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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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GDAŃSK UNIVERSITY OF TECHNOLOGY

FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING

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.

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Title: Activated sodium percarbonate-ozone (SPC/O_3) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1,4-dioxane in water
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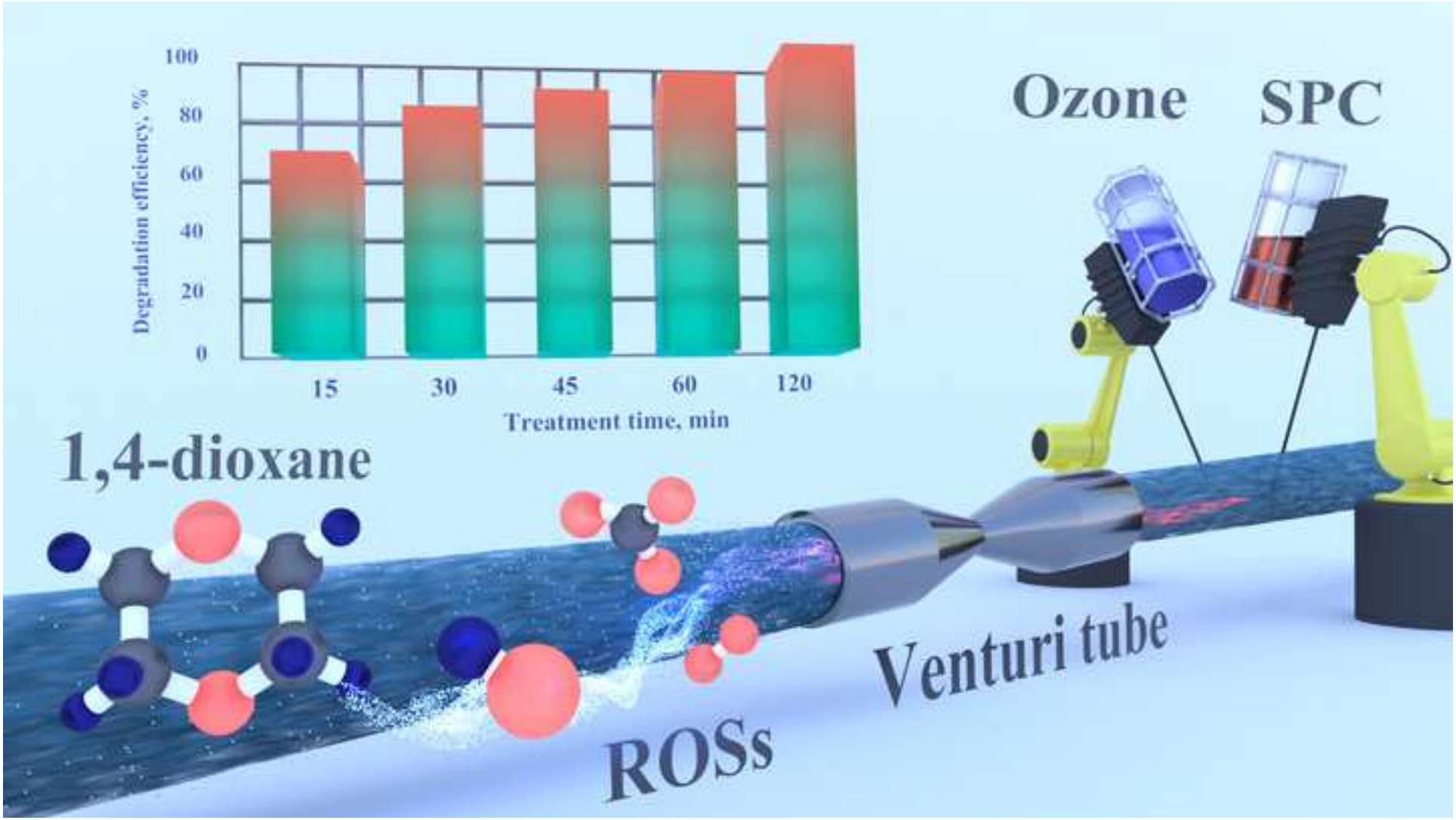
Graphical Abstract



Highlights

- Synergistic HC/SPC/O_3 process for degradation of emerging environmental pollutants
- Superior performance of HC/SPC/O_3 comparing to HC/H_2O_2/O_3
- 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_3) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1,4-dioxane in water.

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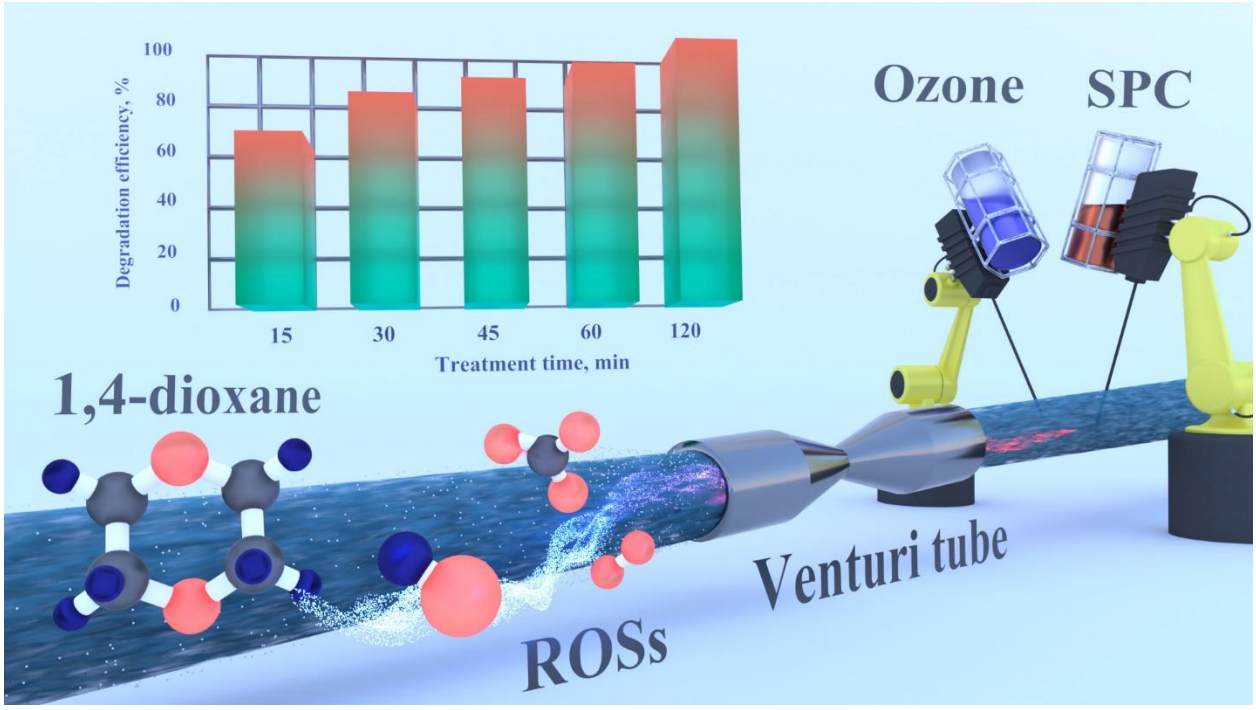
Graphical abstract



Abstract

Hydrodynamic cavitation (HC) was employed to activate sodium percarbonate (SPC) and ozone (O_3) 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 (C_v) 0.27, pH 5, molar ratio of oxidant to pollutant (r_{ox}) 8, ozone dose of 0.86 g h^{-1} under 25±2 ºC with initial concentration of 1,4-dioxane 100 ppm. The application of HC with SPC/O_3 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/O_3 was superior as compared to HC/H_2O_2/O_3, suggesting that the presence of SPC has a significant role in degradation of 1,4-dioxane. Radical quenching experiment revealed highest contribution of hydroxyl ($HO^{\bullet}$) radicals in the degradation of 1,4-dioxane among carbonate ($CO_3^{\bullet-}$) and superoxide ($O_2^{\bullet-}$) radicals. The presence of co-existing anions resulted in an inhibitory effect in the following order: SO_4^{2-} > NO_3^- > 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 (E_{EO}) for best process was 176,79 kWh·m^{-3}·$order^{-1}$. Total cost of treatment was estimated as approx. 20 USD/m^3. These findings confirmed the SPC as an efficient, environmentally-friendly alternative to H_2O_2 and broadened the scope of HC-based AOPs for water and wastewater treatment.

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

1. Introduction

1,4-dioxane also named as 1,4-diethylene oxide, an important stabilizer of chlorinated solvents has found a wide variety of industrial applications such as aerosol additive, wetting and dispersing agent. It is also 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 groundwaters [2,3]. Such widespread occurrence of 1,4-dioxane is mainly originated due to the improper disposal of the effluents, resistance of 1,4-dioxane to biodegradation and merely complete miscibility 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 [1,4]. In connection with this, stringent water quality standards regulating the concentration of 1,4-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, 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 highly reactive radical species appeared to be promising green technologies for remediation of 1,4-dioxane from aqueous environment [5,8–11].

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

scavenging or radical recombination reactions raising the issue of H_2O_2 dosage and introduction mode optimization.

Recently, studies on H_2O_2-based AOPs are focused on sodium percarbonate (SPC), namely $Na_2CO_3 \times 1.5H_2O_2$ 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]. Attempts on SPC activation have been made using Fe^{2+} [22–24], graphene oxide [25], protonated g-C_3N_4 [26], zero valent iron (ZVI) [27], vanadium (IV) [28], UV [29] and ultrasound [21]. Unlike H_2O_2, the oxidation capacity of SPC-based AOPs is conditioned by a variety of ROS, including superoxide ($O_2^{\bullet-}$) and carbonate ($CO_3^{\bullet-}$) radicals. The latter is generated through the consumption of HO$^\bullet$ radicals and exhibit lower oxidation potential of 1.78 V at pH 7 [30]. In spite of this, $CO_3^{\bullet-}$ radicals selectively react with organic pollutants containing electron rich functional groups. For instance, as an electron acceptor $CO_3^{\bullet-}$ radical rapidly reacts with *p*-substituted phenols and anilines with a rate constant of 10^7-10^8 M^{-1} s^{-1} and 10^5-10^7 M^{-1} s^{-1}, respectively [31–33]. Moreover, the concentration of $CO_3^{\bullet-}$ radicals in sunlit surface water appeared to be two orders of magnitude higher than HO$^\bullet$ radicals under the same conditions [34]. Therefore, SPC-based AOPs are seemed to be a preferable option for the degradation of organic pollutants bearing electron rich moieties and, particularly, 1,4-dioxane.

Although, AOPs are considered as effective and environmentally friendly techniques for the degradation organic contaminants, the industrial implementation of AOPs in water treatment schemes is hindered. To achieve a satisfactory level of degradation, the application of traditional AOPs require high operational 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 of hybrid processes based on cavitation and AOPs showed encouraging results anticipating the implementation of novel technologies in water/wastewater treatment [36–39]. Cavitation is an emerging technique which is often employed to improve the effectiveness of AOPs. The key mechanism relying behind the cavitation phenomenon relate to the formation, growth and violent collapse of cavitation 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 radical species through to the pyrolytic disassociation of water or proceed the activation of H_2O_2, O_3 and other peroxides. Owing to the continuous flow operation, high cavitational 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/O_3 process under
85 hydrodynamic cavitation (HC); ii). to understand the synergy in HC/SPC/O_3 the degradation kinetics of
86 1,4-dioxane in sole and coupled processes; iii). to identify the reactive species in HC/SPC/O_3 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/O_3.
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. H_2O_2 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 $M\Omega cm^{-1}$) 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

a mechanical stirrer, temperature indicator and water condenser to maintain the reaction temperature. Sequential pumping system (MS 801-4, 1360 min^{-1}, TECHTOP® MOTOR, Shanghai, China) connected with electromagnetic flowmeter (MPP 600 by MAGFLO®) was used to circulate water through the cavitating device and by-pass line. The cavitating device consisted of brass Venturi tube with 2-mm ID of the throat section. Digital manometers (Suku, Germany) were mounted on the upstream and downstream 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 containing 100 ppm of 1,4-dioxane was added in the feed tank and treated for 120 min at 20±2 ºC. Sample aliquots of 20 mL were collected at regular time interval. The SPC solution was injected through the port with inner porous membrane to attain the required molar ratio of SPC to 1,4-dioxane. Dry air with a certain flow rate was connected to a Tytan 32 (Erem, Poland) ozone generator to purge ozone to the upstream line of Venturi tube. All experiments were performed in duplicate and experimental errors were within 5%.

2.3 *Analysis*

Prior to GC analyses, dispersive liquid-liquid microextraction (DLLME) was employed to extract 1,4-dioxane from water samples. The procedure of DLLME was as follows: 5 µL 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 µL 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 ºC (5 min) ramped at 10 ºC/min to 275 ºC (5 min), detector temperature 275 ºC. 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.

The identification of 1,4-dioxane degradation products was performed using a GCMSQP2010SE (Shimadzu, Japan) gas chromatograph (GC) coupled to a mass spectrometer (MS). A capillary column (100 m × 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 ºC and GC-MS transfer line temperature was 310 ºC. The oven temperature program was 40 ºC (isothermal for 5 min) ramped at 5 ºC/min to 220 ºC. Ion source (EI, 70 eV) temperature was 200 ºC. A mass-to-charge ratio of 34 to 220 m/z was selected for SCAN mode analysis of byproducts.

The concentration of O_3 in introduced gaseous oxidant stream was measured by iodometric titration method. The experimental setup consisted of ozone generator (Erem 32, Poland) and two connected gas washing bottles in series. Each bottle was filled with 400 mL of acidified (pH 3) KI (2% w/w) solution to trap O_3. The compressed dry air containing O_3 was bubbled through KI solution using a sintered glass disc located in the bottom half of bottles. A standardized 0.001 N $Na_2S_2O_3$ solution was used as a titrant and 5% (w/v) starch solution as an indicator. The dose of O_3 at carrier gas flow rate of 0.5, 1.0, 1.5, 2.0 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 organic carbon (TOC) was measured using TOC-LCSH instrument (Shimadzu, Japan). All tubing connecting ozone generator with HC reactor and gas absorption bottles were made of PTFE (Teflon).

3. Results and discussion

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]:

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

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 ρ is the density of the treated liquid.

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

$$ln\frac{C_0}{C_t} = kt, \tag{2}$$

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.

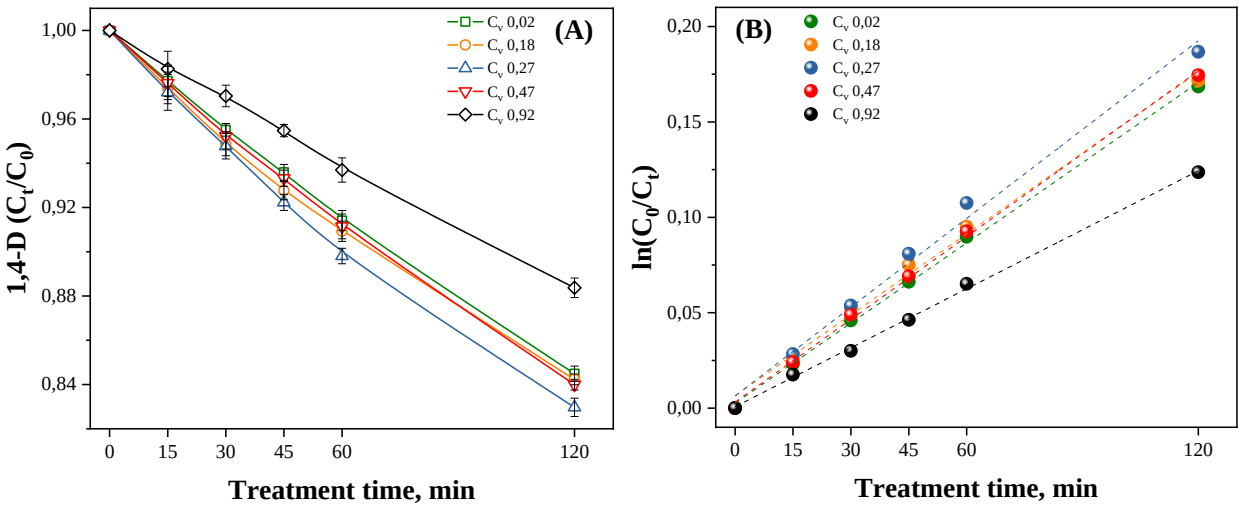


Figure 1. Effect of C_v on the degradation 1,4-dioxane in sole HC: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ($[1,4\text{-D}]_0$ 100 ppm, pH_0 5, 20±2 ºC).

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 1.03×10^{-3} min^{-1} to 1.43×10^{-3} 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

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

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
$k \times 10^{-2}$, min^{-1}	0.140	0.141	0.155	0.145	0.103
R^2	0.998	0.993	0.992	0.998	0.999

3.2 *Enhanced degradation of 1,4-dioxane by HC/SPC/O_3*

The degradation efficiency of HC/O_2, HC/O_3, HC/SPC, SPC/O_3 and HC/SPC/O_3 towards 1,4-dioxane was 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 nuclei for the growth of cavitation bubbles as a gas is purged to the upstream line of Venturi tube. Furthermore, about 24.34 and 22.76% of 1,4-dioxane degradation were obtained within 120 min in HC/O_3 and HC/SPC, respectively. These observations indicate the increase of number of reactive radicals produced in the presence of oxidants according to **Eqs. 3-7** [20,40,48,49]. The generation of radicals was increased further and reflected in 56.02% of 1,4-dioxane degradation in 120 min as O_3 was combined with SPC in the absence of HC. Although, the radicals in SPC/O_3 are produced according to peroxone process as shown in **Eqs. 8, 9** [45], the presence of SPC initiates chain reactions to yield radicals through the decomposition of O_3 and H_2O_2. Particularly, alternative decomposition routes of O_3 and H_2O_2 with formation of HO_2^- are occurred under the alkaline pH of SPC (**Eqs. 10, 11**) [45,50]. Obtained HO_2^- participate in a series of radical chain reactions and are eventually converted to highly reactive $HO^{\bullet}$ radicals. Coupling of HC with SPC/O_3 significantly increased the degradation efficiency of 1,4-dioxane giving 99.34% in 120 min. The observed enhancement of 1,4-dioxane degradation in SPC/O_3 is

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_3 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.

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

$$O^{\bullet} + H_2O + \text{cavitation} \rightarrow 2HO^{\bullet} \quad (4)$$

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

$$HO^{\bullet} + CO_3^{2-} \rightarrow CO_3^{\bullet-} + HO^{-} \quad (6)$$

$$HO^{\bullet} + HCO_3^{-} \rightarrow CO_3^{\bullet-} + H_2O \quad (7)$$

$$O_3 + H_2O_2 \rightarrow O_2 + HO^{\bullet} + HO_2^{\bullet} \quad (8)$$

$$O_3 + HO_2^{\bullet} \rightarrow HO^{\bullet} + 2O_2 \quad (9)$$

$$O_3 + HO^{-} \rightarrow HO_2^{-} + O_2 \quad (10)$$

$$H_2O_2 \leftrightarrow HO_2^{-} + H^{+} \quad (11)$$

As shown in **Table 2**, the pseudo-first-order rate constant of 1,4-dioxane degradation HC/O_2, HC/O_3, HC/SPC and SPC/O_3 were 1.70 × 10^{-3}, 2.32 × 10^{-3}, 2.12 × 10^{-3}, 6.60 × 10^{-3} min^{-1}, respectively, whereas the *k* value in HC/SPC/O_3 was 4.04 × 10^{-2} min^{-1}. Obtained *k* values demonstrate the distinct superiority of the hybrid HC/SPC/O_3 over the binarily integrated processes in degradation of 1,4-dioxane. The synergistic index (ξ) of HC/SPC/O_3 calculated using *k* values according to **Eq. 12** was 4.32, which indicates a remarkable synergy occurred in HC/SPC/O_3 in comparison with the cumulative effect of individual processes. Although the value of ξ in HC/H_2O_2/O_3 was 3.83, the degradation efficiency of 1,4-dioxane was 95.16% after 120 min, whereat the reaction constant was lower by 1.54 × 10^{-2} min^{-1} compared to HC/SPC/O_3.

$$\xi = \frac{k_{HC/SPC/O3}}{k_{SPC/O3}+k_{HC}+(k_{HC/SPC}-k_{HC})+(k_{HC/O3}-k_{HC})}, \quad (12)$$

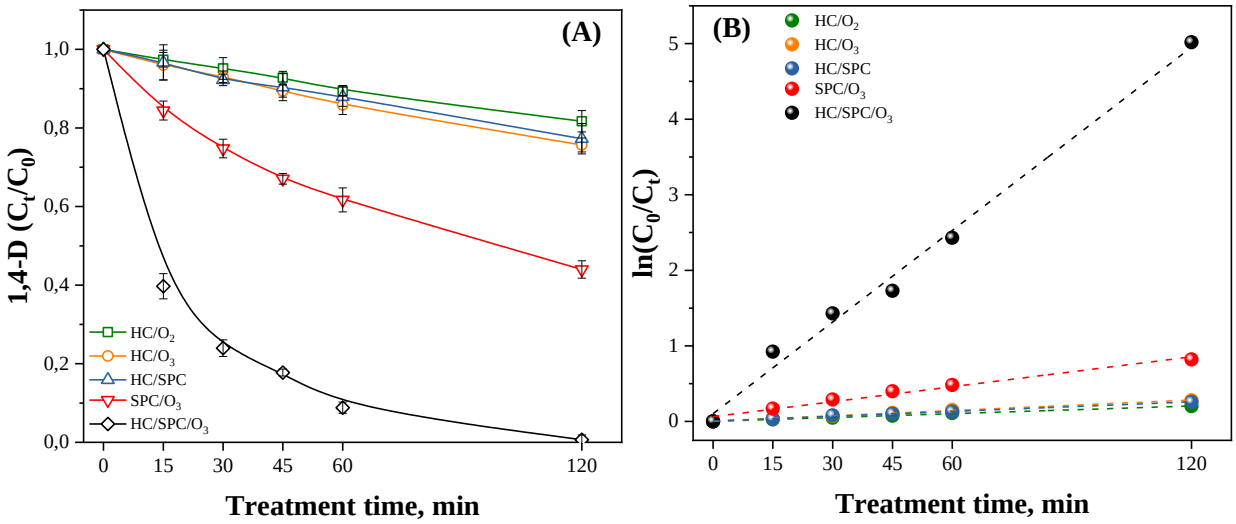


Figure 2. Effect of different processes on the degradation 1,4-D: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ([1,4-D]$_0$ 100 ppm, C_v 0.27, SPC r_{ox} 8, [O_3] 0.86 g h^{-1}, pH$_0$ 5, 20±2 ºC).

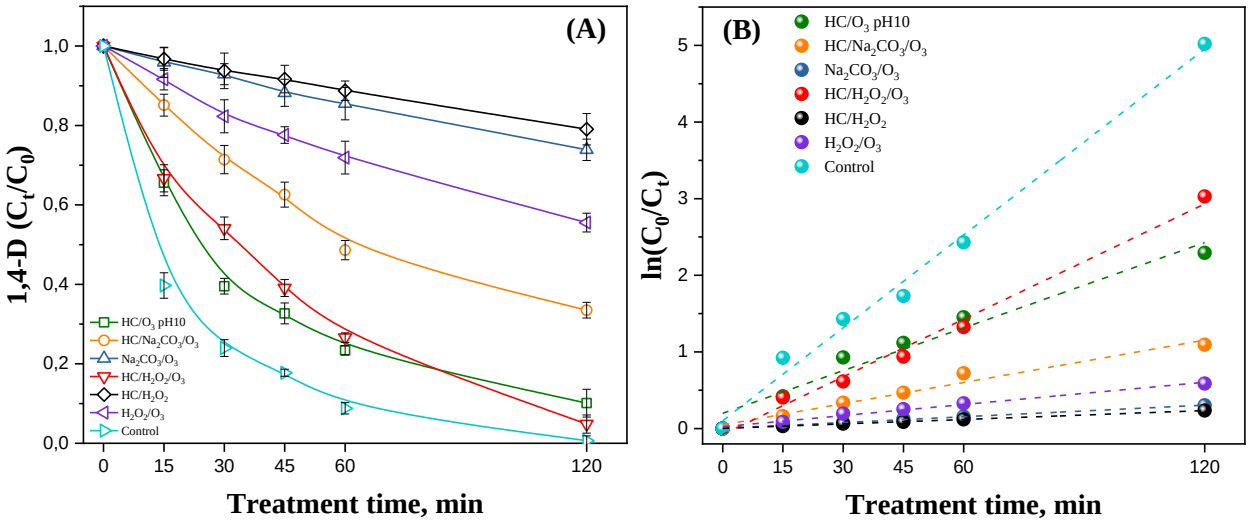


Figure 3. Effect of various processes on the degradation 1,4-D: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ([1,4-D]$_0$ 100 ppm, C_v 0.27, Na_2CO_3=H_2O_2 r_{ox} 8, [O_3] 0.86 g h^{-1}, 20±2 ºC).

To further clarify the role of SPC in degradation of 1,4-dioxane by HC/SPC/O_3, a series of additional experiments, including addition of sodium carbonate, have been conducted. As depicted in **Fig. 3a**, HC/Na_2CO_3/O_3 resulted in 66.50% of 1,4-dioxane degradation within 120 min, whereas it was only 26.11% for O_3/Na_2CO_3 in the absence of HC, indicating a considerable contribution of HC in decomposition of O_3. On the other hand, a discernable improve of 1,4-dioxane degradation was observed when comparing HC/Na_2CO_3/O_3 and Na_2CO_3/O_3 with corresponding HC/SPC/O_3 and SPC/O_3. Thus, the

degradation efficiency of 1,4-dioxane in HC/Na_2CO_3/O_3 was lower by 32.84% compared to HC/SPC/O_3, while it was 29.91% for Na_2CO_3/O_3 and SPC/O_3. Corresponding *k* values (**Table 2**) were increased from 9.22×10^{-3} to 4.04×10^{-2} min^{-1} for HC/Na_2CO_3/O_3 and HC/SPC/O_3 and from 2.52×10^{-3} to 6.60×10^{-3} min^{-1} for Na_2CO_3/O_3 and SPC/O_3, respectively. In addition, application of H_2O_2 in HC/O_3 improved the degradation efficiency of 1,4-dioxane by 70.82% after 120 min. These results signify the essential role of H_2O_2 in formation of radical species in HC/SPC/O_3. Nevertheless, the degradation efficiency attained by 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 increased the degradation efficiency to 65.55%, due to the promoted O_3 decomposition, however, HC/O_3 at pH 10 showed lower efficiency than HC/SPC/O_3. Although, HCO_3^- and CO_3^{2-} anions are anticipated to scavenge of $HO^{\bullet}$ radicals (**Eqs. 6, 7**) and slowly react with 1,4-dioxane (~10^5 M^{-1} s^{-1}) [51–53], these findings suggest, a partial participation of $HCO_3^{\bullet}$ and $CO_3^{\bullet-}$ radicals in degradation of 1.4-dioxane. Therefore, the contribution of $HCO_3^{\bullet}$ and $CO_3^{\bullet-}$ radicals should be further clarified (detailed investigation is presented in section 3.6).

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

Type of process	***k* × 10^{-2}, min^{-1}**	**R^2**
HC/O_2	0.170	0.996
HC/H_2O_2	0.194	0.999
HC/SPC	0.212	0.995
HC/O_3	0.232	0.997
Na_2CO_3/O_3	0.252	0.998
H_2O_2/O_3, pH10	0.483	0.991
SPC/O_3	0.660	0.980
HC/Na_2CO_3/O_3	0.922	0.973
HC/O_3, pH10	1.857	0.963
HC/H_2O_2/O_3, pH10	2.506	0.991
HC/SPC/O_3	4.041	0.992

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_3. In order to determine the optimal dosage of SPC, the degradation of 1,4-dioxane 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 the degradation of 1,4-dioxane was improved to 18.34, 22.11, 27.52 and 37.15% in 120 min, respectively. 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 1.55×10^{-3} to 3.42×10^{-3} min^{-1} as compared to sole HC. With an increase of SPC dosage to r_{ox} 10, 31.94% of 1,4-dioxane was degraded in 120 and k was estimated as 3.14×10^{-3} min^{-1}. These results suggest that the increase of SPC dosage above the optimal value led to the quench of $HO^{\bullet}$ radicals. Undesired $HO^{\bullet}$ consumption of radicals can be caused by unreacted H_2O_2, saturated O_2 and radical recombination reactions, which mainly lead to the formation of secondary radical species with lower oxidation potential (**Eqs. 13-19**) [20,48]. In this study, the degradation efficiency of 1,4-dioxane in HC/SPC was highest at r_{ox} 8 and the competition of scavenging reactions intensified at r_{ox} 10. Such trend regarding to SPC activation has been addressed by previous studies [50,54]. According to the obtained results, r_{ox} 8 was selected as the optimal SPC dosage for further experiments.

$$HO^{\bullet} + H_2O_2 + \text{cavitation} \rightarrow HO_2^{\bullet} + H_2O \quad (13)$$

$$HO^{\bullet} + O_2 + \text{cavitation} \rightarrow HO_2^{\bullet} + O^{\bullet} \quad (14)$$

$$HO^{\bullet} + HO_2^{\bullet} + \text{cavitation} \rightarrow H_2O_2 \quad (15)$$

$$HO^{\bullet} + HO^{\bullet} + \text{cavitation} \rightarrow H_2O_2 \quad (16)$$

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

$$O_2^{\bullet -} + HO^{\bullet} \rightarrow HO^- + O_2 \quad (18)$$

$$CO_3^{\bullet -} + H_2O_2 \rightarrow HCO_3^- + HO_2^{\bullet} \quad (19)$$

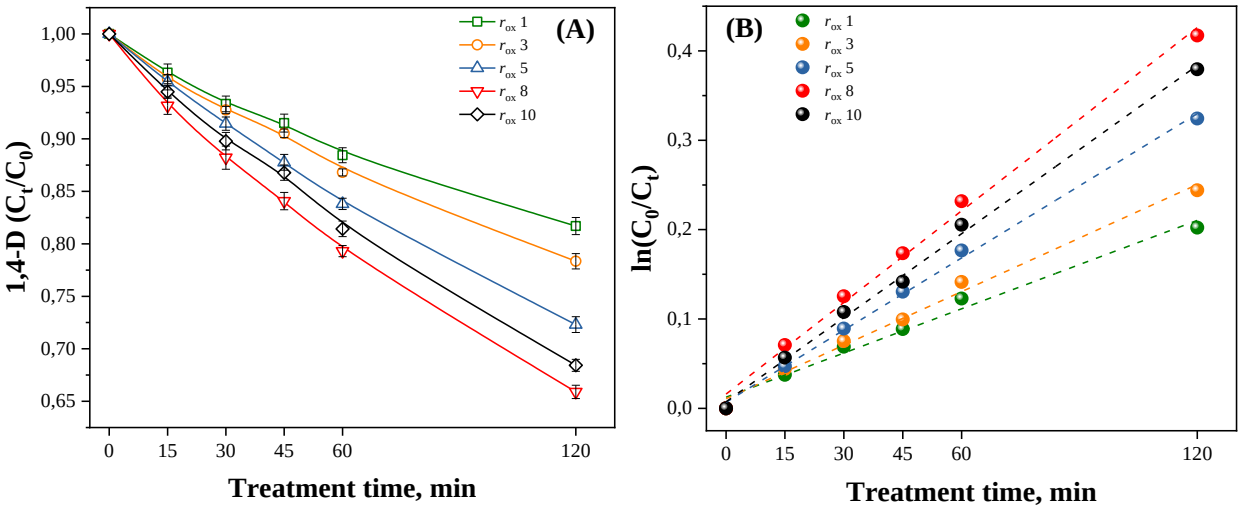


Figure 4. Effect of SPC r_{ox} on the degradation 1,4-D in HC/SPC: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ([1.4-D]$_0$ 100 ppm, C_v 0.27, pH$_0$ 5, 20±2 ºC).

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

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 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 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 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 min, respectively. As given in **Table 4**, the increase of O_3 dosage from 0.23 to 0.86 g h^{-1} accelerated the rate constant of 1,4-dioxane degradation from 4.11 × 10^{-3} to 4.04 × 10^{-2} min^{-1}, respectively, while it was 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 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** [55,56]. On the other hand, overpressure at Venturi tube inlet and the turbulence induced by HC provide high transfer rate of O_3 from gaseous phase into the liquid. In such scenario, the contact of O_3 with H_2O_2 is enhanced resulting in effective utilization of O_3. Particularly, the impact of HC is obvious when comparing HC/SPC/O_3 and SPC/O_3 (**Fig. 2**), whereat 99.34 and 56.02% of 1,4-dioxane was degraded in 120 min and k values were 4.04 × 10^{-2} and 6.60 × 10^{-3} min^{-1}, respectively. The outlet concentration of O_3 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 enhanced utilization efficiency of O_3 due to the effect of HC.

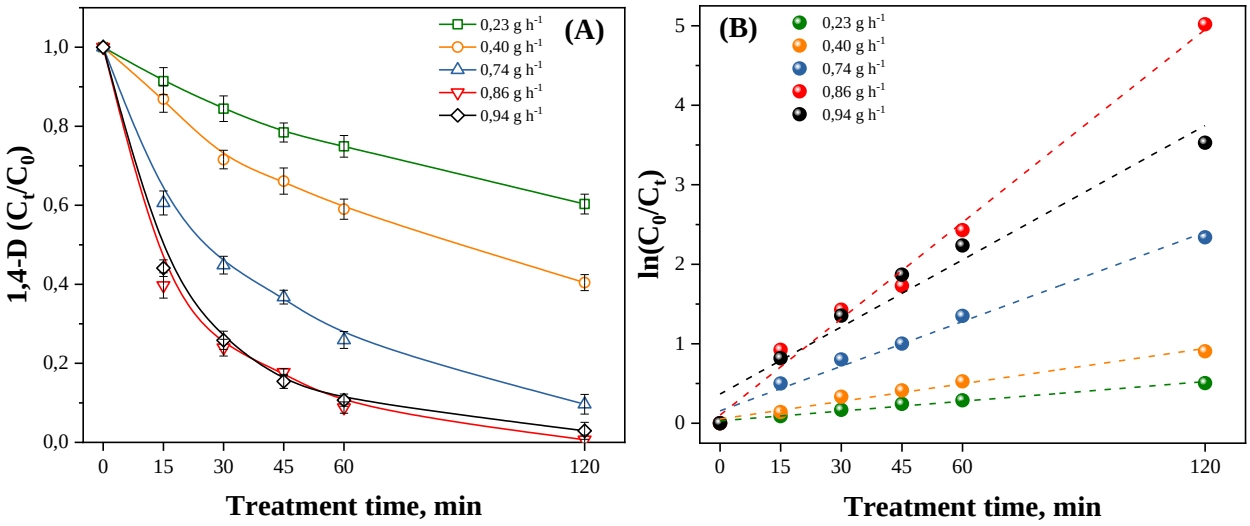


Figure 5. Effect of O_3 dosage on the degradation 1,4-D in HC/SPC/O_3: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ([1,4-D]$_0$ 100 ppm, C_v 0.27, SPC r_{ox} 8, pH$_0$ 5, 20±2 ºC).

Although, an increase of inlet O_3 dosage increases the partial pressure of O_3 in gas phase and, thus, improves the O_3 mass transfer [54], the increase of O_3 dosage to 0.94 g h^{-1} decreased the degradation 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 be ascribed to the scavenging effect of high O_3 dosage, whereat a considerable amount of O_3 was disintegrated to the consumption $HO^{\bullet}$ radicals by dissolved O_3 as described in **Eq. 20** [57]:

$$HO^{\bullet} + O_3 \rightarrow HO_2^{\bullet} + O_2 \quad (20)$$

Table 4. Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O_3 at r_{ox} 8 and different O_3 dosage.

	O_3 dosage, g h^{-1}				
	0.23	0.40	0.74	0.86	0.94
k × 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

To evaluate the improving effect of O_3 on HC/SPC, the degradation of 1,4-dioxane in HC/SPC/O_3 was conducted with fixed dosage of O_3 at 0.86 g h^{-1} 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_3 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 × 10^{-3} to 4.04 × 10^{-2} min^{-1} at r_{ox} 8, whereas the 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

ratio between SPC and O_3 substantially defines the oxidative capacity of HC/SPC/O_3 towards 1,4-dioxane.

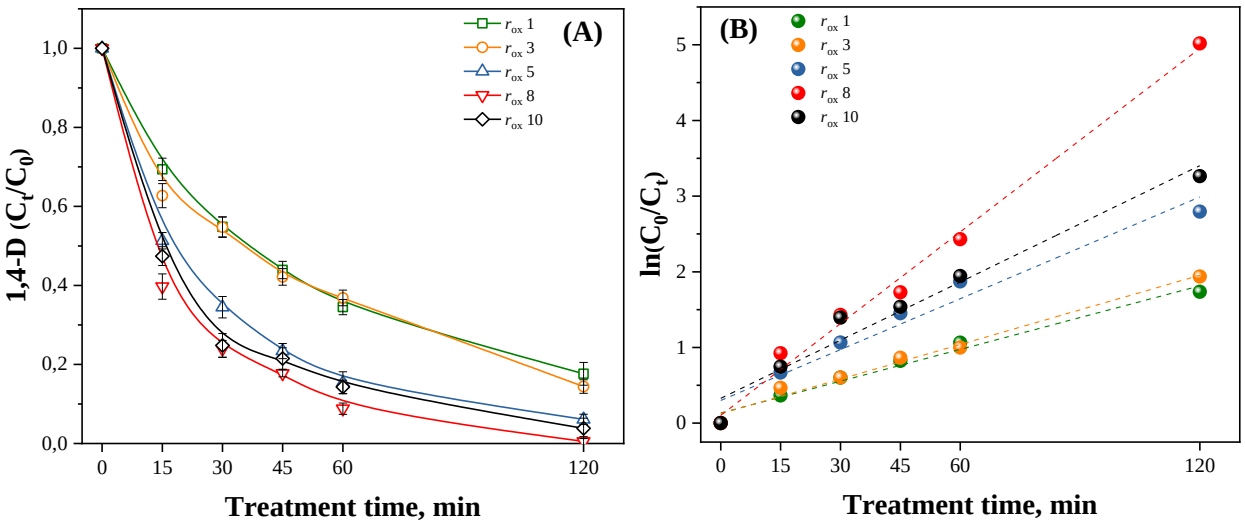


Figure 6. Effect of fixed O_3 dosage on the degradation 1,4-D in HC/SPC/O_3 with various SPC r_{ox}: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ([1,4-D]$_0$ 100 ppm, C_v 0.27, [O_3] 0.86 g h^{-1}, pH_0 5, 20±2 ºC.

Table 5. Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O_3 at 0.86 g h^{-1} O_3 dosage and different r_{ox}.

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

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_3 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_3 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_3 process.

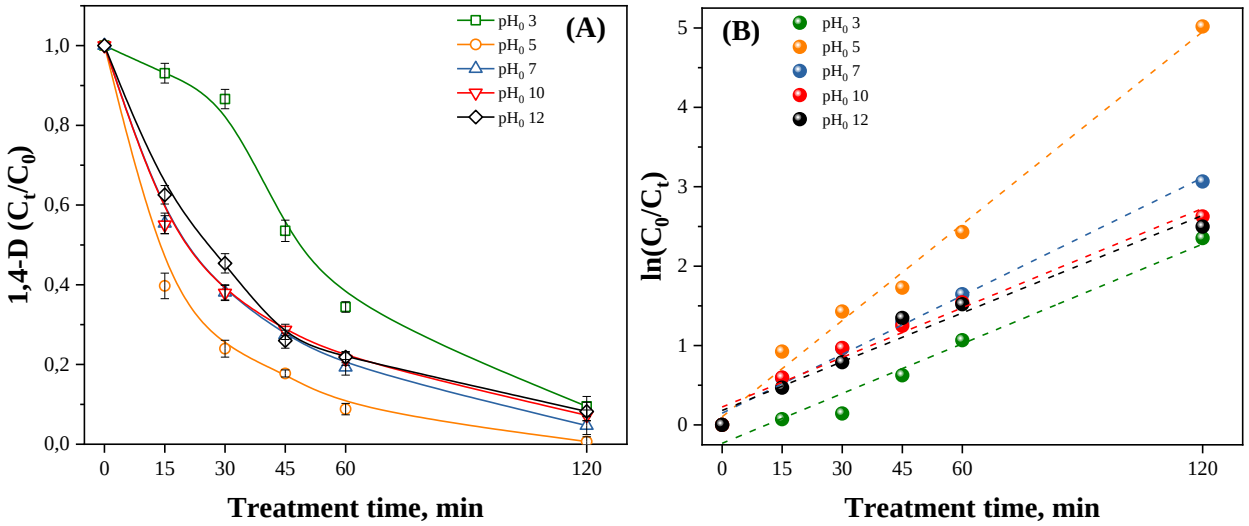


Figure 7. Effect of pH_0 on the degradation 1,4-D in HC/SPC/O_3: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ([1,4-D]$_0$ 100 ppm, C_v 0.27, SPC r_{ox} 8, [O_3] 0.86 g h^{-1}, 20±2 °C).

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 highest resulting in 90.49% of 1,4-dioxane degradation within 120 min. This is attributed to the lower decomposition rate of O_3 at acidic conditions, so the direct oxidation of 1,4-dioxane by molecular O_3 is predominant at pH_0 3. Since O_3 possess lower redox potential than HO$^\bullet$ radicals, the direct oxidation proceeded slowly resulting in the *k* value of 2.09×10^{-2} min^{-1} (**Table 6**). In contrast, the rate constant of 1,4-dioxane degradation was markedly increased to 4.04×10^{-2} min^{-1} at pH_0 5, indicating high concentration of generated radical species. This can be ascribed to the radical route of 1,4-dioxane degradation *via* indirect O_3 oxidation and additional supply of HO$^\bullet$ radicals due to the patrial dissociation 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_3 as illustrated in **Eqs. 21-23** [58]. The detrimental effect of $pH_0 < 5$ coincides with the pH change depicted in **Fig. 8**. Particularly, the degradation efficiency of 1,4-dioxane in HC/SPC/O_3 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 treatment.

$$HO_2^- + O_3 \rightarrow HO_5^- \quad (21)$$

$$HO_5^- \rightarrow HO_2^\bullet + O_3^- \quad (22)$$

$$O_3^- + H_2O \rightarrow O_2 + HO^\bullet + HO^- \quad (23)$$

$$HO_2^- + HO^\bullet \rightarrow HO_2^{\bullet -} + H_2O \quad (24)$$

Table 6. Kinetic parameters of 1,4-dioxane degradation in HC/SPC/O_3 at different pH_0.

	pH_0 3	pH_0 5	pH_0 7	pH_0 10	pH_0 12
$k \times 10^{-2}$, min^{-1}	2.091	4.041	2.471	2.084	2.047
R^2	0.968	0.992	0.993	0.977	0.968

Although alkaline pH promotes the decomposition of O_3, the degradation efficiency of 1,4-dioxane in HC/SPC/O_3 at pH_0 10 and 12 was slightly decreased to 92.76 and 91.78%, respectively. Such trend can be interpreted with an excessive production of HO_2^- (**Eq. 10**), which act as a scavenger of $HO^\bullet$ radicals (**Eq. 24**) [50,54,58].

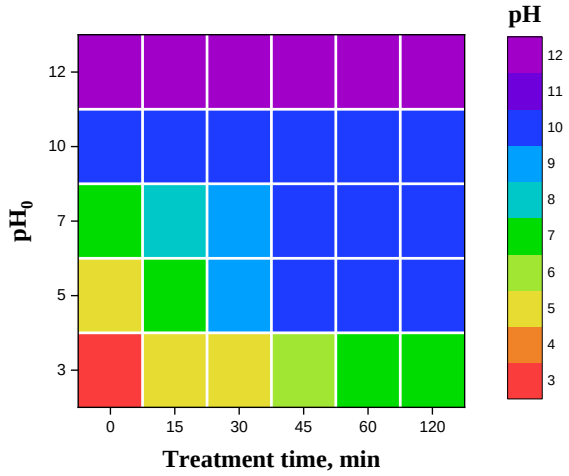


Figure 8. The map of pH change throughout the degradation 1,4-D in HC/SPC/O_3 at various pH_0 ([1,4-D]$_0$ 100 ppm, C_v 0.27, SPC r_{ox} 8, [O_3] 0.86 g h^{-1}, 20±2 ºC).

3.6 *Identification of reactive species in HC/SPC/O_3*

Beside $HO^\bullet$ radicals, $O_2^{\bullet -}$ and $CO_3^{\bullet -}$ radicals could be generated in HC/SPC/O_3 according to **Eqs. 4-9, 17** and participate in the degradation of 1,4-dioxane. To evaluate the contribution of reactive species in degradation of 1,4-dioxane, quenching experiments were conducted. Isopropyl alcohol (IPA), phenol (PhOH), chloroform (CLF), *para*-benzoquinone (*p*-BQ) and sodium azide (NaN_3) were utilized as 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 $HO^\bullet$ radicals (3.9×10^9 M^{-1} s^{-1}) and slowly responds to $CO_3^{\bullet -}$ and $O_2^{\bullet -}$ radicals, with a rate constant of 4.0×10^4 M^{-1} s^{-1} and 1.0×10^6 M^{-1} s^{-1}, respectively [59,60]. Additionally, the reaction of $HO^\bullet$ radicals with IPA proceeds faster than with 1,4-dioxane (2.8×10^9 M^{-1} s^{-1}), H_2O_2 (2.7

× 10^7 M^{-1} s^{-1}), HCO_3^- (8.5 × 10^6 M^{-1} s^{-1}) and CO_3^{2-} (3.9 × 10^8 M^{-1} s^{-1}) [61–63], hence, IPA was selected to study the existence of $HO^•$ radicals. On the other hand, PhOH was used to confirm the occurrence of $O_2^{•-}$ radicals as PhOH preferentially reacts with $HO^•$ (6 × 10^8 M^{-1} s^{-1}) and $CO_3^{•-}$ (1.2 × 10^9 M^{-1} s^{-1}) radicals [60,64]. Additionally, the impact of $O_2^{•-}$ radicals was explored using *p*-BQ and CLF, which rapidly react with a second-order rate constant of 9.6 × 10^8 M^{-1} s^{-1} and 3.9 × 10^{10} M^{-1} s^{-1}, respectively [39,59,65]. As 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 × 10^{-2} to 2.58 × 10^{-3} min^{-1} (**Table 7**) in the presence of IPA. This illustrates the predominant role of $HO^•$ radicals. The degradation efficiency of 1,4-dioxane was inhibited to 13.52% in 120 min with addition of PhOH, suggesting the contribution of $O_2^{•-}$ radicals in 1,4-dioxane degradation. Based on these it can be proposed that for HC/SPC/O_3 highest contribution to degradation had $HO^•$ radicals, with moderate role of $CO_3^{•-}$ and minor role of $O_2^{•-}$. In contrast, the quenching experiments using *p*-BQ and CLF suppressed the degradation efficiency of 1,4-dioxane by 52.99 and 29.21% in 120 min, respectively, suggesting a considerable involvement of $O_2^{•-}$ radicals in degradation of 1,4-dioxane. It must be taken into account, that both scavengers, but especially *p*-BQ also in some part can react with other radicals including $HO^•$, thus these tests are discussed as they confirmed contribution of superoxide radical in degradation. Additional aspect that overlays on the performed tests relates to the fact, that although PhOH is low reactive towards $O_2^{•-}$ radicals (5.8 × 10^2 M^{-1} s^{-1}), scavenging of $HO^•$ radicals prohibits the regeneration of $O_2^{•-}$ radicals through **Eq. 17**. In light of this "doubled" scavenging effect of PhOH it is confirmed that $O_2^{•-}$ contributed to the degradation effect.

In the case of *p*-BQ and CLF, available (not scavenged so fast) $HO^•$ 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 $HO^•$ and $HO_2^•$ radicals can lead to the generation of singlet oxygen ($^1O_2$) species through the following reactions [66]:

$$O_2^{•-} + HO^• \rightarrow {}^1O_2 + HO^- \quad (25)$$

$$O_2^{•-} + HO_2^• + H^+ \rightarrow {}^1O_2 + H_2O_2 \quad (26)$$

To elucidate the formation of $^1O_2$ species, NaN_3 was added to quench $^1O_2$ with a rate constant of 1×10^9 M^{-1} s^{-1} [67]. Quenching experiments using NaN_3 inhibited the degradation efficiency of 1,4-dioxane by 5.03%, whereat the corresponding degradation rate constant was decreased from 4.04×10^{-2} to 2.29×10^{-2} min^{-1}. These observations suggest a negligible contribution of $^1O_2$ in the degradation of 1,4-dioxane by HC/SPC/O_3. Performed experiments provide general identification of ROSs. Besides above quenching experiments, other techniques (e.g., electron paramagnetic resonance) can be suggested for the extensive and more detailed analysis of ROSs in HC/SPC/O_3, as scavengers may interrupt radical chain reactions of O_3 decomposition and consume O_3 [68,69].

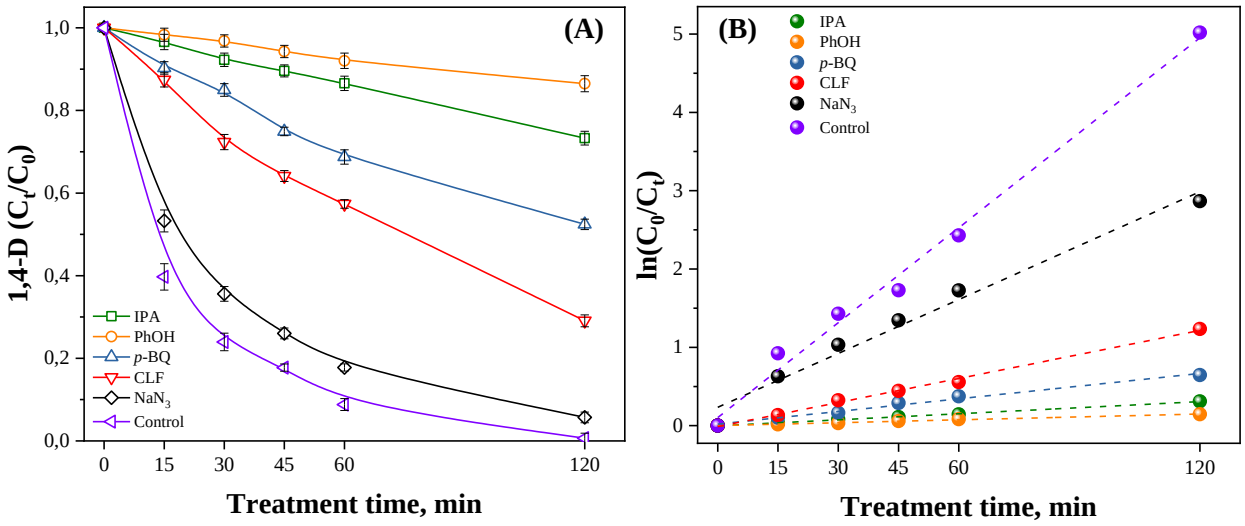


Figure 9. Effect of scavengers on the degradation 1,4-D in HC/SPC/O_3: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ([1,4-D]$_0$ 100 ppm, C_v 0.27, SPC r_{ox} 8, [O_3] 0.86 g h^{-1}, [SPC]:[Scavenger] = 1:10, 20±2 °C).

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

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

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

Inorganic anions such as Cl^-, NO_3^- and SO_4^{2-} are inherently present in natural water [70,71] and might affect the performance of HC/SPC/O_3. Since the practical implementation of HC/SPC/O_3 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_3 was conducted in 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. 10a**, the presence of Cl^- anions resulted in a slight inhibitory effect decreasing the degradation efficiency of 1,4-dioxane from 99.34 to 95.74% within 120 min. The inhibition effect of Cl^- anions is commonly ascribed to the formation chlorine species (i.e., $Cl^•$ and $Cl_2^{•-}$) through the passage of reactions consuming of $HO^•$ radicals as shown in **Eqs. 27-29**. However, the reaction of Cl^- anions with $HO^•$ radicals is negligible at circumneutral conditions due to the fast reverse reaction [72]. In this study, the inhibitory effect of Cl^- anions can be explained due to the interaction of Cl^- anions with O_3, which become relevant at high Cl^- concentration. Such interaction competes with H_2O_2 for O_3 consumption and lead to the formation of hypochlorite which exist in equilibrium with HClO (**Eqs. 30, 31**) and is not oxidized by O_3 [72–74]. The inhibitory effect of 1,4-dioxane degradation in HC/SPC/O_3 found to be more deteriorate with addition of NO_3^- and SO_4^{2-} anions. Thus, the presence of NO_3^- and SO_4^{2-} anions declined the degradation efficiency of HC/SPC/O_3 towards 1,4-dioxane by 7.51 and 12.28% in 120 min, respectively. Although, sulfate radicals ($SO_4^{•-}$) formed *via* **Eq. 32** [75], exhibit relatively high oxidation potential and selectivity towards electron-rich moieties, the presence of precursor SO_4^{2-} anions showed the highest inhibitory effect. This phenomenon can be referred to the decrease of the reduction potential of $SO_4^{•-}$ radicals caused by the high concentration of SO_4^{2-} anions [39]. As depicted in **Table 8**, the degradation rate constant of 1,4-dioxane in presence of Cl^-, NO_3^- and SO_4^{2-} anions in comparison with the process 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}, respectively. In this study, the inhibitory effect of anions towards the degradation of 1,4-dioxane was in the following order: $SO_4^{2-} > NO_3^- > Cl^-$.

$$Cl^- + HO^• \rightarrow HOCl^{•-} \quad (27)$$

$$HOCl^{•-} + H^+ \rightarrow Cl^• + H_2O \quad (28)$$

$$Cl^• + Cl^- \rightarrow Cl_2^{•-} \quad (29)$$

$$Cl^- + O_3 \rightarrow OCl^- + O_2 \quad (30)$$

$$OCl^- \leftrightarrow HOCl \qquad pK_a\ 7.5 \quad (31)$$

$$SO_4^{2-} + HO^• \rightarrow SO_4^{•-} + HO^- \quad (32)$$

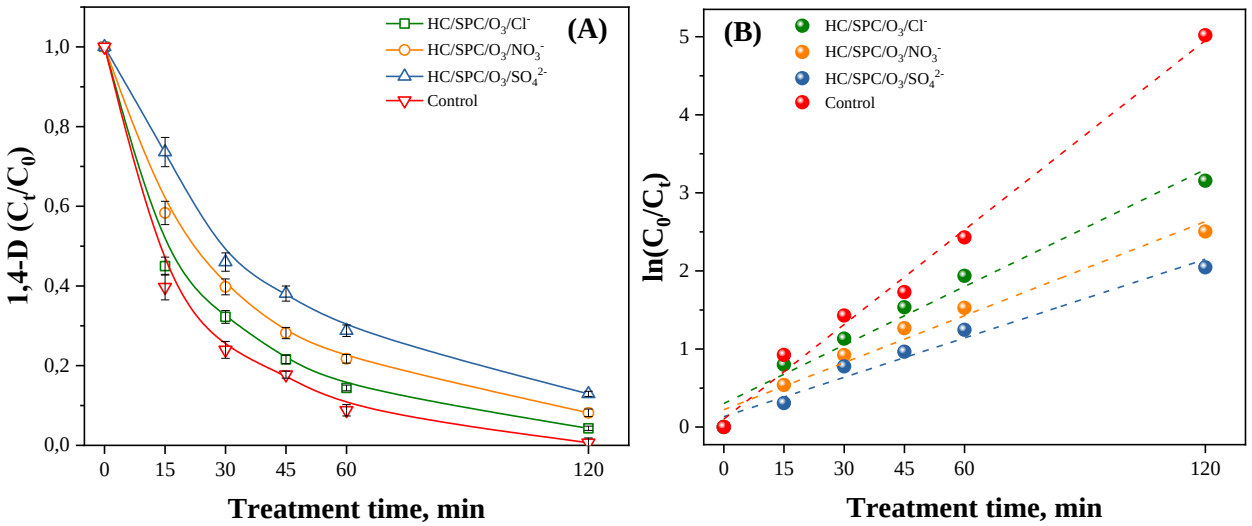


Figure 10. Effect of anions on the degradation 1,4-D in HC/SPC/O_3: (a) degradation efficiency, (b) pseudo-first-order kinetic plots ($[1,4\text{-D}]_0$ 100 ppm, C_v 0.27, SPC r_{ox} 8, $[O_3]$ 0.86 g h^{-1}, [SPC]:[Anion] = 1:10, 20±2 ºC).

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_3 in the presence of anions.

	Type of anion		
	Cl^-	NO_3^-	SO_4^{2-}
$k \times 10^{-2}$, min^{-1}	2.497	2.009	1.681
R^2	0.972	0.972	0.973

3.8 *Degradation pathway of 1,4-dioxane in HC/SPC/O_3*

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/O_3, 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/O_3, an initial concentration of 1000 ppm was adopted at fixed optimal r_{ox}. Based on the analysis of results, ethylene glycol diformate (EGDF) was

identified as the main intermediate of 1,4-dioxane degradation in HC/SPC/O_3 and the proposed degradation pathway is presented in **Fig. 11**.

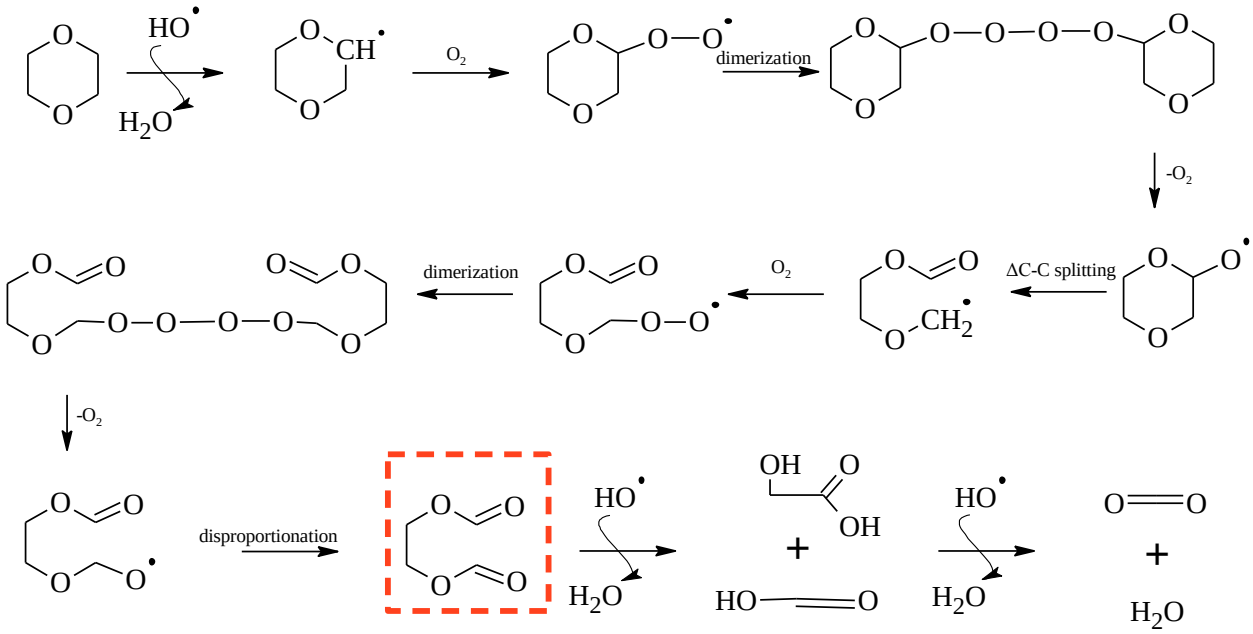


Figure 11. The proposed degradation pathway of 1,4-dioxane in HC/SPC/O_3.

The initial step of the oxidative degradation of 1,4-dioxane proceeds through the attack of radical species with H-abstraction to form 1,4-dioxanyl radical. In the presence of oxygen 1,4-dioxanyl radicals are converted to peroxyl radicals, which are further transformed into α-oxyl radicals [9,76,77]. The latter is recognized as a primary precursor of 1,4-dioxane degradation associated with AOPs. The presence of EGDF in the treated samples supports the ring opening mechanism of α-oxyl radical *via* ΔC-C splitting at the α-C position [76,78]. The obtained radical reacts with oxygen and undergoes dimerization to form tetraoxide, which is further fragmented to yield EGDF. Subsequent attack of HO• radicals causes fragmentation of EGDF with formation of low-molecular intermediates (e.g., glycolic, formic acids), 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-product of 1,4-dioxane degradation, the mechanism pathway of ΔC-C splitting was predominant in HC/SPC/O_3. This result is consistent with the radical-type mechanism of 1,4-dioxane degradation previously described for other AOPs.

3.9 *Economical evaluation*

Assessment of the economic feasibility of HC/SPC/O_3 was based on the energy efficiency and the treatment cost of 1,4-dioxane 100 ppm model solution, calculated for various studied processes compiled in **Table 9.** The cost of treatment was estimated using electric energy per order (E_{EO}), which is defined as [79,80]:

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

, where P_{el} is electric power (kW), t – time of treatment (min), V – volume of the treated solution (L), C_0 and C_t are the initial and final concentration of the pollutant. Since $\log (C_0/C_t) = kt$, the equation can be written as follows:

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

The parameter E_{EO} (kWh $m^{-3}order^{-1}$) describes the amount of energy required to degrade 90% of pollutant in 1 m^3 of the contaminated liquid. The calculations were conducted considering the power of HC system and O_3 generator, which were 0.16 and 0.38 kW, respectively. In this study, the E_{EO} values of 1,4-dioxane degradation using HC/O_3 pH10, HC/H_2O_2/O_3, HC/SPC/O_3 were 222.97, 165.89 and 102.65 kWh $m^{-3}order^{-1}$, respectively (**Table 9**). The adaptation of SPC in HC/SPC/O_3 decreased the energy consumption by 117 and 62% as compared to HC/O_3 pH10 and HC/H_2O_2/O_3, respectively. This is attributed the higher degradation efficiency of HC/SPC/O_3, which allowed to shorten the treatment time of 1,4-dioxane and, 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_2O_2/O_3 cost, while SPC accounted 6.4% of the total cost in HC/SPC/O_3. However, the higher effectiveness of HC/SPC/O_3 provided a reduction of the total treatment cost by 52% as compared to HC/H_2O_2/O_3.

In general, the ranges of E_{EO} values determined for ozonation, peroxone and UV-based AOPs are 0.041-0.73, 0.86-5.96 and 0.73-499 kWh m^{-3}, respectively, and can be substantially large depending on the pollutant's persistency [81]. Interestingly, the degradation of 1,4-dioxane using electro-peroxone and photo-electro-peroxone, according to data reported in the literature required 27.57 and 23.82 kWh m^{-3} [10,11] (details of calculations are provided in **Supplementary data**). However, these values have only theoretically meaning as they were calculated using the theoretical energy required for O_3 generation and assuming the average cell voltage as 7.8 V [82,83]. It is well known that energetic effectiveness of ozone 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 photo-electro-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	k, min^{-1}	E_{EO}, kWh $m^{-3}order^{-1}$	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

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

** The cost of industrial grade H_2O_2 and SPC were assumed as 500, 550 USD/ton, respectively [84,85].

4. Conclusions

HC/SPC/O_3 appears to be an effective alternative for the degradation of 1,4-dioxane resulting in 99.34% in 120 min with a k of 4.04×10^{-2} min^{-1}. Compared to traditional peroxone process, HC/SPC/O_3 required relatively lower dosages of SPC (r_{ox} 8) and O_3 (0.86 g h^{-1}), which is promising for practical implementation in terms of economical feasibility. Concentrations of SPC and O_3 above/below the optimal dosage were found detrimental due to the scavenging of radical species. The presence of CO_3^{2-} in HC/SPC/O_3 enabled the promotion of O_3 decomposition through the increase of pH and participated in radical chain reactions to provide more reactive species. $HO^{\bullet}$ radicals were determined as predominant radical species in HC/SPC/O_3 according to the quenching experiments, which proposed the contribution of reactive species in 1,4-dioxane degradation in order of $HO^{\bullet} > CO_3^{\bullet-} > O_2^{\bullet-}$. The studied co-existing inorganic anions suppressed the effectiveness of HC/SPC/O_3, whereat the inhibitory effect of SO_4^{2-} anions was higher than that of NO_3^- and Cl^- anions. The products of 1,4-dioxane degradation in HC/SPC/O_3 were detected using GC-MS and the degradation pathway was proposed. The oxidation pathway included several transformation steps with formation of ethylene glycol diformate, which is consistent with radical

route degradation 1,4-dioxane reported previously. This work highlights the potential application of SPC in peroxone process as an effective, safe and sustainable replacement to H_2O_2 under HC.

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References

[1] M.J. Zenker, R.C. Borden, M.A. Barlaz, Occurrence and Treatment of 1,4-Dioxane in Aqueous Environments, Environ. Eng. Sci. 20 (2003) 423–432. doi:10.1089/109287503768335913.

[2] 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.

[3] A. Yasuhara, Chemical components in leachates from hazardous wastes landfills in Japan, Toxicol. Environ. Chem. 51 (1995) 113–120. doi:10.1080/02772249509358229.

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

[5] H. Barndõk, 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, Chem. Eng. J. 284 (2016) 112–121. doi:10.1016/J.CEJ.2015.08.097.

[6] C.D. Adams, P.A. Scanlan, N.D. Secrist, Oxidation and biodegradability enhancement of 1, 4-dioxane using hydrogen peroxide and ozone, Environ. Sci. Technol. 28 (1994) 1812–1818.

[7] H. Barndõk, D. Hermosilla, C. Negro, Á. Blanco, Comparison and Predesign Cost Assessment of Different Advanced Oxidation Processes for the Treatment of 1,4-Dioxane-Containing Wastewater from the Chemical Industry, ACS Sustain. Chem. Eng. 6 (2018) 5888–5894. doi:10.1021/acssuschemeng.7b04234.

[8] M.P. Rayaroth, D. Oh, C.S. Lee, Y.G. Kang, Y.S. Chang, In situ chemical oxidation of contaminated groundwater using a sulfidized nanoscale zerovalent iron–persulfate system: Insights from a box-type study, Chemosphere. 257 (2020) 127117. doi:10.1016/j.chemosphere.2020.127117.

[9] S. Sonawane, K. Fedorov, M.P. Rayaroth, G. Boczkaj, Degradation of 1,4-dioxane by sono-activated persulfates for water and wastewater treatment applications, Water Resour. Ind. 28 (2022) 100183. doi:10.1016/J.WRI.2022.100183.

[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.

[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.

[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.

[13] N. Takahashi, T. Hibino, H. Torii, S. Shibata, S. Tasaka, J. Yoneya, M. Matsuda, H. Ogasawara, K. Sugimoto, T. Fujioka, Evaluation of O3/UV and O3/H2O2 as Practical Advanced Oxidation Processes for Degradation of 1,4-Dioxane, Ozone Sci. Eng. 35 (2013) 331–337. 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.

[15] H. Chen, J. Wang, Degradation and mineralization of ofloxacin by ozonation and peroxone (O3/H2O2) process, Chemosphere. 269 (2020) 128775. doi:10.1016/j.chemosphere.2020.128775.

[16] I. Epold, N. Dulova, Y. Veressinina, M. Trapido, Application of Ozonation, UV Photolysis, Fenton Treatment and other Related Processes for Degradation of Ibuprofen and Sulfamethoxazole in Different Aqueous Matrices, J. Adv. Oxid. Technol. 15 (2012) 354–364. doi:doi:10.1515/jaots-2012-0215.

[17] M. Gągol, A. Przyjazny, G. Boczkaj, Highly effective degradation of selected groups of organic compounds by cavitation based AOPs under basic pH conditions, Ultrason. Sonochem. 45 (2018) 257–266. doi:10.1016/j.ultsonch.2018.03.013.

[18] G. Boczkaj, A. Fernandes, P. Makoś, Study of Different Advanced Oxidation Processes for Wastewater Treatment from Petroleum Bitumen Production at Basic pH, Ind. Eng. Chem. Res. (2017). doi:10.1021/acs.iecr.7b01507.

[19] G. Boczkaj, A. Fernandes, Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review, Chem. Eng. J. 320 (2017) 608–633.

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, Environ. Res. 200 (2021) 111371. doi:10.1016/J.ENVRES.2021.111371.

[21] A. Eslami, F. Mehdipour, K.Y.A. Lin, H. Sharifi Maleksari, F. Mirzaei, F. Ghanbari, Sono-photo activation of percarbonate for the degradation of organic dye: The effect of water matrix and identification of by-products, J. Water Process Eng. 33 (2020) 100998. doi:10.1016/J.JWPE.2019.100998.

[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. doi:10.1016/J.SCITOTENV.2021.149382.

[23] Z. Miao, X. Gu, S. Lu, X. Zang, X. Wu, M. Xu, L.B.B. Ndong, Z. Qiu, Q. Sui, G.Y. Fu, Perchloroethylene (PCE) oxidation by percarbonate in Fe2+-catalyzed aqueous solution: PCE performance and its removal mechanism, Chemosphere. 119 (2015) 1120–1125. doi:10.1016/J.CHEMOSPHERE.2014.09.065.

[24] X. Zang, X. Gu, S. Lu, Z. Miao, X. Zhang, X. Fu, G.Y. Fu, Z. Qiu, Q. Sui, Enhanced degradation of trichloroethene by sodium percarbonate activated with Fe(II) in the presence of citric acid, 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. 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. 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
639 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 Site-
642 selective Oxidizing Agent of Guanine in Double-stranded Oligonucleotides *, J. Biol. Chem. 276
643 (2001) 24621–24626. doi:10.1074/jbc.M101131200.
644 [31] J.S. Moore, G.O. Phillips, A. Sosnowski, Reaction of carbonate radical anion with substituted
645 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.
654 [35] B.C. Hodges, E.L. Cates, J.-H. Kim, Challenges and prospects of advanced oxidation water
655 treatment processes using catalytic nanomaterials, Nat. Nanotechnol. 13 (2018) 642–650.
656 doi:10.1038/s41565-018-0216-x.
657 [36] K. Fedorov, K. Dinesh, X. Sun, R. Darvishi Cheshmeh Soltani, Z. Wang, S. Sonawane, G.
658 Boczkaj, Synergistic effects of hybrid advanced oxidation processes (AOPs) based on
659 hydrodynamic cavitation phenomenon – A review, Chem. Eng. J. 432 (2022) 134191.
660 doi:10.1016/J.CEJ.2021.134191.
661 [37] E. Cako, R. Darvishi Cheshmeh Soltani, X. Sun, G. Boczkaj, Desulfurization of raw naphtha cuts

using hybrid systems based on acoustic cavitation and advanced oxidation processes (AOPs), Chem. Eng. J. 439 (2022) 135354. doi:10.1016/J.CEJ.2022.135354.

[38] A.J. Barik, P.R. Gogate, Hybrid treatment strategies for 2,4,6-trichlorophenol degradation based on combination of hydrodynamic cavitation and AOPs, Ultrason. Sonochem. 40 (2018) 383–394. doi:10.1016/j.ultsonch.2017.07.029.

[39] K. Fedorov, X. Sun, G. Boczkaj, Combination of hydrodynamic cavitation and SR-AOPs for 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 Intensif. 71 (2013) 59–69. doi:10.1016/j.cep.2013.03.001.

[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. doi:10.1016/J.CEP.2018.04.010.

[42] M. Dular, T. Griessler-Bulc, I. Gutierrez-Aguirre, E. Heath, T. Kosjek, A. Krivograd Klemenčič, M. Oder, M. Petkovšek, N. Rački, M. Ravnikar, A. Šarc, B. Širok, M. Zupanc, M. Žitnik, B. Kompare, Use of hydrodynamic cavitation in (waste)water treatment, Ultrason. Sonochem. 29 (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. doi:10.1002/jssc.201701464.

[44] B. Wang, H. Su, B. Zhang, Hydrodynamic cavitation as a promising route for wastewater 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. doi:10.1016/J.CEJ.2018.01.049.

[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.
699 [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.
705 [51] S.D. Patton, M.C. Dodd, H. Liu, Degradation of 1,4-dioxane by reactive species generated during
706 breakpoint chlorination: Proposed mechanisms and implications for water treatment and reuse, J.
707 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.
713 [54] X. Yu, M. Kamali, P. Van Aken, L. Appels, B. Van der Bruggen, R. Dewil, Synergistic effects of
714 the combined use of ozone and sodium percarbonate for the oxidative degradation of dichlorvos, J.
715 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

(Peroxone Process): A Revision of Current Mechanistic Concepts Based on Thermokinetic and Quantum-Chemical Considerations, Environ. Sci. Technol. 44 (2010) 3505–3507. doi:10.1021/es100277d.

[57] S. Tang, D. Yuan, Y. Rao, M. Li, G. Shi, J. Gu, T. Zhang, Percarbonate promoted antibiotic decomposition in dielectric barrier discharge plasma, J. Hazard. Mater. 366 (2019) 669–676. doi:10.1016/J.JHAZMAT.2018.12.056.

[58] H. Guo, D. Li, Z. Li, S. Lin, Y. Wang, S. Pan, J. Han, Promoted elimination of antibiotic sulfamethoxazole in water using sodium percarbonate activated by ozone: Mechanism, degradation pathway and toxicity assessment, Sep. Purif. Technol. 266 (2021) 118543. doi:10.1016/J.SEPPUR.2021.118543.

[59] P. Yan, Q. Sui, S. Lyu, H. Hao, H.F. Schröder, W. Gebhardt, Elucidation of the oxidation mechanisms and pathways of sulfamethoxazole degradation under Fe(II) activated percarbonate treatment, Sci. Total Environ. 640–641 (2018) 973–980. doi:10.1016/J.SCITOTENV.2018.05.315.

[60] Y. Xiao, X. Liu, Y. Huang, W. Kang, Z. Wang, H. Zheng, Roles of hydroxyl and carbonate radicals in bisphenol a degradation via a nanoscale zero-valent iron/percarbonate system: influencing factors and mechanisms, RSC Adv. 11 (2021) 3636–3644. doi:10.1039/D0RA08395J.

[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. doi:https://doi.org/10.1016/j.jwpe.2017.06.015.

[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. doi:https://doi.org/10.1016/j.cej.2012.01.107.

[63] J.C. Crittenden, S. Hu, D.W. Hand, S.A. Green, A kinetic model for H2O2/UV process in a completely mixed batch reactor, Water Res. 33 (1999) 2315–2328. doi:https://doi.org/10.1016/S0043-1354(98)00448-5.

[64] J. Gao, X. Duan, K. O'Shea, D.D. Dionysiou, Degradation and transformation of bisphenol A in UV/Sodium percarbonate: Dual role of carbonate radical anion, Water Res. 171 (2020) 115394. doi:10.1016/J.WATRES.2019.115394.

[65] A.L. Teel, R.J. Watts, Degradation of carbon tetrachloride by modified Fenton's reagent, J.

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

778 of coexisting anions, Chem. Eng. J. 416 (2021) 129163. doi:10.1016/J.CEJ.2021.129163.
779 [76] M.I. Stefan, J.R. Bolton, Mechanism of the Degradation of 1,4-Dioxane in Dilute Aqueous
780 Solution Using the UV/Hydrogen Peroxide Process, Environ. Sci. Technol. 32 (1998) 1588–1595.
781 doi:10.1021/es970633m.
782 [77] H. Barndõk, D. Hermosilla, C. Han, D.D. Dionysiou, C. Negro, Á. Blanco, Degradation of 1,4-
783 dioxane from industrial wastewater by solar photocatalysis using immobilized NF-TiO2 composite
784 with monodisperse TiO2 nanoparticles, Appl. Catal. B Environ. 180 (2016) 44–52.
785 doi:10.1016/J.APCATB.2015.06.015.
786 [78] B. Li, J. Zhu, Simultaneous degradation of 1,1,1-trichloroethane and solvent stabilizer 1,4-dioxane
787 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
790 technologies for biodiesel production and processing of hydrocarbon streams: A perspective on
791 key fundamentals, missing process data and economic feasibility – A review, Ultrason. Sonochem.
792 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
800 thiamethoxam abatement by ozonation and ozone-based advanced oxidation processes, J. Hazard.
801 Mater. 390 (2020) 122180. doi:10.1016/J.JHAZMAT.2020.122180.
802 [83] H. Wang, S. Yuan, J. Zhan, Y. Wang, G. Yu, S. Deng, J. Huang, B. Wang, Mechanisms of
803 enhanced total organic carbon elimination from oxalic acid solutions by electro-peroxone process,
804 Water Res. 80 (2015) 20–29. doi:10.1016/J.WATRES.2015.05.024.
805 [84] Y. Li, D. Wang, G. Yang, X. Yuan, L. Yuan, Z. Li, Q. Xu, X. Liu, Q. Yang, W. Tang, L. Jiang, H.
806 Li, Q. Wang, B. Ni, In-depth research on percarbonate expediting zero-valent iron corrosion for

807 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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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: