










## Hydrodynamic cavitation-enhanced activation of sodium percarbonate for estrogen removal

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### ABSTRACT

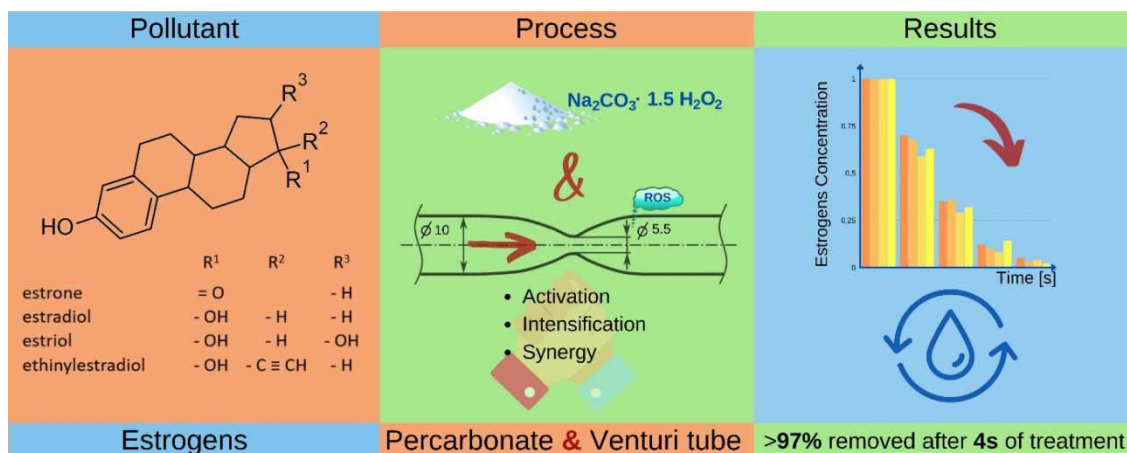
The present paper investigated the potential of hydrodynamic cavitation (HC) as an effective tool for activating sodium percarbonate (SPC). The method's efficiency was demonstrated by effectively removing estrogens, which are pollutants that have adverse impacts on aquatic ecosystems. The effects of the SPC concentration, temperature of solution, and cavitation time were evaluated. After SPC/HC treatment, the removal of estrogens was monitored by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Already after 4 s of treatment and 24 h of reaction time, more than 97% of estrogens (initial concentration of 300 ng/L) were removed. The effect of post-treatment time is not considered in several papers, even though it seems to be crucial and is discussed here. The results were supported by the values of degradation rate constants, which fit the pseudo-first-order kinetic model. We also verified that HC alone was not effective for estrogen removal under the selected conditions. The sustainability of the SPC/HC system was evaluated based on electric energy per order calculation. The combination of SPC and HC is a promising approach for rapidly degrading micropollutants such as estrogenic compounds without the need for additional technological steps, such as pH or temperature adjustment.

**Key words:** activation, estrogen, hydrodynamic cavitation, organic pollutants, sodium percarbonate, water treatment

### HIGHLIGHTS

- A novel method of SPC activation by HC.
- Fast, effective, and environmentally friendly removal of estrogens.
- Practical technology capable of treating tens of m<sup>3</sup> per hour.
- The method is applicable to a broad spectrum of organic pollutants.

## GRAPHICAL ABSTRACT



## INTRODUCTION

Estrogens such as naturally occurring estrone (E1), 17 $\beta$ -estradiol (E2), and estriol (E3), as well as the synthetic 17 $\alpha$ -ethinylestradiol (EE2), are contaminants that are causing particular environmental concern (Kuster *et al.* 2004, 2008; Meffe & de Bustamante 2014; Barreiros *et al.* 2016). They represent one group of so-called endocrine-disrupting chemicals, compounds altering the function of the endocrine system, and consequently have adverse health effects on intact organisms even at ng/L levels (Lafont & Mathieu 2007; Pessoa *et al.* 2014; Adeel *et al.* 2017; Vilela *et al.* 2018). Therefore, the European Decision E.U. 2015/495 included E1, E2, and EE2 in the 'watch-list' of the Water Framework Directive (E.U.). Estrogens enter the environment through insufficient wastewater treatment and animal waste disposal (Sarmah *et al.* 2006; Atkinson *et al.* 2012; Tiedeken *et al.* 2017). The typical concentrations of these substances in wastewater treatment plant effluents and surface water can reach up to tens ng/L (Meffe & de Bustamante 2014; Adeel *et al.* 2017), but occasionally they can exceed 500 ng/L (Tiedeken *et al.* 2017). As the conventional methods of estrogen removal fail, other processes, including sorption, membrane filtration, biodegradation, photolysis, and advanced oxidation processes (AOPs), have been investigated (Rosenfeldt *et al.* 2007; Pereira *et al.* 2012; Silva *et al.* 2012).

Recently, the AOPs have been used in advanced water treatment processes as an efficient, rapid, and simple technology. During AOPs, oxygen radicals such as hydroxyl radicals ( $\cdot\text{OH}$ ) (Miklos *et al.* 2018) or sulfate radicals (Wen *et al.* 2022) are formed, as highly reactive species that interact usually unselectively with target molecules, in quantity sufficient to oxidize the majority of organic pollution present. These technologies involve different activation methods and can potentially utilize several diverse mechanisms. The AOPs could be broadly classified into chemical (e.g.  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  and persulfate), photolytic (e.g. ultra violet (UV)/oxidant or UV/photocatalyst), electrochemical (e.g.  $\text{TiO}_2$  electrodes), catalytic (e.g. Fenton process), and physical (e.g. ultrasound, plasma discharge, microwave) or combinations of them. Each of these particular techniques has its benefits and drawbacks, including the formation of toxic transformation products, which can have similar or increased toxicity relative to the parent compounds (Tufail *et al.* 2021). Thus, to overcome the drawbacks or increase the efficiency of pollution degradation, the use of combinations of different mechanisms is advantageous (Silva *et al.* 2012; Tufail *et al.* 2020). In addition to effectiveness, the operational costs, sustainability, and general feasibility are definitely of great importance.

Sodium percarbonate (SPC;  $\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$ ), as a solid carrier of  $\text{H}_2\text{O}_2$ , acts similarly and has several advantages compared to the liquid phase. The main benefits are its stability and safe handling, its environmentally nature with no toxic residues, effectiveness across a wide pH range, and its relatively low cost (Ma *et al.* 2020; Zhang *et al.* 2021). In addition, SPC decomposition products ( $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ) can act as a buffer for an undesired pH decrease. Although SPC can directly decompose various pollutants, catalyst or energy activation enhances the degradation efficiency. In an activated SPC system, hydroxyl, superoxide, and carbonate radicals are generated (Zhang *et al.* 2021). In order to activate the SPC, various chemicals such as transition metal ions, ozone, and  $\text{FeOCl}$  (Miao *et al.* 2015; Fu *et al.* 2016, 2017; Guo *et al.* 2021) and physical approaches such as discharge plasma (Wang *et al.* 2018; Tang *et al.* 2019), UV light (Sindelar *et al.* 2014), and microwaves

(Zuo *et al.* 2020) were tried. The combination of chemical and physical methods seems to be a reasonably promising and effective method of degrading pollutants.

Hydrodynamic cavitation (HC) belongs to the up-and-coming physical methods of AOPs (Zupanc *et al.* 2013; Dular *et al.* 2016; Marsalek *et al.* 2020; Panda *et al.* 2020). HC occurs when water is forced through a tapering device (Venturi tube, orifice plate, or convergent-divergent nozzle). The gaseous microbubbles are formed after liquid passing through the constriction because of a drop in local pressure. Subsequently, these cavities collapse violently downstream due to the pressure recovery. This phenomenon is accompanied by an increase in local temperature, causing water molecules to dissociate and form reactive oxygen species (Zheng *et al.* 2022). Combining HC with other AOPs is quite a novel approach and offers several advantages, such as higher degradation efficiencies, cost effectiveness, and a reduction in chemicals utilized which means lower environmental impact (Wang *et al.* 2021). The combination of HC and SPC has been proven to degrade lignocellulose in corn stovers (Nakashima *et al.* 2016). Most recently, the HC was used as an activator in a hybrid system of SPC and ozone to remove 1,4-dioxane (Fedorov *et al.* 2023).

This paper studies the degradation of estrogens using SPC activated by HC. We hypothesized that HC could promote the dissolution rate and activate the SPC without any further activation by heating or adding chemicals. Such a process should be more economically convenient and environmentally acceptable. The work focuses on optimizing the new treatment technology for removing organic micropollutants in treated wastewater, especially on the effects of SPC dosage, the number of cavitation cycles (time), and the temperature.

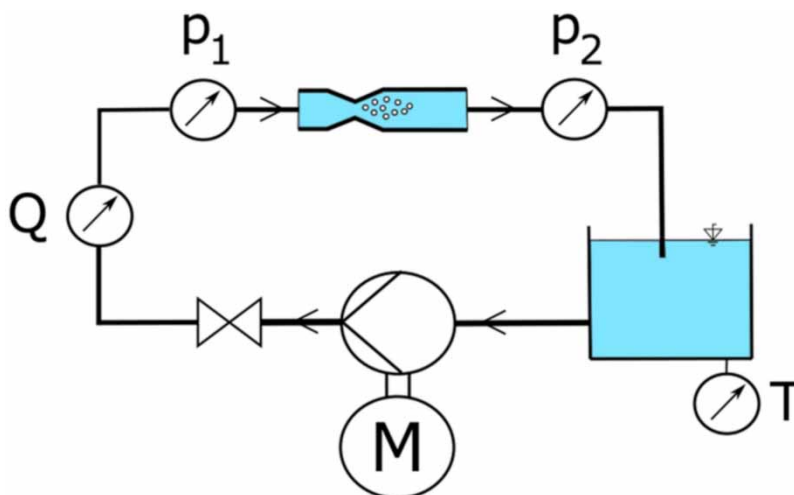
## MATERIALS AND METHODS

### Chemicals and materials

Standard compounds of estrone ( $\geq 99\%$ ),  $17\beta$ -estradiol ( $\geq 98\%$ ), estriol ( $\geq 98\%$ ), and  $17\alpha$ -ethinylestradiol ( $\geq 98\%$ ), as well as all solvents and reagents, were purchased from Sigma-Aldrich (St. Louis, MO, USA). Internal standards  $17\beta$ -estradiol- $d_4$  and  $17\alpha$ -ethinylestradiol- $d_4$  were acquired from C/D/N Isotopes Inc. (Pointe-Claire, Quebec, Canada). All standards were prepared in HPLC-grade methanol. Methanol, acetonitrile, and acetone (HPLC grade), formic acid, hydrochloric acid, SPC (sesquihydrate, available in  $H_2O_2$  20–30%), titanium (IV) oxysulfate in a sulfuric acid solution, dansyl chloride, and sodium bicarbonate were used.

### Degradation experiments

The experiments were carried out on a hydraulic circuit (see Figure 1), which consisted of an opened tank, a centrifugal pump driven by an electric motor (Calpeda BTM 70/A, 0.75 kW) and a plexiglass Venturi tube ( $d_1 = 10$  mm outer diameter and  $d_2 = 5.5$  mm inner diameter), and convergent-divergent sections were smoothly connected by spline-like and control valve. The circuit was operated in a circular mode at a flow rate of 0.5 L/s having an inlet pressure of 450 kPa. Flow ( $Q$ ) is measured



**Figure 1** | Hydraulic circuit with the Venturi tube ( $p_1$ ,  $p_2$  – pressure sensors;  $Q$  – flowmeter;  $T$  – thermometer).

using a FLOMAG DN10 magnetic-induction flowmeter, with pressure readings taken upstream ( $p_1$ ) and downstream ( $p_2$ ) using a DMP331 pressure sensor by BD Sensors, and the temperature is measured using a HSO-502 1A2L thermometer by HIT.

The operating point is characterized by the cavitation number ( $\sigma$ ), which is defined according to the following equation:

$$\sigma = (p_2 - p_{\text{vapor}}) / (\rho \cdot (v_T^2 / 2)) \quad (1)$$

where  $p_2$  (Pa) is the downstream pressure,  $v_T$  (m/s) is the velocity in the throat section of the Venturi tube,  $\rho$  is a liquid density ( $\text{kg/m}^3$ ), and  $p_{\text{vapor}}$  (Pa) is the saturated vapor pressure, and its value is determined as a function of the measured temperature according to the International Association for the Properties of Water and Steam (IAPWS) polynomial fit. The operating point was kept as close as possible to  $\sigma = 0.95$  for all experimental runs.

The tank was filled with 2 L of the aqueous solution containing 300 ng/L of each estrogen. The SPC in concentrations of 80 and 200 mg/L was added. Neither the ionic strength nor the pH of the solutions was adjusted to minimize operating steps, so that the procedure remained economical and suitable for practical implementation. The pH value, temperature, and conductivity were measured by the Combo pH/EC meter (Hanna, HI 98129). After collection, the samples were left to stand for 3 and 24 h before the LC-MS/MS analysis.

The degradation constant ( $k$ ) of estrogens was obtained by fitting the data to the kinetic model of pseudo-first-order (Sun *et al.* 2019; Perondi *et al.* 2020).

$$-\ln(C_t/C_0) = k \cdot t \quad (2)$$

where  $C_0$  and  $C_t$  represent here the initial and actual concentrations (ng/L) at time  $t$  (min), respectively, and  $k$  is the constant rate of pseudo-first-order ( $\text{min}^{-1}$ ).

### LC-MS/MS analysis

Prior to analysis, the estrogens were extracted from water samples using SPE Oasis<sup>®</sup> HLB (500 mg, 6 mL) cartridges (Waters, Milford, MA, USA) according to Sadilek *et al.* (2016) with slight changes (for more details, see Supplementary Material, p. S2).

In this study, the Agilent 1260 Infinity high-performance liquid chromatography system (Agilent Technologies, CA, USA) combined with the Agilent 6460 TripleQuad mass spectrometer (Agilent Technologies, CA, USA) equipped with electrospray ionization interface were used for estrogen quantification. The separation was achieved using Poroshell 120 EC-C18 ( $2.1 \times 100$  mm;  $2.7 \mu\text{m}$ ) fitted with a security guard column of the same packing material (Agilent Technologies, CA, USA). The mobile phases A and B consisted of formic acid (7 mM) and acetonitrile, respectively. A gradient raising the acetonitrile from 50 to 100% in 10 min, then held for 1 min, was used. The flow rate was  $350 \mu\text{L}/\text{min}$ , and the injection volume was  $10 \mu\text{L}$ . Mass data were acquired using the MassHunter Workstation software (Agilent Technologies, CA, USA) with multiple reaction monitoring (MRM) in the positive mode. The detector settings were capillary voltage 3,500 V, nozzle voltage 2,000 V, gas temperature ( $\text{N}_2$ )  $200^\circ\text{C}$ , gas flow  $10 \text{ mL}/\text{min}$ , nebulizer 50 psi, sheath gas temperature ( $\text{N}_2$ )  $350^\circ\text{C}$ , and sheath gas flow  $10 \text{ mL}/\text{min}$ . MRM transitions of protonated dansyl-derivatives to 171 and 156 were used for the quantification and qualification of the estrogens.

### Content of hydrogen peroxide

The colorimetric method previously described was used to determine the content of hydrogen peroxide (Eisenberg 1943). This method is based on a specific reaction between hydrogen peroxide and titanil ions, resulting in a yellow complex of per-titanic acid with absorption maxima at 407 nm. The sample was mixed with the titanium reagent in a ratio of 2:1 (sample: reagent, v/v), and the absorbance was measured using a Spark<sup>™</sup> multimode microplate reader (Tecan, Austria).

### Statistical analysis

Statistical analyses were performed using GraphPad Prism 7.04 (GraphPad Software Inc., CA, USA). A  $t$ -test was used to determine the differences between individual groups of samples. A probability level of  $p < 0.05$  was considered statistically significant. All data are represented as mean  $\pm$  SD of relative concentrations (related to the initial concentration).

## RESULTS AND DISCUSSION

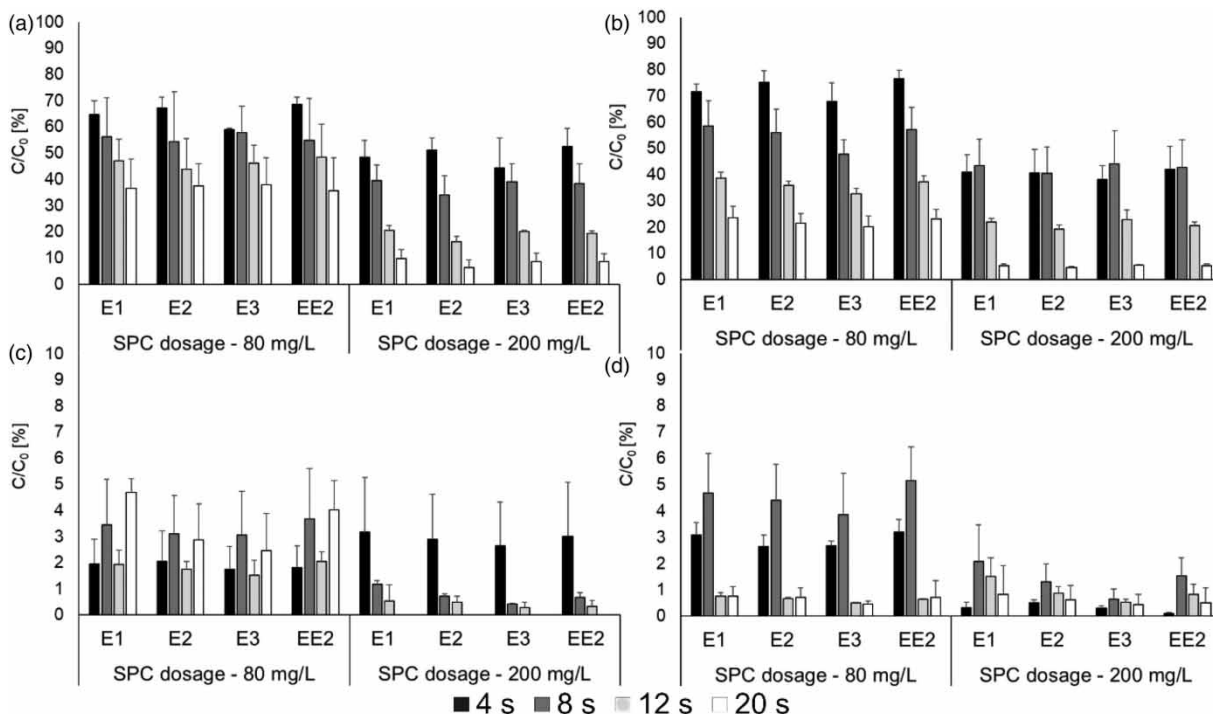
### Effect of SPC dosage

We assessed the estrogen removal using two concentrations of SPC, at 80 and 200 mg/L, which correspond to 20 and 50 mg/L of  $H_2O_2$ . The experiments were performed in deionized water at laboratory temperature ( $T = 21.9^\circ C$ ). The treating time was set up to 4, 8, 12, and 20 s, which corresponds to 1, 2, 3, and 5 passages through the cavitation device. The effect of the SPC dosage on estrogen degradation is graphically illustrated at room temperature in Figure 2(a) and at an elevated temperature of  $60^\circ C$  in Figure 2(b).

It is evident from Figure 2 that a higher SPC concentration increased the estrogen degradation rate, especially after a longer period of cavitation. With increasing cavitation time from 4 to 20 s, the estrogen degradation went from 31 to 62% once 80 mg/L of SPC was added. Furthermore, the degradation increased from 47 to 90% when 200 mg/L of SPC was used. The observation was supported by comparing degradation rate constants (see Table 1 and Figure S1). The increase in the amount of SPC more than doubled the corresponding kinetic constants.

As SPC was used for estrogen removal for the first time in this study, we compared our results with the corresponding dose of liquid  $H_2O_2$  used by other authors. For example, Perondi *et al.* (2020) employed a combination of  $H_2O_2$  (15 mg/L) and UV to remove E2 from surface water, and they obtained constants that were 100 times lower than those reached in our experiments. In that case, 60 min of treatment was needed to remove 89% of E2. In another study, Sun *et al.* (2019) combined  $H_2O_2$  (0.7 mg/L) with 2.5 mg of  $O_3$  to remove E1, E2, and EE2. They generated ozone from high-purity oxygen and reached the estrogen removal efficiency of 89.7, 84.5 and 90.5% for E1, E2, and EE2 after 10 min treatment with reaction rate constants of 0.18, 0.22, and  $0.24 \text{ min}^{-1}$ , respectively. Our experiments achieved 90% removal using 200 mg/L of SPC (equal to 50 mg/L of  $H_2O_2$ ) in 20 s treatment without any ozone needed. Other studies focusing on eliminating estrogens using  $H_2O_2$ -based methods are given in Table 2.

The oxidation process of estrogens involves the orbitally controlled reactions that are initiated by an attack on the aromatic ring (C3, C4, and C5 positions). The OH functional group of estrogens can also be oxidized (to the carbonyl group by



**Figure 2** | Decrease in estrogen content at different SPC/HC treatment conditions and post-treatment time (a) SPC/HC; post-treatment time = 3 h (b) SPC/HC +  $60^\circ C$ ; SPC heated to  $60^\circ C$ ; post-treatment time = 3 h (c) SPC/HC; post-treatment time = 24 h (d) SPC/HC +  $60^\circ C$ ; post-treatment time = 24 h. All experiments were conducted without pH adjustment. Data represent mean over three repetitions and standard deviations are indicated by whiskers. The initial concentration of estrogens was 300 ng/L.

**Table 1** | The pseudo-first-rate constants of estrogens degradation;  $r > 0.97$ 

Conditions	$k_{E1}$ ( $\text{min}^{-1}$ )	$k_{E2}$ ( $\text{min}^{-1}$ )	$k_{E3}$ ( $\text{min}^{-1}$ )	$k_{EE2}$ ( $\text{min}^{-1}$ )
SPC/HC (80 mg/L)	3.41	3.46	3.38	3.42
SPC/HC (80 mg/L; 60°C)	4.42	4.69	5.10	4.49
SPC/HC (200 mg/L)	7.27	8.44	7.58	7.59
SPC/HC (200 mg/L; 60°C)	8.41	8.89	8.26	8.43

**Table 2** | Estrogen removal using the H<sub>2</sub>O<sub>2</sub>-based method

Method	Estrogen	Efficiency	Reference
UV/H <sub>2</sub> O <sub>2</sub> (25 mg/L)	EE2 (1,000 µg/L)	>99% in 60 min	Silveira <i>et al.</i> (2022)
UV/H <sub>2</sub> O <sub>2</sub> (15 mg/L)	E2 (200 µg/L)	89% in 60 min	Perondi <i>et al.</i> (2020)
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> (2.5 mg/0.7 mg/L)	E1, E2, EE2 (50 µg/L)	>85% in 10 min	Sun <i>et al.</i> (2019)
UV/H <sub>2</sub> O <sub>2</sub> (5 mM)	E1, E2, EE2 (5 µM)	99% in 45 min	Gabet <i>et al.</i> (2021)
UV/H <sub>2</sub> O <sub>2</sub> (3 mg/L)	E2, EE2 (100 µg/L)	>99% in 10 min	Chaves <i>et al.</i> (2020)
UV/H <sub>2</sub> O <sub>2</sub> (15 mg/L)	E1, E2, EE2 (50 µg/L)	>76% in 50 min	Ma <i>et al.</i> (2015)
Fe-III-TAML/H <sub>2</sub> O <sub>2</sub> (4 mM)	EE2 (10 µM)	>99% in 20 min	Chen <i>et al.</i> (2012)
SPC/HC (~20 mg/L H <sub>2</sub> O <sub>2</sub> )	E1, E2, E3, EE2 (300 ng/L)	97% in 4 s	This study

TAML, tetra-amido macrocyclic ligands.

deprotonation) (Rokhina & Suri 2012). Due to incomplete mineralization, the transformation products can be formed during the AOP processes. An overview of possible transformation products is summarized in the literature (Pereira *et al.* 2011; Perondi *et al.* 2020). Cedat *et al.* (2016) tested the removal of E1, E2, and EE2 in the mixture using the UV/H<sub>2</sub>O<sub>2</sub> process. Alongside the degradation rate constants of hormones, they also measured the estrogenic activity removal rate constants. They found that they are in the same range, suggesting that no high estrogenic or toxic by-products (tested on *Vibrio fischeri*) were formed during the oxidation process. Contrarily, Silveira *et al.* (2022) used *Ceriodaphnia silvestrii* as the test organism for the toxicity assay after UV-assisted peroxidation of EE2 and demonstrated the likelihood of an acute effect occurring in the aquatic environment. Therefore, before considering a full-scale pilot, the ecotoxicological evaluation should also be a part of the process.

Our previous study (Pribilova *et al.* 2022) investigated the synergy of HC and sodium persulfate (0.1 mM). We obtained similar results regarding the efficiency of estrogen degradation (Table S1) and electric energy per order (EEO) under the same operating conditions (see the SPC activation section for details), but the rate constants were 2–3 times lower. In that case, sulfur-based radicals were also involved in estrogen degradation.

The pH and conductivity of the solutions were also monitored throughout the process (Figure S2). After the addition of SPC at a dose of 80 mg/L, the pH of the solution averaged 9.5 and dropped to 9.1 after a 20-s treatment. A slight decrease was also observed when a dose of 200 mg/L was used; in this case, the initial pH value was 10.2 and dropped to 10.0. Such high values could pose a potential risk to the environment, but it should be noted that the experiments were conducted in distilled water. Moreover, in real wastewater, the buffering capacity of SPC could be an advantage.

In SPC-based AOP, hydroxyl radicals are usually confirmed to be the primary reactive species coming from the cleavage of H<sub>2</sub>O<sub>2</sub> (Li *et al.* 2023). In an alkaline solution, H<sub>2</sub>O<sub>2</sub> decomposes via a reaction with OH<sup>-</sup> to form a hydroperoxide ion (HO<sub>2</sub><sup>-</sup>), which reduces another H<sub>2</sub>O<sub>2</sub> to form O<sub>2</sub> and OH<sup>-</sup> (Equations (3) and (4)) (Ma *et al.* 2018).



Thus, the solution's pH affects the decomposition efficiency by changing the concentration of hydrogen and hydroxides, which affects the formation of free radicals. Moreover, the oxidation potential of hydroxyl radicals is pH dependent and

decreases from 2.8 V at pH = 3.0 to 1.5 V in basic conditions. However, the coexisting carbonate ions in SPC show significant potential in converting OH<sup>•</sup> into other reactive species and compensating for the radical quenching effect caused by HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>. Ma *et al.* (2018) showed that HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> has additional activating effects on H<sub>2</sub>O<sub>2</sub> and increases its oxidation potency via reactive peroxymonocarbonate (HCO<sub>4</sub><sup>-</sup>) formation. The generated HCO<sub>4</sub><sup>-</sup> would undergo homolysis of the O – O bond to further give rise to OH<sup>•</sup>, O<sub>2</sub><sup>-</sup>, CO<sub>3</sub><sup>-</sup>, HO<sub>2</sub><sup>•</sup>, and <sup>1</sup>O<sub>2</sub> (Equations (5)–(10)).

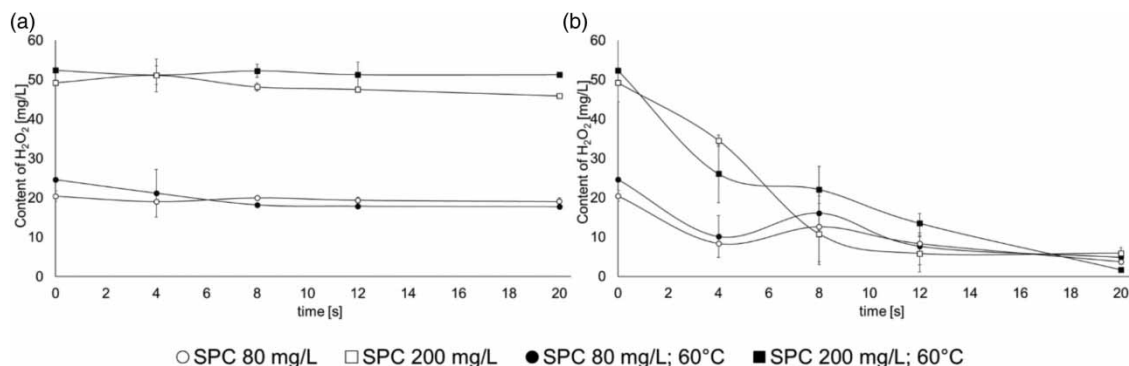


### Effect of temperature

Liu *et al.* stated in their review (Liu *et al.* 2021) that temperature is a key parameter affecting the efficiency of the SPC-activated system. Therefore, we examined the effect of temperature on SPC activation. Our results showed no significant impact on estrogen removal when the solution of SPC was heated to 60°C and combined with HC (compare Figure 2(a) and 2(b)). Similarly, the observation was confirmed by the values of the rate constants, which increased moderately with increased temperature (see Table 1). However, the differences between the individual rate constants ranged from 0.45 to 1.72 min<sup>-1</sup>. In contrast, Ma *et al.* (2018) found that sole SPC is highly affected by increased temperature. They observed that as the temperature increased from 4 to 30°C, the peroxide rate constants increased by two orders of magnitude (from 8.26 × 10<sup>-3</sup> to 7.69 × 10<sup>-1</sup> h<sup>-1</sup>). The difference we observed can be most probably explained by the fact that during the process of HC, high local temperatures (up to 5,000 K; Zupanc *et al.* 2013) occur; thus, the influence of solution temperature is negligible. This could be advantageous since water treatment operates under different weather and temperature conditions (depending on the season). Additionally, the duration of our whole process is so short, as it took place in units of tens of seconds, and thus, it was not affected by the temperature of the solution.

### Effect of reaction time after SPC/HC

Our study examined the effect of subsequent degradation reactions after SPC/HC, where the estrogen content was evaluated after standing for 24 h in laboratory conditions. Our results show that giving the reaction enough time to take place significantly impacts the removal efficiency. As shown in Figure 2 (see Figure 2(c) and 2(d)), the process of estrogen degradation continued over time, and their concentration was subsequently reduced to 5% or less of the initial one. The representative chromatograms of each estrogen can be seen in Figure S3–S5. Correspondingly, we observed a sharp decrease in peroxide content (Figure 3), which dropped dramatically after 24 h. Moreover, after 24 h of post-treatment time using 80 mg/L of SPC and 4 s of cavitation, we detected only trace estrogen concentrations (near the limit of quantification) using LC-MS/MS. These results highlighted the importance of post-treatment processes. It is rarely discussed that molecules such as pharmaceuticals or estrogenic compounds, as in this case, do not need further treatment, or a higher concentration of chemicals or energy, which is problematic for economic or ecological reasons, but need just the post-reaction time to degrade substances successfully. This fact is not properly discussed in the scientific literature, but contrary, the majority of experiments are measured and evaluated just a few hours after treatment. Looking at the results presented in Figure 2, it is clear that the degradation of estrogenic compounds and probably also other organic compounds can react with hydrogen peroxide for a longer time, which is supported also by Figure 3, proving that hydrogen peroxide concentration decreases after 24 h but only slightly 3 h after treatment. We would like to open a discussion on the processes going on during this time as well as the practical point of view, like saving the treatment chemicals and energy needed for AOPs. In practice, a holding tank could then be included behind the cavitation unit to allow the reaction mixture to react.



**Figure 3** | Content of hydrogen peroxide (in mg/L) measured (a) 3 h after cavitation and (b) 24 h after cavitation. Data represent mean over three repetitions and standard deviations are indicated by whiskers.

### Synergistic effect

In the HC process, the cavity collapse releases a large amount of energy, is accompanied by extremely high local temperatures and pressures, and therefore is supposed to induce reaction enhancement. The HC produces enhanced heat transfer and mass transfer. *Zheng et al. (2022)* have called the cavities ‘microreactors’, in which the trapped molecules thermally decompose during the collapse phase. Besides the physical effects, chemical reactions take place during the HC process. Due to the high energy, water molecules are dissociated and reactive oxygen species are formed. The main reactions involved in this process are as follows (Equations (9) and (10)) (*Amin et al. 2010; Zheng et al. 2022*):



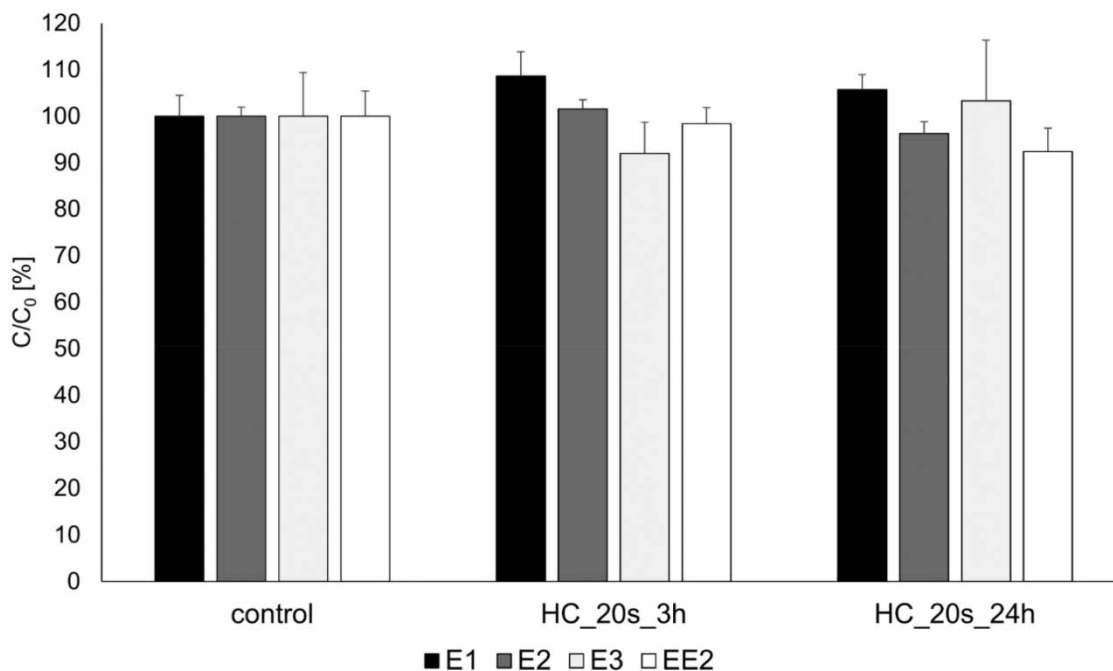
Therefore, we investigated the effectiveness of HC itself on estrogen degradation after the 20-s treatment. The estrogen and hydrogen peroxide content was analyzed at 3 and 24 h after the HC treatment. However, the results from this experiment (shown in *Figure 4*) revealed that the sole HC could not degrade the estrogens. Even though several authors suggest that hydroxyl radicals and, subsequently, hydrogen peroxide are formed during the HC (Equation (10)), the measured values of hydrogen peroxide in our case were 0.2 and 0.3 mg/L after 3 and 24 h, respectively. This is most probably because the HC treatment alone could not produce enough radicals in such a short time (20 s). Thus, in this case, the main benefit of the HC is its physical contribution, such as the intensive mixing of the solution or thermal decomposition of  $\text{H}_2\text{O}_2$  coming from SPC, rather than its direct contribution to the pollutant degradation.

### SPC activation

SPC, calcium percarbonate, or peroxydicarbonate are per-oxo substances, which are used in chemical engineering or water treatment as oxidizing substances. Most commonly, the SPC is used as a solid carrier of hydrogen peroxide because it is considered safer to transport and store, has lower explosive potential than liquid hydrogen peroxide, is suitable for longer storage, and is an environmentally friendly oxidant. It is particularly important for one practical reason: SPC can react in a wide range of pH compared to a broad spectrum of different Fenton-like reactions. The practical use of SPC is supported by the fact that carbonate radicals boost a multiple reactive oxygen species (multi-ROS) process (Equation (5)–(10)), where reactions can generate superoxide radicals, singlet oxygen, or hydroxyl radicals (*Li et al. 2021*). This process was elucidated by *Li et al. (2021)* as the mechanism of SPC activation by  $\text{CuFeS}_2$ . The resulting  $\text{OH}^\cdot$  via the traditional heterogeneous Fenton system reacts with carbonate ions to form additional ROS.

Even though SPC can react with pollutants directly, dominantly due to hydrogen peroxide, to reach the maximum effect of SPC oxidation potential, activated SPC enhances decomposing potential, which is why appropriate SPC activation is recommended. Two types of SPC activation can be differentiated: (i) homogenous and (ii) heterogeneous. Homogenous activation is based on direct contact with reactants, which is typically activated by increased temperature, UV, ozone, microwave, ultrasound, or discharge plasma activation (*Liu et al. 2021*). Heterogeneous activation requires the addition of other chemicals, which is dominantly based on transition metal ions, especially iron. The forms of iron ions depend on the





**Figure 4** | Relative estrogen concentration after 20-s HC, measured 3 and 24 h after treatment. The HC experiments were performed in deionized water ( $\kappa = 2 \mu\text{S}/\text{cm}$ ;  $\text{pH} = 5.58$ ;  $T = 21.6^\circ\text{C}$ ). Data represent the mean of three repetitions and whiskers indicate standard deviations.

technology used and vary from ferrate ( $\text{Fe}^{6+}$ ), through  $\text{Fe}^{2+/3+}$  used in modified Fenton reactions up to nano zero-valent iron (Fu *et al.* 2017; Liu *et al.* 2021). Recently, the degradation of sulfamethazine via the activation of 157 mg/L SPC by 500 mg/L chalcopyrite ( $\text{CuFeS}_2$ ) was published (Li *et al.* 2021). The concentration of SPC used in their study was between the concentrations used in our research. Moreover, the chalcopyrite used in the concentration of 500 mg/L can contaminate water with copper. HC is quite a novel way of homogenous activation of SPC, which does not need any chemicals or expensive activation such as ozone, UV, or heating. HC provides the opportunity to treat realistic volumes of water (the outlet of wastewater treatment plants in tens  $\text{m}^3/\text{h}$ ). HC, in combination with hydrogen peroxide, provides synergic effects (Marsalek *et al.* 2020) and represents a promising tool for the intensification of AOP reactions, particularly for the cheap and environmentally responsible activation of SPC for organic pollutant removal.

Although the SPC/HC system can be easily scaled up, the method's energy consumption and sustainability must be considered before this step. As a comparison tool for different AOP techniques, EEO ( $\text{kWh}/\text{m}^3/\text{order}$ ) is used (Miklos *et al.* 2018). EEO represents the consumption of electric power in kilowatt-hours (kWh) required to reduce a contaminant concentration by one order of magnitude in a unit volume and is independent of pollutant concentration. EEO was calculated as follows:

$$\text{EEO} = P \cdot t \cdot 1,000 / (V \cdot \log(C_0/C_t)) \quad (13)$$

where  $P$  is the rated power of the pump (kW),  $C_0$  and  $C_t$  represent here the initial and actual concentrations (ng/L) at time  $t$  (h), respectively, and  $V$  is the volume (L) of the treated solution. The results for both SPC dosages and 4-s long treatment performed in deionized water with the initial concentration of 300 ng/L are summarized in Table 3.

Other effects of HC also have to be mentioned because they significantly contribute to SPC activation. First, these are high-shear stresses that enhance the disintegration of SPC. The second effect is connected with the multiphase bubbly flow with

**Table 3** | EEO values ( $\text{kWh}/\text{m}^3/\text{order}$ ) of estrogens for 4-s long SPC/HC treatment

SPC dosage	$E_{\text{EO}}$ (E1)	$E_{\text{EO}}$ (E2)	$E_{\text{EO}}$ (E3)	$E_{\text{EO}}$ (EE2)
SPC/HC (80 mg/L)	2.20	2.42	1.81	2.55
SPC/HC (200 mg/L)	1.32	1.43	1.18	1.50

important velocity gradients, which help in the mixing process. It is interesting and important to note that while medium velocity in the Venturi tube throat is around 20 m/s, the bubble wall, during the collapse, moves with velocities higher by two orders of magnitude, and also the velocity of the microjet can reach up to the velocity of sound in liquid medium.

In the case of heat-combined SPC/HC, energy consumption would be higher because the energy of external heating, depending on the heating source, must be considered. According to the calculated values, the SPC/HC system belongs to group 2 (1–100 kWh/m<sup>3</sup>/order); thus, the methods are likely quite energy-intensive for most practical applications, but they might still provide attractive solutions for specific challenges, and full-scale applicability of these processes should be further investigated.

Our experiments showed that activation of SPC via HC is potent and green technology. Although the energy consumption belongs to group 2, the process does not require any other heating, UV radiation, or adding additional chemicals that could burden the environment. However, further experiments evaluating different water matrices should be continued as the experiments were performed in deionized water. The toxicity and estrogenicity tests should also be considered when considering a full-scale pilot.

## CONCLUSIONS

We investigated the possibility of SPC activation via HC and demonstrated its usefulness for the simultaneous degradation of four estrogens: E1, E2, E3, and EE2 in an aqueous solution. By the synergistic action of these two AOP methods, more than 97% of the investigated pollutants were removed. Post-treatment processes played an important role. The experimental results indicated that the proposed treatment method was independent of the solution temperature. All tested estrogens compete to react with the generated radicals because the individual reaction constants were similar. The proposed process is a promising technique for the efficient removal of estrogens from aqueous solution. The advantage of our proposed activation is its low operating costs compared to other combinations, such as the heating of the solution. In addition, this method does not require any additional chemicals, e.g. to adjust pH or increase efficiency, so it does not pose an additional burden on the environment. HC can treat large volumes of water, which is important for any practical applications; thus, we expect that this practical and environmentally safe technology can help clean waters, for example, as the tertiary treatment.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

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