

Advanced Oxidation Processes Integrated with Hydrodynamic Cavitation and Nanomaterials for Wastewater Treatment: Mechanisms, Applications, and Future Perspectives — A Comprehensive Review

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Abstract- The rapid industrialization and urbanization worldwide have led to the discharge of complex, bio-refractory organic pollutants into water bodies, posing severe threats to ecosystems and human health. Conventional wastewater treatment methods often fail to achieve complete mineralization of these recalcitrant compounds. Advanced oxidation processes (AOPs) have emerged as powerful technologies capable of generating highly reactive hydroxyl radicals ($\cdot\text{OH}$) for non-selective oxidation of organic pollutants. However, standalone AOPs face challenges including high energy consumption, mass transfer limitations, and incomplete mineralization. This comprehensive review examines the synergistic integration of hydrodynamic cavitation (HC) with AOPs and nanomaterials as a transformative approach for wastewater treatment. The fundamental mechanisms of hydrodynamic cavitation—including the formation, growth, and implosive collapse of cavities generating localized extreme conditions—are systematically analyzed. The review explores HC integration with various AOPs including Fenton, photocatalysis, ozonation, and persulfate activation, highlighting the synergistic effects that enhance $\cdot\text{OH}$ production and pollutant degradation kinetics. The role of nanomaterials as catalysts in HC-based hybrid systems is critically evaluated, with emphasis on TiO_2 , ZnO , zero-valent iron, carbon-based nanomaterials, and composite catalysts. Key operating parameters including inlet pressure, cavitation number, solution pH, catalyst loading, and reactor geometry are examined for their influence on degradation efficiency. Applications for diverse pollutant classes—dyes, pharmaceuticals, phenolics, pesticides, and emerging contaminants—are comprehensively reviewed. Energy efficiency and cavitation yield analyses provide quantitative comparisons between hybrid and standalone processes. Finally, current challenges, scale-up considerations, and future research directions are discussed, emphasizing the potential of HC-AOP-nanomaterial hybrid systems as sustainable, cost-effective solutions for industrial wastewater treatment.

Keywords: Hydrodynamic cavitation; advanced oxidation processes; nanomaterials; wastewater treatment; heterogeneous catalysis; Fenton; photocatalysis; ozonation; persulfate activation; emerging contaminants

I. INTRODUCTION

The Global Water Pollution Challenge

Water pollution has become one of the most pressing environmental challenges of the twenty-first century. Rapid industrialization, agricultural intensification, and urbanization have resulted in the discharge of complex chemical mixtures into water bodies worldwide [1]. Industrial effluents from textile, pharmaceutical, petrochemical, and

manufacturing sectors contain a wide array of organic pollutants including synthetic dyes, active pharmaceutical ingredients, pesticides, phenolics, and endocrine-disrupting compounds [2]. Many of these pollutants are bio-refractory, meaning they resist conventional biological treatment processes and persist in the environment [3].

The presence of these contaminants in aquatic ecosystems poses significant risks. Synthetic dyes, even at low concentrations, reduce light penetration

and photosynthetic activity in water bodies [4]. Pharmaceuticals and personal care products can induce chronic toxicity in aquatic organisms and contribute to antimicrobial resistance [5]. Phenolic compounds are toxic to aquatic life even at parts-per-billion levels [6]. The detection of these "emerging contaminants" in drinking water sources has raised serious concerns about potential human health effects [7].

Limitations of Conventional Treatment Technologies

Conventional wastewater treatment typically involves primary (physical sedimentation), secondary (biological oxidation), and sometimes tertiary (advanced) treatment stages [8]. While effective for removing suspended solids, biodegradable organics, and nutrients, these conventional processes have significant limitations:

Biological treatment: Activated sludge processes and other biological methods are effective for readily biodegradable compounds but fail to mineralize recalcitrant organic pollutants [9]. Many industrial chemicals are designed to be stable and resist biodegradation. Furthermore, high pollutant concentrations can be toxic to microorganisms, inhibiting treatment performance [10].

Physical separation: Coagulation-flocculation, adsorption onto activated carbon, and membrane filtration transfer pollutants from one phase to another rather than destroying them [11]. This creates secondary waste streams requiring further treatment or disposal.

Conventional chemical oxidation: Chlorination and other traditional chemical oxidants may form toxic disinfection by-products and often achieve only partial oxidation of complex organic molecules [12]. These limitations have driven intensive research into advanced oxidation processes capable of achieving complete mineralization of organic pollutants to CO_2 , H_2O , and inorganic ions [13].

Advanced Oxidation Processes: Principles and Challenges

Advanced oxidation processes (AOPs) are characterized by the generation of highly reactive hydroxyl radicals ($\bullet\text{OH}$), which possess an oxidation potential ($E^0 = 2.80 \text{ V}$) second only to fluorine among common oxidants [14]. Hydroxyl radicals react non-selectively with most organic compounds at near-diffusion-limited rates ($10^8\text{-}10^{10} \text{ M}^{-1} \text{ s}^{-1}$), attacking pollutant molecules through hydrogen abstraction, electrophilic addition, and electron transfer mechanisms [15].

Common AOPs include:

- Fenton processes: Fe^{2+} catalyzes H_2O_2 decomposition to generate $\bullet\text{OH}$ [16]
- Photocatalysis: Semiconductor catalysts (TiO_2 , ZnO) irradiated with UV light generate electron-hole pairs that produce reactive oxygen species [17]
- Ozonation: O_3 reacts directly with pollutants or decomposes to form $\bullet\text{OH}$ [18]
- Persulfate activation: $\text{SO}_4^{\bullet-}$ radicals with high oxidation potential (2.5-3.1 V) [19]
- Electrochemical oxidation: Direct or indirect oxidation at electrode surfaces [20]

Despite their potential, standalone AOPs face several challenges:

Mass transfer limitations: The reaction between short-lived $\bullet\text{OH}$ and pollutants is limited by the rate at which pollutants contact reactive sites [21].

High chemical consumption: Fenton and related processes require continuous addition of H_2O_2 and catalysts [22].

Energy intensity: UV lamps for photocatalysis and ozone generators consume substantial electrical energy [23].

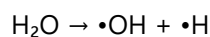
Incomplete mineralization: Some AOPs achieve only partial oxidation, potentially forming transformation products more toxic than parent compounds [24].

Catalyst recovery: Suspended nanoparticle catalysts require separation steps, adding process complexity [25].

Hydrodynamic Cavitation: A Platform for Process Intensification

Hydrodynamic cavitation (HC) has emerged as a promising platform technology for intensifying AOP performance [26]. Cavitation refers to the formation, growth, and implosive collapse of vapor-filled cavities in a liquid medium subjected to rapid pressure changes [27]. In hydrodynamic cavitation, this is achieved by passing liquid through constrictions such as orifice plates, venturi tubes, or rotor-stator assemblies, where the local velocity increases and pressure drops below the vapor pressure of the liquid [28].

The implosive collapse of cavitation bubbles generates localized "hotspots" with extraordinary conditions: temperatures reaching 5000-10,000 K, pressures up to 1000 atm, and heating/cooling rates exceeding 10^{10} K/s [29]. Under these extreme conditions, water molecules undergo thermal dissociation to generate $\bullet\text{OH}$ radicals [30]:



Furthermore, cavitation enhances mass transfer through microturbulence, shock waves, and liquid micro-jets [31]. These effects can:

- Increase contact between pollutants and reactive species
- Disrupt pollutant aggregates and enhance accessibility
- Activate catalysts through surface cleaning and defect generation
- Promote decomposition of oxidants (H_2O_2 , O_3) to generate additional radicals [32]

Nanomaterials as Catalysts in AOPs

Nanomaterials offer unique advantages as catalysts for AOPs due to their high specific surface area, abundant active sites, tunable surface chemistry, and size-dependent optical and electronic properties [33]. Common nanomaterials investigated for AOP applications include:

Metal oxide nanoparticles: TiO_2 , ZnO , Fe_2O_3 , CuO , and mixed oxides [34]

Zero-valent metals: nZVI (nanoscale zero-valent iron), nano-Cu, nano-Ag [35]

Carbon-based nanomaterials: Carbon nanotubes, graphene oxide, graphitic carbon nitride [36]

Nanocomposites: Bimetallic nanoparticles, supported catalysts, magnetic nanocomposites for easy recovery [37]

When integrated with hydrodynamic cavitation, nanomaterials can serve as:

- Heterogeneous catalysts enhancing radical generation
- Adsorbents concentrating pollutants near reactive sites
- Nucleation sites for cavity formation
- Photocatalysts activated by cavitation-induced sonoluminescence [38]

Scope and Organization of This Review

This comprehensive review examines the state-of-the-art in hybrid wastewater treatment systems integrating advanced oxidation processes, hydrodynamic cavitation, and nanomaterials. The specific objectives are:

- To elucidate fundamental mechanisms of hydrodynamic cavitation and its role in intensifying AOPs
- To systematically review HC-AOP-nanomaterial hybrid systems for various pollutant classes
- To analyze key operating parameters and their influence on degradation efficiency
- To evaluate energy efficiency and economic considerations
- To identify current challenges and future research directions

The review is organized as follows: Section 2 presents the fundamental principles of hydrodynamic cavitation. Section 3 examines mechanisms of cavitation-AOP synergy. Section 4 reviews nanomaterial catalysts for HC-based

systems. Section 5 provides comprehensive coverage of applications for different pollutant classes. Section 6 analyzes operating parameters and optimization strategies. Section 7 addresses energy efficiency and scale-up considerations. Section 8 discusses current challenges and future perspectives.

II. FUNDAMENTALS OF HYDRODYNAMIC CAVITATION

Principles of Cavitation

Cavitation occurs when the local pressure in a liquid falls below its vapor pressure, causing vaporization and formation of vapor-filled cavities (bubbles or cavities) [39]. These cavities subsequently collapse when they encounter regions of higher pressure, releasing concentrated energy.

The cavitation phenomenon is characterized by the cavitation number (C_v), a dimensionless parameter defined as [40]:

$$C_v = (P_2 - P_v) / (\frac{1}{2}\rho v_0^2)$$

where:

- P_2 = recovered pressure downstream of the constriction (Pa)
- P_v = vapor pressure of the liquid (Pa)
- ρ = liquid density (kg/m^3)
- v_0 = velocity at the constriction (m/s)

Cavitation inception typically occurs at $C_v \leq 1$, with lower values indicating more intense cavitation [41]. However, optimal cavitation for wastewater treatment requires balancing cavity formation with effective collapse.

Hydrodynamic Cavitation Reactor Configurations

Several reactor geometries have been developed for hydrodynamic cavitation:

Orifice plates: Circular plates with one or multiple holes through which liquid passes [42]. Multi-hole orifices provide higher cavitation yield by generating multiple cavitation events simultaneously. Key design parameters include hole diameter, hole number, plate thickness, and hole arrangement.

Venturi tubes: Convergent-divergent nozzles that accelerate flow through a throat section [43]. Venturi geometries offer advantages including reduced clogging, more uniform cavitation, and easier scalability compared to orifice plates.

Rotor-stator assemblies: High-shear devices where cavitation is generated by rapid rotation of a rotor within a stator [44]. These devices can achieve intense cavitation but have higher energy consumption.

Swirl-type reactors: Generate cavitation through vortex formation, creating cavitation clouds with unique flow patterns [45].

Cavitation Bubble Dynamics

The life cycle of a cavitation bubble involves three stages [46]:

Formation (nucleation): Cavities originate from pre-existing gas nuclei in the liquid, often stabilized in crevices of suspended particles or reactor walls. Nanoparticles can serve as nucleation sites, potentially lowering the energy required for cavitation inception [47].

Growth: Bubbles grow through vaporization of liquid into the cavity and diffusion of dissolved gases. Growth continues while the bubble remains in the low-pressure region.

Collapse: Upon entering a high-pressure region, bubbles implode violently. For symmetric collapse near a rigid boundary, spherical convergence produces a liquid jet directed toward the boundary, along with shock wave emission [48]. Asymmetric collapse generates microturbulence and shear forces.

The collapse temperature (T_{max}) can be estimated from the adiabatic compression equation [49]:

$$T_{\text{max}} = T_0 [P_m(\gamma-1)/P_v]$$

where T_0 is bulk liquid temperature, P_m is pressure at collapse, P_v is vapor pressure, and γ is the specific heat ratio.

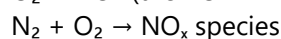
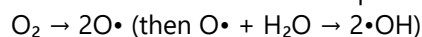
Physical and Chemical Effects of Cavitation

Cavitation produces multiple effects relevant to wastewater treatment:

Mechanical effects:

- Shock waves (pressure pulses up to 1000 bar) disrupt pollutant aggregates and microbial cells [50]
- Micro-jets (velocities up to 100 m/s) erode surfaces and enhance mass transfer [51]
- Turbulence and acoustic streaming improve mixing and contact [52]
- Thermal effects: Localized high temperatures promote thermolytic reactions and activate catalysts [53].

Chemical effects: Water dissociation generates $\bullet\text{OH}$, $\bullet\text{H}$, and other radicals. Dissolved gases (O_2 , N_2) can form additional reactive species [54]:



Factors Affecting Cavitation Intensity

Inlet pressure: Increasing inlet pressure raises velocity through the constriction, reducing cavitation number and increasing cavity formation. However, beyond an optimal pressure, cavities may not collapse effectively or may coalesce into vapor clouds that dampen collapse intensity [55].

Geometric parameters: Hole diameter, throat dimensions, and constriction geometry determine velocity profiles and pressure recovery. Smaller orifices generate more intense cavitation but increase energy consumption [56].

Liquid properties: Viscosity, surface tension, and vapor pressure influence cavitation inception and intensity. Higher vapor pressure facilitates cavitation but may reduce collapse temperature [57].

Dissolved gases: The type and concentration of dissolved gases affect radical formation. Monoatomic gases (Ar , He) yield higher collapse temperatures than diatomic gases (N_2 , O_2) [58].

Temperature: Higher temperatures increase vapor pressure, promoting cavitation but potentially reducing collapse intensity [59].

III. MECHANISMS OF SYNERGY: HYDRODYNAMIC CAVITATION WITH AOPS

HC/H₂O₂ Systems

Hydrogen peroxide alone is a relatively weak oxidant for many recalcitrant pollutants. However, HC enhances H_2O_2 oxidation through multiple mechanisms [60]:

- Thermal dissociation of H_2O_2 in collapsing cavities: $\text{H}_2\text{O}_2 \rightarrow 2\bullet\text{OH}$
- Enhanced mass transfer of H_2O_2 to pollutant molecules
- Cavitation-induced activation of H_2O_2 at catalyst surfaces

The optimal H_2O_2 concentration must balance enhanced radical production against scavenging effects at high concentrations ($\text{H}_2\text{O}_2 + \bullet\text{OH} \rightarrow \text{HO}_2\bullet + \text{H}_2\text{O}$) [61].

HC/Fenton and HC/Fenton-like Systems

The Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \bullet\text{OH} + \text{OH}^-$) is one of the most effective AOPs, but faces limitations including narrow optimal pH range (2.8-3.5), iron sludge production, and slow $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycling [62].

HC integration addresses these limitations [63]:

- Cavitation accelerates Fe^{3+} reduction back to Fe^{2+} through radical reactions and thermal effects
- Enhanced mass transfer increases contact between Fe^{2+} and H_2O_2
- Cavitation can activate heterogeneous iron catalysts (iron oxides, zero-valent iron)
- Mechanical disruption prevents catalyst agglomeration

The "pseudo staggered effect" observed in HC-photocatalysis-peroxide systems demonstrates that

cavitation can dramatically enhance Fenton-like processes [64].

HC/Photocatalysis

Photocatalysis relies on semiconductor irradiation to generate electron-hole pairs that produce reactive oxygen species. HC integration enhances photocatalysis through [65]:

Catalyst activation: Cavitation cleans catalyst surfaces, removing adsorbed intermediates and exposing fresh active sites. Shock waves can also create surface defects that enhance photocatalytic activity.

Enhanced mass transfer: Microturbulence brings pollutants to catalyst surfaces more effectively.

Sonoluminescence: Cavitation collapse emits light across a broad spectrum (including UV) that can activate photocatalysts even without external illumination [66].

De-agglomeration: Cavitation breaks up nanoparticle aggregates, increasing effective surface area.

HC/Ozonation

Ozonation is widely used for disinfection and micropollutant oxidation. HC intensifies ozonation through [67]:

- Enhanced ozone mass transfer due to microturbulence
- Thermal decomposition of ozone to generate $\bullet\text{OH}$
- Formation of additional radicals from ozone reactions with cavitation-generated $\bullet\text{H}$ and $\bullet\text{OH}$
- Improved ozone utilization efficiency
- HC/O₃ systems achieve higher pollutant degradation with lower ozone doses compared to conventional ozonation [68].

HC/Persulfate Activation

Sulfate radical-based AOPs have gained attention due to $\text{SO}_4\bullet^-$ high oxidation potential (2.5-3.1 V) and longer half-life compared to $\bullet\text{OH}$ [69]. Persulfate

($\text{S}_2\text{O}_8^{2-}$) can be activated by heat, UV, transition metals, or cavitation.

HC activates persulfate through [70]:

- Thermal activation in collapsing cavities ($T > 50^\circ\text{C}$ sufficient for activation)
- Radical-mediated activation ($\bullet\text{H} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4\bullet^- + \text{SO}_4^{2-} + \text{H}^+$)
- Enhanced contact with heterogeneous activators (metal oxides, zero-valent metals)

Multiple Oxidation Mechanisms in HC-AOP Systems

Hybrid HC-AOP systems benefit from multiple simultaneous oxidation pathways [71]:

Direct cavitation oxidation: $\bullet\text{OH}$ from water dissociation

Enhanced chemical oxidation: Activated oxidants (H_2O_2 , O_3 , persulfate) generate additional radicals

Thermal degradation: High localized temperatures directly pyrolyze pollutants near collapsing cavities

Shear degradation: Mechanical forces break down high molecular weight pollutants

Catalytic oxidation: Enhanced activity of suspended or immobilized catalysts

The synergy factor (f) can be quantified as [72]:

$$f = \frac{k(\text{HC+AOP})}{[k(\text{HC}) + k(\text{AOP})]}$$

where k represents pseudo-first-order rate constants. Synergy factors >1 indicate positive synergy, with values of 2-5 commonly reported for HC-AOP combinations [73].

IV. NANOMATERIALS FOR HC-INTEGRATED AOP SYSTEMS

Design Criteria for Nanocatalysts in HC Environments

Nanomaterials intended for HC-AOP applications must satisfy specific requirements [74]:

Cavitation stability: Resistance to mechanical degradation from shock waves and micro-jets

Dispersion stability: Resistance to agglomeration under cavitation-induced turbulence

Surface activity: Abundant active sites for radical generation

Recyclability: Easy separation and reuse (magnetic properties advantageous)

Chemical stability: Resistance to leaching and deactivation in aggressive oxidative environments

Metal Oxide Nanoparticles

Titanium dioxide (TiO₂): The most widely studied photocatalyst for wastewater treatment. In HC-photocatalysis systems, TiO₂ benefits from cavitation-induced de-agglomeration, surface cleaning, and sonoluminescence activation [75]. Anatase TiO₂ shows higher activity than rutile due to greater surface area and more favorable band structure [76].

Zinc oxide (ZnO): ZnO offers similar bandgap to TiO₂ (3.2-3.3 eV) but higher electron mobility and quantum efficiency [77]. Sarvothaman and colleagues demonstrated that HC-photocatalysis-peroxide systems with ZnO achieved cavitation yields 5 times higher than acoustic cavitation counterparts [64]. However, ZnO suffers from photocorrosion in aqueous environments, which cavitation may exacerbate.

Iron oxides (Fe₂O₃, Fe₃O₄): Magnetic iron oxide nanoparticles serve as recoverable Fenton-like catalysts [78]. Magnetite (Fe₃O₄) contains both Fe²⁺ and Fe³⁺, facilitating electron transfer and radical generation. HC enhances iron oxide catalytic activity through surface activation and improved mass transfer [79].

Mixed metal oxides: Spinel (CoFe₂O₄, ZnFe₂O₄, CuFe₂O₄) and perovskites offer tunable catalytic properties [80]. These materials can simultaneously catalyze multiple AOPs (Fenton, persulfate activation, photocatalysis) in HC systems.

Zero-Valent Metal Nanoparticles

Nanoscale zero-valent iron (nZVI): nZVI is a powerful reducing agent and Fenton catalyst [81]. In HC systems, nZVI benefits from [82]:

- Surface activation by cavitation-induced oxide layer removal
- Enhanced corrosion rates generating Fe²⁺ for Fenton reactions
- Improved dispersion preventing agglomeration
- Synergistic effects with H₂O₂ and persulfate
- Bimetallic nanoparticles: Fe/Cu, Fe/Pd, and Fe/Ni nanoparticles combine the reducing power of nZVI with catalytic hydrodechlorination activity of noble metals [83]. These materials are particularly effective for chlorinated pollutant degradation.

Carbon-Based Nanomaterials

Carbon nanotubes (CNTs): CNTs adsorb pollutants while catalyzing radical generation from peroxides and persulfate [84]. Their high aspect ratio and mechanical strength resist cavitation damage.

Graphene and graphene oxide: Graphene-based materials offer exceptional surface area, electron mobility, and functionalizable surface chemistry [85]. Graphene oxide (GO) contains oxygen functional groups that can participate in radical generation.

Graphitic carbon nitride (g-C₃N₄): This metal-free photocatalyst has gained attention for visible-light activity and stability [86]. HC enhances g-C₃N₄ dispersion and can provide mechanical exfoliation to increase surface area.

Carbon black and activated carbon: Low-cost carbon materials can serve as catalyst supports or direct catalysts for persulfate activation [87].

Nanocomposites and Supported Catalysts

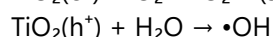
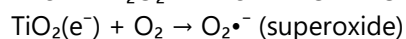
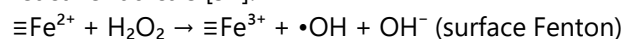
Magnetic nanocomposites: Core-shell structures (Fe₃O₄@SiO₂, Fe₃O₄@TiO₂) combine magnetic recoverability with catalytic functionality [88]. The magnetic core enables easy separation using external magnets, while the shell provides catalytic activity and protects the core from oxidation.

Supported catalysts: Immobilizing nanoparticles on larger supports (zeolites, silica, alumina) facilitates recovery while maintaining high catalytic activity [89]. HC can enhance mass transfer to supported catalysts without dislodging nanoparticles.

Metal-organic frameworks (MOFs): MOFs offer ultra-high surface area and tunable porosity [90]. Some MOFs (MIL-88, ZIF-8) show Fenton-like or photocatalytic activity. However, MOF stability under cavitation requires careful evaluation.

Mechanisms of Nanocatalyst Action in HC Systems

Radical generation: Nanocatalysts accelerate decomposition of H_2O_2 , O_3 , and persulfate to reactive radicals [91]:



Pollutant adsorption: High surface area nanomaterials concentrate pollutants near radical generation sites, enhancing degradation kinetics [92].

Cavitation nucleation: Nanoparticles can serve as nucleation sites for cavitation bubbles, potentially lowering the energy threshold for cavitation inception [93].

Surface activation: Cavitation mechanically activates catalyst surfaces through cleaning, defect creation, and particle size reduction [94].

V. APPLICATIONS FOR POLLUTANT CLASSES

Dyes and Textile Wastewater

Synthetic dyes represent a major class of industrial pollutants, with over 100,000 commercially available dyes and 700,000 tons annually produced worldwide [95]. Dyes are designed to resist degradation, making them challenging targets for conventional treatment.

Azo dyes: The most common dye class, characterized by -N=N- bonds. Methyl orange, Congo red, Reactive Black 5, and Acid Orange 7 have been extensively studied in HC-AOP systems [96]. Azo bond cleavage is the initial degradation step, followed by aromatic ring opening.

A comprehensive review by Egyptian researchers examined HC-based dye degradation, concluding that HC combined with AOPs achieved significantly higher removal than standalone processes [97]. Optimal conditions typically include:

- Inlet pressure: 3-8 bar depending on reactor geometry
- pH: Acidic conditions (pH 3-4) favor Fenton-based systems; near-neutral pH for photocatalysis
- Catalyst loading: 0.1-1.0 g/L for nanoparticle catalysts
- Oxidant concentration: 100-1000 mg/L H_2O_2
- HC/Fenton for dye removal: HC combined with Fenton achieved 95-99% decolorization of various azo dyes within 30-60 minutes, compared to 60-70% for Fenton alone [98]. The synergy arises from enhanced Fe^{3+} reduction and improved mass transfer.

HC/Photocatalysis for dyes: TiO_2 and ZnO nanoparticles under UV or solar irradiation combined with HC showed 2-5 fold enhancement in degradation rates [99]. The pseudo staggered effect observed in HC-photocatalysis-peroxide systems proved particularly effective [64].

HC/Persulfate for dyes: Persulfate activated by HC achieved 90% degradation of Acid Orange 7 within 45 minutes, with sulfate radicals as the primary oxidizing species [100].

Pharmaceutical and Personal Care Products

Pharmaceuticals and personal care products (PPCPs) are emerging contaminants of concern detected worldwide in wastewater, surface water, and even drinking water [101]. These compounds are designed for biological activity and often resist biodegradation.

Antibiotics: Amoxicillin, ciprofloxacin, sulfamethoxazole, and tetracycline have been targeted in HC-AOP studies [102]. Antibiotic degradation is particularly important to prevent development of antimicrobial resistance in environmental bacteria.

Non-steroidal anti-inflammatory drugs (NSAIDs): Diclofenac, ibuprofen, and naproxen are frequently detected in wastewater [103]. Diclofenac is notably susceptible to photodegradation, making HC-photocatalysis combinations effective.

Hormones: 17β -estradiol and 17α -ethinylestradiol (synthetic estrogen) are endocrine disruptors active at parts-per-trillion levels [104]. HC-based systems achieve rapid hormone degradation.

X-ray contrast media: Iodinated contrast agents like iohexol and iopromide are highly recalcitrant [105]. HC/ozonation and HC/persulfate show promise for these compounds.

Research at Tel Aviv University has focused on catalytic ozonation and peroxonation for pharmaceutical degradation, emphasizing the importance of understanding transformation product toxicity [106]. Even when parent compounds are removed, transformation products may retain biological activity or exhibit enhanced toxicity.

Phenolic Compounds

Phenols and substituted phenols are common industrial pollutants from petrochemical, pesticide, and pharmaceutical manufacturing [107]. Phenol itself is a model compound for AOP studies due to its well-characterized degradation pathway.

Phenol: HC alone achieves partial phenol degradation (20-40%) through $\bullet\text{OH}$ attack [108]. HC/Fenton achieves 80-95% phenol removal within 60 minutes, with catechol and hydroquinone as primary intermediates before ring opening to carboxylic acids and finally CO_2 [109].

Chlorophenols: 2-chlorophenol, 4-chlorophenol, and pentachlorophenol are priority pollutants due to toxicity and persistence [110]. HC combined with nZVI or Fenton achieves rapid dechlorination followed by ring cleavage.

Nitrophenols: p-nitrophenol and 2,4-dinitrophenol are explosive manufacturing intermediates and toxic pollutants [111]. The electron-withdrawing nitro groups make these compounds resistant to

electrophilic attack, requiring high $\bullet\text{OH}$ fluxes achievable in HC-AOP systems.

Sarvothaman and colleagues emphasized that the most influential AOP should form the basis for hybrid process design, with complementary AOPs selected based on pollutant characteristics [64]. For phenol, photocatalysis as the primary process combined with cavitation and peroxide proved optimal.

Pesticides and Herbicides

Agricultural runoff containing pesticides and herbicides contaminates surface and groundwater worldwide [112]. Many pesticides are designed for environmental stability and biological activity.

Organophosphorus pesticides: Malathion, parathion, and chlorpyrifos are acetylcholinesterase inhibitors [113]. HC/Fenton achieves rapid degradation through oxidative cleavage of P=S and P-O bonds.

Carbamates: Carbaryl and aldicarb are susceptible to $\bullet\text{OH}$ attack at the carbamate linkage [114].

Chlorinated pesticides: Endosulfan, lindane, and DDT (though banned in many countries) persist in the environment [115]. HC combined with nZVI achieves reductive dechlorination followed by oxidative mineralization.

Herbicides: Atrazine, diuron, and glyphosate have been studied in HC-AOP systems [116]. Atrazine degradation proceeds through dealkylation and dechlorination pathways.

Industrial Chemicals and Emerging Contaminants

Per- and polyfluoroalkyl substances (PFAS): PFAS are "forever chemicals" resistant to all but the most aggressive treatment methods [117]. HC alone shows promise for PFAS degradation through pyrolytic mechanisms in collapsing cavities [118]. Combining HC with persulfate or electrochemical oxidation may enhance PFAS destruction.

Microplastics: Plastic particles accumulate in aquatic environments and adsorb other pollutants [119]. HC can fragment microplastics while potentially degrading polymer chains through $\bullet\text{OH}$ attack,

though complete mineralization remains challenging.

Endocrine-disrupting chemicals (EDCs): Beyond pharmaceuticals, industrial chemicals like bisphenol A (BPA) and nonylphenol exhibit estrogenic activity [120]. HC-AOP systems achieve rapid EDC degradation, with toxicity assays confirming detoxification.

VI. OPERATING PARAMETERS AND OPTIMIZATION

Inlet Pressure and Cavitation Number

Inlet pressure is the most critical operating parameter for HC systems, determining velocity through constrictions and thus cavitation intensity [121]. For each reactor-pollutant system, an optimal pressure exists:

Below optimum: Insufficient cavitation intensity, limited $\bullet\text{OH}$ generation

Above optimum: Cavitation clouds form, dampening collapse intensity; increased energy consumption without proportional benefit

For orifice plates, optimal pressures typically range from 3-8 bar, while venturi systems may operate optimally at lower pressures (2-5 bar) [122]. The cavitation number should be maintained below 1 for effective cavitation, with values of 0.1-0.5 typically optimal.

Solution pH

pH influences multiple aspects of HC-AOP performance [123]:

$\bullet\text{OH}$ oxidation: $\bullet\text{OH}$ oxidation potential decreases slightly at high pH ($E^0 = 2.7$ V at pH 0, 2.3 V at pH 14), but the effect is modest.

Fenton chemistry: Optimal pH 2.8-3.5 for homogeneous Fenton; heterogeneous Fenton catalysts may operate effectively at higher pH.

Photocatalyst surface charge: TiO_2 point of zero charge \sim pH 6.5; below this, surface positive charges attract anionic pollutants.

Pollutant speciation: Ionization state affects pollutant partitioning to cavitation bubbles and susceptibility to oxidation.

H_2O_2 stability: H_2O_2 decomposes rapidly at high pH, potentially wasting oxidant.

Catalyst Loading and Type

Nanocatalyst loading must be optimized for each system [124]:

Too low: Insufficient active sites for radical generation

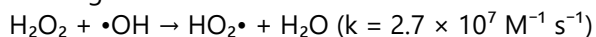
Too high: Catalyst agglomeration reduces effective surface area; turbidity screens UV in photocatalytic systems; excess catalyst may scavenge radicals

Optimal loadings typically range from 0.1-2.0 g/L depending on catalyst density, surface area, and activity. Catalyst recovery and reuse require consideration in process economics.

Oxidant Concentration

For HC systems incorporating H_2O_2 , O_3 , or persulfate, oxidant concentration requires careful optimization [125]:

H_2O_2 : Optimal $[\text{H}_2\text{O}_2]$ depends on pollutant concentration and catalyst loading. Excess H_2O_2 scavenges $\bullet\text{OH}$:



Persulfate: Similar scavenging effects occur at high concentrations.

Ozone: HC enhances ozone mass transfer and utilization, reducing required ozone dose by 30-50% compared to conventional ozonation [126].

Temperature

Bulk temperature affects cavitation intensity and reaction kinetics [127]:

Cavitation intensity: Higher temperature increases vapor pressure, promoting cavity formation but

reducing collapse temperature (more vapor in cavities cushions collapse).

Reaction kinetics: Rate constants generally increase with temperature following Arrhenius behavior.

Optimal temperature: Typically 30-50°C for most HC-AOP systems, balancing cavitation intensity with kinetic enhancement.

Reactor Geometry

Reactor design significantly influences HC-AOP performance [128]:

Orifice vs. venturi: Venturi tubes generally provide more uniform cavitation and lower energy consumption, while orifice plates may achieve higher peak intensities [129].

Multiple orifices: Increasing hole number while maintaining total flow area increases cavitation yield through multiple cavitation events [130].

Geometric ratios: For orifice plates, thickness-to-diameter ratio of 1-3 typically optimal; for venturi, convergence/divergence angles of 20-30° are common.

Reactor volume: Larger volumes increase residence time but may reduce cavitation intensity per unit volume.

VII. ENERGY EFFICIENCY AND SCALE-UP CONSIDERATIONS

Cavitation Yield

Cavitation yield (CY) is a key performance metric defined as [131]:

$CY = (\text{Pollutant degraded, mg}) / (\text{Energy input, kJ})$
 This metric enables comparison between different HC configurations and with competing technologies. Typical CY values range from 0.1-10 mg/kJ depending on pollutant and system design [132].

Sarvothaman and colleagues reported that HC-photocatalysis-peroxide systems achieved cavitation yields 5 times higher than acoustic

cavitation counterparts, demonstrating the energy efficiency of hydrodynamic over acoustic cavitation [64].

Electrical Energy per Order (EE/O)

EE/O is a figure of merit for AOP systems defined as the electrical energy required to reduce pollutant concentration by one order of magnitude in 1 m³ of water [133]:

$EE/O \text{ (kWh/m}^3\text{)} = (P \times t \times 1000) / (V \times \log(C_i/C_f))$
 where P is power (kW), t is time (h), V is volume (L), and C_i/C_f is the concentration reduction factor.

For HC-based systems, EE/O values of 10-100 kWh/m³ are typical, competitive with other AOPs [134]. Optimization can reduce EE/O substantially.

Hybrid vs. Standalone Processes

Comparative studies consistently demonstrate that HC-AOP-nanomaterial hybrid systems outperform standalone processes [135]:

Process	Degradation Efficiency	Energy Consumption	Synergy Factor
HC alone	20-40%	Moderate	-
Fenton alone	60-80%	Low chemical	-
HC/Fenton	90-99%	Moderate	1.5-3.0

Process	Degradation Efficiency	Energy Consumption	Synergy Factor
Photocatalysis alone	50-80%	High (UV lamps)	-
HC/Photocatalysis	85-98%	Moderate	1.8-4.0
Ozonation alone	70-90%	High (O ₃ generation)	-
HC/Ozonation	95-99%	Moderate	1.6-2.5

Scale-Up Challenges and Solutions

Scaling HC reactors from laboratory to industrial scale presents several challenges [136]:

Geometric similarity: Maintaining cavitation characteristics requires careful scaling of constriction geometry. Computational fluid dynamics (CFD) modeling guides scale-up [137].

Multiple units: Parallel operation of multiple HC devices provides redundancy and flexibility [138].
Pump selection: High-pressure pumps for large flows require significant capital investment; optimizing pressure requirements reduces costs.

Catalyst recovery: Magnetic separation, membrane filtration, or immobilization strategies enable catalyst reuse at scale [139].

Continuous operation: Most industrial applications require continuous rather than batch operation, with implications for reactor design and process control.

Economic Analysis

Capital and operating costs for HC-AOP systems depend on [140]:

Capital costs: Pumps, reactors, piping, instrumentation, catalyst inventory

Operating costs: Electricity (pumping), chemicals (H₂O₂, catalysts), maintenance

Treatment cost estimates: \$0.5-5.0 per m³ treated depending on pollutant loading and treatment objectives [141].

Cost comparisons favor HC-AOP over conventional AOPs for many applications due to lower energy consumption and chemical usage [142].

VIII. CURRENT CHALLENGES AND FUTURE PERSPECTIVES

Mechanistic Understanding

Despite extensive research, several mechanistic questions remain [143]:

- Quantitative relationship between cavitation intensity and •OH generation
- Role of nanocatalysts in cavitation nucleation and bubble dynamics
- Fate of transformation products and toxicity assessment
- Contribution of different reactive species under various conditions
- Advanced characterization tools (in situ spectroscopy, laser diagnostics, high-speed imaging) coupled with computational modeling will address these knowledge gaps [144].

Catalyst Stability and Reusability

Nanocatalyst deactivation mechanisms in HC environments require systematic study [145]:

- Mechanical attrition from shock waves
- Surface oxidation or reduction

- Fouling by adsorbed intermediates
- Leaching of active components

Developing robust catalysts with long-term stability under cavitation is essential for industrial adoption.

Transformation Product Identification and Toxicity

Parent compound degradation does not guarantee detoxification [146]. Some AOPs generate transformation products more toxic than original pollutants. Comprehensive toxicity assessment using:

- In vitro bioassays (e.g., Microtox, algal toxicity, Daphnia magna)
- In silico prediction (QSAR models)
- High-resolution mass spectrometry for product identification must accompany degradation studies [147]. Machine learning approaches for predicting transformation product toxicity are under development [106].

Real Wastewater Matrices

Most studies use synthetic wastewater with single pollutants. Real wastewater contains complex matrices with [148]:

- Multiple pollutants competing for •OH
- Natural organic matter (scavengers)
- Inorganic ions (carbonates, chlorides) affecting radical chemistry
- Variable pH and suspended solids Validating HC-AOP performance with real industrial effluents is critical for technology translation.

Integration with Renewable Energy

The energy intensity of AOPs can be mitigated by integration with renewable energy sources [149]:

- Solar-powered photocatalytic HC systems
- Wind-powered pumping for HC generation
- Energy recovery from pressure let-down in industrial processes

Machine Learning and Process Optimization

Machine learning is transforming HC-AOP research [150]:

Predictive modeling: Neural networks predict degradation efficiency from operating parameters

Optimization: Genetic algorithms identify optimal conditions minimizing energy consumption

High-throughput screening: ML models prioritize catalyst formulations for experimental testing

Mechanistic insight: Feature importance analysis reveals key parameters controlling performance

Emerging Hybrid Configurations

Novel hybrid systems under investigation include:

HC/electrochemical oxidation: Cavitation enhances mass transfer to electrodes while electrochemical generation of oxidants supplements radical production [151].

HC/microbial fuel cells: Pre-treatment by HC enhances biodegradability for subsequent biological treatment [152].

HC/membrane processes: Cavitation controls membrane fouling while AOPs degrade retained pollutants [153].

HC with nanobubbles: Hydrodynamically generated nanobubbles (50-500 nm) offer long residence times and high surface area for ozone delivery [154].

Quintero-González and colleagues demonstrated that ozone nanobubbles generated by hydrodynamic cavitation achieved 99.8% suspended solids removal and 90% COD reduction in municipal wastewater [155].

Regulatory and Commercialization Pathways

Transitioning HC-AOP from laboratory to market requires [156]:

- Demonstration at pilot scale (1-100 m³/day)
- Validation with real industrial wastewaters

- Regulatory approval for treated water discharge/reuse
- Technology transfer partnerships
- Life cycle assessment confirming environmental benefits

Several companies now offer commercial HC reactors for wastewater treatment, though integration with AOPs and nanomaterials remains largely at development stage [157].

IX. CONCLUSIONS

The integration of advanced oxidation processes with hydrodynamic cavitation and nanomaterials represents a transformative approach to wastewater treatment, addressing the limitations of conventional technologies for recalcitrant pollutant degradation. This comprehensive review has established:

Fundamental principles: Hydrodynamic cavitation generates extreme localized conditions through bubble formation and collapse, producing $\bullet\text{OH}$ radicals while enhancing mass transfer and catalyst activity. The cavitation number (C_v) governs cavitation intensity, with optimal values of 0.1-0.5 for wastewater treatment.

Synergistic mechanisms: HC integration with Fenton, photocatalysis, ozonation, and persulfate activation achieves synergy factors of 1.5-5.0 through multiple enhancement pathways including enhanced radical generation, improved mass transfer, catalyst activation, and pollutant disruption.

Nanomaterial roles: Nanocatalysts (TiO_2 , ZnO, nZVI, carbon-based materials, magnetic nanocomposites) serve as heterogeneous catalysts, adsorbents, cavitation nuclei, and recoverable active phases in HC-AOP systems. The combination of cavitation with nanomaterials addresses catalyst deactivation through surface cleaning while enhancing catalytic activity.

Pollutant applications: HC-AOP-nanomaterial systems effectively degrade diverse pollutant classes including dyes (95-99% removal), pharmaceuticals

(80-95%), phenolic compounds (85-98%), pesticides, and emerging contaminants. The pseudo staggered effect in HC-photocatalysis-peroxide systems demonstrates particular promise.

Operating parameters: Optimal performance requires systematic optimization of inlet pressure (3-8 bar), pH (pollutant-dependent), catalyst loading (0.1-2.0 g/L), oxidant concentration, temperature (30-50°C), and reactor geometry.

Energy efficiency: Cavitation yields of 0.1-10 mg/kJ and EE/O values of 10-100 kWh/m³ position HC-AOP competitively with conventional AOPs, with hybrid systems offering 30-50% energy savings.

Scale-up considerations: Industrial implementation requires addressing catalyst recovery, continuous operation, real wastewater complexity, and economic viability. Treatment costs of \$0.5-5.0 per m³ are achievable.

Future directions: Mechanistic understanding, catalyst stability, toxicity assessment, renewable energy integration, machine learning optimization, and emerging hybrid configurations will drive continued advancement.

The convergence of hydrodynamic cavitation, advanced oxidation, and nanotechnology offers a powerful platform for sustainable wastewater treatment. As research progresses from laboratory fundamentals to pilot validation and commercial deployment, these hybrid systems are positioned to play an increasingly important role in addressing the global challenge of water pollution and enabling water reuse in a circular economy.

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