connected
113 with electromagnetic flowmeter (MPP 600 by MAGFLO®) was used to circulate water through the
114 cavitating device and by-pass line. The cavitating device consisted of brass Venturi tube with 2-mm ID of
115 the throat section. Digital manometers (Suku, Germany) were mounted on the upstream and downstream
116 lines of Venturi tube to measure the pressure. Polytetrafluoroethylene (PTFE) pipes and stainless-steel
117 joints were used to connect the units. In a typical experimental procedure, 5 L of model solution
118 containing 100 ppm of 1,4-dioxane was added in the feed tank and treated for 120 min at 20±2 °C.
119 Sample aliquots of 20 mL were collected at regular time interval. The SPC solution was injected through
120 the port with inner porous membrane to attain the required molar ratio of SPC to 1,4-dioxane. Dry air
121 with a certain flow rate was connected to a Tytan 32 (Erem, Poland) ozone generator to purge ozone to
122 the upstream line of Venturi tube. All experiments were performed in duplicate and experimental errors
123 were within 5%.

124 2.3 Analysis

125 Prior to GC analyses, dispersive liquid-liquid microextraction (DLLME) was employed to extract 1,4-
126 dioxane from water samples. The procedure of DLLME was as follows: 5 µL of internal standard
127 (cyclohexanone) were added to 10 mL of samples. Then 0.9 mL mixture of dispersing and extraction
128 solvent composed of dichloromethane and acetone (50:40). After 1 min shaking, the samples were
129 centrifugated for 10 min at 5000 rpm (EBA 8S, Hettich, Germany). A 300 µL of organic phase were
130 extracted and placed in glass conical inserts for analysis [9,43].

131 A quantitative analysis of 1,4-dioxane concentration was studied using a Clarus 500 (Perkin Elmer, USA)
132 gas chromatograph equipped with flame ionization detector (GC-FID). A capillary column (60 m × 0.32
133 mm ID, 1.8 µm DB624, Agilent, USA) was used is separations. Parameters setting of GC-FID were as
134 follows: temperature program - 50 °C (5 min) ramped at 10 °C/min to 275 °C (5 min), detector
135 temperature 275 °C. A nitrogen was used as carrier gas with volumetric flowrate of 5 mL/min. Detector
136 gases flow rate: air 450 mL/min, hydrogen 40 mL/min.

137 The identification of 1,4-dioxane degradation products was performed using a GCMSQP2010SE
138 (Shimadzu, Japan) gas chromatograph (GC) coupled to a mass spectrometer (MS). A capillary column
139 (100 m × 0.2 mm ID, 0.1 µm DHA, Restek, USA) was used for separation of analytes. A hydrogen

140 (supplied from PGX500 hydrogen generator, Perkin Elmer, USA) was used as carrier gas (1 mL/min),
141 injection port temperature was 300 °C and GC-MS transfer line temperature was 310 °C. The oven
142 temperature program was 40 °C (isothermal for 5 min) ramped at 5 °C/min to 220 °C. Ion source (EI, 70
143 eV) temperature was 200 °C. A mass-to-charge ratio of 34 to 220 m/z was selected for SCAN mode
144 analysis of byproducts.

145 The concentration of O₃ in introduced gaseous oxidant stream was measured by iodometric titration
146 method. The experimental setup consisted of ozone generator (Erem 32, Poland) and two connected gas
147 washing bottles in series. Each bottle was filled with 400 mL of acidified (pH 3) KI (2% w/w) solution to
148 trap O₃. The compressed dry air containing O₃ was bubbled through KI solution using a sintered glass
149 disc located in the bottom half of bottles. A standardized 0.001 N Na₂S₂O₃ solution was used as a titrant
150 and 5% (w/v) starch solution as an indicator. The dose of O₃ at carrier gas flow rate of 0.5, 1.0, 1.5, 2.0
151 and 2.5 L min⁻¹ were determined as 0.23, 0.40, 0.74, 0.86 and 0.94 g h⁻¹, respectively. The content of total
152 organic carbon (TOC) was measured using TOC-LCSH instrument (Shimadzu, Japan). All tubing
153 connecting ozone generator with HC reactor and gas absorption bottles were made of PTFE (Teflon).

154 **3. Results and discussion**

155 *3.1 Effect of cavitation number*

156 Cavitation conditions (e.g., size of cavitation bubbles, dynamics) are defined by the factors, such as a
157 geometry of the cavitating device, flow velocity, temperature, content of dissolved gases and suspended
158 particles. The intensity of cavitation directly depends on the turbulence intensity of the liquid and number
159 of generated cavities. The turbulence intensity, in turn, is related to geometry of the cavitating device and
160 flow conditions of the liquid [44]. The relation between flow conditions and the cavitation intensity can
161 be defined using cavitation number (C_v). Thus, the determination of optimal C_v is required for the
162 regulation of flow conditions to get max cavitation events and can be expressed as follows [45–47]:

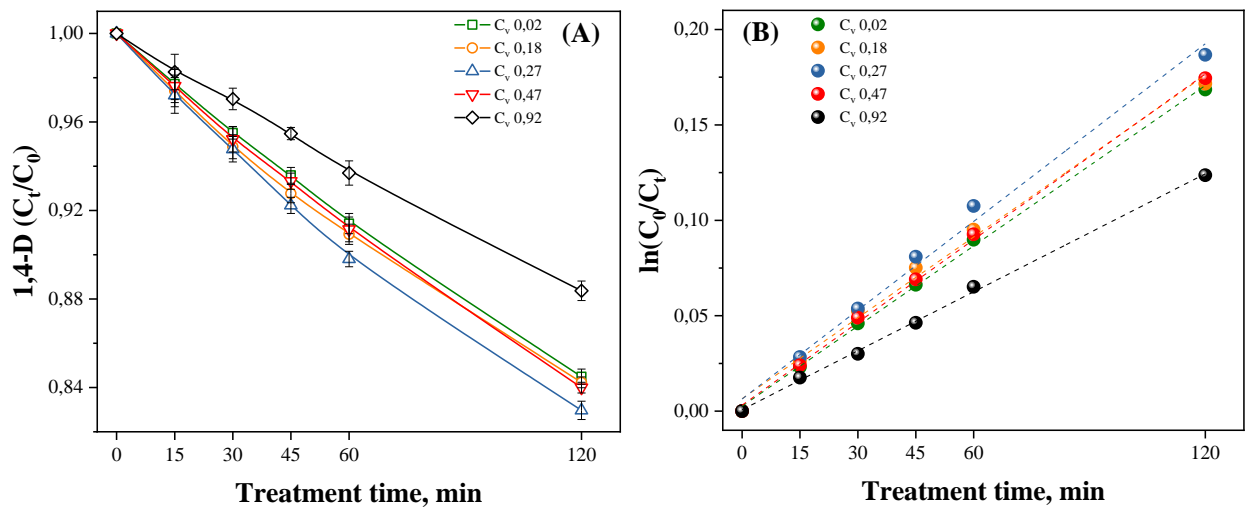
$$163 \quad C_v = \frac{p_2 - p_v}{\frac{1}{2}u_0^2 \rho}, \quad (1)$$

164 where, p₂ is the recovered downstream pressure, p_v – vapor pressure of the liquid, u₀ is liquid linear
165 velocity at the throat of cavitating constriction and ρ is the density of the treated liquid.

166 In this study, the effectiveness of sole HC towards 1,4-dioxane degradation was performed varying the
 167 liquid velocity to determine the optimal C_v . All studies in this paper were performed for primary
 168 concentration of dioxane 100 ppms. This concentration was selected to address effectiveness of studied
 169 processes to concentration level that can be expected in the industrial effluents. Dioxane is well soluble in
 170 water. Concentration values much higher than 100 ppms, are not expected, as in such case simple
 171 purification processes based on adsorption or membrane treatment would be effectively used. Pseudo-
 172 first-order model with regard to the concentration of 1,4-dioxane was employed to depict the degradation
 173 kinetics (Eq. 2).

$$174 \quad \ln \frac{C_0}{C_t} = kt, \quad (2)$$

175 where C_0 and C_t are initial and instant concentration of 1,4-dioxane, respectively, k represents the
 176 degradation rate constant and t is the treatment time. The rate constant of each process was calculated by
 177 plotting $\ln(C_0/C_t)$ against time of treatment.



178
 179 **Figure 1.** Effect of C_v on the degradation 1,4-dioxane in sole HC: (a) degradation efficiency, (b) pseudo-
 180 first-order kinetic plots ($[1,4-D]_0$ 100 ppm, pH_0 5, 20 ± 2 °C).

181 As depicted in **Fig. 1a**, the percent degradation of 1,4-dioxane was 11.63, 16.01 and 17.03% for C_v 0.92,
 182 0.47 to 0.27, respectively. The degradation rate constant was increased from $1.03 \times 10^{-3} \text{ min}^{-1}$ to $1.43 \times$
 183 10^{-3} min^{-1} (**Table 1**) with a reduction of C_v from 0.92 to 0.27. These observations indicated that the
 184 increase of the liquid velocity and, subsequently, inlet pressure, increased the cavitation intensity, which
 185 is reflected in higher degradation of 1,4-dioxane. However, the continuous reduction of C_v to 0.18 and



186 0.02 resulted in 15.76 and 15.51% of 1,4-dioxane degradation, respectively. The rate constants of 1,4-
 187 dioxane degradation using C_v 0.18 and 0.02 were 1.41×10^{-3} and $1.40 \times 10^{-3} \text{ min}^{-1}$, respectively. Similar
 188 findings were extensively reported and attributed due to supercavitation or so-called choked cavitation,
 189 which occurs beyond the critical level of inlet pressure in Venturi tube. In choked cavitation, a large
 190 number of generated cavities undergo mutual coalescence yielding a vaporous cavity cloud with reduced
 191 collapse pressure [39,44]. Based on the obtained results, 0.27 was selected as the optimal C_v for the rest
 192 of experiments.

193 **Table 1.** Kinetic parameters of 1,4-dioxane degradation in sole HC at different C_v .

	Cavitation number (C_v)				
	0.02	0.18	0.27	0.47	0.92
$k \times 10^{-2}, \text{ min}^{-1}$	0.140	0.141	0.155	0.145	0.103
R^2	0.998	0.993	0.992	0.998	0.999

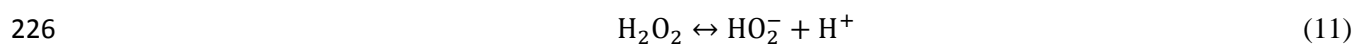
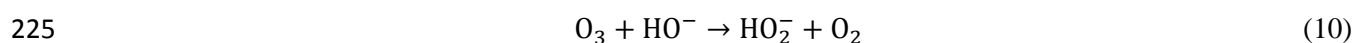
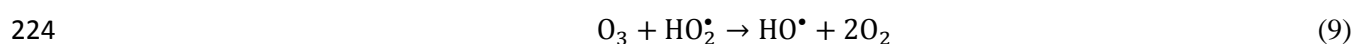
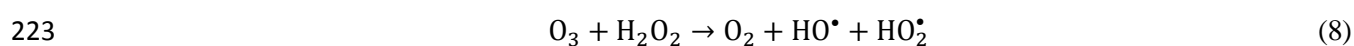
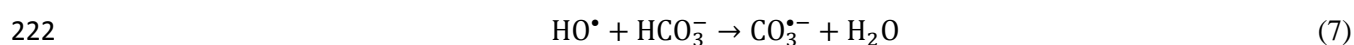
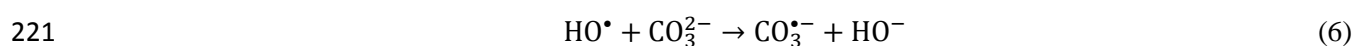
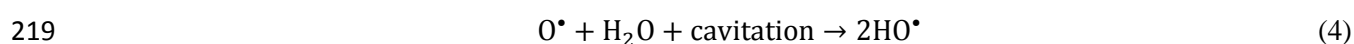
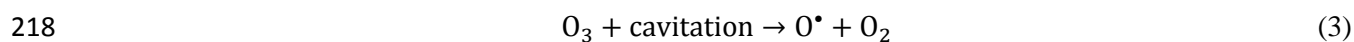
194

195 3.2 Enhanced degradation of 1,4-dioxane by HC/SPC/O₃

196

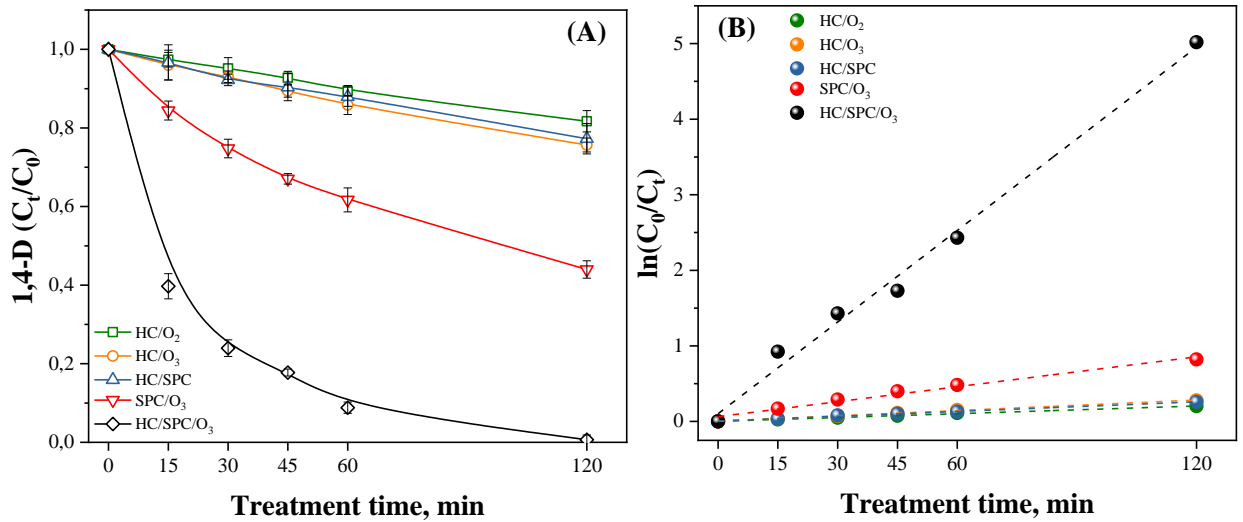
197 The degradation efficiency of HC/O₂, HC/O₃, HC/SPC, SPC/O₃ and HC/SPC/O₃ towards 1,4-dioxane was
 198 examined and depicted in **Fig. 2a**. According to **Fig. 2a**, 18.29% of 1,4-dioxane was degraded in 120 min,
 199 showing higher degradation efficiency than sole HC. This can be explained by formation of additional
 200 nuclei for the growth of cavitation bubbles as a gas is purged to the upstream line of Venturi tube.
 201 Furthermore, about 24.34 and 22.76% of 1,4-dioxane degradation were obtained within 120 min in
 202 HC/O₃ and HC/SPC, respectively. These observations indicate the increase of number of reactive radicals
 203 produced in the presence of oxidants according to **Eqs. 3-7** [20,40,48,49]. The generation of radicals was
 204 increased further and reflected in 56.02% of 1,4-dioxane degradation in 120 min as O₃ was combined
 205 with SPC in the absence of HC. Although, the radicals in SPC/O₃ are produced according to peroxone
 206 process as shown in **Eqs. 8, 9** [45], the presence of SPC initiates chain reactions to yield radicals through
 207 the decomposition of O₃ and H₂O₂. Particularly, alternative decomposition routes of O₃ and H₂O₂ with
 208 formation of HO₂⁻ are occurred under the alkaline pH of SPC (**Eqs. 10, 11**) [45,50]. Obtained HO₂⁻
 209 participate in a series of radical chain reactions and are eventually converted to highly reactive HO[•]
 210 radicals. Coupling of HC with SPC/O₃ significantly increased the degradation efficiency of 1,4-dioxane
 211 giving 99.34% in 120 min. The observed enhancement of 1,4-dioxane degradation in SPC/O₃ is

212 presumably attributed to the following beneficial factors provided by HC: i). thermal effect of so-called
 213 “hot spots” due the adiabatic collapse of cavitation bubbles assisted the cleavage of chemical bonds
 214 accelerating radical chain reactions; ii). continuous circulation along with shock waves improved the
 215 utilization of O₃ and facilitated the overall mass transfer in the system; iii). owing to the extreme
 216 conditions in “hot spots”, HC continuously produces radical species, thus, promoting the chain radical
 217 reactions.



227 As shown in **Table 2**, the pseudo-first-order rate constant of 1,4-dioxane degradation HC/O₂, HC/O₃,
 228 HC/SPC and SPC/O₃ were 1.70×10^{-3} , 2.32×10^{-3} , 2.12×10^{-3} , $6.60 \times 10^{-3} \text{ min}^{-1}$, respectively, whereas
 229 the k value in HC/SPC/O₃ was $4.04 \times 10^{-2} \text{ min}^{-1}$. Obtained k values demonstrate the distinct superiority of
 230 the hybrid HC/SPC/O₃ over the binarily integrated processes in degradation of 1,4-dioxane. The
 231 synergistic index (ξ) of HC/SPC/O₃ calculated using k values according to **Eq. 12** was 4.32, which
 232 indicates a remarkable synergy occurred in HC/SPC/O₃ in comparison with the cumulative effect of
 233 individual processes. Although the value of ξ in HC/H₂O₂/O₃ was 3.83, the degradation efficiency of 1,4-
 234 dioxane was 95.16% after 120 min, whereat the reaction constant was lower by $1.54 \times 10^{-2} \text{ min}^{-1}$
 235 compared to HC/SPC/O₃.

$$\xi = \frac{k_{\text{HC/SPC/O}_3}}{k_{\text{SPC/O}_3} + k_{\text{HC}} + (k_{\text{HC/SPC}} - k_{\text{HC}}) + (k_{\text{HC/O}_3} - k_{\text{HC}})} \quad (12)$$

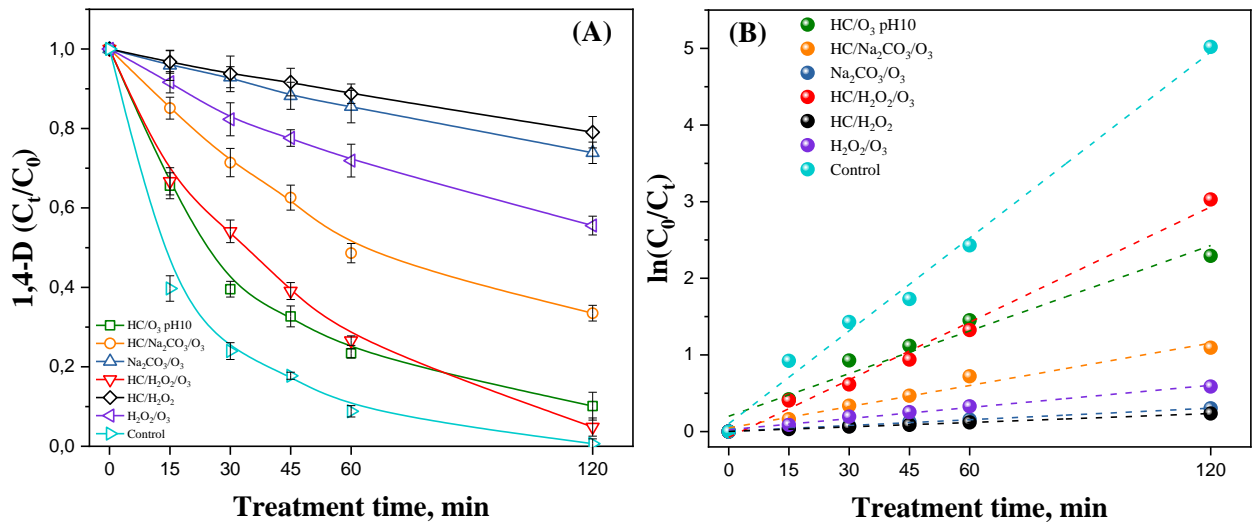


237

238 **Figure 2.** Effect of different processes on the degradation 1,4-D: (a) degradation efficiency, (b) pseudo-

239

first-order kinetic plots ([1,4-D]₀ 100 ppm, C_v 0.27, SPC *r*_{ox} 8, [O₃] 0.86 g h⁻¹, pH₀ 5, 20±2 °C).



240

241 **Figure 3.** Effect of various processes on the degradation 1,4-D: (a) degradation efficiency, (b) pseudo-

242

first-order kinetic plots ([1,4-D]₀ 100 ppm, C_v 0.27, Na₂CO₃=H₂O₂ *r*_{ox} 8, [O₃] 0.86 g h⁻¹, 20±2 °C).

243

To further clarify the role of SPC in degradation of 1,4-dioxane by HC/SPC/O₃, a series of additional

244

experiments, including addition of sodium carbonate, have been conducted. As depicted in **Fig. 3a**,

245

HC/Na₂CO₃/O₃ resulted in 66.50% of 1,4-dioxane degradation within 120 min, whereas it was only

246

26.11% for O₃/Na₂CO₃ in the absence of HC, indicating a considerable contribution of HC in

247

decomposition of O₃. On the other hand, a discernable improve of 1,4-dioxane degradation was observed

248

when comparing HC/Na₂CO₃/O₃ and Na₂CO₃/O₃ with corresponding HC/SPC/O₃ and SPC/O₃. Thus, the

249 degradation efficiency of 1,4-dioxane in HC/Na₂CO₃/O₃ was lower by 32.84% compared to HC/SPC/O₃,
 250 while it was 29.91% for Na₂CO₃/O₃ and SPC/O₃. Corresponding *k* values (**Table 2**) were increased from
 251 9.22×10^{-3} to $4.04 \times 10^{-2} \text{ min}^{-1}$ for HC/Na₂CO₃/O₃ and HC/SPC/O₃ and from 2.52×10^{-3} to 6.60×10^{-3}
 252 min^{-1} for Na₂CO₃/O₃ and SPC/O₃, respectively. In addition, application of H₂O₂ in HC/O₃ improved the
 253 degradation efficiency of 1,4-dioxane by 70.82% after 120 min. These results signify the essential role of
 254 H₂O₂ in formation of radical species in HC/SPC/O₃. Nevertheless, the degradation efficiency attained by
 255 HC/H₂O₂/O₃ was significantly lower than HC/SPC/O₃. Similarly, the increase of pH to 10 in HC/O₃
 256 increased the degradation efficiency to 65.55%, due to the promoted O₃ decomposition, however, HC/O₃
 257 at pH 10 showed lower efficiency than HC/SPC/O₃. Although, HCO₃⁻ and CO₃²⁻ anions are anticipated to
 258 scavenge of HO[•] radicals (**Eqs. 6, 7**) and slowly react with 1,4-dioxane ($\sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [51–53], these
 259 findings suggest, a partial participation of HCO₃⁻ and CO₃⁻ radicals in degradation of 1,4-dioxane.
 260 Therefore, the contribution of HCO₃⁻ and CO₃⁻ radicals should be further clarified (detailed investigation
 261 is presented in section 3.6).

262 **Table 2.** Kinetic parameters of 1,4-dioxane degradation in studied processes.

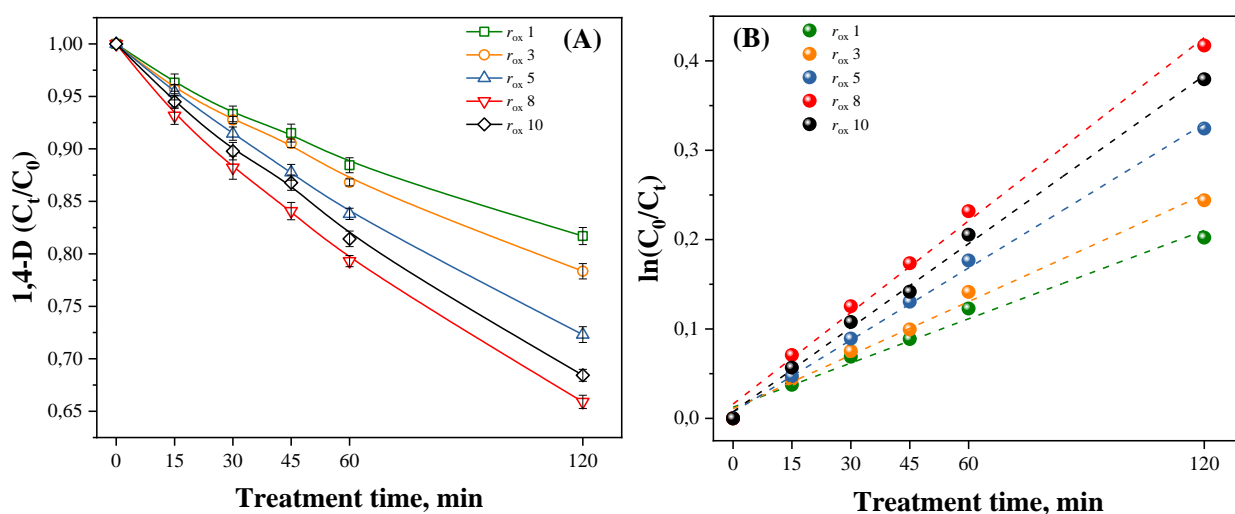
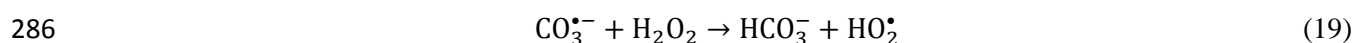
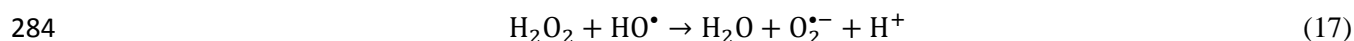
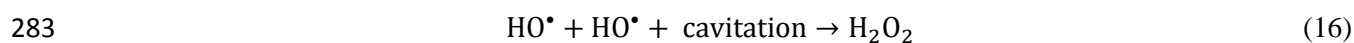
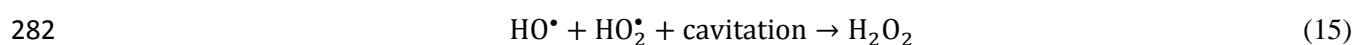
Type of process	<i>k</i> × 10 ⁻² , min ⁻¹	R ²
HC/O ₂	0.170	0.996
HC/H ₂ O ₂	0.194	0.999
HC/SPC	0.212	0.995
HC/O ₃	0.232	0.997
Na ₂ CO ₃ /O ₃	0.252	0.998
H ₂ O ₂ /O ₃ , pH10	0.483	0.991
SPC/O ₃	0.660	0.980
HC/Na ₂ CO ₃ /O ₃	0.922	0.973
HC/O ₃ , pH10	1.857	0.963
HC/H ₂ O ₂ /O ₃ , pH10	2.506	0.991
HC/SPC/O ₃	4.041	0.992

263

264 3.3 Effect of SPC dosage

265 Since SPC is a precursor of radical species, the dose of added SPC critically affects the effectiveness and
 266 operational cost of HC/SPC/O₃. In order to determine the optimal dosage of SPC, the degradation of 1,4-
 267 dioxane was performed in HC/SPC with *r*_{ox} ranging from 1 to 10, where the value of *r*_{ox} represents the

268 molar ratio of SPC to 1,4-dioxane. As presented in **Fig. 4a**, with the addition of SPC at r_{ox} 1, 3, 5, and 8
 269 the degradation of 1,4-dioxane was improved to 18.34, 22.11, 27.52 and 37.15% in 120 min, respectively.
 270 The maximum degradation of 1,4-dioxane was attained at r_{ox} 8, whereat the rate constant of 1,4-dioxane
 271 degradation (**Table 3**) was increased from 1.55×10^{-3} to $3.42 \times 10^{-3} \text{ min}^{-1}$ as compared to sole HC. With
 272 an increase of SPC dosage to r_{ox} 10, 31.94% of 1,4-dioxane was degraded in 120 and k was estimated as
 273 $3.14 \times 10^{-3} \text{ min}^{-1}$. These results suggest that the increase of SPC dosage above the optimal value led to the
 274 quench of HO^\bullet radicals. Undesired HO^\bullet consumption of radicals can be caused by unreacted H_2O_2 ,
 275 saturated O_2 and radical recombination reactions, which mainly lead to the formation of secondary radical
 276 species with lower oxidation potential (**Eqs. 13-19**) [20,48]. In this study, the degradation efficiency of
 277 1,4-dioxane in HC/SPC was highest at r_{ox} 8 and the competition of scavenging reactions intensified at r_{ox}
 278 10. Such trend regarding to SPC activation has been addressed by previous studies [50,54]. According to
 279 the obtained results, r_{ox} 8 was selected as the optimal SPC dosage for further experiments.



287

288 **Figure 4.** Effect of SPC r_{ox} on the degradation 1,4-D in HC/SPC: (a) degradation efficiency, (b) pseudo-
 289 first-order kinetic plots ($[1,4-D]_0$ 100 ppm, C_v 0.27, pH_0 5, 20 ± 2 °C).

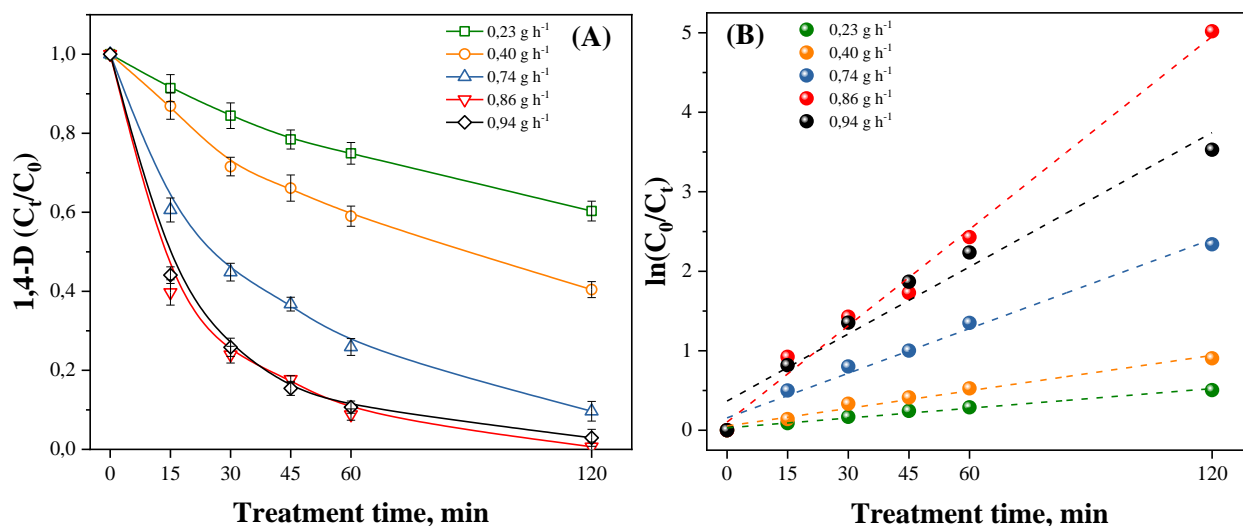
290 **Table 3.** Kinetic parameters of 1,4-dioxane degradation in HC/SPC at different r_{ox} .

	r_{ox} 1	r_{ox} 3	r_{ox} 5	r_{ox} 8	r_{ox} 10
$k \times 10^{-2}, \text{min}^{-1}$	0.165	0.200	0.269	0.342	0.314
R^2	0.984	0.991	0.998	0.995	0.997

291

292 3.4 Effect of O_3 dosage

293 To investigate the effect of O_3 dosage, the degradation of 1,4-dioxane was performed in HC/SPC at r_{ox} 8
 294 varying the dosage of O_3 in the range of 0.23-0.94 g h⁻¹. As can be seen from **Fig. 5a**, the increase of O_3
 295 dosage from 0.23 to 0.94 g h⁻¹ improved the degradation of 1,4-dioxane. Thus, 39.65, 59.55, 90.35 and
 296 99.34% of 1,4-dioxane were degraded in HC/SPC with O_3 dosage of 0.23, 0.40, 0.74 and 0.86 g h⁻¹ in 120
 297 min, respectively. As given in **Table 4**, the increase of O_3 dosage from 0.23 to 0.86 g h⁻¹ accelerated the
 298 rate constant of 1,4-dioxane degradation from 4.11×10^{-3} to 4.04×10^{-2} min⁻¹, respectively, while it was
 299 3.74×10^{-3} min⁻¹ for HC/SPC at r_{ox} 8 in absence of O_3 . These finding suggest that the improvement effect
 300 in HC/SPC/ O_3 was due to the reaction of O_3 and H_2O_2 yielding HO^\bullet radicals according to **Eqs. 8,9**
 301 [55,56]. On the other hand, overpressure at Venturi tube inlet and the turbulence induced by HC provide
 302 high transfer rate of O_3 from gaseous phase into the liquid. In such scenario, the contact of O_3 with H_2O_2
 303 is enhanced resulting in effective utilization of O_3 . Particularly, the impact of HC is obvious when
 304 comparing HC/SPC/ O_3 and SPC/ O_3 (**Fig. 2**), whereat 99.34 and 56.02% of 1,4-dioxane was degraded in
 305 120 min and k values were 4.04×10^{-2} and 6.60×10^{-3} min⁻¹, respectively. The outlet concentration of O_3
 306 during HC/SPC/ O_3 was determined as 0.135 g h⁻¹, while it was 0.384 g h⁻¹ for SPC/ O_3 , confirming the
 307 enhanced utilization efficiency of O_3 due to the effect of HC.



308

309 **Figure 5.** Effect of O₃ dosage on the degradation 1,4-D in HC/SPC/O₃: (a) degradation efficiency, (b)
 310 pseudo-first-order kinetic plots ([1,4-D]₀ 100 ppm, C_v 0.27, SPC *r*_{ox} 8, pH₀ 5, 20±2 °C).

311 Although, an increase of inlet O₃ dosage increases the partial pressure of O₃ in gas phase and, thus,
 312 improves the O₃ mass transfer [54], the increase of O₃ dosage to 0.94 g h⁻¹ decreased the degradation
 313 efficiency to 97.12% resulting in the decrease of *k* from 4.04 × 10⁻² to 2.82 × 10⁻² min⁻¹. Such effect can
 314 be ascribed to the scavenging effect of high O₃ dosage, whereat a considerable amount of O₃ was
 315 disintegrated to the consumption HO[•] radicals by dissolved O₃ as described in Eq. 20 [57]:

316



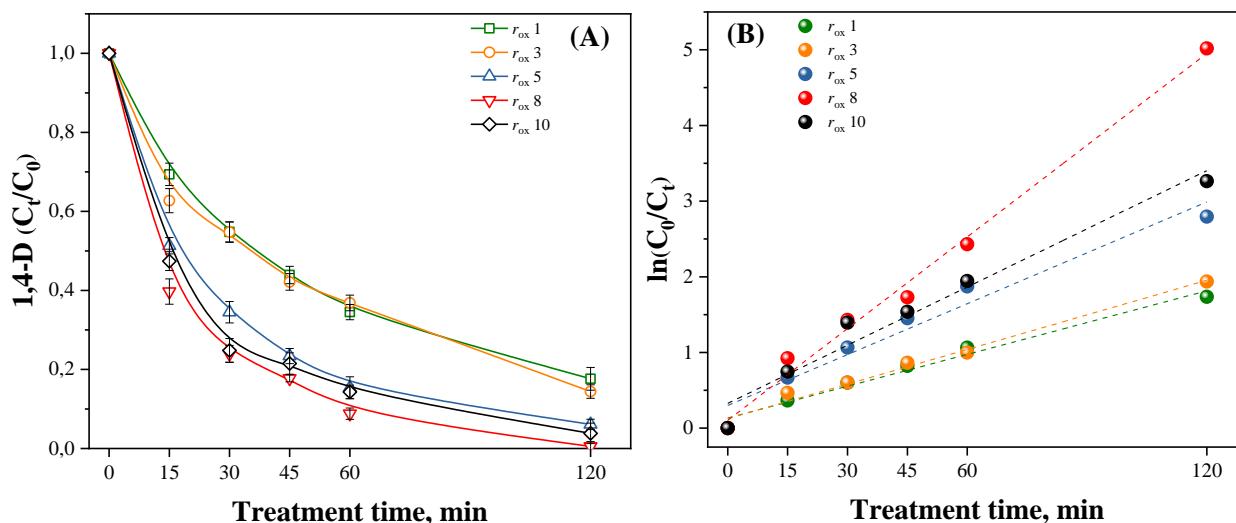
317 **Table 4.** Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O₃ at *r*_{ox} 8 and different O₃ dosage.

	O ₃ dosage, g h ⁻¹				
	0.23	0.40	0.74	0.86	0.94
<i>k</i> × 10 ⁻² , min ⁻¹	0.411	0.740	1.873	4.041	2.815
R ²	0.984	0.980	0.986	0.992	0.961

318

319 To evaluate the improving effect of O₃ on HC/SPC, the degradation of 1,4-dioxane in HC/SPC/O₃ was
 320 conducted with fixed dosage of O₃ at 0.86 g h⁻¹ and varying SPC *r*_{ox} in the range of 1-10. As shown in
 321 **Fig. 6a**, the degradation efficiency of 1,4-dioxane at *r*_{ox} 1, 3, 5, 8 and 10 were improved from 18.34,
 322 22.11, 27.52, 37.15% and 31.94% to 82.36, 85.58, 93.89, 99.34 and 96.18%, respectively. The
 323 improvement effect of O₃ addition was the highest at *r*_{ox} 8, which is clearly observed in **Table 5**. The
 324 degradation rate of 1,4-dioxane was improved from 3.73 × 10⁻³ to 4.04 × 10⁻² min⁻¹ at *r*_{ox} 8, whereas the
 325 corresponding *k* was increased from 3.20 × 10⁻³ to 2.56 × 10⁻² min⁻¹ at *r*_{ox} 10. These findings show that the

326 ratio between SPC and O₃ substantially defines the oxidative capacity of HC/SPC/O₃ towards 1,4-
 327 dioxane.



328

329

330 **Figure 6.** Effect of fixed O₃ dosage on the degradation 1,4-D in HC/SPC/O₃ with various SPC r_{ox} : (a)
 331 degradation efficiency, (b) pseudo-first-order kinetic plots ($[1,4-D]_0$ 100 ppm, C_v 0.27, $[O_3]$ 0.86 g h⁻¹,
 332 pH₀ 5, 20±2 °C.

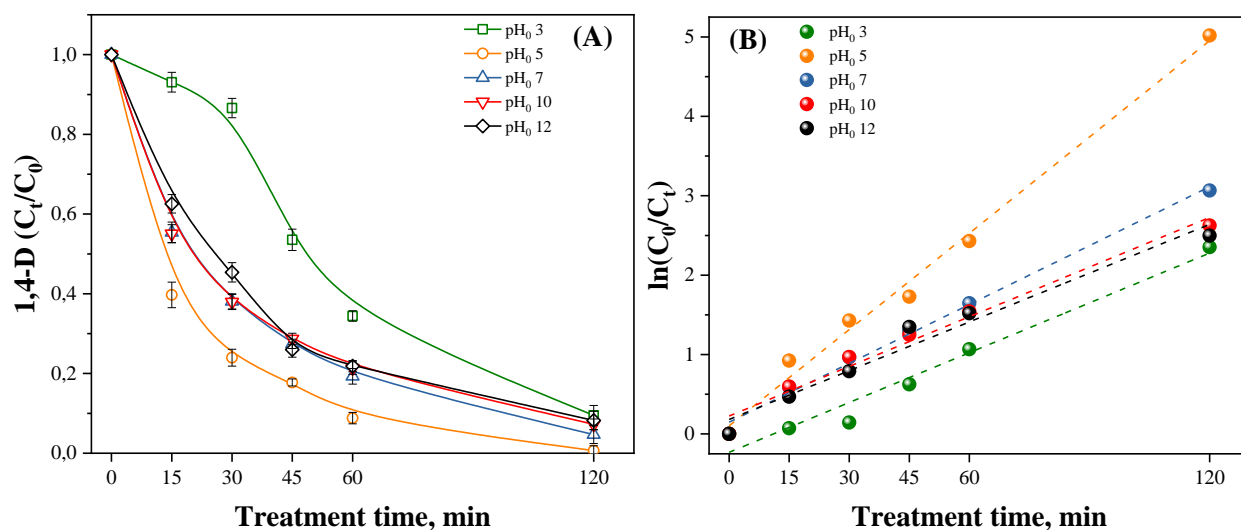
333 **Table 5.** Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O₃ at 0.86 g h⁻¹ O₃ dosage and
 334 different r_{ox} .

	r_{ox} 1	r_{ox} 3	r_{ox} 5	r_{ox} 8	r_{ox} 10
$k \times 10^{-2}, \text{min}^{-1}$	1.401	1.524	2.242	4.041	2.563
R^2	0.979	0.984	0.956	0.992	0.963

335

336 3.5 Effect of initial pH

337 The solution pH is an important parameter, which significantly affect the production of reactive species
 338 and, hence, the overall performance of HC/SPC/O₃ for the degradation of 1,4-dioxane. The effect of pH
 339 also determines the oxidation potential of generated radical species, interaction between SPC and O₃ and
 340 the state of the pollutant and oxidants in treated media. **Fig 7a** illustrates the effect of initial pH in the
 341 range of 3-12 on the degradation of 1,4-dioxane in HC/SPC/O₃ process.



342

343

344 **Figure 7.** Effect of pH₀ on the degradation 1,4-D in HC/SPC/O₃: (a) degradation efficiency, (b) pseudo-
 345 first-order kinetic plots ([1,4-D]₀ 100 ppm, C_v 0.27, SPC *r*_{ox} 8, [O₃] 0.86 g h⁻¹, 20±2 °C).

346 According to **Fig. 7a**, the highest degradation efficiency was reached at pH₀ 5 (non-adjusted), while pH₀
 347 3, 7, 10 and 12 were detrimental. Among the tested pH values, the inhibitory effect of pH₀ 3 was the
 348 highest resulting in 90.49% of 1,4-dioxane degradation within 120 min. This is attributed to the lower
 349 decomposition rate of O₃ at acidic conditions, so the direct oxidation of 1,4-dioxane by molecular O₃ is
 350 predominant at pH₀ 3. Since O₃ possess lower redox potential than HO[•] radicals, the direct oxidation
 351 proceeded slowly resulting in the *k* value of $2.09 \times 10^{-2} \text{ min}^{-1}$ (**Table 6**). In contrast, the rate constant of
 352 1,4-dioxane degradation was markedly increased to $4.04 \times 10^{-2} \text{ min}^{-1}$ at pH₀ 5, indicating high
 353 concentration of generated radical species. This can be ascribed to the radical route of 1,4-dioxane
 354 degradation *via* indirect O₃ oxidation and additional supply of HO[•] radicals due to the partial dissociation
 355 of H₂O₂. The latter is initiated by the transformation of H₂O₂ to yield HO₂⁻ (**Eq. 11**), which further react
 356 with O₃ as illustrated in **Eqs. 21-23** [58]. The detrimental effect of pH₀ < 5 coincides with the pH change
 357 depicted in **Fig. 8**. Particularly, the degradation efficiency of 1,4-dioxane in HC/SPC/O₃ at pH₀ 3 was
 358 markedly enhanced from 6.92 to 46.47% when the pH was increased from 3 to 6 after 45 min of
 359 treatment.

360

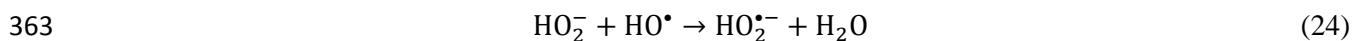


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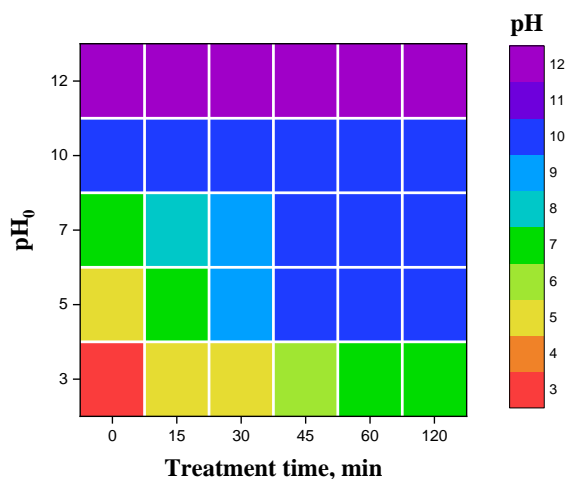


364 **Table 6.** Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O₃ at different pH₀.

	pH ₀ 3	pH ₀ 5	pH ₀ 7	pH ₀ 10	pH ₀ 12
$k \times 10^{-2}, \text{min}^{-1}$	2.091	4.041	2.471	2.084	2.047
R ²	0.968	0.992	0.993	0.977	0.968

365

366 Although alkaline pH promotes the decomposition of O₃, the degradation efficiency of 1,4-dioxane in
 367 HC/SPC/O₃ at pH₀ 10 and 12 was slightly decreased to 92.76 and 91.78%, respectively. Such trend can be
 368 interpreted with an excessive production of HO₂⁻ (Eq. 10), which act as a scavenger of HO[•] radicals (Eq.
 369 24) [50,54,58].



370

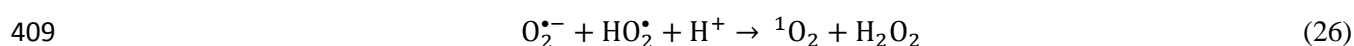
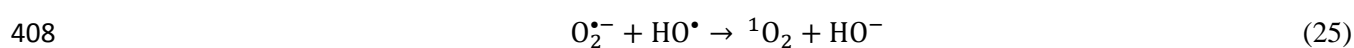
371 **Figure 8.** The map of pH change throughout the degradation 1,4-D in HC/SPC/O₃ at various pH₀ ([1,4-
 372 D]₀ 100 ppm, C_v 0.27, SPC r_{ox} 8, [O₃] 0.86 g h⁻¹, 20±2 °C).

373 3.6 Identification of reactive species in HC/SPC/O₃

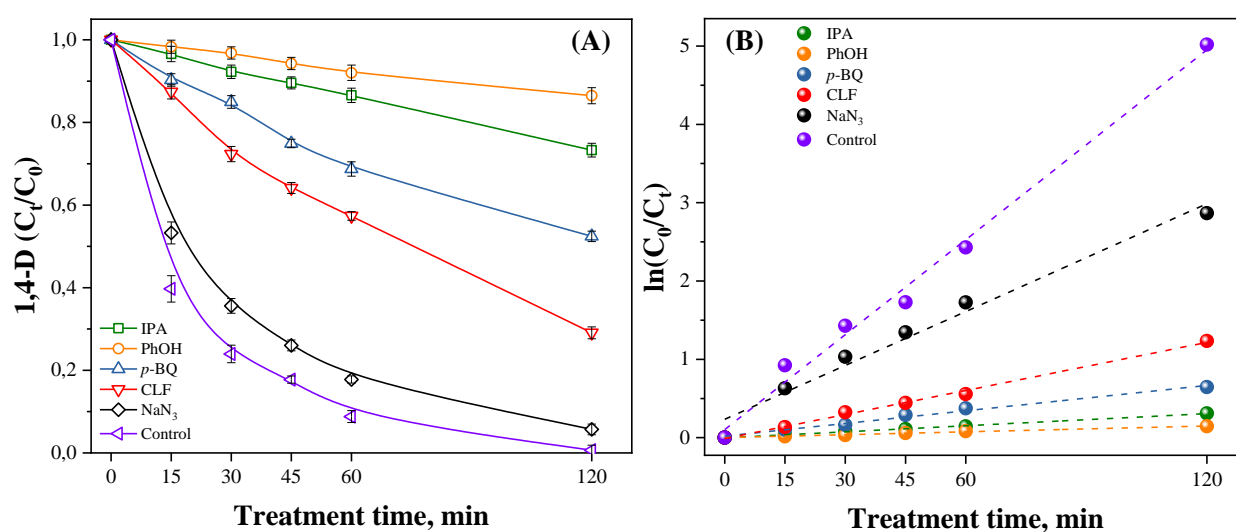
374 Beside HO[•] radicals, O₂^{•-} and CO₃^{•-} radicals could be generated in HC/SPC/O₃ according to Eqs. 4-9, 17
 375 and participate in the degradation of 1,4-dioxane. To evaluate the contribution of reactive species in
 376 degradation of 1,4-dioxane, quenching experiments were conducted. Isopropyl alcohol (IPA), phenol
 377 (PhOH), chloroform (CLF), *para*-benzoquinone (*p*-BQ) and sodium azide (NaN₃) were utilized as
 378 scavenging agents. The molar ratio of scavenger to SPC was set as 10:1 to ensure the effective quenching
 379 of radicals. IPA rapidly reacts with HO[•] radicals ($3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and slowly responds to CO₃^{•-} and O₂^{•-}
 380 radicals, with a rate constant of $4.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively [59,60]. Additionally,
 381 the reaction of HO[•] radicals with IPA proceeds faster than with 1,4-dioxane ($2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), H₂O₂ (2.7

382 $\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), HCO_3^- ($8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and CO_3^{2-} ($3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [61–63], hence, IPA was selected to
 383 study the existence of HO^\bullet radicals. On the other hand, PhOH was used to confirm the occurrence of $\text{O}_2^{\bullet-}$
 384 radicals as PhOH preferentially reacts with HO^\bullet ($6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and $\text{CO}_3^{\bullet-}$ ($1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) radicals
 385 [60,64]. Additionally, the impact of $\text{O}_2^{\bullet-}$ radicals was explored using *p*-BQ and CLF, which rapidly react
 386 with a second-order rate constant of $9.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $3.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, respectively [39,59,65]. As
 387 observed from **Fig. 9a**, the degradation efficiency of 1,4-dioxane was declined from 99.34 to 26.71%
 388 after 120 min and the corresponding rate constants were decreased from 4.04×10^{-2} to $2.58 \times 10^{-3} \text{ min}^{-1}$
 389 (**Table 7**) in the presence of IPA. This illustrates the predominant role of HO^\bullet radicals. The degradation
 390 efficiency of 1,4-dioxane was inhibited to 13.52% in 120 min with addition of PhOH, suggesting the
 391 contribution of $\text{O}_2^{\bullet-}$ radicals in 1,4-dioxane degradation. Based on these it can be proposed that for
 392 HC/SPC/ O_3 highest contribution to degradation had HO^\bullet radicals, with moderate role of $\text{CO}_3^{\bullet-}$ and minor
 393 role of $\text{O}_2^{\bullet-}$. In contrast, the quenching experiments using *p*-BQ and CLF suppressed the degradation
 394 efficiency of 1,4-dioxane by 52.99 and 29.21% in 120 min, respectively, suggesting a considerable
 395 involvement of $\text{O}_2^{\bullet-}$ radicals in degradation of 1,4-dioxane. It must be taken into account, that both
 396 scavengers, but especially *p*-BQ also in some part can react with other radicals including HO^\bullet , thus these
 397 tests are discussed as they confirmed contribution of superoxide radical in degradation. Additional aspect
 398 that overlays on the performed tests relates to the fact, that although PhOH is low reactive towards $\text{O}_2^{\bullet-}$
 399 radicals ($5.8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$), scavenging of HO^\bullet radicals prohibits the regeneration of $\text{O}_2^{\bullet-}$ radicals through
 400 **Eq. 17**. In light of this “doubled” scavenging effect of PhOH it is confirmed that $\text{O}_2^{\bullet-}$ contributed to the
 401 degradation effect.

402 In the case of *p*-BQ and CLF, available (not scavenged so fast) HO^\bullet radicals promoted the continuous
 403 regeneration of $\text{O}_2^{\bullet-}$ radicals (**Eq. 17**). Interestingly, the inhibitory effect of hydrophobic and more volatile
 404 CLF (which tends to move into the cavitation bubble - a place in the system that is less polar than water
 405 and preferred by volatile compounds) was lower than *p*-BQ implying that the formation of $\text{O}_2^{\bullet-}$ radicals
 406 proceeds mainly in bulk liquid phase. Subsequent oxidation of $\text{O}_2^{\bullet-}$ radicals by HO^\bullet and HO_2^\bullet radicals can
 407 lead to the generation of singlet oxygen ($^1\text{O}_2$) species through the following reactions [66]:



410 To elucidate the formation of $^1\text{O}_2$ species, NaN_3 was added to quench $^1\text{O}_2$ with a rate constant of 1×10^9
 411 $\text{M}^{-1} \text{s}^{-1}$ [67]. Quenching experiments using NaN_3 inhibited the degradation efficiency of 1,4-dioxane by
 412 5.03%, whereat the corresponding degradation rate constant was decreased from 4.04×10^{-2} to 2.29×10^{-2}
 413 min^{-1} . These observations suggest a negligible contribution of $^1\text{O}_2$ in the degradation of 1,4-dioxane by
 414 HC/SPC/ O_3 . Performed experiments provide general identification of ROSs. Besides above quenching
 415 experiments, other techniques (e.g., electron paramagnetic resonance) can be suggested for the extensive
 416 and more detailed analysis of ROSs in HC/SPC/ O_3 , as scavengers may interrupt radical chain reactions of
 417 O_3 decomposition and consume O_3 [68,69].



418
 419 **Figure 9.** Effect of scavengers on the degradation 1,4-D in HC/SPC/ O_3 : (a) degradation efficiency, (b)
 420 pseudo-first-order kinetic plots ($[1,4\text{-D}]_0$ 100 ppm, C_v 0.27, SPC r_{ox} 8, $[\text{O}_3]$ 0.86 g h^{-1} , $[\text{SPC}]:[\text{Scavenger}]$
 421 $= 1:10$, $20 \pm 2 \text{ }^\circ\text{C}$).

422 **Table 7.** Kinetic parameters of 1,4-dioxane degradation in HC/SPC/ O_3 in the presence of scavengers.

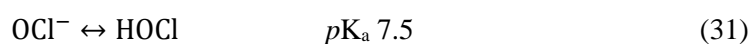
	Type of scavenger				
	IPA	PhOH	<i>p</i> -BQ	CLF	NaN_3
$k \times 10^{-2}, \text{min}^{-1}$	0.258	0.124	0.539	1.023	2.294
R^2	0.998	0.991	0.989	0.996	0.978

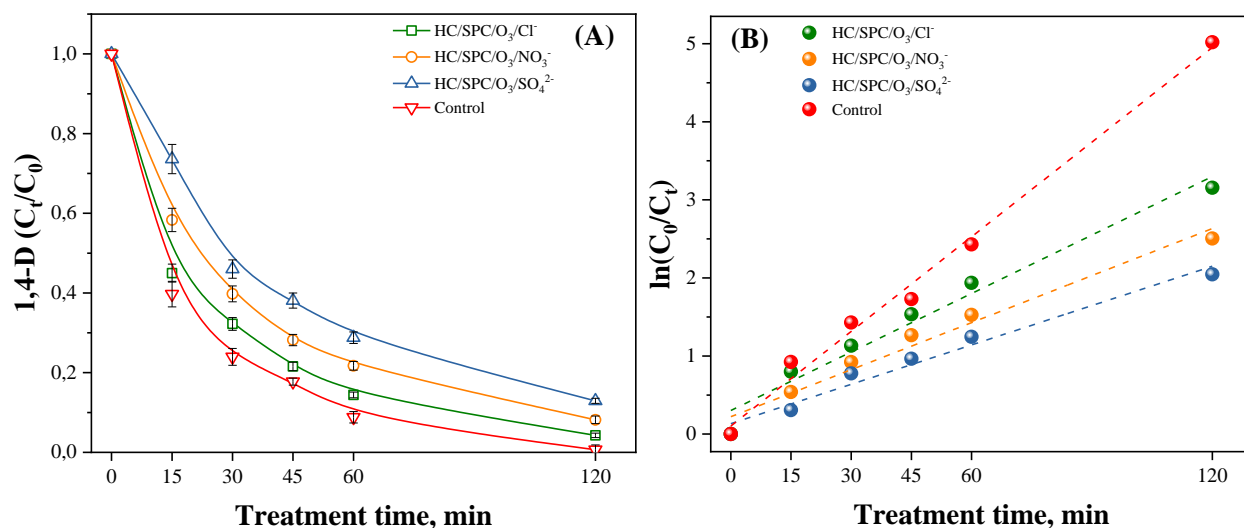
423
 424 **3.7 The effect of co-existing inorganic anions on HC/SPC/ O_3**

425 Inorganic anions such as Cl^- , NO_3^- and SO_4^{2-} are inherently present in natural water [70,71] and might
 426 affect the performance of HC/SPC/ O_3 . Since the practical implementation of HC/SPC/ O_3 assumes the
 427 treatment of contaminated natural water, the study of the effect of inorganic anions is required. To



428 evaluate the effect of inorganic anions, the degradation of 1,4-dioxane in HC/SPC/O₃ was conducted in
 429 the presence of Cl⁻, NO₃⁻ and SO₄²⁻, whereat the molar ratio of anion to SPC was 10:1. As shown, in **Fig.**
 430 **10a**, the presence of Cl⁻ anions resulted in a slight inhibitory effect decreasing the degradation efficiency
 431 of 1,4-dioxane from 99.34 to 95.74% within 120 min. The inhibition effect of Cl⁻ anions is commonly
 432 ascribed to the formation chlorine species (i.e., Cl[•] and Cl₂^{•-}) through the passage of reactions consuming
 433 of HO[•] radicals as shown in **Eqs. 27-29**. However, the reaction of Cl⁻ anions with HO[•] radicals is
 434 negligible at circumneutral conditions due to the fast reverse reaction [72]. In this study, the inhibitory
 435 effect of Cl⁻ anions can be explained due to the interaction of Cl⁻ anions with O₃, which become relevant
 436 at high Cl⁻ concentration. Such interaction competes with H₂O₂ for O₃ consumption and lead to the
 437 formation of hypochlorite which exist in equilibrium with HClO (**Eqs. 30, 31**) and is not oxidized by O₃
 438 [72–74]. The inhibitory effect of 1,4-dioxane degradation in HC/SPC/O₃ found to be more deteriorate
 439 with addition of NO₃⁻ and SO₄²⁻ anions. Thus, the presence of NO₃⁻ and SO₄²⁻ anions declined the
 440 degradation efficiency of HC/SPC/O₃ towards 1,4-dioxane by 7.51 and 12.28% in 120 min, respectively.
 441 Although, sulfate radicals (SO₄^{•-}) formed *via* **Eq. 32** [75], exhibit relatively high oxidation potential and
 442 selectivity towards electron-rich moieties, the presence of precursor SO₄²⁻ anions showed the highest
 443 inhibitory effect. This phenomenon can be referred to the decrease of the reduction potential of SO₄^{•-}
 444 radicals caused by the high concentration of SO₄²⁻ anions [39]. As depicted in **Table 8**, the degradation
 445 rate constant of 1,4-dioxane in presence of Cl⁻, NO₃⁻ and SO₄²⁻ anions in comparison with the process
 446 without additives was decreased from 4.04 × 10⁻² to 2.50 × 10⁻², 2.01 × 10⁻² and 1.68 × 10⁻² min⁻¹,
 447 respectively. In this study, the inhibitory effect of anions towards the degradation of 1,4-dioxane was in
 448 the following order: SO₄²⁻ > NO₃⁻ > Cl⁻.





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Figure 10. Effect of anions on the degradation 1,4-D in HC/SPC/O₃: (a) degradation efficiency, (b)

pseudo-first-order kinetic plots ($[1,4-D]_0$ 100 ppm, C_v 0.27, SPC r_{ox} 8, $[O_3]$ 0.86 g h⁻¹, $[SPC]:[Anion] =$

1:10, 20±2 °C).

It is worth to mention, that in overall the inhibitory effect of anions was relatively low. In all cases above 80% degradation was obtained in 120 minutes. Applied concentration of anions was relatively high, thus in many real case scenarios it can be expected to be much lower. Thus, the developed system provides satisfactory performance to be implemented for treatment of real effluents.

Table 8. Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O₃ in the presence of anions.

	Type of anion		
	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
$k \times 10^{-2}, \text{min}^{-1}$	2.497	2.009	1.681
R ²	0.972	0.972	0.973

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3.8 Degradation pathway of 1,4-dioxane in HC/SPC/O₃

Highly reactive and non-selective behavior of radical species induces a broad variety of structural transformations to the target pollutant. These transformations can lead to the formation of by-products, which present toxicity higher than the parent compound. To better understand the transformation mechanism of 1,4-dioxane under HC/SPC/O₃, the intermediates present in treated samples were identified and analyzed by GC-MS using SCAN mode. In order to detect minor intermediates and, thus propose an accurate pathway of 1,4-dioxane degradation in HC/SPC/O₃, an initial concentration of 1000 ppm was adopted at fixed optimal r_{ox} . Based on the analysis of results, ethylene glycol diformate (EGDF) was

473 identified as the main intermediate of 1,4-dioxane degradation in HC/SPC/O₃ and the proposed
 474 degradation pathway is presented in **Fig. 11**.

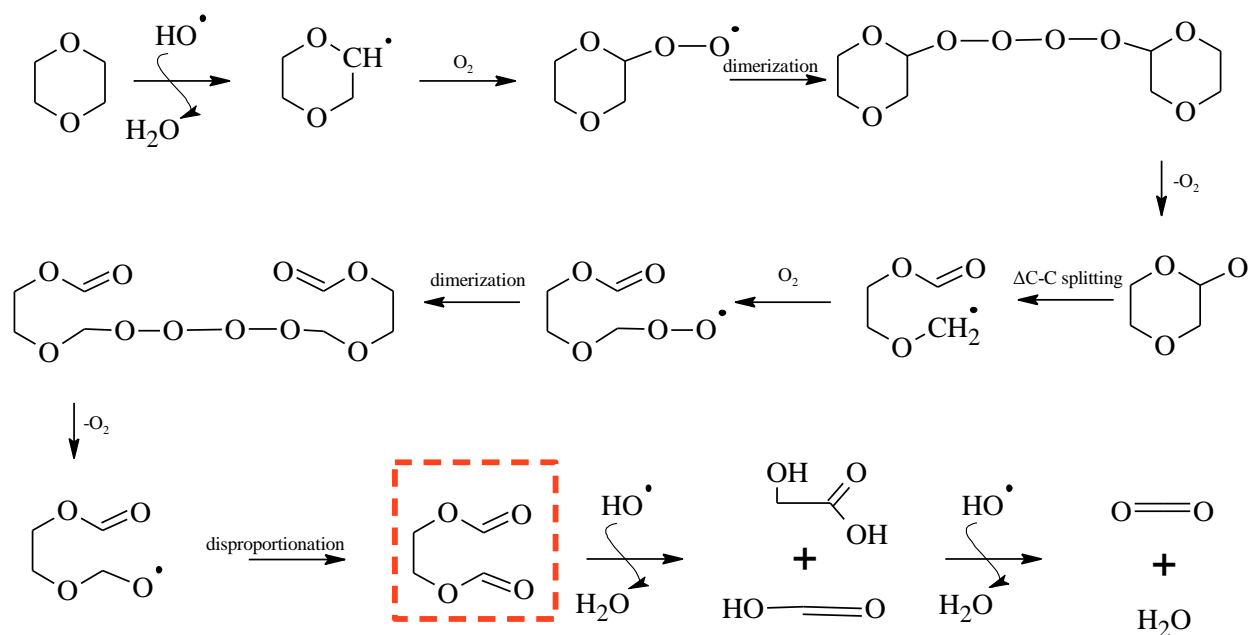


Figure 11. The proposed degradation pathway of 1,4-dioxane in HC/SPC/O₃.

478 The initial step of the oxidative degradation of 1,4-dioxane proceeds through the attack of radical species
 479 with H-abstraction to form 1,4-dioxanyl radical. In the presence of oxygen 1,4-dioxanyl radicals are
 480 converted to peroxy radicals, which are further transformed into α -oxyl radicals [9,76,77]. The latter is
 481 recognized as a primary precursor of 1,4-dioxane degradation associated with AOPs. The presence of
 482 EGDF in the treated samples supports the ring opening mechanism of α -oxyl radical *via* Δ C-C splitting at
 483 the α -C position [76,78]. The obtained radical reacts with oxygen and undergoes dimerization to form
 484 tetraoxide, which is further fragmented to yield EGDF. Subsequent attack of HO• radicals causes
 485 fragmentation of EGDF with formation of low-molecular intermediates (e.g., glycolic, formic acids),
 486 which are further converted to CO₂ and H₂O. TOC analysis of the samples showed up to 95% of TOC
 487 removal confirming the mineralization of 1,4-dioxane (**Fig. S2**). Since, EDGF was found as the main by-
 488 product of 1,4-dioxane degradation, the mechanism pathway of Δ C-C splitting was predominant in
 489 HC/SPC/O₃. This result is consistent with the radical-type mechanism of 1,4-dioxane degradation
 490 previously described for other AOPs.

491

492 3.9 Economical evaluation

493 Assessment of the economic feasibility of HC/SPC/O₃ was based on the energy efficiency and the
494 treatment cost of 1,4-dioxane 100 ppm model solution, calculated for various studied processes compiled
495 in **Table 9**. The cost of treatment was estimated using electric energy per order (E_{EO}), which is defined as
496 [79,80]:

$$497 \quad E_{EO} = \frac{P_{el} \times t \times 1000}{V \times 60 \times \log\left(\frac{C_0}{C_t}\right)} \quad (33)$$

498 , where P_{el} is electric power (kW), t – time of treatment (min), V – volume of the treated solution (L), C₀
499 and C_t are the initial and final concentration of the pollutant. Since log (C₀/C_t) = kt, the equation can be
500 written as follows:

$$501 \quad E_{EO} = \frac{38.4 \times P_{el}}{V \times k} \quad (34)$$

502 The parameter E_{EO} (kWh m⁻³order⁻¹) describes the amount of energy required to degrade 90% of pollutant
503 in 1 m³ of the contaminated liquid. The calculations were conducted considering the power of HC system
504 and O₃ generator, which were 0.16 and 0.38 kW, respectively. In this study, the E_{EO} values of 1,4-dioxane
505 degradation using HC/O₃ pH10, HC/H₂O₂/O₃, HC/SPC/O₃ were 222.97, 165.89 and 102.65 kWh m⁻³
506 order⁻¹, respectively (**Table 9**). The adaptation of SPC in HC/SPC/O₃ decreased the energy consumption
507 by 117 and 62% as compared to HC/O₃ pH10 and HC/H₂O₂/O₃, respectively. This is attributed the higher
508 degradation efficiency of HC/SPC/O₃, which allowed to shorten the treatment time of 1,4-dioxane and,
509 thereby decreased the energy consumption by HC pump and O₃ generator. Owing to cheaper industrial
510 price, H₂O₂ constituted only 0.8% of HC/H₂O₂/O₃ cost, while SPC accounted 6.4% of the total cost in
511 HC/SPC/O₃. However, the higher effectiveness of HC/SPC/O₃ provided a reduction of the total treatment
512 cost by 52% as compared to HC/H₂O₂/O₃.

513 In general, the ranges of E_{EO} values determined for ozonation, peroxone and UV-based AOPs are 0.041-
514 0.73, 0.86-5.96 and 0.73-499 kWh m⁻³, respectively, and can be substantially large depending on the
515 pollutant's persistency [81]. Interestingly, the degradation of 1,4-dioxane using electro-peroxone and
516 photo-electro-peroxone, according to data reported in the literature required 27.57 and 23.82 kWh m⁻³
517 [10,11] (details of calculations are provided in **Supplementary data**). However, these values have only
518 theoretical meaning as they were calculated using the theoretical energy required for O₃ generation and
519 assuming the average cell voltage as 7.8 V [82,83]. It is well known that energetic effectiveness of ozone
520 generators is far away from theoretical assumptions.

521 In this study, E_{EO} values were obtained based on nominal power of HC pump for used flowrate and real
 522 power consumption of ozone generator. Therefore, the values of E_{EO} of HC-based AOPs for degradation
 523 of 1,4-dioxane were generally higher as compared to reported in literature electro-peroxone and photo-
 524 electro-peroxone. On the other hand, data presented in the cited papers do not allow to use typical formula
 525 for E_{EO} that is commonly used and implemented in current paper. In addition, design of energy efficient
 526 treatment systems will allow to reach more optimistic E_{EO} values reported in the literature.

527 **Table 9.** Evaluated cost of treatment of HC-based AOPs for degradation of 1,4-dioxane.

Process	k, min^{-1}	$E_{EO}, \text{kWh m}^{-3}\text{order}^{-1}$	Cost of energy*, USD	Amount of oxidant, kg	Cost of oxidant**, USD	Total cost, USD	Efficiency, %
HC/O ₃ pH10	0.0186	222.97	24.53	-	-	24.53	89.89
HC/Peroxone	0.025	165.89	18.25	0.306	0.15	18.40	95.16
HC/SPC/O ₃	0.0404	102.65	11.29	1.413	0.78	12.07	99.34

528 *The cost of energy was estimated based on the average electricity cost for industrial customers in Poland
 529 - 0.11 USD/kWh.

530 ** The cost of industrial grade H₂O₂ and SPC were assumed as 500, 550 USD/ton, respectively [84,85].

531 4. Conclusions

532 HC/SPC/O₃ appears to be an effective alternative for the degradation of 1,4-dioxane resulting in 99.34%
 533 in 120 min with a k of $4.04 \times 10^{-2} \text{min}^{-1}$. Compared to traditional peroxone process, HC/SPC/O₃ required
 534 relatively lower dosages of SPC (r_{ox} 8) and O₃ (0.86 g h⁻¹), which is promising for practical
 535 implementation in terms of economical feasibility. Concentrations of SPC and O₃ above/below the
 536 optimal dosage were found detrimental due to the scavenging of radical species. The presence of CO₃²⁻ in
 537 HC/SPC/O₃ enabled the promotion of O₃ decomposition through the increase of pH and participated in
 538 radical chain reactions to provide more reactive species. HO• radicals were determined as predominant
 539 radical species in HC/SPC/O₃ according to the quenching experiments, which proposed the contribution
 540 of reactive species in 1,4-dioxane degradation in order of HO• > CO₃^{•-} > O₂^{•-}. The studied co-existing
 541 inorganic anions suppressed the effectiveness of HC/SPC/O₃, whereat the inhibitory effect of SO₄²⁻ anions
 542 was higher than that of NO₃⁻ and Cl⁻ anions. The products of 1,4-dioxane degradation in HC/SPC/O₃ were
 543 detected using GC-MS and the degradation pathway was proposed. The oxidation pathway included
 544 several transformation steps with formation of ethylene glycol diformate, which is consistent with radical

545 route degradation 1,4-dioxane reported previously. This work highlights the potential application of SPC
546 in peroxone process as an effective, safe and sustainable replacement to H₂O₂ under HC.

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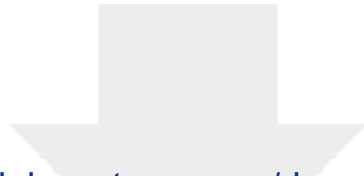
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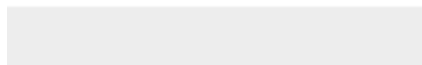
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Supplementary Material

Supplementary data of HC-SPC-O3 for CEJ 14 DEC.pdf



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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: