

Article

Effective Degradation of 1,4-Dioxane by UV-Activated Persulfate: Mechanisms, Parameters and Environmental Impacts

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Abstract: There is more and more research focusing on the removal of dioxane by advanced oxidation technology at this stage, and this study investigated the efficacy of an advanced oxidation system with UV-activated persulfate (UV/PDS). This method had the advantages of fast reaction rate, simple equipment and convenient operation. Free radical quenching test and electron paramagnetic resonance (EPR) analysis showed that the main active radicals in the reaction system were $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$. This study also investigated that the optimal parameters were the initial PDS dosage of 3 mM, the UV intensity of 0.190 mW/cm², the pH between 5 and 7 and the initial dioxane concentration of 50 mg/L. Additionally, after a reaction time of 150 min, the total organic carbon (TOC) content still remained at 83.53%, which revealed that the mineralization degree of organic matter was not fully achieved through UV/PDS treatment. The concentration of SO_4^{2-} in the reaction system was 74.69 mg·L⁻¹, which complied with the standard concentration specified. Furthermore, the cytotoxicity of the system exhibited an initial increase followed by a subsequent decrease, under the influence of the intermediates. It showed that the technology could efficiently degrade organic pollutants.

Keywords: ultraviolet; persulfate; dioxane; advanced oxidation; degradation



Citation: Zhu, X.; Qiu, J.; Wang, Y.; Tang, Y.; Zhang, Y. Effective Degradation of 1,4-Dioxane by UV-Activated Persulfate: Mechanisms, Parameters and Environmental Impacts. *Water* **2024**, *16*, 1281. <https://doi.org/10.3390/w16091281>

Academic Editor: Alexandre T. Paulino

Received: 8 April 2024
Revised: 18 April 2024
Accepted: 23 April 2024
Published: 29 April 2024



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1. Introduction

Emerging pollutants are widely present in the environment, resulting in non-negligible potential environmental risks [1]. In recent years, emerging contaminants identified include pharmaceuticals and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), pesticides, disinfection byproducts (DBPs), antibiotic-resistant bacteria (ARBs), antibiotic-resistant genes (ARGs) and others [2]. Since these substances are not routinely monitored, they enter the environment uncontrolled and present ecological and environmental health risks. A typical emerging pollutant, 1,4-dioxane, is a colorless and volatile cyclic ether at room temperature, originating from leakages and untreated emissions during industrial use and storage. Because dioxane is water soluble, it poses a potential risk to drinking water sources [3,4]. Some studies have shown that dioxane concentrations in contaminated groundwater could be as high as 2800 µg·L⁻¹ [5,6]. It is also a known liver carcinogen that has other potential adverse health effects. The International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) has included dioxane in its list of group II carcinogens (2B) [3].

Scientists used advanced oxidation processes to decompose refractory emerging pollutants because traditional purification was not effective in removing many types of compounds [7]. Dioxane is refractory to general chemical treatment techniques due to its relatively stable physicochemical properties and water solubility, and these conventional physicochemical treatments are inefficient for dioxane removal, putting it at risk of secondary diffusion and pollution [8–10]. Microorganisms are often used to treat various

organic pollutants in water. However, since dioxane is a co-pollutant of chlorinated organic solvents, organic substances such as trichloroethylene can significantly inhibit its biodegradation rate [11,12].

More and more studies have used advanced oxidation techniques to degrade dioxane. Kishimoto et al. improved the degradation efficiency of dioxane by the sequential process of electro-oxidation followed by UV photolysis (EO/UV), which was more effective in the rapid removal of 1,4-dioxane under an unsteady pollutant loading than the single electro-oxidation [13]. Advanced oxidation techniques with potent oxidizing properties (such as hydroxyl radicals, sulfate radicals and ozone) can completely destroy the chemical structure of dioxane, so as to effectively degrade dioxane in water. This study has shown that the ozone-based advanced oxidation process was significantly affected by pH value in the removal of dioxane, so the widespread use of this technology was limited [14]. Compared with hydroxyl radicals, sulfate radicals have a higher selectivity for organic pollutants, undergoing oxidation with a secondary reaction rate constant of 10^5 – 10^9 [15]. Usually, they are effective for oxidizing organic pollutants, such as dioxins, at pH = 2.0–8.0 [16,17]. Due to the higher half-life of sulfate radicals, they can contact and react with organic pollutants more adequately in water, resulting in higher oxidant utilization efficiency [18]. The primary precursor substances for generating sulfate radicals are peroxymonosulfate (PMS) and persulfate (PDS), and sulfate radicals are generated when the O-O bond is broken (Equations (1) and (2)). PDS has a high redox potential and can directly degrade some organic pollutants.



UV-activated persulfate PDS to generate sulfate radicals to degrade organic pollutants with simple equipment, management and UV technology has been applied in conventional water treatment and deep treatment [19]. The UV activation mode of action is shown in Equation (3), where PDS absorbed the energy radiated from UV light, causing the O-O bond in PDS to break and generate sulfate radicals. The molar absorption coefficient of PDS at a UV wavelength of 254 nm is $21.1 \text{ M}^{-1} \cdot \text{cm}^{-1}$ with a quantum yield of $0.7 \text{ M} \cdot \text{Einstein}^{-1}$, which is higher than that of H_2O_2 and peroxydisulfate (PMS) under the same conditions [20].



Compared with UV activation, thermal activation, transition metal ion activation and alkali activation can activate PDS and degrade the target organic pollutants. Still, they exhibit some characteristic limitations [21–23]. The surface and underground water temperatures are usually below $20 \text{ }^\circ\text{C}$, whereas PDS activation typically occurs at $\geq 60 \text{ }^\circ\text{C}$. When the volume of the water to be treated is large, heating it to $\geq 60 \text{ }^\circ\text{C}$ is unrealistic because of the huge energy waste and uncontrollable costs [24–27]. PDS often needs to be activated under strong alkali conditions to release sulfate radicals, requiring an enormous amount of alkali in the water body [26]. The corrosion resistance of the relevant water treatment equipment should be considered to avoid negative impacts of water quality [28]. In the existing studies, although the activation of H_2O_2 - $\text{S}_2\text{O}_8^{2-}$ by Fe^{2+} and NaOH was shown to achieve the removal of dioxane as well, the long reaction time, high economic cost and low efficiency were its limitations [29]. The activation of peroxydisulfate by $\text{Pd}/\text{Al}_2\text{O}_3$, despite having achieved the effective removal of dioxane, needs to take into account the change in the post-treatment water quality and the removal of Pd, which may increase the operating cost [30]. Like the Fenton reaction, PDS activation by transition metal ions is generally faster under acidic conditions, limiting its use scenarios for organic pollutants [17]. In addition, few studies are known to have systematically investigated the degradation efficacy of advanced oxidation techniques with UV-activated PDS for dioxane. After reviewing a large number of studies, it was found that few studies systematically investigated the degradation efficacy of advanced oxidation techniques with UV-activated PDS for dioxane. The pollution effect of the reaction system on the environment was

also neglected. In this study, the quantitative research method was used to make a more comprehensive and perfect addition to this research field.

The purposes of this study were: (i) to investigate the degradation effect of advanced oxidation technology based on UV-activated persulfate on dioxane and to analyze the main reactive radicals in the reaction system by free radical quenching experiments and electron spin resonance, (ii) to analyze the effects of different parameters (persulfate concentration, UV irradiation intensity, initial dioxane concentration and pH value) on the degradation effect of dioxane, and (iii) to analyze the changes of water quality in the reaction system to investigate the influence of the technology on the water environment when degrading organic pollutants, and provide a theoretical basis for controlling the pollution problems caused by dioxane.

2. Materials and Methods

2.1. Experimental Setup

The test setup was a UV Quasi-Parallel Beam Apparatus (Collimated Beam Apparatus) (Figure 1) consisting of a UV light source (PHILIPS, Shanghai, China, 75W TUV HO), a reaction dish, a magnetic stirrer and a lifting table.

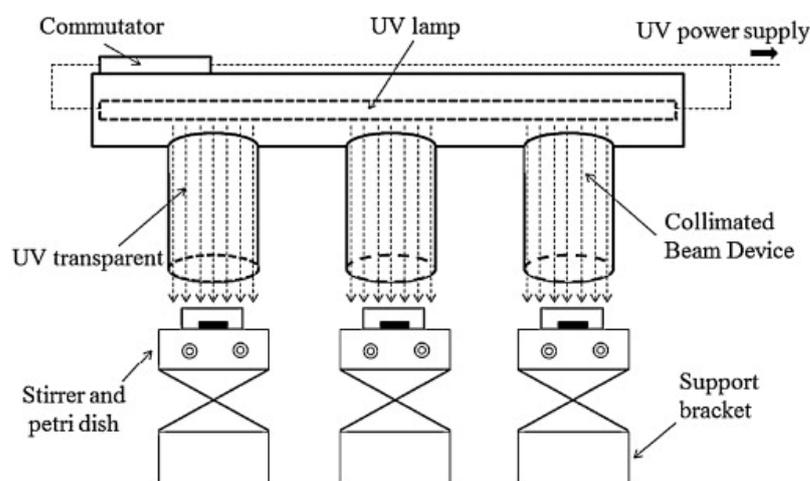


Figure 1. Diagram of UV/persulfate reaction unit.

2.2. Materials

The 1,4-dioxane (GC) and potassium persulfate (GR) was purchased from Macklin Biochemical Technology Co., Ltd., Shanghai, China. Sodium chloride (GR), anhydrous sodium carbonate (GR), sodium humate (AR), methanol (GC grade), tert-butyl alcohol (ACS), anhydrous ethanol (GC grade), ferrous sulfate heptahydrate (ACS) and 5,5-dimethyl-1-pyrrolidine-N-oxide ($\geq 97\%$) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium nitrate (AR) and sulfuric acid were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, while sodium hydroxide ($\geq 98.0\%$) was purchased from Sigma-Aldrich Company, St. Louis, MO, USA. All test solutions were prepared using ultrapure water (Milli-Q, Billerica, MA, USA) with an $18.25 \text{ M}\Omega$ resistivity.

2.3. Experimental

The light source of the UV quasi-parallel beam apparatus was 254 nm, equipped with a 75 W low-pressure mercury lamp. The average UV irradiation intensity of the reaction dish was $0.190 \text{ mW}\cdot\text{cm}^{-2}$, and the UV quasi-parallel beam apparatus was preheated for 30 min before the reaction started to stabilize the UV lamp irradiation intensity. PDS was prepared before each test and the concentration of the mother solution was $50 \text{ mg}\cdot\text{L}^{-1}$. The initial PDS concentration was 2 mM, with a pH of 6.9. Next, 100 mL of this reaction system was added to the reaction petri dish and the magnetic stirring was maintained at 300 rpm. Using 50 mM ethanol solution at different times, 5 mL was added to the headspace sample

bottle and the acquired samples were stored at 4 °C in a refrigerator until further analysis. The reaction was carried out for triplicate to verify on the validity of the produced results.

2.4. Analytical Methods

Dioxane was detected using a Trace DSQII-MS GC/MS (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an HP5-MS column (30 m × 53 mm × 0.25 μm). The headspace injection was performed by adding 3 g of NaCl into each headspace vial with a 15 min incubation time, 350 rpm shaking speed, 65 °C heating temperature and an 800 μL sample size. The injection port and ion source were set at 222 °C and 200 °C, respectively. The carrier gas was high-purity helium with a shunt ratio of 1:10, passed at 1.2 mL·min⁻¹ flow rate. The heating-up procedure was to maintain the temperature at 35 °C for 3 min, and then increased to 65 °C at 20 °C·min⁻¹ for 1 min. The SIM mode was used for the mass spectrometry (*m/z* = 58, 88).

The PDS concentration was detected using the iodometric method. PDS oxidized potassium iodide to iodine monomer (I₃) due to its strong oxidizing property, and the rate of I₃ production during the oxidation process was linearly related to the concentration of PDS. The absorbance at 352 nm was measured by UV spectrophotometer after 1 min of reaction with 10 mL of PDS solution with 0.05 g of NaHCO₃ and 0.86 g of potassium iodide with rapid stirring. The concentration of PDS was calculated indirectly by the absorbance value, and the standard curve between PDS concentration and absorbance is shown in Figure S1.

Methods for toxicity testing of organic matter: Hamster ovary cell sublines were seeded in 96-well plates and then precultured in a titanium dioxide incubator at 37 °C in 5% CO₂ for 24 h. Then, the precultured cells were starved with serum-free medium for 12 h and the samples to be tested were added: 5 μL Cell Counting Kit-8 reagent (CCK8) was added to one of the 96-well plates, and the same procedure was repeated after 72 h in the remaining 96-well plates. The 96-well plates after the above treatment were placed in an incubator for 3 h, and their absorbance at 450 nm was measured by a microplate reader.

3. Results and Discussion

3.1. Degradation of Dioxane by UV, PDS and UV/PDS

Figure 2 shows the results of dioxane degradation using UV alone, PDS alone and UV/PDS combined. After 150 min of reaction, PDS at a concentration of 2 mM and UV irradiation alone had a very low effect on the degradation of dioxane in water, with both removing about 20% of dioxane. When the UV was activated with PDS (2 mM), the removal rate of dioxane reached more than 93% after 150 min, which was significantly better than the results when UV and PDS were used alone. The kinetic analysis of the experimental results showed that the degradation process of dioxane under UV basically conformed to the proposed first-order kinetic equation (Figure S2). The degradation pattern of the proposed first-order kinetic equation can be expressed as Equations (4) and (5).

$$-\frac{d[1,4\text{-Dioxane}]}{dt} = k[1,4\text{-Dioxane}] \quad (4)$$

$$\text{Ln} \frac{[1,4\text{-Dioxane}]}{[1,4\text{-Dioxane}]_0} = -kt \quad (5)$$

where [1,4-dioxane] is the concentration of dioxane in solution (mM), *t* is the time (min), [1,4-dioxane]₀ is the initial dioxane concentration in solution (mM) and *k* is the apparent reaction rate constant for dioxane (min⁻¹).

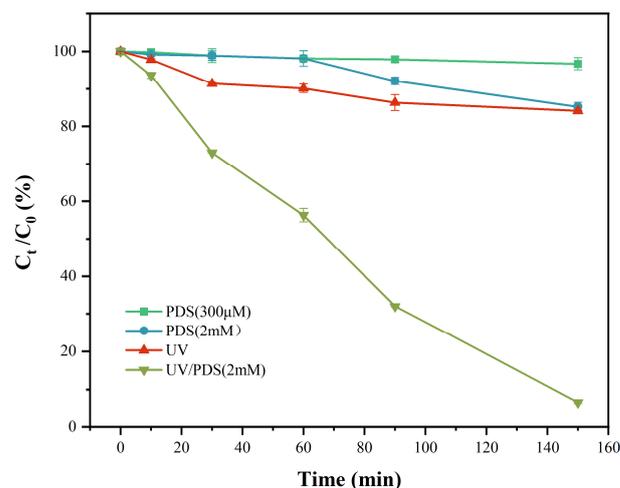


Figure 2. The degradation efficiency of dioxane by PDS, UV and UV/PDS (C_0 is the initial dioxane concentration and C_t is the residual dioxane concentration).

Comparing the existing studies, when degrading dioxane with similar concentration, it took at least 4 h to achieve complete dioxane removal by Fe^{2+} activation of persulfate and hydrogen peroxide, and the NaOH activation was less efficient and took longer to remove dioxane [29]. Therefore, the use of UV/PDS combination could significantly improve the degradation efficiency of dioxane and save the cost. UV-activated PDS could be considered as an advanced oxidation technology capable of efficiently degrading dioxane in water.

3.2. Analysis of Free Radical Species in the UV/PDS Reaction System

In the combined UV/PDS system, PDS was activated by 254 nm UV light to produce $\text{SO}_4^{\cdot-}$, which further reacts in water to form $\cdot\text{OH}$ with a similarly high redox capacity. It was considered as the primary mechanism for degrading organic pollutants, relying on the advanced oxidation system of UV/PDS. The free radicals in the UV/PDS system were determined by free radical quenching and electron spin paramagnetic resonance (EPR) analysis and ethanol (EtOH) was capable of quenching $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ at high reaction rates. However, tert-butyl alcohol (TBA) reacted with $\cdot\text{OH}$ at a significantly higher rate ($\sim 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$) than with $\text{SO}_4^{\cdot-}$ ($\sim 10^5 \text{ M}^{-1}\cdot\text{s}^{-1}$). We assumed that TBA only exerted a good quenching effect on $\cdot\text{OH}$ [31].

Figure 3 illustrates that dioxane removal in all four test sets with quencher addition was significantly lower than without. In the initial stage of the reaction, the added quencher concentration had little effect on the dioxane degradation rate. It was due to the low concentration of radicals generated in the water at this time. As the reaction proceeded, a higher concentration of reactive radicals was generated in the low quencher concentration system. Finally, dioxane removal was only 19.43% at 150 min and 34.93% at 150 min when 100 mM EtOH and 100 mM TBA were added, recording a 71.54% and 56.04% decrease, respectively (compared with that without quencher). The results showed that the reactive radicals generated in UV-activated PDS also had a large amount of $\cdot\text{OH}$ in addition to $\text{SO}_4^{\cdot-}$, all of which had a significant effect on the degradation of dioxane. The results were consistent with quasi-first-order kinetics (Figure S3), with higher free radical concentrations leading to faster reaction rates.

In this study, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a radical trapping agent reacted with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ radicals (with a shorter half-life in solution) to generate stable spin adducts. The study relied on the EPR spectral analysis of the solution to obtain the active substance (Figure 4). Compared with the sampling results at 0 min, the spectral results at various times after the reaction commenced showed that the reaction system contains DMPO-SO (peak signal intensity 1:1:1:1) and DMPO-OH (peak signal intensity 1:2:2:1) [32,33]. Also, the peak signal intensities confirmed that $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ increased in sequence during the reaction, which matched the dioxane degradation rate.

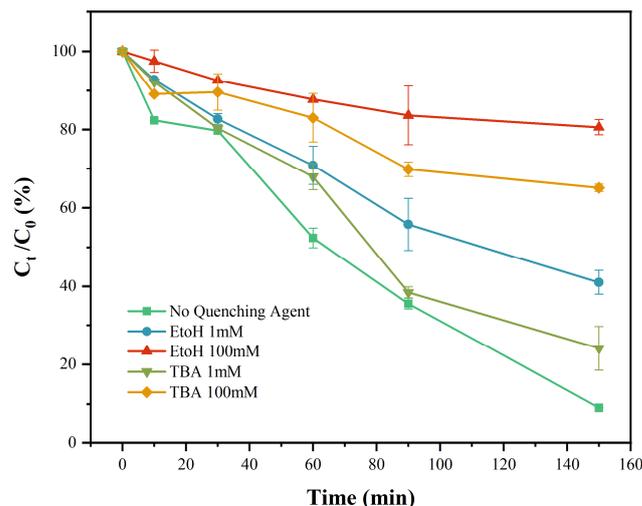


Figure 3. Effect of TBA and EtOH on degradation of 1,4-dioxane.

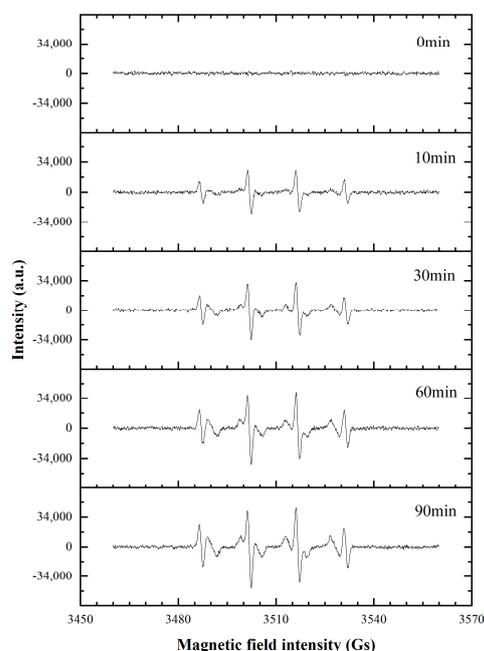


Figure 4. EPR adduct spectra of DMPO-OH and DMPO-SO₄⁻.

3.3. Parameters of UV/PDS Degradation of Dioxane

The advanced oxidation technology of UV/PDS had the advantages of fast reaction rate, simple equipment and convenient operation. In this study, we investigated the effects of various parameters on dioxane degradation in a UV/PDS system by changing the reaction conditions (e.g., PDS dosage and UV intensity) and water conditions (e.g., target pollutant concentration and pH value). The PDS concentration varied between 300 and 50 mM, and the results are shown in Figure 5a. The dioxane degradation efficiency was more than 90% after 150 min of reaction in all cases. When the dosage exceeded 10 mM, the dioxane degradation efficiency could reach more than 95% in 30 min. Overall, similar to the degradation of organic matter in medical wastewater treated by PDS oxidation technology, the removal efficiency of dioxane increased significantly with the PDS dosage [34]. However, some studies have indicated that an excessive dosage of PDS led to a decrease in the degradation efficiency of target pollutants. For instance, Tang et al. found that the removal efficiency of organic matter increased with the dose of oxidant, and it decreased when the dose of PDS exceeded 40 mM [35]. It was due to the fact that excessive PDS dosage lowered

the degradation efficiency of dioxane (Equations (6) and (7)), as excess SO_4^- underwent self-quenching to produce S_2O_8^- [32,36]. In addition, the PDS dose of 50mM did not show a decrease in degradation efficiency, conjecturing that this dose did not represent the upper limit of the oxidant dose that could be administered. The optimal dose of PDS was 3 mM.

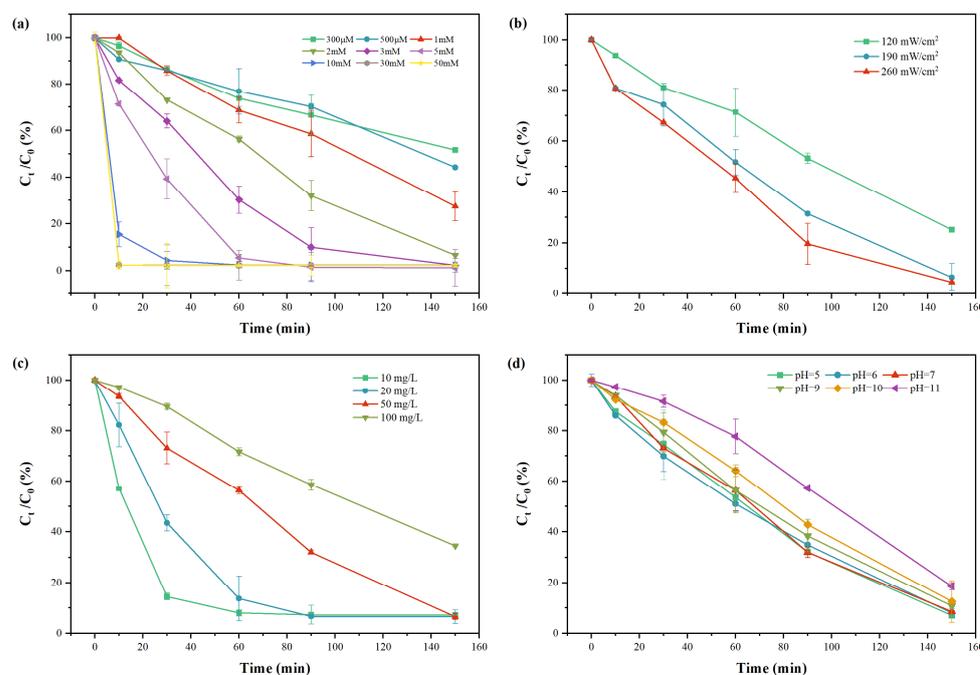
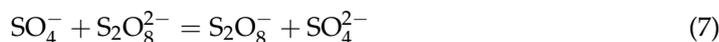


Figure 5. Effect of parameters (a) PDS dosage, (b) UV intensity, (c) 1,4-dioxane initial concentrations and (d) initial pH values on the UV/PDS degradation of 1,4-dioxane.

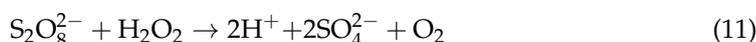
Figure 5b shows that degradation efficiency of dioxane increased with UV radiation intensity and exposure time. Further, the experimental data were subjected to the proposed first-order kinetic simulation (Figure S4). The data under the three irradiation intensities conformed adequately with the proposed first-order kinetic equation. As the irradiation intensities increased, the apparent reaction rate constants of the system also increased sequentially to 8.94×10^{-3} , 1.75×10^{-2} , and $2.04 \times 10^{-2} \cdot \text{min}^{-1}$, respectively. As a component of this reaction system, UV activated the PDS, so the increased UV intensity significantly promoted the degradation rate of target pollutants. The stronger UV irradiation, the more PDS O-O bonds were broken, generating more active substances to complete the dioxane degradation. However, there was a limit of active radicals that could be generated due to a certain initial PDS concentration. When enough radicals have been generated by the time of the reaction, the effect of UV intensity was reduced. Although the degradation rate in the reaction process varied with different UV irradiation intensities, the final degradation efficiency remained similar between $0.190 \text{ mW}/\text{cm}^2$ and $0.260 \text{ mW}/\text{cm}^2$. According to Ma. Y et al.'s study, UV irradiation intensity impacted the degradation rate during the reaction process without affecting the ultimate degradation efficiency [37]. Therefore, it was advisable to select the most cost-effective process parameters for practical applications, which $0.190 \text{ mW}/\text{cm}^2$ was deemed optimal UV irradiation intensity for dioxane degradation using the UV/PDS system in this study.

The above results demonstrated the feasibility of this system, but the upper limit of the degradable dioxane concentration of this system remained to be determined. While other conditions of the reaction system were kept unchanged, Figure 5c demonstrates that

the degradation efficiency exceeded 90% for all dioxane concentrations tested (10 mg/L, 20 mg/L, and 50 mg/L) after 150 min. However, when the dioxane concentration was increased to 100 mg/L, the degradation efficiency dropped significantly to only 65.50%. As the initial dioxane concentration continued to increase, the degradation efficacy of the UV/PDS system decreased gradually. Additionally, when the initial concentration of dioxane increased from 10 to 100 mg·L⁻¹, the corresponding apparent reaction rate constant decreased from 4.26×10^{-2} to 7.16×10^{-3} min⁻¹ (Figure S5) under the reaction conditions. This change was related to the number of reactive substances exposed to the target pollutant in the reaction system. When the concentration of dioxane increased, the number of reactive radicals to which a single dioxane could be exposed correspondingly decreased, lowering the reaction rate. A similar conclusion was demonstrated in the study of the UV-activated PDS degradation of carbamazepine in water [38]. The direct irradiation of UV₂₅₄ light did not effectively degrade dioxane, suggesting that intermediate products generated during the degradation process of organic pollutants might compete with PDS for UV radiation. This competition inhibited the formation of SO₄⁻ and reduced the likelihood of collision between dioxane and reactive free radicals [37,39]. Therefore, it was necessary to increase the intensity of UV irradiation in order to enhance the degradation efficiency when treating high concentrations of dioxane. It also could be determined that an initial dioxane concentration of 50 mg/L was optimal at this UV irradiation intensity.

Changes in pH values could affect the advanced oxidation reaction system in several ways. When the system was alkaline, more ·OH was generated from SO₄⁻. pH differences might also change the morphology of the target pollutants, as they had different pKa values. In this study, we investigated the effect of the initial reaction pH on the degradation efficiency of dioxane (Figure 5d). The results show that the system had a wide range of dioxane degradation at pH values. When the initial pH values of the reaction system were 5, 6, 7, 9, 10, and 11, dioxane degradation efficiency for 150 min was 92.98%, 91.94%, 91.44%, 89.19%, 87.47%, and 81.32%, respectively. Conversely, the degradation efficiency of dioxane was similar, nearly identical, under acidic and neutral conditions, whereas a significant decrease was observed in alkaline solutions. Particularly at pH 11, the degradation efficiency reached only 22.33% after 60 levels of degradation were achieved within approximately 20 min in acidic or neutral solutions. The UV/PDS degradation of dioxane also was consistent well with the proposed first-order kinetic equation (Figure S6), corresponding to reaction rate constants of 1.72×10^{-2} , 1.61×10^{-2} , 1.62×10^{-2} , 1.46×10^{-2} , 1.35×10^{-2} and 1.08×10^{-2} ·min⁻¹. The reaction rate decreased with the increased initial pH of the system. This phenomenon could be ascribed to the change in the active radical species in the system at various pH values.

In alkaline solutions, SO₄⁻ and ·OH react with excess OH⁻ in solution as shown in Equations (8)–(11) [40], reducing the concentration of free radicals, thereby lowering the dioxane degradation efficiency. Huang et al. showed that under acidic and neutral conditions (pH = 2–7), S₂O₈²⁻ forms SO₄⁻ after bond breaking [41]. However, under weakly alkaline conditions (pH = 8–10), SO₄⁻ co-existed with ·OH, while in strongly alkaline conditions (pH > 10), ·OH became the primary active substance [41]. Because ·OH was less oxidizing under alkaline conditions, it was less effective in treating wastewater under alkaline conditions than under acid or neutral conditions. Thus, adjusting the pH between 5 and 7 could achieve the best degradation efficiency.



3.4. Changes in Water Quality Conditions during UV/PDS Degradation

By analyzing PDS consumption, the generation of sulfate, the change in total organic carbon (TOC) in the system and toxicity in water reflected the change in water quality during the degradation. We evaluated the change in UV/PDS reaction system's water quality and provided a theoretical basis for the feasibility of applying it to the actual water.

In the reaction system, the concentration of PDS (as the oxidant) changed, reflecting the extent of the reaction. PDS concentration in the reaction system decreased continuously after the reaction commenced (Figure 6). During the reaction, the PDS decreased by approximately 0.1 mM after 30 min. However, it took approximately 60 min of reaction to consume another 0.1 mM of PDS. After 150 min, PDS residual concentration was 1.71 mM, while at the same time the degradation efficiency of dioxane reached 93.44% (according to Section 3.3). Considering the dioxane degradation efficiency and the starting PDS concentration, the dioxane degradation was reduced by 51.68% after 150 min when the PDS initial concentration was 300 μM . Therefore, we speculated that dioxane activation by UV irradiation was not a linear process, and the rate of reactive free radical generation by PDS was notably based on the PDS concentration in the system.

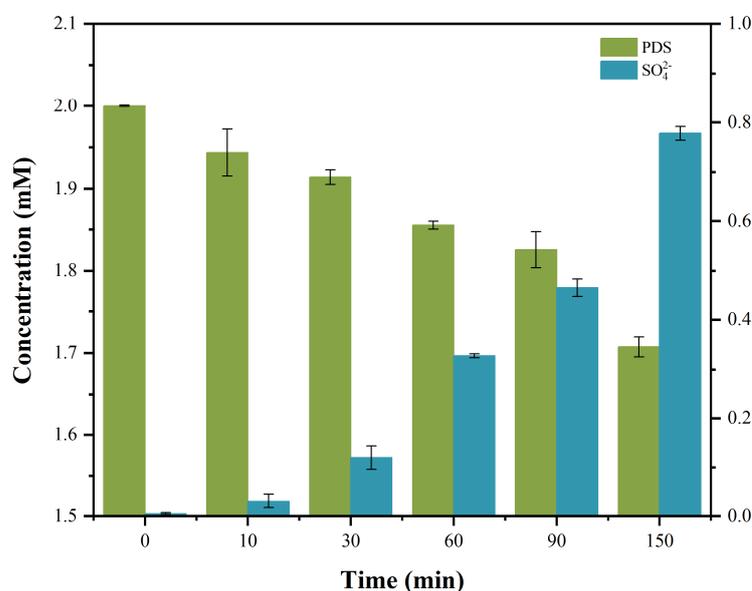


Figure 6. Changes of PDS and SO_4^{2-} concentrations in the system during the reaction.

UV/PDS and other advanced oxidation systems are based on sulfate radicals generating sulfate during the reaction, and sulfate can threaten the water environment's safety. China has set the threshold value of sulfate content at 300 mg/L in the Standards for drinking water quality (GB5749-2022) [42]. This study attempted to determine the sulfate generation in this reaction system. Figure 6 illustrates that the SO_4^{2-} concentration in the system increased with reaction time, and the concentration of SO_4^{2-} produced was about twice that of PDS consumed, consistent with the decomposition law in Equation (12). When the reaction was carried out for 150 min, the SO_4^{2-} concentration in the system was 0.778 mM, i.e., 74.69 $\text{mg}\cdot\text{L}^{-1}$, which satisfied the standard limits. UV/PDS system effectively degraded dioxane while generating SO_4^{2-} at standard concentrations. Thus, the pollution of the aquatic environment caused by this system while degrading organic pollutants was within the controllable range.



Various advanced oxidation techniques can mineralize organic matter in the system, i.e., by oxidizing and decomposing organic pollutants into inorganic substances, such as carbon dioxide and water. We analyzed the mineralized dioxane by detecting total

organic carbon (TOC) in the system. As Figure 7 illustrates, the TOC concentration in the reaction system during the dioxane degradation decreased as the reaction progressed. After 150 min, only 6.56% of dioxane was left in the system, while the TOC level was 83.53% high. This value indicated that dioxane was not completely and directly mineralized in the system. The possible reason was that dioxane was not directly converted into carbon dioxide and water during the degradation but transformed into other smaller organic molecules. According to Sonawane S. et al.'s study, the collision between dioxane and reactive free radicals led to the formation of the main precursor intermediate, namely 1,4-dioxan- α -oxyl radical, through a series of transformations. Ethylene glycol diformate (EGDF) and diethylene glycol were produced by different fissions and oxidation pathways. Ultimately, glyoxylic acid and acetic acid served as the primary degradation products [43]. So, the TOC surplus was significantly higher than the target pollutants.

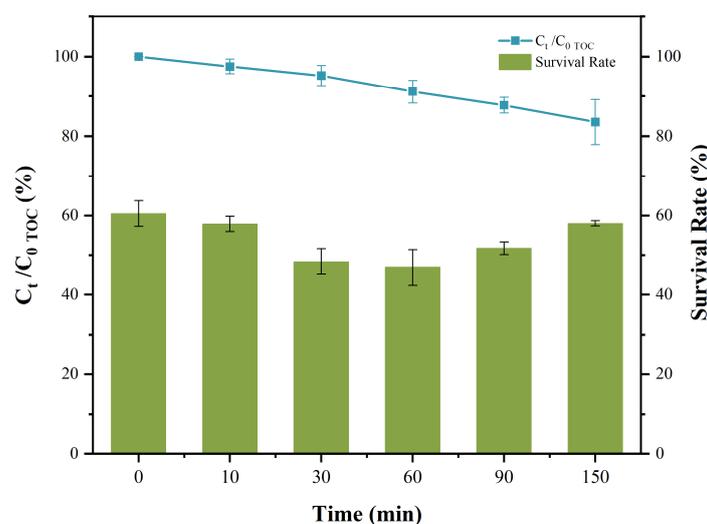


Figure 7. Changes in TOC and the toxicity assessment during the reaction (C_0 is the initial TOC concentration and C_t is the residual TOC concentration).

The CCK8 method determined the system's effect on cell suspension activity at different reaction times, which helped to evaluate the effect of various intermediate products on the cytotoxicity during this reaction system. The reaction system had the most significant effect on cell survival at 60 min (Figure 7) when the cell survival was 46.81%. Therefore, dioxane generated intermediates in the middle of the reaction that were somewhat more toxic than themselves, such as diethylene glycol mentioned above, an organic compound with biological toxicity [44,45]. Toxicity may also increase in the early stages of the reaction as a result of the synergistic effect of the parent compound and transformation products. As the reaction proceeded, the toxicity of the system gradually decreased again, probably because the target pollutants and other intermediates were converted to less toxic substances. And the mineralization of organic matter in the system further increased. This result was consistent with studies comparing the changes in cytotoxicity of AOPs during the removal of benzene and dioxane. Li W. et al. found that for aromatic compounds, intermediates with high cytotoxicity were generated at the beginning of the oxidation reaction, but with the extension of time, the oxidant could completely remove the parent compounds and oxidized products, reducing the generation of toxic oxidation by-products [46]. And the degradation effect of UV/S₂O₈²⁻ was more stable than that of UV/H₂O₂ [46]. The studies of potential reaction product types and degradation mechanisms in the UV/PDS system should be further explored in subsequent studies and use other analytical methods (e.g., SPE, SPME) to detect intermediates that are less volatile than the parent compound to facilitate the assessment of the applicability of this technology in practical water treatment processes.

4. Conclusions

This study investigated the degradation effect of advanced oxidation technology with UV-activated PDS on the emerging pollutant dioxane. The types of active substances in the reaction system were determined by quenching tests and EPR spectroscopic analyses and the effect of the technical parameters and water quality during the degradation were analyzed. Additionally, the presence of secondary pollution in the system was investigated by monitoring the changes in the water quality.

- (1) Compared with previous studies, the results show that the advanced oxidation technology of UV/PDS can effectively degrade dioxane by more than 90%. Additionally, because the advanced oxidation technology of UV/PDS has the advantages of fast reaction rate, simple equipment and convenient operation, it can be applied to water treatment processes for degrading dioxane in actual water.
- (2) The quenching test with varied concentration gradients and the EPR experiment proved that SO_4^- and $\cdot\text{OH}$ influenced dioxane degradation in the reaction system of UV-activated PDS.
- (3) Changes in the technical parameters of this reaction system significantly altered dioxane degradation. When the oxidizing agent (PDS) concentration or the UV intensity were increased, the rate of dioxane degradation increased significantly. Additionally, there existed an upper limit on the speculative amount of PDS, as excessive administration may exert inhibitory effects. However, the concentration of 50mM/L did not surpass this threshold in this study. In addition, the pH value of the reaction system influenced dioxane degradation, particularly under alkaline conditions, leading to a significant inhibitory effect. The reason for this was that the active radical species in the system changed under varied pH values, thereby altering the dioxane degradation. Analyzing the effect of the initial dioxane concentration proved that the number of active substances accessible in the reaction system drove the degradation efficiency of target pollutants. Also, it revealed that the accessibility of reactive radicals to a single dioxane decreased correspondingly as the dioxane concentration increased, leading to a decrease in reaction rate. The optimal reaction conditions were an initial PDS dosage of 3 mM, UV intensity of 0.190 mM/cm^2 , pH between 5 and 7 and an initial dioxane concentration of 50 mg/L.
- (4) The rate at which PDS generated active radicals during the reaction was related to its concentration. Meanwhile, SO_4^{2-} concentration in the system was 0.778 mM, corresponding to the consumption of PDS. Moreover, the pollutant in the water was within a controllable concentration range. When the reaction was carried out for 150 min, 6.78% of dioxane but 83.53% of TOC remained, indicating reduced dioxin degradation, i.e., dioxane was incompletely mineralized and was converted into other small molecules. The system's toxicity fluctuated as the reaction progressed, and there was a notable degree of toxicity to the cells. The intermediate products were more toxic, which could also be verified by the above degradation pathways.
- (5) In subsequent studies, we will investigate the removal of other emerging contaminants such as antibiotic resistance genes and chloroquine phosphate (CQP), an anti-new coronavirus drug, by UV-activated persulfate advanced oxidation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w16091281/s1>, Figure S1: PDS Concentration Detection Standard Curve; Figure S2: Kinetics model of UV and UV/PDS on 1,4-dioxane removal; Figure S3: Kinetics Model of TBA and EtOH on 1,4-Dioxane removal; Figure S4: Kinetics model of UV intensity variation on 1,4-dioxane removal; Figure S5: Kinetics model of 1,4-dioxane initial concentrations variation on its removal; Figure S6: Kinetics model of pH values variation on 1,4-dioxane removal.

Author Contributions: Conceptualization, X.Z. and J.Q.; methodology, X.Z. and J.Q.; software, Y.W. and Y.T.; validation, X.Z., J.Q., Y.W. and Y.T.; formal analysis, X.Z., J.Q. and Y.W.; investigation, X.Z. and Y.W.; resources, X.Z., J.Q. and Y.T.; data curation, J.Q., Y.W. and Y.T.; writing—original draft

preparation, X.Z.; writing—review and editing, X.Z., J.Q., Y.W., Y.T. and Y.Z.; visualization, Y.W. and Y.T.; supervision, Y.Z.; project administration, Y.Z. and Y.T.; funding acquisition, Y.Z. and Y.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (No. 52070145, 51778453).

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Mohamed, A.-M.O.; Paleologos, E.K. *Fundamentals of Geoenvironmental Engineering: Understanding Soil, Water, and Pollutant Interaction and Transport*; Butterworth-Heinemann: Oxford, UK, 2017.
2. Mishra, R.K.; Mentha, S.S.; Misra, Y.; Dwivedi, N. Emerging pollutants of severe environmental concern in water and wastewater: A comprehensive review on current developments and future research. *Water-Energy Nexus* **2023**, *6*, 74–95. [[CrossRef](#)]
3. Chiang, S.Y.; Anderson, R.; Wilken, M.; Walecka-Hutchison, C. Practical perspectives of 1,4-dioxane investigation and remediation. *Remediat. J.* **2016**, *27*, 7–27. [[CrossRef](#)]
4. Xu, F.; Zhou, Z. Introduction to toxicological study on 1,4-dioxane. *J. Environ. Occup. Med.* **2010**, *27*, 554–556.
5. Isaacson, C.; Mohr, T.K.G.; Field, J.A. Quantitative determination of 1,4-dioxane and tetrahydrofuran in groundwater by solid phase extraction GC/MS/MS. *Environ. Sci. Technol.* **2006**, *40*, 7305–7311. [[CrossRef](#)] [[PubMed](#)]
6. Pollitt, K.J.G.; Kim, J.-H.; Peccia, J.; Elimelech, M.; Zhang, Y.; Charkoftaki, G.; Hodges, B.; Zucker, I.; Huang, H.; Deziel, N.C.; et al. 1,4-Dioxane as an emerging water contaminant: State of the science and evaluation of research needs. *Sci. Total. Environ.* **2019**, *690*, 853–866. [[CrossRef](#)] [[PubMed](#)]
7. Shanmugavel, S.P.; Kumar, G.; Gunasekaran, M. Recent progress in mineralization of emerging contaminants by advanced oxidation process: A review. *Environ. Pollut.* **2024**, *341*, 122842.
8. Klečka, G.; Gonsior, S. Removal of 1,4-dioxane from wastewater. *J. Hazard. Mater.* **1986**, *13*, 161–168. [[CrossRef](#)]
9. Myers, M.A.; Johnson, N.W.; Marin, E.Z.; Pornwongthong, P.; Liu, Y.; Gedalanga, P.B.; Mahendra, S. Abiotic and bioaugmented granular activated carbon for the treatment of 1,4-dioxane-contaminated water. *Environ. Pollut.* **2018**, *240*, 916–924. [[CrossRef](#)] [[PubMed](#)]
10. Adamson, D.T.; de Blanc, P.C.; Farhat, S.K.; Newell, C.J. Implications of matrix diffusion on 1,4-dioxane persistence at contaminated groundwater sites. *Sci. Total. Environ.* **2016**, *562*, 98–107. [[CrossRef](#)] [[PubMed](#)]
11. Li, F.; Deng, D.; Li, M. Distinct catalytic behaviors between two 1,4-dioxane-degrading monooxygenases: Kinetics, inhibition, and substrate range. *Environ. Sci. Technol.* **2019**, *54*, 1898–1908. [[CrossRef](#)] [[PubMed](#)]
12. Mahendra, S.; Grostern, A.; Alvarez-Cohen, L. The impact of chlorinated solvent co-contaminants on the biodegradation kinetics of 1,4-dioxane. *Chemosphere* **2013**, *91*, 88–92. [[CrossRef](#)] [[PubMed](#)]
13. Kishimoto, N.; Miki, T. Sequential Process of Electro-Oxidation Followed by UV Photolysis (EO/UV) as a Simple Advanced Oxidation Process. *Ozone Sci. Eng.* **2023**, *45*, 528–535. [[CrossRef](#)]
14. Andaluri, G.; Suri, R. Removal of 1,4-Dioxane and Volatile Organic Compounds from Groundwater Using Ozone-Based Advanced Oxidation Process. *Ozone Sci. Eng.* **2017**, *39*, 423–434. [[CrossRef](#)]
15. Neta, P.; Huie, R.E.; Ross, A.B. Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027–1284. [[CrossRef](#)]
16. Rosario-Ortiz, F.L.; Wert, E.C.; Snyder, S.A. Evaluation of UV/H₂O₂ treatment for the oxidation of pharmaceuticals in wastewater. *Water Res.* **2010**, *44*, 1440–1448. [[CrossRef](#)] [[PubMed](#)]
17. Oh, W.-D.; Dong, Z.; Lim, T.-T. Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: Current development, challenges and prospects. *Appl. Catal. B Environ.* **2016**, *194*, 169–201. [[CrossRef](#)]
18. Lee, J.; von Gunten, U.; Kim, J.-H. Persulfate-based advanced oxidation: Critical assessment of opportunities and roadblocks. *Environ. Sci. Technol.* **2020**, *54*, 3064–3081. [[CrossRef](#)] [[PubMed](#)]
19. Vela, N.; Fenoll, J.; Garrido, I.; Pérez-Lucas, G.; Flores, P.; Hellín, P.; Navarro, S. Reclamation of agro-wastewater polluted with pesticide residues using sunlight activated persulfate for agricultural reuse. *Sci. Total. Environ.* **2019**, *660*, 923–930. [[CrossRef](#)] [[PubMed](#)]
20. 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](#)]
21. Wang, G.; Zhou, S.; Wang, D.; Feng, L.; Xu, Y.; Huang, L. Study on influence factors of treating landfill leachate by ultraviolet-activated persulfate system. *Environ. Sci. Pollut. Res.* **2021**, *28*, 52981–52992. [[CrossRef](#)] [[PubMed](#)]
22. Feng, Y.; Wu, D.; Li, H.; Bai, J.; Hu, Y.-B.; Liao, C.-Z.; Li, X.-Y.; Shih, K. Activation of persulfates using siderite as a source of ferrous ions: Sulfate radical production, stoichiometric efficiency, and implications. *ACS Sustain. Chem. Eng.* **2018**, *6*, 3624–3631. [[CrossRef](#)]

23. Zhou, Z.; Liu, X.; Sun, K.; Lin, C.; Ma, J.; He, M.; Ouyang, W. Persulfate-based advanced oxidation processes (AOPs) for organic-contaminated soil remediation: A review. *Chem. Eng. J.* **2019**, *372*, 836–851. [[CrossRef](#)]
24. Zhao, L.; Hou, H.; Fujii, A.; Hosomi, M.; Li, F. Degradation of 1,4-dioxane in water with heat-and Fe²⁺-activated persulfate oxidation. *Environ. Sci. Pollut. Res.* **2014**, *21*, 7457–7465. [[CrossRef](#)] [[PubMed](#)]
25. Lee, Y.; Lo, S.; Kuo, J.; Hsieh, C. Decomposition of perfluorooctanoic acid by microwaveactivated persulfate: Effects of temperature, pH, and chloride ions. *Front. Environ. Sci. Eng.* **2011**, *6*, 17–25. [[CrossRef](#)]
26. Hori, H.; Nagaoka, Y.; Murayama, M.; Kutsuna, S. Efficient decomposition of perfluorocarboxylic acids and alternative fluorochemical surfactants in hot water. *Environ. Sci. Technol.* **2008**, *42*, 7438–7443. [[CrossRef](#)]
27. 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](#)]
28. Lominchar, M.; Santos, A.; de Miguel, E.; Romero, A. Remediation of aged diesel contaminated soil by alkaline activated persulfate. *Sci. Total. Environ.* **2017**, *622–623*, 41–48. [[CrossRef](#)] [[PubMed](#)]
29. Yan, N.; Liu, F.; Liu, B.; Brusseau, M.L. Treatment of 1,4-dioxane and trichloroethene co-contamination by an activated binary persulfate-peroxide oxidation process. *Environ. Sci. Pollut. Res.* **2018**, *25*, 32088–32095. [[CrossRef](#)] [[PubMed](#)]
30. Feng, Y.; Lee, P.H.; Wu, D.; Shih, K. Surface-bound sulfate radical-dominated degradation of 1,4-dioxane by alumina-supported palladium (Pd/Al₂O₃) catalyzed peroxymonosulfate. *Water Res.* **2017**, *120*, 12–21. [[CrossRef](#)]
31. Gao, L.; Guo, Y.; Zhan, J.; Yu, G.; Wang, Y. Assessment of the validity of the quenching method for evaluating the role of reactive species in pollutant abatement during the persulfate-based process. *Water Res.* **2022**, *221*, 118730. [[CrossRef](#)]
32. Ouyang, D.; Yan, J.; Qian, L.; Chen, Y.; Han, L.; Su, A.; Zhang, W.; Ni, H.; Chen, M. Degradation of 1,4-dioxane by biochar supported nano magnetite particles activating persulfate. *Chemosphere* **2017**, *184*, 609–617. [[CrossRef](#)] [[PubMed](#)]
33. Duan, X.; Sun, H.; Kang, J.; Wang, Y.; Indrawirawan, S.; Wang, S. Insights into heterogeneous catalysis of persulfate activation on dimensional-structured nanocarbons. *ACS Catal.* **2015**, *5*, 4629–4636. [[CrossRef](#)]
34. Lin, M.; Liu, M.; Wu, J.; Owens, G.; Chen, Z. Green synthesis of Mn₂O₃ activated PDS to degrade estril in medical wastewater and its degradation pathway. *Chem. Eng. J.* **2024**, *484*, 149713. [[CrossRef](#)]
35. Tang, J.; Yang, J.; Chen, Y.; Zhang, X.; Zhang, A. Comparative study of Fe⁰-H₂O₂, Fe⁰-PMS and Fe⁰-PDS systems for the removal of refractory organics from bio-treated landfill leachate. *J. Environ. Chem. Eng.* **2023**, *11*, 111173. [[CrossRef](#)]
36. 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](#)]
37. Ma, Y.; Wang, Z.; Yang, W.; Chen, C.; Li, J.; He, R.; Liu, S. Insights into the radical and nonradical oxidation degradation of ciprofloxacin in peroxydisulfate activation by ultraviolet light. *J. Water Process. Eng.* **2022**, *49*, 103184. [[CrossRef](#)]
38. Naiyun, G.; Xuhan, H.; Jing, D. Study on UV-activated persulfate oxidation of carbamazepine in water. *J. Huazhong Univ. Sci. Technol.* **2013**, *41*, 117–122.
39. Fujioka, T.; Kodamatani, H.; Tran, H.D.M.; Fujioka, A.; Hino, K.; Yoshikawa, T.; Inoue, D.; Ikehata, K. Degradation of N-nitrosamines and 1,4-dioxane using vacuum ultraviolet irradiation (UV254+185 nm or UV172 nm). *Chemosphere* **2021**, *278*, 130326. [[CrossRef](#)]
40. Lau, T.K.; Chu, W.; Graham, N.J. The aqueous degradation of butylated hydroxyanisole by UV/S₂O₈²⁻: Study of reaction mechanisms via dimerization and mineralization. *Environ. Sci. Technol.* **2007**, *41*, 613–619. [[CrossRef](#)] [[PubMed](#)]
41. Huang, Y.-F.; Huang, Y.-H. Identification of produced powerful radicals involved in the mineralization of bisphenol A using a novel UV-Na₂S₂O₈/H₂O₂-Fe (II, III) two-stage oxidation process. *J. Hazard. Mater.* **2009**, *162*, 1211–1216. [[CrossRef](#)]
42. GB 5749-2022; Standards for Drinking Water Quality; State Administration of Market Supervision and Administration of the People's Republic of China, Standardization Administration of the People's Republic of China. Standards Press of China: Beijing, China, 2022.
43. Sonawane, S.; Fedorov, K.; Rayaroth, M.P.; Boczkaj, G. Degradation of 1,4-dioxane by sono-activated persulfates for water and wastewater treatment applications. *Water Resour. Ind.* **2022**, *28*, 100183. [[CrossRef](#)]
44. Tornambè, A.; Manfra, L.; Mariani, L.; Faraponova, O.; Onorati, F.; Savorelli, F.; Cicero, A.M.; Lamberti, C.V.; Magaletti, E. Toxicity evaluation of diethylene glycol and its combined effects with produced waters of off-shore gas platforms in the Adriatic Sea (Italy): Bioassays with marine/estuarine species. *Mar. Environ. Res.* **2012**, *77*, 141–149. [[CrossRef](#)] [[PubMed](#)]
45. Marraffa, J.M. Diethylene glycol. In *Encyclopedia of Toxicology*, 4th ed.; Wexler, P., Ed.; Academic Press: Oxford, UK, 2024; pp. 739–742.
46. Li, W. *Sulfate Radical-Based Advanced Oxidation Treatment for Groundwater Water Treatment and Potable Water Reuse*; University of California: Riverside, CA, USA, 2017; p. 254.

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