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A Comparative Study of Advanced Oxidation Processes for Pentachlorophenol Degradation

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Abstract

Pentachlorophenol (PCP) is a priority pollutant that is highly resistant to conventional water treatment methods. Advanced Oxidation Processes (AOPs) offer an efficient approach by combining oxidants with activators to produce radicals. Hydrogen peroxide (H_2O_2) and peroxydisulfate ($S_2O_8^{2-}$) are oxidants with symmetrical peroxide bonds that effectively generate radicals through energy transfer. However, each produces distinct radicals, followed by different degradation mechanisms. A comprehensive comparison is crucial for adopting effective AOP technologies. This study evaluates the kinetic performance and cost-effectiveness of AOPs using H_2O_2 and $S_2O_8^{2-}$, activated by ultrasound (US), UV light (UVC and VUV), and their combinations. H_2O_2 demonstrated superior performance, particularly under UV light, due to its pH stability and higher reactivity with PCP. The combination of US and VUV irradiation resulted in the highest degradation rates, with the addition of H_2O_2 yielding the best overall performance ($k = 0.75$ min^{-1}). Increasing the temperature enhanced PCP degradation across all systems, with the US–VUV–H_2O_2 system achieving the highest rate at 35°C ($k = 0.91$ min^{-1}). The VUV-H_2O_2 system recorded the lowest activation energy ($E_a = 4.77$ kJ mol^{-1}), indicating greater efficiency. H_2O_2-based systems, particularly VUV-H_2O_2 and UVC-H_2O_2, emerged as the most efficient and cost-effective options, with the lowest energy consumption (4.65–4.80 kWh m^{-3}) and costs (Rp8,825–Rp9,064/m^{-3}). These results highlight H_2O_2 in UV configurations as the optimal choice for PCP degradation, offering effective treatment with reduced energy and chemical requirements.

1. Introduction

Pentachlorophenol (PCP), a highly chlorinated hydrocarbon, has been extensively used as a wood preservative and biocide [1]. Its chemical stability has contributed to extensive contamination of both terrestrial and aquatic ecosystems, enabling its accumulation and transmission through the food chain [2]. Furthermore, PCP's acute and chronic toxicity, along with its carcinogenic properties, have led to its classification as a priority pollutant by the US EPA, with a maximum contaminant level of 0.001 mg/L for drinking water [3]. In Indonesia, the permissible PCP concentration in drinking water is set at 0.009 mg/L [4]. Given these factors, the removal of PCP is crucial in water reclamation processes. Both biological and chemical methods have been explored for PCP remediation. However, PCP is considered one of the most toxic and treatment-resistant compounds when using conventional activated sludge processes [3]. Advanced oxidation processes (AOPs) have demonstrated significant effectiveness in degrading chlorophenols and chlorobenzenes, making them a promising approach for PCP remediation [5].

AOPs involve the combination of oxidants, such as hydrogen peroxide H_2O_2 or persulfate salts, with activators to generate highly reactive free radicals. Persulfate salts are commonly found in the form of peroxymonosulfate (HSO_5^-) and peroxydisulfate ($S_2O_8^{2-}$). These radicals effectively degrade pollutants by breaking them down into less harmful substances through a process known as mineralization [6]. The generation of free radicals occurs in situ via energy or electron transfer reactions. Energy-activated AOPs are highly effective at rapidly breaking down persistent pollutants without the use of harsh chemicals, thereby minimizing the risk of secondary pollution [7, 8]. This efficiency is further enhanced when symmetrical peroxide oxidants, such as H_2O_2 and $S_2O_8^{2-}$, are used. These oxidants undergo homolytic cleavage of the peroxide (-O-O-) bond, resulting in the formation of two identical radicals, hydroxyl radicals (·OH) or sulfate radicals ($SO_4^{\cdot-}$), which serve as the primary oxidants [9].

Both ·OH and $SO_4^{\cdot-}$ radicals are highly reactive and capable of oxidizing a wide range of organic compounds; however, the mechanisms by which they degrade pollutants can differ significantly. $SO_4^{\cdot-}$ primarily reacts through electron transfer reactions, whereas ·OH can also engage in hydrogen-atom abstraction in addition to electron transfer [10]. These distinct reaction pathways lead to varying degradation efficiencies and outcomes. Consequently, understanding and evaluating the differences in performance between the two symmetrical oxidants, H_2O_2 and $S_2O_8^{2-}$, is essential. These oxidants generate unique radicals and follow different mechanisms, which can profoundly impact their effectiveness in treating specific pollutants.

Energy inputs for AOPs encompass ultrasound, light, and heat. US irradiation, recognized for its environmental compatibility and effectiveness, operates by inducing cavitation in liquids at frequencies ranging from 20 to 1,000 kHz. This process involves the formation, growth, and collapse of bubbles, releasing extreme localized conditions—temperatures up to 5,000 K and pressures reaching 1,000 atm—which activate oxidants to produce free radicals [11], as shown in Equations (1) and (2). Additionally, ultrasound can break water molecules to generate hydroxyl radicals, as described in Equation (3).

$$H_2O_2 \overset{US}{\rightarrow} 2 \cdot OH \tag{1}$$

$$S_2O_8^{2-} \overset{US}{\rightarrow} 2SO_4^{\bullet-} \tag{2}$$

$$H_2O \overset{US}{\rightarrow} \cdot OH + \cdot H \tag{3}$$

Similarly, light energy plays a critical role in photochemical AOPs, where UV light in the range of ~200–280 nm effectively promotes the generation of ·OH or $SO_4^{\cdot-}$ radicals. UV-based processes are considered clean, simple, and often more efficient than purely chemical AOPs [7]. UVC light is commonly used, though to further enhance radical production, vacuum-UV (VUV) light is employed, which emits wavelengths of 185 nm and 254 nm simultaneously [12]. The chemical reactions representing radical formation by UV-based AOPs are presented in Equations (4) and (5). Moreover, VUV-185 nm light is highly absorbed by water (with an absorption coefficient of 1.8 cm^{-1}), making it particularly effective for activating water molecules to generate radicals efficiently [13], as illustrated in Equation (6).

$$H_2O_2 + hv \rightarrow 2 \ \cdot OH \tag{4}$$

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\bullet-} \tag{5}$$

$$H_2O \ + hv \ (185 \ nm) \rightarrow OH \ + \cdot H \tag{6}$$

Considering the predominant yet distinct mechanisms involved in AOPs using H_2O_2 and $S_2O_8^{2-}$ activated by US and ultraviolet light (UVC and VUV), or their combinations, understanding the effectiveness of each approach is essential for evaluating performance and applicability. Previous studies have mostly examined these processes individually. For instance, H_2O_2 and $S_2O_8^{2-}$ activated by US were compared for the removal of phenol from aqueous solutions, with results indicating that the combination of US/$S_2O_8^{2-}$ achieved the highest efficiency, exceeding 90% [14]. UV/H_2O_2 and UV/$S_2O_8^{2-}$ processes have also been evaluated for degrading acetamiprid, where the UV/$S_2O_8^{2-}$ process showed the best performance, with a rate constant of 0.11 min^{-1} [15].

In another study, the individual and combined effects of UV and US in activating $S_2O_8^{2-}$ were investigated for the degradation of tetracycline in aqueous solution. The highest removal efficiency—approximately 96.29%—was achieved using the combined UV/US/$S_2O_8^{2-}$ process, outperforming the individual treatments [16]. Since energy-activated AOPs are seen as effective and environmentally friendly for contaminant removal, assessing their energy consumption is crucial for evaluating economic feasibility. Although energy-per-order comparisons of various AOPs have been reported [17], persulfate-based systems were not included. Furthermore, most prior studies evaluated H_2O_2 and $S_2O_8^{2-}$ activation separately, under different conditions, targeting different pollutants, and using varying evaluation parameters—making fair comparisons difficult.

Although several review papers have discussed sonolytic and photolytic AOPs [18, 19, 20, 21], direct experimental comparisons conducted under uniform conditions remain scarce. Therefore, a systematic investigation into both the individual and combined effects of these AOPs under standardized experimental settings is essential to accurately evaluate their degradation kinetics and economic feasibility. To date, no single study has comprehensively assessed these aspects within a unified experimental framework. This study aims to address this gap by providing a thorough comparison of various energy-activated AOPs for the degradation of PCP, contributing valuable insights for the effective implementation of AOP technologies in the treatment of PCP-contaminated wastewater.

2. Experimental

2.1. Chemicals and Reagents

All chemicals used in the experiments were of analytical reagent grade. Pentachlorophenol (C_6Cl_5OH, 97%) and sodium persulfate ($Na_2S_2O_8^{2-}$, 99%) were purchased from Sigma-Aldrich Inc., USA. Hydrogen peroxide (H_2O_2, 35%) was obtained from Daejung Chemicals & Metals, Korea. Temperature regulation was achieved using a cooling system. Water used for reagent preparation was purified using a Millipore reverse osmosis system with a resistivity of 18.2 MΩ·cm. Acetic acid (CH_3COOH, 100%, HPLC grade) was purchased from J.T. Baker Chemical Co., and acetonitrile (99.9%, HPLC grade) was purchased from Duksan Pure Chemical Co.

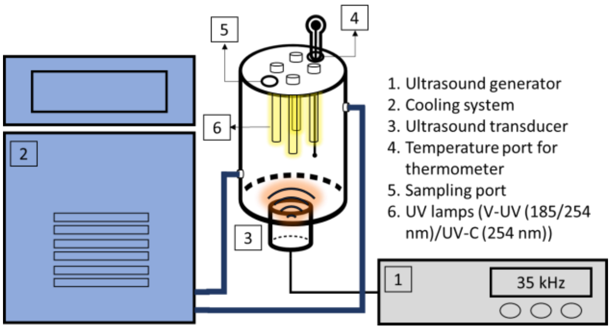

Figure 1. Reactor setup for photolytic and sonolytic experiments

2.2. Experimental Setup and Analysis Method

The experimental setup for the photolytic and sonolytic degradation of PCP is illustrated in Figure 1. The degradation experiments were conducted in a capped cylindrical glass batch reactor (Φ 100 × H 200 mm, total volume: 1.50 L, experimental volume: 1 L). A single piezoelectric transducer with an area of approximately 1590.4 mm^2 (PZT, Tamura, Japan) was installed beneath the reactor to irradiate ultrasound from the bottom. The transducer was connected to an ultrasonic generator (Mirae Ultrasonic MEGA-100, Korea), allowing control of the power and frequency, set at 35 kHz and 70 W, respectively. For photolytic experiments, the reactor was equipped with either four UVC lamps (254 nm, 10 W each) or four VUV lamps (185/254 nm, 10 W each), each measuring 150 mm in length. The lamps were partially submerged, with approximately 77.3 mm of their length in contact with the water. The temperature of the reactor was maintained using a water jacket surrounding the reactor to ensure stable operating conditions.

At specific time intervals, 1 mL of the solution was sampled, filtered through a 0.22 µm Millipore membrane, and mixed with 1 mL of methanol to completely terminate the oxidation process. The experiments were conducted as single runs; therefore, the results primarily serve as preliminary comparative data to highlight trends. The PCP concentration was analyzed using a high-performance liquid chromatography (HPLC) system (Agilent 1260 Infinity) equipped with a Poroshell 120 EC-C18 column (4.6 × 150 mm, 5 µm) and a diode array detector set at 300.5 nm. The mobile phase consisted of 70% acetonitrile and 30% aqueous acetic acid (5%), delivered at a flow rate of 1 mL/min [22].

2.3. Kinetic Analysis

The residual concentration of PCP in the solution was used to determine the kinetic constants. The kinetic constants were derived using the pseudo-first-order kinetic model, considering that it is commonly applied in AOPs research [23, 24, 25]. In addition, this model was chosen due to the condition in which the oxidant is used in excess compared to the target contaminant. In this experiment, the initial concentration of PCP and the concentrations of oxidants (either H_2O_2 or $S_2O_8^{2-}$) corresponded to a 1:10 ratio. Under such conditions, the concentration of the oxidant is assumed to remain relatively constant throughout the reaction, and the reaction rate depends primarily on the concentration of PCP. The equation for the pseudo-first-order kinetic model is represented in Equation (7).

$$\frac{dC}{dt} = -k_1 C \tag{7}$$

Where, C represents the concentration of PCP, t denotes time, and k is the kinetic constant. The activation energy parameters for PCP decomposition were determined using the Arrhenius equation (Equation (8)).

$$lnk = lnA - \left(\frac{E_a}{RT}\right) \tag{8}$$

Where, A is the Arrhenius constant, R is the universal gas constant (8.3144598 J mol^{-1}K^{-1}), T refers to the absolute temperature (K), k represents the reaction rate constant (min^{-1}), E_a denotes the activation energy (kJ mol^{-1}). This equation was applied in the lnk vs. $\frac{1}{T}$ format, where the slope gives the value of $\frac{-E_a}{R}$ from where E_a can be calculated.

3. Results and Discussion

3.1. Effect of Different Combinations of Oxidant and Energy Input

Figure 2 illustrates the kinetic rate constant (k) of PCP degradation for various combinations of oxidants (H_2O_2 and $S_2O_8^{2-}$) activated by different energy inputs, including US, VUV, UVC, US-VUV, and US-UVC. The complete kinetic degradation profiles of PCP over time are presented in Figure S1.

When comparing H_2O_2 and $S_2O_8^{2-}$ as oxidants, H_2O_2 consistently outperforms $S_2O_8^{2-}$ in most energy activation methods, particularly those involving light-based activation (VUV, UVC, US-VUV, and US-UVC), as evidenced by the higher k values. These results align with previous studies that demonstrated higher k for clonidine, benzoic acid, and nitrobenzene under UV/H_2O_2 systems compared to UV/$S_2O_8^{2-}$ systems [26, 27]. Similarly, UV/H_2O_2 achieved better removal efficiency than HSO_5^--based systems for 23 tested micropollutants [28].

The first explanation is likely due to the fact that this system operates at nearly neutral pH. H_2O_2 is more stable and effective across a wider pH range (typically pH 3–9), making it well-suited for neutral conditions. In contrast, $S_2O_8^{2-}$ performance is more pH-dependent and typically requires acidic conditions (pH < 3) for optimal activation [26]. This highlights the practical advantage of H_2O_2 for real-world applications under neutral pH conditions, where $S_2O_8^{2-}$ efficacy may be limited.

Furthermore, PCP exhibits higher reactivity with •OH than with $SO_4^{\bullet-}$. This difference can be attributed to PCP's molecular structure: the five chlorine atoms attached to the benzene ring reduce the oxidation state of the carbon atoms, making them more susceptible to attack by •OH. •OH are known to preferentially target carbon atoms with lower oxidation states in the early stages of the degradation process, which explains the superior degradation kinetics achieved with H_2O_2 as the oxidant [29].

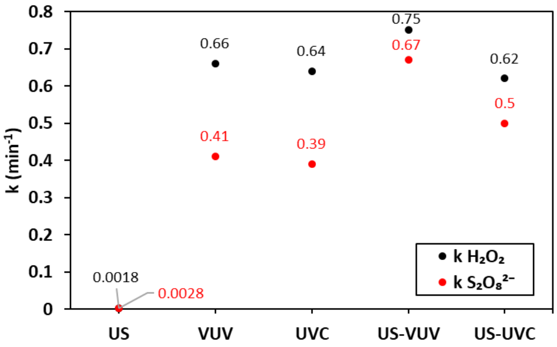

Figure 2. Kinetic constant of PCP degradation using different combinations of oxidant and energy input ($[PCP]_0$ = 10 mg/L; $[H_2O_2]_0/[S_2O_8^{2-}]_0$ = 0.4 mM; US frequency = 35 kHz; US power = 70W; UV power = 10 W(each); T = 25°C; and initial pH = 6 ± 0.2)

However, under US activation alone, $S_2O_8^{2-}$ achieves a higher k value of k = 0.0028 min⁻¹ compared to H_2O_2 (k = 0.0018 min⁻¹). This indicates that the cavitation effects generated by US are more effective at $S_2O_8^{2-}$ to produce $SO_4^{\cdot -}$ than at activating H_2O_2 to generate •OH [23, 30]. UV light activates $S_2O_8^{2-}$ through photolysis, which depends on the direct absorption of UV photons by molecules. The molar absorption coefficient (ε) of $S_2O_8^{2-}$ at a UV wavelength of 254 nm is 21.1 M⁻¹cm⁻¹, slightly higher than that of H_2O_2 (ε = 18.6 M⁻¹cm⁻¹) [31, 32].

In terms of energy inputs to activate oxidants, the US alone results in the lowest k for both oxidants. In contrast, both VUV and UVC light significantly enhance k. For H_2O_2, the k reaches 0.66 min⁻¹ with VUV and 0.64 min⁻¹ with UVC, while for $S_2O_8^{2-}$, the k values improve to 0.41 min⁻¹ (VUV) and 0.39 min⁻¹ (UVC). UV activation provides consistent, high-energy photons that efficiently cleave peroxide bonds through photolysis, ensuring rapid and uniform radical generation. This is attributed to both oxidants' strong absorption of UVC light at 254 nm and even higher absorption at VUV wavelengths (185 nm), which deliver more energetic photons for effective bond cleavage. For instance, H_2O_2 has an absorption coefficient of approximately 240 M⁻¹cm⁻¹ at 185 nm, significantly higher than its absorption at 254 nm (18.6 M⁻¹cm⁻¹). Similarly, $S_2O_8^{2-}$ demonstrates a much stronger absorption at 185 nm, with an absorption coefficient of approximately 350 M⁻¹cm⁻¹, compared to 21.1 M⁻¹cm⁻¹ at 254 nm [33, 34].

Combining US with VUV energy inputs achieves the highest k for PCP degradation. For H_2O_2, the k reaches 0.75 min⁻¹, while for $S_2O_8^{2-}$, k increases to 0.67 min⁻¹. This synergistic effect arises from the physical effect of cavitation, which provides the intense mixing to utilize the UV light irradiation effectively [35, 36, 37, 38]. Among all tested configurations, the combination of H_2O_2 with US-VUV delivers the highest k, showcasing the powerful synergy between ultrasound and VUV light. Although $S_2O_8^{2-}$ also performs effectively, it generally shows slightly lower k, likely due to the slower reaction mechanisms associated with $SO_4^{\cdot -}$ compared to •OH. This highlights the superior performance of H_2O_2 in energy-activated AOP systems, particularly under combined US-VUV conditions.

3.2. Effect of Initial Temperature

Temperature is a critical factor in redox systems, as it directly influences the activation energy required to initiate the reaction. To evaluate the effect of temperature on PCP degradation, experiments were conducted at 15, 25, and 35°C. The choice of these temperatures represents different environmental and operational scenarios: 25°C reflects average ambient temperatures in temperate regions and standard laboratory conditions, 15°C simulates colder environments or industrial settings with cooling systems, and 35°C represents warmer climates or tropical regions. This range allows for a comprehensive understanding of how temperature impacts the efficiency of the degradation process.

The effect of temperature on PCP degradation shows a clear trend of increased degradation rates with rising temperatures for both H_2O_2 and $S_2O_8^{2-}$ across various energy activation methods, as shown in Figure 3(a) for H_2O_2 and 3(b) for $S_2O_8^{2-}$. The highest k achieved in the US- VUV-H_2O_2 system, where k reaches 0.91 min⁻¹ at 35°C. The observed enhancement in degradation rates with increasing temperature can be attributed to its role in lowering activation energy. Elevated temperatures facilitate faster cleavage of peroxide bonds and improve radical formation efficiency in both H_2O_2 and $S_2O_8^{2-}$ systems [39]. This effect is particularly pronounced in systems employing VUV or US-VUV, where the combination of photolysis, cavitation, and thermal effects enhances radical generation and reaction kinetics [20].

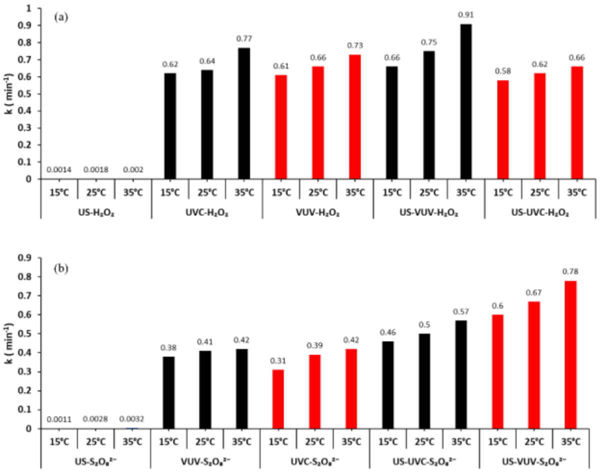

Figure 3. Kinetic constant of PCP degradation using various energy input at various temperature to activate (a) H_2O_2, and (b) $S_2O_8^{2-}$ ($[PCP]_0$ = 10 mg/L; $[H_2O_2]_0/[S_2O_8^{2-}]_0$ = 0.4 mM; US frequency = 35 kHz; US power = 70W; UV power = 10 W (each); and initial pH = 6 ± 0.2)

Table 1. Economic comparison of PCP degradation in distilled water by various AOPs systems

System	E_{EO} (kWh m^{-3})	Oxidant conc. (mM)	Cost		Total cost (/m^{-3})
			Electricity (kWh^{-1})	Chemical (kg^{-1})	
US-$S_2O_8^{2-}$	1920.00	0.004	Rp3,157,478	Rp1,090,000	Rp4,247,478
VUV-$S_2O_8^{2-}$	7.49	0.004	Rp12,322	Rp1,090,000	Rp1,102,322
UVC-$S_2O_8^{2-}$	7.88	0.004	Rp12,954	Rp1,090,000	Rp1,102,954
US-VUV-$S_2O_8^{2-}$	12.61	0.004	Rp20,736	Rp1,090,000	Rp1,110,736
US-UVC-$S_2O_8^{2-}$	16.90	0.004	Rp27,786	Rp1,090,000	Rp1,117,786
US-H_2O_2	2986.67	0.004	Rp4,911,633	Rp1,171	Rp4,912,804
VUV-H_2O_2	4.65	0.004	Rp7,654	Rp1,171	Rp8,825
UVC-H_2O_2	4.80	0.004	Rp7,894	Rp1,171	Rp9,064
US-VUV-H_2O_2	11.26	0.004	Rp18,524	Rp1,171	Rp19,695
US-UVC-H_2O_2	13.63	0.004	Rp22,408	Rp1,171	Rp23,579

Condition: $[PCP]_0$ = 10 mg/L; $[H_2O_2]_0/[S_2O_8^{2-}]_0$ = 0.4 mM; US frequency = 35 kHz; US power = 70W; UV power = 10 W(each); T = 25°C; and initial pH =5.8 ± 0.2.

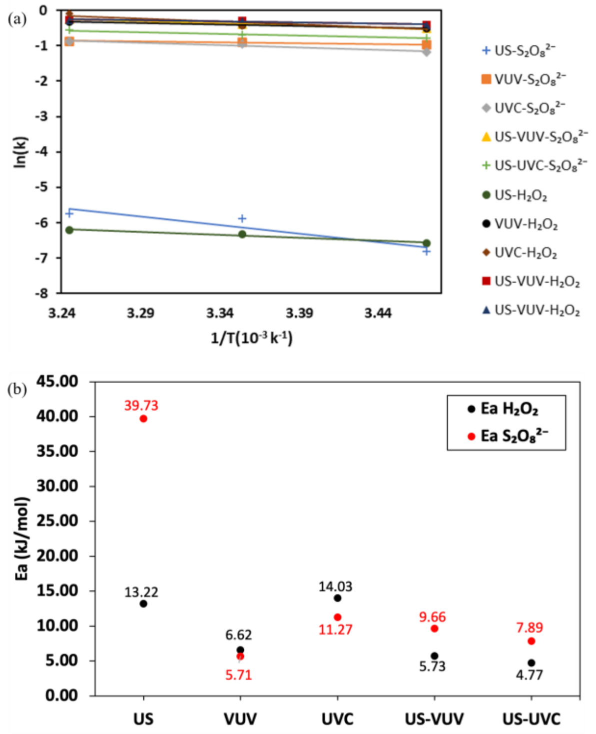

Figure 4. Arrhenius plot of the pseudo first order rate constants, and (b) activation energy of PCP degradation using different combinations of oxidant and energy input ($[PCP]_0$ = 10 mg/L; $[H_2O_2]_0/[S_2O_8^{2-}]_0$ = 0.4 mM; US frequency = 35 kHz; US power = 70W; UV power = 10 W(each); T = 25°C; and initial pH = 6 ± 0.2)

The Arrhenius equation was applied to calculate E_a value. Activation energy refers to the minimum energy required to initiate a chemical reaction. The Arrhenius plots for all the systems are given in Figure 4(a), which accordingly shows that k increases with an increase in temperature. The calculated E_a for PCP decomposition using all combinations of oxidant and energy inputs is shown in Figure 4(b). The highest E_a is observed in the US system with $S_2O_8^{2-}$ (E_a = 39.73 kJ mol^{-1}), indicating the limited efficiency of the US alone in activating $S_2O_8^{2-}$ for $SO_4^{\cdot-}$ generation. This value is in the order of magnitude of previously reported tetracycline degradation using the same system, with a value of E_a of 32.01 kJ mol^{-1} [40].

In contrast, the lowest E_a is recorded in the US-UVC system with H_2O_2 (E_a = 4.77 kJ mol^{-1}), which is eight times lower than US activated alone. Furthermore, compared to other reported PCP degradation methods, such as heat-activated persulfate (E_a = 105.60 kJ mol^{-1}) [41] and H_2O_2 activated by magnetite (E_a = 47.00 kJ mol^{-1}) [42], the US-UVC system demonstrates a significantly lower energy requirement. This highlights the strong synergistic effect of combining US cavitation with UV light, which effectively reduces the energy barrier for ·OH production.

3.3. Energy and Cost Comparison

An economic evaluation of the AOP systems in this study was conducted using the electrical energy per order (E_{EO}) metric. E_{EO} is a quantitative parameter used to assess the energy consumption of AOPs, aiding both technical development and practical applications. It represents the amount of electrical energy, measured in kilowatt-hours (kWh), required to degrade a contaminant concentration (C) by one order of magnitude in a unit volume, such as 1 m³ (1000 L), of contaminated water. E_{EO} is particularly suitable for scenarios where the contaminant concentration is low, and the reaction follows first-order kinetics with respect to C. This makes it highly relevant to this study, as PCP is classified as a micropollutant [43]. In this study, E_{EO} (kWh m^{-3}) of an idealized batch reactor was calculated using Equation (9).

$$E_{EO} = \frac{P38.4}{Vk} \tag{9}$$

Where, P represents the input power (kW) of the US, UVC, and/or VUV utilized in each system, V denotes the volume of treated water (L), and k corresponds to the first-order rate constant (min^{-1}).

Furthermore, the cost analysis in Indonesian Rupiah was conducted based on the calculated E_{EO} values and is summarized in Table 1. The electricity price per kWh was determined using the rates set by the Indonesian National Electricity Company (PLN) as of January 2025, while the chemical costs were derived from the per-kilogram pricing of Sigma Aldrich products. A detailed summary of the economic comparison to treat 1 m³ of PCP-contaminated water is presented in Table 1.

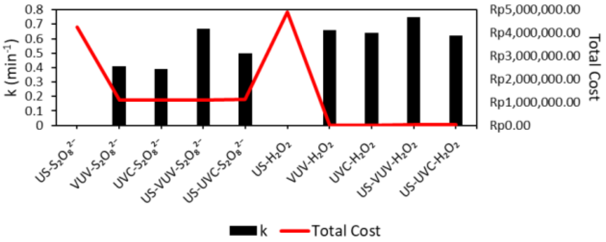

Figure 5. Plot of reaction rate constants for PCP degradation using various AOP methods versus treatment costs for each method

The most efficient and cost-effective systems are VUV-H_2O_2 (4.65 kWh/m^3, Rp8,825/m^3) and UVC-H_2O_2 (4.80 kWh/m^3, Rp9,064/m^{-3}), which have the lowest E_{EO} values and total costs. In contrast, persulfate systems like US-$S_2O_8^{2-}$ show the highest E_{EO} (1920 kWh m^{-3}) and total cost (Rp4,247,478/m^3), making it the least economical option. While UV-based $S_2O_8^{2-}$ systems (VUV-$S_2O_8^{2-}$ and UVC-$S_2O_8^{2-}$) are more efficient, they still have higher total costs compared to H_2O_2 systems. Overall, H_2O_2, particularly in UV configurations, proves to be the most energy-efficient and cost-effective choice for treating PCP-contaminated water, as illustrated in Figure 5. It is also evident that H_2O_2 use is more economical than UV/$S_2O_8^{2-}$ systems due to the high cost of persulfate.

Previously reported results have shown that the E_{EO} amount for US is 31.72 times more than that combination with UV for H_2O_2-based AOPs [44], which aligns with the findings of this study. Furthermore, E_{EO} values for various pharmaceuticals and personal care products treated by UV/H_2O_2 have been reported to range from 0.017 to 2.26 kWh/m^3 [45], while for UV/$S_2O_8^{2-}$, the values for degradation of heliotrine and its N-oxide were 0.28 and 0.43 kWh/m^3, respectively [46]. The results of this study offer a more comprehensive comparison of the energy requirements for each method. This leads to the recommendation of UV combined with H_2O_2 as the most environmentally and economically favorable option—minimizing both electricity and chemical consumption while ensuring rapid pollutant degradation.

4. Conclusion

This study compares various AOPs, including combinations of H_2O_2 and $S_2O_8^{2-}$ activated by US and UV light (UVC and VUV), or their combinations, to degrade PCP in distilled water. The comparison focuses on kinetic performance and cost-effectiveness. H_2O_2 generally outperforms $S_2O_8^{2-}$, especially under UV activation, due to its better pH stability and better reactivity with $\cdot OH$. While $S_2O_8^{2-}$ shows higher k with US alone, its performance is limited by pH dependence and slower reaction speeds. The combination of US and VUV activation produces the highest k for both oxidants, with H_2O_2 showing the best overall results (k = 0.75 min^{-1}). Higher temperatures improve PCP degradation for all the systems, with the highest rate (k = 0.91 min^{-1}) observed in the US-VUV-H_2O_2 system at 35°C. The lowest activation energy (E_a 4.77 kJ·mol^{-1}) was found in the US-UVC-H_2O_2 system, indicating higher efficiency. H_2O_2-based systems, particularly VUV-H_2O_2 and UVC-H_2O_2, demonstrated the highest efficiency and cost-effectiveness, with the lowest E_{EO} values (4.65–4.80 kWh m^{-3}) and treatment costs (Rp8,825–Rp9,064/m^{-3}). This study highlights H_2O_2, especially in UV configurations, as the best choice for PCP degradation, offering reduced energy use, lower chemical consumption, and effective treatment. The study provides valuable insights into the efficiency of different AOPs for PCP degradation, but it has some limitations. Specifically, it does not explore radical production or the formation of intermediate products, which are important for understanding the degradation mechanism. Additionally, the type of interaction between combined AOPs—whether synergistic, additive, or antagonistic—was not quantitatively assessed, which could offer a deeper understanding of their combined effects. Future research should focus on these aspects, including synergy analysis, to optimize AOPs and improve their application to other contaminants.

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References

[1] M. A. Boncz, H. Bruning, W. H. Rulkens, E. J. R. Sudhölter, G. H. Harmsen, J. W. Bijsterbosch, Kinetic and mechanistic aspects of the oxidation of chlorophenols by ozone, *Water Science and Technology*, 35, 4, (1997), 65-72 https://doi.org/10.2166/wst.1997.0087

[2] Hai-Yan Ma, Lixia Zhao, Liang-Hong Guo, Hui Zhang, Feng-Jie Chen, Wan-Chao Yu, Roles of reactive oxygen species (ROS) in the photocatalytic degradation of pentachlorophenol and its main toxic intermediates by TiO_2/UV, *Journal of Hazardous Materials*, 369, (2019), 719-726 https://doi.org/10.1016/j.jhazmat.2019.02.080

[3] P. K. Andrew Hong, Yu Zeng, Degradation of pentachlorophenol by ozonation and biodegradability of intermediates, *Water Research*, 36, 17, (2002), 4243-4254 https://doi.org/10.1016/S0043-1354(02)00144-6

[4] Kementerian Kesehatan Republik Indonesia, *Peraturan Menteri Kesehatan Republik Indonesia Nomor 492/MENKES/PER/IV/2010 tentang Persyaratan Kualitas Air Minum*, Kementerian Kesehatan RI, Jakarta, 2010,

[5] Marc Pera-Titus, Verónica García-Molina, Miguel A. Baños, Jaime Giménez, Santiago Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Applied Catalysis B: Environmental*, 47, 4, (2004), 219-256 https://doi.org/10.1016/j.apcatb.2003.09.010

[6] Jiangfang Yu, Haopeng Feng, Lin Tang, Ya Pang, Guangming Zeng, Yue Lu, Haoran Dong, Jiajia Wang, Yani Liu, Chengyang Feng, Jingjing Wang, Bo Peng, Shujing Ye, Metal-free carbon materials for persulfate-based advanced oxidation process: Microstructure, property and tailoring, *Progress in Materials Science*, 111, (2020), 100654 https://doi.org/10.1016/j.pmatsci.2020.100654

[7] Manju Kurian, Advanced oxidation processes and nanomaterials -a review, *Cleaner Engineering and*

Technology, 2, (2021), 100090 https://doi.org/10.1016/j.clet.2021.100090

[8] Jingquan Wang, Jing Deng, Erdeng Du, Hongguang Guo, Reevaluation of radical-induced differentiation in UV-based advanced oxidation processes (UV/hydrogen peroxide, UV/peroxydisulfate, and UV/chlorine) for metronidazole removal: Kinetics, mechanism, toxicity variation, and DFT studies, *Separation and Purification Technology*, 301, (2022), 121905 https://doi.org/10.1016/j.seppur.2022.121905

[9] Tugba Olmez-Hanci, Idil Arslan-Alaton, Comparison of sulfate and hydroxyl radical based advanced oxidation of phenol, *Chemical Engineering Journal*, 224, (2013), 10-16 https://doi.org/10.1016/j.cej.2012.11.007

[10] P. Neta, V. Madhavan, Haya Zemel, Richard W. Fessenden, Rate constants and mechanism of reaction of sulfate radical anion with aromatic compounds, *Journal of the American Chemical Society*, 99, 1, (1977), 163-164 https://doi.org/10.1021/ja00443a030

[11] Fassi Soumia, Christian Petrier, Effect of potassium monopersulfate (oxone) and operating parameters on sonochemical degradation of cationic dye in an aqueous solution, *Ultrasonics Sonochemistry*, 32, (2016), 343-347 https://doi.org/10.1016/j.ultsonch.2016.03.032

[12] Ran Yin, Claire E. Anderson, Jing Zhao, Alexandria B. Boehm, William A. Mitch, Controlling contaminants using a far-UVC-based advanced oxidation process for potable reuse, *Nature Water*, 1, 6, (2023), 555-562 https://doi.org/10.1038/s44221-023-00094-5

[13] Yi-Lin Zhang, Wen-Long Wang, Min-Yong Lee, Zheng-Wei Yang, Qian-Yuan Wu, Nan Huang, Hong-Ying Hu, Promotive effects of vacuum-UV/UV (185/254 nm) light on elimination of recalcitrant trace organic contaminants by UV-AOPs during wastewater treatment and reclamation: A review, *Science of The Total Environment*, 818, (2022), 151776 https://doi.org/10.1016/j.scitotenv.2021.151776

[14] H. Almasi, Gh. Asgari, M. Leili, Z. Sharifi, A. Seid-Mohammadi, The Study of Phenol Removal from Aqueous Solutions Using Oxidizing Agents of Peroxide Hydrogen, Persulfate and Periodate Activated by Ultrasound, *Journal of Rafsanjan University of Medical Sciences*, 15, 9, (2017), 835-848

[15] Liwei Chen, Tianming Cai, Chuan Cheng, Zhuang Xiong, Dahu Ding, Degradation of acetamiprid in UV/H_2O_2 and UV/persulfate systems: A comparative study, *Chemical Engineering Journal*, 351, (2018), 1137-1146 https://doi.org/10.1016/j.cej.2018.06.107

[16] Mohammad Malakootian, Seyedeh Nastaran Asadzadeh, Removal of tetracycline from aqueous solution by ultrasound and ultraviolet enhanced persulfate oxidation, *Desalination and Water Treatment*, 197, (2020), 191-199 https://doi.org/10.5004/dwt.2020.25975

[17] Naresh N. Mahamuni, Yusuf G. Adewuyi, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: A review with emphasis on cost estimation, *Ultrasonics Sonochemistry*, 17, 6, (2010), 990-1003 https://doi.org/10.1016/j.ultsonch.2009.09.005

[18] Tanisha Kathuria, Anjali Mehta, Sudhanshu Sharma, Sudesh Kumar, Review on ultrasound-enhanced activation of persulfate/peroxymonosulfate in hybrid advanced oxidation technologies, *Chemical Engineering Communications*, 211, 10, (2024), 1645-1669 https://doi.org/10.1080/00986445.2024.2358372

[19] Tessora Young, Make Geng, Lin Lin, Selma Mededovic Thagard, Oxidative Degradation of Bisphenol A: A Comparison Between Fenton Reagent, UV, UV/H_2O_2 and Ultrasound, *Journal of Advanced Oxidation Technologies*, 16, 1, (2013), 89-101 https://doi.org/10.1515/jaots-2013-0109

[20] H. C. Yap, Y. L. Pang, S. Lim, A. Z. Abdullah, H. C. Ong, C. H. Wu, A comprehensive review on state-of-the-art photo-, sono-, and sonophotocatalytic treatments to degrade emerging contaminants, *International Journal of Environmental Science and Technology*, 16, 1, (2019), 601-628 https://doi.org/10.1007/s13762-018-1961-y

[21] Ana L. Camargo-Perea, Ainhoa Rubio-Clemente, Gustavo A. Peñuela, Use of Ultrasound as an Advanced Oxidation Process for the Degradation of Emerging Pollutants in Water, *Water*, 12, 4, (2020), 1068 https://doi.org/10.3390/w12041068

[22] Yeyuan Xiao, Cecilia De Araujo, Chun Chau Sze, David C. Stuckey, Controlling a toxic shock of pentachlorophenol (PCP) to anaerobic digestion using activated carbon addition, *Bioresource Technology*, 181, (2015), 303-311 https://doi.org/10.1016/j.biortech.2015.01.080

[23] George Z. Kyzas, Nezamaddin Mengelizadeh, Morteza khodadadi Saloot, Samaneh Mohebi, Davoud Balarak, Sonochemical degradation of ciprofloxacin by hydrogen peroxide and persulfate activated by ultrasound and ferrous ions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 642, (2022), 128627 https://doi.org/10.1016/j.colsurfa.2022.128627

[24] Qiongfang Wang, Yisheng Shao, Naiyun Gao, Wenhai Chu, Xiang Shen, Xian Lu, Juxiang Chen, Yanping Zhu, Degradation kinetics and mechanism of 2,4-Di-tert-butylphenol with UV/persulfate, *Chemical Engineering Journal*, 304, (2016), 201-208 https://doi.org/10.1016/j.cej.2016.06.092

[25] N. Daneshvar, M. A. Behnajady, M. Khayyat Ali Mohammadi, M. S. Seyed Dorraji, UV/H_2O_2 treatment of Rhodamine B in aqueous solution: Influence of operational parameters and kinetic modeling, *Desalination*, 230, 1, (2008), 16-26 https://doi.org/10.1016/j.desal.2007.11.012

[26] Ying-Hong Guan, Jin Chen, Li-Jun Chen, Xin-Xin Jiang, Qiang Fu, Comparison of UV/H_2O_2, UV/PMS, and UV/PDS in Destruction of Different Reactivity Compounds and Formation of Bromate and Chlorate, *Frontiers in Chemistry*, 8, (2020), https://doi.org/10.3389/fchem.2020.581198

[27] Ruiyang Xiao, Lei He, Zonghao Luo, Richard Spinney, Zongsu Wei, Dionysios D. Dionysiou, Feiping Zhao, An experimental and theoretical study on the degradation of clonidine by hydroxyl and sulfate radicals, *Science of The Total Environment*, 710, (2020), 136333 https://doi.org/10.1016/j.scitotenv.2019.136333

[28] J. Rodríguez-Chueca, E. Laski, C. García-Cañibano, M. J. Martín de Vidales, Á Encinas, B. Kuch, J. Marugán, Micropollutants removal by full-scale UV-C/sulfate radical based Advanced Oxidation Processes, *Science of The Total Environment*, 630, (2018), 1216-1225 https://doi.org/10.1016/j.scitotenv.2018.02.279

[29] Pengfei Gan, Yichun Sun, Yunyi Li, Wen Liu, Jiangyu Ye, Meiping Tong, Jialiang Liang, The degradation of municipal solid waste incineration leachate by UV/persulfate and UV/H_2O_2 processes: The different selectivity of $SO_4^{\cdot -}$ and $^{\cdot}OH$, *Chemosphere*, 311, (2023), 137009 https://doi.org/10.1016/j.chemosphere.2022.137009

[30] Jongbok Choi, Dukyoung Lee, Younggyu Son, Ultrasonic activation of persulfate for removal of aqueous pollutants: cavitational versus thermal mechanisms, *Current Opinion in Chemical Engineering*, 48, (2025), 101136 https://doi.org/10.1016/j.coche.2025.101136

[31] Xiuneng Zhu, Jie Qiu, Yexing Wang, Yulin Tang, Yongji Zhang, Effective Degradation of 1,4-Dioxane by UV-Activated Persulfate: Mechanisms, Parameters and Environmental Impacts, *Water*, 16, 9, (2024), 1281 https://doi.org/10.3390/w16091281

[32] David B. Miklos, Christian Remy, Martin Jekel, Karl G. Linden, Jörg E. Drewes, Uwe Hübner, Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review, *Water Research*, 139, (2018), 118-131 https://doi.org/10.1016/j.watres.2018.03.042

[33] Marlo S. Morgan, Paul F. Van Trieste, Stephanie M. Garlick, Martin J. Mahon, Allan L. Smith, Ultraviolet molar absorptivities of aqueous hydrogen peroxide and hydroperoxyl ion, *Analytica Chimica Acta*, 215, (1988), 325-329 https://doi.org/10.1016/S0003-2670(00)85294-0

[34] Jaesang Lee, Urs von Gunten, Jae-Hong Kim, Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks, *Environmental Science & Technology*, 54, 6, (2020), 3064-3081 https://doi.org/10.1021/acs.est.9b07082

[35] Kirill Fedorov, Kumaravel Dinesh, Xun Sun, Reza Darvishi Cheshmeh Soltani, Zhaohui Wang, Shirish Sonawane, Grzegorz Boczkaj, Synergistic effects of hybrid advanced oxidation processes (AOPs) based on hydrodynamic cavitation phenomenon – A review, *Chemical Engineering Journal*, 432, (2022), 134191 https://doi.org/10.1016/j.cej.2021.134191

[36] Ritesh Patidar, Vimal Chandra Srivastava, Mechanistic and kinetic insights of synergistic mineralization of ofloxacin using a sono-photo hybrid process, *Chemical Engineering Journal*, 403, (2021), 125736 https://doi.org/10.1016/j.cej.2020.125736

[37] Seungmin Na, Yun-Gyong Ahn, Mingcan Cui, Jeehyeong Khim, Significant diethyl phthalate (DEP) degradation by combined advanced oxidation process in aqueous solution, *Journal of Environmental Management*, 101, (2012), 104-110 https://doi.org/10.1016/j.jenvman.2012.01.028

[38] Oualid Hamdaoui, Emmanuel Naffrechoux, Sonochemical and photosonochemical degradation of 4-chlorophenol in aqueous media, *Ultrasonics Sonochemistry*, 15, 6, (2008), 981-987 https://doi.org/10.1016/j.ultsonch.2008.03.011

[39] Sanzeeda Baig Shuchi, Md Burhan Kabir Suhan, Sufian Bin Humayun, Muhammad Enamul Haque, Md Shahinoor Islam, Heat-activated potassium persulfate treatment of Sudan Black B dye: Degradation kinetic and thermodynamic studies, *Journal of Water Process Engineering*, 39, (2021), 101690 https://doi.org/10.1016/j.jwpe.2020.101690

[40] Gholam Hossein Safari, Simin Nasseri, Amir Hossein Mahvi, Kamyar Yaghmaeian, Ramin Nabizadeh, Mahmood Alimohammadi, Optimization of sonochemical degradation of tetracycline in aqueous solution using sono-activated persulfate process, *Journal of Environmental Health Science and Engineering*, 13, (2015), 76 https://doi.org/10.1186/s40201-015-0234-7

[41] Linning Yin, Junyan Wei, Yumeng Qi, Zhengnan Tu, Ruijuan Qu, Chao Yan, Zunyao Wang, Feng Zhu, Degradation of pentachlorophenol in peroxymonosulfate/heat system: Kinetics, mechanism, and theoretical calculations, *Chemical Engineering Journal*, 434, (2022), 134736 https://doi.org/10.1016/j.cej.2022.134736

[42] Xiaofei Xue, Khalil Hanna, Mustapha Abdelmoula, Nansheng Deng, Adsorption and oxidation of PCP on the surface of magnetite: Kinetic experiments and spectroscopic investigations, *Applied Catalysis B: Environmental*, 89, 3, (2009), 432-440 https://doi.org/10.1016/j.apcatb.2008.12.024

[43] James R. Bolton, Keith G. Bircher, William Tumas, Chadwick A. Tolman, Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems (IUPAC Technical Report), *Pure and Applied Chemistry*, 73, 4, (2001), 627-637 https://doi.org/10.1351/pac200173040627

[44] Mohammad A. Behnajady, Behrouz Vahid, Nasser Modirshahla, Mohammad Shokri, Evaluation of electrical energy per order (E_{EO}) with kinetic modeling on the removal of Malachite Green by US/UV/H_2O_2 process, *Desalination*, 249, 1, (2009), 99-103 https://doi.org/10.1016/j.desal.2008.07.025

[45] Kaiheng Guo, Zihao Wu, Shuwen Yan, Bo Yao, Weihua Song, Zhechao Hua, Xuewen Zhang, Xiujuan Kong, Xuchun Li, Jingyun Fang, Comparison of the UV/chlorine and UV/H_2O_2 processes in the degradation of PPCPs in simulated drinking water and wastewater: Kinetics, radical mechanism and energy requirements, *Water Research*, 147, (2018), 184-194 https://doi.org/10.1016/j.watres.2018.08.048

[46] Menghong Gao, Shuili Yu, Li'an Hou, Xingli Ji, Rongsheng Ning, Ying Xu, Lei Li, Treatment of emerging pyrrolizidine alkaloids in drinking water by UV/persulfate process: Kinetics, energy efficiency and degradation pathway, *Chemical Engineering Journal*, 490, (2024), 151852 https://doi.org/10.1016/j.cej.2024.151852