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Variation of pH and Composite Dosage on the Photocatalytic Activity of CuO/Epoxy Composites: An expanded review

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Abstract

This review consolidates current evidence on how solution pH and composite dosage (loading) govern the photocatalytic activity of CuO/epoxy composites for water treatment. Mechanistically, pH modulates surface charge relative to the CuO p_{Hpzc} (~8–9), pollutant speciation, band-edge alignment, and ROS pathways, while dosage shapes active-site density and the internal light field of pigmented epoxy films. Across supported CuO and polymer-immobilized oxides, the literature consistently shows best performance near neutral to slightly acidic pH (≈5–7), whereas very acidic or strongly alkaline media introduce instability, unfavorable adsorption, or enhanced recombination. Dosage exhibits a single-peak dependence: increasing loading improves rates up to an optimum, after which scattering/shading and aggregation lower the effective photon flux; practical ranges cluster around 0.3–1.0 g·L⁻¹ (slurry equivalents) or ~0.1–2 wt% for thin epoxy coatings when thickness and areal loading are reported. Comparative data from ZnO/epoxy under sunlight/visible irradiation confirm the same qualitative pH and loading trends, supporting transferable optimization rules. The review concludes with practical windows for lab screening and highlights the need for thickness-resolved optical/kinetic reporting and long-cycle stability testing in real effluents.

Keywords: CuO; Epoxy; Photocatalysis; pH; Catalyst Loading; Reactive Oxygen Species; Wastewater

1. Introduction

Photocatalysis is an advanced oxidation route in which light-excited semiconductors generate reactive oxygen species (ROS) able to oxidize and mineralize persistent organics under mild, often solar-driven conditions [1,2]. Compared with conventional treatments, photocatalysis can reduce chemical inputs and secondary waste while targeting dyes, pharmaceuticals, and other refractory pollutants [2–4]. Within this family of materials, copper (II) oxide (CuO) is compelling because its narrow band gap (~1.2–1.9 eV) enables visible-light activation, and its stability and low-cost favor scale-up for environmental applications [2–4,5]. The main practical drawback of nanoparticulate CuO is agglomeration and difficult recovery, which depress apparent kinetics and reusability in slurry reactors [3,4].

Embedding CuO in epoxy addresses these constraints by immobilizing particles, limiting aggregation, and enabling straightforward reuse as films or coatings on glass, metal, or ceramics [3,14,16]. Epoxy provides mechanical robustness and chemical resistance, but performance depends strongly on microstructure: good dispersion, controlled film thickness, and appropriate oxide loading are needed to avoid diffusion penalties and optical losses in pigmented layers [14,16,19]. When these factors are tuned, immobilized CuO can approach the activity of powders while simplifying post-treatment separation and repeated cycling [3,14].

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Two operating variables dominate performance in CuO/epoxy systems: solution pH and composite dosage (loading). pH governs catalyst surface charge relative to CuO's point of zero charge (typically near pH 8–9), pollutant speciation, and ROS pathways; very acidic or highly alkaline media can also undermine structural stability or raise charge-carrier recombination [11–13,15–16]. Across supported CuO and polymer-immobilized oxides, the literature repeatedly shows best rates near neutral to slightly acidic conditions (\approx pH 5–7), where adsorption thermodynamics and ROS formation are jointly favorable [11–12,17,20]. The second lever—dosage—controls active-site density and photon transport. Increasing loading boosts activity up to a single optimum; further addition causes scattering/shading and aggregation, reducing the effective photon flux and accessible surface [2,12–14,19]. For immobilized coatings, this “effective dosage” is captured by oxide wt.%, film thickness, and areal loading rather than slurry concentration [14,16,19].

Finally, polymer-bound ZnO systems provide a useful analog for cross-checking trends when direct CuO/epoxy datasets are limited. ZnO/epoxy coatings exhibit the same qualitative pH-rate profile and the same rise-to-optimum behavior with loading under sunlight/visible conditions, reinforcing transferable optimization windows for epoxy-based photocatalysts [18,21,22]. Building on this context, the present review focuses on how pH and dosage co-determine CuO/epoxy performance, compiles representative operating ranges, and highlights practical considerations for lab-scale screening and coating design [2–4,11–12,14,16,18,21,22].

2. Photocatalytic Mechanism of CuO/Epoxies Composites

Under illumination at energies \geq the band gap, CuO generates electron-hole pairs that participate in interfacial redox chemistry; conduction-band electrons reduce dissolved O_2 to superoxide ($\cdot O_2^-$), while valence-band holes oxidize surface H_2O/OH^- to hydroxyl radicals ($\cdot OH$), and the resulting ROS oxidize adsorbed organics toward mineralization [1,9–11]. In epoxy-immobilized architectures, the polymer provides a mechanically robust, chemically resistant host that suppresses particle agglomeration and limits catalyst loss while enabling handling and reuse; when dispersion is uniform and films are thin, optical attenuation and diffusive barriers are minimized so that photon utilization and mass transfer improve relative to loosely packed powders [3,12,14,16]. Beyond simple immobilization, the polymer-oxide interface governs charge separation and transport: interfacial traps and local electric fields can either assist spatial separation of carriers or promote non-radiative recombination, so controlling oxide loading, dispersion quality, and film thickness is central to sustaining a high steady-state ROS flux [12,14,16]. Solution chemistry then co-modulates the pathway: pH shifts surface charge relative to the point of zero charge (typically near 8–9 for CuO), alters pollutant speciation and adsorption thermodynamics, and changes band-edge alignment with solution redox couples; mildly acidic to near-neutral media often balance adsorption and stability, whereas strong acid/base can accelerate recombination or induce surface instability that quenches activity [11–13,15–16,20]. Composite dosage dictates the density of accessible active sites and the internal light field; loadings below the optical/kinetic optimum under-utilize photons, while excessive pigment creates scattering/shading and longer diffusion paths that raise recombination, reducing effective quantum efficiency despite higher nominal surface area [2,12–14,19]. Dissolved oxygen acts as the primary electron acceptor ($O_2 + e^- \rightarrow \cdot O_2^-$), and subsequent solution reactions generate additional oxidants (e.g., $\cdot OH$ via $\cdot O_2^-/HO_2\cdot$ chains or H_2O_2 intermediates), so maintaining adequate O_2 transport through the coating and boundary layer is also important; collectively, the interplay of light absorption, charge generation and separation, interfacial adsorption, and ROS kinetics—each tuned by pH and composite loading—sets the observed photocatalytic rate in CuO/epoxy systems [1–3,9–12,14–16,19–20].

3. Effect of pH on Photocatalytic Activity

CuO's surface charge reverses around its point of zero charge (typically near pH 8–9), favoring adsorption of anionic species below that range and cationic species above it [11–13]. pH simultaneously tunes pollutant ionization and ROS pathways; mildly alkaline conditions increase OH^- availability for $\cdot OH$ formation, whereas highly acidic or strongly basic media can induce catalyst instability (e.g., leaching/etching) or elevate charge-carrier recombination [12,15–16]. Across epoxy-immobilized oxides and supported CuO systems, slightly acidic to neutral pH (\approx 5–7) frequently maximizes apparent kinetics by balancing adsorption and structural stability [11–12,17,20]. Polymer-immobilized ZnO under sunlight shows the same qualitative pH profile—low rates in strong acid, a rise toward neutral/mild base, and a decline again at high pH—providing a relevant analog for CuO/epoxy optimization [21,22].

Additional nuance. The effective pH response depends on synthesis route and surface chemistry: the pH pzc of CuO can shift with particle size, surface hydroxylation, and dopants, which changes the crossover between anion- and cation-selective adsorption [11–13]. pH also alters band-edge positions and flat-band potentials, modifying the driving force for O_2 reduction and H_2O/OH^- oxidation; near-neutral media often maximize ROS yield without compromising film integrity [12,15–16]. In epoxy films, local microenvironments may deviate from bulk pH because of buffering and slower

ion transport inside the polymer, so reporting bulk pH alongside ionic strength and (when available) the coating's areal loading improves reproducibility across studies [14,16,19–20]. Finally, very low pH can promote Cu leaching, while very high pH may passivate surfaces or thicken hydration layers—both scenarios reduce long-term activity despite transient adsorption gains [12,15–16,20].

Table 1 Effect of pH on CuO/epoxy photocatalysis

pH	Composite dosage ($\text{g}\cdot\text{L}^{-1}$)	Degradation efficiency (%)	Observation
3	0.5	60–75	Strong protonation; good anionic adsorption but possible instability [11,16]
5	0.5	75–88	Favorable adsorption and ROS balance [11–12]
6–7	0.75	85–92	Often near-optimal trade-off [11–12,20]
9	1.0	70–85	Better for cationic pollutants; can raise recombination [12,15]
10	1.0	60–75	Strong negative surface charge; unfavorable for anionic adsorption [12,15]

4. Effect of Composite Dosage on Photocatalytic Performance

Composite dosage (loading) controls the density of accessible active sites and the internal light field of CuO/epoxy systems. At low loading, photon absorption and site availability are insufficient, limiting apparent kinetics; increasing the dosage raises both until a single optimum is reached. Beyond that point, additional solids induce Mie scattering and shading, bury active surface within crowded pigment domains, and lengthen diffusion paths inside the coating, which collectively elevate recombination and reduce the effective quantum efficiency [2,12–14,19]. In immobilized formats, the “effective dosage” is best reported as oxide wt% together with film thickness and areal loading, because identical wt.% at different thicknesses can yield very different rates due to optical attenuation and mass-transfer constraints [14,16,19]. Good dispersion postpones aggregation and preserves accessible area, whereas over-pigmented or poorly dispersed films suffer crowding and partially inactive regions. Typical laboratory optima cluster around $0.3\text{--}1.0\text{ g}\cdot\text{L}^{-1}$ in slurry equivalents or $\sim 0.1\text{--}2\text{ wt.}\%$ in thin epoxy coatings (with explicit thickness), but the exact maximum shifts with reactor optics, pollutant concentration, and solution chemistry [2,13–14,19]. Consistent rise-to-maximum behavior followed by decline at higher loading is also observed for polymer-immobilized ZnO under sunlight/visible conditions, reinforcing the generality of these trends for epoxy-bound photocatalysts [18,21,22]. Because adsorption and ROS turnover are pH-dependent, the optimum loading can move with pollutant charge and ionic strength; reporting pH, ionic strength, thickness, and areal loading alongside performance is therefore essential for reproducibility [2,12–14,19,21–22].

Table 2 Composite dosage vs. performance

Dosage ($\text{g}\cdot\text{L}^{-1}$)	pH	Degradation efficiency (%)	Observation
0.25	6	60–68	Limited active-site density [13]
0.50	6	80–90	Balanced sites vs. light penetration [2,13]
0.75	6	88–94	Near maximum before scattering [13,21]
1.00	6	85–90	Onset of shading/scattering [2,14]
1.50	6	80–86	Aggregation and photon attenuation [13,19]

5. Comparative Insights with Other Polymer-Immobilized Oxides

Across epoxy-immobilized metal oxides, pH and loading govern performance through the same coupled mechanisms—electrostatic adsorption, ROS pathways, and photon transport—so the qualitative response of ZnO/epoxy and TiO₂/epoxy mirrors that of CuO/epoxy: rates are typically highest near neutral pH at moderate loadings and decline at extremes due to adsorption penalties, accelerated recombination, or optical losses [15,18,20–22]. The principal material distinction is spectral: CuO is intrinsically visible-light responsive because of its narrow band gap, whereas

TiO₂ generally requires UV photons unless surface-modified or doped; ZnO can operate under UV/solar but is more vulnerable to photocorrosion in acidic media and over prolonged irradiation [15,18,20–22]. Despite these differences, immobilization quality—oxide dispersion within the polymer, film thickness, and areal loading—dominates practical outcomes in all three systems: uniform dispersion suppresses agglomeration and improves interfacial contact, thin optically transparent films reduce scattering and shorten diffusion paths, and reporting areal loading alongside thickness enables reproducible comparisons across laboratories [3,14,18–20]. Heterojunction strategies are transferable as well: coupling CuO with ZnO or conductive/porous phases can facilitate charge separation and broaden the operating window, but the same trade-offs remain—over-pigmented layers introduce shading, while overly dilute coatings under-utilize incident photons [14,18–20]. In short, once immobilized, CuO/epoxy, ZnO/epoxy, and TiO₂/epoxy are governed by the same device-level constraints, with CuO offering the pragmatic advantage of visible-light activation and ZnO/TiO₂ serving as useful benchmarks for pH and loading optimization under similar reactor optics [15,18,20–22; 3,14,18–20].

6. Practical Operating Windows and Outlook

For lab-scale screening, pH = 5–8 is a robust starting window (finer steps around 6–7 for common dyes/pharmaceuticals), avoiding extremes (<3 or >11) unless targeting specific ionic pollutants [11–12,20–22]. For dosage, explore 0.3–1.0 g·L⁻¹ in slurry analogs or thin epoxy films at 0.1–2 wt.% with controlled thickness; always report film thickness and areal loading (e.g., mg·cm⁻²) to enable reproducibility and fair cross-study comparison [2,13–14,19]. If baseline activity is low, consider conductive/porous modifiers (e.g., rGO, SiO₂, biopolymers) to promote charge separation and mechanical robustness, but avoid over-pigmentation that induces optical shading; dispersion quality should be verified and maintained across samples [6–8,10,17]. Because immobilized coatings reshape photon transport, performance reporting should also include irradiance and spectral distribution, reactor geometry/optical path, and ionic strength, since these parameters can shift the apparent optimum for both pH and loading [2,13–14,19].

Looking forward, priority areas include coupling optical modeling with thickness-resolved kinetics to rationalize the single-peak response to loading, systematic long-cycle stability tests in real effluents (including fouling and matrix-effects), and the design of hybrid CuO systems that sustain activity under low irradiance through improved charge management and interfacial engineering [14,16,19]. Standardized datasets that jointly report pH, ionic strength, film thickness/areal loading, and light metrics will accelerate benchmarking and scale-up of CuO/epoxy photocatalysts for continuous-flow water treatment [2,13–14,19–22].

7. Conclusion

CuO/epoxy composites are credible visible-light photocatalysts that merge intrinsic CuO activity with the handling and reusability advantages of polymer immobilization. Across the literature, performance is dominated by two levers—solution pH and composite dosage—because they co-tune adsorption thermodynamics, band-edge driving forces, photon transport, and charge-carrier recombination. A consistent outcome is that near-neutral to slightly acidic pH (≈5–7) and moderate loading deliver the best trade-off between ROS generation and structural stability, whereas very acidic or strongly alkaline media and over-pigmented coatings introduce instability, unfavorable adsorption, or optical penalties that depress apparent kinetics [2–4,11–12,14,16]. Comparative evidence from polymer-immobilized ZnO corroborates the same qualitative pH and loading dependencies under sunlight/visible irradiation, suggesting generalizable optimization rules for epoxy-based photocatalysts [18,21,22].

Practically, effective screening should report pH, ionic strength, irradiance/spectrum, oxide wt.%, film thickness, and areal loading to enable reproducibility and rational comparison across studies. Within these reporting standards, thin, well-dispersed coatings tend to outperform thick, opaque layers, and coupling modest loading with pH near neutrality is a robust starting point for common dyes and pharmaceuticals [2–4,11–12,14,16,18,21,22]. Looking ahead, integrating optical modeling with thickness-resolved kinetics, along with long-cycle stability in real effluents, will be key to translating CuO/epoxy from lab exploration to reliable continuous-flow operation.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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