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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. --Manuscript Draft--

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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:	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 4.04×10-2 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- > CI 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, $\Delta$ C-C splitting at the α-C position, subsequent dimerization, fragmentation and mineralization. Electric energy per order (EEO) for best process was 102.65 kWh·m-3·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.
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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. doi:10.1016/J.WATRES.2015.05.024.



## 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

GDAŃSK UNIVERSITY OF TECHNOLOGY G. Narutowicza 11/12 80-233 Gdańsk, Poland tel +48 697970303

e-mail: grzegorz.boczkaj@pg.edu.pl www.pg.edu.pl



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## Highlights

- Synergistic HC/SPC/O<sub>3</sub> process for degradation of emerging environmental pollutants
- Superior performance of HC/SPC/O<sub>3</sub> comparing to HC/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>
- 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/O<sub>3</sub>) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1,4-dioxane in water.

Kirill Fedorov<sup>1</sup>, Manoj P. Rayaroth<sup>2</sup>, Noor S. Shah<sup>3</sup>, Grzegorz Boczkaj<sup>1,4,\*</sup>

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

<sup>2</sup>GREMI, UMR 7344, Université d'Orléans, CNRS, 45067 Orléans, France.

<sup>3</sup>Department of Environmental Sciences, COMSATS University Islamabad, Vehari Campus 61100, Pakistan.

<sup>4</sup>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

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## Graphical abstract



#### 1 Abstract

Hydrodynamic cavitation (HC) was employed to activate sodium percarbonate (SPC) and ozone (O<sub>3</sub>) to 2 degrade recalcitrant 1,4-dioxane. The degradation efficiency >99% with a rate constant of  $4.04 \times 10^{-2}$  min<sup>-1</sup> 3 4 was achieved in 120 min under the optimal conditions of cavitation number ( $C_v$ ) 0.27, pH 5, molar ratio of oxidant to pollutant ( $r_{ox}$ ) 8, ozone dose of 0.86 g h<sup>-1</sup> under 25±2 °C with initial concentration of 1,4-5 dioxane 100 ppm. The application of HC with SPC/O<sub>3</sub> increased the degradation efficiency by 43.32% in 6 120 min, confirming a synergistic effect between the coupled processes. In addition, the degradation 7 8 efficiency of 1,4-dioxane in HC/SPC/O<sub>3</sub> was superior as compared to HC/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>, suggesting that the presence of SPC has a significant role in degradation of 1,4-dioxane. Radical quenching experiment 9 10 revealed highest contribution of hydroxyl (HO') radicals in the degradation of 1,4-dioxane among carbonate ( $CO_3$ ) and superoxide ( $O_2$ ) radicals. The presence of co-existing anions resulted in an 11 inhibitory effect in the following order:  $SO_4^{2-} > NO_3^{-} > Cl^{-}$ . Based on GC-MS analysis, ethylene glycol 12 13 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,  $\Delta C$ -C 14 15 splitting at the  $\alpha$ -C position, subsequent dimerization, fragmentation and mineralization. Electric energy per order (E<sub>EO</sub>) for best process was 176,79 kWh·m<sup>-3</sup>·order<sup>-1</sup>. Total cost of treatment was estimated as 16 17 approx. 20 USD/m<sup>3</sup>. These findings confirmed the SPC as an efficient, environmentally-friendly alternative to H<sub>2</sub>O<sub>2</sub> and broadened the scope of HC-based AOPs for water and wastewater treatment. 18

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

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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 occurrence of 1,4-dioxane has been detected in municipal water supply, landfill leachate and 30 groundwaters [2,3]. Such widespread occurrence of 1,4-dioxane is mainly originated due to the improper 31 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 potentially (Class B2) carcinogenic to human by the United States Environmental Protection Agency 34 [1,4]. In connection with this, stringent water quality standards regulating the concentration of 1,4-35 36 dioxane in water have been adopted to reduce the health risk. However, the conventional water treatment methods based on biodegradation were found ineffective towards 1,4-dioxane [5-7]. Therefore, 37 38 tremendous efforts have been devoted for the development of technologies to degrade 1,4-dioxane in water. Among the tested technologies, advanced oxidation processes (AOPs) based on the generation of 39 40 highly reactive radical species appeared to be promising green technologies for remediation of 1,4-41 dioxane from aqueous environment [5,8–11].

As a part of AOPs,  $H_2O_2$  produces hydroxyl (HO<sup> $\cdot$ </sup>) radicals with an extremely strong oxidation capacity 42  $(E^0 2.8 \text{ V})$ , which can allow to achieve complete mineralization of treated organic pollutants [12]. The 43 44 production of HO<sup> $\cdot$ </sup> radicals is generally proceeded through the combination of H<sub>2</sub>O<sub>2</sub> with oxidants (PS, PMS), catalysts (Fe<sup>2+</sup>, TiO<sub>2</sub>) or energy input (ultrasound, UV-irradiation). Among the combined 45 processes,  $H_2O_2/O_3$  is a well-known and powerful method denominated as peroxone, which involves 46 47 direct and indirect oxidation of pollutants. The effectiveness of  $H_2O_2/O_3$  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<sup>•</sup> radicals are generated *via* the accelerated decomposition of  $O_3$  initiated by  $H_2O_2$  and alternative activation of  $H_2O_2$  by  $O_3$ . Nevertheless, the use of 50 H<sub>2</sub>O<sub>2</sub> is associated with serious safety concerns related with a risk of explosion during the transportation 51 52 and corrosion of equipment. Moreover, the application of  $H_2O_2$  in AOPs is commonly related with selfscavenging or radical recombination reactions raising the issue of  $H_2O_2$  dosage and introduction mode optimization.

55 Recently, studies on H<sub>2</sub>O<sub>2</sub>-based AOPs are focused on sodium percarbonate (SPC), namely Na<sub>2</sub>CO<sub>3</sub>  $\times$ 56  $1.5H_2O_2$  as a safe and cheap alternative to  $H_2O_2$ . Besides, this trend is reasoned with a number of advantages such as prevention of acidification of treated media and wide operating pH range [20,21]. 57 Attempts on SPC activation have been made using  $Fe^{2+}$  [22–24], graphene oxide [25], protonated g-C<sub>3</sub>N<sub>4</sub> 58 [26], zero valent iron (ZVI) [27], vanadium (IV) [28], UV [29] and ultrasound [21]. Unlike H<sub>2</sub>O<sub>2</sub>, the 59 60 oxidation capacity of SPC-based AOPs is conditioned by a variety of ROS, including superoxide  $(O_2^{-})$ and carbonate (CO3<sup>-</sup>) radicals. The latter is generated through the consumption of HO<sup>-</sup> radicals and 61 exhibit lower oxidation potential of 1.78 V at pH 7 [30]. In spite of this, CO<sub>3</sub><sup>-</sup> radicals selectively react 62 with organic pollutants containing electron rich functional groups. For instance, as an electron acceptor 63 CO3<sup>-</sup> radical rapidly reacts with *p*-substituted phenols and anilines with a rate constant of 10<sup>7</sup>-10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> 64 and 10<sup>5</sup>-10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively [31–33]. Moreover, the concentration of CO<sub>3</sub><sup>--</sup> radicals in sunlit surface 65 water appeared to be two orders of magnitude higher than HO<sup>•</sup> radicals under the same conditions [34]. 66 Therefore, SPC-based AOPs are seemed to be a preferable option for the degradation of organic 67 68 pollutants bearing electron rich moieties and, particularly, 1,4-dioxane.

Although, AOPs are considered as effective and environmentally friendly techniques for the degradation 69 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 integration of AOPs with cavitation is a promising route for the improvement of AOPs. The development 73 of hybrid processes based on cavitation and AOPs showed encouraging results anticipating the 74 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, regions of extreme conditions or so-called "hot spots" are created. Such conditions are capable to form 79 radical species through to the pyrolytic disassociation of water or proceed the activation of  $H_2O_2$ ,  $O_3$  and 80 other peroxides. Owing to the continuous flow operation, high cavitational yield and effectiveness 81

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/O<sub>3</sub> process under 85 hydrodynamic cavitation (HC); ii). to understand the synergy in HC/SPC/O<sub>3</sub> the degradation kinetics of 1,4-dioxane in sole and coupled processes; iii). to identify the reactive species in  $HC/SPC/O_3$  by 86 quenching experiments using specific radical scavengers; iv). to perform the degradation under 87 environmental relevant conditions varying pH and in the presence of inorganic anions; and finally, y), to 88 89 identify the transformation products and elucidate the mechanism of 1,4-dioxane degradation in 90 HC/SPC/O<sub>3</sub>.

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- 92 **2.** Materials and methods
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1,4-dioxane (reagent grade, p.a., 99%), sodium nitrate (pure), sodium hydroxide (pure p.a., 98.8%), 96 97 chloroform (pure p.a.), acetone, dichloromethane, 2-propanol (pure p.a.), hydrogen peroxide (pure p.a., 30%), potassium iodide (pure p.a.) and sodium thiosulfate pentahydrate (acs pure p.a.) were purchased 98 99 from POCH (Poland). Sodium percarbonate (avail. H<sub>2</sub>O<sub>2</sub> 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 grade and were used as received without purification. Ultrapure quality water (18.2 M $\Omega$ cm<sup>-1</sup>) from 104 105 Millipore<sup>®</sup> system (Direct-Q UV-R model) was used for preparation of reaction solution.

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107 2.2 Experimental procedure

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

<sup>94 2.1</sup> Chemicals

111 a mechanical stirrer, temperature indicator and water condenser to maintain the reaction temperature. 112 Sequential pumping system (MS 801-4, 1360 min<sup>-1</sup>, TECHTOP<sup>®</sup> MOTOR, Shanghai, China) connected with electromagnetic flowmeter (MPP 600 by MAGFLO®) was used to circulate water through the 113 114 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 joints were used to connect the units. In a typical experimental procedure, 5 L of model solution 117 118 containing 100 ppm of 1,4-dioxane was added in the feed tank and treated for 120 min at  $20\pm2$  °C. Sample aliquots of 20 mL were collected at regular time interval. The SPC solution was injected through 119 120 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

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

A quantitative analysis of 1,4-dioxane concentration was studied using a Clarus 500 (Perkin Elmer, USA) gas chromatograph equipped with flame ionization detector (GC-FID). A capillary column (60 m × 0.32 mm ID, 1.8 um DB624, Agilent, USA) was used is separations. Parameters setting of GC-FID were as follows: temperature program - 50 °C (5 min) ramped at 10 °C/min to 275 °C (5 min), detector temperature 275 °C. A nitrogen was used as carrier gas with volumetric flowrate of 5 mL/min. Detector 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  $\times$  0.2 mm ID, 0.1 um DHA, Restek, USA) was used for separation of analytes. A hydrogen (supplied from PGX500 hydrogen generator, Perkin Elmer, USA) was used as carrier gas (1 mL/min),
injection port temperature was 300 °C and GC-MS transfer line temperature was 310 °C. The oven
temperature program was 40 °C (isothermal for 5 min) ramped at 5 °C/min to 220 °C. Ion source (EI, 70
eV) temperature was 200 °C. A mass-to-charge ratio of 34 to 220 m/z was selected for SCAN mode
analysis of byproducts.

145 The concentration of  $O_3$  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 O<sub>3</sub>. The compressed dry air containing O<sub>3</sub> was bubbled through KI solution using a sintered glass 149 disc located in the bottom half of bottles. A standardized 0.001 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was used as a titrant and 5% (w/v) starch solution as an indicator. The dose of O<sub>3</sub> at carrier gas flow rate of 0.5, 1.0, 1.5, 2.0 150 151 and 2.5 L min<sup>-1</sup> were determined as 0.23, 0.40, 0.74, 0.86 and 0.94 g h<sup>-1</sup>, respectively. The content of total organic carbon (TOC) was measured using TOC-LCSH instrument (Shimadzu, Japan). All tubing 152 connecting ozone generator with HC reactor and gas absorption bottles were made of PTFE (Teflon). 153

#### 154 **3. Results and discussion**

#### 155 3.1 *Effect of cavitation number*

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

$$C_{\nu} = \frac{p_2 - p_V}{\frac{1}{2}u_0^2 \rho},\tag{1}$$

where,  $p_2$  is the recovered downstream pressure,  $p_v$  – vapor pressure of the liquid,  $u_0$  is liquid linear velocity at the throat of cavitating constriction and  $\rho$  is the density of the treated liquid.

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In this study, the effectiveness of sole HC towards 1,4-dioxane degradation was performed varying the 166 liquid velocity to determine the optimal C<sub>v</sub>. All studies in this paper were performed for primary 167 168 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. Pseudofirst-order model with regard to the concentration of 1,4-dioxane was employed to depict the degradation 172 173 kinetics (Eq. 2).

$$ln\frac{c_0}{c_t} = kt,$$
(2)

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



Figure 1. Effect of C<sub>v</sub> on the degradation 1,4-dioxane in sole HC: (a) degradation efficiency, (b) pseudo first-order kinetic plots ([1,4-D]<sub>0</sub> 100 ppm, pH<sub>0</sub> 5, 20±2 °C).

As depicted in **Fig. 1a**, the percent degradation of 1,4-dioxane was 11.63, 16.01 and 17.03% for  $C_v 0.92$ , 0.47 to 0.27, respectively. The degradation rate constant was increased from  $1.03 \times 10^{-3} \text{ min}^{-1}$  to  $1.43 \times 10^{-3} \text{ min}^{-1}$  (**Table 1**) with a reduction of  $C_v$  from 0.92 to 0.27. These observations indicated that the increase of the liquid velocity and, subsequently, inlet pressure, increased the cavitation intensity, which 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  $1.41 \times 10^{-3}$  and  $1.40 \times 10^{-3}$  min<sup>-1</sup>, 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.

**Table 1**. Kinetic parameters of 1,4-dioxane degradation in sole HC at different C<sub>v</sub>.

	Cavitation number (C <sub>v</sub> )						
	0.02	0.18	0.27	0.47	0.92		
$k \times 10^{-2}, \min^{-1}$	0.140	0.141	0.155	0.145	0.103		
$\mathbb{R}^2$	0.998	0.993	0.992	0.998	0.999		

<sup>194</sup> 

195 3.2 Enhanced degradation of 1,4-dioxane by HC/SPC/O<sub>3</sub>

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197 The degradation efficiency of HC/O<sub>2</sub>, HC/O<sub>3</sub>, HC/SPC, SPC/O<sub>3</sub> and HC/SPC/O<sub>3</sub> 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, showing higher degradation efficiency than sole HC. This can be explained by formation of additional 199 200 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  $HC/O_3$  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  $O_3$  was combined 205 with SPC in the absence of HC. Although, the radicals in  $SPC/O_3$  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  $O_3$  and  $H_2O_2$ . Particularly, alternative decomposition routes of  $O_3$  and  $H_2O_2$  with 208 formation of HO<sub>2</sub><sup>-</sup> are occurred under the alkaline pH of SPC (Eqs. 10, 11) [45,50]. Obtained HO<sub>2</sub><sup>-</sup> participate in a series of radical chain reactions and are eventually converted to highly reactive HO' 209 radicals. Coupling of HC with  $SPC/O_3$  significantly increased the degradation efficiency of 1,4-dioxane 210 giving 99.34% in 120 min. The observed enhancement of 1,4-dioxane degradation in SPC/O<sub>3</sub> is 211

presumably attributed to the following beneficial factors provided by HC: i). thermal effect of so-called "hot spots" due the adiabatic collapse of cavitation bubbles assisted the cleavage of chemical bonds accelerating radical chain reactions; ii). continuous circulation along with shock waves improved the utilization of O<sub>3</sub> and facilitated the overall mass transfer in the system; iii). owing to the extreme conditions in "hot spots", HC continuously produces radical species, thus, promoting the chain radical reactions.

218 
$$O_3 + \text{cavitation} \rightarrow O^{\bullet} + O_2$$
 (3)

219 
$$0^{\bullet} + H_2 0 + \text{cavitation} \rightarrow 2H0^{\bullet}$$
 (4)

220 
$$H_2O_2 + \text{cavitation} \rightarrow HO^{\bullet} + HO^{\bullet}$$
 (5)

221 
$$HO^{\bullet} + CO_3^{2-} \to CO_3^{\bullet-} + HO^{-}$$
 (6)

222 
$$HO^{\bullet} + HCO_3^- \to CO_3^{\bullet-} + H_2O$$
 (7)

223 
$$0_3 + H_2 O_2 \to O_2 + HO^{\bullet} + HO_2^{\bullet}$$
 (8)

$$0_3 + \mathrm{HO}_2^{\bullet} \to \mathrm{HO}^{\bullet} + 2\mathrm{O}_2 \tag{9}$$

225 
$$0_3 + H0^- \to H0_2^- + 0_2$$
 (10)

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \tag{11}$$

As shown in Table 2, the pseudo-first-order rate constant of 1,4-dioxane degradation HC/O<sub>2</sub>, HC/O<sub>3</sub>, 227 HC/SPC and SPC/O<sub>3</sub> were  $1.70 \times 10^{-3}$ ,  $2.32 \times 10^{-3}$ ,  $2.12 \times 10^{-3}$ ,  $6.60 \times 10^{-3}$  min<sup>-1</sup>, respectively, whereas 228 229 the k value in HC/SPC/O<sub>3</sub> was  $4.04 \times 10^{-2}$  min<sup>-1</sup>. Obtained k values demonstrate the distinct superiority of the hybrid HC/SPC/O<sub>3</sub> over the binarily integrated processes in degradation of 1,4-dioxane. The 230 synergistic index ( $\xi$ ) of HC/SPC/O<sub>3</sub> calculated using k values according to Eq. 12 was 4.32, which 231 232 indicates a remarkable synergy occurred in  $HC/SPC/O_3$  in comparison with the cumulative effect of 233 individual processes. Although the value of  $\xi$  in HC/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> was 3.83, the degradation efficiency of 1,4dioxane was 95.16% after 120 min, whereat the reaction constant was lower by  $1.54 \times 10^{-2}$  min<sup>-1</sup> 234 235 compared to HC/SPC/O<sub>3</sub>.



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]<sub>0</sub> 100 ppm, C<sub>v</sub> 0.27, SPC r<sub>ox</sub> 8, [O<sub>3</sub>] 0.86 g h<sup>-1</sup>, pH<sub>0</sub> 5, 20±2 °C).



241 Figure 3. Effect of various processes on the degradation 1,4-D: (a) degradation efficiency, (b) pseudofirst-order kinetic plots ([1,4-D]<sub>0</sub> 100 ppm, C<sub>v</sub> 0.27, Na<sub>2</sub>CO<sub>3</sub>=H<sub>2</sub>O<sub>2</sub> r<sub>ox</sub> 8, [O<sub>3</sub>] 0.86 g h<sup>-1</sup>, 20±2 °C). 242

243 To further clarify the role of SPC in degradation of 1,4-dioxane by HC/SPC/O<sub>3</sub>, a series of additional 244 experiments, including addition of sodium carbonate, have been conducted. As depicted in Fig. 3a, HC/Na<sub>2</sub>CO<sub>3</sub>/O<sub>3</sub> resulted in 66.50% of 1,4-dioxane degradation within 120 min, whereas it was only 245 26.11% for O<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> in the absence of HC, indicating a considerable contribution of HC in 246 247 decomposition of  $O_3$ . On the other hand, a discernable improve of 1,4-dioxane degradation was observed 248 when comparing HC/Na<sub>2</sub>CO<sub>3</sub>/O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>/O<sub>3</sub> with corresponding HC/SPC/O<sub>3</sub> and SPC/O<sub>3</sub>. Thus, the

249	degradation efficiency of 1,4-dioxane in HC/Na <sub>2</sub> CO <sub>3</sub> /O <sub>3</sub> was lower by 32.84% compared to HC/SPC/O <sub>3</sub> ,
250	while it was 29.91% for Na <sub>2</sub> CO <sub>3</sub> /O <sub>3</sub> and SPC/O <sub>3</sub> . Corresponding $k$ values ( <b>Table 2</b> ) were increased from
251	$9.22\times10^{\text{-3}}$ to $4.04\times10^{\text{-2}}$ min^{\text{-1}} for HC/Na_2CO_3/O_3 and HC/SPC/O_3 and from $2.52\times10^{\text{-3}}$ to $6.60\times10^{\text{-3}}$
252	min <sup>-1</sup> for $Na_2CO_3/O_3$ and SPC/O <sub>3</sub> , respectively. In addition, application of $H_2O_2$ in HC/O <sub>3</sub> improved the
253	degradation efficiency of 1,4-dioxane by 70.82% after 120 min. These results signify the essential role of
254	$H_2O_2$ in formation of radical species in HC/SPC/O <sub>3</sub> . Nevertheless, the degradation efficiency attained by
255	$HC/H_2O_2/O_3$ was significantly lower than $HC/SPC/O_3$ . Similarly, the increase of pH to 10 in $HC/O_3$
256	increased the degradation efficiency to 65.55%, due to the promoted $O_3$ decomposition, however, HC/O <sub>3</sub>
257	at pH 10 showed lower efficiency than HC/SPC/O <sub>3</sub> . Although, HCO <sub>3</sub> <sup>-</sup> and CO <sub>3</sub> <sup>2-</sup> anions are anticipated to
258	scavenge of HO' radicals (Eqs. 6, 7) and slowly react with 1,4-dioxane (~ $10^5$ M <sup>-1</sup> s <sup>-1</sup> ) [51–53], these
259	findings suggest, a partial participation of $HCO_3$ and $CO_3$ radicals in degradation of 1.4-dioxane.
260	Therefore, the contribution of $HCO_3$ and $CO_3$ radicals should be further clarified (detailed investigation
261	is presented in section 3.6).

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

Type of process	$k \times 10^{-2}, \min^{-1}$	$\mathbb{R}^2$
HC/O <sub>2</sub>	0.170	0.996
HC/H <sub>2</sub> O <sub>2</sub>	0.194	0.999
HC/SPC	0.212	0.995
HC/O <sub>3</sub>	0.232	0.997
Na <sub>2</sub> CO <sub>3</sub> /O <sub>3</sub>	0.252	0.998
H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> , pH10	0.483	0.991
SPC/O <sub>3</sub>	0.660	0.980
HC/Na <sub>2</sub> CO <sub>3</sub> /O <sub>3</sub>	0.922	0.973
HC/O <sub>3</sub> , pH10	1.857	0.963
HC/H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> , pH10	2.506	0.991
HC/SPC/O <sub>3</sub>	4.041	0.992

263

264 3.3 Effect of SPC dosage

Since SPC is a precursor of radical species, the dose of added SPC critically affects the effectiveness and operational cost of HC/SPC/O<sub>3</sub>. In order to determine the optimal dosage of SPC, the degradation of 1,4dioxane was performed in HC/SPC with  $r_{ox}$  ranging from 1 to 10, where the value of  $r_{ox}$  represents the

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 8 268 269 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 degradation (**Table 3**) was increased from  $1.55 \times 10^{-3}$  to  $3.42 \times 10^{-3}$  min<sup>-1</sup> as compared to sole HC. With 271 an increase of SPC dosage to  $r_{ox}$  10, 31.94% of 1,4-dioxane was degraded in 120 and k was estimated as 272  $3.14 \times 10^{-3}$  min<sup>-1</sup>. These results suggest that the increase of SPC dosage above the optimal value led to the 273 274 quench of HO<sup>•</sup> radicals. Undesired HO<sup>•</sup> consumption of radicals can be caused by unreacted H<sub>2</sub>O<sub>2</sub>, 275 saturated O<sub>2</sub> 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.

280 
$$H0^{\bullet} + H_2O_2 + cavitation \rightarrow HO_2^{\bullet} + H_2O$$
(13)

281 
$$H0^{\bullet} + O_2 + \text{cavitation} \rightarrow HO_2^{\bullet} + 0^{\bullet}$$
(14)

$$H0^{\bullet} + H0_2^{\bullet} + \text{cavitation} \rightarrow H_2O_2$$
(15)

283 
$$H0^{\bullet} + H0^{\bullet} + \text{cavitation} \rightarrow H_2O_2$$
 (16)

284 
$$H_2O_2 + HO^{\bullet} \to H_2O + O_2^{\bullet-} + H^+$$
 (17)

285 
$$0_2^{\bullet-} + H0^{\bullet} \to H0^- + 0_2$$
 (18)

286 
$$CO_3^{\bullet-} + H_2O_2 \to HCO_3^- + HO_2^{\bullet}$$
 (19)



**Figure 4.** Effect of SPC *r*<sub>ox</sub> on the degradation 1,4-D in HC/SPC: (a) degradation efficiency, (b) pseudo-

289

first-order kinetic plots ([1.4-D]<sub>0</sub> 100 ppm, C<sub>v</sub> 0.27, pH<sub>0</sub> 5, 20±2 °C).

	$r_{\rm ox}$ 1	$r_{\rm ox}$ 3	$r_{\rm ox} 5$	$r_{\rm ox} 8$	<i>r</i> <sub>ox</sub> 10	
$k \times 10^{-2}, \min^{-1}$	0.165	0.200	0.269	0.342	0.314	
$\mathbb{R}^2$	0.984	0.991	0.998	0.995	0.997	

290	Table 3. Kinetic	parameters of 1,4-dioxane degradation in HC/SPC at different $r_{ox}$ .
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291

**292** 3.4 *Effect of*  $O_3$  *dosage* 

To investigate the effect of  $O_3$  dosage, the degradation of 1,4-dioxane was performed in HC/SPC at  $r_{ox}$  8 293 294 varying the dosage of  $O_3$  in the range of 0.23-0.94 g h<sup>-1</sup>. As can be seen from **Fig. 5a**, the increase of  $O_3$ dosage from 0.23 to 0.94 g h<sup>-1</sup> improved the degradation of 1,4-dioxane. Thus, 39.65, 59.55, 90.35 and 295 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<sup>-1</sup> in 120 296 min, respectively. As given in **Table 4**, the increase of  $O_3$  dosage from 0.23 to 0.86 g h<sup>-1</sup> accelerated the 297 rate constant of 1,4-dioxane degradation from  $4.11 \times 10^{-3}$  to  $4.04 \times 10^{-2}$  min<sup>-1</sup>, respectively, while it was 298 299  $3.74 \times 10^{-3}$  min<sup>-1</sup> for HC/SPC at  $r_{ox}$  8 in absence of O<sub>3</sub>. These finding suggest that the improvement effect 300 in HC/SPC/O<sub>3</sub> was due to the reaction of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> yielding HO<sup>•</sup> 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<sub>3</sub> from gaseous phase into the liquid. In such scenario, the contact of O<sub>3</sub> with H<sub>2</sub>O<sub>2</sub> is enhanced resulting in effective utilization of O<sub>3</sub>. Particularly, the impact of HC is obvious when 303 comparing HC/SPC/O<sub>3</sub> and SPC/O<sub>3</sub> (Fig. 2), whereat 99.34 and 56.02% of 1,4-dioxane was degraded in 304 120 min and k values were  $4.04 \times 10^{-2}$  and  $6.60 \times 10^{-3}$  min<sup>-1</sup>, respectively. The outlet concentration of O<sub>3</sub> 305 306 during HC/SPC/O<sub>3</sub> was determined as 0.135 g h<sup>-1</sup>, while it was 0.384 g h<sup>-1</sup> for SPC/O<sub>3</sub>, confirming the enhanced utilization efficiency of  $O_3$  due to the effect of HC. 307





Although, an increase of inlet O<sub>3</sub> dosage increases the partial pressure of O<sub>3</sub> in gas phase and, thus, improves the O<sub>3</sub> mass transfer [54], the increase of O<sub>3</sub> dosage to 0.94 g h<sup>-1</sup> decreased the degradation efficiency to 97.12% resulting in the decrease of *k* from  $4.04 \times 10^{-2}$  to  $2.82 \times 10^{-2}$  min<sup>-1</sup>. Such effect can be ascribed to the scavenging effect of high O<sub>3</sub> dosage, whereat a considerable amount of O<sub>3</sub> was disintegrated to the consumption HO<sup>•</sup> radicals by dissolved O<sub>3</sub> as described in **Eq. 20** [57]:

$$\mathrm{HO}^{\bullet} + \mathrm{O}_3 \to \mathrm{HO}_2^{\bullet} + \mathrm{O}_2 \tag{20}$$

**Table 4**. Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O<sub>3</sub> at  $r_{ox}$  8 and different O<sub>3</sub> dosage.

	O <sub>3</sub> dosage, g h <sup>-1</sup>						
	0.23	0.40	0.74	0.86	0.94		
$k \times 10^{-2}, \min^{-1}$	0.411	0.740	1.873	4.041	2.815		
$\mathbb{R}^2$	0.984	0.980	0.986	0.992	0.961		

316

To evaluate the improving effect of O<sub>3</sub> on HC/SPC, the degradation of 1,4-dioxane in HC/SPC/O<sub>3</sub> was conducted with fixed dosage of O<sub>3</sub> at 0.86 g h<sup>-1</sup> and varying SPC  $r_{ox}$  in the range of 1-10. As shown in **Fig. 6a**, the degradation efficiency of 1,4-dioxane at  $r_{ox}$  1, 3, 5, 8 and 10 were improved from 18.34, 22.11, 27.52, 37.15% and 31.94% to 82.36, 85.58, 93.89, 99.34 and 96.18%, respectively. The improvement effect of O<sub>3</sub> addition was the highest at  $r_{ox}$  8, which is clearly observed in **Table 5**. The degradation rate of 1,4-dioxane was improved from  $3.73 \times 10^{-3}$  to  $4.04 \times 10^{-2}$  min<sup>-1</sup> at  $r_{ox}$  8, whereas the corresponding *k* was increased from  $3.20 \times 10^{-3}$  to  $2.56 \times 10^{-2}$  min<sup>-1</sup> at  $r_{ox}$  10. These findings show that the



327 dioxane.



335

328

Figure 6. Effect of fixed O<sub>3</sub> dosage on the degradation 1,4-D in HC/SPC/O<sub>3</sub> with various SPC  $r_{ox}$ : (a) degradation efficiency, (b) pseudo-first-order kinetic plots ([1,4-D]<sub>0</sub> 100 ppm, C<sub>v</sub> 0.27, [O<sub>3</sub>] 0.86 g h<sup>-1</sup>, pH<sub>0</sub> 5, 20±2 °C.

**Table 5.** Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O<sub>3</sub> at 0.86 g h<sup>-1</sup> O<sub>3</sub> dosage and different  $r_{ox}$ .

	$r_{\rm ox}$ 1	$r_{\rm ox} 3$	$r_{\rm ox} 5$	$r_{\rm ox} 8$	<i>r</i> <sub>ox</sub> 10	
$k \times 10^{-2}, \min^{-1}$	1.401	1.524	2.242	4.041	2.563	
$\mathbb{R}^2$	0.979	0.984	0.956	0.992	0.963	

#### 336 3.5 Effect of initial pH

The solution pH is an important parameter, which significantly affect the production of reactive species and, hence, the overall performance of HC/SPC/O<sub>3</sub> for the degradation of 1,4-dioxane. The effect of pH also determines the oxidation potential of generated radical species, interaction between SPC and O<sub>3</sub> and the state of the pollutant and oxidants in treated media. **Fig 7a** illustrates the effect of initial pH in the range of 3-12 on the degradation of 1.4-dioxane in HC/SPC/O<sub>3</sub> process.





Figure 7. Effect of pH<sub>0</sub> on the degradation 1,4-D in HC/SPC/O<sub>3</sub>: (a) degradation efficiency, (b) pseudofirst-order kinetic plots ([1,4-D]<sub>0</sub> 100 ppm, C<sub>v</sub> 0.27, SPC  $r_{ox}$  8, [O<sub>3</sub>] 0.86 g h<sup>-1</sup>, 20±2 °C).

346 According to Fig. 7a, the highest degradation efficiency was reached at  $pH_0$  5 (non-adjusted), while  $pH_0$ 3, 7, 10 and 12 were detrimental. Among the tested pH values, the inhibitory effect of  $pH_0$  3 was the 347 348 highest resulting in 90.49% of 1,4-dioxane degradation within 120 min. This is attributed to the lower 349 decomposition rate of  $O_3$  at acidic conditions, so the direct oxidation of 1,4-dioxane by molecular  $O_3$  is 350 predominant at  $pH_0$  3. Since  $O_3$  possess lower redox potential than HO' radicals, the direct oxidation proceeded slowly resulting in the k value of  $2.09 \times 10^{-2} \text{ min}^{-1}$  (**Table 6**). In contrast, the rate constant of 351 1.4-dioxane degradation was markedly increased to  $4.04 \times 10^{-2}$  min<sup>-1</sup> at pH<sub>0</sub> 5, indicating high 352 concentration of generated radical species. This can be ascribed to the radical route of 1,4-dioxane 353 354 degradation via indirect O<sub>3</sub> oxidation and additional supply of HO<sup>•</sup> radicals due to the patrial dissociation 355 of  $H_2O_2$ . The latter is initiated by the transformation of  $H_2O_2$  to yield  $HO_2^-$  (Eq. 11), which further react with O<sub>3</sub> as illustrated in Eqs. 21-23 [58]. The detrimental effect of  $pH_0 < 5$  coincides with the pH change 356 357 depicted in **Fig. 8**. Particularly, the degradation efficiency of 1,4-dioxane in HC/SPC/O<sub>3</sub> at  $pH_0$  3 was markedly enhanced from 6.92 to 46.47% when the pH was increased from 3 to 6 after 45 min of 358 treatment. 359

360

- $\mathrm{HO}_2^- + \mathrm{O}_3 \to \mathrm{HO}_5^- \tag{21}$
- $HO_5^- \to HO_2^\bullet + O_3^- \tag{22}$
- 362  $O_3^- + H_2 O \to O_2 + HO^{\bullet} + HO^-$  (23)

364	Table 6.	Kinetic	parameters	of 1,4	-dioxane	degradati	on ir	n HC/SP	$C/O_3$ at	different	$pH_0$
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	pH <sub>0</sub> 3	$pH_0 5$	$pH_0 7$	pH <sub>0</sub> 10	pH <sub>0</sub> 12	
$k \times 10^{-2}, \min^{-1}$	2.091	4.041	2.471	2.084	2.047	
$\mathbb{R}^2$	0.968	0.992	0.993	0.977	0.968	

365

Although alkaline pH promotes the decomposition of  $O_3$ , the degradation efficiency of 1,4-dioxane in HC/SPC/O<sub>3</sub> at pH<sub>0</sub> 10 and 12 was slightly decreased to 92.76 and 91.78%, respectively. Such trend can be interpreted with an excessive production of HO<sub>2</sub><sup>-</sup> (**Eq. 10**), which act as a scavenger of HO<sup>•</sup> radicals (**Eq. 24**) [50,54,58].



370

Figure 8. The map of pH change throughout the degradation 1,4-D in HC/SPC/O<sub>3</sub> at various pH<sub>0</sub> ([1,4-D]<sub>0</sub> 100 ppm, C<sub>v</sub> 0.27, SPC  $r_{ox}$  8, [O<sub>3</sub>] 0.86 g h<sup>-1</sup>, 20±2 °C).

373 3.6 Identification of reactive species in HC/SPC/O<sub>3</sub>

374 Beside HO' radicals,  $O_2^{-}$  and  $CO_3^{-}$  radicals could be generated in HC/SPC/O<sub>3</sub> 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  $(NaN_3)$  were utilized as 378 scavenging agents. The molar ratio of scavenger to SPC was set as 10:1 to ensure the effective quenching of radicals. IPA rapidly reacts with HO<sup>•</sup> radicals  $(3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$  and slowly responds to CO<sub>3</sub><sup>•-</sup> and O<sub>2</sub><sup>•-</sup> 379 radicals, with a rate constant of  $4.0 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> and  $1.0 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>, respectively [59,60]. Additionally, 380 381 the reaction of HO<sup>•</sup> radicals with IPA proceeds faster than with 1,4-dioxane  $(2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ , H<sub>2</sub>O<sub>2</sub> (2.7

 $\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ), HCO<sub>3</sub><sup>-</sup> (8.5  $\times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) and CO<sub>3</sub><sup>2-</sup> (3.9  $\times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) [61–63], hence, IPA was selected to 382 study the existence of HO' radicals. On the other hand, PhOH was used to confirm the occurrence of O<sub>2</sub>. 383 radicals as PhOH preferentially reacts with HO<sup>•</sup> ( $6 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>) and CO<sub>3</sub><sup>•-</sup> ( $1.2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>) radicals 384 [60,64]. Additionally, the impact of  $O_2^{-}$  radicals was explored using p-BQ and CLF, which rapidly react 385 with a second-order rate constant of  $9.6 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> and  $3.9 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>, respectively [39,59,65]. As 386 387 observed from Fig. 9a, the degradation efficiency of 1,4-dioxane was declined from 99.34 to 26.71% after 120 min and the corresponding rate constants were decreased from  $4.04 \times 10^{-2}$  to  $2.58 \times 10^{-3}$  min<sup>-1</sup> 388 (Table 7) in the presence of IPA. This illustrates the predominant role of HO<sup>•</sup> radicals. The degradation 389 390 efficiency of 1,4-dioxane was inhibited to 13.52% in 120 min with addition of PhOH, suggesting the 391 contribution of  $O_2$  radicals in 1,4-dioxane degradation. Based on these it can be proposed that for 392 HC/SPC/O<sub>3</sub> highest contribution to degradation had HO<sup>•</sup> radicals, with moderate role of CO<sub>3</sub><sup>•</sup> and minor 393 role of  $O_2$ . 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 O<sub>2</sub><sup>-</sup> 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, 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  $O_2^{-}$ 399 radicals (5.8  $\times$  10<sup>2</sup> M<sup>-1</sup> s<sup>-1</sup>), scavenging of HO<sup>•</sup> radicals prohibits the regeneration of O<sub>2</sub><sup>•-</sup> radicals through Eq. 17. In light of this "doubled" scavenging effect of PhOH it is confirmed that  $O_2$  contributed to the 400 401 degradation effect.

In the case of *p*-BQ and CLF, available (not scavenged so fast) HO<sup>•</sup> radicals promoted the continuous regeneration of  $O_2^{-*}$  radicals (**Eq. 17**). Interestingly, the inhibitory effect of hydrophobic and more volatile CLF (which tends to move into the cavitation bubble - a place in the system that is less polar than water and preferred by volatile compounds) was lower than *p*-BQ implying that the formation of  $O_2^{-*}$  radicals proceeds mainly in bulk liquid phase. Subsequent oxidation of  $O_2^{-*}$  radicals by HO<sup>•</sup> and HO<sub>2</sub><sup>•</sup> radicals can lead to the generation of singlet oxygen (<sup>1</sup>O<sub>2</sub>) species through the following reactions [66]:

408

$$0_2^{\bullet-} + H0^{\bullet} \to {}^10_2 + H0^{-}$$
 (25)

409 
$$0_2^{\bullet-} + H0_2^{\bullet} + H^+ \to {}^10_2 + H_20_2$$
 (26)

To elucidate the formation of  ${}^{1}O_{2}$  species, NaN<sub>3</sub> was added to quench  ${}^{1}O_{2}$  with a rate constant of  $1 \times 10^{9}$ 410 411  $M^{-1}$  s<sup>-1</sup> [67]. Quenching experiments using NaN<sub>3</sub> inhibited the degradation efficiency of 1,4-dioxane by 5.03%, whereat the corresponding degradation rate constant was decreased from  $4.04 \times 10^{-2}$  to  $2.29 \times 10^{-2}$ 412 min<sup>-1</sup>. These observations suggest a negligible contribution of  ${}^{1}O_{2}$  in the degradation of 1,4-dioxane by 413 414 HC/SPC/O<sub>3</sub>. 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<sub>3</sub>, as scavengers may interrupt radical chain reactions of 417  $O_3$  decomposition and consume  $O_3$  [68,69].



418

Figure 9. Effect of scavengers on the degradation 1,4-D in HC/SPC/O<sub>3</sub>: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ([1,4-D]<sub>0</sub> 100 ppm, C<sub>v</sub> 0.27, SPC  $r_{ox}$  8, [O<sub>3</sub>] 0.86 g h<sup>-1</sup>, [SPC]:[Scavenger] = 1:10, 20±2 °C).

**Table 7**. Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O<sub>3</sub> in the presence of scavengers.

	Type of scavenger							
	IPA	PhOH	p-BQ	CLF	NaN <sub>3</sub>			
$k \times 10^{-2}, \min^{-1}$	0.258	0.124	0.539	1.023	2.294			
<b>R</b> <sup>2</sup>	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<sub>3</sub>

Inorganic anions such as Cl<sup>-</sup>,  $NO_3^{-}$  and  $SO_4^{2-}$  are inherently present in natural water [70,71] and might affect the performance of HC/SPC/O<sub>3</sub>. Since the practical implementation of HC/SPC/O<sub>3</sub> assumes the treatment of contaminated natural water, the study of the effect of inorganic anions is required. To

evaluate the effect of inorganic anions, the degradation of 1,4-dioxane in HC/SPC/O<sub>3</sub> was conducted in 428 the presence of  $Cl^{-}$ ,  $NO_{3}^{-}$  and  $SO_{4}^{2-}$ , whereat the molar ratio of anion to SPC was 10:1. As shown, in **Fig.** 429 10a, the presence of Cl<sup>-</sup> anions resulted in a slight inhibitory effect decreasing the degradation efficiency 430 of 1,4-dioxane from 99.34 to 95.74% within 120 min. The inhibition effect of Cl<sup>-</sup> anions is commonly 431 432 ascribed to the formation chlorine species (i.e., Cl<sup> $\cdot$ </sup> and Cl<sub>2</sub><sup> $\cdot$ </sup>) through the passage of reactions consuming 433 of HO<sup>•</sup> radicals as shown in Eqs. 27-29. However, the reaction of Cl<sup>-</sup> anions with HO<sup>•</sup> radicals is 434 negligible at circumneutral conditions due to the fast reverse reaction [72]. In this study, the inhibitory effect of Cl<sup>-</sup> anions can be explained due to the interaction of Cl<sup>-</sup> anions with O<sub>3</sub>, which become relevant 435 at high Cl<sup>-</sup> concentration. Such interaction competes with H<sub>2</sub>O<sub>2</sub> for O<sub>3</sub> consumption and lead to the 436 437 formation of hypochlorite which exist in equilibrium with HClO (Eqs. 30, 31) and is not oxidized by O<sub>3</sub> [72–74]. The inhibitory effect of 1,4-dioxane degradation in HC/SPC/O<sub>3</sub> found to be more deteriorate 438 with addition of  $NO_3^-$  and  $SO_4^{2-}$  anions. Thus, the presence of  $NO_3^-$  and  $SO_4^{2-}$  anions declined the 439 degradation efficiency of HC/SPC/O<sub>3</sub> towards 1,4-dioxane by 7.51 and 12.28% in 120 min, respectively. 440 Although, sulfate radicals (SO<sub>4</sub><sup>•</sup>) formed via Eq. 32 [75], exhibit relatively high oxidation potential and 441 selectivity towards electron-rich moieties, the presence of precursor SO<sub>4</sub><sup>2-</sup> anions showed the highest 442 443 inhibitory effect. This phenomenon can be referred to the decrease of the reduction potential of SO4. radicals caused by the high concentration of  $SO_4^{2-}$  anions [39]. As depicted in **Table 8**, the degradation 444 rate constant of 1,4-dioxane in presence of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions in comparison with the process 445 without additives was decreased from  $4.04 \times 10^{-2}$  to  $2.50 \times 10^{-2}$ ,  $2.01 \times 10^{-2}$  and  $1.68 \times 10^{-2}$  min<sup>-1</sup>, 446 447 respectively. In this study, the inhibitory effect of anions towards the degradation of 1,4-dioxane was in the following order:  $SO_4^{2-} > NO_3^{-} > Cl^{-}$ . 448

454

$$Cl^- + HO^{\bullet} \to HOCl^{\bullet-}$$
(27)

$$HOCl^{\bullet-} + H^+ \to Cl^{\bullet} + H_2O$$
(28)

451 
$$\operatorname{Cl}^{\bullet} + \operatorname{Cl}^{-} \to \operatorname{Cl}_{2}^{\bullet-}$$
 (29)

$$Cl^{-} + 0_3 \to OCl^{-} + 0_2$$
 (30)

453 
$$OCI^- \leftrightarrow HOCl \qquad pK_a \ 7.5$$
 (31)

 $\mathrm{SO}_4^{2-} + \mathrm{HO}^{\bullet} \to \mathrm{SO}_4^{\bullet-} + \mathrm{HO}^{-} \tag{32}$ 



456 **Figure 10.** Effect of anions on the degradation 1,4-D in HC/SPC/O<sub>3</sub>: (a) degradation efficiency, (b) 457 pseudo-first-order kinetic plots ([1,4-D]<sub>0</sub> 100 ppm, C<sub>v</sub> 0.27, SPC  $r_{ox}$  8, [O<sub>3</sub>] 0.86 g h<sup>-1</sup>, [SPC]:[Anion] = 458 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/O<sub>3</sub> in the presence of anions.

		Type of anio	n
	Cl-	NO <sub>3</sub> -	SO4 <sup>2-</sup>
$k \times 10^{-2}, \min^{-1}$	2.497	2.009	1.681
<b>R</b> <sup>2</sup>	0.972	0.972	0.973

464

#### 465 3.8 Degradation pathway of 1,4-dioxane in HC/SPC/O<sub>3</sub>

466 Highly reactive and non-selective behavior of radical species induces a broad variety of structural 467 transformations to the target pollutant. These transformations can lead to the formation of by-products, 468 which present toxicity higher than the parent compound. To better understand the transformation 469 mechanism of 1,4-dioxane under HC/SPC/O<sub>3</sub>, the intermediates present in treated samples were identified 470 and analyzed by GC-MS using SCAN mode. In order to detect minor intermediates and, thus propose an 471 accurate pathway of 1,4-dioxane degradation in HC/SPC/O<sub>3</sub>, an initial concentration of 1000 ppm was 472 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  $HC/SPC/O_3$  and the proposed





475 476

477

Figure 11. The proposed degradation pathway of 1,4-dioxane in HC/SPC/O<sub>3</sub>.

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 peroxyl radicals, which are further transformed into  $\alpha$ -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  $\alpha$ -oxyl radical via  $\Delta$ C-C splitting at 483 the  $\alpha$ -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  $CO_2$  and  $H_2O$ . TOC analysis of the samples showed up to 95% of TOC removal confirming the mineralization of 1,4-dioxane (Fig. S2). Since, EDGF was found as the main by-487 product of 1,4-dioxane degradation, the mechanism pathway of  $\Delta$ C-C splitting was predominant in 488 HC/SPC/O<sub>3</sub>. This result is consistent with the radical-type mechanism of 1,4-dioxane degradation 489 previously described for other AOPs. 490

491

493 Assessment of the economic feasibility of HC/SPC/O<sub>3</sub> 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

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

498 , where  $P_{el}$  is electric power (kW), t – time of treatment (min), V – volume of the treated solution (L), C<sub>0</sub> 499 and C<sub>t</sub> are the initial and final concentration of the pollutant. Since log (C<sub>0</sub>/C<sub>t</sub>) = *k*t, the equation can be 500 written as follows:

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

The parameter  $E_{EO}$  (kWh m<sup>-3</sup>order<sup>-1</sup>) describes the amount of energy required to degrade 90% of pollutant 502 503 in 1 m<sup>3</sup> of the contaminated liquid. The calculations were conducted considering the power of HC system 504 and  $O_3$  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/O<sub>3</sub> pH10, HC/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>, HC/SPC/O<sub>3</sub> were 222.97, 165.89 and 102.65 kWh m<sup>-</sup> 506 <sup>3</sup>order<sup>-1</sup>, respectively (**Table 9**). The adaptation of SPC in  $HC/SPC/O_3$  decreased the energy consumption 507 by 117 and 62% as compared to  $HC/O_3$  pH10 and  $HC/H_2O_2/O_3$ , respectively. This is attributed the higher 508 degradation efficiency of HC/SPC/O<sub>3</sub>, which allowed to shorten the treatment time of 1.4-dioxane and, 509 thereby decreased the energy consumption by HC pump and  $O_3$  generator. Owing to cheaper industrial price,  $H_2O_2$  constituted only 0.8% of HC/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> cost, while SPC accounted 6.4% of the total cost in 510 HC/SPC/O<sub>3</sub>. However, the higher effectiveness of HC/SPC/O<sub>3</sub> provided a reduction of the total treatment 511 512 cost by 52% as compared to  $HC/H_2O_2/O_3$ .

513 In general, the ranges of E<sub>EO</sub> 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<sup>-3</sup>, 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<sup>-3</sup> 517 [10,11] (details of calculations are provided in **Supplementary data**). However, these values have only 518 theoretically meaning as they were calculated using the theoretical energy required for O<sub>3</sub> 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.

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

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

Process	<i>k</i> , min <sup>-1</sup>	E <sub>EO</sub> , kWh m <sup>-3</sup> order <sup>-1</sup>	Cost of energy <sup>*</sup> ,	Amount of oxidant, kg	Cost of oxidant <sup>**</sup> ,	Total cost,	Efficiency, %
			USD		USD	USD	
HC/O <sub>3</sub> 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 <sub>3</sub>	0.0404	102.65	11.29	1.413	0.78	12.07	99.34

<sup>\*</sup>The cost of energy was estimated based on the average electricity cost for industrial customers in Poland

529 - 0.11 USD/kWh.

531 **4.** Conclusions

532 HC/SPC/O<sub>3</sub> 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  $4.04 \times 10^{-2}$  min<sup>-1</sup>. Compared to traditional peroxone process, HC/SPC/O<sub>3</sub> required 534 relatively lower dosages of SPC ( $r_{ox}$  8) and O<sub>3</sub> (0.86 g h<sup>-1</sup>), which is promising for practical implementation in terms of economical feasibility. Concentrations of SPC and O<sub>3</sub> above/below the 535 optimal dosage were found detrimental due to the scavenging of radical species. The presence of  $CO_3^{2-}$  in 536 537  $HC/SPC/O_3$  enabled the promotion of  $O_3$  decomposition through the increase of pH and participated in 538 radical chain reactions to provide more reactive species. HO' radicals were determined as predominant radical species in HC/SPC/O<sub>3</sub> according to the quenching experiments, which proposed the contribution 539 of reactive species in 1,4-dioxane degradation in order of HO' >  $CO_3$  · >  $O_2$  ·. The studied co-existing 540 541 inorganic anions suppressed the effectiveness of HC/SPC/O<sub>3</sub>, whereat the inhibitory effect of SO<sub>4</sub><sup>2-</sup> anions was higher than that of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> anions. The products of 1,4-dioxane degradation in HC/SPC/O<sub>3</sub> were 542 detected using GC-MS and the degradation pathway was proposed. The oxidation pathway included 543 544 several transformation steps with formation of ethylene glycol diformate, which is consistent with radical

<sup>&</sup>lt;sup>\*\*</sup> The cost of industrial grade  $H_2O_2$  and SPC were assumed as 500, 550 USD/ton, respectively [84,85].

- 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  $H_2O_2$  under HC.

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- 550 References
- 551 [1] M.J. Zenker, R.C. Borden, M.A. Barlaz, Occurrence and Treatment of 1,4-Dioxane in Aqueous
  552 Environments, Environ. Eng. Sci. 20 (2003) 423–432. doi:10.1089/109287503768335913.
- A. Abe, Distribution of 1,4-dioxane in relation to possible sources in the water environment, Sci.
  Total Environ. 227 (1999) 41–47. doi:10.1016/S0048-9697(99)00003-0.
- 555 [3] A. Yasuhara, Chemical components in leachates from hazardous wastes landfills in Japan,

556 Toxicol. Environ. Chem. 51 (1995) 113–120. doi:10.1080/02772249509358229.

557 [4] C.A. Act, R. Act, R. Act, Environmental protection agency (EPA), Rep. Carcinog. 168 (2006).

558 [5] H. Barndők, L. Blanco, D. Hermosilla, Á. Blanco, Heterogeneous photo-Fenton processes using

zero valent iron microspheres for the treatment of wastewaters contaminated with 1,4-dioxane,

560 Chem. Eng. J. 284 (2016) 112–121. doi:10.1016/J.CEJ.2015.08.097.

- 561 [6] C.D. Adams, P.A. Scanlan, N.D. Secrist, Oxidation and biodegradability enhancement of 1, 4562 dioxane using hydrogen peroxide and ozone, Environ. Sci. Technol. 28 (1994) 1812–1818.
- 563 [7] H. Barndők, D. Hermosilla, C. Negro, Á. Blanco, Comparison and Predesign Cost Assessment of
- 564 Different Advanced Oxidation Processes for the Treatment of 1,4-Dioxane-Containing
- 565 Wastewater from the Chemical Industry, ACS Sustain. Chem. Eng. 6 (2018) 5888–5894.

566 doi:10.1021/acssuschemeng.7b04234.

- 567 [8] M.P. Rayaroth, D. Oh, C.S. Lee, Y.G. Kang, Y.S. Chang, In situ chemical oxidation of
  568 contaminated groundwater using a sulfidized nanoscale zerovalent iron-persulfate system:
- Insights from a box-type study, Chemosphere. 257 (2020) 127117.
- 570 doi:10.1016/j.chemosphere.2020.127117.
- 571 [9] S. Sonawane, K. Fedorov, M.P. Rayaroth, G. Boczkaj, Degradation of 1,4-dioxane by sono572 activated persulfates for water and wastewater treatment applications, Water Resour. Ind. 28
  573 (2022) 100183. doi:10.1016/J.WRI.2022.100183.
- 574 [10] W. Shen, Y. Wang, J. Zhan, B. Wang, J. Huang, S. Deng, G. Yu, Kinetics and operational

- parameters for 1,4-dioxane degradation by the photoelectro-peroxone process, Chem. Eng. J. 310
  (2017) 249–258. doi:10.1016/J.CEJ.2016.10.111.
- 577 [11] H. Wang, B. Bakheet, S. Yuan, X. Li, G. Yu, S. Murayama, Y. Wang, Kinetics and energy
- efficiency for the degradation of 1,4-dioxane by electro-peroxone process, J. Hazard. Mater. 294
  (2015) 90–98. doi:10.1016/j.jhazmat.2015.03.058.
- 580 [12] M.P. Rayaroth, C.T. Aravindakumar, N.S. Shah, G. Boczkaj, Advanced oxidation processes
- (AOPs) based wastewater treatment unexpected nitration side reactions a serious environmental
  issue: A review, Chem. Eng. J. 430 (2022) 133002. doi:10.1016/J.CEJ.2021.133002.
- 583 [13] N. Takahashi, T. Hibino, H. Torii, S. Shibata, S. Tasaka, J. Yoneya, M. Matsuda, H. Ogasawara,
- 584 K. Sugimoto, T. Fujioka, Evaluation of O3/UV and O3/H2O2 as Practical Advanced Oxidation
- 585 Processes for Degradation of 1,4-Dioxane, Ozone Sci. Eng. 35 (2013) 331–337.
- 586 doi:10.1080/01919512.2013.795851.
- [14] M. Abdi, M. Balagabri, H. Karimi, H. Hossini, S.O. Rastegar, Degradation of crystal violet (CV)
  from aqueous solutions using ozone, peroxone, electroperoxone, and electrolysis processes: a
  comparison study, Appl. Water Sci. 10 (2020) 168. doi:10.1007/s13201-020-01252-w.
- 590 [15] H. Chen, J. Wang, Degradation and mineralization of ofloxacin by ozonation and peroxone
- 591 (O3/H2O2) process, Chemosphere. 269 (2020) 128775. doi:10.1016/j.chemosphere.2020.128775.
- 592 [16] I. Epold, N. Dulova, Y. Veressinina, M. Trapido, Application of Ozonation, UV Photolysis,
- 593 Fenton Treatment and other Related Processes for Degradation of Ibuprofen and
- 594 Sulfamethoxazole in Different Aqueous Matrices, J. Adv. Oxid. Technol. 15 (2012) 354–364.

595 doi:doi:10.1515/jaots-2012-0215.

- 596 [17] M. Gągol, A. Przyjazny, G. Boczkaj, Highly effective degradation of selected groups of organic
  597 compounds by cavitation based AOPs under basic pH conditions, Ultrason. Sonochem. 45 (2018)
  598 257–266. doi:10.1016/j.ultsonch.2018.03.013.
- 599 [18] G. Boczkaj, A. Fernandes, P. Makoś, Study of Different Advanced Oxidation Processes for
  600 Wastewater Treatment from Petroleum Bitumen Production at Basic pH, Ind. Eng. Chem. Res.
  601 (2017). doi:10.1021/acs.iecr.7b01507.
- 602 [19] G. Boczkaj, A. Fernandes, Wastewater treatment by means of advanced oxidation processes at
  603 basic pH conditions: A review, Chem. Eng. J. 320 (2017) 608–633.

- 604 doi:10.1016/J.CEJ.2017.03.084.
- [20] X. Liu, S. He, Y. Yang, B. Yao, Y. Tang, L. Luo, D. Zhi, Z. Wan, L. Wang, Y. Zhou, A review on
   percarbonate-based advanced oxidation processes for remediation of organic compounds in water,
- 607 Environ. Res. 200 (2021) 111371. doi:10.1016/J.ENVRES.2021.111371.
- 608 [21] A. Eslami, F. Mehdipour, K.Y.A. Lin, H. Sharifi Maleksari, F. Mirzaei, F. Ghanbari, Sono-photo
  609 activation of percarbonate for the degradation of organic dye: The effect of water matrix and
- 610 identification of by-products, J. Water Process Eng. 33 (2020) 100998.
- 611 doi:10.1016/J.JWPE.2019.100998.
- 612 [22] X. Ling, J. Deng, C. Ye, A. Cai, S. Ruan, M. Chen, X. Li, Fe(II)-activated sodium percarbonate
- for improving sludge dewaterability: Experimental and theoretical investigation combined with the
- evaluation of subsequent utilization, Sci. Total Environ. 799 (2021) 149382.
- 615 doi:10.1016/J.SCITOTENV.2021.149382.
- 616 [23] Z. Miao, X. Gu, S. Lu, X. Zang, X. Wu, M. Xu, L.B.B. Ndong, Z. Qiu, Q. Sui, G.Y. Fu,
- 617 Perchloroethylene (PCE) oxidation by percarbonate in Fe2+-catalyzed aqueous solution: PCE
- 618 performance and its removal mechanism, Chemosphere. 119 (2015) 1120–1125.
- 619 doi:10.1016/J.CHEMOSPHERE.2014.09.065.
- 620 [24] X. Zang, X. Gu, S. Lu, Z. Miao, X. Zhang, X. Fu, G.Y. Fu, Z. Qiu, Q. Sui, Enhanced degradation
- 621 of trichloroethene by sodium percarbonate activated with Fe(II) in the presence of citric acid,
- 622 Water Supply. 17 (2016) 665–673. doi:10.2166/ws.2016.117.
- [25] U. Farooq, M. Danish, S. Lu, M.L. Brusseau, M. Naqvi, X. Fu, X. Zhang, Q. Sui, Z. Qiu, Efficient
  transformation in characteristics of cations supported-reduced graphene oxide nanocomposites for
  the destruction of trichloroethane, Appl. Catal. A Gen. 544 (2017) 10–20.
- 626 doi:10.1016/J.APCATA.2017.07.007.
- [26] D. Li, Y. Xiao, M. Pu, J. Zan, S. Zuo, H. Xu, D. Xia, A metal-free protonated g-C3N4 as an
  effective sodium percarbonate activator at ambient pH conditions: Efficiency, stability and
  mechanism, Mater. Chem. Phys. 231 (2019) 225–232.
- 630 doi:10.1016/J.MATCHEMPHYS.2019.04.016.
- [27] M. Danish, X. Gu, S. Lu, U. Farooq, W.Q. Zaman, X. Fu, Z. Miao, M.L. Brusseau, A. Ahmad, M.
  Naqvi, An efficient catalytic degradation of trichloroethene in a percarbonate system catalyzed by

- 633 ultra-fine heterogeneous zeolite supported zero valent iron-nickel bimetallic composite, Appl.
- 634 Catal. A Gen. 531 (2017) 177–186. doi:10.1016/J.APCATA.2016.11.001.
- 635 [28] L. Li, J. Huang, X. Hu, S. Zhang, Q. Dai, H. Chai, L. Gu, Activation of sodium percarbonate by
- 636 vanadium for the degradation of aniline in water: Mechanism and identification of reactive
- 637 species, Chemosphere. 215 (2019) 647–656. doi:10.1016/J.CHEMOSPHERE.2018.10.047.
- 638 [29] J. Rivas, O. Gimeno, T. Borralho, F. Beltrán, Influence of oxygen and free radicals promoters on
- the UV-254 nm photolysis of diclofenac, Chem. Eng. J. 163 (2010) 35–40.
- 640 doi:10.1016/J.CEJ.2010.07.027.
- 641 [30] V. Shafirovich, A. Dourandin, W. Huang, N.E. Geacintov, The Carbonate Radical Is a Site642 selective Oxidizing Agent of Guanine in Double-stranded Oligonucleotides \*, J. Biol. Chem. 276
- 643 (2001) 24621–24626. doi:10.1074/jbc.M101131200.
- J.S. Moore, G.O. Phillips, A. Sosnowski, Reaction of carbonate radical anion with substituted
  phenols, Int. J. Radiat. Biol. 31 (1977) 605.
- 646 [32] J.P. Huang, S.A. Mabury, A new method for measuring carbonate radical reactivity toward
  647 pesticides, Environ. Toxicol. Chem. 19 (2000) 1507.
- 648 [33] M.P. Rayaroth, U.K. Aravind, C.T. Aravindakumar, Effect of inorganic ions on the ultrasound
  649 initiated degradation and product formation of triphenylmethane dyes, Ultrason. Sonochem. 48
  650 (2018) 482–491. doi:10.1016/j.ultsonch.2018.07.009.
- 651 [34] S. Canonica, T. Kohn, M. Mac, F.J. Real, J. Wirz, U. von Gunten, Photosensitizer Method to
  652 Determine Rate Constants for the Reaction of Carbonate Radical with Organic Compounds,
- 653 Environ. Sci. Technol. 39 (2005) 9182–9188. doi:10.1021/es051236b.
- [35] B.C. Hodges, E.L. Cates, J.-H. Kim, Challenges and prospects of advanced oxidation water
  treatment processes using catalytic nanomaterials, Nat. Nanotechnol. 13 (2018) 642–650.
  doi:10.1038/s41565-018-0216-x.
- [36] K. Fedorov, K. Dinesh, X. Sun, R. Darvishi Cheshmeh Soltani, Z. Wang, S. Sonawane, G.
  Boczkaj, Synergistic effects of hybrid advanced oxidation processes (AOPs) based on
  hydrodynamic cavitation phenomenon A review, Chem. Eng. J. 432 (2022) 134191.
  doi:10.1016/J.CEJ.2021.134191.
- 661 [37] E. Cako, R. Darvishi Cheshmeh Soltani, X. Sun, G. Boczkaj, Desulfurization of raw naphtha cuts

- 662 using hybrid systems based on acoustic cavitation and advanced oxidation processes (AOPs),
- 663 Chem. Eng. J. 439 (2022) 135354. doi:10.1016/J.CEJ.2022.135354.
- 664 [38] A.J. Barik, P.R. Gogate, Hybrid treatment strategies for 2,4,6-trichlorophenol degradation based
  665 on combination of hydrodynamic cavitation and AOPs, Ultrason. Sonochem. 40 (2018) 383–394.
- doi:10.1016/j.ultsonch.2017.07.029.
- 667 [39] K. Fedorov, X. Sun, G. Boczkaj, Combination of hydrodynamic cavitation and SR-AOPs for
  668 simultaneous degradation of BTEX in water, Chem. Eng. J. (2020).
- doi:10.1016/j.cej.2020.128081.
- [40] P.R. Gogate, G.S. Bhosale, Comparison of effectiveness of acoustic and hydrodynamic cavitation
  in combined treatment schemes for degradation of dye wastewaters, Chem. Eng. Process. Process
  [72] Intensif. 71 (2013) 59–69. doi:10.1016/j.cep.2013.03.001.
- 673 [41] M. Gągol, A. Przyjazny, G. Boczkaj, Effective method of treatment of industrial effluents under
- basic pH conditions using acoustic cavitation A comprehensive comparison with hydrodynamic
  cavitation processes, Chem. Eng. Process. Process Intensif. 128 (2018) 103–113.
- 676 doi:10.1016/J.CEP.2018.04.010.
- 677 [42] M. Dular, T. Griessler-Bulc, I. Gutierrez-Aguirre, E. Heath, T. Kosjek, A. Krivograd Klemenčič,
- 678 M. Oder, M. Petkovšek, N. Rački, M. Ravnikar, A. Šarc, B. Širok, M. Zupanc, M. Žitnik, B.
- 679 Kompare, Use of hydrodynamic cavitation in (waste)water treatment, Ultrason. Sonochem. 29

680 (2016) 577–588. doi:10.1016/J.ULTSONCH.2015.10.010.

- [43] P. Makoś, A. Fernandes, G. Boczkaj, Method for the simultaneous determination of monoaromatic
  and polycyclic aromatic hydrocarbons in industrial effluents using dispersive liquid–liquid
  microextraction with gas chromatography–mass spectrometry, J. Sep. Sci. 41 (2018) 2360–2367.
- 684 doi:10.1002/jssc.201701464.
- 685 [44] B. Wang, H. Su, B. Zhang, Hydrodynamic cavitation as a promising route for wastewater
  686 treatment A review, Chem. Eng. J. 412 (2021) 128685. doi:10.1016/J.CEJ.2021.128685.
- [45] M. Gągol, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation
  processes based on cavitation A review, Chem. Eng. J. 338 (2018) 599–627.
- 689 doi:10.1016/J.CEJ.2018.01.049.
- 690 [46] P.R. Gogate, A.B. Pandit, HYDRODYNAMIC CAVITATION REACTORS: A STATE OF THE

- 691 ART REVIEW, Rev. Chem. Eng. 17 (2001) 1–85. doi:10.1515/revce.2001.17.1.1.
- 692 [47] A. Mukherjee, A. Mullick, P. Vadthya, S. Moulik, A. Roy, Surfactant degradation using
- 693 hydrodynamic cavitation based hybrid advanced oxidation technology: A techno economic
- 694 feasibility study, Chem. Eng. J. 398 (2020) 125599. doi:10.1016/J.CEJ.2020.125599.
- 695 [48] G. Boczkaj, M. Gągol, M. Klein, A. Przyjazny, Effective method of treatment of effluents from
  696 production of bitumens under basic pH conditions using hydrodynamic cavitation aided by
- 697 external oxidants, Ultrason. Sonochem. 40 (2018) 969–979.
- 698 doi:10.1016/J.ULTSONCH.2017.08.032.
- [49] J.A.I. Pimentel, C. Di Dong, S. Garcia-Segura, R.R.M. Abarca, C.W. Chen, M.D.G. de Luna,
- 700 Degradation of tetracycline antibiotics by Fe2+-catalyzed percarbonate oxidation, Sci. Total

701 Environ. 781 (2021) 146411. doi:10.1016/J.SCITOTENV.2021.146411.

- 702 [50] C. Tan, Q. Xu, H. Zhang, Z. Liu, S. Ren, H. Li, Enhanced removal of coumarin by a novel
- 703 O3/SPC system: Kinetic and mechanism, Chemosphere. 219 (2019) 100–108.
- 704 doi:10.1016/J.CHEMOSPHERE.2018.11.194.
- [51] S.D. Patton, M.C. Dodd, H. Liu, Degradation of 1,4-dioxane by reactive species generated during
  breakpoint chlorination: Proposed mechanisms and implications for water treatment and reuse, J.
  Hazard. Mater. Lett. 3 (2022) 100054. doi:https://doi.org/10.1016/j.hazl.2022.100054.
- 708 [52] P. Neta, R.E. Huie, A.B. Ross, Rate Constants for Reactions of Inorganic Radicals in Aqueous
- 709 Solution, J. Phys. Chem. Ref. Data. 17 (1988) 1027–1284. doi:10.1063/1.555808.
- 710 [53] V. Maurino, P. Calza, C. Minero, E. Pelizzetti, M. Vincenti, Light-assisted 1,4-dioxane

711 degradation, Chemosphere. 35 (1997) 2675–2688. doi:https://doi.org/10.1016/S0045-

712 6535(97)00322-6.

- [54] X. Yu, M. Kamali, P. Van Aken, L. Appels, B. Van der Bruggen, R. Dewil, Synergistic effects of
  the combined use of ozone and sodium percarbonate for the oxidative degradation of dichlorvos, J.
  Water Process Eng. 39 (2021) 101721. doi:10.1016/J.JWPE.2020.101721.
- 716 [55] M. Gągol, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation
  717 processes based on cavitation A review, Chem. Eng. J. 338 (2018) 599–627.
- 718 doi:10.1016/j.cej.2018.01.049.
- 719 [56] G. Merényi, J. Lind, S. Naumov, C. von Sonntag, Reaction of Ozone with Hydrogen Peroxide

721 Quantum-Chemical Considerations, Environ. Sci. Technol. 44 (2010) 3505–3507. 722 doi:10.1021/es100277d. 723 [57] S. Tang, D. Yuan, Y. Rao, M. Li, G. Shi, J. Gu, T. Zhang, Percarbonate promoted antibiotic 724 decomposition in dielectric barrier discharge plasma, J. Hazard. Mater. 366 (2019) 669–676. 725 doi:10.1016/J.JHAZMAT.2018.12.056. H. Guo, D. Li, Z. Li, S. Lin, Y. Wang, S. Pan, J. Han, Promoted elimination of antibiotic 726 [58] 727 sulfamethoxazole in water using sodium percarbonate activated by ozone: Mechanism, degradation pathway and toxicity assessment, Sep. Purif. Technol. 266 (2021) 118543. 728 729 doi:10.1016/J.SEPPUR.2021.118543. 730 [59] P. Yan, Q. Sui, S. Lyu, H. Hao, H.F. Schröder, W. Gebhardt, Elucidation of the oxidation 731 mechanisms and pathways of sulfamethoxazole degradation under Fe(II) activated percarbonate 732 treatment, Sci. Total Environ. 640–641 (2018) 973–980. doi:10.1016/J.SCITOTENV.2018.05.315. Y. Xiao, X. Liu, Y. Huang, W. Kang, Z. Wang, H. Zheng, Roles of hydroxyl and carbonate 733 [60] 734 radicals in bisphenol a degradation via a nanoscale zero-valent iron/percarbonate system: 735 influencing factors and mechanisms, RSC Adv. 11 (2021) 3636-3644. doi:10.1039/D0RA08395J. 736 [61] M. Bagheri, M. Mohseni, Pilot-scale treatment of 1,4-dioxane contaminated waters using 185 nm radiation: Experimental and CFD modeling, J. Water Process Eng. 19 (2017) 185-192. 737 738 doi:https://doi.org/10.1016/j.jwpe.2017.06.015. 739 [62] G. Imoberdorf, M. Mohseni, Kinetic study and modeling of the vacuum-UV photoinduced degradation of 2,4-D, Chem. Eng. J. 187 (2012) 114-122. 740 doi:https://doi.org/10.1016/j.cej.2012.01.107. 741 J.C. Crittenden, S. Hu, D.W. Hand, S.A. Green, A kinetic model for H2O2/UV process in a 742 [63] 743 completely mixed batch reactor, Water Res. 33 (1999) 2315–2328. 744 doi:https://doi.org/10.1016/S0043-1354(98)00448-5. J. Gao, X. Duan, K. O'Shea, D.D. Dionysiou, Degradation and transformation of bisphenol A in 745 [64] UV/Sodium percarbonate: Dual role of carbonate radical anion, Water Res. 171 (2020) 115394. 746 747 doi:10.1016/J.WATRES.2019.115394. 748 A.L. Teel, R.J. Watts, Degradation of carbon tetrachloride by modified Fenton's reagent, J. [65]

(Peroxone Process): A Revision of Current Mechanistic Concepts Based on Thermokinetic and

720

749		Hazard. Mater. 94 (2002) 179–189. doi:10.1016/S0304-3894(02)00068-7.
750	[66]	Y. Nosaka, A.Y. Nosaka, Generation and Detection of Reactive Oxygen Species in Photocatalysis,
751		Chem. Rev. 117 (2017) 11302–11336. doi:10.1021/acs.chemrev.7b00161.
752	[67]	S. Zhu, X. Li, J. Kang, X. Duan, S. Wang, Persulfate Activation on Crystallographic Manganese
753		Oxides: Mechanism of Singlet Oxygen Evolution for Nonradical Selective Degradation of
754		Aqueous Contaminants, Environ. Sci. Technol. 53 (2019) 307-315. doi:10.1021/acs.est.8b04669.
755	[68]	Y. Guo, J. Long, J. Huang, G. Yu, Y. Wang, Can the commonly used quenching method really
756		evaluate the role of reactive oxygen species in pollutant abatement during catalytic ozonation?,
757		Water Res. 215 (2022) 118275. doi:https://doi.org/10.1016/j.watres.2022.118275.
758	[69]	Y. Wang, G. Yu, Challenges and pitfalls in the investigation of the catalytic ozonation mechanism:
759		A critical review, J. Hazard. Mater. 436 (2022) 129157.
760		doi:https://doi.org/10.1016/j.jhazmat.2022.129157.
761	[70]	J. Wang, S. Wang, Effect of inorganic anions on the performance of advanced oxidation processes
762		for degradation of organic contaminants, Chem. Eng. J. 411 (2021) 128392.
763		doi:10.1016/J.CEJ.2020.128392.
764	[71]	M.P. Rayaroth, U.K. Aravind, C.T. Aravindakumar, Effect of inorganic ions on the ultrasound
765		initiated degradation and product formation of triphenylmethane dyes, Ultrason. Sonochem. 48
766		(2018) 482-491. doi:10.1016/J.ULTSONCH.2018.07.009.
767	[72]	U. von Gunten, Ozonation of drinking water: Part II. Disinfection and by-product formation in
768		presence of bromide, iodide or chlorine, Water Res. 37 (2003) 1469–1487.
769		doi:https://doi.org/10.1016/S0043-1354(02)00458-X.
770	[73]	W.R. Haag, J. Hoigné, Ozonation of water containing chlorine or chloramines. Reaction products
771		and kinetics, Water Res. 17 (1983) 1397-1402. doi:https://doi.org/10.1016/0043-1354(83)90270-
772		1.
773	[74]	A. Asghar, H. V Lutze, J. Tuerk, T.C. Schmidt, Influence of water matrix on the degradation of
774		organic micropollutants by ozone based processes: A review on oxidant scavenging mechanism, J.
775		Hazard. Mater. 429 (2022) 128189. doi:https://doi.org/10.1016/j.jhazmat.2021.128189.
776	[75]	M. Khajeh, M.M. Amin, A. Fatehizadeh, T.M. Aminabhavi, Synergetic degradation of atenolol by
777		hydrodynamic cavitation coupled with sodium persulfate as zero-waste discharge process: Effect

- of coexisting anions, Chem. Eng. J. 416 (2021) 129163. doi:10.1016/J.CEJ.2021.129163.
- [76] M.I. Stefan, J.R. Bolton, Mechanism of the Degradation of 1,4-Dioxane in Dilute Aqueous
- Solution Using the UV/Hydrogen Peroxide Process, Environ. Sci. Technol. 32 (1998) 1588–1595.
  doi:10.1021/es970633m.
- 782 [77] H. Barndők, D. Hermosilla, C. Han, D.D. Dionysiou, C. Negro, Á. Blanco, Degradation of 1,4-
- 783dioxane from industrial wastewater by solar photocatalysis using immobilized NF-TiO2 composite
- with monodisperse TiO2 nanoparticles, Appl. Catal. B Environ. 180 (2016) 44–52.
- 785 doi:10.1016/J.APCATB.2015.06.015.
- [78] B. Li, J. Zhu, Simultaneous degradation of 1,1,1-trichloroethane and solvent stabilizer 1,4-dioxane
  by a sono-activated persulfate process, Chem. Eng. J. 284 (2016) 750–763.
- 788 doi:10.1016/j.cej.2015.08.153.
- 789 [79] E. Cako, Z. Wang, R. Castro-Muñoz, M.P. Rayaroth, G. Boczkaj, Cavitation based cleaner
- technologies for biodiesel production and processing of hydrocarbon streams: A perspective on
- key fundamentals, missing process data and economic feasibility A review, Ultrason. Sonochem.
  88 (2022) 106081. doi:https://doi.org/10.1016/j.ultsonch.2022.106081.
- 793 [80] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-Merit for the Technical
- 794 Development and Application of Advanced Oxidation Processes, 1 (1996) 13–17.
- 795 doi:doi:10.1515/jaots-1996-0104.
- 796 [81] N. Wardenier, Z. Liu, A. Nikiforov, S.W.H. Van Hulle, C. Leys, Micropollutant elimination by
- 797 O3, UV and plasma-based AOPs: An evaluation of treatment and energy costs, Chemosphere. 234
  798 (2019) 715–724. doi:10.1016/J.CHEMOSPHERE.2019.06.033.
- 799 [82] 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.
- [83] 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. doi:10.1016/J.WATRES.2015.05.024.
- [84] Y. Li, D. Wang, G. Yang, X. Yuan, L. Yuan, Z. Li, Q. Xu, X. Liu, Q. Yang, W. Tang, L. Jiang, H.
  Li, Q. Wang, B. Ni, In-depth research on percarbonate expediting zero-valent iron corrosion for

- conditioning anaerobically digested sludge, J. Hazard. Mater. 419 (2021) 126389.
- 808 doi:https://doi.org/10.1016/j.jhazmat.2021.126389.
- 809 [85] A. Fernandes, M. Gągol, P. Makoś, J.A. Khan, G. Boczkaj, Integrated photocatalytic advanced
- 810 oxidation system (TiO2/UV/O3/H2O2) for degradation of volatile organic compounds, Sep. Purif.
- 811 Technol. 224 (2019) 1–14. doi:https://doi.org/10.1016/j.seppur.2019.05.012.

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Supplementary Material

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### **Declaration of interests**

**X** 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: