

Covalent Organic Frameworks and Porous Organic Polymers for Photocatalytic Antibiotic Degradation: Structure–Property Relationships, Trade-Offs, Environmental Safety, and Technical Scale-Up

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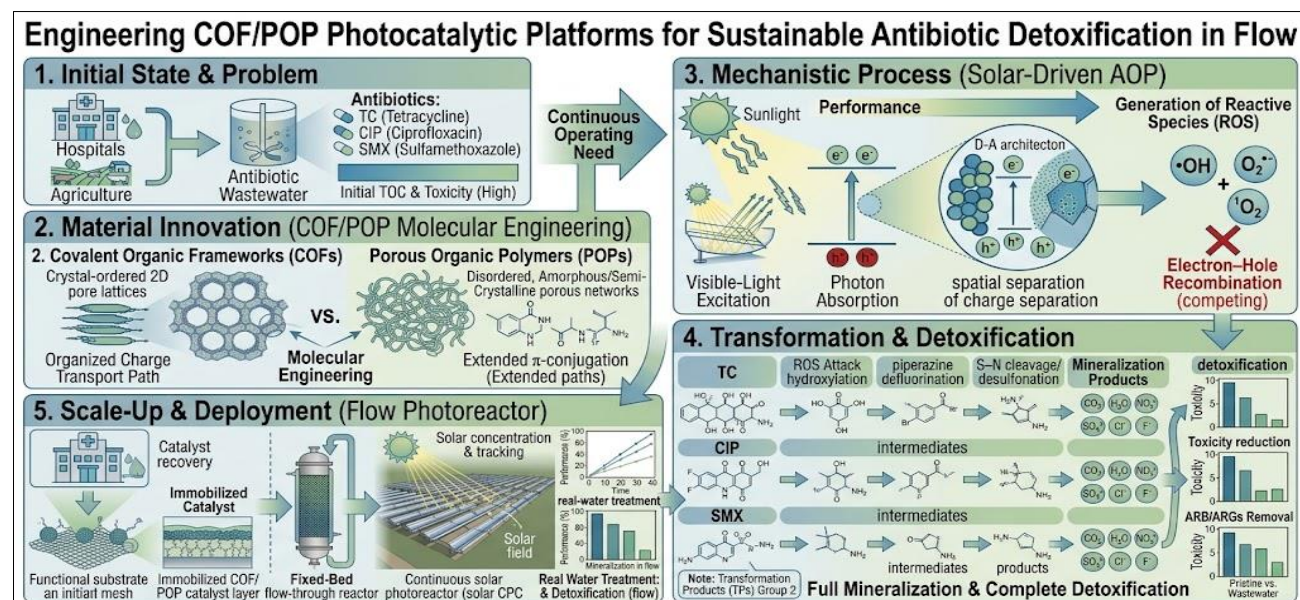
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Abstract



Graphical Abstract

Antibiotic contamination in aquatic ecosystems drives the dissemination of antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs). While heterogeneous photocatalysis using metal-free porous organic polymers (POPs) and covalent organic frameworks (COFs) offers a sustainable remediation strategy, current literature predominantly focuses on parent pollutant disappearance rather than fundamental degradation bottlenecks. This review critically addresses this gap by evaluating the inherent molecular trade-offs governing COF/POP design, the mechanistic pathways of real-water matrix interference, and the ecotoxicity of transformation products. Furthermore, we provide a critical Life Cycle Assessment (LCA) and Techno-Economic Analysis (TEA) perspective on synthesis versus performance, concluding with a standardized reporting checklist to guide future research toward practical, pilot-scale implementation.

Keywords: Antibiotic Contamination, Aquatic Ecosystems, Antibiotic-Resistant Bacteria (ARB), Antibiotic Resistance Genes (ARGs), Heterogeneous Photocatalysis, Covalent Organic Frameworks (COFs).

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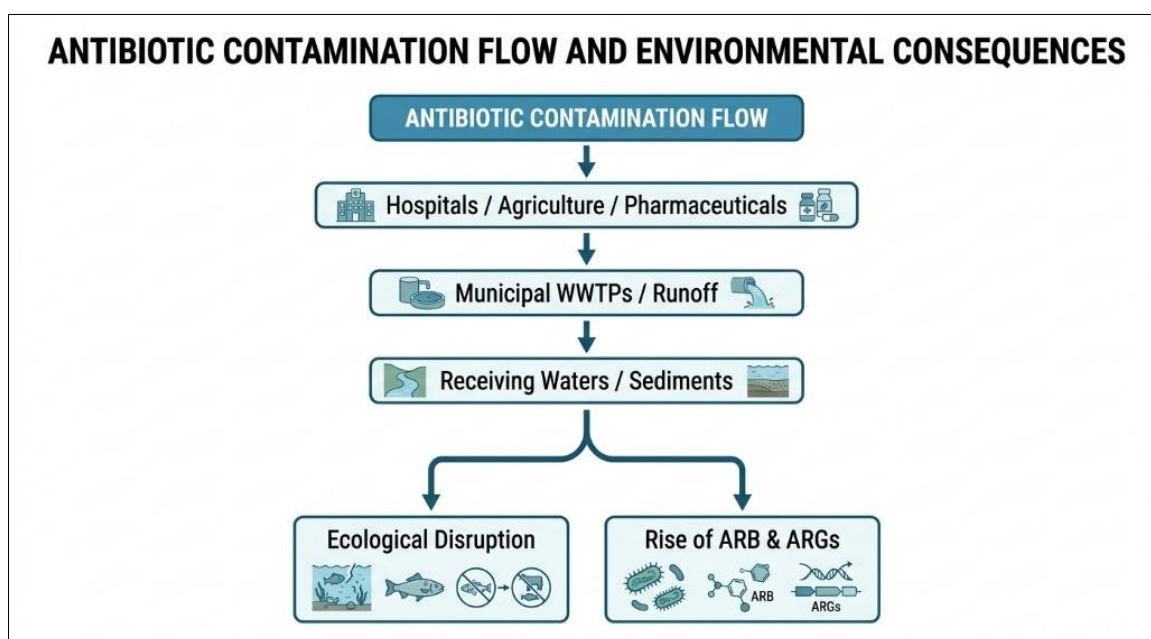
1. INTRODUCTION

The global presence of antibiotics in water environment became among the most critical environmental and public health issues in the recent decades [1, 2]. Pharmaceutical classes such as tetracyclines (TC), fluoroquinolones, e.g., ciprofloxacin (CIP), sulfonamides, e.g., sulfamethoxazole (SMX), macrolides, and β -lactam are widely utilized in human, livestock, veterinary and aquaculture productions [4, 5]. Their widespread and persistent use led to their continued release in municipal sewage, hospital wastewater, agricultural drainage, pharmaceutical production wastewater and in aquaculture activities. As a result of incomplete metabolism in humans and animals, 30-90% of the used antibiotics are excreted as the parent compound or active metabolite into the aquatic environment [2, 7].

Conventional organic pollutants can be subjected to relatively fast degradation. In contrast, it has been found that antibiotics can behave as pseudo-persistent pollutants due to repeated inputs into aquatic environments from various sources that balances their removal via natural attenuation mechanisms. So, wastewater treatment plant (WWTP) effluents, surface

waters, groundwater, sediments and even, occasionally, drinking water sources may contain antibiotics [2–5]. Even at trace concentrations, their continuous environmental presence is of considerable concern because antibiotics are biologically active compounds specifically designed to interfere with essential cellular processes in microorganisms.

The environmental consequences of antibiotic contamination extend beyond the direct toxicity of the parent compounds. Continuous exposure to sub-inhibitory antibiotic concentrations can exert selective pressure on microbial communities, favoring organisms that possess resistance mechanisms. This process can accelerate the selection, enrichment, and dissemination of antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs) [1, 6]. Aquatic environments can therefore function not only as receiving compartments for pharmaceutical contaminants but also as potential reservoirs and transmission pathways for antimicrobial resistance (AMR). The coexistence of antibiotics, resistant microorganisms, resistance genes, and mobile genetic elements may further facilitate horizontal gene transfer and contribute to the environmental dissemination of resistance [1, 6].



Flowchart 1

The ongoing release of antibiotics into the water environment takes place via diverse but linked pathways. Hospitals and healthcare institutions release antibiotic residues and metabolites into the environment via domestic wastewater while agriculture contributes its share through livestock manure, veterinary pharmaceuticals, and agricultural run-off. When treatment and discharge management are insufficient, pharmaceutical production plants may produce a stream of the effluent containing high concentrations of antibiotics. Another significant source of antimicrobials,

is aquaculture, where these agents can be applied directly into aquatic production systems and residual compounds can be released into adjacent water and sediment [2, 4, 7].

Even conventional wastewater treatment plants (WWTPs) are capable of removing bulk organics, suspended solids, nutrients and most other conventional contaminants efficiently; they have not, however, been designed to remove pharmaceutical residues at trace levels fully. Some antibiotics may be biodegraded in

activated sludge and other biological treatment systems, but the degradation rate is highly dependent on antibiotic class, chemical structure, physical-chemical properties, biodegradability, operational parameters, sludge retention time and microbial community structure [2, 7]. Biologically persistent antibiotics may, therefore, pass through treatment systems and be discharged to receiving waters.

The persistence of these pollutants underscores the demand for novel treatment strategies that would destroy, rather than transfer, antibiotic molecules between the compartments of the environment. Consequently, adsorption, membrane filtration, biological treatment, ozonation, electrochemical oxidation and advanced oxidation processes (AOPs) has been widely investigated for the treatment of pharmaceutical wastewater. Among these, heterogeneous photocatalysis has received great interest because it can exploit the light energy to trigger highly reactive oxidation processes that might lead to the decomposition of the parent pharmaceutical molecule into smaller, less toxic compounds and, in favorable situations, to the final mineralization [8–10].

Advanced oxidation processes (AOPs) such as heterogeneous photocatalysis are based on the direct utilization of light energy for the production of reactive

charge carriers and ROS, which can be considered as water-soluble precursors of ozone. These active metabolites may react with chemically inert functional groups in the antibiotics and start an array of reactions, which includes oxidation, hydroxylation, dealkylation, deamination, cleavage of bonds, and the opening of rings [8–10]. Ideally, the transformations proceed in the direction of mineralization, resulting in the generation of relatively benign inorganic compounds such as CO_2 , H_2O , NH_4^+ , NO_3^- , SO_4^{2-} , and Cl^- , which are dependent on the elemental makeup of the parent antibiotic [8–10].

Nevertheless, rapid parent antibiotic disappearance does not necessarily mean complete detoxification. Photocatalytic processing can produce transformation products which may have a residual biologic activity or toxicity other than that of the parent compound. Thus, evaluation of the photocatalytic efficiency should consider also mineralization, identification of transformation products and ecotoxicological tests beside antibiotic disappearance. The parameters including total organic carbon (TOC) removal, chemical oxygen demand reduction, degradation kinetics and biological toxicity are expected to supply a supplementary information on the real performance of the treatment system.

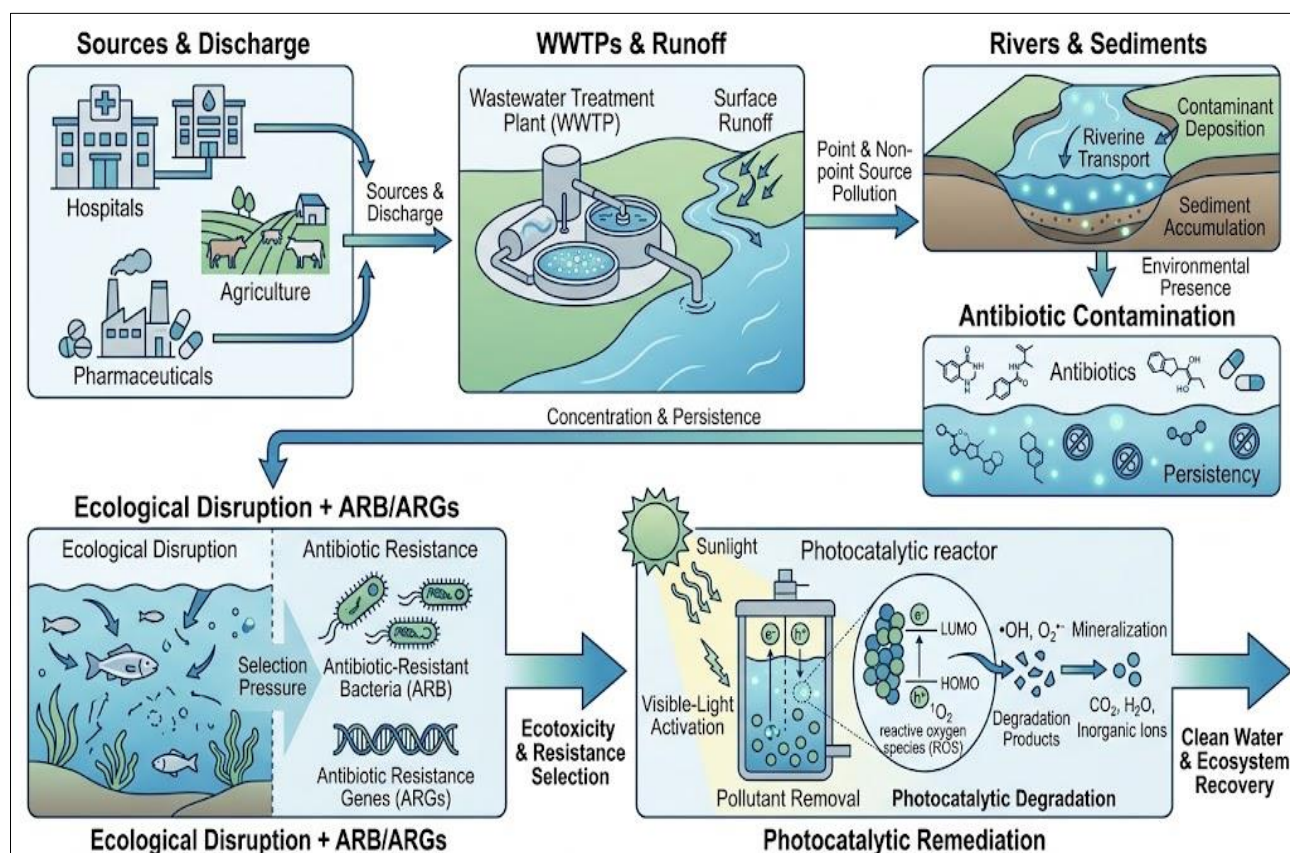


Figure 1: Major sources, environmental dissemination, and consequences of antibiotic contamination in aquatic systems [1, 2, 4–7]

2. LIMITATIONS OF CONVENTIONAL PHOTOCATALYSTS AND EMERGENCE OF POROUS ORGANIC FRAMEWORKS

2.1 Limitations of Conventional Photocatalysts

Traditional inorganic semiconductors such as TiO_2 and $\text{g-C}_3\text{N}_4$ have been widely studied for pharmaceutical contaminant degradation due to their chemical stability, photocatalytic activity and the relatively low cost of [11-14, ... 20]. However, their usage is limited by some inherent weaknesses. The bandgap of TiO_2 is known to be relatively large, so it cannot take advantage of a considerable part of visible solar radiation. Moreover, re-bonding of photogenerated electron-hole pairs may — render them less available for surface redox reactions. Limited surface area and inadequate adsorption of certain pharmaceutical

molecules may also weaken the efficiency of pollutants with photocatalytically active sites [11-14].

Metal-free semiconductor graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has therefore become a promising candidate for visible-light-driven environmental photocatalysis [18-20], but it is still a challenging task to develop high performance $\text{g-C}_3\text{N}_4$ based materials. The pure $\text{g-C}_3\text{N}_4$ might also be limited by fast charge recombination, limited surface area, and partial utilization of solar spectrum. These drawbacks have motivated the exploration of different strategies such as physical modifications, heterojunctions, doped systems or other metal-free photocatalytic systems with enhanced charge separation, light harvesting and pollutant diffusion.

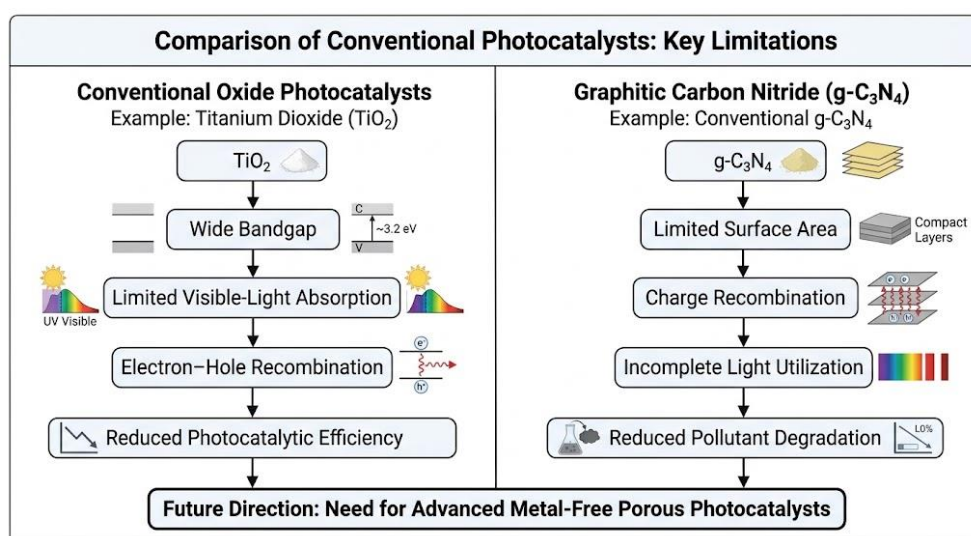


Figure 2: Major limitations of conventional TiO_2 and $\text{g-C}_3\text{N}_4$ photocatalysts and the motivation for developing advanced porous organic photocatalysts [11–14, 18–20]

2.2 Emergence of Porous Organic Polymers and Covalent Organic Frameworks

Porous organic polymers (POPs) and covalent organic frameworks (COFs) have emerged as promising metal-free alternatives for photocatalytic environmental remediation [18, 38]. These materials provide an unusual combination of permanent porosity, extended π -conjugation, tunable electronic structures, and chemically adjustable surface functionality. Their molecular structures can be designed by selecting appropriate organic building blocks and covalent linkages, allowing researchers to modify pore size, surface polarity, light absorption, charge-carrier behavior, and adsorption characteristics.

COFs are distinguished by their ordered and often crystalline architectures, in which organic building blocks are connected through covalent bonds to produce periodic two-dimensional (2D) or three-dimensional (3D) porous networks [21, 22]. Their structural regularity provides well-defined channels that can facilitate molecular diffusion and potentially support directional charge transport. By incorporating donor and

acceptor components into the framework, the electronic structure can also be engineered to promote charge separation and broaden light absorption [22, 28].

POPs represent a broader class of porous organic materials that includes conjugated microporous polymers (CMPs), covalent triazine frameworks (CTFs), and related porous polymer networks [36–41]. Their structures are generally less ordered than those of crystalline COFs, but their irreversible covalent connections can provide excellent chemical and hydrolytic stability. In particular, C–C-linked and triazine-containing frameworks can withstand harsh aqueous environments while maintaining permanent porosity and chemically accessible functional groups [36, 37, 41].

Constructed entirely through strong covalent bonds such as C–C, C–N, and C=N, these organic frameworks feature customizable pore geometries, extended π -conjugation, high chemical and hydrolytic resistance, and a complete absence of intentionally incorporated toxic metal species [21, 26, 36, 41]. Their

metal-free nature is particularly relevant to environmental applications because it can reduce concerns associated with secondary metal-ion release during prolonged photocatalytic operation.

Another important advantage of COFs and POPs is their structural tunability. The incorporation of electron-donating and electron-withdrawing units can modify the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, while changes in conjugation length and molecular connectivity can influence optical bandgaps and charge-carrier transport. Similarly, functional groups can be introduced to increase hydrophilicity, hydrophobicity, electrostatic interactions, hydrogen bonding, or π - π interactions with antibiotic molecules. These features create opportunities to simultaneously optimize adsorption and photocatalytic degradation.

The relationship between adsorption and photocatalysis is particularly important for antibiotic remediation. Adsorption can concentrate antibiotic molecules near photocatalytically active sites, increasing the probability of interaction with photogenerated charge carriers and reactive oxygen species (ROS). Conversely, degradation of adsorbed molecules can continuously regenerate surface sites, potentially supporting sustained pollutant removal. Thus, the overall performance of a COF or POP photocatalyst is governed not by a single structural parameter but by the combined effects of light

harvesting, adsorption, charge generation, charge separation, charge transport, ROS formation, and accessibility of reactive sites.

Despite these advantages, several challenges remain before COF- and POP-based photocatalysts can be considered fully mature technologies for practical wastewater treatment. Laboratory studies frequently employ simplified aqueous systems containing a single antibiotic at relatively high concentrations. Real wastewater, in contrast, contains dissolved organic matter, inorganic ions, suspended solids, competing contaminants, and microorganisms that can interfere with adsorption and photocatalytic reactions. Furthermore, catalyst recovery, mechanical stability, light penetration, reactor configuration, long-term performance, and large-scale synthesis must be considered when translating these materials from laboratory experiments to continuous treatment systems.

Therefore, the development of next-generation COF and POP photocatalysts requires a comprehensive understanding of their structure–property–performance relationships. Such understanding is essential for connecting molecular-level design with macroscopic photocatalytic activity and for determining whether improvements observed under laboratory conditions can be maintained in realistic water matrices and scalable reactor systems.

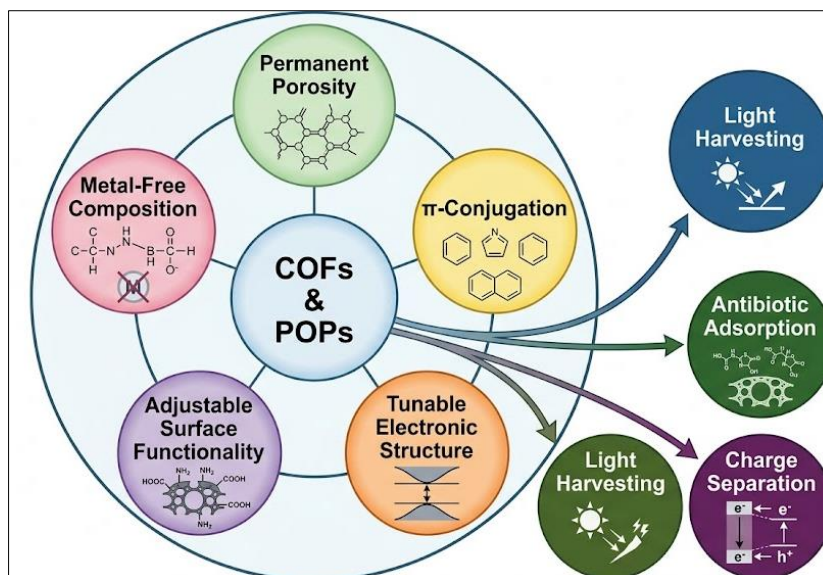


Figure 3: Key structural features of COFs and POPs that support photocatalytic antibiotic degradation [18, 21, 22, 26, 36–41]

2.3 Fundamentals of Photocatalytic Antibiotic Degradation

Rather than relying on basic textbook redox equations, charge-carrier dynamics in porous organic materials must be understood through their linkage-dependent photophysics. Photon absorption promotes electrons from the highest occupied molecular orbital

(HOMO) to the lowest unoccupied molecular orbital (LUMO), generating excitons. The efficiency of exciton dissociation depends heavily on the framework's covalent linkage chemistry:

- **Imine Linkages ($-C=N-$):** Provide moderate polarization, but are prone to localized exciton trapping due to structural flexibility.

- **β -Ketoenamine Linkages:** Irreversible keto-enamine tautomerism creates strong internal electron withdrawal, significantly lowering exciton binding energy and driving rapid charge separation.
- **Triazine Rings (C_3N_3):** Act as electron-deficient nodes that pull photogenerated electrons, suppressing electron-hole recombination.

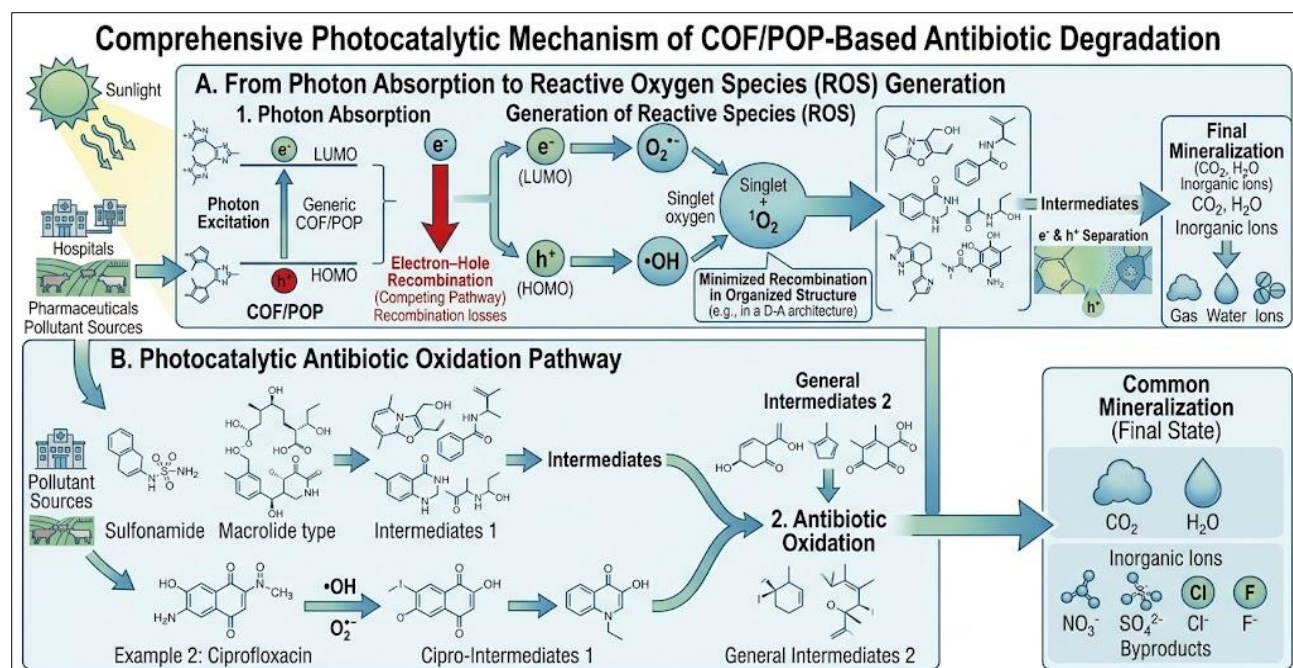
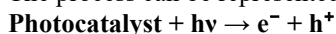


Figure 4: Simplified mechanism of photocatalytic antibiotic degradation over COF and POP photocatalysts [9, 15, 18, 22]

2.3.1 Photon Absorption and Charge-Carrier Generation

The first stage of photocatalysis is the absorption of photons with energy equal to or greater than the optical bandgap of the photocatalyst. When the framework absorbs suitable photons, electrons in the highest occupied molecular orbital (HOMO) can be promoted to the lowest unoccupied molecular orbital (LUMO), generating excited electrons and corresponding holes.

The process can be represented as:



where $h\nu$ represents the incident photon energy, e^- represents the photogenerated electron, and h^+ represents the photogenerated hole.

The efficiency of this initial step depends strongly on the optical and electronic structure of the material. A photocatalyst with a suitable bandgap can utilize a broader fraction of the incident solar spectrum, whereas an excessively wide bandgap restricts photon utilization. COFs and POPs offer considerable flexibility in this regard because their organic building blocks can be systematically modified to tune their electronic structures and extend light absorption toward the visible region.

The generation of photocarriers, however, does not automatically result in efficient photocatalysis. Following excitation, electrons and holes can either migrate toward the surface and participate in redox reactions or recombine within the framework. Rapid recombination represents a major loss pathway because the energy of the photogenerated carriers is dissipated without contributing to pollutant degradation [15, 16].

2.3.2 Charge Migration and Separation

Photogenerated electrons and holes after the photon absorption must also go through the photocatalyst itself to be involved in surface reactions. Thus, an effective spatial separation of these charge carriers is critical in high photocatalytic activity.

For POFs, π -conjugated pathways at the molecular level can enable charge transport by the electronic communication between closest aromatic/conjugated units. Ordered COF structure may also offer more or less defined channels for charge migration, whereas charge transport in amorphous POPs may resemble hopping transport through localized such as electronically coupled regions [22, 28, 43].

Donor-acceptor architectures are a key approach to enhance charge separation. Electron-donating and electron-withdrawing groups may induce an internal electronic asymmetry that facilitates

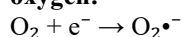
directional charge migration and diminishes the chance of electron-hole recombination. Therefore, the photocatalytic performance of the assembled framework can be greatly affected by controlling the donor and acceptor moieties in the spatial arrangement at the molecular level [28, 35].

Separation charge might be measured effectively with physical methods like photoluminescence (PL) spectroscopy, time-resolved PL (TRPL), transient photocurrent (TPC) measurements, electrochemical impedance spectroscopy (EIS), and electron paramagnetic resonance (EPR) spectroscopy. These methods yield complementary information on recombination patterns, charge-transfer efficiency, interfacial resistance, and ROS formation.

2.3.3 Surface Redox Reactions

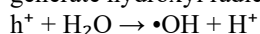
Once separated charge carriers reach the photocatalyst surface, they participate in oxidation and reduction reactions involving adsorbed antibiotic molecules, water, hydroxide ions, dissolved oxygen, and other species present in the aqueous matrix.

Photogenerated electrons can reduce dissolved oxygen:

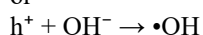


The resulting superoxide radical can participate in subsequent reactions that generate additional reactive species or directly attack susceptible functional groups within antibiotic molecules.

Photogenerated holes are strong oxidizing agents and can directly oxidize adsorbed organic molecules or react with water and hydroxide species to generate hydroxyl radicals:



or



The relative contribution of direct hole oxidation and ROS-mediated oxidation depends on the photocatalyst's electronic structure, surface chemistry, dissolved oxygen concentration, pH, and the chemical structure of the target antibiotic.

2.3.4 Pollutant Mineralization

The final stage involves the progressive oxidation and cleavage of the antibiotic molecule. Initial reactions may involve hydroxylation, dealkylation, deamination, dehalogenation, sulfonamide cleavage, piperazine-ring oxidation, or other structure-specific transformations. These reactions can generate smaller intermediate molecules that undergo further oxidation.

Ideally, successive oxidation reactions ultimately convert the organic carbon into CO_2 and H_2O , while heteroatoms are released as inorganic species such

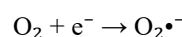
as NH_4^+ , NO_3^- , SO_4^{2-} , Cl^- , or F^- , depending on the molecular composition of the antibiotic.

Therefore, the complete photocatalytic process should be distinguished from the simple disappearance of the parent antibiotic. A high percentage of antibiotic removal measured by chromatographic analysis may indicate transformation rather than complete mineralization. For this reason, total organic carbon (TOC) analysis and identification of transformation products are important complementary approaches for evaluating the true environmental effectiveness of photocatalytic treatment [8, 57, 59].

2.4 Reactive Oxygen Species (ROS) Pathways

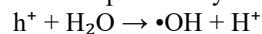
Reactive oxygen species (ROS) are central to the photocatalytic degradation of antibiotics because they provide highly reactive intermediates capable of attacking chemically stable pharmaceutical structures. The nature, concentration, lifetime, and relative contribution of ROS depend on the photocatalyst's band structure, surface functionality, dissolved oxygen concentration, solution pH, light wavelength, and molecular structure of the target antibiotic [15, 17].

Photogenerated electrons located in the lowest unoccupied molecular orbital (LUMO) can reduce dissolved molecular oxygen to superoxide radicals:



The generated superoxide radical ($\text{O}_2^{\bullet -}$) can subsequently participate in protonation, electron-transfer, and disproportionation reactions, producing secondary reactive oxygen species. Depending on the reaction environment, these pathways may contribute to the formation of hydrogen peroxide (H_2O_2) and ultimately hydroxyl radicals ($\bullet\text{OH}$). Because $\text{O}_2^{\bullet -}$ is less oxidizing than $\bullet\text{OH}$, its contribution may involve selective oxidation and electron-transfer reactions rather than exclusively non-selective mineralization.

Photogenerated holes (h^+), on the other hand, possess strong oxidation capability and can directly oxidize adsorbed antibiotic molecules. They can also react with surface hydroxyl groups, hydroxide ions, or water to produce hydroxyl radicals:



or



The hydroxyl radical is highly reactive and relatively non-selective, allowing it to attack aromatic rings, heterocyclic structures, alkyl substituents, amino groups, and other chemically susceptible functional groups within antibiotic molecules [11, 15]. This broad reactivity is particularly important for the degradation of structurally complex antibiotics containing multiple aromatic and heterocyclic rings.

In addition to $O_2^{\bullet-}$ and $\bullet OH$, singlet oxygen (1O_2) may contribute to antibiotic degradation. Unlike $\bullet OH$, which generally exhibits highly non-selective oxidation behavior, 1O_2 can display greater selectivity toward electron-rich organic moieties. Its generation may involve energy-transfer processes from photoexcited organic frameworks or reactions involving superoxide-derived intermediates [15, 17].

Therefore, photocatalytic antibiotic degradation should be considered a network of parallel and consecutive oxidation pathways rather than a single ROS-mediated reaction. The relative contribution of direct h^+ oxidation, $O_2^{\bullet-}$, $\bullet OH$, and 1O_2 can vary substantially between different COF and POP structures. Establishing the dominant reactive species is consequently important for understanding degradation

mechanisms and predicting the transformation products generated during treatment.

ROS contributions can be experimentally investigated using radical scavenging experiments, electron paramagnetic resonance (EPR) spectroscopy, selective fluorescent probes, and controlled-atmosphere experiments. For example, the addition of a $\bullet OH$ scavenger can help determine whether hydroxyl radicals contribute significantly to antibiotic degradation, whereas experiments conducted under oxygen-deficient conditions can provide information regarding the importance of oxygen-derived species. Such mechanistic investigations are particularly valuable because high apparent removal efficiency alone does not establish which reactive pathway is responsible for pollutant transformation.

Table 1: Major Reactive Oxygen Species and Their Roles in Antibiotic Degradation

Reactive Species	Formation Pathway	Standard Redox Potential (V vs. NHE)	Primary Function in Antibiotic Degradation
Hydroxyl radical ($\bullet OH$)	$h^+ + H_2O / OH^-$	+1.99 to +2.80	Non-selective cleavage of aromatic rings and complex bonds [11, 15]
Superoxide radical ($O_2^{\bullet-}$)	$O_2 + e^-$	-0.16	Initial oxidation, dealkylation, and electron transfer [15]
Singlet oxygen (1O_2)	Energy transfer from excited framework	+0.65 to +0.85	Selective oxidation of electron-rich aromatic moieties [15]
Photogenerated holes (h^+)	Direct extraction from HOMO	+1.50 to +3.00	Direct oxidation of surface-adsorbed antibiotic molecules [11, 15]

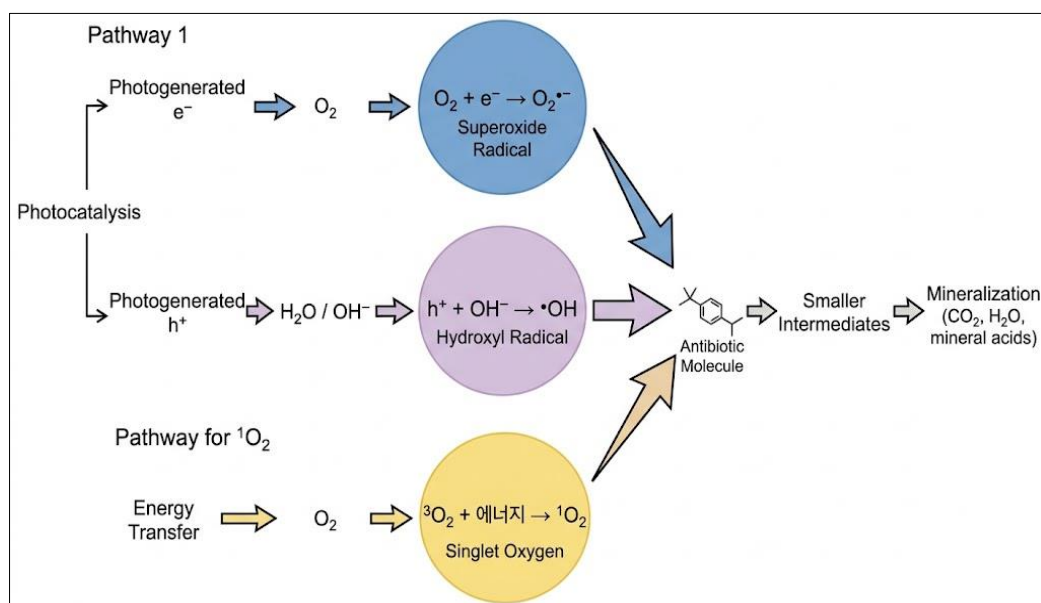


Figure 5: Principal reactive oxygen species pathways involved in photocatalytic antibiotic degradation [15, 17].

3. STRUCTURE-PROPERTY-PERFORMANCE RELATIONSHIPS IN POPs AND COFs

The photocatalytic efficacy of porous organic framework materials relies strongly on the molecular engineering of their organic building blocks, covalent linkages, pore architecture, conjugation pathways, surface functionality, and electronic structure [22, 28, 39, 40]. Unlike conventional inorganic semiconductors, for

which the chemical composition of the semiconductor is often relatively fixed, COFs and POPs offer an unusually broad molecular design space. Their photocatalytic properties can be modified by changing the identity and geometry of the monomers, donor-acceptor combinations, linkage chemistry, degree of conjugation, pore dimensions, and surface functional groups.

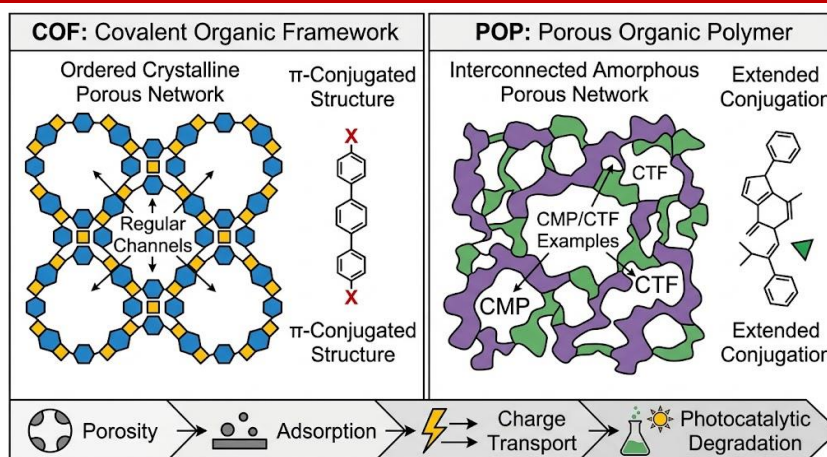


Figure 6: Simplified structural comparison of covalent organic frameworks (COFs) and porous organic polymers (POPs) and their influence on photocatalytic performance [21, 22, 28, 36–41]

This structural tunability provides an opportunity to establish direct relationships between molecular structure and photocatalytic performance. In the context of antibiotic degradation, an effective material must simultaneously provide sufficient light absorption, efficient generation and separation of

photogenerated charge carriers, accessible adsorption sites, rapid mass transport, and appropriate redox potentials for the formation of reactive species. Consequently, high surface area alone is insufficient to guarantee high photocatalytic activity.

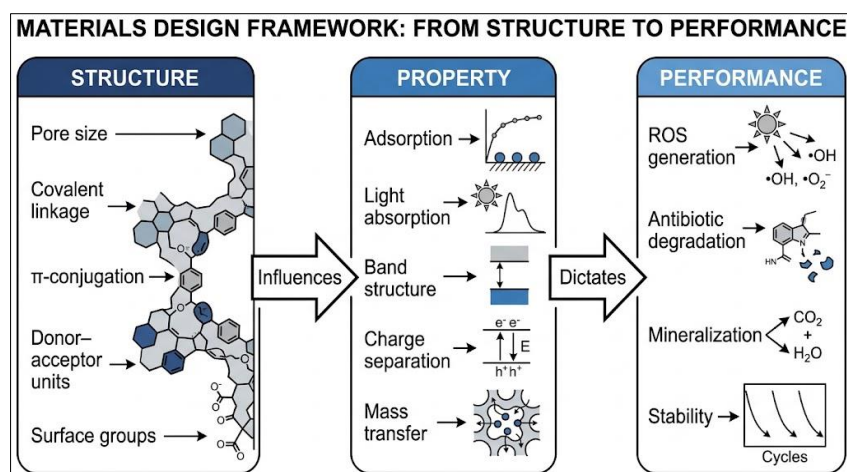
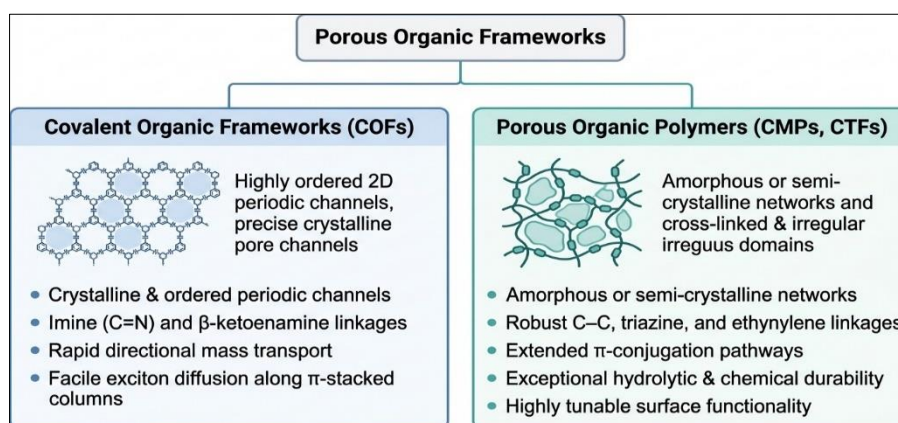


Figure 7: Structure–property–performance relationship governing COF/POP photocatalytic activity toward antibiotic degradation [22, 28, 35, 39, 40]

2.1 Porous Organic Framework Design



Flowchart 2

The structural distinction between COFs and POPs provides the foundation for understanding their different photocatalytic behaviors. COFs are generally characterized by long-range structural order and periodic pore channels, whereas many POPs exhibit amorphous or semi-crystalline networks with irregular pore distributions [21, 31, 36, 38]. Nevertheless, both classes can be engineered to possess high surface areas, extended conjugation, and chemically accessible active sites.

The structure–property relationship can be considered through several interconnected parameters:

Molecular Building Blocks → Covalent Linkages → Pore Architecture → Electronic Structure → Charge Dynamics → ROS Generation → Antibiotic Degradation

A change at any stage of this sequence can influence the final photocatalytic performance of the material.

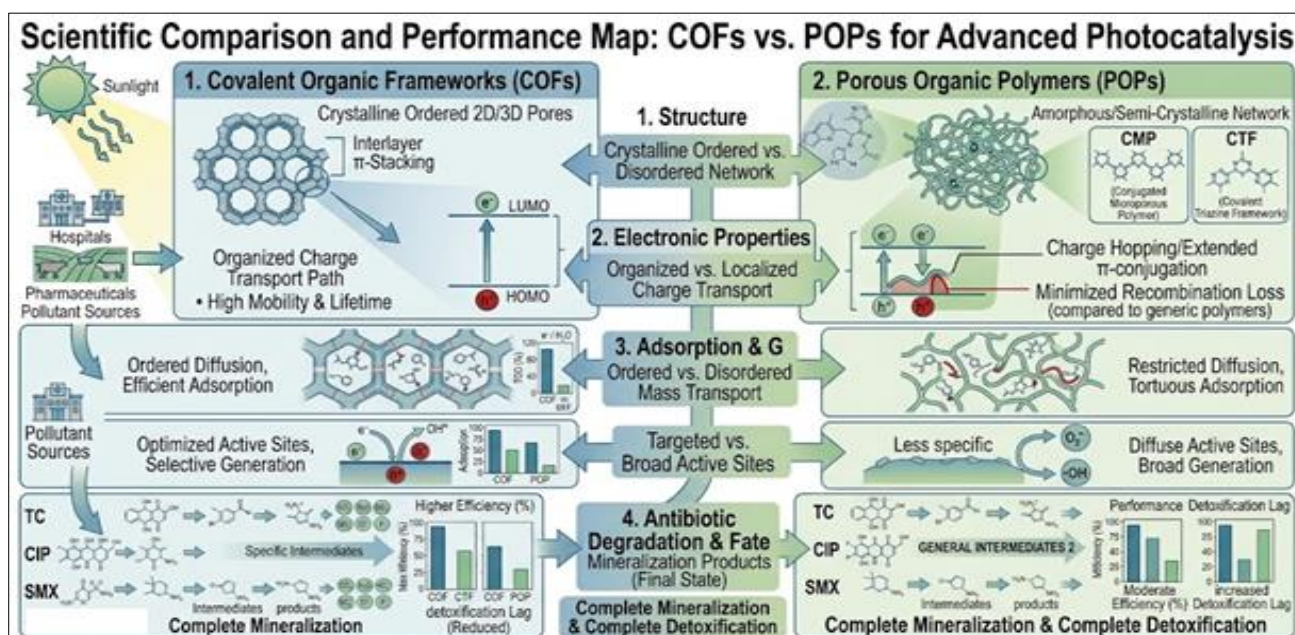


Figure 8: Comparative structure–property–performance map of COFs and POPs for photocatalytic antibiotic degradation [21, 22, 28, 36–41, 43, 48]

3.2 Covalent Organic Frameworks: Crystallinity and Ordered Porosity

Covalent organic frameworks are constructed by linking molecular building blocks through strong covalent bonds to generate permanently porous crystalline structures [21, 32, 33]. Their periodic architectures can provide well-defined channels and molecularly organized pathways for mass transport and charge migration.

The crystalline nature of COFs is particularly relevant to photocatalysis because structural order can reduce the randomness associated with molecular transport and electronic communication. In a well-organized framework, the spatial arrangement of conjugated units may facilitate movement of photoexcited carriers and reduce the number of structural defects that act as recombination centers.

The pore architecture also influences the interaction between antibiotics and the photocatalyst. Antibiotic molecules are structurally diverse and may contain aromatic rings, heterocycles, ionizable functional groups, and hydrophobic domains. Therefore, pore size and surface chemistry must be compatible with

the molecular dimensions and physicochemical properties of the target contaminant.

Ordered Pore Channels

The presence of relatively uniform pore channels can facilitate molecular diffusion and reduce mass-transfer limitations. One-dimensional channels may provide relatively direct pathways for antibiotic molecules to access internal surfaces, whereas interconnected two- and three-dimensional pore systems can provide multiple transport pathways [24, 29].

This feature is particularly important for bulky antibiotics such as tetracyclines and fluoroquinolones. If the pore aperture is too small, the antibiotic molecule may be unable to enter the internal pore system, resulting in underutilization of the theoretical surface area. Conversely, appropriately sized pores can promote adsorption and increase the local concentration of antibiotic molecules near photocatalytically active regions.

Therefore, the BET surface area should not be considered independently of pore accessibility. A material with a lower nominal surface area but highly accessible active sites may outperform a material with a

larger surface area in which a substantial fraction of the pores are inaccessible to the target contaminant.

3.3 Porous Organic Polymers: Network Structure and Chemical Stability

Porous organic polymers constitute a broader family of permanently porous organic networks and include conjugated microporous polymers (CMPs), covalent triazine frameworks (CTFs), and other cross-linked polymeric structures [36–41].

Unlike many COFs, which rely on reversible bond formation to achieve crystalline order, POP synthesis frequently involves irreversible coupling reactions. This kinetic control can result in disordered structures but may simultaneously provide excellent chemical and hydrolytic stability [36, 38].

Conjugated Microporous Polymers

CMPs have extended π -conjugated backbones, which allow electronic communication along the polymer chains [39, 43]. Its conjugated structure allows absorption of visible light and charge transfer pathways after photoexcitation.

Using different electron-rich and electron-poor building blocks, the optical properties of the CMPs can be modulated. Extension of conjugation length, the insertion of planar aromatic moieties or the design of donor–acceptor structures modulate the energy levels of the frontier orbitals, and also lead to a reduction of the optical bandgap.

Nevertheless, too much chain rigidity or aggregation may lead to detrimental effects. Strong π – π stacking or closely packed aggregates favor non-radiative energy relaxation or charge recombination. Hence, the synthesis of conjugated POPs should involve a compromise between maintaining good electronic connectivity and having sufficient porosity and accessibility.

Covalent Triazine Frameworks

CTFs are nitrogen-rich porous polymers generally constructed from aromatic nitrile precursors through trimerization reactions [37, 41]. The resulting triazine rings possess electron-deficient characteristics and can influence both the electronic structure and surface polarity of the framework.

The presence of nitrogen-containing sites can improve interactions with polar antibiotic molecules through hydrogen bonding, electrostatic interactions, and dipole-related interactions. These features may enhance adsorption while simultaneously influencing the electronic properties of the photocatalyst.

The strong covalent nature of the triazine-containing framework also provides excellent resistance toward chemical degradation, making CTFs attractive

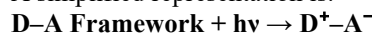
candidates for aqueous applications in which long-term structural stability is required [37, 41, 47].

3.4 Donor–Acceptor Engineering and Electronic Structure

One of the most effective approaches for improving photocatalytic performance is the construction of donor–acceptor (D–A) architectures [28, 35]. In these systems, electron-donating and electron-withdrawing molecular units are incorporated into the same porous framework.

Upon illumination, the donor component can facilitate electron generation, while the acceptor component provides a favorable destination for electron transfer. This spatial separation can reduce the probability of electron–hole recombination and increase the lifetime of charge carriers available for surface reactions.

A simplified representation is:



where D represents the electron-donating component and A represents the electron-accepting component.

The resulting internal charge-transfer process can broaden the absorption spectrum and promote separation of photogenerated carriers. Such molecular engineering is particularly valuable for solar photocatalysis because visible-light utilization is a major factor determining practical solar conversion efficiency [28, 35].

The relative positions of the HOMO and LUMO are also important because they determine whether the photogenerated electrons and holes possess sufficient thermodynamic driving force to produce ROS. A material with excellent visible-light absorption but insufficient redox potential may not generate the reactive species required for effective antibiotic degradation.

Thus, optimization requires a balance between:

Light Absorption + Charge Separation + Redox Potential + Surface Accessibility rather than maximizing any single property.

3.5 Role of π -Conjugation in Photocatalytic Performance

Extended π -conjugation is a defining feature of many photocatalytically active COFs and POPs. Conjugated aromatic units allow electronic delocalization across the framework and can facilitate charge transport between neighboring structural units [39, 43].

Greater conjugation can reduce the energy required for electronic excitation and thereby promote visible-light absorption. However, the relationship between conjugation and photocatalytic activity is not necessarily linear. Excessive conjugation, aggregation,

or planar stacking may increase the probability of charge recombination.

Consequently, molecular design should aim for sufficient conjugation to facilitate light harvesting and charge transport while preserving porous channels and spatial separation of charge carriers.

In COFs, π - π stacking between adjacent two-dimensional layers may additionally influence charge transport. Depending on the stacking arrangement and interlayer distance, these interactions can either facilitate carrier movement or promote recombination. Therefore, interlayer organization represents another important structural parameter when designing high-performance photocatalytic COFs.

3.6 Surface Functionality and Antibiotic Adsorption

The surface chemistry of a COF or POP strongly affects its interaction with antibiotic molecules. Antibiotics contain multiple functional groups, including amino, hydroxyl, carboxyl, carbonyl, sulfonamide, and heterocyclic groups. Depending on solution pH, these groups can exist in different protonation states, influencing the electrostatic interaction between the antibiotic and photocatalyst.

Surface functional groups can promote antibiotic adsorption through:

- Hydrogen bonding
- Electrostatic attraction
- π - π interactions
- Hydrophobic interactions
- Dipole-dipole interactions
- Pore confinement

Adsorption is not merely a preliminary separation process; it can directly influence photocatalytic degradation by concentrating antibiotic molecules near reactive sites. When adsorption and photocatalytic oxidation occur simultaneously, the local concentration of the pollutant at the catalyst surface may increase, improving the probability of reaction with photogenerated charge carriers and ROS.

However, excessively strong adsorption can also become counterproductive if reaction products remain strongly bound to the framework and block active sites. Therefore, an ideal photocatalyst should exhibit a balance between strong enough adsorption for effective pollutant enrichment and sufficiently reversible interactions to permit product desorption and regeneration of active sites.

3.7 Pore Size, Surface Area, and Mass Transport

Porosity is one of the defining characteristics of COFs and POPs. The internal surface area provides potential locations for antibiotic adsorption and photocatalytic reactions. However, photocatalytic

performance depends on both the quantity and accessibility of these sites.

Micropores can provide high adsorption capacity because of their large internal surface area and strong confinement effects. Mesopores, in contrast, can facilitate faster molecular diffusion and reduce transport limitations. Hierarchical pore systems containing micro-, meso-, and macropores can therefore provide complementary advantages.

A simplified relationship can be expressed as:

High Surface Area + Accessible Pores + Efficient Mass Transport = High Utilization of Active Sites

For antibiotic degradation, pore architecture should ideally be designed according to the molecular dimensions of the target contaminant. Bulky antibiotic molecules may experience steric limitations in ultramicroporous structures, whereas larger mesoporous channels can facilitate diffusion into the catalyst interior.

Therefore, reporting only BET surface area does not provide sufficient information to predict photocatalytic performance. Pore-size distribution, pore connectivity, adsorption behavior, and molecular accessibility should also be considered.

3.8 Chemical and Hydrolytic Stability

Long-term stability is particularly important for photocatalysts intended for wastewater treatment. A material that exhibits high initial degradation efficiency but undergoes structural degradation after repeated irradiation would have limited practical value.

COFs and POPs can display high chemical stability because of their covalently bonded frameworks [25, 26, 36, 41]. However, stability depends strongly on the chemical nature of the linkage. Early imine-linked COFs may be susceptible to hydrolysis under strongly acidic or basic conditions, whereas β -ketoenamine-linked structures generally provide enhanced resistance [25, 26].

Similarly, C-C-linked POPs and triazine-based frameworks can exhibit high resistance to hydrolysis and chemical attack [36, 37]. Such stability is particularly advantageous for wastewater applications involving variable pH and complex chemical matrices.

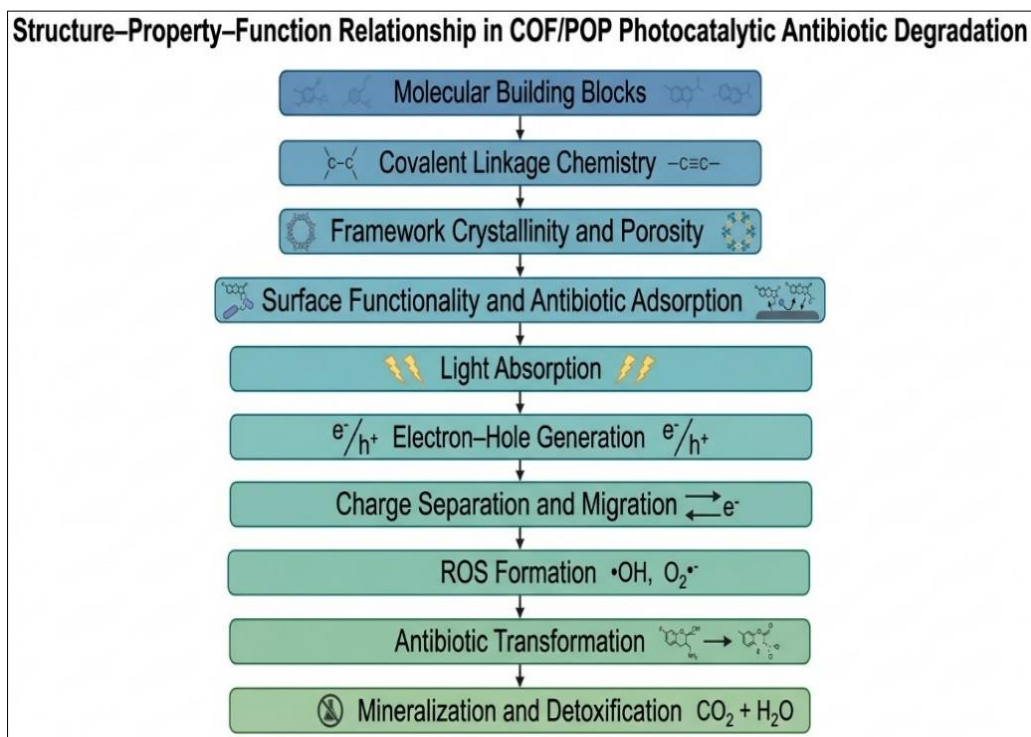
Repeated-cycle experiments should therefore evaluate:

- Photocatalytic activity after multiple cycles
- Structural integrity after irradiation
- Changes in BET surface area
- Changes in crystallinity or framework order
- Changes in optical properties
- Potential release of organic building blocks or degradation products

A stable photocatalyst should retain both its structural integrity and photocatalytic function during repeated treatment cycles.

3.9 Linking Structure to Photocatalytic Performance

The relationship between structural characteristics and photocatalytic antibiotic degradation can be summarized as follows:



Flowchart 3

This framework demonstrates that photocatalytic performance is a multivariable property. High surface area alone does not guarantee efficient degradation, nor does strong visible-light absorption necessarily result in complete mineralization. The most effective COF and POP photocatalysts are those in which pore architecture, surface chemistry, electronic structure, charge dynamics, and redox properties are simultaneously optimized.

Accordingly, future development should move beyond empirical optimization based solely on degradation percentages and instead establish quantitative structure–property–performance relationships. Such an approach can enable rational prediction of photocatalytic behavior and facilitate the

design of materials specifically tailored for different antibiotic classes and real wastewater conditions [22, 28, 39, 40].

COMPREHENSIVE COMPARISON: COFs VS. GENERAL POPs

Both covalent organic frameworks (COFs) and porous organic polymers (POPs) are porous, metal-free organic materials that can be engineered for photocatalytic environmental remediation. However, they differ substantially in terms of structural order, pore organization, charge-transport behavior, chemical stability, and synthetic scalability [22, 38, 39, 60]. These differences directly influence antibiotic adsorption, light utilization, charge separation, reactive oxygen species generation, and overall degradation performance.

Table 2: Comparison of Structural and Functional Characteristics of COFs and POPs

Feature / Metric	Covalent Organic Frameworks (COFs)	Porous Organic Polymers (POPs / CMPs / CTFs)
Crystallinity and Order	High; ordered 2D/3D periodic lattices [21, 31, 33]	Low to amorphous; disordered interconnected networks [36, 38]
Pore Structure	Uniform, mono-sized 1D/3D channels [25, 32]	Broad, hierarchical micro- to mesoporous distribution [38, 48]
BET Surface Area	800–3,000 m ² g ⁻¹ [21, 24]	500–2,400 m ² g ⁻¹ [36, 37, 39]
Mass Transfer Kinetics	Fast diffusion through relatively non-tortuous pore channels [22, 29]	Moderate diffusion through more tortuous random pore pathways [38]
Charge-Carrier Mobility	High along orderly stacked π - π columns [23, 28]	Variable; localized hopping across disordered domains [43, 60]

Feature / Metric	Covalent Organic Frameworks (COFs)	Porous Organic Polymers (POPs / CMPs / CTFs)
Hydrolytic / Chemical Stability	Moderate to high; linkage dependent, with imine < β -ketoenamine stability [25, 26]	Generally high; non-reversible C–C and triazine linkages provide high stability [36, 37, 41]
Metal-Leaching Risk	Very low; metal-free organic composition [22, 50]	Very low; metal-free organic composition [40, 54]
Synthesis Scalability	More challenging; requires controlled crystallization conditions [31, 34]	Generally easier; kinetically controlled polymerization reactions [36, 38]

3.10 Critical Trade-Offs in Molecular Design

Designing high-performance COF and POP photocatalysts requires navigating competing structural

and photophysical constraints. Maximizing one performance metric often introduces trade-offs in operational stability or charge separation.

Table 3: Design Parameters for Photocatalytic COFs

Design Parameter	Primary Benefit	Inherent Trade-Off / Drawback	Mitigation Strategy
High Crystallinity (COFs)	Ordered channels for fast diffusion and directional charge mobility.	Reversible linkages (e.g., imine) suffer from low hydrolytic stability in acidic/basic water.	Post-synthetic linkage conversion or β -ketoenamine hybridization.
Extended π-Conjugation	Narrows the optical bandgap to maximize visible-light absorption.	Increases exciton binding energy and layer stacking, accelerating e^-/h^+ recombination.	Incorporate twisted or non-planar donor–acceptor (D–A) units to interrupt stacking.
Strong D–A Architectures	Promotes spatial charge separation and internal electric fields.	Shifts in band-edge positions can decrease the thermodynamic driving force needed for ROS formation.	Fine-tune donor-to-acceptor ratios to balance light absorption and redox potential.
High Surface Area / Micro-porosity	Enhances adsorption capacity for target antibiotics.	Small micropores suffer from mass-transfer resistance and site blocking by natural organic matter.	Engineer hierarchical micro–mesoporous structures.

4.1 Key Structural Differences

Crystallinity vs. Amorphicity

The most fundamental distinction between COFs and general POPs is their degree of structural order. COFs are generally synthesized through reversible bond-forming reactions that allow structural error correction during framework formation. This dynamic process promotes long-range crystallinity and produces relatively well-defined pore architectures [21, 31].

The resulting structural order can be advantageous for photocatalysis because regularly arranged conjugated building blocks can provide more predictable pathways for electronic communication and molecular diffusion. In contrast, many POPs are formed through irreversible cross-linking reactions. Their networks therefore tend to be amorphous or only partially ordered, resulting in broader pore-size distributions and less-defined charge-transport pathways [36, 38].

However, amorphicity should not automatically be interpreted as a disadvantage. The highly cross-linked structures of POPs can provide excellent chemical stability and may contain a large number of accessible defects and chemically active sites. Therefore, the optimal degree of structural order depends on the intended application and the balance between charge transport, porosity, stability, and adsorption.

Mass Transport and Accessibility

Pore architecture directly influences the movement of antibiotic molecules from the bulk solution toward photocatalytically active sites. The relatively ordered and interconnected channels of many COFs can minimize diffusion limitations and facilitate transport of pharmaceutical molecules through the framework [24, 29].

This characteristic is particularly relevant for antibiotics with relatively large and complex molecular structures, including tetracyclines and fluoroquinolones. When pore dimensions are appropriately matched with molecular dimensions, antibiotics can penetrate the framework and interact with internal active sites rather than being restricted to the external surface.

POPs generally exhibit more irregular and tortuous pore networks. Although these structures can provide substantial surface area, some internal sites may be less accessible because of pore constrictions or dense polymeric domains [38, 48]. Consequently, the practical adsorption capacity may differ from the theoretical surface area measured by gas adsorption.

This distinction emphasizes that BET surface area alone is insufficient for predicting photocatalytic performance. Pore connectivity, pore-mouth accessibility, molecular diffusion coefficients, surface chemistry, and antibiotic size must also be considered.

Charge Transport and Photocatalytic Activity

The ordered stacking of conjugated units in some COFs can facilitate directional charge migration and reduce charge-transfer resistance [23, 28]. Efficient charge transport increases the probability that photogenerated electrons and holes will reach the surface before recombination.

In POPs, charge transport can be more heterogeneous because conjugated domains may be separated by structural irregularities. Charge carriers may therefore migrate through localized hopping or between electronically connected domains [43, 60]. Nevertheless, donor–acceptor engineering, extended conjugation, heteroatom incorporation, and appropriate cross-linking can significantly improve charge separation in POP systems.

Thus, structural order represents one factor controlling charge transport, but it is not the sole determinant. The electronic nature of the building blocks, conjugation length, energy-level alignment, defects, and donor–acceptor interactions can all influence the ultimate photocatalytic response.

Stability Profiles

Chemical and hydrolytic stability are critical for photocatalysts intended for prolonged aqueous treatment. Early generations of imine-linked COFs could undergo hydrolysis under strongly acidic or basic conditions, potentially compromising their crystallinity and photocatalytic activity [25].

The development of more robust linkages, including β -ketoenamine structures, has substantially improved the aqueous stability of COFs [26]. Similarly, fully conjugated C–C-linked POPs and triazine-based frameworks can exhibit strong resistance to hydrolysis and chemical attack [36, 37, 58].

Consequently, material stability should be evaluated under conditions that resemble the intended wastewater application rather than solely under ideal laboratory conditions. Repeated irradiation cycles, changes in pH, dissolved salts, natural organic matter, and the presence of competing pollutants may all influence long-term structural integrity.

Overall Performance Trade-Off

The comparison between COFs and POPs indicates that neither material class is universally superior. COFs offer advantages associated with structural order, well-defined porosity, and potentially more efficient charge migration, whereas POPs can provide exceptional chemical robustness, flexible molecular design, and comparatively straightforward synthesis.

The selection of an appropriate framework should therefore be based on the target antibiotic, water matrix, illumination source, reactor configuration, required stability, and desired regeneration strategy. Rational material selection rather than simple comparison of degradation percentages is essential for translating laboratory-scale photocatalytic results into practical environmental applications.

5. ENVIRONMENTAL SAFETY, INTERMEDIATE TOXICITY, AND DEGRADATION PATHWAYS

A critical requirement for photocatalytic remediation is verifying that treatment results in genuine detoxification rather than merely transforming the parent antibiotic into potentially toxic intermediate products [7, 57, 59]. Disappearance of the parent antibiotic from chromatographic measurements does not necessarily demonstrate complete destruction of its biological activity.

Photocatalytic oxidation generally proceeds through multiple consecutive reactions. The initial attack of ROS can generate hydroxylated, dealkylated, deaminated, dehalogenated, or ring-opened products. Some of these transformation products may be less toxic than the parent compound, whereas others may retain antimicrobial activity or exhibit different ecological effects.

Therefore, an environmentally meaningful evaluation should combine chemical analysis with mineralization measurements and biological toxicity testing.

- Integrated Toxicity Assessment
- Analytical Identification
- LC–MS/MS pathway mapping
- Identification of transformation and cleavage products
- Total organic carbon (TOC) mineralization tracking
- Biological Ecotoxicity Assays
- *Vibrio fischeri* bioluminescence inhibition
- *Daphnia magna* acute immobilization
- *E. coli* antimicrobial activity

The integration of these approaches allows researchers to distinguish between parent-compound removal, chemical transformation, and actual detoxification. LC–MS/MS can identify transformation products, while TOC measurements provide evidence for the extent of carbon mineralization. Biological assays can then determine whether the treated water retains measurable toxicity or antimicrobial activity [57, 59].

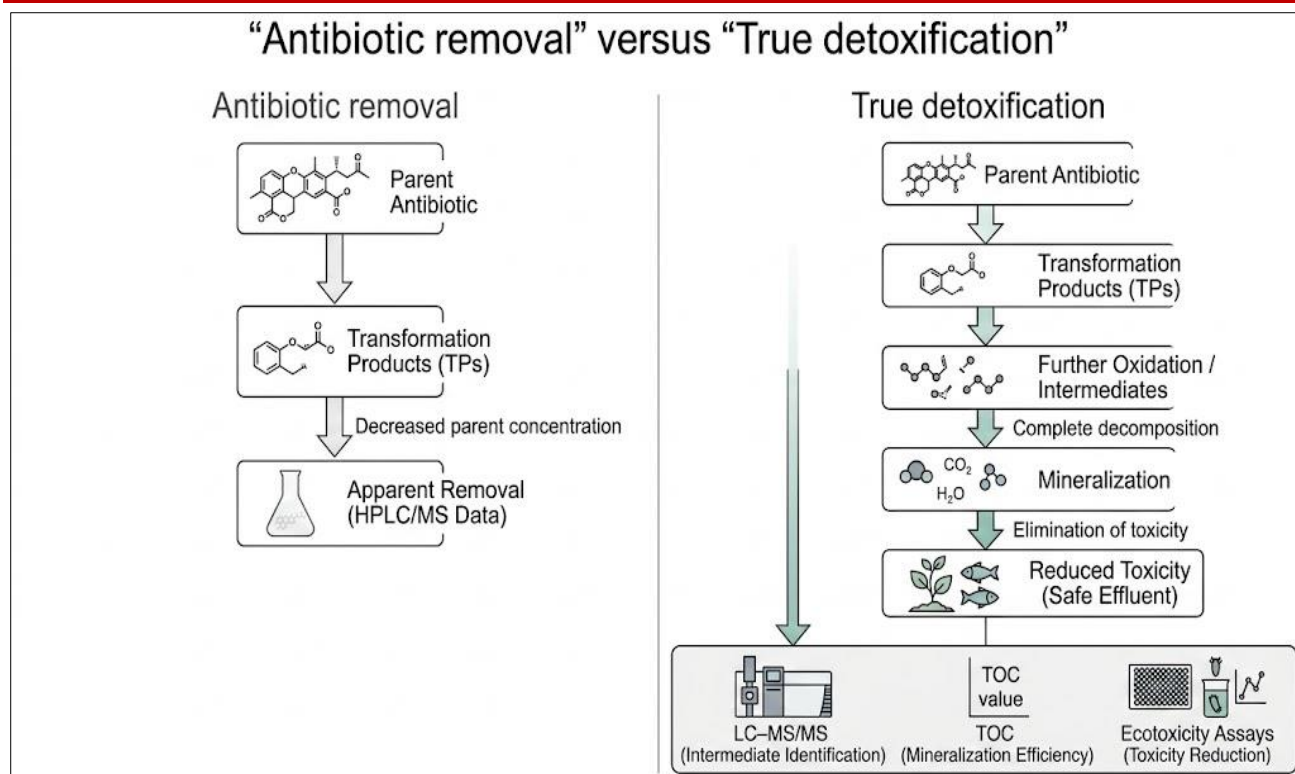


Figure 9: Distinction between parent-antibiotic removal, transformation, and complete detoxification during photocatalytic treatment [7, 57, 59]

5.1 Benchmark Antibiotic Degradation Pathways

Different antibiotic classes exhibit different degradation pathways because their molecular structures

contain distinct functional groups and chemically reactive sites.

Table 4: Representative Photocatalytic Degradation Pathways of Selected Antibiotics

Target Antibiotic	Initial ROS Attack Pathway	Major Intermediate Reactions	Final Mineralization End-Products
Tetracycline (TC)	$\bullet\text{OH}$ / h^+ hydroxylation [9, 15]	Demethylation, deamination, and ring-opening cleavage [8, 53]	CO_2 , H_2O , NH_4^+ [8, 59]
Ciprofloxacin (CIP)	$\text{O}_2^{\bullet-}$ / $\bullet\text{OH}$; piperazine oxidation [9, 59]	Defluorination, piperazine-ring cleavage, and quinolone oxidation [52, 59]	CO_2 , H_2O , NO_3^- , F^- [53, 59]
Sulfamethoxazole (SMX)	$^1\text{O}_2$ / $\bullet\text{OH}$; sulfonamide cleavage [15, 50]	S–N bond cleavage, aniline hydroxylation, and desulfonation [50, 53]	CO_2 , H_2O , SO_4^{2-} , NO_3^- [8, 53]

Tetracycline

Tetracycline contains multiple aromatic and oxygen- and nitrogen-containing functional groups, making it susceptible to hydroxyl radical attack and direct oxidation by photogenerated holes. Hydroxylation can be followed by demethylation, deamination, and progressive cleavage of the tetracyclic structure [8, 53]. Complete mineralization requires further oxidation of the resulting low-molecular-weight intermediates.

Ciprofloxacin

Ciprofloxacin contains a quinolone core, piperazine substituent, and fluorine-containing functional group. Initial oxidation frequently occurs at the piperazine moiety, followed by ring cleavage and

defluorination [52, 59]. These transformations can produce multiple intermediates before further oxidation yields inorganic products such as F^- and nitrogen-containing species.

Sulfamethoxazole

Sulfamethoxazole contains a sulfonamide linkage connecting an aniline moiety with an isoxazole ring. ROS-mediated oxidation can induce S–N bond cleavage, hydroxylation, and desulfonation [50, 53]. Because sulfur- and nitrogen-containing fragments can persist as intermediate species, monitoring of inorganic sulfur and nitrogen products is important when assessing mineralization.

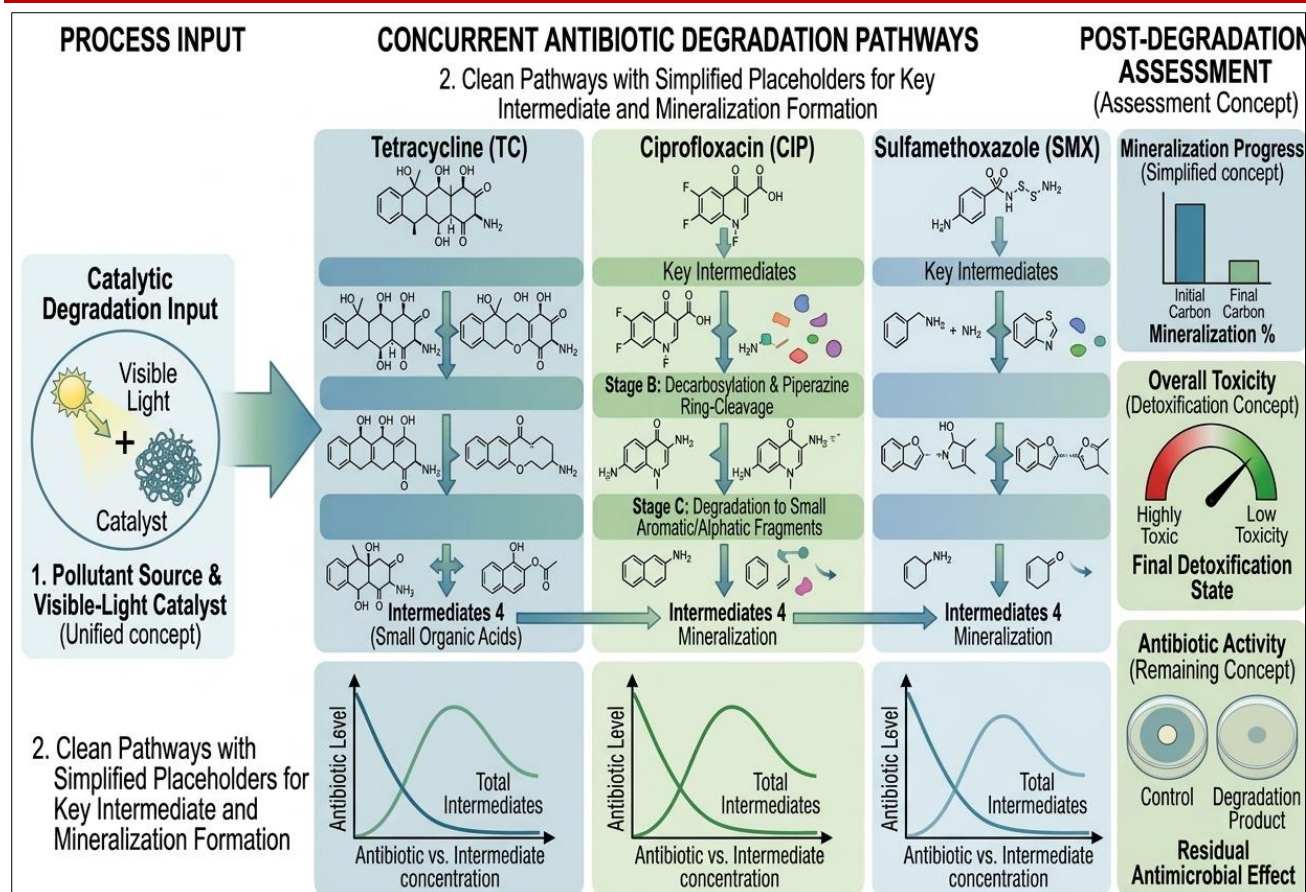


Figure 10: Simplified representative transformation pathways of tetracycline, ciprofloxacin, and sulfamethoxazole during photocatalytic degradation [8, 50, 52, 53, 59]

5.2 Environmental Safety of COF/POP Catalysts

Unlike many metal-containing photocatalytic systems, metal-free COFs and POPs can substantially reduce concerns associated with heavy-metal ion release into treated water [22, 40, 50, 54]. This characteristic is particularly valuable for long-term environmental applications because catalyst-derived metal ions may otherwise introduce secondary contamination.

Potential concerns associated with metals such as Cr, Co, Pb, and Cd include toxicity toward aquatic organisms and persistence in environmental compartments. Metal-free organic frameworks therefore offer an important safety advantage when they remain structurally stable throughout repeated treatment cycles [7, 57].

However, the designation "metal-free" does not by itself guarantee complete environmental safety. The framework itself may release soluble organic fragments if its covalent bonds degrade, and residual monomers or synthesis-derived impurities may also require

consideration. Consequently, future studies should assess framework stability, possible organic leachates, transformation products, and toxicity after repeated photocatalytic cycles.

6. TECHNICAL SCALE-UP AND REAL-WORLD APPLICATION

Transitioning COF- and POP-based photocatalysts from laboratory-scale powder suspensions to continuous industrial systems requires careful consideration of reactor design, catalyst recovery, light utilization, mass transfer, hydraulic retention time, and long-term material stability [10, 56].

Although slurry photocatalytic systems often provide excellent contact between the catalyst and contaminant, separating fine photocatalyst particles from treated water can be technically and economically challenging. Immobilization strategies can overcome this limitation by anchoring the photocatalyst onto mechanically stable supports.

Simplifying Scale-up: Lab to Industry Roadmap for Photocatalysis

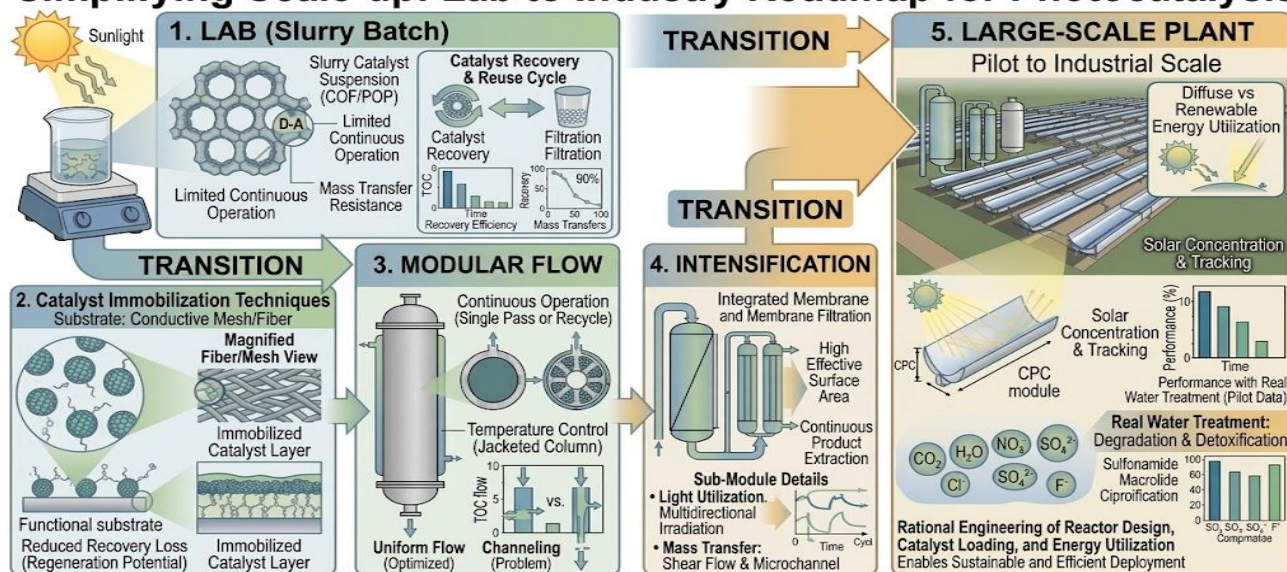


Figure 11: Scale-up and engineering strategies for COF/POP-based photocatalytic wastewater treatment [10, 29, 50, 52, 56]

6.1 Immobilization Strategies

To circumvent costly post-treatment filtration, catalyst aggregation, and particle loss, COFs and POPs can be immobilized onto porous or mechanically stable supports [29, 50, 52]. Immobilization can facilitate catalyst recovery and enable continuous operation while reducing the release of fine particles into treated water.

Electrospun Nanofibrous Membranes

Incorporating COFs into polymeric nanofibers provides a high surface-to-volume ratio while maintaining mechanical flexibility and continuous flow-through capability [29, 50]. The interconnected fibrous structure can expose photocatalytically active regions to the water phase and reduce the diffusion distance between the contaminant and the photocatalyst.

Hydrogel Encapsulation

Entrapping POP powders within alginate, chitosan, or PVDF-based hydrogel beads can facilitate catalyst recovery and enable their use in packed-bed or gravity-driven systems [52, 54]. The porous matrix can provide physical confinement while maintaining contact between the photocatalyst and aqueous contaminants.

However, immobilization must be carefully optimized because excessive encapsulation can shield active sites or introduce additional diffusion resistance. Therefore, the support material should maintain sufficient porosity and light accessibility while providing adequate mechanical stability.

6.2 Comparison of Photocatalytic Reactor Configurations

Table 4: Comparison of Photocatalytic Reactor Configurations for COF/POP Applications

Reactor Configuration	Operating Mode	Mass Transfer Rate	Catalyst Recovery Effort	Technology Readiness Level (TRL)
Slurry Batch Reactor	Batch	High [10]	Complex; requires centrifugation/filtration [50]	TRL 2–3; laboratory scale [9]
Fixed-Bed Column Reactor	Continuous	Moderate [10, 56]	Unnecessary; immobilized bed [29, 56]	TRL 4–5; pilot scale [56]
Membrane Photoreactor	Continuous	High [29, 56]	Integrated; internal membrane rejection [29]	TRL 4–5; pilot scale [56]
Compound Parabolic Collector (CPC)	Continuous / Solar	High [10, 56]	Integrated / Fixed [10, 56]	TRL 6–7; demonstration scale [10, 56]

Among these configurations, slurry reactors are useful for fundamental laboratory investigations because they maximize catalyst–pollutant contact. However, catalyst recovery remains a major limitation. Fixed-bed and membrane-based configurations offer improved opportunities for continuous operation because the

photocatalyst can remain within the reactor while treated water passes through the system [29, 56].

Solar CPC systems are particularly attractive for large-scale environmental applications because they can utilize naturally available solar radiation. Their practical performance, however, depends on solar intensity,

reactor geometry, catalyst optical properties, and the composition of the treated water [10, 56].

6.3 Interference in Real-Water Matrices

Real municipal and industrial effluents contain numerous substances that can interfere with photocatalytic degradation. Natural organic matter (NOM), bicarbonate (HCO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), and other dissolved species can compete with antibiotics for adsorption sites or react with photogenerated ROS [3, 5, 52].

For example, NOM may absorb incident light and reduce photon availability, while inorganic anions can alter ROS chemistry and surface charge. These matrix effects may result in substantially lower degradation rates than those observed in ultrapure laboratory water.

Polymer-backbone tuning and incorporation of hydrophobic functional groups, ionic linkages, or selective recognition sites can improve antibiotic capture in complex water matrices [40, 51]. However, such modifications should be evaluated under realistic wastewater conditions rather than solely in simplified single-solute systems.

Future studies should therefore include representative real-water matrices, competing contaminants, environmentally relevant antibiotic concentrations, repeated-use experiments, and toxicity assessments. This would provide a more realistic evaluation of whether the observed laboratory photocatalytic performance can translate into practical wastewater treatment.

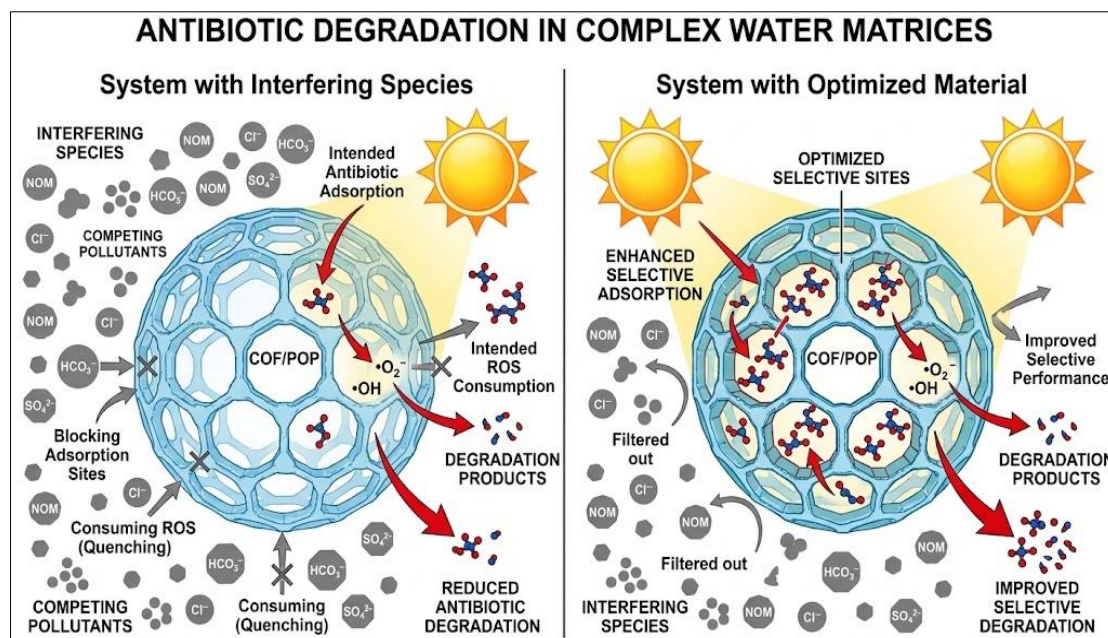


Figure 12: Effects of representative real-water matrix components on antibiotic adsorption and photocatalytic degradation over COF/POP materials [3, 5, 40, 51, 52]

In real wastewater matrices, degradation performance drops significantly compared to ultrapure water due to specific chemical interference mechanisms:

- **Natural Organic Matter (NOM):**
 - *Inner Filter Effect:* NOM absorbs incoming UV–Vis light, shielding the photocatalyst.
 - *Competitive Scavenging:* NOM reacts non-selectively with $\bullet\text{OH}$ radicals.
 - *Active Site Blocking:* Large humic molecules sterically block pore entrances.
- **Inorganic Anions (Cl^- , HCO_3^- , SO_4^{2-}):**
 - *Radical Quenching:* These ions scavenge highly reactive $\bullet\text{OH}$ radicals to form lower-reactivity radical species ($\text{Cl}\bullet$, $\text{CO}_3^{\bullet-}$, $\text{SO}_4^{\bullet-}$), thereby slowing degradation rates.

6.4 Techno-Economic Analysis (TEA) and Life Cycle Assessment (LCA) Perspective

Although COFs and POPs offer metal-free photocatalysis, their overall environmental footprint must be critically evaluated.

- **Solvent & Energy Footprint:** Traditional solvothermal COF synthesis requires toxic organic solvents (e.g., 1,4-dioxane and mesitylene) and multi-day heating at high temperatures.
- **Environmental Net-Benefit:** An LCA perspective requires that the embodied energy and solvent footprint of framework synthesis do not outweigh the environmental benefits of removing trace antibiotic pollutants.
- **Scalable Green Alternatives:** Mechanochemical grinding, room-temperature

aqueous synthesis, and continuous-flow polymerization are essential to make COF/POP scale-up environmentally and economically viable.

7. CONCLUSIONS AND FUTURE PERSPECTIVES

Covalent organic frameworks (COFs) and porous organic polymers (POPs) represent promising metal-free platforms for solar-driven antibiotic remediation [22, 38, 49]. Their structural tunability, high pore accessibility, strong light-harvesting capacity, adjustable electronic structures, and chemical stability provide several advantages over conventional photocatalytic materials [24, 35, 40].

The major strength of these materials lies in the ability to control their properties at the molecular level. By selecting appropriate building blocks, covalent linkages, pore dimensions, donor–acceptor combinations, and surface functional groups, researchers can potentially design photocatalysts specifically targeted toward different antibiotic classes.

Nevertheless, several barriers must be addressed before widespread implementation. These include synthesis cost, scalability, catalyst recovery, long-term stability, realistic wastewater performance, transformation-product toxicity, and standardized evaluation protocols. In particular, future research should move beyond reporting only the percentage removal of the parent antibiotic and should simultaneously consider mineralization, toxicity reduction, catalyst stability, and energy efficiency.

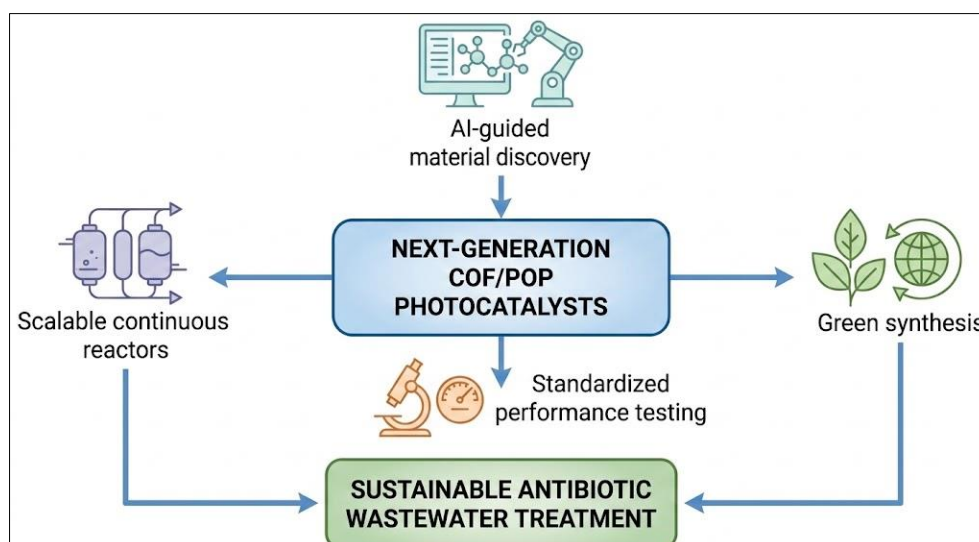


Figure 13: Key research priorities for advancing COF/POP photocatalysts toward sustainable antibiotic wastewater treatment [31, 34, 35, 51, 56, 57]

Emerging Priorities

AI/Machine Learning-Guided Discovery

Computational models and machine-learning approaches can be used to screen large numbers of possible molecular building blocks, covalent linkages, pore structures, and donor–acceptor combinations before experimental synthesis [31, 35]. Such approaches could accelerate the identification of frameworks with suitable band alignment, optical absorption, adsorption affinity, and charge-separation characteristics.

A future design workflow could therefore follow:

Database Generation → Molecular Descriptors
→ Machine-Learning Prediction → Candidate
Selection → Experimental Validation → Model
Refinement

This iterative strategy could reduce experimental trial-and-error and facilitate the discovery of high-performance COF and POP photocatalysts.

Green Synthesis and Scalability

The environmental sustainability of COF and POP production should also be considered alongside their application in wastewater treatment. Conventional solvothermal synthesis may require large quantities of organic solvents, elevated temperatures, and prolonged reaction times. Replacing these procedures with mechanochemical grinding, aqueous synthesis, low-temperature routes, or continuous-flow polymerization could reduce energy and solvent consumption [34, 51].

Green synthesis should therefore become an important criterion when evaluating the overall sustainability of these materials. A photocatalyst that efficiently removes antibiotics but requires a highly energy-intensive synthesis route may provide limited net environmental benefit.

Standardized Reporting

Consistent benchmark protocols should be established for total organic carbon (TOC) removal,

apparent reaction-rate constants (k_{app}), antibiotic removal efficiency, quantum efficiency, catalyst stability, and ecotoxicity under realistic wastewater conditions [8, 56, 57].

Final Perspective

Ultimately, the successful development of COF- and POP-based photocatalytic systems will depend on integrating materials chemistry, photophysics, environmental engineering, toxicity assessment, and

reactor design. The next generation of research should therefore focus not simply on achieving higher antibiotic removal percentages, but on developing stable, recyclable, scalable, low-energy, and genuinely detoxifying treatment systems capable of functioning in complex real-water environments.

To enable meaningful cross-study comparisons, future investigations should adhere to the following reporting guidelines:

Table 5: Proposed Minimum Reporting Checklist for COF/POP Photocatalysis

Parameter Category	Minimum Required Data to Report	Standard Unit / Measurement Standard
Material Characteristics	BET Surface Area, Pore Size Distribution, Optical Bandgap, Linkage Type	$\text{m}^2 \text{g}^{-1}$, nm, eV, FTIR/NMR verification
Reaction Conditions	Catalyst Dosage, Pollutant Concentration, Solution pH, Temperature, Volume	g L^{-1} , mg L^{-1} , pH value, $^{\circ}\text{C}$, mL/L
Light Source Parameters	Light Source Type, Spectrum/Cut-off Filter, Light Intensity, Illumination Area	W m^{-2} or mW cm^{-2} , nm, cm^2
Performance Metrics	k_{app} (Kinetic Rate), Apparent Quantum Yield (AQY), TOC Removal	min^{-1} , %, % TOC removal
Matrix & Ecotoxicity	Matrix Composition (TOC/COD, Ions), Standardized Bioassays	mg L^{-1} , Bioassays (<i>V. fischeri</i> , <i>D. magna</i>)

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