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Rapid AOP Method for Estrogens Removal via Persulfate Activated by Hydrodynamic Cavitation

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Abstract: The production and use of manufactured chemicals have risen significantly in the last few decades. With interest in preserving and improving the state of the environment, there is also growing interested in new technologies for water purification and wastewater treatment. One frequently discussed technological group is advanced oxidation processes (AOPs). AOPs using sulphur-based radicals appear to reduce the volume of organic contaminants in wastewater significantly. The use of persulfate has excellent potential to successfully eliminate the number of emerging contaminants released into the environment. The main disadvantage of sulphur-based AOPs is the need for activation. We investigated an economically and environmentally friendly solution based on hydrodynamic cavitation, which does not require heating or additional activation of chemical substances. The method was evaluated for emerging contaminant removal research, specifically for the group of steroid estrogens. The mixture of estrone (E1), 17β-estradiol (E2), estriol (E3), and 17α-ethinylestradiol (EE2) was effectively eliminated and completely removed during a treatment that lasted just a few seconds. This novel method can be used in a broad spectrum of water treatment processes or as the intensification of reactions in chemical engineering technologies.

Keywords: hydrodynamic cavitation; advanced oxidation processes; estrogens removal; water treatment; persulfate activation

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1. Introduction

Steroid estrogens (Figure 1) are representatives of a group of pollutants called endocrine disruptors. Their increased environmental presence poses a potential risk to wildlife and human health, even at low concentrations. Estrogens are suspected of causing the development of certain defects and diseases, such as reproduction dysfunction, metabolic diseases, cancer, and many others. The suggested link to the increased numbers of patients with breast cancer—the most diagnosed cancer in women—is alarming [1]. Besides harming humans and animals, steroid estrogens also affect plant growth [2].

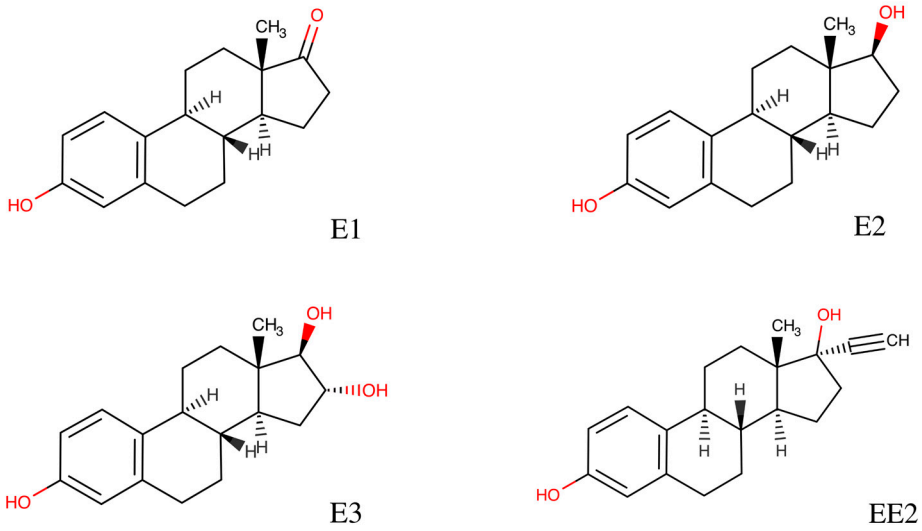

Figure 1. Chemical structure of selected estrogens.

The physical-chemical properties of these compounds play an essential role in predicting their fate in the environment. Estrogens are poorly soluble in water. The values of the octanol/water coefficient (K_{ow})—defined as the ratio of the concentration of a compound in n-octanol and water under equilibrium conditions at a specific temperature—indicate slightly hydrophobic behavior and, thereby, a tendency to sorb to the solid phase and thus be retained in the environment [3,4]. Most estrogens are excreted from the body in the urine in conjugated form. These polar conjugates are biologically inactive and more soluble in water. Nevertheless, at the influent of the wastewater treatment plant, primarily unconjugated estrogens are found, indicating hydrolysis of the conjugates prior to entering the treatment plant caused by bacteria like *E. coli* [4].

The crucial factor in polluting the environment with these substances is inadequate wastewater treatment. Although there are already methods that can satisfactorily reduce concentrations of various pollutants entering the environment, their application in practice are both technologically and economically demanding. On the other hand, wastewater treatment research has been actively producing new technologies based on various mechanisms with various efficiency levels. Traditional Fenton and Fenton-like processes, ozonization, UV-based methods, or other heterogenous photocatalyzed processes have been studied, modified, and intensified for over two decades [5]. Significant development has been achieved in advanced oxidation processes (AOPs) based on highly reactive radicals.

Sulphate radical ($SO_4^{\bullet -}$)-based AOPs play a significant role in advanced wastewater treatment development. Sulphate radicals are usually generated from persulfate (PS), supplied as $Na_2S_2O_8$, or less commonly from peroxymonosulphate (PMS) in the form of 2 $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ [6]. It should be noted that the PS method is more cost-effective and, in practice, more user-friendly than PMS [7]. Sodium persulfate is a white crystalline compound highly soluble in water (73 g/100 g H_2O at 25 °C [6,8], providing easy manipulation. Although PS is a powerful oxidant, some form of activation needs to be used for pollutant degradation at a reasonable rate [7]. Many papers have already been published on PS activation; some introduce potentially environmentally responsible technologies, such as thermolysis or photolysis.

Heat- or UV-activated persulfate has a significant advantage as it does not require additional chemicals, thus it is a potentially environmentally responsible technology. However, it is necessary to consider the cost and impact of using the electric energy needed for UV lamps or other additional energy to heat the system. Moreover, it must be recognized that heating is not economical because thermal heating has been classified as pollution, nor is it ecological [6] in recent literature. Table 1 lists some examples of PS activation methods.

Table 1. Examples of PS activation methods.

Method	Pollutant	Efficiency	Commentary	Reference
UV and/or transition metals: Fe(II), Fe(III), Co(II), Ag(I)	2,4-dichlorophenol	99.9% within 4 h	The high scavenging effect, possible inhibition by dissolved oxygen, secondhand water contamination with high concentrations of metal ions, prolonged reaction time	[9]
Iron-based nanoparticles (bimetallic zero valent nanoparticles) Fe/PS process	trichloroethylene	>99% in 20 s reaction time	High cost and potential environmental risk caused by nanoparticles	[10]
PS and PMS activation by electrophilic transition metal cations (Ag^+ and Co^{2+}), UV ($300 < \lambda < 400$ nm) and/or heat ($T = 30$ °C)	microcystin-LR	~77% in 10 min	Best results achieved at lower pH (pH = 3) and higher PS concentrations [PMS]/[MC-LR] molar ratio = 100	[11]
Magnetite nanoparticles/PS	norfloxacin	90% within 60 min	The concentration of PS 1 mM; dose of nanoparticles: 0.3 g L^{-1}; adjusted pH = 4.0	[12]
TiO_2/light/PS	acetaminophen	up to 100% in 9 h, pH 9	High costs and complicated in practice (high dose of PS, pH adjustment, prolonged reaction time)	[13]
Phenols/PS	nitrobenzene	over 60% in 8 h, pH 11.5	Addition of hazardous chemicals and the need for significant pH adjustment, prolonged reaction time	[14]
PS activated by quinones	PCBs	over 60% in 1 h, over 80% in 2 h	The mechanism of persulfate activation was primarily elucidated	[15]
PS activated by Fe^{2+}	diuron, ibuprofen and caffeine	>90% in 240 min	pH adjustment needed; kinetics model primarily evaluated	[16]
PS activated by nitrogen-modified carbon nanotubes	phenol	>90% under 30 min	Phenol concentration = 20 ppm; catalyst dose 0.2 g L	[17]
PS/activated carbon	Azo dye (orange 7)	80% degradation and 50% mineralization in 5 h	The activation effectiveness decreased by adsorption of the pollutant on the catalyst	[18]
Thermally activated PS	59 volatile organic compounds	>90% in 72 h	The best results were achieved in combination with 5 g l^{-1} of $Na_2S_2O_8$ at 40 °C for 72 h	[19]

Table 1. *Cont.*

Method	Pollutant	Efficiency	Commentary	Reference
Thermally activated PS	antipyrine	80% removal within 2 h	Anaerobic conditions favoured degradation (20%)	[20]
UV/PS	sulfamethazine	>95% in 45 min	Photolysis (22.0%), persulfate oxidation (15.10%), UV/H_2O_2 (87.5%) efficiencies were also investigated	[21]
UV/PS	cylindrospermopsin	>99% in 20 min	UV (less than 5%) and UV/H_2O_2 (~20%) efficiencies were also investigated	[22]
UV/PS	2,4,6-trichloroanisole	>80% in 30 min	Mechanism and kinetics were primarily investigated	[23]
PS/sonolysis	carbamazepine	89.4% in 120 min, pH 3.0	PS and ultrasound efficiencies were also investigated; PS alone with less than 50% and ultrasound with less than 5%	[24]
PS/sonolysis	bisphenol A	>90% under 60 min	High temperatures enhanced sulfate radical formation but impeded sonochemical activity.By-products were also investigated	[25]

Both environmentally and economically sustainable methods are still needed in optimal wastewater treatment technology. The methods mentioned above are only effective to a certain extent and are associated with high time requirements. Experiments are usually performed within tens of minutes, sometimes up to two or three hours, once for days [9–30]. Such a time delay is difficult to achieve in real-life water treatment. Therefore, we present results with a time allowance of a few seconds and an efficiency comparable to or higher than previously published alternatives.

We studied hydrodynamic cavitation (HC) as a persulfate activation process, which is presented as an essential step in persulfate-based AOPs. Hydrodynamic cavitation is based on lowering the pressure in the system, causing the formation of imploding bubbles and a local increase in temperature. The imploding process generates a shock wave with enough energy to produce radicals that are the basis of AOP [31,32]. The main advantage is that there is no need for other added substances nor pH adjustment, and it requires significantly shorter treatment time (seconds) and saves energy (the system does not need to be heated, and cavitation can be provided just with the gravitation-based flow).

2. Materials and Methods

2.1. Chemicals and Reagents

Estrone standards (E1; 99%): 17β-estradiol (E2; 98%), estriol (E3; 98%), and 17α-ethinylestradiol (EE2; 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). As internal standards for the quantification of estrogens, deuterated 17β-estradiol (E2D) was used for the quantification of estrone, estradiol, and estriol, and deuterated 17α-ethinylestradiol (EE2D) for the quantification of ethinylestradiol cations, both purchased from C/D/N Isotopes Inc. (Pointe-Claire, QC, Canada). The solvents methanol and

acetonitrile for LC-MS and acetone for HPLC were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ultra-purified distilled water was produced directly in the laboratory using a Millipore system (Merck KGaA, Darmstadt, Germany).

Formic acid was used as the mobile phase (0.7 mM), hydrochloric acid to adjust the pH of the samples before analysis, dansyl chloride (1 mg mL in acetone) in the derivatization of estrogens to increase the sensitivity of the method, and sodium bicarbonate (100 mM; pH = 10.5) as a derivatization buffer.

For the experiments, $Na_2S_2O_8$ was purchased from Sigma-Aldrich (St. Louis, MO, USA), and KI and $NaHCO_3$, which was used in the spectrophotometric determination of PS, from Penta, s.r.o., (Czech Republic).

2.2. Experiment Design

The experiments were performed on two litres of spiked water with an estrogen concentration of 300 ng L^{-1} in the cavitation unit consisting of a tank, a pump, Venturi tube, and control valves (Figure 2). The unit operates in circulation mode at speed flow 0.45 L s^{-1}, inlet pressure 450 kPa, and pump power 0.75 kW. The experiment was performed in three variants: (i) PS activation by HC, (ii) with thermal activation of persulfate (60 °C) combined with HC, and (iii) with HC only.

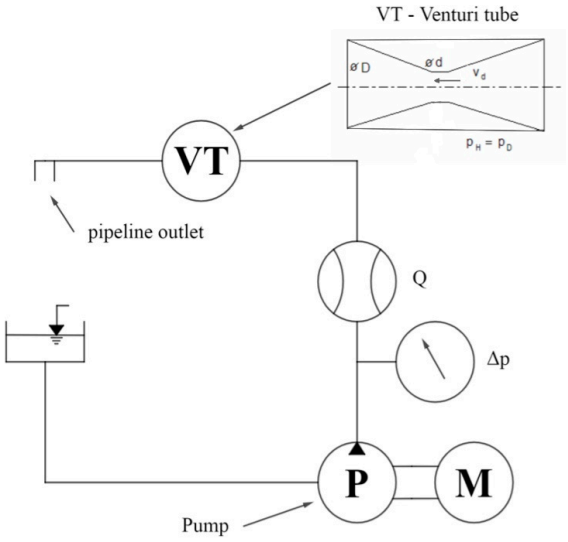

Figure 2. Design of laboratory cavitation equipment.

The PS dose was chosen to be 0.1 mM in accordance with the available literature dealing with a similar topic with a low time requirement and a task to keep the dose at a reasonable level [12,19–25,31].

Treated water was circulated through the system and sampled after 4, 8, 12, and 20 s of treatment (1, 2, 3, and 5 cycles through the system). The monitored parameters include pH, conductivity, persulfate, and estrogen concentrations. With regard to future research, neither the ionic strength nor the pH of the solutions was adjusted in any way to minimize the operational steps, hence the procedure was as economical as possible and potentially suitable for practical implementation. The pH, temperature, and conductivity were measured using a Combo pH/EC meter (Hanna, HI 98129). As the sulfate radical is more stable and, therefore, has a longer lifetime than the hydroxyl radical and a slower reaction rate [33], after collection, the samples were untouched for 3 h and 24 h, allowing the degradation of destabilized molecules sufficient time to take place.

2.3. Analytical Method

The analytical method of estrogen analysis has already been published and described [34]. The sample was analysed using the HPLC/MS (QQQ) system by Agilent

Technologies (Santa Clara, CA, USA). The column used for analysis was Poroshell 120 EC-C18 (2.1 × 100 mm, 2.7 µm); the mobile phase was a mixture of 7 mM HCOOH and acetonitrile with a flow of 0.35 mL min^{-1}. In short, the pH of 50 mL of the sample was adjusted to pH = 3 (±0.2), extracted with an SPE cartridge (Waters Oasis hydrophilic-lipophilic balance (HLB) cartridges) to 8 mL of methanol, dried, reconstituted in 20 µL of acetone, derivatized with dansyl chloride, dried again, and dissolved in 1 mL of 40% methanol.

Spectrophotometric analysis was used to determine the persulfate concentration. Exactly 1 mL of reagent (KI/$NaHCO_3$) was added to 200 µL of the sample [35], and the sample was mixed well and allowed to react for 20 min in the dark. The reaction product was analysed at 394 nm in a 96-well plate using a SparkTM multimode microplate reader (Tecan, Austria).

3. Results

All the experiments were performed using a persulfate concentration of 0.1 mM. In the first set, the system was activated by hydrodynamic cavitation only (without heating). As can be seen in Figure 3, after only one cycle through the cavitation unit (t = 4 s), the concentration of the estrogen mixture drops to approximately 60% of the initial concentration. After 24 h, the concentration lowered to a fraction of the initial amount. Simultaneously, a decrease in persulfate content in the mixture was observed, confirming its consumption in estrogens removal (see Figure 3B).

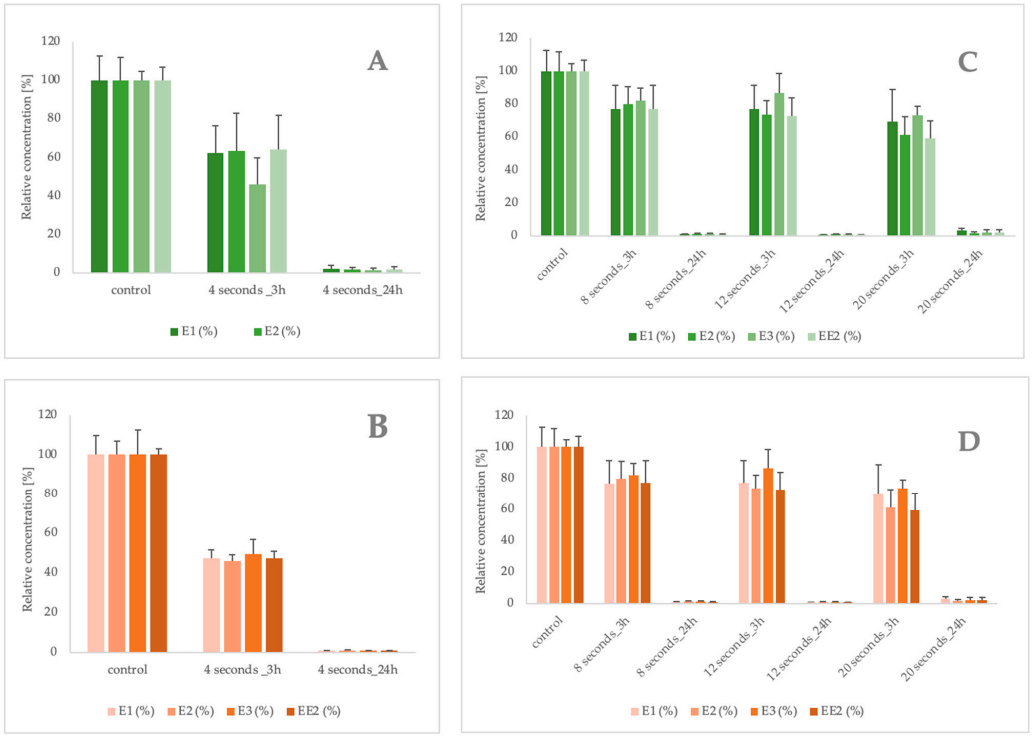

Figure 3. (**A**) Relative concentration of estrogens after treatment with persulfate (0.1 mM) activated by HC; (**B**) Relative concentration of estrogens after treatment with persulfate (0.1 mM) activated by HC combined with heat (60 °C); (**C**) Relative concentration of estrogens treated with persulfate (0.1 mM) activated by HC (8, 12, and 20 s treatment) analysed 3 and 24 h after reaction; (**D**) Relative concentration of estrogens treated with persulfate (0.1 mM) activated by the combination of HC (8, 12, and 20 s treatment) and heat (60 °C) analysed 3 and 24 h after the reaction.

The second set of experiments was performed by combining heat and HC activation. The combined activation showed slightly less pronounced results 3 h after treatment, but no significant difference was observed after 24 h (Figure 3B).

Although the most significant data obtained are related to a single flow through the cavitation device, degradation after 2, 3, and 5 cycles (8, 12, and 20 s) was also observed. Within 3 h, post-reaction processes occurred, and more intensive estrogen removal was observed. However, after 24 h, these differences disappeared, and PS activated by hydrodynamic cavitation destroyed 95–99% of the selected estrogenic compounds, similar to the PS activated by HC and 60 °C heating (compare Figure 3C,D).

The graphical results are supported by the calculation of the rate constants in Table 2. Based on the kinetic model of pseudo-first order, degradation constants (k) of estrogens were calculated according to Formula (1):

$$-\ln\left(\frac{c_t}{c_0}\right) = k \times t, \quad (1)$$

where c_0 and c_t represent the initial concertation and concentration at time t (min), respectively [32,36].

Table 2. The pseudo-first-rate constants of estrogens degradation; r > 0.97.

Conditions	k_{E1} (min^{-1})	k_{E2} (min^{-1})	k_{E3} (min^{-1})	k_{EE2} (min^{-1})
PS 0.1 mM + HC	1.24	1.51	0.94	1.2
PS 0.1 mM (heat activated 60 °C) + HC	1.15	1.40	1.68	1.54

PS concentration was also monitored during the experiments. The results show that only about half of the dosed PS was needed (Figure 4), and there is room for possible dose reduction. Moreover, no significant difference in PS concentrations was observed between the sets with and without thermal activation.

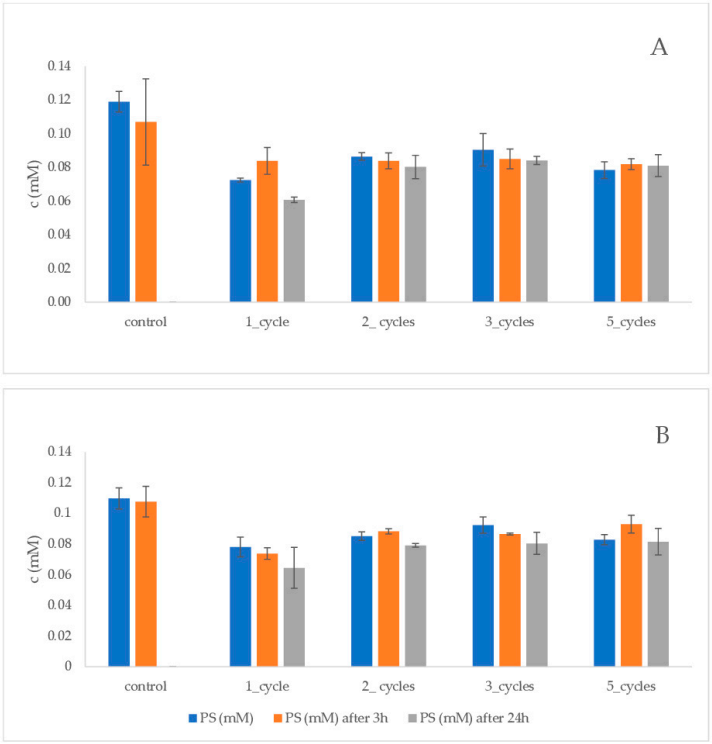

Figure 4. (**A**) Concentration of PS after treatment with PS (0.1 mM) activated by HC; 1, 2, 3, and 5 cycles through the unit corresponding with 4, 8, 12, and 20 s of treatment; (**B**) Concentration of PS after treatment with PS (0.1 mM) activated by HC combined with heat (60 °C); 1, 2, 3, and 5 cycles through the unit corresponding with 4, 8, 12, and 20 s of treatment.

To evaluate the effect of HC alone, a set of experiments was performed without added PS. Figure 5 shows that HC alone does not eliminate estrogens and only acts as a tool to activate PS.

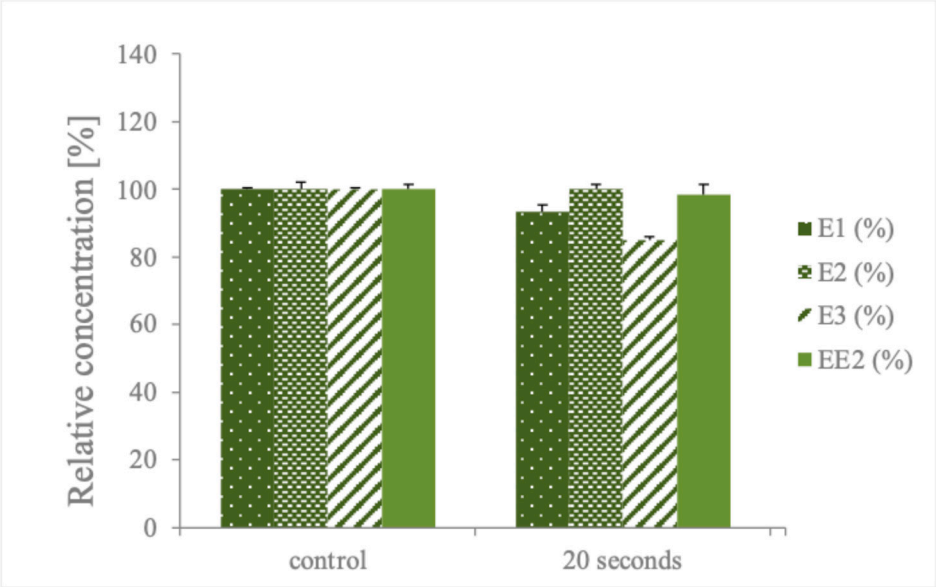

Figure 5. Relative concentration of estrogens after treatment with HC only.

Simultaneously, the pH value was monitored for all samples. It can be seen (Figure 6) that the pH value decreases slightly with an increasing number of cycles (longer reaction time). This phenomenon is possibly caused by the formation of sulphates in the aqueous solution [37]. This trend was observed for both the HC-only and HC-heat-activated sets. However, even in this case, no difference was observed between the two variants.

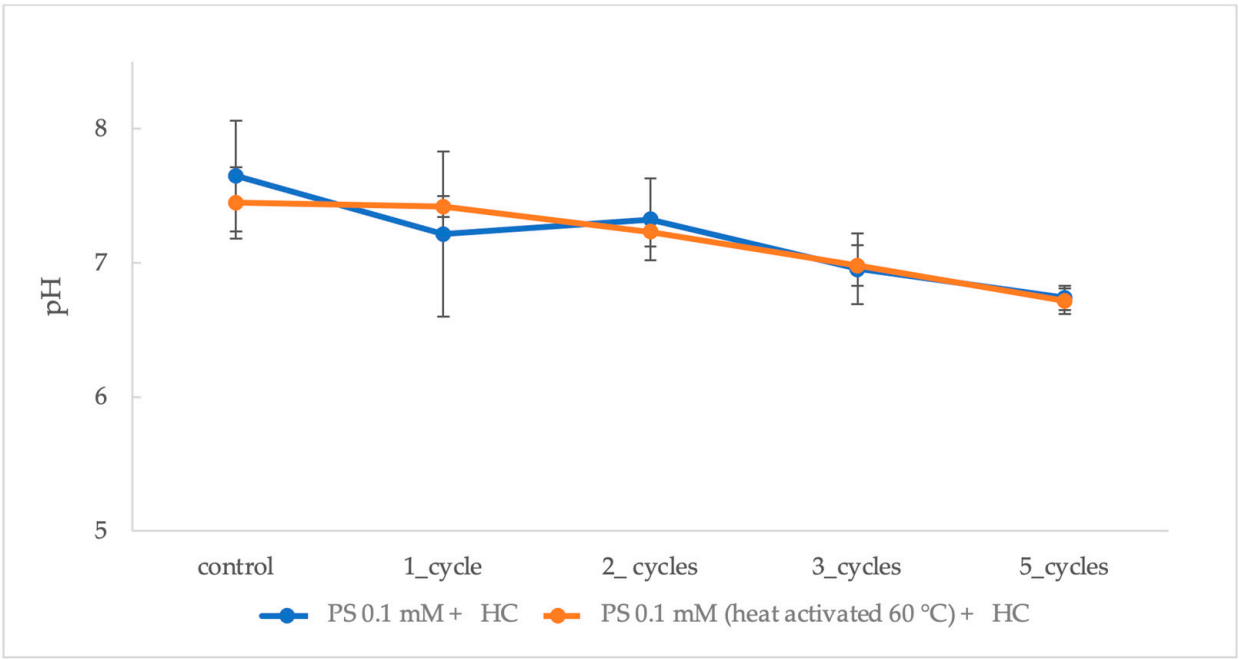

Figure 6. The pH levels of samples after treatment with PS (0.1 mM) activated by HC; 1, 2, 3, and 5 cycles through the unit corresponding with 4, 8, 12, and 20 s of treatment, and after treatment with PS (0.1 mM) activated by HC combined with heat (60 °C); 1, 2, 3, and 5 cycles through the unit corresponding with 4, 8, 12, and 20 s of treatment.

For the purpose of the cost comparison of some advanced oxidation processes, electricity consumption can be used [33]. Electric energy per mass (E_{EM}) and Electric energy per order (E_{EO}) were reported to be useful for calculating different types of treatment [38,39]. When contaminant concentrations are greater than 10 mg L^{-1}, E_{EM} should be applied, while E_{EO} should be applied when contaminant concentrations are less than 10 mg L^{-1}. To calculate treatment costs for the estrogen's concentrations, (300 µg L^{-1}) E_{EO} was selected. E_{EO} values (kWh m^{-3} $order^{-1}$) were calculated using the following Formula (2) [38].

$$E_{EO} = \frac{P_{HC} \times t \times 1000}{\log\left(\frac{c_i}{c_f}\right) \times V}, \quad (2)$$

where P_{HC} is the rated power of the pump (kW) in the HC system, t is the treatment time (h), c_i and c_f are the initial and final concentrations (mol L^{-1}) of each estrogen, and V is the reaction volume (L).

Calculated values in kWh m^{-3} $order^{-1}$ for PS 0.1 mM activated by HC, 4 s long treatment are E_{EO}(E1) = 2.02, E_{EO}(E2) = 2.10, E_{EO}(E3) = 1.12, and E_{EO}(EE2) = 2.15. In the case of PS 0.1 mM activated by the combination of HC and heat, the energy of external heating depending on the heating source must be considered, so the formula cannot be applied. Obviously, energy consumption is much higher in heat-combined activation as compared to the case of HC activation.

4. Discussion

Our experiment setup is unique due to the short time needed for the actual treatment and the lack of need for additional system heating. For comparison, the study performed on wastewater to eliminate frequently occurring pharmaceuticals using PS was accomplished at increased temperatures of 55, 64, and 75 °C. To achieve at least a 50% decrease in the concentration of the monitored drugs, the wastewater had to be heated up to 75 °C and allowed to react for 50 min (PS concentration ≤ 500 µM) [30].

Other studies focusing on eliminating estrogens by AOP produced results in reducing concentration, summarised in Table 3 [26].

Table 3. Estrogen removal based on AOP with focus on PS-based AOP.

Method	Estrogen	Efficiency	Reference
Fenton oxidation	EE2 (200 µg L^{-1})	100% in 10 min	[27]
Photo-Fenton	E2 (272 µg L^{-1})	86.4% in 8 h	[28]
Photo-Fenton	E2 (1 mg L^{-1})	98% in 60 min	[29]
PS/modified Fenton-like process	E2 (6 mg L^{-1})	100% in 90 min	[30]
PS/UV	E1, E2 and EE2 (5 µM)	over 95% in 5 min	[31]
UVC/PS/TiO_2 (on ceramic membrane)	E2 and EE2 (100 µg L^{-1})	uder 45% (radiation time 4.6 s)	[40]
PS activated on nanoscale zero-valent iron loaded porous graphitized biochar	E2 (3 mg L^{-1})	100% in 45 min	[41]
PS/visible light/Bi_2WO_6/Fe_3O_4	E2 (5 mg L^{-1})	~70% in 60 min	[42]
PS activated by reduced graphene oxide–elemental silver/magnetite nanohybrids	EE2 (10 µM)	~90% in 15 min	[43]
PS/ultrasound	E2 (5 mg L^{-1})	over 90% in 90 min	[44]
PS/ultrasound	E1, E2, E3 and EE2 (17–239 ng L^{-1}), real wastewater sample	over 95% in 10 min	[45]
PS/HC	E1, E2, E3 and EE2 (300 µg L^{-1})	99% in 4 s treatment	This study

Although these methods show promising efficiencies, some even in a relatively short time, Fenton-like oxidations are specific for the relatively high amount of waste and the demand for added chemicals and/or energy [46]. For example, to eliminate EE2 200 μg L^{-1} within 10 min, 5 mg L^{-1} of Fe^{2+} and 8.6 mg L^{-1} of H_2O_2 is needed [26].

Promising results were observed in the literature: using UV-activated PS (c = 40 mg L^{-1}), 50% of the E2 concentration was removed in deionized water within 5 min. However, in natural wastewater, it was necessary to increase the concentration of PS to 200 mg L^{-1} to achieve similar results [47]. Comparable results were observed in a study degrading E1, E2, and EE2 (5 μM) in 5 min (PS dose 5 mM, pH = 6, UV-B) [31]. UV-based activation of PS has been shown to be fast and effective. The main disadvantage in comparison to a PS/HC system is the need for a UV source, which represents extra operation costs.

Furthermore, heating activation was performed to eliminate the common pharmaceutical drug ibuprofen. The temperature required to achieve the half-life of 3.6 min (initial concentration 20.36 μM) was 70 °C [48]. When using a PS concentration of 2 mM and 50 °C temperature conditions, more than 360 min were required to remove at least 50% of the sulfamethoxazole. For other sulfonamides, at least 6 min were required to halve the initial concentration [49].

Another drug, the antibiotic chloramphenicol, was degraded by combining PS/UV. The experiments were performed under natural conditions, and complete elimination was achieved within 1 h [50]. Similarly time-consuming is the successful degradation of the beta-blocker bisoprolol, which requires thermal activation of PS for at least 60 °C and a contact time of 1 h [51]. A study combining thermal and UV activation on municipal wastewater achieved E2 removal of over 90% within an hour [52].

Based on the available literature, it is assumed that $SO_4^{-}\bullet$ and HO• radicals are involved in removing estrogens by HC-activated PS [45,52]. HC-based treatment has also been reported to promote the generation of $HO_2\bullet$ and $O_2^{\bullet-}$ radicals [53,54]. Nevertheless $SO_4^{-}\bullet$ and HO• are significantly stronger oxidants than $HO_2\bullet$ and $O_2^{-}\bullet$ [53].

The positive synergy of PS and HC has already been proven on the degradation of polycyclic aromatic hydrocarbons in sediments removing PAH by 79% in 60 min [39]. Our set-up proves the ability of HC-activated PS to effectively eliminate estrogens in a short time, even in a flow-through-like system.

Since AOPs represent a large number of various processes, they are difficult to compare with each other from different points of view. Based on E_{EO} values, AOP can be classified into three groups:

- <1 kWh m^{-3} $order^{-1}$ for representing a realistic range for full-scale application,
- 1–100 kWh m^{-3} $order^{-1}$ for a group that is possibly too energy intensive for most practical applications, but that can still be recommended for further full-scale-application investigation,
- >100 kWh m^{-3} $order^{-1}$, which is considered as not (yet) energy efficient [55].

Our results show that the PS activated by HC should be classified in group 2. Nevertheless, the financial complexity of AOP processes is highly dependent on operating costs. Here, it is necessary to think about the equipment's lifespan. For comparison, this can be a limiting factor in PS activation in frequently used UV lamps (with a lifespan of around 12,000 h) and other UV-based AOPs. In addition, compared to similarly operating ultrasonic activation, HC has been reported to be 10 times more efficient in the means of electricity consumption [56].

The above examples show that heating, adding additional chemicals, and/or UV radiation are required to eliminate estrogens or other drugs using PS-based AOPs successfully. Compared to using hydrodynamic cavitation as PS activation, all these processes require higher initial costs and high operating costs, whether in the form of increasing energy prices or input chemicals. With the increasing demand for environmental responsibility, there is a growing need for functional "green" technologies, and cavitation activation has the potential to become an example of such technology.

5. Conclusions

We demonstrated that selected estrogens could be effectively eliminated from water during a short treatment time—within seconds. Venturi tube cavitation is an easy-to-install and easy-to-use economically and environmentally friendly technique compared to other known AOP (PS/AOP) alternatives. Based on the presented results, it can be assumed that cavitation acts as persulfate activation. Its main advantage is that it requires neither adding/dosing other substances into the treated water nor heating it, as opposed to methods described in earlier papers. This method can be used in a broad spectrum of water treatment processes or to intensify reactions in chemical engineering technologies. Calculated values of E_{EO} can be used for further comparison with other similar techniques and scale-up.

A lab-scale experiment, which proved the efficiency of PS activation, was conducted in this study. Pilot or other scale-up experiments are required to assess the different processes' efficacy on real wastewater fully. Nonetheless, the short treatment time (4 s), estrogens removal rate 99%, and flow rate of the lab-scale equipment 4.5 m^3 h^{-1} proved that this novel technology for removing estrogenic compounds is promising.

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References

1. Lecomte, S.; Habauzit, D.; Charlier, T.D.; Pakdel, F. Emerging Estrogenic Pollutants in the Aquatic Environment and Breast Cancer. *Genes* **2017**, *8*, 229. [CrossRef]
2. Adeel, M.; Yang, Y.; Wang, Y.; Song, X.; Ahmad, M.A.; Rogers, H.J. Uptake and transformation of steroid estrogens as emerging contaminants influence plant development. *Environ. Pollut.* **2018**, *243*, 1487–1497. [CrossRef]
3. Hamid, H.; Eskicioglu, C. Fate of estrogenic hormones in wastewater and sludge treatment. A review of properties and analytical detection techniques in sludge matrix. *Water Res.* **2012**, *46*, 5813–5833. [CrossRef] [PubMed]
4. Jones-Lepp, T.L.; Stevens, R. Pharmaceuticals and personal care products in biosolids/sewage sludge. the interface between analytical chemistry and regulation. *Anal. Bioanal. Chem.* **2007**, *387*, 1173–1183. [CrossRef]
5. Munter, R. Advanced oxidation processes—Current status and prospects, in: Proceedings of the Estonian Academy of Science. *Chemistry* **2001**, *50*, 59–80.
6. Ike, I.A.; Linden, K.G.; Orbell, J.D.; Duke, M. Critical review of the science and sustainability of persulphate advanced oxidation processes. *Chem. Eng. J.* **2018**, *338*, 651–669. [CrossRef]
7. Zhang, T.; Chen, Y.; Wang, Y.; Le Roux, J.; Yang, Y.; Croué, J.-P. Efficient Peroxydisulfate Activation Process Not Relying on Sulfate Radical Generation for Water Pollutant Degradation. *Environ. Sci. Technol.* **2014**, *48*, 5868–5875. [CrossRef]
8. FMC. Persulfates Technical Information, in, FMC Corporation. 2001. Available online: http://www.peroxychem.com/media/90826/aod_brochure_persulfate.pdf (accessed on 3 March 2022).
9. Anipsitakis, G.P.; Dionysiou, D.D. Transition metal/UV-based advanced oxidation technologies for water decontamination. *Appl. Catal. B Environ.* **2004**, *54*, 155–163. [CrossRef]
10. Al-Shamsi, M.A.; Thomson, N.R.; Forsey, S.P. Iron based bimetallic nanoparticles to activate peroxygens. *Chem. Eng. J.* **2013**, *232*, 555–563. [CrossRef]
11. Antoniou, M.G.; de la Cruz, A.A.; Dionysiou, D.D. Degradation of microcystin-LR using sulfate radicals generated through photolysis, thermolysis and e− transfer mechanisms. *Appl. Catal. B Environ.* **2010**, *96*, 290–298. [CrossRef]

12. Ding, D.; Liu, C.; Ji, Y.; Yang, Q.; Chen, L.; Jiang, C.; Cai, T. Mechanism insight of degradation of norfloxacin by magnetite nanoparticles activated persulfate: Identification of radicals and degradation pathway. *Chem. Eng. J.* **2017**, *308*, 330–339. [CrossRef]
13. Lin, J.C.-T.; de Luna, M.D.G.; Aranzamendez, G.L.; Lu, M.-C. Degradations of acetaminophen via a K2S2O8 -doped TiO2 photocatalyst under visible light irradiation. *Chemosphere* **2016**, *155*, 388–394. [CrossRef]
14. Ahmad, M.; Teel, A.L.; Watts, R.J. Mechanism of Persulfate Activation by Phenols. *Environ. Sci. Technol.* **2013**, *47*, 5864–5871. [CrossRef] [PubMed]
15. Fang, G.; Gao, J.; Dionysiou, D.D.; Liu, C.; Zhou, D. Activation of Persulfate by Quinones: Free Radical Reactions and Implication for the Degradation of PCBs. *Environ. Sci. Technol.* **2013**, *47*, 4605–4611. [CrossRef]
16. Rodriguez, S.; Santos, A.; Romero, A. Oxidation of priority and emerging pollutants with persulfate activated by iron: Effect of iron valence and particle size. *Chem. Eng. J.* **2017**, *318*, 197–205. [CrossRef]
17. Sun, H.; Kwan, C.; Suvorova, A.; Ang, H.M.; Tadé, M.O.; Wang, S. Catalytic oxidation of organic pollutants on pristine and surface nitrogen-modified carbon nanotubes with sulfate radicals. *Appl. Catal. B Environ.* **2014**, *154–155*, 134–141. [CrossRef]
18. Yang, S.; Yang, X.; Shao, X.; Niu, R.; Wang, L. Activated carbon catalyzed persulfate oxidation of Azo dye acid orange 7 at ambient temperature. *J. Hazard. Mater.* **2011**, *186*, 659–666. [CrossRef]
19. Huang, K.-C.; Zhao, Z.; Hoag, G.E.; Dahmani, A.; Block, P.A. Degradation of volatile organic compounds with thermally activated persulfate oxidation. *Chemosphere* **2005**, *61*, 551–560. [CrossRef]
20. Tan, C.; Gao, N.; Deng, Y.; Rong, W.; Zhou, S.; Lu, N. Degradation of antipyrine by heat activated persulfate. *Sep. Purif. Technol.* **2013**, *109*, 122–128. [CrossRef]
21. Gao, Y.-Q.; Gao, N.-Y.; Deng, Y.; Yang, Y.-Q.; Ma, Y. Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. *Chem. Eng. J.* **2012**, *195–196*, 248–253. [CrossRef]
22. He, X.; de la Cruz, A.A.; Dionysiou, D.D. Destruction of cyanobacterial toxin cylindrospermopsin by hydroxyl radicals and sulfate radicals using UV-254nm activation of hydrogen peroxide, persulfate and peroxymonosulfate. *J. Photochem. Photobiol. A Chem.* **2013**, *251*, 160–166. [CrossRef]
23. Luo, C.; Jiang, J.; Ma, J.; Pang, S.; Liu, Y.; Song, Y.; Guan, C.; Li, J.; Jin, Y.; Wu, D. Oxidation of the odorous compound 2,4,6-trichloroanisole by UV activated persulfate: Kinetics, products, and pathways. *Water Res.* **2016**, *96*, 12–21. [CrossRef] [PubMed]
24. Wang, S.; Zhou, N. Removal of carbamazepine from aqueous solution using sono-activated persulfate process. *Ultrason. Sonochem.* **2016**, *29*, 156–162. [CrossRef] [PubMed]
25. Darsinou, B.; Frontistis, Z.; Antonopoulou, M.; Konstantinou, I.; Mantzavinos, D. Sono-activated persulfate oxidation of bisphenol A: Kinetics, pathways and the controversial role of temperature. *Chem. Eng. J.* **2015**, *280*, 623–633. [CrossRef]
26. Frontistis, Z.; Xekoukoulotakis, N.P.; Hapeshi, E.; Venieri, D.; Fatta-Kassinos, D.; Mantzavinos, D. Fast degradation of estrogen hormones in environmental matrices by photo-Fenton oxidation under simulated solar radiation. *Chem. Eng. J.* **2011**, *178*, 175–182. [CrossRef]
27. Feng, X.; Ding, S.; Tu, J.; Wu, F.; Deng, N. Degradation of estrone in aqueous solution by photo-Fenton system. *Sci. Total Environ.* **2005**, *345*, 229–237. [CrossRef]
28. Mboula, V.M.; Héquet, V.; Andrès, Y.; Gru, Y.; Colin, R.; Doña-Rodríguez, J.; Pastrana-Martínez, L.; Silva, A.; Leleu, M.; Tindall, A.; et al. Photocatalytic degradation of estradiol under simulated solar light and assessment of estrogenic activity. *Appl. Catal. B Environ.* **2015**, *162*, 437–444. [CrossRef]
29. Yaping, Z.; Jiangyong, H. Photo-Fenton degradation of 17β-estradiol in presence of α-FeOOHR and H_2O_2. *Appl. Catal. B Environ.* **2008**, *78*, 250–258. [CrossRef]
30. Zhang, P.; Tan, X.; Liu, S.; Liu, Y.; Zeng, G.; Ye, S.; Yin, Z.; Hu, X.; Liu, N. Catalytic degradation of estrogen by persulfate activated with iron-doped graphitic biochar: Process variables effects and matrix effects. *Chem. Eng. J.* **2019**, *378*, 122141. [CrossRef]
31. Gabet, A.; Métivier, H.; de Brauer, C.; Mailhot, G.; Brigante, M. Hydrogen peroxide and persulfate activation using UVA-UVB radiation: Degradation of estrogenic compounds and application in sewage treatment plant waters. *J. Hazard. Mater.* **2021**, *405*, 124693. [CrossRef] [PubMed]
32. Gągol, M.; Przyjazny, A.; Boczkaj, G. Wastewater treatment by means of advanced oxidation processes based on cavitation—A review. *Chem. Eng. J.* **2018**, *338*, 599–627. [CrossRef]
33. Yi, L.; Li, B.; Sun, Y.; Li, S.; Qi, Q.; Qin, J.; Sun, H.; Wang, X.; Wang, J.; Fang, D. Degradation of norfloxacin in aqueous solution using hydrodynamic cavitation: Optimization of geometric and operation parameters and investigations on mechanism. *Sep. Purif. Technol.* **2021**, *259*, 118166. [CrossRef]
34. Sadílek, J.; Spálovská, P.; Vrana, B.; Vávrová, M.; Maršálek, B.; Šimek, Z. Comparison of extraction techniques for isolation of steroid oestrogens in environmentally relevant concentrations from sediment. *Int. J. Environ. Anal. Chem.* **2016**, *96*, 1022–1037. [CrossRef]
35. Wacławek, S.; Grübel, K.; Černík, M. Simple spectrophotometric determination of monopersulfate. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2015**, *149*, 928–933. [CrossRef]
36. Perondi, T.; Michelon, W.; Junior, P.R.; Knoblauch, P.M.; Chiareloto, M.; Moreira, R.D.F.P.M.; Peralta, R.A.; Düsman, E.; Pokrywiecki, T.S. Advanced oxidative processes in the degradation of 17β-estradiol present on surface waters: Kinetics, byproducts and ecotoxicity. *Environ. Sci. Pollut. Res.* **2020**, *27*, 21032–21039. [CrossRef]

37. Xia, X.; Zhu, F.; Li, J.; Yang, H.; Wei, L.; Li, Q.; Jiang, J.; Zhang, G.; Zhao, Q. A Review Study on Sulfate-Radical-Based Advanced Oxidation Processes for Domestic/Industrial Wastewater Treatment: Degradation, Efficiency, and Mechanism. *Front. Chem.* **2020**, *8*, 592056. [CrossRef]
38. Bolton, J.R.; Bircher, K.G.; Tumas, W.; Tolman, C.A. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems (IUPAC Technical Report). *Pure Appl. Chem.* **2001**, *73*, 627–637. [CrossRef]
39. Hung, C.-M.; Huang, C.-P.; Chen, C.-W.; Dong, C.-D. Hydrodynamic cavitation activation of persulfate for the degradation of polycyclic aromatic hydrocarbons in marine sediments. *Environ. Pollut.* **2021**, *286*, 117245. [CrossRef]
40. Castellanos, R.M.; Presumido, P.H.; Dezotti, M.; Vilar, V.J. Ultrafiltration ceramic membrane as oxidant-catalyst/water contactor to promote sulfate radical AOPs: A case study on 17β-estradiol and 17α-ethinylestradiol removal. *Environ. Sci. Pollut. Res.* **2022**, *29*, 42157–42167. [CrossRef]
41. Ding, J.; Xu, W.; Liu, S.; Liu, Y.; Tan, X.; Li, X.; Li, Z.; Zhang, P.; Du, L.; Li, M. Activation of persulfate by nanoscale zero-valent iron loaded porous graphitized biochar for the removal of 17β-estradiol: Synthesis, performance and mechanism. *J. Colloid Interface Sci.* **2021**, *588*, 776–786. [CrossRef]
42. Liu, Y.; Guo, H.; Zhang, Y.; Tang, W. Feasible oxidation of 17β-estradiol using persulfate activated by Bi 2 WO 6 /Fe 3 O 4 under visible light irradiation. *RSC Adv.* **2016**, *6*, 79910–79919. [CrossRef]
43. Park, C.M.; Heo, J.; Wang, D.; Su, C.; Yoon, Y. Heterogeneous activation of persulfate by reduced graphene oxide–elemental silver/magnetite nanohybrids for the oxidative degradation of pharmaceuticals and endocrine disrupting compounds in water. *Appl. Catal. B Environ.* **2018**, *225*, 91–99. [CrossRef]
44. Alvarez Corena, J.R.; Bergendahl, J.A. Effect of pH, temperature, and use of synergistic oxidative agents on the ultrasonic degradation of tris-2-chloroethyl phosphate, gemfibrozil, and 17β estradiol in water. *J. Environ. Chem. Eng.* **2021**, *9*, 105005. [CrossRef]
45. Choi, J.; Cui, M.; Lee, Y.; Ma, J.; Kim, J.; Son, Y.; Khim, J. Hybrid reactor based on hydrodynamic cavitation, ozonation, and persulfate oxidation for oxalic acid decomposition during rare-earth extraction processes. *Ultrason. Sonochem.* **2019**, *52*, 326–335. [CrossRef] [PubMed]
46. Domingues, E.; Silva, M.J.; Vaz, T.; Gomes, J.; Martins, R.C. Sulfate radical based advanced oxidation processes for agro-industrial effluents treatment: A comparative review with Fenton's peroxidation. *Sci. Total Environ.* **2022**, *832*, 155029. [CrossRef]
47. Angkaew, A.; Sakulthaew, C.; Satapanajaru, T.; Poapolathep, A.; Chokejaroenrat, C. UV-activated persulfate oxidation of 17β-estradiol: Implications for discharge water remediation. *J. Environ. Chem. Eng.* **2019**, *7*, 102858. [CrossRef]
48. Ghauch, A.; Tuqan, A.M.; Kibbi, N. Ibuprofen removal by heated persulfate in aqueous solution: A kinetics study. *Chem. Eng. J.* **2012**, *197*, 483–492. [CrossRef]
49. Ji, Y.; Fan, Y.; Liu, K.; Kong, D.; Lu, J. Thermo activated persulfate oxidation of antibiotic sulfamethoxazole and structurally related compounds. *Water Res.* **2016**, *87*, 1–9. [CrossRef]
50. Ghauch, A.; Baalbaki, A.; Amasha, M.; El Asmar, R.; Tantawi, O. Contribution of persulfate in UV-254 nm activated systems for complete degradation of chloramphenicol antibiotic in water. *Chem. Eng. J.* **2017**, *317*, 1012–1025. [CrossRef]
51. Ghauch, A.; Tuqan, A.M. Oxidation of bisoprolol in heated persulfate/H_2O systems: Kinetics and products. *Chem. Eng. J.* **2012**, *183*, 162–171. [CrossRef]
52. Sakulthaew, C.; Chokejaroenrat, C.; Satapanajaru, T.; Chirasatienpon, T.; Angkaew, A. Removal of 17β-Estradiol Using Persulfate Synergistically Activated Using Heat and Ultraviolet Light. *Water Air Soil Pollut.* **2020**, 231. [CrossRef]
53. Joshi, S.M.; Gogate, P.R. Intensification of industrial wastewater treatment using hydrodynamic cavitation combined with advanced oxidation at operating capacity of 70 L. *Ultrason. Sonochem.* **2019**, *52*, 375–381. [CrossRef]
54. Zhang, Q.; Zhao, H.; Dong, Y.; Zhu, X.; Liu, X.; Li, H. A novel ternary MQDs/NCDs/TiO_2 nanocomposite that collaborates with activated persulfate for efficient RhB degradation under visible light irradiation. *New J. Chem.* **2021**, *45*, 1327–1338. [CrossRef]
55. Miklos, D.B.; Remy, C.; Jekel, M.; Linden, K.G.; Drewes, J.E.; Hübner, U. Evaluation of advanced oxidation processes for water and wastewater treatment—A critical review. *Water Res.* **2018**, *139*, 118–131. [CrossRef] [PubMed]
56. Gogate, P.R. Cavitational reactors for process intensification of chemical processing applications: A critical review. *Chem. Eng. Process. Process Intensif.* **2008**, *47*, 515–527. [CrossRef]