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A Unified Kinetic–Process Framework for Advanced Oxidation Processes: From Radical Chemistry to Reactor-Scale Performance in Wastewater Treatment

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Abstract

Advanced oxidation processes (AOPs) are widely investigated for the removal of persistent organic contaminants from wastewater, yet their full-scale application remains limited by matrix effects, energy demand, and scale-up challenges. A key difficulty lies in linking intrinsic reaction kinetics to reactor-scale performance under realistic conditions.

This work develops a unified kinetic–process framework that integrates radical generation, matrix-dependent scavenging, and transport phenomena within a system-level description. The apparent first-order rate constant (k_{app}) is interpreted as an emergent parameter governing observable treatment performance.

Analysis of representative wastewater matrices shows that hydroxyl-radical consumption is dominated by dissolved organic carbon and inorganic species, reducing effective radical availability by several orders of magnitude compared to laboratory systems. This explains the discrepancy between intrinsic reactivity and observed degradation rates.

AOP performance is further controlled by coupled kinetic–transport regimes, where mass transfer, radiation attenuation, and hydrodynamics constrain radical availability and lead to non-linear scaling. A dimensionless formulation based on Damköhler, Sherwood, cavitation, Reynolds, and optical thickness parameters provides a consistent basis for interpreting rate-limiting mechanisms.

From an engineering perspective, treatment time and energy demand are inversely related to k_{app}, emphasizing the need for matrix-aware design and process integration. The proposed framework provides a scalable and energy-efficient basis for AOP implementation in wastewater treatment.

Keywords: Advanced oxidation process; apparent rate constant; reaction kinetics; radical scavenging; energy efficiency; scaling-up; wastewater treatment.

1. Introduction

The increasing occurrence of micropollutants in aquatic environments has fundamentally altered the objectives of wastewater treatment. Conventional biological processes, while highly effective for biodegradable organic matter and nutrient removal, are not designed to eliminate persistent dissolved contaminants such as pharmaceuticals, endocrine-disrupting compounds, and per- and polyfluoroalkyl substances (PFAS) [1–3]. These compounds are frequently detected at trace concentrations (ng/L–µg/L) yet may exert significant ecological and toxicological effects due to persistence, bioaccumulation, and biological activity [4,5].

In modern plants, oxidation is usually a **tertiary or quaternary** step, placed after biological treatment and preferably after solids polishing, because suspended solids, nitrite, bicarbonate/carbonate, and dissolved organic matter consume oxidants and radicals non-productively [1,13,28]. That is why full-scale micropollutant control programs in Europe have typically upgraded biologically treated effluents with ozonation, activated carbon, or combinations of polishing steps rather than trying to oxidize raw wastewater directly [11,13,28].

Oxidative treatment in water proceeds through two broad routes [6,7,13]. The first is **selective direct oxidation** by a molecular oxidant such as ozone, free chlorine, ferrate, or electro-generated active chlorine. The second is **non-selective radical oxidation**, dominated in most AOPs by hydroxyl radical, HO•, with a standard redox potential near 2.8 V; sulfate radicals and chlorine radicals can also contribute in some systems.

Advanced oxidation processes (AOPs) are defined as systems in which strong oxidants are activated to generate highly reactive radical species (e.g., •OH, $SO_4^{\bullet-}$), enabling rapid and largely non-selective oxidation of a wide range of contaminants, with overall performance governed by the balance between radical generation, scavenging, and transport phenomena. In contrast to direct oxidation, AOPs rely on transient radical species rather than molecular oxidants as the primary reactive agents.

This distinction is critical not only mechanistically but also for predictive modeling of treatment performance [6,7]. Systems based on ozone (O_3), hydrogen peroxide (H_2O_2), ultraviolet irradiation (UV), Fenton chemistry, and more recently hydrodynamic cavitation and electrochemical oxidation, have demonstrated high removal efficiencies under optimized conditions [8–10].

However, despite this extensive body of research, the large-scale implementation of AOPs in municipal wastewater treatment plants remains limited. The primary reasons include high energy consumption, sensitivity to water matrix composition, formation of by-products, and challenges associated with reactor scale-up and process control [11,12]. In many cases, removal efficiencies reported at laboratory scale cannot be reproduced under real wastewater conditions due to radical scavenging, mass transfer limitations, and hydraulic constraints.

A key limitation in the current literature is the separation between **reaction-level understanding** and **process-level implementation**. Most studies focus either on:

- Fundamental reaction chemistry under controlled conditions, or
- Empirical process performance without mechanistic interpretation.

This fragmentation limits the ability to develop predictive, scalable, and economically viable AOP systems [13,18,29].

This work addresses this gap by proposing a **kinetic–process framework** that integrates:

- Radical reaction kinetics.
- Water matrix effects.
- Reactor hydrodynamics and transport phenomena.
- Energy and operational constraints.

Unlike previous studies that treat kinetics and process performance separately, this work establishes a unified kinetic–process framework that quantitatively links radical chemistry, matrix scavenging, and reactor-scale transport phenomena. The key novelty lies in interpreting the apparent rate constant (k_{app}) as an emergent system parameter that integrates these effects, enabling predictive understanding of AOP performance across scales. This approach provides a mechanistic basis for process design, optimization, and scale-up under realistic wastewater conditions.

2. Direct and Radical Oxidation Kinetics in Wastewater Treatment

2.1 General Reaction Mechanism

Direct oxidation pathways associated with ozone or hydrogen peroxide are generally useful for electron-rich moieties such as activated aromatics, amines, phenols, olefins, and some sulfur-containing pharmaceuticals but play only a limited role in overall COD removal. In contrast, significant COD reduction requires non-selective oxidation by hydroxyl radicals, which are capable of degrading bulk organic matter. This direct oxidation by molecular oxidants such as ozone, chlorine, or ferrate follows second-order kinetics and can be expressed as:

$$\frac{dC}{dt} = -k_{\mathrm{ox}} \cdot C \cdot [\mathrm{Ox}]$$

where:
C= pollutant concentration (mol·L^{-1})
[Ox]= oxidant concentration (mol·L^{-1})
k_{ox}= second-order rate constant (L·mol^{-1}·s^{-1})

Typical values of k_{ox} for ozone range from 10^3 to 10^6 L·mol^{-1}·s^{-1} depending on the compound structure, with higher values observed for electron-rich moieties such as phenols and amines [7,13,16].

Radical oxidation is broader in scope and often faster across many classes of organic compounds, but it is also more vulnerable to matrix scavenging by bicarbonate, carbonate, nitrite, dissolved organic carbon, and background solutes. While radical oxidation offers fast and non-selective degradation of a wide range of organic compounds, its efficiency can be significantly reduced in real water matrices. Naturally occurring species such as bicarbonate, carbonate, nitrite, and dissolved organic carbon act as radical scavengers, consuming reactive radicals and limiting their availability for target pollutant removal. Therefore, process performance strongly depends on water composition, and appropriate pre-treatment or higher

oxidant dosing may be required to maintain efficiency. These kinetic distinctions and their implications for process performance are well documented in the AOP literature [6–8,13, 28].

Radical oxidation (primarily via hydroxyl radical, HO•) in aqueous systems is fundamentally governed by **competitive kinetics** between target pollutants and matrix constituents. The degradation rate of a pollutant i can be expressed as:

$$\frac{dC_i}{dt} = -k_{OH,i} \cdot [\cdot OH] \cdot C_i$$

where:
$k_{OH,i}$= second-order rate constant for the reaction of •OH with species i (typically 10^8–10^{10} L·mol^{-1}·s^{-1}).
$[\cdot OH]$ = hydroxyl radical concentration (mol·L^{-1})

Unlike molecular oxidants, hydroxyl radicals are not externally dosed but are generated in situ and exist at very low steady-state concentrations. Their concentration can be estimated using a steady-state approximation under well-mixing conditions:

$$[\cdot OH]_{app} = \frac{R_{gen}}{\sum k_{OH,i} C_i} = \frac{R_{gen}}{k_{scav}}$$

where:
R_{gen} = radical generation rate (mol·L^{-1}·s^{-1}).
k_{scav} = total scavenging terms of full matrix including the target pollutants (s^{-1}).
$k_{OH,i}$ = second-order rate constant for species i (L·mol^{-1}·s^{-1}).
C_i = concentration of species i (mol·L^{-1}) in the matrix.

The denominator represents the **total scavenging capacity of the matrix**, including both target pollutants and background constituents such as dissolved organic carbon (DOC), bicarbonate, and carbonate.

At this point, we could define an observed, apparent or effective first-order rate constant (k_{app}) for a specific pollutant *j*:

$$k_{app,j} = k_{OH,j}[\cdot OH]_{app} = k_{OH,j} \frac{R_{gen}}{k_{scav}}$$

Under typical municipal wastewater conditions, this term may exceed the contribution of target pollutants by orders of magnitude because of **the matrix scavenging term** or **background scavenging capacity**, making it the primary determinant of AOP efficiency in municipal wastewater.

Additionally, AOPs are fundamentally governed by radical chain reactions that can be described through three principal stages [6,7,18,19]:

Initiation:
Generation of reactive species (primarily •OH) from oxidant precursors:

- H_2O_2 + Ultraviolet radiation (UV) → 2 •OH
- H_2O + Hydrodynamic cavitation (HC) → •OH + •H
- $Fe^{2+} + O_3 + H_2O \rightarrow Fe^{3+} + \cdot OH + OH^- + O_2$
- $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$

Radical attack on organic substrates (R):

- $\bullet OH + R \rightarrow R\bullet + H_2O$
- $R\bullet + O_2 \rightarrow ROO\bullet \rightarrow$ degradation intermediates

Termination:

Radical recombination or quenching:

- $\bullet OH + \bullet OH \rightarrow H_2O_2$ ($\sim 5 \times 10^9$ L·mol^{-1}·s^{-1})
- $\bullet OH + CO_3^{2-} \rightarrow CO_3\bullet^- + OH^-$ ($\sim 3.9 \times 10^8$ L·mol^{-1}·s^{-1})
- $\bullet OH + HCO_3^- \rightarrow CO_3\bullet^- + H_2O$ ($\sim 8.5 \times 10^6$ L·mol^{-1}·s^{-1})
- $\bullet HO\cdot + DOC \rightarrow oxidized\ products$ ($\sim 10^4$ - 10^6 L·mol^{-1}·s^{-1})
- $\bullet HO\cdot + polluant \rightarrow oxidized\ products$ ($\sim 10^8 - 10^{10}$ L·mol^{-1}·s^{-1})

Although ozonation can generate hydroxyl radicals, radical formation remains only a partial conversion pathway. Reported wastewater ozonation data indicate an average molar ·OH yield of approximately 21 ± 3% per mole of ozone consumed [23], demonstrating that only a limited fraction of consumed ozone is converted into non-selective radical oxidants. This provides a practical basis for relating ozone consumption to cumulative radical generation efficiency in real treatment systems.

$$[\cdot OH]_{produced} = Y_{OH} \cdot O_3^{consumed}$$

Where: $Y_{OH} = 0.21$ [23].

This expression represents an empirical lumped yield and does not capture the detailed radical chain mechanism or pH-dependent ozone decomposition kinetics.

As shown in Figure 1, hydroxyl-radical generation increases approximately linearly with ozone consumption, but the slope remains far below unity. This indicates that radical formation during ozonation is inherently limited and that ozone consumption should not be interpreted as equivalent to radical production. Under typical wastewater conditions, a substantial fraction of ozone is consumed through direct reactions with matrix constituents and intermediate species rather than being transformed into ·OH.

This limited radical yield has important consequences for process design. Even when ozone transfer and consumption are efficient, the resulting radical exposure remains constrained by the intrinsic chemistry of ozone decomposition and by the scavenging capacity of the matrix. Therefore, increasing ozone dose does not lead to a proportional increase in effective radical concentration, reinforcing the need to evaluate ozonation performance in terms of both ozone consumption and radical utilization efficiency.

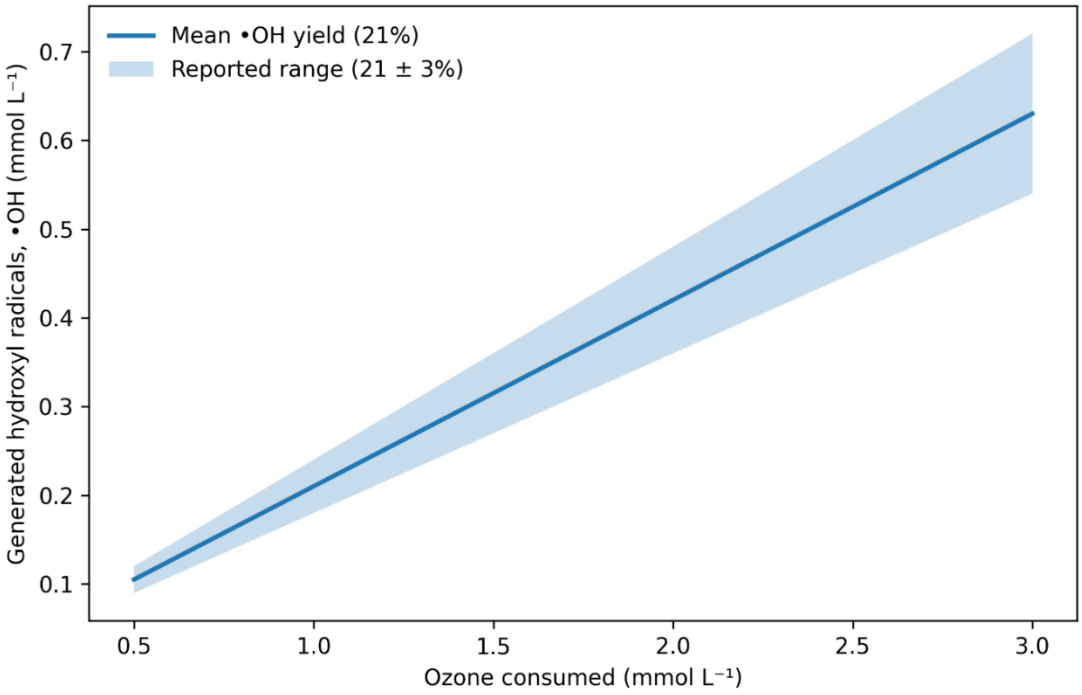

Figure 1. Calculated hydroxyl radical production as a function of ozone consumption using a literature reported OH yield of 0.21 mol OH per mol O_3 [23].

2.2 Scavenging Effect

From a design perspective, the performance of advanced oxidation processes (AOPs) can be interpreted within a competition-kinetics framework, in which removal efficiency is governed by the distribution of hydroxyl radicals between target pollutants and background matrix constituents. This can be expressed using the dimensionless parameter:

$$\eta_j = \frac{k_{OH,j} C_j}{k_{scav}}$$

where $k_{scav} = \sum_i k_{OH,i}\, C_i$ represents the total scavenging capacity of the matrix.

The set of η_i values therefore satisfies the normalization condition, reflecting conservation of radical consumption across all competing reaction pathways:

$$\sum_i \eta_i = 1$$

Under steady-state radical conditions and assuming well-mixed systems:

$$[\cdot OH] = \frac{R_{gen}}{k_{scav}}$$

and the pollutant degradation rate becomes:

$$-\frac{dC_j}{dt} = k_{OH,j}[\cdot OH]C_j = R_{gen}\eta_j$$

Here, R_{gen} is the volumetric rate of hydroxyl-radical generation and represents the source term of the radical balance. It is not an intrinsic property of the oxidant, but a process-dependent parameter governed by energy input, reactor configuration, and transport phenomena.

The pollutant degradation rate formulation highlights that the degradation rate is directly governed by the radical utilization efficiency, rather than by radical generation alone.

The dimensionless parameter η_j can be interpreted as the **radical utilization efficiency**, also referred to as a radical selectivity factor toward pollutant *j*, representing the fraction of generated hydroxyl radicals that effectively react with the target compound rather than being consumed by background matrix constituents.

In practical wastewater systems, $\eta_j \ll 1$, indicating that only a small fraction of radicals contributes to target pollutant degradation and reflecting dominant radical scavenging by background constituents. The theoretical limit $\eta_j \to 1$, corresponding to negligible scavenging, is not attainable under realistic conditions.

This framework explains why:

- waters with identical oxidant doses may exhibit significantly different removal efficiencies,
- dissolved organic carbon (DOC), alkalinity, and nitrite strongly influence process performance, and
- temperature effects are often secondary compared to matrix effects.

Consequently, reliable prediction of AOP performance requires:

- estimation of total scavenging capacity,
- use of experimentally derived pseudo-first-order rate constants, and
- avoidance of over-reliance on intrinsic reaction kinetics alone.

AOP performance in real wastewater is governed by matrix-controlled radical competition rather than by oxidant dosage alone. Hence, the performance of AOPs depends on the balance between radical generation, useful reactions, and scavenging losses [13,14,19,28].

Example: For diclofenac, $k_{OH} \approx 1\times10^{9}$ L·mol^{-1}·s^{-1}, yet removal efficiency may decrease from >90% in ultrapure water to <60% in secondary effluent due to matrix scavenging.

To illustrate this interplay, Table 1 first summarizes the major hydroxyl-radical scavengers relevant to wastewater AOP systems, including their reaction mechanisms, approximate rate constants, and engineering implications. Building on this qualitative overview, Table 2 then presents estimated pseudo-first-order scavenging-rate contributions $\left(k_{\mathrm{OH},i}C_i\right)$ for a representative secondary-effluent matrix based on literature-reported concentrations and reaction rate constants [13,25,26,28]. Bicarbonate and carbonate concentrations were derived from reported alkalinity and pH, while micropollutant concentrations were taken from typical effluent measurements by Tixier et al. (2003).

Table 1 shows that intrinsic reactivity alone does not determine the importance of a scavenger. In practical wastewater matrices, radical consumption depends on the product of reaction rate

constant and concentration. Therefore, the relative contribution of each component is better represented by pseudo-first-order scavenging terms, as summarized in Table 2.

Table 1. Key hydroxyl-radical scavengers, reaction mechanisms, and engineering implications in wastewater AOP systems.

Representative species	Reaction mechanism with •OH	Typical k_{OH}(L·mol^{-1}·s^{-1})	Engineering impact
Carbamazepine (CBZ)	•OH + CBZ → transformation products (aromatic addition, H-abstraction)	~10^9	Fast intrinsic kinetics, but negligible contribution due to low concentration; used as benchmark micropollutant
Diclofenac (DCF)	•OH + DCF → hydroxylated intermediates and ring-opening products	~10^9–10^{10}	Highly reactive compound: rapid degradation in clean systems but strongly suppressed in real wastewater
Bicarbonate (HCO_3^-)	•OH + HCO_3^- → $CO_3^{\bullet-}$ + H_2O	~8.5×10^6	Major inorganic scavenger; converts •OH into less reactive carbonate radicals, reducing oxidation efficiency
Carbonate (CO_3^{2-})	•OH + CO_3^{2-} → $CO_3^{\bullet-}$ + OH^-	~3.9×10^8	Strong scavenger at alkaline pH; contributes significantly to radical loss in high-alkalinity waters
Nitrite (NO_2^-)	•OH + NO_2^- → $NO_2^{\bullet}$ + OH^-	~1.0×10^{10}	Highly reactive scavenger even at low concentrations; can significantly reduce radical availability
Bulk organic matter (EfOM / COD)	•OH + EfOM → oxidized intermediates and radical species	~10^4–10^6 (effective range)	Dominant radical sink; complex mixture with distributed reactivity; controls overall radical utilization efficiency

Table 2. Estimated pseudo-first-order scavenging rates $(k_{OH,i}C_i)$ contributions in a representative secondary Effluent**.**

Component	Typical Concentration (C_i)	Unit	Second-Order Rate Constant with •OH ($k_{OH,i}$) (L·mol^{-1}·s^{-1}) [a]	Pseudo-First-Order Scavenging Rate ($k_{OH,i}C_i$) (s^{-1}) [a]	Fraction of Total Scavenging (%) [b]
Target Micropollutants					
Carbamazepine (CBZ)	10	µg/L	2.6×10^9 [c]	2.6×10^1	<0.01
Diclofenac (DCF)	10	µg/L	3.0×10^9 [c]	3.0×10^1	<0.01
Inorganic Scavengers					
Bicarbonate (HCO_3^-)	2.47	mM	5.7×10^7 [d]	1.4×10^5	16.9
Carbonate (CO_3^{2-})	0.36	mM	1.5×10^8 [d]	5.3×10^4	6.2
Nitrite (NO_2^-)	55	µM	3.2×10^9 [d]	1.8×10^4	1.9
Bulk Organic Matter					
Dissolved Organic Carbon (DOC)[e]	4.4	mgC/L	– [f]	2.3×10^5	74.8
Total Scavenging Capacity ($k_{scav} = \Sigma k_{OH,i}C_i$)			–	**3.1×10^5**	**100**

[a] Units are shown below the column header.
[b] Fraction of total scavenging capacity: $(k_{OH,i}C_i) / (k_{scav}) \times 100$.
[c] Representative second-order rate constants for reaction with •OH in water at 25 °C (Klamerth et al., 2009; Buxton et al., 1988).
[d] Rate constants from Buxton et al. (1988) and Deng & Zhao (2015).
[e] Pseudo-first-order scavenging rate for DOC estimated from fractional scavenging distribution reported for secondary effluent (Ervens et al., 2003); f_{DOC} = 75% of total scavenging capacity.
[f] DOC consists of a complex mixture of compounds with a wide range of reactivities; therefore, a single second-order rate constant is not representative. Its contribution is included as a bulk pseudo-first-order term derived from fractional distribution (see Section 2.2).

Note: Table 2 values are internally consistent estimates based on literature data and typical effluent characteristics. They represent order-of-magnitude contributions and are not expected to be system-specific measurements.

The contribution of dissolved organic carbon (DOC) is represented as a bulk pseudo-first-order scavenging term. Because effluent organic matter consists of a complex mixture of compounds with a wide range of reactivities, it cannot be described by a single second-order rate constant. Instead, its contribution is estimated using reported fractional scavenging distributions for similar wastewater matrices.

The total scavenging capacity is calculated from the sum of the pseudo-first-order contributions listed in Table 2:

$$k_{\mathrm{scav}} = \sum k_{\mathrm{OH,i}}\, C_{\mathrm{i}} \approx 3.1{\times}105\ \mathrm{s}{-}1$$

The DOC contribution is then obtained from its fractional share:

$$k_{scav,DOC} = f_{DOC} \cdot k_{scav} = 0.748 \times 3.1 \times 10^5 = 2.3 \times 10^5\ \mathrm{s}^{-1}$$

This approach provides an internally consistent illustrative estimate and should not be interpreted as a predictive or independently validated calculation. The resulting values are intended to provide an order-of-magnitude representation of scavenging contributions rather than system-specific quantities.

The estimated pseudo-first-order scavenging rates indicate that hydroxyl-radical consumption in wastewater is dominated by background matrix constituents rather than by target micropollutants. Despite their high intrinsic second-order rate constants ($k_{OH} \approx 10^9$–10^{10} L·mol^{-1}·s^{-1}), carbamazepine and diclofenac exhibit pseudo-first-order scavenging rates on the order of 10^1 s^{-1}, reflecting their low environmental concentrations.

In contrast, inorganic carbon species, particularly bicarbonate and carbonate, contribute significantly higher scavenging rates (10^4–10^5 s^{-1}) due to their substantially higher concentrations. The dominant contribution arises from dissolved organic carbon (DOC), which exhibits an estimated scavenging rate on the order of 10^5 s^{-1}, reflecting both its abundance and distributed reactivity.

Overall, the total scavenging capacity of the wastewater matrix exceeds the contribution of target micropollutants by several orders of magnitude. Although the exact values depend on matrix assumptions, this imbalance is consistent with experimental observations reported in the literature [13,18] and confirms that radical utilization efficiency is primarily governed by competition with background constituents.

The estimated pseudo-first-order scavenging rates are visualized in Figure 2, allowing direct comparison between target micropollutants and major matrix components. The figure highlights that bulk organic matter and inorganic carbon species dominate radical consumption by 3-4 orders of magnitude compared to target pollutants (micropollutants).

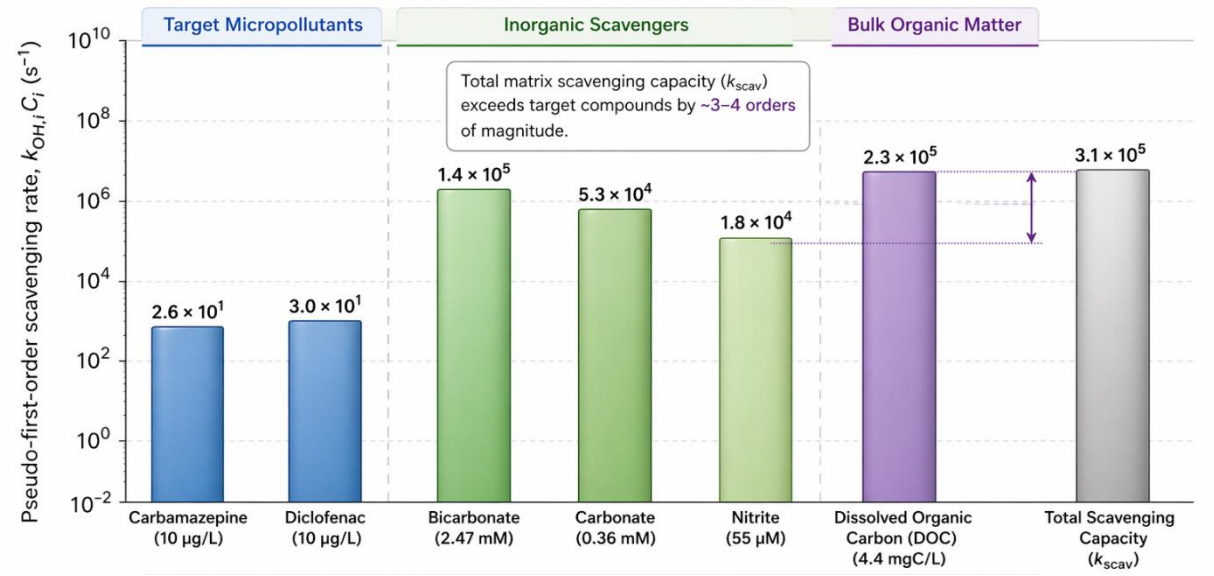

Figure 2. Estimated pseudo-first-order hydroxyl-radical scavenging rates ($k_{\mathrm{OH},i}C_i$) in a representative secondary-effluent matrix.

To further illustrate this effect, Figure 3 presents the normalized radical utilization efficiency (η_i), representing the fraction of hydroxyl radicals consumed by each component:

$$\eta_i = \frac{k_{OH,i}C_i}{k_{scav}}$$

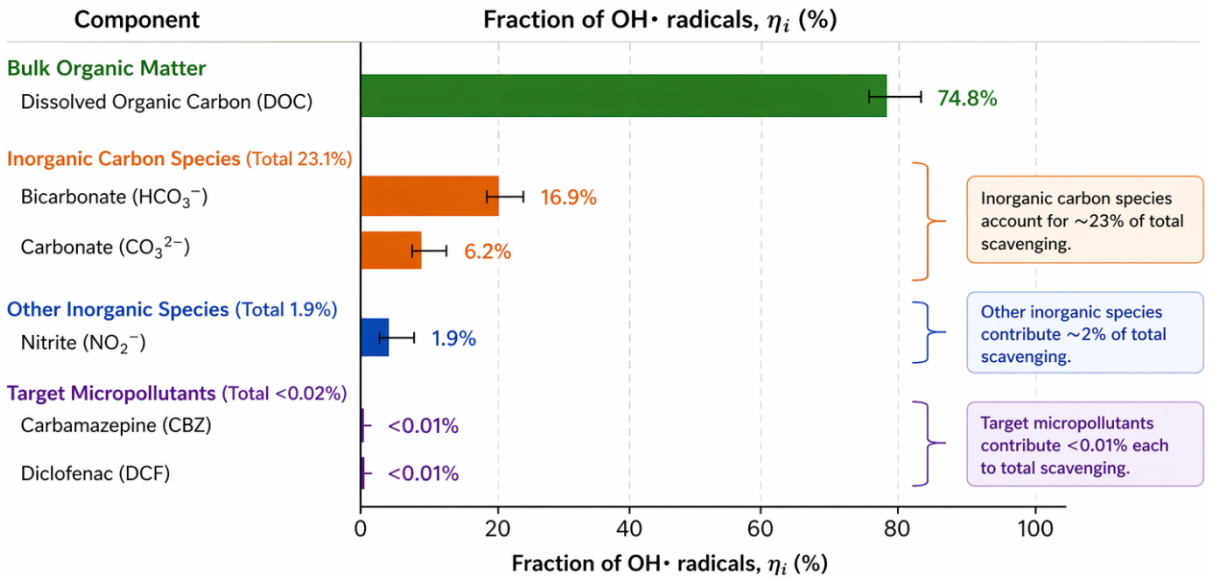

Figure 3. Estimated fraction of hydroxyl radicals reacting with individual components i in a representative secondary-effluent matrix, expressed as $(\eta_i = 100.k_{\mathrm{OH},i}C_i/k_{\mathrm{scav}})$.

This representation converts kinetic terms into a direct measure of radical utilization. Under representative secondary-effluent conditions, the contributions of carbamazepine and diclofenac are negligible (<0.01%), whereas DOC accounts for approximately 75% of total scavenging, followed by bicarbonate (~17%), carbonate (~6%), and nitrite (~2%).

Although these values are estimated, they are consistent with experimentally observed scavenging distributions [13,18,28] and illustrate the dominant role of matrix composition in controlling radical utilization. In practical terms, the vast majority of hydroxyl radicals are consumed by background constituents rather than by the target pollutants.

This strong imbalance explains the discrepancy between laboratory-scale and real wastewater performance. In systems with low scavenging capacity, a larger fraction of radicals is available for pollutant degradation, leading to high apparent removal efficiencies. In contrast, under realistic conditions, the effective radical concentration is reduced by competing reactions, resulting in lower apparent rate constants (k_{app}) and reduced treatment performance.

To further illustrate the practical implications of matrix-controlled scavenging, the effect of residual dissolved organic carbon (DOC) is examined by varying its concentration in the treated effluent.

Figure 4 shows the relationship between DOC concentration and the fraction of radicals reacting with carbamazepine (10 µg/L), expressed as radical utilization efficiency (η) and normalized efficiency (η/η_{max}). The analysis assumes constant inorganic scavenger contributions and proportional variation of the DOC-related scavenging term.

The results indicate that increasing DOC from 0.5 to 4.4 mgC/L reduces η by approximately an order of magnitude, demonstrating the dominant role of DOC in limiting radical utilization. This behavior is consistent with the competition-kinetics framework, where total scavenging capacity controls radical partitioning.

From a process design perspective, maximizing η toward target pollutants—rather than maximizing radical generation alone—is the central objective of efficient AOP operation.

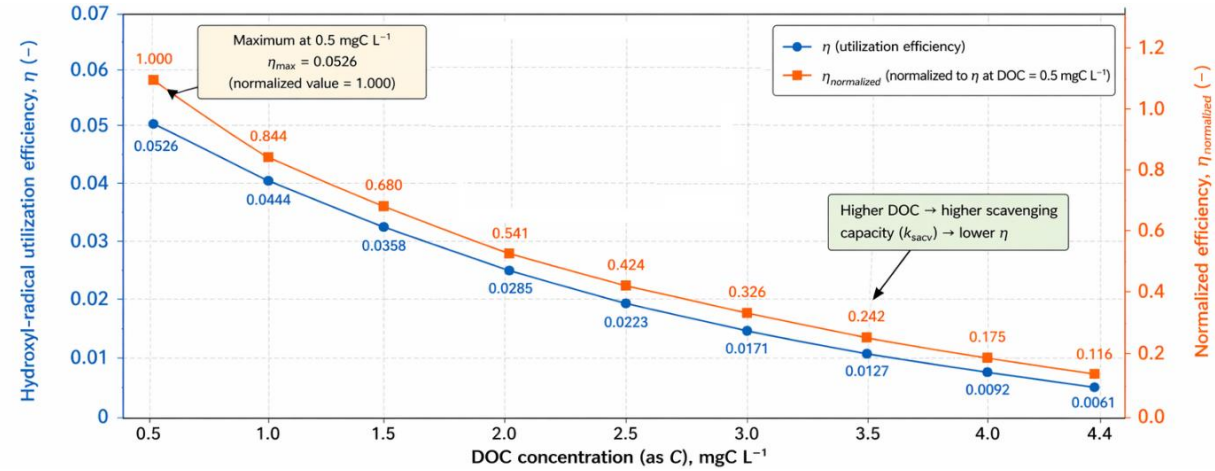

Figure 4. Effect of residual dissolved organic carbon (DOC) after pretreatment on hydroxyl-radical utilization efficiency (η) taking CBZ (10 µ.g/L) as targeted pollutant in a representative secondary-effluent matrix.

From an engineering perspective, changes in radical utilization directly affect process performance. Figure 5 shows the corresponding effect on normalized treatment time and energy demand, represented as proportional to $1/k_{app}$. Treatment time and energy demand are expressed relative to their minimum values to emphasize the performance penalty associated with increasing scavenging.

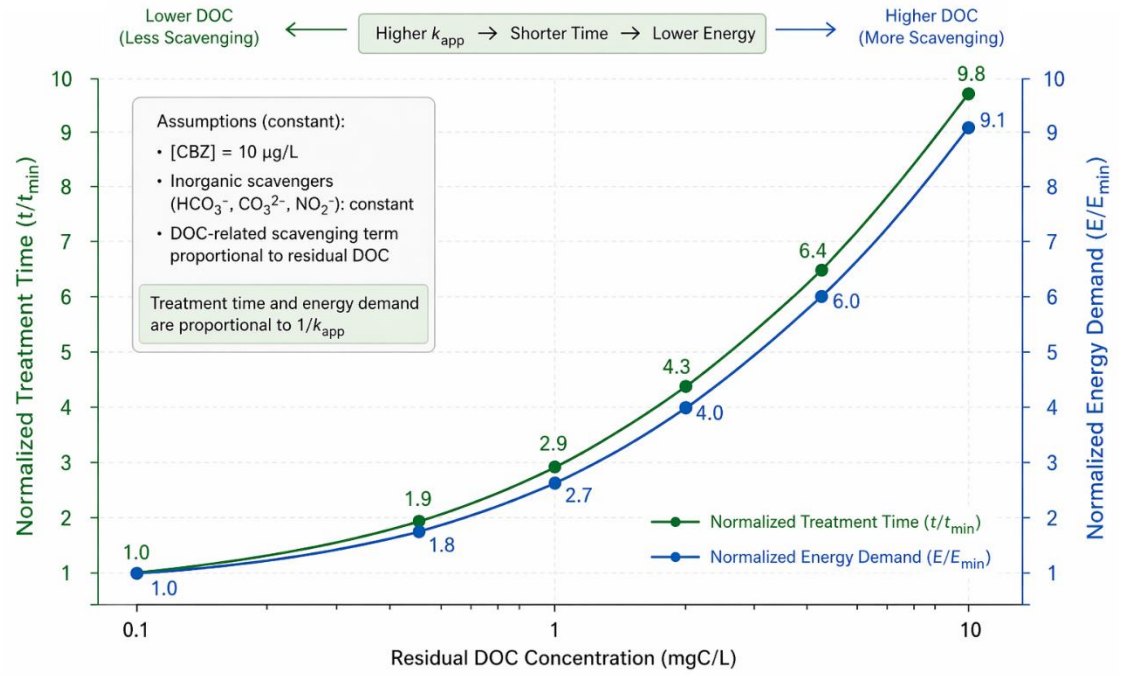

Figure 5. Effect of residual dissolved organic carbon (DOC) after pretreatment on normalized treatment time and energy demand (proportional to $1/k_{app}$) in advanced oxidation processes.

As k_{app} is inversely related to total scavenging capacity, reduction of DOC leads to higher effective reaction rates, shorter treatment times, and lower energy consumption. This highlights the importance of upstream removal of bulk organic matter in improving AOP efficiency.

These results provide quantitative support for the common practice of applying AOPs as tertiary or quaternary treatment steps following biological treatment and solids removal. By reducing the concentration of dominant scavengers, pretreatment enhances radical availability and improves oxidant and energy utilization.

Overall, the analysis reinforces the interpretation of the apparent rate constant (k_{app}) as a system-level parameter governed by matrix composition and underscores the importance of integrated process design in advanced oxidation systems.

In ozone-based systems, pollutant degradation proceeds through two concurrent pathways: selective direct oxidation by molecular ozone and non-selective oxidation mediated by hydroxyl radicals formed during ozone decomposition. As shown in Figure 1, only a limited fraction of the consumed ozone is converted into hydroxyl radicals, with a representative yield of approximately 0.21 mol •OH per mol O_3 consumed under typical wastewater conditions [23].

Consequently, the contribution of the radical pathway is inherently constrained, not only by its partial formation from ozone but also by rapid scavenging within the wastewater matrix. This dual limitation explains why the high intrinsic reactivity of hydroxyl radicals does not directly translate into proportional treatment performance and why increasing ozone dose does not necessarily result in a corresponding increase in degradation rates.

Hydrogen peroxide (H_2O_2) represents an alternative oxidant that differs fundamentally from ozone in its reactivity and mode of action. Under typical aqueous conditions, H_2O_2 exhibits only weak direct oxidation capacity toward most organic micropollutants, as its reactions are kinetically slow and highly selective. Consequently, its direct use as an oxidant in wastewater treatment is limited.

Instead, H_2O_2 is primarily applied as a radical precursor in advanced oxidation processes (AOPs), where activation methods such as UV irradiation or hydrodynamic cavitation, reaction with ozone (peroxone), or catalytic decomposition (Fenton chemistry) are used to generate hydroxyl radicals. These processes enable rapid and non-selective oxidation of a wide range of contaminants. Nevertheless, the effectiveness of these systems remains strongly influenced by matrix-dependent radical scavenging, such that the overall treatment efficiency is governed by the balance between radical generation and competitive consumption by background constituents.

From a process perspective, oxidation efficiency is therefore governed by the combined effects of oxidant partitioning between direct and indirect pathways and matrix-controlled radical competition. This highlights the importance of evaluating AOP performance using system-level parameters that account for both radical generation and scavenging processes.

2.3 Kinetic Regimes and Rate Limitations

In real wastewater systems, the performance of advanced oxidation processes (AOPs) is rarely governed by intrinsic reaction kinetics alone [13,18,29]. Instead, the overall degradation rate results from the coupling of **chemical reaction kinetics, mass transfer, and radiation transport phenomena**, each of which may become rate-limiting depending on operating conditions.

2.3.1 Chemical Kinetics Control

Chemical kinetics control dominates when oxidant and radical availability are sufficiently high and transport limitations are negligible. Under these conditions, the degradation rate is governed by intrinsic reaction kinetics:

$$r = k_{\mathrm{OH}} \cdot [\cdot OH] \cdot C$$

where:

- $k_{\mathrm{OH}} \approx 10^{8}$–$10^{10}$ L·mol^{-1}·s^{-1}
- C= pollutant concentration.

This regime is typically approached in **well-mixed laboratory systems with low scavenger concentrations**, where radical generation is efficient and uniformly distributed.

However, even in this regime, the effective/apparent rate constant k_{app} remains dependent on matrix composition through radical scavenging.

2.3.2 Mass Transfer Control

Mass transfer limitations are particularly relevant in processes involving gas–liquid interactions, such as ozonation. In such systems, the rate of ozone transfer from the gas phase into the liquid phase can limit the overall reaction rate [13,19]:

$$\frac{dC_{O_3}}{dt} = k_L a\left(C^*_{O_3} - C_{O_3}\right) - r_{\text{reaction}}$$

where:

- $k_L a$= volumetric mass transfer coefficient (s^{-1}).
- $C^*_{O_3}$= saturation concentration of ozone.
- C_{O_3}= dissolved ozone concentration.

The volumetric mass transfer coefficient $k_L a$ becomes a critical parameter, as gas–liquid transfer often limits ozone availability in the liquid phase and thus constrains the overall oxidation rate.

As a result, increasing ozone dosage does not necessarily increase degradation rates if mass transfer is limiting.

2.3.3 Radiation Transfer Control

In UV-based AOP systems (e.g., UV/H_2O_2), the generation of radicals depends on photon absorption, which is governed by radiation transport within the reactor. The local photon flux decreases exponentially with depth according to the Beer–Lambert law:

$$I = I_0\, e^{-\alpha x}$$

where:

- I= local light intensity.
- α= absorption coefficient.
- x= optical path length.

Radiation transfer is strongly affected by:

- Turbidity and suspended solids.
- Dissolved organic matter (UV absorbance).
- Reactor geometry and lamp configuration.

Therefore, a non-uniform UV distribution leads to spatial heterogeneity in radical generation and reduced overall efficiency. Additionally, UV attenuation by dissolved organic matter reduces radical generation efficiency [16,17].

2.3.4 Coupling of Regimes and Non-Linear Behavior

In practical systems, these regimes do not act independently but are strongly coupled [13,18,29]. The overall degradation rate can be conceptualized as:

$$r_{\text{overall}} = \min(r_{\text{kinetics}}, r_{\text{mass transfer}}, r_{\text{radiation}})$$

In other words, the overall rate is controlled by the slowest process and can be approximated as being controlled by the dominant limiting step. Nevertheless, this expression represents a conceptual approximation of rate-limiting behavior rather than a strict mechanistic relationship.

As a result, improvements in one domain (e.g., increasing oxidant dose) may have limited effect if another process (e.g., mass transfer or light penetration) is rate-limiting.

The performance of AOP systems is governed by the interplay between reaction kinetics and transport phenomena, and transitions between regimes lead to non-linear scaling behavior that complicates process design and scale-up.

2.3.5 Dimensionless Analysis and Scaling Criteria

The interplay between reaction kinetics, mass transfer, and radiation transport in advanced oxidation processes (AOPs) can be further formalized using dimensionless numbers that characterize the relative importance of these processes [13,18,29]. These parameters are essential for scaling analysis and for identifying rate-limiting regimes across reactor configurations.

A key dimensionless group is the **Damköhler number (Da)**, defined as the ratio of the characteristic reaction rate to the transport rate:

$$\text{Da} = \frac{k_{app}\, L}{u}$$

or, more generally,

$$\text{Da} = \frac{\text{reaction rate}}{\text{transport rate}}$$

where L is a characteristic length scale and u is the flow velocity.

• $\text{Da} \ll 1$: reaction-limited regime; transport or hydraulic residence is fast relative to the apparent chemical conversion rate.
• $\text{Da} \gg 1$: transport- or mixing-limited regime; chemical conversion is fast relative to delivery, mixing, or residence-time constraints.

In ozonation systems, mass transfer limitations can be further characterized by the **Sherwood number (Sh)**:

$$\text{Sh} = \frac{k_L\, L}{D}$$

where k_L is the liquid-side mass transfer coefficient and D is the molecular diffusivity. The Sherwood number relates convective mass transfer to diffusion and governs ozone availability in the liquid phase.

For hydrodynamic cavitation systems, the key dimensionless parameter is the **cavitation number** [10,20], which expresses the tendency of a liquid flow to undergo cavitation:

$$\sigma = \frac{P_\infty - P_v}{\frac{1}{2}\rho u^2}$$

where P_∞ is the reference static pressure, P_v is the vapor pressure of the liquid, ρ is the liquid density, and u is the characteristic flow velocity.

The cavitation number represents the ratio of pressure forces to inertial forces and determines the onset and intensity of cavitation:

- $\sigma \gg 1$: no cavitation
- $\sigma \approx 1$: incipient cavitation
- $\sigma \ll 1$: developed cavitation with intense bubble collapse

In AOP applications, the cavitation number links reactor geometry and operating pressure to bubble formation, collapse intensity, localized radical generation, and energy dissipation. Hence, within an appropriate operating range, lower cavitation numbers are generally associated with more intense bubble collapse and increased radical generation rates (R_{gen}), directly influencing the apparent rate constant k_{app}. Additionally, maintaining comparable σ values is essential when translating hydrodynamic cavitation performance from laboratory to pilot or full scale.

In addition, the flow regime can be characterized by the **Reynolds number (Re)** [29]:

$$\mathrm{Re} = \frac{\rho u L}{\mu}$$

where L is a characteristic length scale and μ is the dynamic viscosity.

The Reynolds number determines the degree of turbulence and mixing, which influence bubble distribution, collapse frequency, and mass transfer. In practical cavitation reactors, turbulent conditions ($\mathrm{Re} \gg 10^4$) are typically required to sustain effective cavitation and radical production.

Together, $\sigma$and Reprovide a dimensionless description of cavitation intensity and hydrodynamic conditions, enabling consistent comparison and scale-up of cavitation-based AOP systems.

In UV-based systems, radiation transport can be characterized using an **optical thickness parameter** derived from the Beer–Lambert law:

$$\tau = \alpha L$$

where α is the absorption coefficient and L is the optical path length.

• $\tau \ll 1$: uniform radiation field.
• $\tau \gg 1$: strong attenuation and non-uniform radical generation.

These dimensionless parameters provide a unified framework for interpreting AOP performance across scales. In particular, the apparent rate constant k_{app} can be interpreted as a function of the governing dimensionless groups:

$$k_{app} = f(Da, Sh, \sigma, Re, \tau)$$

This formulation is consistent with multi-parameter scaling approaches in chemical engineering, where system performance is governed by interacting dimensionless groups rather than by individual variables alone [29].

Consequently, scale-up of AOP systems requires considering not only similar operating conditions but also comparable dimensionless numbers, ensuring that the relative contributions of reaction kinetics, transport processes, and radiation effects remain consistent.

2.4 Selectivity and Oxidation Pathways

Although hydroxyl radicals (•OH) are commonly described as "non-selective" oxidants due to their very high redox potential (E° ≈ 2.8 V) [6,7,18], their reactivity in aqueous systems is in fact **kinetically selective** and strongly dependent on molecular structure and reaction pathways.

The rate of oxidation is governed by compound-specific second-order rate constants:

$$r = k_{\mathrm{OH}} \cdot [\cdot OH] \cdot C$$

where k_{OH} **varies significantly** depending on the chemical nature of the target compound.

2.4.1 Structure–Reactivity Relationships

Hydroxyl radical reactions proceed primarily via [8,16]:

- Hydrogen abstraction (aliphatic compounds).
- Addition to double bonds or aromatic rings.
- Electron transfer (less common in neutral systems).

As a result, the following trends are observed:

- **Electron-rich aromatic compounds** (e.g., phenols, anilines, many pharmaceuticals) exhibit high reactivity, with: $k_{\mathrm{OH}} \approx 10^{9}$–$10^{10}$ L·mol^{-1}·s^{-1}
- **Compounds with activated π-systems** (e.g., dyes, chromophores) undergo rapid radical addition, leading to efficient degradation and decolorization.

This structure-dependent reactivity is illustrated in Figure 6, which compares second-order reaction rate constants for representative wastewater-relevant contaminants with ozone and hydroxyl radicals. The selected compounds include diclofenac (DCF), carbamazepine (CBZ),

sulfamethoxazole (SMX), metoprolol (MTP), benzotriazole (BTZ), and acesulfame (ACE), which span a range of structures and reactivities commonly encountered in municipal wastewater and are frequently used as indicator compounds in oxidation studies.

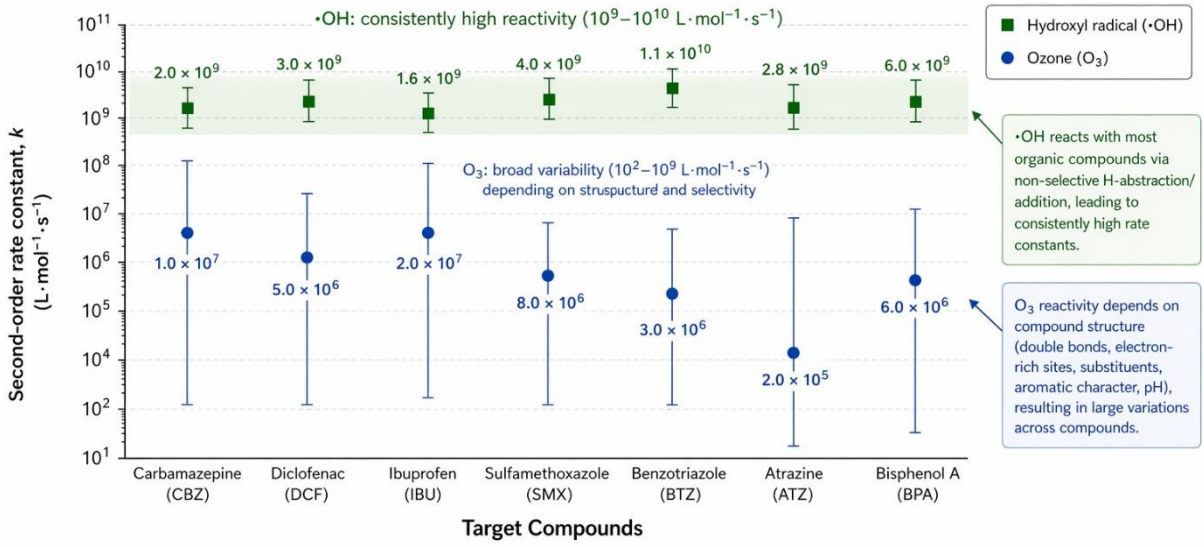

Figure 6. Comparison of intrinsic second-order rate constants for reactions with ozone (k_{O_3}) and hydroxyl-radical (k_{OH}) for representative wastewater-relevant micropollutants.

Figure 6 highlights the fundamental difference between selective molecular oxidation and non-selective radical oxidation. The reaction rate constants for ozone vary over several orders of magnitude, depending on molecular structure, functional groups, and speciation. For example, compounds such as diclofenac (DCF), carbamazepine (CBZ), and benzotriazole (BTZ) do not have a single, fixed structure in aqueous solution. They exist in different ionic and neutral forms depending on pH and can adopt multiple conformations. Consequently, ozone reactivity and the corresponding second-order rate constants are not unique but represent an average or typical value under the reported experimental conditions.

In contrast, hydroxyl-radical rate constants remain consistently high for all compounds, typically in the range of 10^9–10^{10} L·mol^{-1}·s^{-1}, indicating a largely non-selective oxidation mechanism. This explains why compounds that are resistant to direct ozone oxidation can still be effectively degraded in systems where hydroxyl radicals are generated.

However, despite this high intrinsic reactivity, the overall contribution of hydroxyl radicals to pollutant degradation in wastewater systems remains constrained by limited radical formation and strong matrix scavenging, as discussed in previous sections. Therefore, Figure 6 should be interpreted as a representation of intrinsic molecular reactivity rather than actual process performance, which is governed by the combined effects of kinetics, concentration, and matrix interactions.

2.4.2 Resistant Compounds and Bond Strength Effects

In contrast, compounds with strong chemical bonds or low electron density exhibit significantly lower reactivity:

- **Saturated aliphatic compounds**:
    - Lower reactivity due to stronger C–H bonds.
    - $k_{OH} \approx 10^6$–10^8 L·mol^{-1}·s^{-1}.
- **Fully halogenated compounds (e.g., PFAS)** [5,11]:
    - Extremely stable C–F bonds (~485 kJ/mol).
    - Limited susceptibility to •OH attack.
    - Very low effective degradation rates under conventional AOP conditions.

2.4.3 Reaction Pathways and Transformation Behavior

It is important to distinguish between:

- **Partial oxidation (transformation):** Initial radical attack is rapid.
- **Complete mineralization (CO_2, H_2O)**: Subsequent degradation steps are slower and may form intermediates.

This explains why:

- **Color removal (dyes)** is fast.
- **COD removal** is significantly slower.

2.4.4 Practical Implications for AOP Application

Based on these kinetic and mechanistic considerations, AOPs are generally most effective for:

- Aromatic pharmaceuticals (e.g., diclofenac, carbamazepine).
- Phenolic and electron-rich compounds.
- Dyes and chromophoric molecules.

In contrast, AOP performance is often limited for:

- Fully halogenated compounds (e.g., PFAS).
- Small, highly stable molecules (e.g., short-chain acids).
- Compounds lacking reactive functional groups.

Despite their high oxidation potential, hydroxyl radicals exhibit strong kinetic selectivity governed by molecular structure, such that AOP efficiency is controlled by compound-specific reaction pathways rather than oxidant strength alone.

3. Reactor Engineering and Process Constraints

The performance of oxidation processes, and particularly advanced oxidation processes (AOPs), at scale is strongly influenced by reactor design, as reaction kinetics are inherently coupled with transport phenomena and hydrodynamics [13,18,29]. These effects can be

interpreted in terms of dimensionless numbers such as the Damköhler, Sherwood, cavitation and Reynolds numbers, which determine the relative importance of reaction and transport processes.

In **ozonation systems**, the overall reaction rate is frequently limited by gas–liquid mass transfer, which governs the availability of dissolved ozone:

$$r_{O_3} = k_L a\left(C^*_{O_3} - C_{O_3}\right)$$

where $k_L a$ is the volumetric mass transfer coefficient. bubble size distribution, interfacial area, and mixing intensity therefore play a critical role in determining process efficiency.

In **UV-based systems**, radical generation depends on photon absorption, which is constrained by optical path length and light attenuation:

$$I = I_0 e^{-\alpha x}$$

As a result, turbidity, dissolved organic matter, and reactor geometry directly affect the spatial distribution of UV intensity and, consequently, radical formation.

In **cavitation systems**, oxidation efficiency is governed by hydrodynamic conditions, including pressure drop, flow regime, and reactor geometry, which control bubble formation, collapse intensity, and localized radical generation [10,20]. These conditions are commonly described using the cavitation number (σ) and Reynolds number (Re), which characterize cavitation intensity and flow regime, respectively.

At reactor scale, imperfect mixing and transport limitations lead to non-uniform radical distribution. This results in:

- Localized regions of high radical concentration (over-oxidation).
- Zones with insufficient oxidant exposure (under-treatment).
- Reduced overall process efficiency.

At scale, AOP performance is limited by transport non-uniformities, leading to spatial variations in radical concentration. These effects reduce effective k_{app} and overall efficiency.

Mass transfer limitations increase with scale due to non-linear scaling of k_La [13]. Similarly, UV systems suffer from light attenuation and non-uniform photon distribution [17].

illustrative example: Hydrodynamic cavitation-assisted AOP intensification

Hydrodynamic cavitation (HC) can be interpreted not only as an oxidation process, but also as a reactor-scale intensification platform for advanced oxidation processes. Bubble collapse produces localized high-temperature and high-pressure microenvironments, while also enhancing turbulence, micromixing, and interfacial renewal. Within the kinetic–process framework proposed here, HC-assisted AOP performance is therefore governed by coupled chemical and transport effects, including radical generation, oxidant utilization, matrix scavenging, gas–liquid mass transfer, and hydrodynamic conditions.

Conceptually, the apparent rate constant may be expressed as:

$$k_{\mathrm{app}} = f\left(R_{\mathrm{gen}}, k_{\mathrm{scav}}, \sigma, Re, k_L a, \phi_{\mathrm{Ox}}\right)$$

where R_{gen} is the radical generation rate, k_{scav} is the total matrix scavenging capacity, σ is the cavitation number, Re is the Reynolds number, $k_L a$ is the volumetric gas–liquid mass-transfer coefficient, and ϕ_{Ox} represents oxidant utilization efficiency.

Pilot-scale data reported for a 70 L hydrodynamic cavitation system treating high-COD industrial wastewater provide a useful quantitative example of this intensification behavior [30]. In that study, HC alone produced only limited COD removal, approximately 6.1% after 180 min, with a pseudo-first-order rate constant of 0.3×10^{-3} min^{-1}. In contrast, the addition of oxidants significantly increased both COD removal and apparent kinetics. The rate constant increased to 2.1×10^{-3} $\mathrm{min}^{-1}$for HC/H_2O_2, 3.2×10^{-3} $\mathrm{min}^{-1}$for HC/Fenton, 3.4×10^{-3} $\mathrm{min}^{-1}$for HC/O_2, and 5.8×10^{-3} $\mathrm{min}^{-1}$for HC/Fenton/O_2. The corresponding COD removal increased from 6.1% for HC alone to 63% for the combined HC/Fenton/O_2 process after 180 min, as shown in Figure 7.

The relative apparent-rate enhancement factor can be defined as:

$$I_k = \frac{k_{\mathrm{app,HC+AOP}}}{k_{\mathrm{app,HC}}}$$

where $k_{\mathrm{app,HC+AOP}}$ is the apparent pseudo-first-order rate constant for the combined cavitation–oxidation process and $k_{\mathrm{app,HC}}$ is the apparent rate constant for HC alone under comparable operating conditions. Based on the reported pilot-scale data, I_k increased from 1.0 for HC alone to approximately 19.3 for HC/Fenton/O_2 [30].

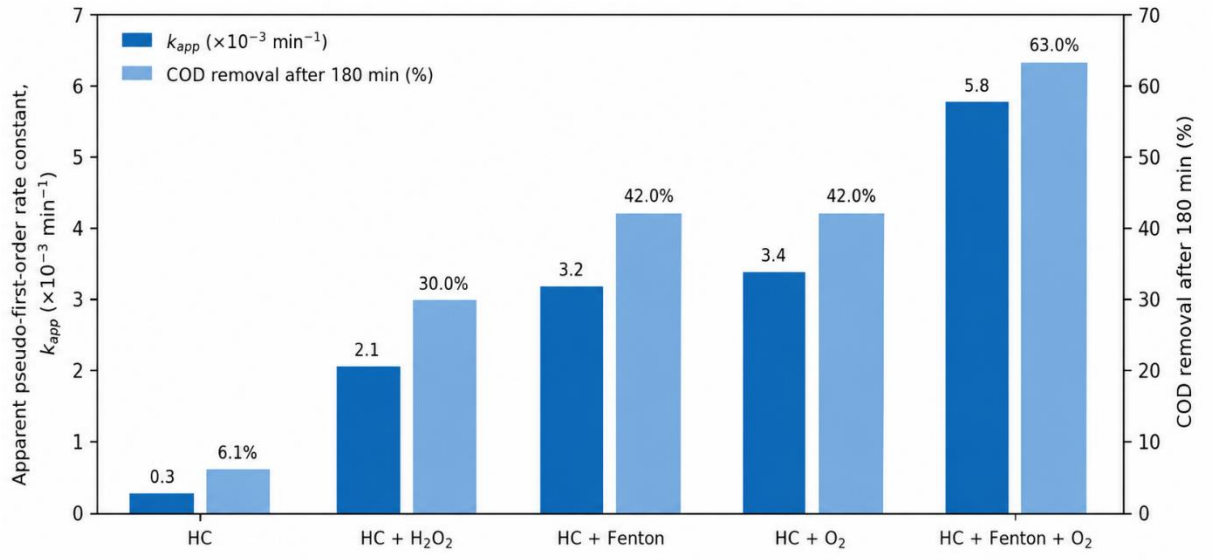

Figure 7. Apparent pseudo-first-order rate constants (k_{app}) and COD removal after 180 min for hydrodynamic cavitation (HC) alone and HC-assisted oxidation systems during pilot-scale treatment of high-COD industrial wastewater. Data adapted from Ref. [30].

These results support the central interpretation of this work: k_{app} is not an intrinsic pollutant property, but a process-level descriptor integrating radical generation, scavenging, oxidant utilization, and transport phenomena. The example also shows that HC is most effective when used as part of a coupled oxidation system rather than as a standalone treatment process. However, such kinetic intensification must be evaluated together with energy consumption, oxidant cost, wastewater composition, and treatment objectives.

4. Energy Efficiency and Process Economics

The practical implementation of advanced oxidation processes (AOPs) is fundamentally constrained by their energy demand and associated operational costs [12,13,28]. While laboratory-scale studies often report high removal efficiencies, these results rarely reflect the true energetic cost of pollutant degradation under realistic conditions.

In addition, AOPs may lead to the formation of transformation by-products, such as bromate during ozonation or partially oxidized intermediates, which can exhibit different toxicity and persistence characteristics. These effects must be considered alongside energy efficiency when evaluating overall process performance and suitability for full-scale application.

AOP performance must be evaluated using **process-relevant energy metrics**, rather than removal percentages alone.

4.1. Volumetric Energy Consumption

$$E_v = \frac{P \cdot t}{V} \left[\text{kWh/m}^3\right]$$

Where:

- P= power input (kW)
- t= treatment time (h)
- V= treated volume (m^3)

The treatment time required for pollutant j depends on the effective radical exposure and can be related to the apparent rate constant as follows:

$$t_j = \frac{1}{k_{\text{app}}} \ln\left(\frac{C_{o,j}}{C_j}\right)$$

$$k_{app,j} = k_{OH,j} \frac{R_{gen}}{k_{scav}}$$

Where:

- $k_{OH,j}$= intrinsic second-order rate constant ($L \cdot mol^{-1} \cdot s^{-1}$).
- $[\cdot OH]$ = effective/apparent hydroxyl radical concentration (mol/L).

Table 3 presents some typical values for effective (or apparent) first-order rate constant k_{app} (s^{-1}), showing the significant decrease in this constant from clean laboratory water to raw wastewater.

The apparent rate constant k_{app} integrates intrinsic reaction kinetics and matrix-dependent radical availability and therefore represents the true operational parameter governing pollutant degradation. Therefore, in advanced oxidation processes, k_{app} is not a property of the pollutant

alone, but an emergent system parameter resulting from the balance between radical generation and competitive scavenging within the water matrix.

Table 3: Typical Values of effective (or apparent) first-order rate constant k_{app}

System	$k_{app}(s^{-1})$
Clean lab water	**0.1 – 1**
Treated wastewater	**0.01 – 0.1**
Raw wastewater	**0.001 – 0.01**

4.2. Energy per Mass of Pollutant Removed (Critical Metric)

$$E_p = \frac{P \cdot t}{V \cdot (C_0 - C)}$$

where:
E_p= energy per mass removed (kWh/kg pollutant)
P= power input (kW)
V= treated volume (m^3)
C_0, C= initial and final pollutant concentration (kg/m^3)

Table 4 presents some typical energy demand ranges applying different AOPs of ozonation, UV/H_2O_2, and cavitation [13].

Table 4: Typical energy ranges are reported for ozonation, UV/H2O2, and cavitation systems [13–15].

Process	Typical Energy Demand	Conditions
Ozonation	10–20 kWh/kg O_3	Transfer efficiency: 60–90%
UV/H_2O_2	0.5–5 kWh/m^3	UV transmittance (500–1500 mJ/cm^2)
Cavitation	0.25–2 kWh/m^3	depending on pressure drop and system scale

Additionally, it is important to notice that the energy demand is proportional to the treatment time and therefore inversely proportional to the effective (or apparent) first-order rate constant k_{app}, as expressed in the following expressions:

$$t = \frac{1}{k_{\text{app}}} \ln\left(\frac{C_0}{C}\right) \Rightarrow E \propto t \propto \frac{1}{k_{\text{app}}}$$

The energetic performance of AOP systems is fundamentally governed by the effective rate constant k_{app}, which reflects the balance between radical generation and matrix scavenging, rather than by oxidant dosage alone. Therefore, a decrease in k_{app}, caused by increased radical scavenging or reduced radical generation, directly leads to longer treatment times and higher energy consumption [13,18]. Nevertheless, this relationship holds under constant operational efficiency assumptions.

5. Integration into Wastewater Treatment Trains

The effective implementation of advanced oxidation processes (AOPs) depends strongly on their placement within the overall treatment train. In practice, AOPs are most commonly applied as **tertiary or quaternary treatment steps**, following biological treatment and solid removal [28].

The primary rationale for this placement is the reduction of radical scavenging and process interference. After biological treatment and clarification, concentrations of suspended solids, dissolved organic carbon (DOC), and particulate matter are significantly reduced, which increases the effective radical availability:

$$\left[\cdot OH\right]_{app} = \frac{R_{gen}}{\sum k_i C_i}$$

Lower background concentrations ($\sum k_i C_i$) lead to higher oxidation efficiency and improved energy utilization.

Since the scavenging term $\sum k_i C_i$ varies significantly with dissolved organic carbon (DOC), alkalinity, nitrite, and other constituents, the required oxidant dose and operating conditions must be **adapted dynamically**.

This applies to:

- Oxidant dosing (O_3, H_2O_2)
- UV intensity and exposure time
- Cavitation intensity (pressure drop, flow regime)
- Combined hybrid systems

This highlights the need for sensor-based and digitally controlled AOP systems capable of adjusting process conditions in response to dynamic influent variability.

Optimal Placement Considerations

- **Post-biological treatment:** Biological processes remove bulk biodegradable organics and nutrients, allowing AOPs to target residual micropollutants more selectively.
- **After solids removal:** Suspended solids and turbidity reduce UV penetration and increase radical scavenging; therefore, filtration or clarification improves AOP performance.
- **Upstream of polishing steps:** AOPs are often placed before adsorption or membrane processes to transform micropollutants into more biodegradable or adsorbable

intermediates. However, oxidation may also generate transformation by-products, which require careful consideration in downstream treatment steps to ensure complete removal and avoid unintended environmental impacts.

Hybrid System Configurations

AOPs are most effective after biological treatment and solids removal, where scavenging is minimized. Hybrid systems combining oxidation, adsorption, and membrane separation improve overall efficiency [14,21,28]:

- **O_3 + activated carbon:** Ozonation partially oxidizes micropollutants and increases their adsorption affinity, while activated carbon removes residual organics and oxidation by-products.
- **UV/H_2O_2 + membranes:** UV-based AOPs degrade dissolved contaminants, while membrane systems (NF/RO) provide physical separation of residual micropollutants and transformation products.
- **Cavitation + oxidants (O_3, H_2O_2):** Cavitation enhances radical generation and mass transfer, improving oxidant utilization and degradation rates in hybrid oxidation systems.

The optimal integration of AOPs relies on positioning them after bulk pollutant removal, where matrix effects are minimized and radical utilization is maximized, rather than applying them as standalone treatment steps.

Adaptive control of oxidant dosing and operating conditions is required due to variability in wastewater composition [22].

6. Scale-Up Challenges

The transition from laboratory to full-scale implementation of advanced oxidation processes (AOPs) is associated with significant challenges, primarily due to the non-linear coupling between reaction kinetics, mass transfer, and hydrodynamics [13,18,29].

A key limitation arises from the **non-linear scaling of mass transfer**, particularly in ozonation systems, where the volumetric mass transfer coefficient ($k_L a$) does not scale proportionally with reactor size. As a result, the transfer of oxidants into the liquid phase becomes less efficient at larger scales, reducing the effective radical generation rate.

At the same time, **hydrodynamic complexity increases**, leading to non-uniform mixing, spatial gradients in oxidant concentration, and heterogeneous radical distribution. These effects directly impact the apparent rate constant k_{app}, which typically decreases under real-scale conditions unless compensated by optimized reactor design and transport enhancement due to increased scavenging and transport limitations [13,20]. The difficulty of scaling AOP systems arises from the inability to preserve key dimensionless parameters (e.g., Damköhler, Sherwood, Cavitation and Reynolds numbers [13,18,29]), leading to shifts in dominant rate-limiting mechanisms.

In addition, energy demand may increase disproportionately with scale if larger systems require higher power input to maintain mixing, pressure, or irradiation intensity [12,29]. Combined

with decreasing reaction efficiency at low pollutant concentrations, this leads to significant **cost escalation**, particularly for high removal targets.

Role of Pilot-Scale Validation

Given these constraints, pilot-scale studies are essential to bridge the gap between laboratory performance and full-scale operation. They allow [18,24,29]:

- **Kinetic verification:** Determination of realistic k_{app} values under actual wastewater conditions.
- **Energy optimization:** Evaluation of energy consumption (kWh/m³ and kWh/kg pollutant) under operational conditions.
- **Process stability assessment:** Analysis of system robustness under variable flow, composition, and loading.

The scale-up of AOP systems is fundamentally constrained by the non-linear interaction between reaction kinetics and transport phenomena, resulting in performance losses that cannot be predicted from laboratory-scale data alone.

These scale-dependent effects often lead to overestimation of process efficiency in laboratory studies and highlight the need for system-specific design and validation.

7. Conclusions

This work presents a unified kinetic–process framework for interpreting the performance of advanced oxidation processes (AOPs) in wastewater treatment by explicitly linking radical reaction kinetics, matrix composition, and reactor-scale transport phenomena [13,18].

The analysis demonstrates that AOP efficiency is governed primarily by matrix-controlled radical scavenging rather than by intrinsic oxidant reactivity alone [13,18,28]. Under realistic wastewater conditions, dissolved organic carbon and inorganic carbon species dominate hydroxyl-radical consumption, significantly reducing effective radical availability and apparent reaction rates compared to laboratory systems.

The apparent first-order rate constant (k_{app}) is identified as a practical system-level descriptor that integrates radical generation, scavenging, and transport limitations. This parameter provides a direct link between chemical kinetics and process performance and explains the discrepancy between laboratory-scale observations and full-scale operation.

The concept of radical utilization efficiency (η) provides a physically meaningful metric for evaluating and optimizing AOP performance under matrix-controlled conditions.

Furthermore, AOP performance is shown to depend on coupled kinetic–transport regimes, in which mass transfer, radiation attenuation, and hydrodynamics impose fundamental constraints. These interactions lead to non-linear behavior and limit the effectiveness of increasing oxidant dosage alone.

From an engineering perspective, treatment time and energy demand are inversely related to k_{app}, emphasizing the importance of reducing matrix scavenging through appropriate

pretreatment and process integration. Accordingly, AOPs are most effective when applied after bulk organic removal, where radical utilization is maximized.

The proposed framework is general in form and applicable to a wide range of AOP systems; however, its quantitative application depends on system-specific parameters, including water matrix composition, target contaminants, and reactor configuration. Nevertheless, it provides a consistent basis for interpreting AOP performance across scales and supports the development of matrix-aware design strategies [29]. Future work should focus on validation under pilot- and full-scale conditions and on extending the framework to dynamic systems with variable water quality.

References

1. Tchobanoglous G. et al. *Wastewater Engineering: Treatment and Resource Recovery*. McGraw-Hill, 2014.
2. Luo Y. et al. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci Total Environ*, 2014. https://doi.org/10.1016/j.scitotenv.2013.12.065
3. Bolong N. et al. A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination*, 2009. https://doi.org/10.1016/j.desal.2008.03.020
4. Deblonde T. et al. Emerging pollutants in wastewater: A review of the literature. *Int J Hyg Environ Health*, 2011. https://doi.org/10.1016/j.ijheh.2011.08.002
5. Nishmitha PS et al. Understanding emerging contaminants in water and wastewater: A comprehensive review on detection, impacts, and solutions. *J Hazard Mater Adv*, 2025. https://doi.org/10.1016/j.hazadv.2025.100755
6. Glaze WH et al. The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. *Ozone Sci Eng*, 1987. https://doi.org/10.1080/01919518708552148
7. von Gunten U. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res*, 2003. https://doi.org/10.1016/S0043-1354(02)00457-8
8. Huber MM et al. Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. *Environ Sci Technol*, 2003. https://doi.org/10.1021/es025896h
9. Sirés I. et al. Electrochemical advanced oxidation processes: today and tomorrow. A review. *Environ Sci Pollut Res*, 2014. https://doi.org/10.1007/s11356-014-2783-1
10. Dular M. et al. Use of hydrodynamic cavitation in (waste)water treatment. *Ultrason Sonochem*, 2016. https://doi.org/10.1016/j.ultsonch.2015.10.010
11. Eggen T. et al. Micropollutant Removal from Wastewater: Facts and Decision-Making Despite Uncertainty. *Environ Sci Technol*, 2015. https://doi.org/10.1021/acs.est.5b02242
12. Gu Y. et al. The feasibility and challenges of energy self-sufficient wastewater treatment plants. *Applied Energy*, 2017. https://doi.org/10.1016/j.apenergy.2017.02.069

13. Miklos DB, Remy C, Jekel M, Linden KG, Drewes JE, Hübner U. Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review. Water Res. 2018; 139:118–131. https://doi.org/10.1016/j.watres.2018.03.042

14. Wang J, Wang S. Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: A review. J Environ Manage. 2016; 182:620–640. https://doi.org/10.1016/j.jenvman.2016.07.049

15. Ikehata K, El-Din MG. Aqueous pesticide degradation by ozonation and ozone-based advanced oxidation processes: A review (Part I). Ozone Sci Eng. 2007; 27:83–114. https://doi.org/10.1080/01919510590925220

16. Lee Y, von Gunten U. Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical). Water Res. 2010; 44:555–566. https://doi.org/10.1016/j.watres.2009.11.045

17. Rosario-Ortiz FL, Wert EC, Snyder SA. Evaluation of UV/H_2O_2 treatment for the oxidation of pharmaceuticals in wastewater. Water Res. 2010; 44:1440–1448. https://doi.org/10.1016/j.watres.2009.10.031

18. Oturan MA, Aaron JJ. Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review. Crit Rev Environ Sci Technol. 2014; 44:2577–2641. https://doi.org/10.1080/10643389.2013.829765

19. Gogate PR, Pandit AB. A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions. Adv Environ Res. 2004; 8:501–551. https://doi.org/10.1016/S1093-0191(03)00032-7

20. Carpenter J, et al., Hydrodynamic cavitation: An emerging technology for the intensification of various chemical and physical processes in a chemical process industry. *eviews in Chemical Engineering*, vol. 33, no. 5, 2017, pp. 433-468. https://doi.org/10.1515/revce-2016-0032

21. Babuponnusami A, Muthukumar K. A review on Fenton and improvements to the Fenton process for wastewater treatment. J Environ Chem Eng. 2014; 2:557–572. https://doi.org/10.1016/j.jece.2013.10.011

22. Parsons S, Jefferson B. Introduction to Potable Water Treatment Processes. Blackwell Publishing; 2006. ISBN:9781405127967 |Online ISBN:9781444305470

23. Lee Y et al, Prediction of Micropollutant Elimination during Ozonation of Municipal Wastewater Effluents: Use of Kinetic and Water Specific Information. Environ. Sci. Technol. 2013; 14: 5872-5881. https://doi.org/10.1021/es400781r

24. Hübner U, et al., Advanced oxidation processes for water and wastewater treatment – Guidance for systematic future research. Heliyon, 2024; 10. https://doi.org/10.1016/j.heliyon.2024.e30402

25. Meyer C, et al., Ozonation of pharmaceuticals and their human metabolites in wastewater—Insights from laboratory experiments and field data. *Environ Sci Technol.* 2025; 59(38):20842–20859. https://doi.org/10.1021/acs.est.5c08128.

26. Tixier C, et al.. Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters. *Environ Sci Technol.* 2003;37(6):1061–1068. https://doi.org/10.1021/es025834r.
27. Buxton GV et al.. Rate constant for reaction of hydroxyl radicals with bicarbonate ions. *Radiat* Phys Chem. 1986;27(3):241–243. https://doi.org/10.1016/1359-0197(86)90059-7.
28. Saylam A. Advances in wastewater treatment: Energy efficiency, micropollutants, and circular resource recovery. Zenodo, 2026. https://zenodo.org/records/19438614
29. Saylam A. Engineering scale-up: Overcoming challenges from lab to industry. ResearchGate, 2025. https://doi.org/10.13140/RG.2.2.24337.49761
30. Joshi, S. M., et al. Intensification of industrial wastewater treatment using hydrodynamic cavitation combined with advanced oxidation at operating capacity of 70 L, Ultrasonics Sonochemistry (2019), 1350-4177. https://doi.org/10.1016/j.ultsonch.2018.12.016