

Article

Sono-Activated Peracetic Acid as a Tunable Advanced Oxidation Process for Water Pollution Control: Kinetics, Radical Pathways, and Operational Windows

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Abstract

High-frequency ultrasound-assisted activation of peracetic acid (PAA) was investigated as a tunable advanced oxidation process for the removal of organic pollutants from water. Sunset Yellow FCF (SSY), a representative anionic azo dye, was used as a probe contaminant in a 425 kHz sonoreactor to clarify the roles of PAA speciation, acoustic cavitation, dissolved gases, oxidant dose, acoustic power, and initial pH. UV spectroscopic analysis showed that PAA exhibits pH-dependent far-UV absorbance associated with acid-base speciation and peroxide equilibria, while ultrasonication promoted simultaneous PAA activation and H_2O_2 accumulation. Compared with PAA alone and ultrasound alone, the combined US/PAA process markedly enhanced SSY decolorization. Under natural conditions, 5 mg/L SSY and 5 mM PAA were completely decolorized within 210 min, with an initial rate of 0.116 mg/L·min, compared with 0.078 and 0.0086 mg/L·min for ultrasound and PAA alone, respectively. The corresponding synergy ratio and synergy index were 1.5 and 1.34. The process exhibited tunable reaction-pathway control, with two favorable pH windows: a strongly acidic region, where interfacial $\text{HO}^\bullet$ -driven sonochemistry and PAA stability are favored, and a mildly alkaline region, where PAA deprotonation promotes peracetate-driven acyl/peroxyl radical-chain propagation. Oxygen saturation improved performance, whereas CO_2 suppressed cavitation-driven activation. Increasing PAA concentration and acoustic power enhanced removal up to practical limits, beyond which radical scavenging and diminishing sonochemical returns became evident. Beyond demonstrating enhanced decolorization, this study distinguishes US/PAA from previously reported UV/PAA, transition-metal/PAA, and ultrasound-only systems by showing how 425 kHz cavitation converts PAA into a tunable hybrid $\text{HO}^\bullet$ /acyl-peroxyl radical network. The main contribution is a mechanistic operating map that links PAA speciation, sonochemical peroxide accumulation, dissolved gas chemistry, acoustic power, oxidant dose, and pH to pollutant-removal performance, thereby defining practical windows for sono-activated PAA treatment of anionic dyes and related recalcitrant contaminants.

Academic Editor: Danilo Russo

Received: 26 May 2026

Revised: 26 June 2026

Accepted: 1 July 2026

Published: 3 July 2026

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Keywords: ultrasonication; peracetic acid; advanced oxidation process; water pollution control; azo dye; radical activation; process intensification

1. Introduction

Colorants from the textile, food, and personal care industries are increasingly recognized as recalcitrant and bioactive contaminants in aquatic environments. Azo dyes, the largest commercial class of synthetic dyes, reduce light penetration, increase oxygen demand, and may release aromatic amines during transformation. These contaminants are therefore relevant not only from the perspective of local effluent quality but also from a broader environmental-health perspective, because persistent aromatic pollutants can be transported through receiving waters, wastewater-reuse pathways, sediment–water interfaces, and interconnected treatment or discharge networks [1,2]. Their high chromophoric stability and limited biodegradability make them difficult to remove by conventional biological or physicochemical treatment, prompting the development of advanced oxidation approaches that generate reactive oxygen species (ROS) and disrupt stable aromatic and azo structures.

In addition to chemical degradation of aromatic pollutants, the compatibility of treated effluents with downstream biological processes and receiving environments must be considered. Residual oxidants such as PAA and H_2O_2 can exert antimicrobial or oxidative-stress effects if discharged before sufficient decay, quenching, or dilution [3].

Recent catalytic degradation systems have provided important benchmarks for the removal of aromatic pollutants, including nitrophenols, phenols, dyes, and related chromophoric contaminants. In particular, heterogeneous metal oxides and mixed-metal nanocomposites are widely investigated because their redox-active surfaces can promote electron transfer, peroxide activation, and reactive oxygen species generation. For example, *p*-nitrophenol is frequently used as a model aromatic pollutant because of its toxicity, persistence, and well-defined spectroscopic response during reduction or oxidative degradation. Recent work [4] on microwave-assisted Sb_2O_3 -CuO nanocomposites demonstrated that rationally designed mixed oxides can enhance catalytic degradation of *p*-nitrophenol, illustrating the current trend toward rapid catalyst synthesis, interfacial redox engineering, and high-efficiency aromatic pollutant removal. These catalyst-based systems provide valuable performance and mechanistic benchmarks for advanced oxidation research.

Unlike heterogeneous metal-based activators, the present US/PAA system does not introduce a solid catalyst; therefore, catalyst leaching, spent-solid management, and secondary metal contamination are not operative variables in this work. Nevertheless, these issues are important when comparing US/PAA with heterogeneous alternatives, because metal-containing solids may require careful control of dissolution, leaching kinetics, and reactive regulation, as illustrated in pyrite-cinder leaching systems [5].

Beyond standalone catalytic or oxidative treatment, practical water treatment schemes increasingly rely on hybrid processes in which oxidation is coupled with downstream separation or membrane polishing. In such configurations, US/PAA can serve as an oxidative pretreatment to decolorize aromatic pollutants, weaken chromophoric structures, and convert persistent molecules into more hydrophilic or more separable transformation products. A subsequent membrane step can then polish the effluent by retaining residual parent pollutants, oxidation by-products, macromolecular organic matter, or inorganic constituents. Recent advances in highly selective membrane fabrication illustrate the rapid progress being made toward precise molecular and ionic separation [6]. Although the present study did not use downstream adsorbents or evaluate material aging, oxidative compatibility should be considered when US/PAA is integrated with membranes, adsorbents, or other polishing units, because residual PAA/ H_2O_2 may affect material lifetime [7].

US/PAA should also be considered alongside other AOP pretreatment strategies developed for real water matrices. Vacuum ultraviolet (VUV)-based oxidation, for

example, has recently been evaluated as an ultrafiltration pretreatment with attention to treatment performance, fouling control, risk assessment, and mechanistic interpretation [8]. Compared with VUV-based pretreatment, which relies on high-energy photochemical activation, US/PAA uses acoustic cavitation to activate PAA/peracetate and generate $\text{HO}^\bullet$ together with longer-lived acyl/peroxyl radicals. Both approaches highlight that oxidative pretreatment should be assessed not only by parent-pollutant removal, but also by matrix effects, residual oxidants, transformation products, membrane behavior, and post-treatment risk.

One such process is high-frequency ultrasound (US, ≥ 100 kHz), a controllable source of short-lived radicals generated by acoustic cavitation. The repeated growth and violent collapse of bubbles create hot spots that split water into $\text{HO}^\bullet$ and $\cdot\text{H}$. Dissolved O_2 channels H atoms to $\text{HO}_2^\bullet$ and ultimately to H_2O_2 . The resulting radical/peroxide matrix drives pollutant oxidation. The yields and selectivity of radicals depend on the frequency, power, and amount of dissolved gas in the reactor. Higher frequencies produce larger steady-state ROS fluxes and favor interfacial pathways, which are advantageous for degrading aromatic chromophores, though they are also prone to mass-transfer limitations [9].

Peracetic acid (PAA) is a peroxycarboxylic acid increasingly used as an oxidant and disinfectant in water and wastewater treatment. Commercial PAA is supplied as an equilibrium mixture containing PAA, hydrogen peroxide, acetic acid, and water, and its reactivity is strongly controlled by acid-base speciation because PAA deprotonates to peracetate near pH 8.2. In contrast to H_2O_2 -based AOPs, activated PAA can generate not only $\text{HO}^\bullet$ but also organic oxygen-centered radicals, mainly acetoxy/acetyloxy radicals ($\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$) and acyl-peroxyl radicals ($\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$, often represented as $\text{CH}_3\text{CO}_3^\bullet$). These longer-lived radicals may diffuse farther from the activation zone and participate in selective electron-transfer, addition, and hydrogen-abstraction reactions in the bulk solution [10–13].

PAA activation has been investigated mainly through UV irradiation, transition-metal catalysis, thermolysis, electrochemical activation, base activation, and heterogeneous catalysts [11–13]. In UV/PAA, direct photolysis of the peroxide bond initiates radical formation, whereas in metal/PAA systems, radical branching is governed by metal redox cycling. Ultrasound-driven PAA activation is less developed but mechanistically distinctive because the activating energy is delivered locally through acoustic cavitation rather than uniformly throughout the bulk solution. During cavitation, collapsing bubbles generate high-temperature/high-pressure hot spots and split water into $\text{HO}^\bullet$ and $\text{H}^\bullet$. These primary sonochemical radicals can then activate PAA by O–O bond cleavage, hydrogen abstraction, and electron-transfer reactions, producing $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$. In oxygenated media, carbon- and acyl-centered intermediates are further converted to peroxyl radicals, reinforcing oxidative chain propagation [12,14].

The selection of ultrasound rather than metal-mediated activation was motivated by both mechanistic and practical considerations. Metal-mediated PAA activation, including Fe-based and other transition-metal systems, can be highly effective because redox cycling promotes peroxide decomposition and radical formation. However, such systems require rational selection of the activator because performance depends on metal speciation, surface chemistry, particle size, catalyst dose, leaching, passivation, recoverability, and water-matrix composition. Recent work [15] on iron-based nanoparticles in dark fermentative biohydrogen production showed that nZVI, $\gamma\text{-Fe}_2\text{O}_3$, and Fe_3O_4 can make different contributions to process kinetics, electron transfer, and microbial structure, illustrating that iron-based nanomaterial effects are application-specific and require careful selection.

The frequency of ultrasound is expected to strongly affect PAA sonolysis and subsequent radical production because acoustic frequency controls bubble growth, collapse intensity, bubble population density, interfacial area, and radical escape into the surrounding liquid. Low-frequency ultrasound generally favors stronger mechanical effects and more violent individual bubble collapse, whereas mid- and high-frequency ultrasound produces smaller, more numerous cavitation bubbles and can enhance chemical effects such as $\text{HO}^\bullet$ and H_2O_2 formation. At very high frequencies, however, shorter acoustic periods may limit bubble growth and reduce collapse intensity, so radical yields are reactor- and condition-dependent. Therefore, PAA sonolysis under ultrasound should be understood as a frequency-dependent process in which direct thermal/homolytic PAA cleavage near collapsing bubbles and indirect $\text{HO}^\bullet/\text{H}^\bullet$ -mediated PAA activation operate simultaneously. In the high-frequency range used here (425 kHz), the process is expected to favor a dense cavitation field, sustained water sonolysis, interfacial radical generation, H_2O_2 accumulation, and conversion of PAA/peracetate into longer-lived acyl and peroxy radicals. This high-frequency mechanism differs from classical UV/PAA and metal/PAA processes because it couples interfacial cavitation chemistry with bulk organic-radical-chain propagation.

In this work, the term ‘tunable’ refers to reaction-pathway control rather than only to changes in apparent degradation rate. In chemical reaction engineering, tunability implies that the operating conditions can bias a reaction network toward one pathway or another. A related concept is encountered in controllable organic synthesis, where reaction conditions can direct tandem transformations toward different products, such as ring-opened or annulated/dechlorinated products in solvent-free O-alkylation of $\text{P}(\text{O})\text{--OH}$ compounds with epichlorohydrocarbons [6]. This reference is not used here as evidence for water treatment, but as a broader example of condition-controlled reaction selectivity. By analogy, US/PAA can be considered tunable because pH, dissolved gas, oxidant dose, and acoustic power shift the relative contributions of interfacial $\text{HO}^\bullet$ attack, PAA/peracetate activation, acyl/peroxy radical-chain propagation, and radical-scavenging or termination reactions.

Recent studies further show that PAA-based AOPs are rapidly evolving beyond classical UV/PAA and metal/PAA systems. For example, ultrasound-activated PAA has been reported to efficiently degrade tetracycline hydrochloride, confirming that ultrasonic irradiation can transform PAA from a relatively weak standalone oxidant into a reactive radical-generating system [14]. Ultrasonic/PAA pre-oxidation has also been explored for algae-laden water treatment, where it modified dissolved organic matter and affected membrane-fouling behavior [16]. In addition, light- and ultrasound-activated PAA systems have been evaluated for bisphenol oxidation, highlighting the importance of physical activation routes for peracid chemistry [17]. Recent reviews [18–20] on PAA-AOPs and ultrasound/oxidant processes emphasize that the field is moving toward hybrid activation platforms in which external energy input, oxidant speciation, radical branching, and water-matrix effects jointly control performance. These recent reports support the relevance of US/PAA, but they also show that systematic data linking PAA speciation, high-frequency cavitation, dissolved gases, pH, oxidant dose, and acoustic power remain limited. The present work addresses this gap using SSY as an anionic azo-dye probe in a 425 kHz sonoreactor.

H_2O_2 is central to many AOPs because it can act both as an oxidant precursor and as a radical scavenger, depending on the reaction environment. Recent progress in electrocatalytic H_2O_2 production has highlighted the importance of controlling H_2O_2 generation rate, selectivity, stability, and utilization efficiency for environmental and oxidative applications [21]. In US/PAA, H_2O_2 originates from water sonolysis, oxygen-mediated radical recombination, and the commercial PAA equilibrium mixture, while it

is consumed through $\text{HO}^\bullet$ scavenging and secondary radical formation. Therefore, H_2O_2 accumulation should be considered a dynamic component of the radical budget rather than only a passive by-product.

Against this background, US/PAA occupies a distinct position among catalytic and AOPs. Unlike solid-catalyst systems such as metal oxide nanocomposites, US/PAA does not rely on a recoverable catalytic surface or catalyst synthesis step. Instead, ultrasound provides a physical activation field through acoustic cavitation, while PAA acts as a molecular oxidant that can be converted into $\text{HO}^\bullet$, acetyloxy, and acyl-peroxyl radicals. Thus, the relevant design variables are not only catalyst composition and surface redox properties, but also acoustic frequency, cavitation intensity, dissolved gas, PAA/peracetate speciation, oxidant dose, and pollutant partitioning near the bubble-liquid interface. This distinction is important because aromatic pollutant degradation in US/PAA is governed by the coupling between interfacial sonochemistry and bulk radical-chain propagation, rather than by surface-mediated catalysis alone.

Despite this progress, high-frequency ultrasound-driven PAA activation remains less understood than UV/PAA and metal/PAA systems, especially with respect to how cavitation frequency, gas composition, pH-dependent PAA/peracetate speciation, H_2O_2 accumulation, and organic radical-chain propagation jointly determine pollutant removal. Several open questions still limit process design and scaling up. First, we must understand how initial pH affects dye-interface partitioning and PAA speciation across its pKa. Second, we must determine how dissolved gases, such as O_2 , Ar, and CO_2 , impact cavitation strength and initiation chemistry. It is also crucial to determine how acoustic power and PAA dosage balance radical initiation versus scavenging and chain propagation. Finally, we must understand how these factors together govern the kinetics and spectral signatures of decolorization. The prior sonochemical literature emphasizes the strong frequency and gas dependencies of radical production, while PAA reviews highlight speciation-driven selectivity. A unified mechanistic dataset spanning these operating levers at 400–500 kHz is scarce.

The novelty of the present study lies in treating US/PAA not simply as a faster oxidation variant, but as a speciation- and cavitation-controlled activation platform. Previous studies have mainly addressed aromatic pollutant removal through heterogeneous catalytic systems, UV/PAA, transition-metal/PAA, or other catalyst-assisted activation routes, while sonochemical dye degradation has often been examined without explicitly considering PAA speciation and organic-radical-chain formation. Here, we integrate PAA far-UV speciation, sonochemical H_2O_2 accumulation, dissolved gas-dependent cavitation chemistry, acoustic-power scaling, oxidant-dose response, and pH-dependent dye/interface behavior in a single high-frequency system. This approach enables reaction-pathway control to be resolved by distinguishing two complementary mechanistic regimes: acid-favored interfacial $\text{HO}^\bullet$ attack near the cavitation-bubble interface and alkaline peracetate-enabled acyl/peroxyl radical-chain oxidation in the bulk liquid. The contribution of this work is therefore both mechanistic and practical: it identifies when PAA enhances ultrasound, when excess PAA or high acoustic power produces diminishing returns, and when dissolved gases promote or suppress sono-activation. These findings provide operational criteria for designing US/PAA processes for anionic dyes and related micropollutants.

In the present study, we address these gaps by using Sunset Yellow FCF (SSY), a representative anionic azo dye, as a probe contaminant in a 425 kHz sonoreactor. Specifically, our goals are to resolve the far-UV spectral behavior of PAA and its evolution under ultrasonication, to link acid–base speciation to the accompanying radical/peroxide background, and to quantify the kinetics of SSY removal by ultrasound alone, by PAA alone, and by their combination across pH, dissolved gas atmospheres, PAA dose, and

acoustic power. Using established radical chemistry ($\text{HO}\cdot/\text{HO}_2\cdot/\text{O}_2\cdot^-/\text{H}_2\text{O}_2$ and acyl/peroxyl species), we interpret the observed trends as shifts between competing reaction pathways and derive actionable operating windows for controlling US/PAA oxidation. By mapping the interplay between interfacial sonochemistry and bulk organic radical chains, this study provides process-level guidance for effectively treating anionic dyes and related micropollutants using US and PAA.

2. Results and Discussion

2.1. PAA Ultrasonication

Figure 1a illustrates the significant impact of pH on the UV spectra of 0.5 mM PAA measured between 190 and 220 nm. Absorbance increases monotonically with increasing pH ($\text{pH } 4 < 6 < 8.2 < 10$) and decreasing wavelength. This behavior directly follows from acid-base speciation. PAA ($\text{pK}_a = 8.2$) is partially deprotonated at pH 8.2 and fully deprotonated at pH 10. The peracetate anion exhibits greater far-UV extinction than the neutral PAA molecule. Additionally, since PAA solutions are in equilibrium with hydrogen peroxide and acetic acid, the alkaline spectra include a contribution from the hydroperoxide anion ($\text{HO}_2\cdot$). The molar absorptivity of $\text{HO}_2\cdot$ in the UV-C region greatly exceeds that of H_2O_2 . The combined effect of peracetate and $\text{HO}_2\cdot$ results in the greatest absorbance at pH 10. The steep short-wavelength rise is characteristic of peroxide-centered $n \rightarrow \sigma^*$ transitions and is also observed for H_2O_2 [22].

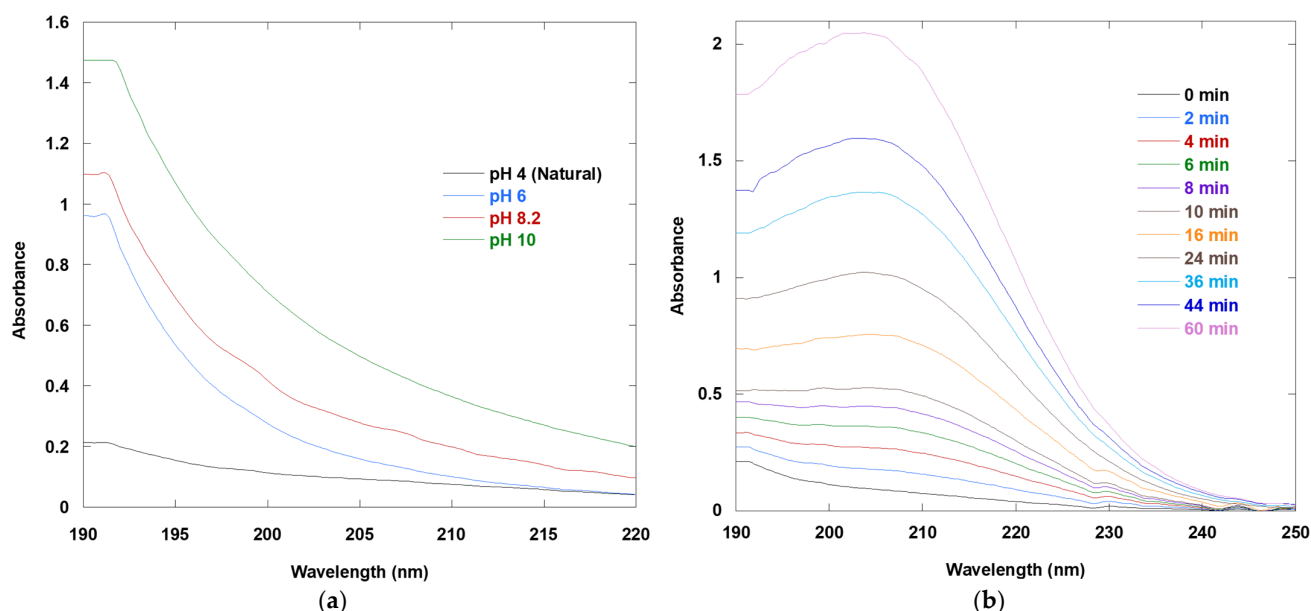


Figure 1. UV spectra of 0.5 mM PAA: (a) pH-dependent spectra recorded at pH 4, 6, 8.2, and 10; and (b) time-dependent spectral evolution at pH 4 during ultrasonication (200 mL, 425 kHz, 100 W).

Figure 1b shows the time-resolved UV spectra (190–250 nm) of 0.5 mM PAA at pH 4 that was exposed to 425 kHz and 100 W of ultrasound. Under these conditions, ultrasound produces hydroxyl ($\text{HO}\cdot$) and hydrogen ($\cdot\text{H}$) radicals through water sonolysis. In aerated media, secondary radicals $\text{HO}_2\cdot$, $\text{O}_2\cdot^-$, and H_2O_2 are formed. Since PAA solutions are in equilibrium with H_2O_2 and acetic acid, ultrasonication couples PAA chemistry to this radical/peroxide matrix. Thus, the time-resolved UV spectra reflect an increasing peroxide background (bulk H_2O_2) with superimposed PAA consumption and activation. The predominant oxidizing species are $\text{HO}\cdot$ (from water) and acetoxyl/peracetyl radicals (from PAA) [12,14]. $\text{HO}_2\cdot$ prevails over $\text{O}_2\cdot^-$ at pH 4, and the radicals recycle back to H_2O_2 . These

findings are consistent with the formation of radicals through sonochemistry at high frequencies and with peracid-AOP mechanisms [12].

At 425 kHz, the observed spectral evolution should be interpreted as the result of coupled high-frequency water sonolysis and PAA activation rather than direct PAA decomposition alone. High-frequency cavitation continuously generates $\text{HO}^\bullet$ and $\text{H}^\bullet$ at or near the bubble-liquid interface. These radicals can react with PAA or peracetate to form $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$, while recombination and oxygen-mediated reactions contribute to H_2O_2 and $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ formation. Therefore, the rising far-UV baseline reflects the superposition of sonochemical H_2O_2 accumulation, PAA/peracetate speciation, and ongoing PAA activation. This interpretation is consistent with emerging views of US/PAA as a hybrid activation process in which localized hot-spot chemistry initiates radical formation and longer-lived PAA-derived organic radicals propagate oxidation in the bulk liquid.

The same qualitative, time-dependent response was observed when the experiment was repeated at pH 6, 8.2, and 10 using the same PAA concentration of 0.5 mM. However, the apparent absorbance amplitude increased with higher pH levels. The response included rapid initial growth, stabilization of the cavitation field midway through the experiment, and renewed growth with longer ultrasonication time. This is expected because the primary sonochemical step, water sonolysis, occurs across a wide pH range. Additionally, net H_2O_2 buildup under ultrasound shows little sensitivity to initial pH between 3 and 11 [23]. Thus, the same rising far-UV baseline (200–230 nm) appears at these pH values. Above the pK_a , PAA progressively deprotonates to peracetate. The $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ pair shifts toward $\text{O}_2^{\bullet-}$ ($\text{pK}_a = 4.8$). At pH 10, a small but increasing amount of H_2O_2 exists as HO_2^- ($\text{pK}_a = 11.6$). These shifts alter radical pathways and can increase apparent absorbance amplitudes because the solution contains more total peroxide and different conjugate bases. Meanwhile, the overall spectral shape (a featureless, deep UV band governed by peroxide $n \rightarrow \sigma^*$ transitions) remains unchanged. This behavior is consistent with three factors: robust H_2O_2 generation during ultrasonication, independent of pH; the equilibrium nature of PAA solutions ($\text{PAA} \rightleftharpoons \text{H}_2\text{O}_2 + \text{acetic acid} + \text{H}_2\text{O}$); and the well-documented UV absorbance of aqueous H_2O_2 in the 200–300 nm range.

The peroxide background can be described semi-quantitatively as the net result of generation and utilization steps. Under high-frequency ultrasound, H_2O_2 is generated mainly through radical recombination and oxygen-mediated reactions. In parallel, commercial PAA solutions already contain H_2O_2 as part of the PAA– H_2O_2 –acetic acid equilibrium. Therefore, the measured far-UV response reflects a total peroxide background rather than a single isolated H_2O_2 contribution. H_2O_2 is also continuously consumed or converted through radical reactions, especially $\text{HO}^\bullet$ scavenging. Thus, H_2O_2 accumulation has a dual role. Moderate H_2O_2 formation indicates active sonolysis and supports the peroxide/radical matrix, whereas excessive H_2O_2 competes with the pollutant for $\text{HO}^\bullet$ and can decrease the effective radical dose available for SSY oxidation.

2.2. Ultrasound/PAA Combination

Figure 2 illustrates the degradation kinetics of SSY via ultrasonication (US: 425 kHz, 100 W), PAA, and the US/PAA method. The experiment was conducted with 5 mg/L of SSY and 5 mM of PAA under natural pH conditions of 3.3. Negligible removal occurred with PAA alone over 270 min, while US alone produced a steady, quasi-exponential decay curve. The US/PAA method removed SSY much faster, attaining total removal at 210 min. This ranking is mechanistically expected. The initial SSY oxidation rate using the US/PAA technique was 0.116 mg/L·min. This rate was then compared to the rates of 0.078 and 0.0086 mg/L·min for US and PAA removals, respectively. These results yielded a synergistic ratio of 1.5 and a synergy index of 1.34.

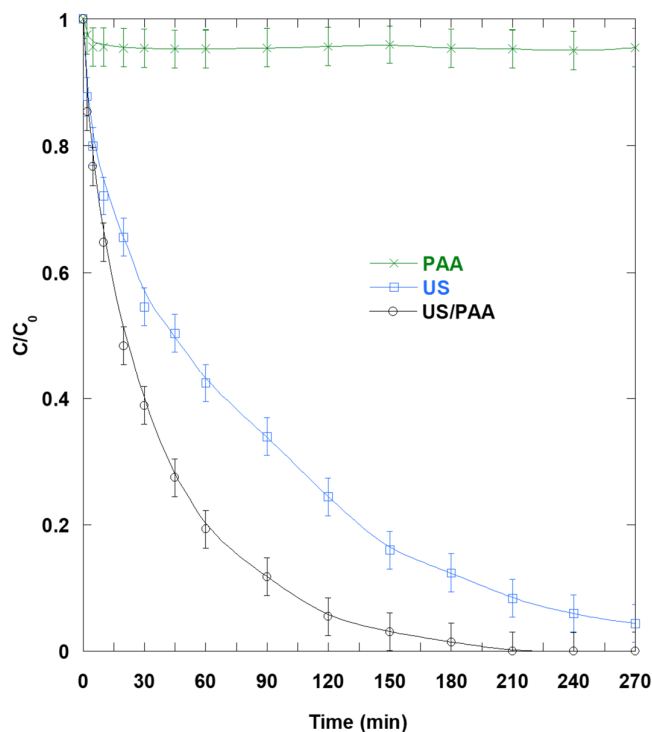


Figure 2. SSY degradation kinetics during PAA treatment, ultrasound alone, and the combined US/PAA process (5 mg/L SSY, 5 mM PAA, 200 mL, pH 3.3, 425 kHz, 100 W).

In water, PAA coexists in equilibrium with H_2O_2 and acetic acid. At acidic pH, PAA remains largely protonated and exhibits only modest direct reactivity toward azo dyes. Consequently, PAA often underperforms as an oxidant for chromophoric organics without an activator. In the US-only case, high-frequency ultrasound drives acoustic cavitation. Bubble collapse thermally splits water into $\text{HO}^\bullet$ and $\text{H}^\bullet$. In aerated solutions, these form $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ and accumulate H_2O_2 . This radical field degrades azo dyes. The US/PAA curve clearly shows synergy. Ultrasound provides $\text{HO}^\bullet$ and $\text{H}^\bullet$ through water sonolysis and activates PAA through both direct hot-spot-assisted O–O bond cleavage near collapsing bubbles and indirect radical-mediated pathways involving $\text{HO}^\bullet/\text{H}^\bullet$ attack on PAA or peracetate. This breaks the peroxy bond, yielding acetoxyl ($\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$) and peracetyl/peroxyl ($\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$) radicals. These radicals complement the indiscriminate oxidation of $\text{HO}^\bullet$ with more selective reaction channels for azo-bond cleavage and aromatic ring opening. The acidic medium (pH 3.3) helps explain the speciation of radicals. Under these conditions, the $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ pair ($\text{pK}_a = 4.8$) favors $\text{HO}_2^\bullet$, and $\text{O}_2^{\bullet-}$ is minor. $\text{HO}_2^\bullet$ is a weaker one-electron oxidant than $\text{HO}^\bullet$. However, $\text{HO}_2^\bullet$ effectively recycles to H_2O_2 , thus sustaining the rising peroxide background generated sonochemically. Meanwhile, $\text{HO}^\bullet$, formed at bubble interfaces and in the liquid, attacks SSY directly and initiates PAA homolysis. This process feeds acyloxy/peroxyl chains. This network illustrates why US/PAA is more effective than US alone and why PAA alone is largely inert. These results illustrate true process intensification, achieved by combining US and PAA, as opposed to using PAA or US alone.

The observed synergy is consistent with recent US/PAA studies [14,16,17] showing that PAA alone is often insufficient for rapid degradation of organic contaminants, whereas ultrasonic activation markedly enhances removal by generating $\text{HO}^\bullet$ and PAA-derived organic radicals. For example, recent work on tetracycline hydrochloride degradation by US/PAA reported rapid pollutant removal after ultrasonic activation of PAA, while ultrasonic/PAA pre-oxidation has also been shown to modify organic matter

in algae-laden water treatment. Similar trends have been reported for bisphenols treated by PAA activated with light or ultrasound. Compared with these recent studies, the present work extends the discussion by focusing on a high-frequency 425 kHz system and by systematically linking kinetic enhancement to pH-dependent PAA/peracetate speciation, dissolved-gas composition, acoustic power, and oxidant dose.

Figure 3a,b depict how the UV-vis. spectra of SSY change over time when subjected to US and US/PAA processing. Figure 3a illustrates the consistent decline in SSY's visible band, centered at 482 nm. This decrease is associated with the $\pi \rightarrow \pi^*$ transition of the azo chromophore. Meanwhile, the near-UV region (300–360 nm) exhibits weaker, transient features. The preferential, monotonic loss of the 482-nm peak is the spectroscopic hallmark of azo-bond scission ($-N=N-$) during radical attack. The smaller bands in the UV region originate from aromatic intermediates, such as hydroxylated or ring-opened naphthalenesulfonates, that subsequently degrade. Fading of the visible maximum is characteristic of sonochemical treatment of azo dyes and reflects the steady radical dose delivered by high-frequency cavitation. At 425 kHz, bubbles efficiently collapse, generating $HO^\bullet$ and $\cdot H$ in water. In aerated media, these yield $HO_2^\bullet$ and $O_2^{\bullet-}$, while H_2O_2 accumulates in the bulk; the exact radical/peroxide matrix that decolorizes azo dyes. Thus, the spectral evolution tracks both the primary $HO^\bullet$ attack on the azo chromophore and the secondary transformation of aromatic fragments.

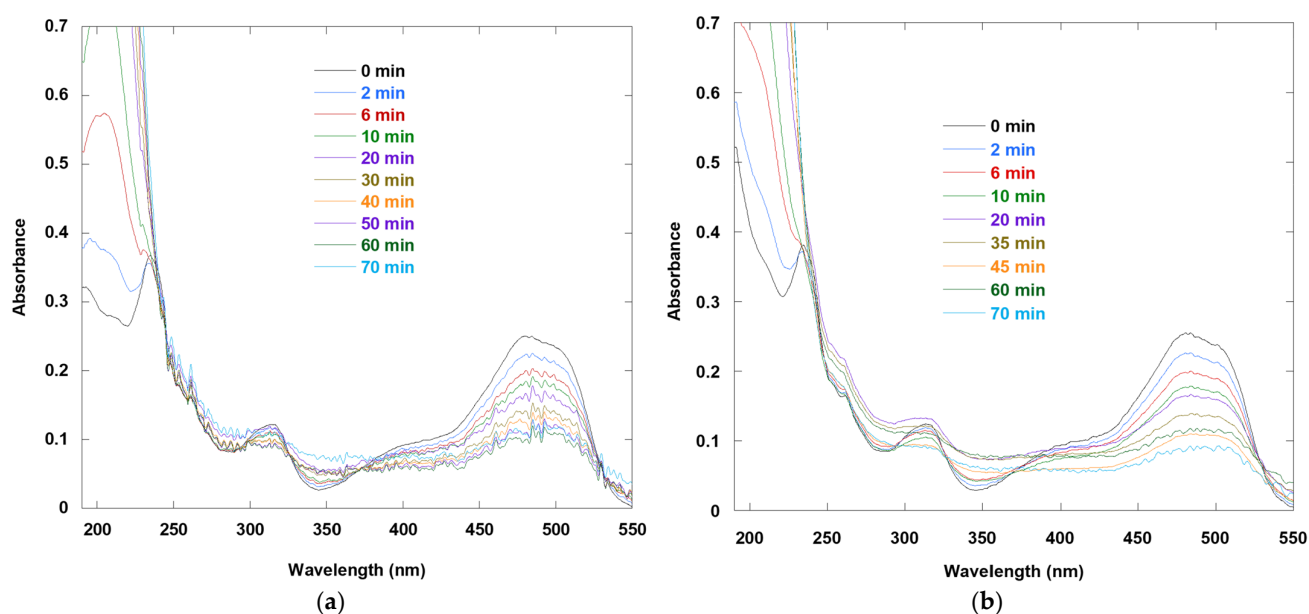


Figure 3. Time-dependent UV-visible spectra of SSY during (a) ultrasound alone and (b) the combined US/PAA process (5 mg/L SSY, 5 mM PAA, 200 mL, pH 3.3, 425 kHz, 100 W).

Figure 3b shows the same qualitative pathway but with faster decay of the 482 nm band and more pronounced, short-lived shoulders in the 300–360 nm region. Ultrasound provides water-derived $HO^\bullet$ and activates PAA by homolyzing the peroxy bond and/or abstracting hydrogen, which forms acyloxy/peracetyl radicals ($CH_3C(O)O^\bullet/CH_3C(O)OO^\bullet$). These radicals are often summarized as $CH_3CO_3^\bullet$. These oxidants complement $HO^\bullet$. $CH_3CO_3^\bullet$ is more selective toward electron-rich sites and aromatic substituents, whereas $HO^\bullet$ indiscriminately attacks the azo linkage and rings. The combined radical pool increases the initial decolorization rate and accelerates the conversion of intermediates. This explains why the transient UV bands crest earlier and the entire spectrum collapses more rapidly under US/PAA than under US alone.

Since the experiments were conducted at pH 3.3, the $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ equilibrium leans toward $\text{HO}_2^\bullet$. This matters in two ways. First, $\text{HO}_2^\bullet$ is a weaker oxidant than $\text{HO}^\bullet$. However, $\text{HO}_2^\bullet$ efficiently recycles to H_2O_2 , which sustains the bulk peroxide background that contributes to the deep-UV slope. Second, $\text{O}_2^{\bullet-}$, which is present in small amounts at this pH, can reduce dyes or intermediates. However, it is quickly protonated near the bubble–liquid interface. The observed far-UV changes are consistent with the growth and turnover of peroxides during ultrasonication because aqueous H_2O_2 exhibits significant absorbance between 200 and 300 nm. Thus, the faster, cleaner collapse of the SSY spectrum in US/PAA is explained by a higher net radical flux ($\text{HO}^\bullet$ + PAA-derived radicals) acting in an oxidative medium that steadily renews peroxides.

Overall, the paired spectra demonstrate classic azo-dye sonochemistry, involving decolorization through azo-bond cleavage and aromatic fragment oxidation. Using US with PAA is more effective than using US alone because ultrasound simultaneously generates radicals from the water and activates the PAA, creating additional mechanistically complementary radicals.

2.3. PAA Concentration Impact

Figure 4 shows how the initial PAA concentration affects SSY degradation via the US/PAA process at two initial dye concentrations of 5 and 10 mg/L (pH 3.3, 425 kHz, and 100 W). Two robust features emerge. First, the degradation rate significantly increases from 0 to approximately 5–15 mM PAA at a fixed dye load and then levels off. Marginal gains are seen with an SSY concentration of 5 mg/L, while slight inhibition occurs with a dye concentration of 10 mg/L. Second, an initial dye concentration of 10 mg/L results in slower fractional removal than a concentration of 5 mg/L with the same PAA dose. High-frequency ultrasound generates $\text{HO}^\bullet/\cdot\text{H}$ via water sonolysis. In aerated media, $\text{HO}_2^\bullet$ and $\text{O}_2^{\bullet-}$ accumulate, resulting in H_2O_2 and dye fading, which is typical of high-frequency sonoreactors. Ultrasound provides water-derived $\text{HO}^\bullet$ and activates PAA. Thus, $\text{HO}^\bullet$ (and other initiators) convert PAA into organic radicals, such as peroxyacetyl and acyloxy ($\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$), which assist $\text{HO}^\bullet$ in cleaving azo bonds and oxidizing aromatic substituents. The net result is an increased rate as the PAA concentration rises. The plateau and occasional slowing at high PAA concentration reflect the transition from productive peroxide activation to radical-budget limitation. At low-to-intermediate PAA doses, cavitation-generated $\text{HO}^\bullet$ and $\cdot\text{H}$ activate PAA/peracetate and increase the formation of $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$, thereby accelerating SSY oxidation. However, when PAA is present in excess, a larger fraction of $\text{HO}^\bullet$ is diverted from dye oxidation toward PAA activation or scavenging. Quantitatively, $\text{HO}^\bullet$ reacts rapidly with PAA, with $k_{\text{HO}^\bullet+\text{PAA}} = 1.3 \pm 0.2 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$ [13], and H_2O_2 also scavenges $\text{HO}^\bullet$, with $k_{\text{HO}^\bullet+\text{H}_2\text{O}_2} = 2.7 \times 10^7 \text{ M}^{-1}\cdot\text{s}^{-1}$ [13]. Therefore, increasing PAA concentration increases the probability that $\text{HO}^\bullet$ will react with PAA/ H_2O_2 rather than directly with SSY. The resulting acyl/peroxyl radicals contribute to oxidation, but they can also undergo self- and cross-termination. This explains why increasing the oxidant dose improves degradation only up to an optimum range, after which additional peroxide mainly increases scavenging and radical termination rather than useful pollutant attack.

For this reason, the effect of PAA concentration should be interpreted in terms of peroxide-utilization efficiency, not simply oxidant availability. A useful apparent metric is the dose-normalized initial degradation rate, $r_0/[\text{PAA}]_0$. Under the baseline conditions used for the synergy test, $r_0 = 0.116 \text{ mg/L}\cdot\text{min}$ at $[\text{PAA}]_0 = 5 \text{ mM}$, giving an apparent dose-normalized initial rate of $0.0232 \text{ mg/L}\cdot\text{min}\cdot\text{mM PAA}$. This value should not be considered an intrinsic kinetic constant because it depends on acoustic power, pH, dissolved gas, reactor geometry, and dye concentration. However, it provides a practical measure of how efficiently the added peroxide oxidant is converted into useful dye-removal capacity

under a defined operating condition. The decrease in marginal benefit at higher PAA doses indicates a lower peroxide-utilization efficiency due to $\text{HO}^\bullet$ scavenging and radical termination.

Dependence on the initial dye concentration stems from where the reactions occur. For azo dyes, sonochemical attack occurs at the interface between bubbles and liquid, as well as in the surrounding liquid layer. As the dye concentration doubles from 5 to 10 mg/L, the radicals become more diluted per molecule. This lowers the observed degradation rate, even when PAA is abundant. Furthermore, the US/PAA pathway introduces bulk-phase organic radicals ($\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$), which are less confined than interfacial $\text{HO}^\bullet$ radicals. Thus, increasing PAA disproportionately favors the higher-load scenario. Nevertheless, the same rise-then-plateau pattern is exhibited.

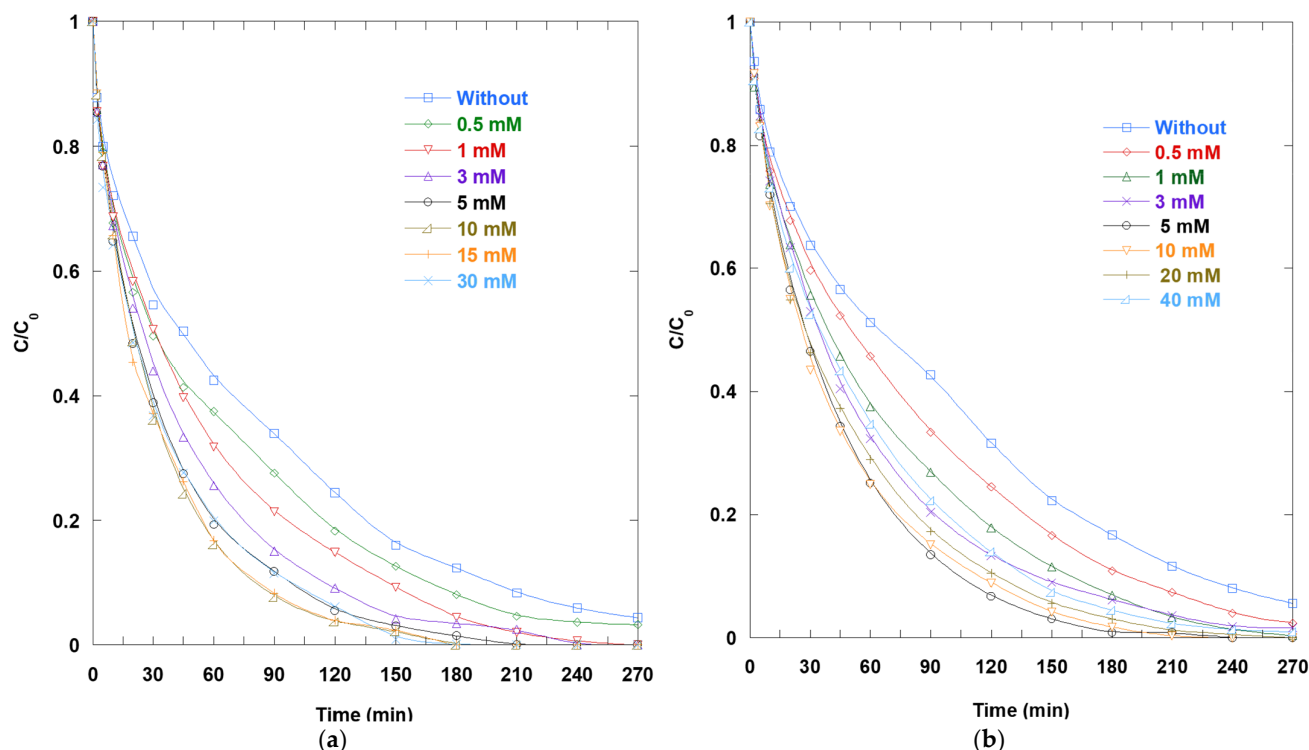


Figure 4. Effect of initial PAA concentration on SSY degradation during the US/PAA process at initial SSY concentrations of (a) 5 mg/L and (b) 10 mg/L. Conditions: 200 mL, pH 3.3, 425 kHz, 100 W. PAA concentrations are indicated in the legends (200 mL, pH 3.3, 425 kHz, 100 W).

Two practical implications follow for process design. First, an economical optimum exists at 425 kHz. Beyond that range, additional PAA mostly converts $\text{HO}^\bullet$ into secondary radicals or is lost to radical–radical reactions. Second, since PAA solutions are in equilibrium with H_2O_2 and acetic acid, the background peroxide pool increases during ultrasonication and participates in the scavenging network. Therefore, when comparing doses, it is important to report and control H_2O_2 alongside PAA.

These trends align with broader observations of the AOP [24,25]. These results also agree with recent PAA-AOP studies showing that increasing the oxidant dose improves degradation only up to an optimum range [14,16,17]. Beyond that range, excess PAA and the associated H_2O_2 background can consume $\text{HO}^\bullet$, favor radical–radical termination, and reduce oxidant utilization efficiency. The present US/PAA system follows this same contemporary trend, but with an added sonochemical constraint: PAA activation depends on the cavitation-generated radical flux, which is controlled by acoustic power, dissolved gas, and reactor frequency. Therefore, the plateau observed at high PAA concentration

should be interpreted not as a failure of PAA activation, but rather as the onset of radical-budget limitation and scavenging under high-frequency ultrasound. First, increasing the oxidant concentration raises the reaction rate until radical production becomes the limiting factor rather than oxidant availability. The production rate depends on power, frequency, and the cavitation field. Second, an excess of oxidant (PAA or H_2O_2) competes with $\text{HO}^\bullet$ radicals for reactants, flattening the dose-response curve.

2.4. Power Impact

Figure 5 illustrates the impact of ultrasonication power on the degradation of SSY via US and US/PAA processes at two initial dye concentrations of 5 and 10 mg/L (5 mM PAA, pH 3.3, 425 kHz). Increasing acoustic power accelerates decolorization for both initial SSY loads under US alone (dashed lines) and under US/PAA (solid lines). The curves retain a quasi-exponential shape. At any given power level, the US/PAA process is more effective than US alone. This is the expected kinetic signature when the removal rate is governed by a steady flux of sonochemical radicals and when PAA supplies additional organic radicals upon activation. High-frequency cavitation (425 kHz) generates an abundance of hydroxyl and hydrogen radicals, producing hydrogen peroxide and causing exponential dye fading through accumulation. Coupling an oxidant, such as PAA, adds acyloxy and peroxyacetyl radicals that complement hydroxyl radicals. This explains the persistent performance gap between the US and US/PAA. At a fixed frequency and geometry, increasing the input power raises the number of active cavitation events and the severity of bubble collapses. Thus, the formation rates of $\text{HO}^\bullet$, $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$, and H_2O_2 increase, resulting in higher rates of dye degradation. Systematic power sweeps demonstrate this monotonic rise in sonochemical activity. However, at sufficiently high powers, shielding/attenuation and bubble coalescence can limit further gains. Consequently, many sonoreactors exhibit diminishing returns rather than unlimited acceleration as power increases. This is evident in the gradual spacing between the 80 and 100 W traces compared to the significant difference between the 40 and 60 W traces.

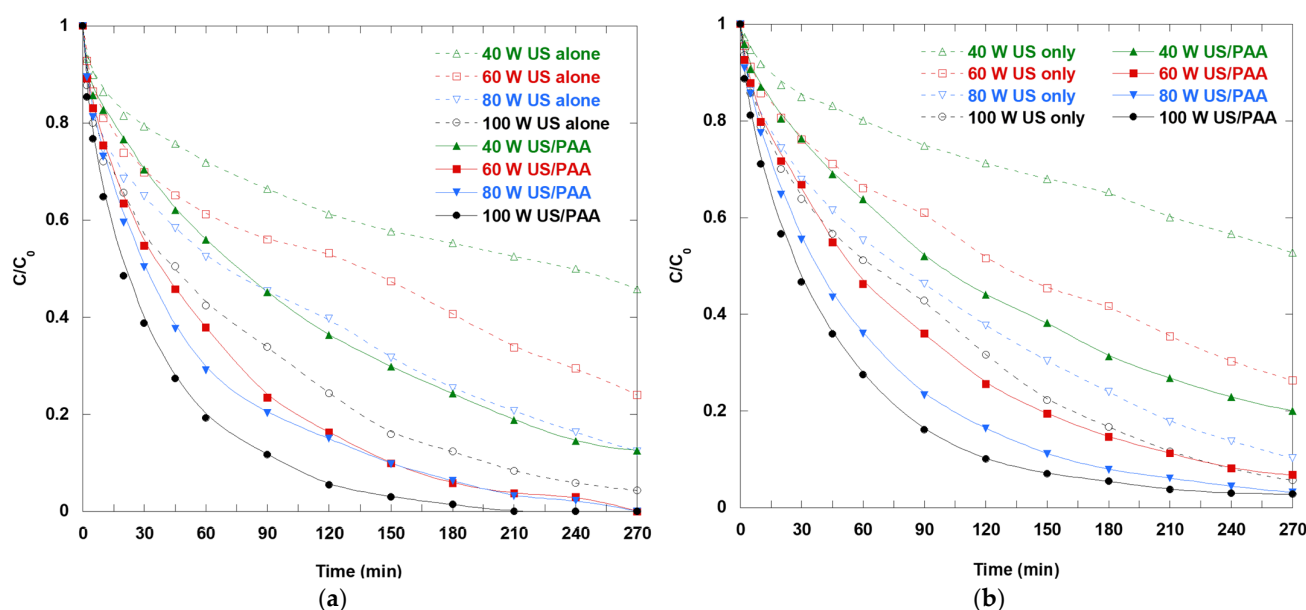


Figure 5. Effect of acoustic power on SSY degradation during ultrasound alone and the combined US/PAA process at initial SSY concentrations of (a) 5 mg/L and (b) 10 mg/L. Conditions: 5 mM PAA, 200 mL, pH 3.3, 425 kHz. Acoustic powers are indicated in the legends. (5 mM PAA, 200 mL, pH 3.3, 425 kHz).

Ultrasound creates water-derived $\text{HO}^\bullet$ and activates PAA. The initiation by $\text{HO}^\bullet$ (and high-temperature homolysis near collapsing bubbles) converts the PAA into peroxyacetyl and acyloxy radicals ($\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$), which selectively target azo bonds and aromatic substituents more effectively than $\text{HO}^\bullet$ does. Since PAA activation is initiated by the same radicals whose production increases with acoustic power, higher power increases both the primary ($\text{HO}^\bullet$) and secondary (PAA-derived) oxidant pools. At the higher SSY load (10 mg/L), each curve is above its 5 mg/L counterpart, indicating a lower degradation rate at the same power level. This stems from radical budget and transport limits. As concentration increases, the $\text{HO}^\bullet$ formed at bubble walls and in the near-interface liquid is distributed among more dye molecules, thereby lowering the per-molecule dose. This is due to competition for radicals and site-limited reactions near cavitation bubbles. Power accelerates the removal process under the US alone (dashed line) and even more so under US/PAA (solid line). These results align with higher radical fluxes at larger powers, as well as PAA activation, which adds acyl and peroxyacetyl radicals that complement $\text{HO}^\bullet$ radicals. Operating around 425 kHz is near the reported optimum window for hydroxyl radical production in many aqueous systems and provides a stable, homogeneous cavitation field. Within this regime, power scaling is highly efficient, as demonstrated by the distinct separation of the 40-, 60-, 80-, and 100-W traces.

At low acoustic power, the cavitation field produces a modest flux of primary radicals ($\text{HO}^\bullet/\text{H} \rightarrow \text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ and H_2O_2). Adding PAA significantly increases the flux in this regime because hydroxyl radicals efficiently activate PAA near collapsing bubbles and within the liquid. This process produces peroxyacetyl and acyloxy radicals ($\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$). These radicals work with hydroxyl radicals to cleave azo bonds and oxidize aromatics. Consequently, the relative improvement of US/PAA over US alone is greatest when the native $\text{HO}^\bullet$ supply is low. High-frequency sonochemistry (approximately 0.3–0.5 MHz) steadily generates radicals. At the lower end of the power sweep, however, radicals limit the system. Thus, PAA-derived radicals accelerate dye loss. As ultrasonication power increases, the cavitation population and collapse intensity rise, pushing $\text{HO}^\bullet$ production toward a higher quasi-steady state. Numerous power sweeps demonstrate this monotonic increase as well as diminishing returns at higher powers due to acoustic attenuation, bubble coalescence, and shorter bubble lifetimes. Therefore, US-only operation rapidly degrades SSY. Under these conditions, adding PAA yields a smaller relative gain because oxidation is limited by radical transport and competition at interfaces rather than radical scarcity. Additionally, the larger oxidant pool formed at higher power levels competes for $\text{HO}^\bullet$. H_2O_2 effectively scavenges $\text{HO}^\bullet$, and $\text{HO}^\bullet$ also reacts with PAA. These factors reduce the marginal benefit of additional PAA at high power levels. Together, these factors cause the US/PAA-over-US gap to shrink as power increases, as observed for both dye loads. This interpretation aligns with power-dependent radical yields and their reduction at high input. It also aligns with PAA activation pathways that generate $\text{CH}_3\text{CO}_3^\bullet$ /acyloxy radicals, which are essential for synergy with ultrasound. Additionally, it aligns with $\text{HO}^\bullet$ scavenging reactions, which become more significant as the peroxide/PAA background increases with power and irradiation time. These findings explain why PAA's impact is most pronounced when acoustic power is low and the system is radical-limited.

PAA dose and acoustic power further tune the reaction network by controlling the radical budget. At low PAA concentration or low acoustic power, the system is radical-limited, and additional PAA or acoustic energy increases the availability of oxidizing species. At intermediate PAA concentration, PAA activation becomes productive, and acyl/peroxyl radical propagation contributes strongly to dye oxidation. At excessive PAA concentration or high accumulated H_2O_2 levels, the pathway shifts toward $\text{HO}^\bullet$

scavenging and radical-radical termination, producing diminishing returns. Therefore, tunability in US/PAA involves optimizing the balance between radical initiation, radical propagation, pollutant attack, and radical loss.

Recent ultrasound/oxidant studies [14,16,17] similarly emphasize that increasing acoustic power enhances oxidant activation only while cavitation events remain productive. At higher power inputs, acoustic shielding, bubble coalescence, attenuation, and radical scavenging can reduce the marginal benefit of additional energy. The present data agree with this view: US/PAA remained faster than US alone at all tested powers, but the relative benefit of PAA decreased as power increased because the system shifted from radical-limited to transport- and scavenging-limited behavior.

Increasing acoustic power results in higher radical generation ($\text{HO}^\bullet/\cdot\text{H}$, $\text{HO}_2^\bullet/\text{O}_2^{\cdot-}$, H_2O_2) and faster decolorization when ultrasound is used alone. The increased $\text{HO}^\bullet$ flux activates PAA more quickly, producing acyloxy radicals ($\text{CH}_3\text{CO}_2^\bullet$) due to the formation of additional oxidative channels. This induces faster US/PAA kinetics at all power levels. At a higher pollutant load, the same amount of radical production is distributed among more targets, resulting in a slower degradation rate.

2.5. Initial pH Impact

Figure 6 shows how the initial solution pH affects SSY degradation when using US alone or the US/PAA method. Ultrasound alone decolorizes much faster under acidic conditions (pH 1–3) than under neutral/alkaline conditions. At pH 11, the curve initially drops quickly and then plateaus. Adding 5 mM PAA (US/PAA) yields the fastest results under acidic (pH 1) and moderately alkaline (pH 9–11) conditions. Neutral conditions (pH 7) are clearly suboptimal. These qualitative trends are consistent with reactant distribution by cavitation, changes in SSY speciation/affinity with pH, and switching of PAA radical chemistry across its pKa. At 425 kHz, the chemistry is dominated by $\text{HO}^\bullet$, which is formed through water sonolysis. pH determines where the dye sits and how effectively radicals can reach it. SSY is a sulfonated azo dye (anionic over most of the pH range), and cavitation bubble interfaces in water are negatively charged above pH 3 due to OH^- adsorption. Anions are electrostatically repelled and therefore spend less time in the interfacial reaction zone. Lowering the pH reduces this repulsion and can partially protonate the azo and phenolic sites. This increases hydrophobicity and interfacial affinity, resulting in faster color loss at pH levels between 1 and 3 than at neutral or alkaline levels. The neutral species/interfacial accumulation principle classically explains how pH affects the sonochemical degradation of ionic contaminants. Alkalinity adds two more penalties. First, background bases (e.g., carbonate and bicarbonate in typical waters) scavenge $\text{HO}^\bullet$ to form the much less reactive $\text{CO}_3^{\cdot-}$, thereby reducing the effective oxidant strength. The rate constants for $\text{HO}^\bullet$ with HCO_3^- and CO_3^{2-} are 8.5×10^6 and $3.9 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$ [26], respectively. Second, H_2O_2 (the product of water sonolysis) decomposes more readily as pH rises, lowering steady-state oxidant levels. Together, these factors account for the shallow, long-tailed decay at pH 6.9–11 in the US-only process.

Adding 5 mM of PAA creates a second source of oxidant that can be activated by ultrasound. PAA has a pKa of 8.2. Below this value, it is largely neutral (PAAH); above this value, the peracetate anion (PAA^-) dominates. When activated by ultrasonication, PAA generates acyl-peroxyl and acetyloxy radicals ($\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$), which diffuse farther and have a longer lifespan than $\text{HO}^\bullet$ radicals. This enables the radicals to attack anionic dyes that evade the bubble interface. These features explain the marked acceleration across all pH levels in the US/PAA process and the appearance of an alkaline optimum. Crucially, PAA speciation flips across its pKa of 8.2. Below pH 8.2, the neutral PAA (PAAH) species dominates, and above pH 8.2, the peracetate anion (PAA^-) becomes abundant. The reaction of $\text{HO}^\bullet$ with PAA^- is more than 10 times faster than with

PAAH, with reported second-order rate constants of 9.97×10^9 versus $9.33 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$ [27]. This efficiently funnels $\text{HO}^\bullet$ into organic radical chains ($\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{O}^\bullet$).

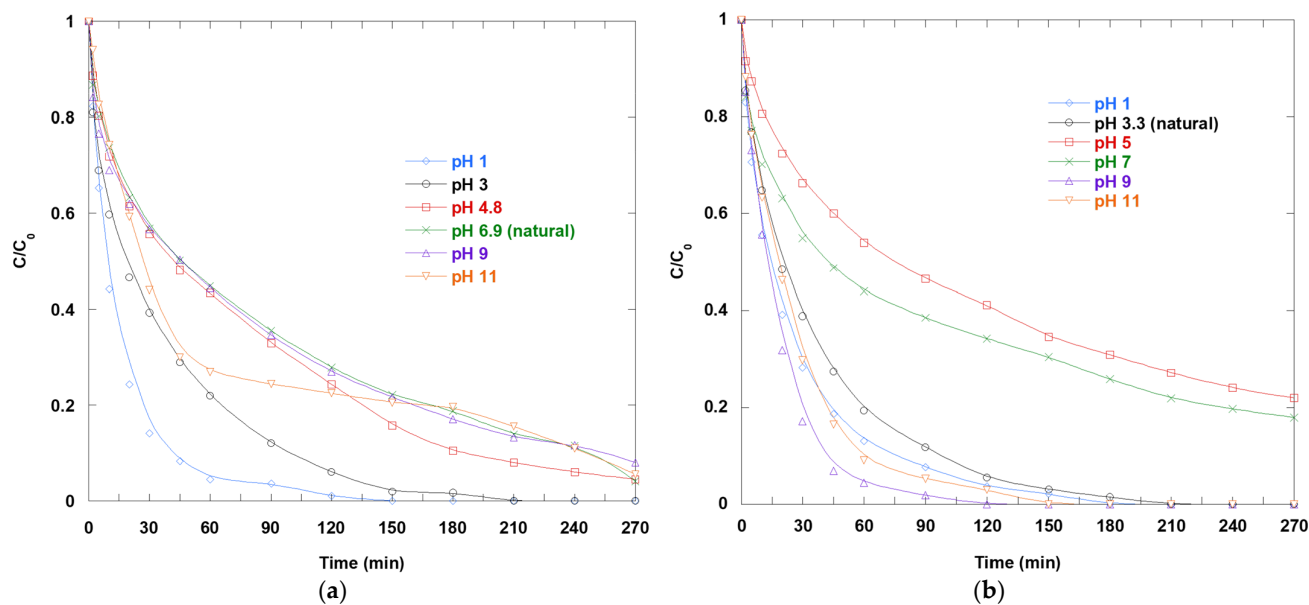


Figure 6. Effect of initial solution pH on SSY degradation during (a) ultrasound alone and (b) the combined US/PAA process (5 mg/L, 5 mM PAA, 200 mL, 425 kHz, 100 W).

It is important to note that this interpretation does not imply that non-radical PAA pathways are absent. Direct oxidation by PAA, base-assisted PAA reactions, and electrophilic reactions involving PAA/peracetate may occur in parallel, particularly under alkaline conditions. However, under the present experimental conditions, these non-radical routes appear to be secondary for SSY decolorization. This conclusion is based on three observations. First, PAA alone produced negligible removal, showing that direct PAA oxidation is insufficient for rapid azo-dye decolorization under the tested conditions. Second, the US/PAA system outperformed both US alone and PAA alone, indicating that ultrasound activates PAA rather than simply adding an independent oxidant. Third, the alkaline enhancement coincides with increased peracetate availability and with the much faster reaction of $\text{HO}^\bullet$ with PAA^- than with neutral PAAH. Therefore, the favorable alkaline window is attributed mainly to ultrasound-initiated peracetate conversion into acyl/peroxyl radicals, while recognizing that minor non-radical reactions may coexist. This pH-dependent behavior illustrates the tunability of the US/PAA reaction network. At low pH, pathway control is achieved mainly by improving dye access to the bubble-liquid interface, where $\text{HO}^\bullet$ production is highest. At mildly alkaline pH, pathway control shifts from interfacial access to chemical speciation because PAA^- becomes more available and reacts rapidly with cavitation-generated $\text{HO}^\bullet$ to initiate acyl/peroxyl radical chains. Therefore, the same US/PAA system can be directed toward either an interfacial $\text{HO}^\bullet$ -dominated regime or a bulk organic-radical-propagation regime by adjusting pH. Within the tested 425 kHz US/PAA system, this shift in PAA speciation provides a plausible explanation for the improved performance at pH 9–11, despite the weaker performance of US alone in the same pH range; however, this pathway assignment should be viewed as condition-specific and dependent on pollutant structure, ultrasound frequency, oxidant dose, gas atmosphere, and matrix composition. Once some $\text{HO}^\bullet$ is produced by cavitation, the PAA^- rapidly converts it into longer-lived organic radicals that effectively work in the bulk. At pH 7, only about 6% of the PAA is deprotonated. This restricts the rapid $\text{HO}^\bullet +$

PAA[−] pathway that initiates organic-radical chains. Meanwhile, the dye remains anionic and is not favored at the bubble interface. In other words, neither the interfacial (acid-favored) nor the chain-propagation (alkaline-favored) pathway is optimal. Consequently, it is the slowest condition in the US/PAA technique. At the very acidic end (pH 1–3.3), two advantages reinforce each other. SSY is less strongly repelled and can partition closer to the bubble interface, where radical fluxes are highest, and PAA solutions are acidic and stable in an acidic environment. The typical product pH is less than 1.8, so homolysis driven by ultrasound can proceed without rapid base-catalyzed decomposition. This results in the steep early-time decay observed at pH 1–3.3 in the US/PAA technique.

Mechanistically, three contributions should be distinguished. Radical oxidation refers to SSY attack by cavitation-generated HO• and by PAA-derived acyloxy/acyl-peroxyl radicals; non-radical pathways refer to possible direct reactions of PAA or PAA[−] with the dye or intermediates; and speciation-driven transformation refers to the pH-controlled shift from neutral PAA to PAA[−], which changes the probability of radical-chain initiation. This distinction follows the broader principle that advanced oxidation systems may involve speciation-controlled transformation in addition to conventional radical oxidation [28].

The US relies almost entirely on interfacial HO• chemistry. Therefore, anything that improves dye residence at the interface, such as a low pH for anions, or anything that preserves HO•, such as a low carbonate concentration, accelerates decolorization. However, when PAA is present, bulk organic radical chains share (and often dominate) the workload. This decouples performance from the strict interfacial requirement, creating a second optimum at an alkaline pH through speciation to PAA[−] and enhanced radical propagation.

For the US, operating in the acidic regime is advantageous for anionic dyes such as SSY because it mitigates electrostatic exclusion from the hot interfacial zone and avoids carbonate scavenging. Expect substantially slower kinetics at neutral to alkaline pH in unbuffered waters. For the US/PAA system, two practical windows are optimal: a very acidic window, which provides fast interfacial access and efficient homolysis, and a moderately alkaline window, which enables PAA[−]-driven radical chains. Neutral pH is the least favorable.

Two attractive windows emerge for the US/PAA system: one very acidic (with fast interfacial access and PAA homolysis) and one moderately alkaline (with PAA[−]-enabled radical chains). Neutral pH is suboptimal. The alkaline window is useful when acidification is impractical, as PAA-derived organic radicals can effectively work in the bulk phase where anionic dyes reside. Thus, the proposed mechanism should be read as a hierarchy of likely pathways under the present conditions rather than as an absolute exclusion of alternative chemistry. At acidic pH, SSY removal is primarily favored by interfacial access to cavitation-generated HO•. At mildly alkaline pH, where PAA[−] becomes more abundant, the data are more consistent with ultrasound-triggered radical-chain propagation involving CH₃C(O)O• and CH₃C(O)OO•. Non-radical PAA reactions may contribute, but they do not account for the observed synergy between US and PAA or for the dependence on acoustic activation.

2.6. Saturating Gases Impact

Figure 7 illustrates the effect of dissolved gas on SSY degradation during ultrasound alone and the US/PAA process. The effect of gas identity should be interpreted in terms of both cavitation chemistry and gas–liquid mass transfer. In ultrasound alone, rapid decolorization under O₂ saturation is consistent with increased steady-state oxidant formation at high frequency. During water sonolysis, bubble collapse produces HO• and H•. Dissolved O₂ traps H• to form HO₂•, which subsequently contributes to H₂O₂

formation and sustains oxidative chemistry in the liquid phase. Thus, O_2 affects not only the thermal and chemical composition of cavitation bubbles, but also the transfer of oxidant-forming species between the gas phase, bubble interface, and surrounding liquid. The rapid decrease in the O_2 -saturated profile is therefore consistent with efficient radical initiation, oxygen transfer, and secondary peroxide formation. Argon is nearly as effective because it is thermally inert, has a high heat capacity ratio ($\gamma = 1.67$), and has a low thermal conductivity. These properties intensify collapses and enhance radical formation. However, argon alone typically falls just short of O_2 because it lacks the ability to chemically trap H atoms. The curve order (O_2 first, Ar second) reflects this. Both air-saturated and non-saturated liquids behave similarly because they both contain air and native nuclei in the absence of forced sparging. Ultrasound acts on these nuclei to initiate cavitation. Therefore, the difference between the two is modest because air is present in both cases. Finally, CO_2 saturation nearly shuts down the chemistry. The high solubility of CO_2 fills the bubbles with a polyatomic gas that has a low γ value and a higher heat capacity. This lowers the collapse temperatures.

Adding 5 mM PAA introduces a second radical source into the cavitation field. Ultrasound promotes PAA homolysis and chain steps that generate acetyloxyl and acylperoxyl radicals ($CH_3C(O)O\cdot$ and $CH_3C(O)OO\cdot$), as well as some $HO\cdot$ radicals. These longer-lived organic radicals diffuse farther into the bulk than $HO\cdot$ and are highly effective at removing azo dyes. Consequently, all curves accelerate and cluster together compared to US alone. Oxygen still plays a role because $R\cdot + O_2 \rightarrow ROO\cdot$ is nearly diffusion-controlled. Thus, O_2 channels carbon-centered and acyl radicals into peroxy radicals that propagate oxidation. This explains why the O_2 -saturated US/PAA curve is the fastest.

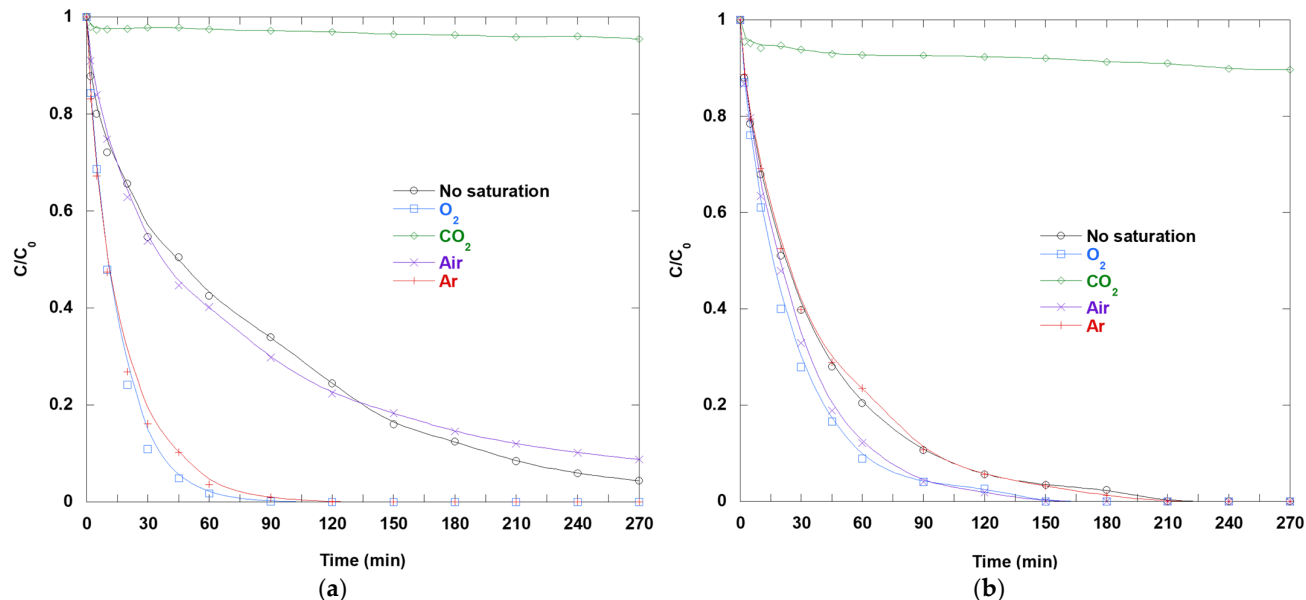


Figure 7. Effect of dissolved gas on SSY degradation during (a) ultrasound alone and (b) the combined US/PAA process (5 mg/L, 5 mM PAA, 200 mL, pH 3.3, 425 kHz, 100 W).

The US/PAA system also has a multiphase-transport dimension. Cavitation bubbles create transient gas–liquid interfaces where $HO\cdot$ and $H\cdot$ are generated, whereas PAA and SSY reside mainly in the aqueous phase. For efficient oxidation, radicals or radical precursors must escape from the interfacial region, and the pollutant must be transported toward reactive zones. PAA-derived acyl/peroxy radicals are longer lived than $HO\cdot$ and can therefore extend oxidation farther into the bulk liquid, partially relaxing the strict

requirement for pollutant accumulation at the bubble interface. This explains why the differences among gases become smaller in US/PAA than in ultrasound alone: once PAA-derived radical chains are initiated, bulk-phase propagation contributes more strongly to the overall removal.

Under US/PAA conditions, argon behaves similarly to air or non-saturated liquid conditions. Once PAA provides an ample supply of organic radicals, the benefit of O_2 's H-atom trapping becomes less significant than in neat sonolysis. Although it still benefits from argon's high-temperature collapse, the gas ranking decreases because, as shown in Figure 7b, radical propagation (fed by PAA) rather than initiation controls the kinetics.

CO_2 performs the worst with PAA. The CO_2 -rich bubble composition limits collapse temperatures and radical initiation. With fewer initiating $HO\cdot/H\cdot$ and less efficient PAA activation, the organic radical chain is starved. CO_2 may decrease or suppress acoustic $HO\cdot$ generation. This explains why the SSY profile is nearly flat, even when an external oxidant (PAA) is present.

From a mass-transfer perspective, dissolved gases control the availability, composition, and persistence of cavitation nuclei. O_2 participates chemically by replenishing oxygen at the bubble-liquid interface and by converting $H\cdot$ and organic radical intermediates into $HO_2\cdot$ and $ROO\cdot$ species. Ar, although chemically inert, promotes more intense bubble collapse because of its high heat-capacity ratio and relatively low thermal conductivity; its main contribution is therefore stronger radical initiation rather than oxygen-mediated propagation. CO_2 behaves differently because its higher solubility and polyatomic nature increase the heat capacity of the bubble contents and reduce collapse intensity. In addition, dissolved CO_2 can shift the carbonate/bicarbonate balance of the solution, which may further influence $HO\cdot$ availability and pollutant oxidation. Thus, the observed gas ranking reflects a coupled balance between gas dissolution, bubble transport, interfacial radical formation, oxygen-assisted propagation, and radical loss.

The identity of the gas controls the temperature and pressure history of the hot spots via γ and thermal conductivity. These factors determine the initiation rates of $H\cdot/HO\cdot$ (radical fragments from PAA) and the in-bubble reaction networks that promote or hinder oxidation. Promotion occurs through O_2 trapping of $H\cdot$ and formation of $HO_2\cdot/H_2O_2$, while hindrance occurs through CO_2 heat sink/cushioning. PAA overlays a bulk-phase radical chain ($CH_3C(O)O\cdot/CH_3C(O)OO\cdot$), which is less sensitive to interfacial localization issues associated with anionic dyes. This allows PAA to minimize differences between gases, except when initiation is significantly curtailed (e.g., with CO_2).

Dissolved gas provides a second pathway-control variable. O_2 favors oxidative propagation by trapping $H\cdot$ and organic radical intermediates to form $HO_2\cdot$ and $ROO\cdot$ species, whereas Ar mainly enhances radical initiation through stronger inertial collapse. CO_2 shifts the network in the opposite direction by lowering collapse intensity and suppressing radical initiation. Thus, gas selection tunes whether US/PAA chemistry is initiation-limited, propagation-favored, or strongly inhibited.

Dissolved gas also affects the quantitative peroxide balance. In O_2 -saturated media, $H\cdot$ atoms generated during bubble collapse are efficiently trapped by O_2 to form $HO_2\cdot$, which subsequently contributes to H_2O_2 formation. This increases the steady-state peroxide background and supports oxidative propagation. In Ar-saturated media, radical initiation is favored by stronger inertial collapse, but the lack of direct O_2 trapping limits oxygen-assisted $HO_2\cdot/H_2O_2$ formation. In CO_2 -saturated media, bubble cushioning reduces collapse intensity and suppresses primary $HO\cdot/H\cdot$ generation, thereby decreasing both PAA activation and sonochemical H_2O_2 formation. Thus, the gas effect reflects not only differences in cavitation temperature but also differences in the rates of peroxide generation and utilization.

The importance of transport is also consistent with broader observations in multiphase aqueous systems [29]. Thus, contaminant removal is controlled not only by intrinsic reaction kinetics but also by the ability of pollutants, oxidants, gases, and reactive interfaces to contact each other within multiphase environments. For US/PAA, this means that dissolved gas selection influences both radical generation and the spatial delivery of reactive species to contaminants.

For ultrasound alone, O₂ or Ar saturation is favorable, whereas CO₂ should be avoided. The activity order O₂ ≥ Ar > air > CO₂ for H₂O₂/HO• production and pollutant decay is consistent with both classical sonochemical principles and recent ultrasound/oxidant studies. For the US/PAA process, oxygenation remains beneficial, but the differences among gases are reduced because PAA-derived acyl/peroxyl radical chains contribute to bulk-phase oxidation. From a process-design standpoint, gas selection should therefore be considered a mass-transfer and reaction-pathway variable. O₂ promotes radical propagation and peroxide formation, Ar enhances collapse-driven initiation, and CO₂ suppresses radical initiation by weakening bubble collapse. These effects may become especially important in scaled reactors, where gas holdup, interfacial area, mixing, and pollutant transport strongly influence the contact between contaminants and reactive species.

Future work may also explore the integration of US/PAA with electrochemical or capacitive separation platforms as part of energy-efficient oxidation–separation treatment trains. In such configurations, US/PAA could be used to degrade aromatic pollutants and reduce chromophoric organic loads, while downstream electrochemical or capacitive processes could assist in removing residual ions, oxidants, or transformation products. Recent advances in flow-electrode capacitive deionization show that improving ionic and electronic transport within flow electrodes is critical for efficient desalination and ion removal [30]. Although not evaluated in the present study, such platforms may provide complementary separation functions after oxidative pretreatment.

3. Materials and Methods

All solutions were prepared with ultrapure water (Milli-Q, 18.2 MΩ·cm). Sunset Yellow FCF (SSY; 90% purity) was obtained from Sigma-Aldrich (Steinheim, Germany). SSY is 2-naphthalenesulfonic acid, 6-hydroxy-5-((4-sulfophenyl)azo)-disodium salt. Peracetic acid solution (32 wt. % in dilute acetic acid) was supplied by Sigma-Aldrich. Unless otherwise noted, the reagents were of analytical grade and used as received without further purification.

Experiments were conducted in a jacketed, cylindrical glass reactor with an internal diameter of 6 cm. A piezoelectric ceramic disk with a diameter of 4 cm, bonded to the reactor base, operated at 425 kHz; the electrical input power varied as required. The liquid temperature was controlled by circulating water through the outer jacket. A thermocouple immersed in the ultrasonicated liquid provided continuous temperature readings. Acoustic power was determined calorimetrically by measuring the temperature increase of the liquid during 5 min of ultrasonication. Ultrapure water was used as the working fluid for this calibration, and the jacket was drained to minimize heat loss to the thermostat and improve the accuracy of the heat balance.

Stock solutions of peracetic acid (PAA, 100 mM) and SSY (100 mg/L) were prepared and stored in the dark at 4 °C. These solutions were used throughout the study. Experiments were performed at 20 °C. The solution pH was adjusted with NaOH or H₂SO₄. For gas-effect tests, the reactor was sparged with the selected gas for 15 min prior to ultrasonication; sparging continued throughout the experiment.

SSY concentrations were quantified by UV–visible spectrophotometry (Mettler Toledo UV7, Greifensee, Switzerland) at λ_{max} = 482 nm. After each measurement, the

sample was returned to the reactor within 30 s to maintain constant ultrasonic power density.

All experiments were performed in triplicate. Unless otherwise indicated, the reported values are the means of three independent runs. We assessed the statistical significance of differences between conditions using two-sided Student's *t*-tests. A *p*-value less than 0.03 was considered significant.

4. Conclusions

The principal novelty of this work is the establishment of a unified mechanistic and operational framework for high-frequency ultrasound-activated PAA, linking cavitation chemistry, PAA speciation, organic-radical-chain formation, dissolved-gas effects, oxidant dose, acoustic power, and pH-dependent dye reactivity. In this framework, 'tunable' means that the dominant oxidation pathway can be shifted by changing the operating conditions: acidic media favor interfacial HO• attack near cavitation bubbles, mildly alkaline media favor PAA[−]-driven acyl/peroxyl radical-chain propagation in the bulk liquid, oxygen promotes peroxyl-radical propagation, CO₂ suppresses radical initiation, and excessive PAA/H₂O₂ shifts the system toward scavenging and radical termination.

The US/PAA process outperformed ultrasound alone across dye loadings and acoustic-power inputs, confirming kinetic synergy at the natural acidic pH of PAA solutions. Initial pH exerted primary control by governing both dye/interfacial partitioning and PAA speciation. With ultrasound alone, acidic media (pH 1–3) were optimal because electrostatic exclusion of the anionic dye from the negatively charged cavitation-bubble interface was reduced, allowing more effective access to the radical-rich interfacial region. At neutral to alkaline pH, lower interfacial affinity and HO• scavenging by carbonate species decreased oxidation efficiency. In the presence of PAA, the pH response became bimodal. Very acidic conditions preserved the interfacial advantage, whereas moderately alkaline media (pH 9–11) promoted PAA deprotonation and enabled the fast HO• + PAA[−] pathway, thereby initiating productive acyl/peroxyl radical chains. The pH-dependent HO₂•/O₂^{•−} equilibrium further contributed to tuning the redox network.

The identity of the dissolved gas modulated cavitation strength and initiation chemistry. O₂ and Ar promoted stronger cavitation activity and higher steady-state oxidant formation, whereas CO₂ acted as a bubble-cushioning gas and substantially suppressed radical generation. Under ultrasound alone, the activity followed the general order O₂ ≥ Ar > air > CO₂. Adding PAA reduced the differences between gases because bulk acyl/peroxyl radical chains carried a larger fraction of the oxidative workload. Nevertheless, oxygenation remained beneficial because O₂ promotes peroxyl-radical propagation through rapid R• + O₂ → ROO• reactions.

PAA dose and acoustic power acted as coupled operational levers. Increasing PAA concentration from zero to the millimolar range accelerated SSY degradation because cavitation-generated HO•/H• initiated PAA activation and produced acetyloxy and acyl-peroxyl radicals. However, beyond the intermediate dose range, the kinetic gains plateaued because excess PAA and accumulated H₂O₂ diverted HO• from dye oxidation and promoted radical–radical termination. Increasing acoustic power enhanced both US and US/PAA rates by increasing the population of active cavitation events and the intensity of bubble collapse, thereby increasing the primary radical flux available for direct dye oxidation and PAA activation.

Under the specific operating conditions investigated here, the results support a radical-dominated US/PAA mechanism in which cavitation-generated HO•/•H initiates PAA/peracetate activation, producing acyloxy and acyl-peroxyl radicals that complement

interfacial $\text{HO}^\bullet$ attack. This conclusion is condition-specific rather than universal: non-radical PAA reactions may coexist, but they appear secondary for SSY decolorization in the present 425 kHz system because PAA alone was ineffective, US/PAA showed clear synergy, and excessive PAA produced radical-scavenging-type diminishing returns.

H_2O_2 accumulation should be interpreted as a dynamic component of the US/PAA radical budget. It is generated through high-frequency water sonolysis, $\text{HO}^\bullet$ recombination, oxygen-mediated $\text{HO}_2^\bullet$ chemistry, and the PAA equilibrium background. At moderate levels, this peroxide pool indicates active cavitation chemistry and supports the oxidative environment. At excessive levels, however, H_2O_2 competes with SSY for $\text{HO}^\bullet$ and shifts the system toward $\text{HO}_2^\bullet$ formation, scavenging, and radical termination. The observed plateau at high PAA concentration is therefore consistent with reduced peroxide-utilization efficiency rather than a simple lack of oxidant availability.

The dissolved-gas results also have mass-transfer and multiphase-transport implications. Gas identity determines not only the collapse temperature of cavitation bubbles but also gas–liquid transfer, bubble population, interfacial area, radical escape, oxygen-assisted propagation, and pollutant access to reactive zones. In this sense, gas selection is a reaction–transport control variable: O_2 favors peroxide formation and peroxy-radical propagation, Ar favors collapse-driven initiation, and CO_2 suppresses radical formation by cushioning bubble collapse. These considerations are important for scale-up and for coupling US/PAA with porous media, membrane polishing, or other separation units, where the efficiency of oxidation depends on both radical chemistry and the transport of contaminants and oxidants across multiphase interfaces.

Although the present work was performed at a fixed frequency of 425 kHz, the mechanistic interpretation emphasizes that US/PAA performance should be frequency-dependent because acoustic frequency controls bubble dynamics, radical flux, interfacial area, H_2O_2 formation, and the balance between direct PAA sonolysis and $\text{HO}^\bullet/\text{H}$ -mediated PAA activation. Compared with prior PAA-based AOPs and ultrasound-only dye-degradation studies, this work shows that the benefit of US/PAA depends on the balance between interfacial $\text{HO}^\bullet$ chemistry and bulk acyl/peroxy radical propagation, which creates distinct acidic and alkaline operating windows and defines the conditions under which synergy is maximized.

Author Contributions: Investigation, validation, data curation, visualization, A.B.; conceptualization, methodology, validation, formal analysis, investigation, resources, data curation, writing—original draft preparation, writing—review and editing, visualization, supervision, project administration, funding acquisition, O.H.; conceptualization, methodology, validation, investigation, resources, visualization, supervision, L.E.B.; resources, validation, visualization, funding acquisition, M.K.H.-K.; validation, visualization, supervision, A.A. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to thank the Ongoing Research Funding Program (ORF-2026-1764), King Saud University, Riyadh, Saudi Arabia, for financial support.

Data Availability Statement: Data are contained within the article.

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

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