


Engineered biochar-metal oxide nanocomposites for targeted dye remediation in textile wastewater

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ABSTRACT

The global textile industry releases nearly 280,000 tons of synthetic dyes each year, generating persistent pollutants that disrupt aquatic ecosystems as well as pose carcinogenic and mutagenic risks. Conventional treatment technologies such as activated carbon adsorption, advanced oxidation processes, and biological degradation often fail to address the complexity of real industrial effluents. This review critically evaluated engineered biochar metal oxide nanocomposites (BMO-NCs) as emerging dual-functional materials that integrate adsorption with photocatalytic degradation for targeted dye removal. The authors highlighted how the tunable surface chemistry, hierarchical porosity, and electronic conductivity of biochar synergize with metal-oxide-driven reactive oxygen species ($\bullet\text{OH}$, $\bullet\text{O}_2^-$, h^+) to enhance degradation pathways. While laboratory studies frequently report >95% dye removal, real-wastewater conditions such as fluctuating pH, high salinity, and competing contaminants significantly reduce performance. To bridge this gap, key research priorities were identified, including mechanistic validation of ROS via in-situ ESR, LC-MS tracking of degradation intermediates, long-term regeneration and metal-leaching assessments, and standardized testing protocols for industrial effluents. This review provided design principles for scalable, safe, and circular-economy-aligned BMO-NCs, underscoring their potential contribution to Sustainable Development Goal 6.

Keywords: biochar-metal oxide nanocomposites, textile wastewater treatment, adsorption-photocatalysis synergy, reactive oxygen species, synthetic dye degradation.

INTRODUCTION

The rising global demand for textiles, printing, leather, paint, food, pharmaceuticals, and other industrial processes have led to the generation

of vast level of contaminated water with synthetic organic dyes (Oguanobi et al., 2025; Periyasamy, 2024; Uddin, 2021). Globally, an estimated 700,000 tons of synthetic dyes are generated annually, with approximately 280,000 tons released

into effluents, making dyes one of the prominent classes of industrial pollutants (Sahu and Poler, 2024; Singh et al., 2024). These dyes are designed for widespread use, contributing to their persistence in aquatic systems. Their presence reduces aesthetic quality as well as poses severe eco-toxicological and health hazards (Rajak et al., 2024). Figure 1 summarizes the principal industrial sources of dye pollution (e.g., textile, leather, printing, paper and pharmaceutical sectors) and the main pathways by which dye-laden effluents impair aquatic ecosystems, reduce water quality, and create human-health risks. The organic dyes, often associated with aromatic structures, reduce light and oxygen penetration, which negatively affects aquatic ecosystems, photosynthesis, and microbial activity (Kumari, 2024; Mukherjee et al., 2024). Furthermore, certain synthetic dyes exhibit carcinogenic, mutagenic, and other adverse health impacts in humans, including cancer and respiratory infections, demand the urgent need for effective remediation strategies before discharge into water bodies (Kumari, 2024; Ramamurthy et al., 2024).

Addressing this critical environmental issue requires innovative remediation technologies that are both effective and sustainable. Numerous techniques, such as, spanning physicochemical, and biological method working on removal of organic dyes from wastewater (N Lotha et al., 2024; Sornaly et al., 2024). Adsorption methods, such as activated carbon, efficiently remove dyes and are simple to use; however, their cost, limited sustainability, and reduced effectiveness against complex dye mixtures restricted their practical applications (Akinnike et al., 2024). Advanced oxidation processes (AOPs), such as photocatalysis, generate reactive oxygen species ($\cdot\text{OH}$, h^+ and $\cdot\text{O}_2^-$) that efficiently degrade pollutants. However, their practical application is limited by high energy requirements, complex setups, and low effectiveness in treating real effluents (Iqbal et al., 2024). Biological methods, while environmentally friendly, often struggle with the recalcitrant nature and structural complexity of many synthetic dyes, which are inherently resistant to biodegradation (Sharma et al., 2024). Despite these advancements, conventional wastewater treatment plants often failed to remove persistent organic dyes, highlighting the need for more robust and effective treatment technologies.

Engineered biochar based nanocomposites (NCs), particularly those incorporating metal

oxides, constitute an emerging and sustainable solution for dye removal (Ahmad et al., 2024; Damahé et al., 2024). Pyrolysis of low-cost waste biomass yield biochar, a material characterized by a high surface area, significant porosity, and tunable surface chemistry. The incorporation of metal oxide can further functionalize biochar, creating the composites capable of the simultaneous adsorption and photocatalytic degradation of pollutants (Awais Ahmad et al., 2024; Attiqah Ahmad et al., 2024). This integration improves surface charge and pH tune-ability, allowing for efficient wastewater management (Kumar et al., 2025). These synergistic properties of metal oxide biochar NCs enable them to produce next-generation materials for integrated dye remediation. The synergistic action of adsorption and photocatalytic degradation allows these NCs to efficiently remove pollutants from complex wastewater, surpassing the performance of conventional treatments (Haleem et al., 2023). Recent studies have demonstrated that the biochar-supported ZnO composites effectively degrade organic dyes such as methylene blue and rhodamine B. The photocatalytic activity is significantly enhanced by the incorporation of ZnO, with biochar providing adsorption sites for the dye molecules (Kaur, 2022). Another study demonstrated the preparation of peanut shell biochar-loaded $\text{TiO}_2/\text{Ce}-\text{C}_3\text{N}_4$ heterojunctions, significantly enhancing photocatalytic activity for methylene blue (MB) degradation under visible light. The composite achieved 100% MB removal after 30 minutes of adsorption and 7 minutes of irradiation, with a rate constant 19 times higher than $\text{Ce}-\text{C}_3\text{N}_4$ and 16 times higher than TiO_2 . The synergistic adsorption-photocatalytic effect and reduced band gap energy contributed to efficient pollutant removal and excellent stability (Li et al., 2024). A similar study synthesized biochar-supported copper oxide composite (BC-CuO) to activate peroxymonosulfate (PMS) for treating highly saline wastewater. The BC-CuO/PMS system achieved rapid removal of various pollutants, including Methylene Blue, Rhodamine B, and Ciprofloxacin, with efficiencies up to 100% under highly saline conditions. The degradation process was dominated by singlet oxygen ($^1\text{O}_2$), and the results suggest that BC-CuO/PMS is a promising technique for removing organic pollutants from complex and saline wastewater systems (Li et al., 2020).

In this study, dye removal using biochar-metal oxide nanocomposites (BMO-NCs) was

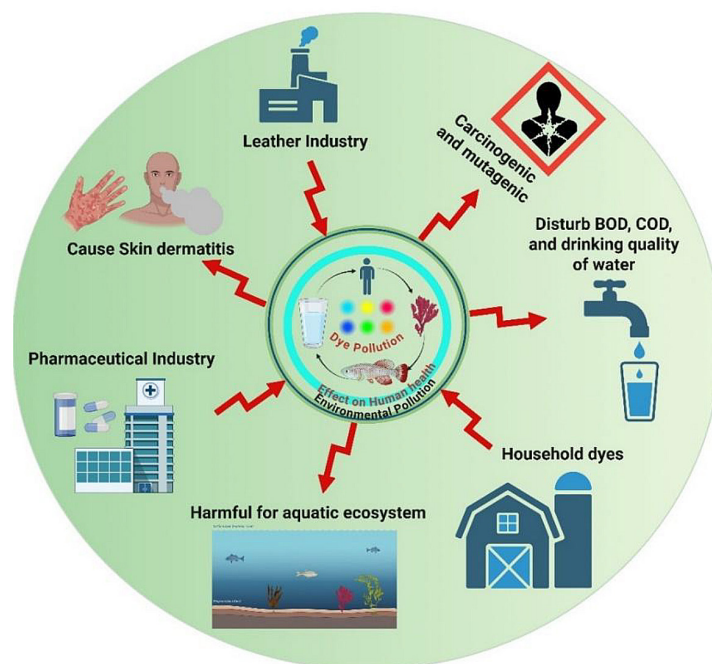


Figure 1. Major industrial sources of dye pollution and their associated environmental and human health impacts, including aquatic ecosystem degradation, water-quality deterioration, skin disorders, and carcinogenic risk

comprehensively examined. Nevertheless, a significant knowledge gap persists between lab scale advancement and practical implementation at the industrial level. Previous studies lack an in depth analysis of real-world complexities, such as dye mixtures, varying pH, salinity, co-contaminants, and comprehensive economic or lifecycle assessments essential for long-term feasibility (Mogashane et al., 2024; Hellal et al., 2025). Future research is required to validate the scalability, regeneration potential, and cost effectiveness of emerging compounds. Unlike conventional reviews focused on synthetic dye solutions, this paper emphasized material performance under real wastewater conditions. The design, mechanisms, and efficacy of BMC-NCs, were critically evaluated with a focus on their practical application in industrial wastewater treatment.

CHEMISTRY-GUIDED DESIGN

Chemistry-guided design serves as the foundational framework for engineering biochar metal oxide nanocomposites (BMO-NCs) with high selectivity, durability, and efficiency for dye remediation under complex wastewater conditions (Amdeha, 2024; Aslam et al., 2024). The performance of BMO-NCs is governed by the interplay between biochar surface chemistry as well as the

electronic and catalytic properties of the incorporated metal oxides (Amdeha, 2024; Zheng et al., 2025). Together, these features define how the composite interacts with cationic, anionic, and structurally diverse azo dyes. At the molecular scale, the adsorption of ionizable dyes in aqueous media is primarily governed by electrostatic interactions, which are strongly modulated by solution pH relative to the point of zero charge of the material (pH_{pzc}) (Sayed et al., 2025; Strebel et al., 2024). Conversely, protonation at $pH < pH_{pzc}$ ($\equiv C-OH + H^+ \rightarrow \equiv C-OH_2^+$) generates a positively charged surface that enhances the binding of sulfonated anionic dyes like Congo Red and Eriochrome Black T (Oluwasina et al., 2024). Such charge-governed behavior is substantiated by zeta potential measurements, surface titrations, and density functional theory (DFT) insights, showing how protonation states alter surface electron density and binding affinity (Qin et al., 2024; Y. Zhang et al., 2024). In realistic textile effluents, the charge behavior of BMO-NCs is governed not only by pH_{pzc} but also by electrical-double-layer (EDL) structure and Donnan ion partitioning. Elevated ionic strength collapses the Debye length and compresses the diffuse layer, attenuating the effective surface potential and diminishing long-range electrostatic attraction a trend consistently observed through reduced magnitude of zeta

potential and lower adsorption of charged dyes at high salinity (George et al., 2024; Kar et al., 2025; Wu, 2022). At high electrolyte concentrations, Stern-layer charge compensation becomes significant: specifically, adsorbing ions (e.g., Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-}) neutralize surface functional groups, suppressing accessible charge sites and reducing chemisorption capacity. Moreover, strong ion pairing (e.g., Na^+ –dye $^-$ or SO_4^{2-} –dye $^+$ complexes) lowers the activity coefficients of ionic dyes, effectively decreasing the fraction of “free” dye available for interaction with active sites. Collectively, EDL compression, Donnan exclusion, Stern-layer compensation, and ion-pairing effects explain the substantial performance disparities observed between deionized laboratory systems and complex saline wastewaters.

Beyond electrostatic attraction, the π – π interactions between the sp^2 -hybridized carbon domains of biochar and aromatic dye rings significantly strengthen the adsorption of cationic dyes, while hydrogen bonding with surface $-\text{OH}$, $-\text{COOH}$, and $-\text{C}=\text{O}$ groups further promotes dye adsorption (Wang et al., 2025). In addition, coordination and Lewis acid base interactions arise when metal centers (e.g. Cu^{2+} , Fe^{3+} , Mn^{3+} , Zn^{2+}) bind electron-rich functional groups on dye molecules (Ahmed et al., 2025). The porous architecture of engineered biochar provides confinement effects and capillary driven pore filling, enabling rapid mass transfer and pre-concentration of pollutants at the catalytic interface. Incorporating metal oxides introduces oxygen vacancies, surface hydroxylation, and tunable redox as well as band-edge properties that strongly affect adsorption and photocatalytic activity (Yang et al., 2025). Oxygen-deficient sites act as electron traps and increase chemisorption, while heterojunction formation between biochar and metal oxides suppresses electron hole recombination and accelerates the generation of reactive oxygen species (Hailili and Gan, 2025). These combined effects significantly amplify the dual-function efficiency of BMO-NCs under visible-light or oxidant-assisted conditions, even in the presence of competing ions and co-contaminants. Chemistry-guided design provides a mechanistic blueprint enabling BMO-NCs to selectively target and efficiently remove cationic dyes, anionic sulfonated dyes, and recalcitrant azo dyes the degradation of which requires both strong adsorption and catalytic bond cleavage. This design philosophy not only rationalizes material performance, but also

provides information on the development of next-generation composites optimized for real industrial wastewater environments. In the following sections, these chemistry-guided principles are further deconstructed into charge-specific design strategies for cationic and anionic dyes, providing a basis for rational tailoring of BMO-NCs for targeted dye remediation.

Charge-specific design strategies

Textile wastewater contains highly conjugated and ionizable dyes that remain mobile due to strong resonance stabilization and hydrophilicity (Periyasamy, 2024; Ran et al., 2024). As a result, the performance of (BMO-NCs) depends not only on porosity or surface area but largely on the electrostatic compatibility between the dye molecules and the engineered surface charge of the composite. Therefore, charge specific design acts as the primary mechanism governing dye recognition, interfacial accumulation, and catalytic activation (Periyasamy, 2024). Surfaces switch between protonated ($-\text{M}-\text{OH}_2^+$, $-\text{NH}_2^+$) and deprotonated ($-\text{M}-\text{O}^-$, $-\text{COO}^-$) states, even a 1–2-unit shift in pH relative to pH_{pzc} may alter adsorption capacity by more than an order of magnitude. This shift modifies electrostatic attraction, reduces competition between protons and dye ions, as well as affects both inner- and outer-sphere complexation pathways (P. Zhang et al., 2024)

ZnO biochar and CuO biochar composites develop negative zeta potentials (-20 to -35 mV) at near-neutral pH, enabling $>95\%$ MB removal through combined electrostatic attraction, π – π stacking, and Lewis base interactions from oxygenated groups on biochar (Ameen et al., 2025; Yadav et al., 2026). Conversely, Mn–CuO@biochar and Fe-modified biochars with high pH_{pzc} values (>5.5) maintain strong positive charge under acidic conditions. These materials achieve $>98\%$ CR and EBT removal due to electrostatic attraction, hydrogen bonding, and Lewis acidic interactions at metal oxide sites (Ullah et al., 2025). In real effluents, competitive ions such as Cl^- and SO_4^{2-} can partially screen electrostatic forces; therefore, maintaining high surface charge density is essential for stable performance under high-ionic-strength conditions (Liu et al., 2025). Charge-specific adsorption also enhances catalytic degradation. Local enrichment of dye molecules at the BMO-NC interface reduces mass-transfer limitations and increases the probability of dye–ROS

interaction (Suthar and Patidar, 2024). Negatively charged surfaces promote O_2 activation and enhance $\bullet O_2^-$ generation, whereas protonated metal oxide sites accelerate H_2O_2 activation and $\bullet OH$ production through Fe^{2+}/Fe^{3+} , Cu^+/Cu^{2+} , and Mn^{3+}/Mn^{4+} redox cycling (Feng et al., 2024; Suthar and Patidar, 2024; Yang et al., 2024). This synergy is especially important for azo dyes, where complete cleavage of the $-N=N-$ bond requires both selective pre-concentration and sustained ROS attack (Oral et al., 2024).

Thus, charge-specific design provides the conceptual framework for achieving selective adsorption, efficient ROS generation, and hybrid adsorption–oxidation pathways. The following subsections translate these principles into targeted strategies for cationic, anionic, and azo dyes, forming a unified design logic for textile wastewater.

Cationic dyes

Cationic dyes, like methylene blue (MB), carry a positive charge in aqueous solutions (Yildirim et al., 2024; Sannino et al., 2024). To effectively remove the dyes through electrostatic attraction, the adsorbent surface should be negatively charged (Attia Ahmad et al., 2024; Ashebir et al., 2024). Moreover, pH significantly influenced the surface charge of an adsorbent link to the point of zero charge (pHpzc) (Adawiyah et al., 2025; Amdeha, 2024). From pHpzc if the pH is increased, the adsorbent surface tend towards negative charge (Oraon et al., 2024), which enhances the electrostatic attraction with positively charge cationic dyes like MB, leading to increased adsorption and degradation efficiencies (Radoor et al., 2024). Studies on $CuO@BSS$ NCs, practical for MB removal, showed their pHpzc was around pH 3.8, and their outer surface charge was negative over a broad pH range above this value (Gomaa et al., 2022). Additionally, if the pH values decrease from point of zero charge (PZC), surface become positive charge due to protonation, causing repulsive forces with cationic dyes and reducing removal efficiency; H^+ ions also compete for active sites at low pH (Ederer et al., 2025; Gomaa et al., 2022). Similarly, another study shows that MB adsorption onto ZnO /biochar is highly pH dependent, with acidic conditions limiting uptake due to H^+ competition, while alkaline conditions enhance electrostatic attraction between the deprotonated biochar surface and cationic MB. As a result, adsorption capacity and removal efficiency

increase sharply with pH and stabilize at higher alkaline values. Similarly, biochar exhibited higher adsorption of MB under alkaline conditions compared to acidic conditions, highlighting the influence solution pH on adsorbent dye interactions (Borthakur et al., 2021; Yan et al., 2024).

For aromatic cationic dyes like MB electrostatic forces and π - π interaction are also crucial for the adsorption (Salahshoori et al., 2024). These interactions occur between graphitic domains present in the biochar structure and aromatic rings in dye molecules (Liang et al., 2024). The degree of aromaticity in the dye molecule plays a crucial role in their interaction with adsorbent. The instant MB from wood biochar removed by potassium hydroxide modified phenol formaldehyde via electrostatic attraction, π - π interactions and pore-filling (Hakami, 2023; Ning et al., 2024) whereas the date palm-derived Fe-modified biochar also removes MB through hydrogen bonding, electrostatic attraction, and π - π interactions (Grabi et al., 2022; Shafiq et al., 2025). Post modification introduces functional groups like hydroxyls and amines to enhance π - π interactions in biochar-based nanocomposites (Guo et al., 2023), as demonstrated in porous ZnO /peanut shell-biochar nanocomposite that achieved high Methylene Blue adsorption (426.44 mg g^{-1}) via π - π and electrostatic mechanism. Figure 2 illustrates the charge-dependent adsorption mechanisms governing the interaction of cationic and anionic dyes with BMO-NC surfaces, emphasizing how pH-driven transitions relative to the pHpzc of the material dictate electrostatic attraction, the π - π interactions, and hydrogen bonding. The schematic highlights how surface protonation at $pH < pHpzc$ enhances uptake of sulfonated anionic dyes through strong Coulombic interactions, whereas deprotonated surfaces at $pH > pHpzc$ favor the adsorption of cationic aromatic dyes via π - π stacking and donor–acceptor interactions. By visualizing these complementary pathways, Figure 2 provides a mechanistic framework explaining how engineered BMO-NCs tailor surface chemistry to achieve high-affinity, dye-specific adsorption under varying wastewater conditions.

Anionic dyes

Congo red (CR) and Eriochrome black T (EBT) are anionic dyes that exhibited a negative charge in solution, owing to the presence of sulfonate groups and other ionizable functional groups in their molecular structures (Al-Zoubi et al.,

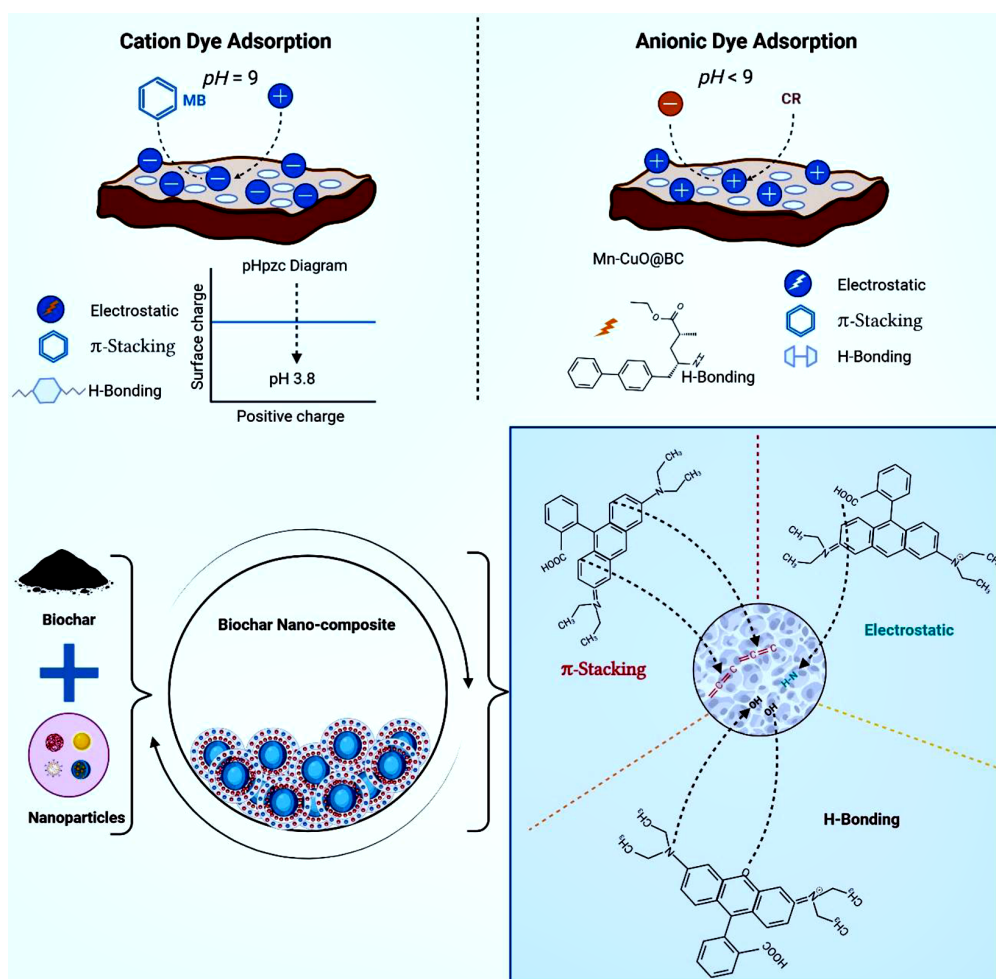


Figure 2. Charge-dependent adsorption mechanisms of cationic and anionic dyes on BMO-NCs, illustrating pH-driven surface charge transitions relative to pHpzc and the dominant interaction pathways electrostatic attraction, π - π stacking, and hydrogen bonding governing dye binding

2020). Effective removal strategies for these dyes often involve the use of positively charged adsorbent surfaces to facilitate electrostatic attraction (Zhang et al., 2019). A positively charged surface can be achieved by adjusting the solution pH to below the material PZC, leading to saturation of positive hydrogen ions on the surface (Al-Amrani et al., 2022). Mn-CuO@BC NCs show that optimal adsorption of anionic dyes like CR and EBT at pH 4, occurred via surface protonation electrostatic attraction. This implies a positively charged surface at low pH, while amine functionalization is discussed in the context of N-doped biochar and as potentially enhancing catalytic activity through improved electron transfer, the provided sources do not explicitly detail amine functionalization or connect it directly as a design strategy for removing anionic dyes like EBT and CR via H^+ saturation at low pH for Mn-CuO@BC NCs. Mn-CuO@BC NCs showed remarkable

adsorption efficiencies of approximately 98% for CR and 95% for EBT. Zeta Potential (ZP) characterization was performed for Mn-CuO@BC to evaluate its stability, and its performance for anionic dyes is better in acidic conditions due to a positively charged surface (Ullah et al., 2025). Similar studies conducted have shown that pH significantly affects the surface charge of adsorbents and their efficiency in removing the Congo Red (CR) dye. The results indicated that pH 2 is the most effective for CR removal, as the adsorbent surfaces acquire a positive charge, promoting electrostatic attraction with the negatively charged dye (Rubangakene et al., 2023).

Azo dyes

The presence of the stable azo bond ($-N=N-$) makes azo dyes a significant environmental hazard (Ramamurthy et al., 2024). Degradation

often involves breaking these bonds, frequently through photocatalysis, which generates reactive oxygen species (ROS) (González and Jaramillo-Fierro, 2025; Qian et al., 2024). Metal oxides embedded into biochar metrics function as catalytic active site, facilitating the production of ROS (Diaz-Uribe et al., 2024). Mn-CuO@BC NCs, containing CuO, were effective in the photocatalytic degradation of azo dyes like CR and EBT. The integration of H_2O_2 with the Mn-CuO@BC system significantly enhanced the photocatalytic degradation of EBT and CR, likely due to the accelerated generation of hydroxyl radical ($\cdot OH$) (Karuppasamy et al., 2022; Ullah et al., 2025). Moreover, other active substances generated during photocatalysis include $\cdot O_2^-$ and h^+ . These active species attack and degrade the complex molecular structures of azo dyes into simpler substances (Selvaraj et al., 2021). Analysis of EBT degradation products suggests that the azo $-N=N-$ double bond is a susceptible site for attack by $\cdot OH$ radicals. Cu/Cu₂O/BC NCs, containing Cu and Cu₂O, generate $\cdot O_2^-$ and h^+ upon exposure to visible light radiation, the azo dye methyl orange undergoes oxidation and reduction reaction resulting in H_2O and CO_2 (Bekele et al., 2024).

Green synthesis routes

The green synthesis of engineered BMO-NCs is crucial for sustainable textile wastewater

remediation, emphasizing circular resource use, low environmental impact, and industrial feasibility. Biomass precursors, such as agronomic residue, marine biomass, and municipal waste significantly influence the porosity, surface chemistry, and mineral content of the resulting biochar, enabling tailored performance and regional valorization (Khandaker et al., 2025). One-pot synthesis methods (e.g., co-pyrolysis) offer energy efficient, solvent minimized fabrication but often sacrifice precise control over nanoparticle crystallinity and dispersion. In turn, two step approaches (e.g., impregnation calcination) provide tunable surface and structural features at the cost of increased processing complexity (Amrute et al., 2021; Pavlenko et al., 2022; Rao et al., 2024). Key synthesis variables, including temperature, pH, activating agents, and metal doping directly impact BET surface area, pH_{pzc}, zeta potential, magnetic separability and heterojunction formation, which are critical for adsorption and photocatalysis (Amdeha, 2024; Weidner et al., 2022). Scalable methods must also address energy efficiency, compatibility with continuous reactor systems, reusability, and regulatory compliance (e.g., metal leaching, waste generation) (Durak, 2023; Tawo and Mbamalu, 2025). Future advancements should prioritize the synthesis strategies that harmonize environmental safety, material performance, and industrial scalability for real-world deployment. Figure 3 shows the

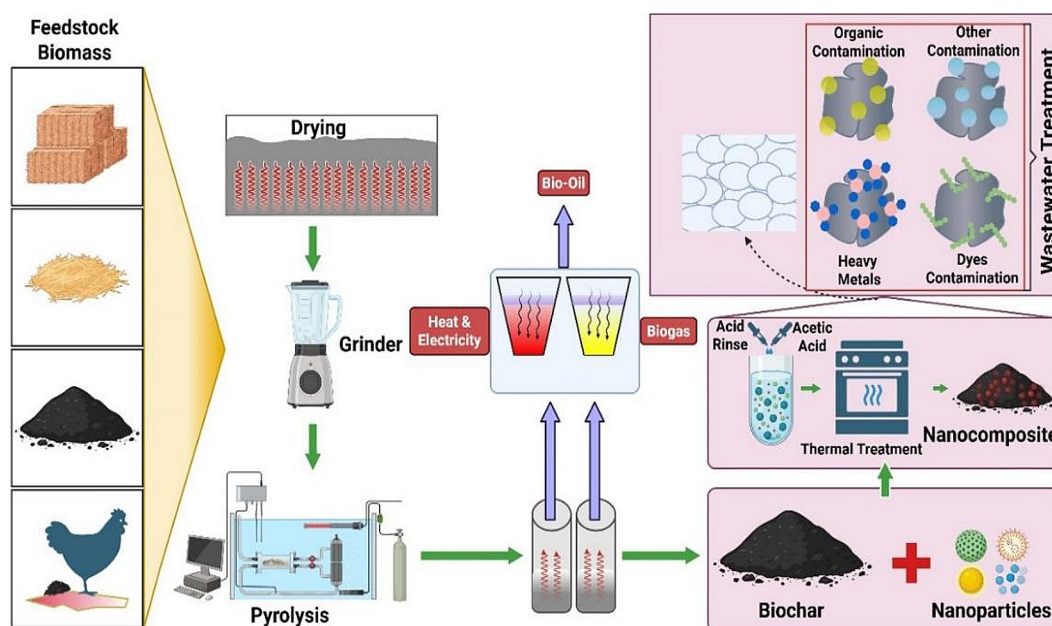


Figure 3. Schematic overview of biochar–metal oxide nanocomposite synthesis from diverse biomass feedstocks through drying, grinding, and pyrolysis, followed by nanoparticle integration and application in wastewater treatment for removing dyes, heavy metals, and organic contaminants

complete synthesis workflow of biochar–metal oxide nanocomposites, beginning with biomass drying, grinding, and pyrolysis to generate a porous carbon framework, followed by metal oxide loading through approaches such as impregnation, hydrothermal treatment, or chemical precipitation. The schematic illustrates how these sequential steps lead to nanoparticle anchoring, surface functionalization, and heterojunction formation, collectively enabling the composite's enhanced adsorption capacity and photocatalytic activity in wastewater treatment.

Comparative analysis of biochar-metal oxide nanocomposites

To rigorously assess the efficiency and scalability of biochar BMO-NCs in dye remediation, a comparative analysis of their physicochemical characteristics, dual-functional performance, and robustness under real effluent conditions is essential. The addition of metal oxides into biochar matrices significantly enhances the surface area, modulates surface charge via pH_{pzc} tuning, and introduces active sites conducive to both adsorption and photocatalysis (Amdeha, 2024; Weidner et al., 2022). Notably, the NCs combining high porosity with appropriate band alignment demonstrate superior dye removal efficiencies (>90%) across varying pH and ionic strength (Zhang et al., 2023). However, performance gaps remain between ideal lab conditions and complex industrial effluents, where co-contaminants, salinity, and fluctuating pH compromise efficacy (Hossain, 2021). Therefore, parameters such as regeneration efficiency, recyclability, and real matrix compatibility are critical for field translation. Table 1 presents a curated comparison of recently developed BMO-NCs, highlighting their compositional features, mechanistic insights, and practical treatment potential.

MECHANISMS OF DYE REMOVAL IN REAL WASTEWATER SYSTEMS

The multifaceted challenges of industrial textile wastewater, characterized by fluctuating pH, high salinity, and co-contaminants, demand more than just high removal efficiencies; they require a fundamental understanding of how engineered BMO-NCs function under harsh, realistic conditions (Dzoujo et al., 2024). While these NCs

leverage a potent synergy of adsorption and photocatalysis for targeted dye removal, their true potential hinges on mechanistic robustness against real-world stressors (Kumar and Singh, 2025). This section dissects the charge transfer pathways, reactive oxygen species (ROS) generation, and interfacial dynamics that govern performance in complex matrices, bridging material design with progress toward clean water and sanitation (Sustainable Development Goal 6).

Synergistic adsorption-photo catalysis in complex matrices

Engineered BMO-NCs typically initiate dye removal through adsorption, an essential pre-concentration step attributed to the essential properties of biochar support (Damahe et al., 2024). Biochar, derived from various biomass sources, possesses various active sites for pollutant capture. The adsorption mechanism involves several mechanisms, such as hydrophobic interactions, pore filling, hydrogen bonding, π - π bonding, and electrostatic interactions between the dye molecules and the biochar surface (Qiu et al., 2022; Tran et al., 2017).

Modifying biochar through metal oxide can further enhance its surface area and introduce new functional groups, thereby increasing its adsorption capacity. Moreover, metal engraving shown to be specifically enhance the biochar surface area, improving its adsorbent properties (Liu and Zhang, 2022). For instance, the ZnO/peanut shell-derived biochar NCs exhibited an 826.44 mg g⁻¹ MB adsorption capacity, significantly improving the recently published adsorbent capacity. Similarly, the adsorption capability of the ZnO/green pea peel biochar (GPBC) NCs amounting to 114.94 mg/g for CR, was particularly higher than for GPBC alone (62.11 mg/g). Modification of date palm-derived biochar with iron (Fe) significantly increased adsorption capacity of MB to 85.21 mg g⁻¹, highlighting the efficiency of the treatment compared to pristine material (Aziz et al., 2024). According to the previous studies, the adsorption follows pseudo-second order kinetics, indicating chemisorption as a predominant mechanism, while adsorption isotherms frequently align with the Langmuir model (Guo et al., 2020). The frequent occurrence of pseudo-second-order kinetics in dye adsorption onto biochar-metal-oxide composites suggests that uptake is influenced by the availability and ionization state of surface

Table 1. Comparative overview of engineered biochar-metal oxide nanocomposites in terms of physicochemical properties, dye removal performance, mechanistic insights, and real wastewater treatment applicability

Composite	BET (m ² /g)	PZC (pH)	Zeta potential (mV)	Target dye(s)	Adsorption capacity (mg/g)	Removal efficiency (%)	Mechanism (s)	Real wastewater performance	References
ZnO/ peanut shell biochar	80.6	3.8	-25 (pH 7)	MB	65.3	88–99.81	Electrostatic	N/A	(Yu et al., 2023)
Mn-CuO@ biochar	3.34	5.5/4.0	+58.8	CR, EBT	10.2	98 CR, 95 EBT	Chemisorption, Langmuir	Retained over seven cycles	(Ullah et al., 2025)
CuO@BSS (barley straw BC)	80.6	3.8	Negative across pH	MB	70.4	85–99	Adsorption + Photocatalysis	Tested (efficiency drops)	(Gomaa et al., 2022)
PEG-ZnO/rGO	45	3		CR	97.462	94	Adsorption	Real river water tested	(Buledi et al., 2024)
MCH-EGDE/ ORNC		4.0		RBBR	168.4	87.5	Freundlich, pseudo-2nd-order	N/A	(Abdulhameed et al., 2024)
AlS/Pin			-20	MG	384.61	89.98	Langmuir, pseudo-2nd-order	N/A	(Kolya & Kang, 2025)
Chitosan-treated nanocomposite	8.9	7.0		MO	172.17	92	Langmuir	N/A	(Waliullah et al., 2023)
Biochar/Ag NPs	72.6	5.2	-27.5	MB	115.2	96.09	Adsorption + Photocatalysis	84% (textile effluent)	(Chakhtouna et al., 2023)
ZnO/GPBC	112.4	7.1	+15 (pH 4)	CR	114.94	93	Adsorption	N/A	(Damahe et al., 2024)
KOH Lychee seed BC	154	7	-12.6	MB	124.5	91	π - π , H-bonding, Langmuir	N/A	(Rawat et al., 2023)
Biochar/Fe oxide (coffee)		6.2		MB, MO	62.1 (MB), 57.1 (MO)	88	Adsorption > Photocatalysis	N/A	(Kochito et al., 2024)
Fe oxide/ Douglas biochar	91.4	5.8	Positive (protonated)	MB	210	96	Adsorption	N/A	(Samaraweera et al., 2023)
FexOy/date palm BC		6.0		MB		93	π - π , H-bonding	N/A (4 cycles reusable)	(Abd-Elhamid et al., 2024)
AWBM (Wakame BC)		5.9		MB, hB, MG	841.6, 33.8, 4066.9	95	Endothermic adsorption	N/A	(Sutar et al., 2022)
EPAC (Enteromorpha BC)		5.6		MB	910	94	Endothermic, pH-dependent	N/A	(Mittal et al., 2022)
Ulva Reticulata BC		2.0		Remazol Orange 3R		91.6	Bio decolorization	N/A	(Kumar et al., 2021)

sites, though strictly speaking the model does not prove chemisorption (Devi et al., 2024). Furthermore, many studies report a distinct intraparticle-diffusion regime, particularly for hierarchically porous materials, indicating that external adsorption followed by pore migration contributes to the overall rate (Ahmaruzzaman et al., 2025). Accordingly, kinetic parameters such as the PSO rate constant (k_2) and intraparticle-diffusion coefficient (k_i/d) may reflect, in a semi-quantitative way, how well surface charge, functional groups and pore architecture have been tuned, especially under varied ionic strength or dye-type conditions.

The initial adsorption step concentrates dye molecules on the NCs surface, enhancing proximity to photocatalytic sites and significantly boosting degradation efficiency, even at low pollutant concentrations (Cheng et al., 2022). Engineered NCs like Mn-CuO@BC have shown dual functional advantages, exhibiting remarkable adsorption of 98% for CR and 95% for EBT, which contributes to their high overall removal efficiency. The best adsorption-photocatalytic effect for the Cu/Cu₂O/BC NCs was observed of BC to Cu/Cu₂O (0.2) at specific mass ratio, highlighting the importance of NCs composition for optimal synergistic

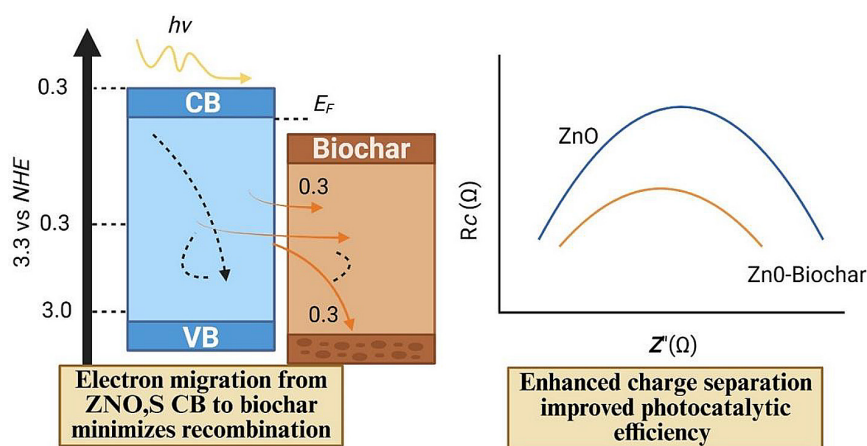


Figure 4. Synergistic adsorption photocatalysis and charge transfer pathways in BMO-NCs enabling enhanced dye degradation under light exposure

performance (Du et al.). Figure 4 shows the charge-transfer behavior of the ZnO–biochar composites, illustrating how photogenerated electrons migrate from the ZnO conduction band to the biochar, reducing electron hole recombination. The left panel depicts band alignment and electron flow under light irradiation, while the right panel shows the reduced charge-transfer resistance (R_{ct}) for the ZnO biochar compared to pure ZnO, confirming enhanced charge separation and improved photocatalytic efficiency.

Charge transfer pathways and ROS generation

Under appropriate light irradiation, the metal oxide component of the BMO-NCs absorbs photons, exciting electrons (e^-) from valance bond (VB) to conduction band (CB) and generating electrons (e^-) in (CB) and holes (h^+) in the VB (Magdalane et al., 2017). A critical aspect of the charge transfer pathway is the efficient separation and transfer process of these photo-generated electron hole pairs, which prevents their rapid recombination and enhances photocatalytic activity (Balapure et al., 2024). The biochar support material perform key role in this by facilitating the migration and transport of these charge carriers due to its electrical conductivity, large surface area, and porosity (Wang et al., 2024). This integration with biochar reduces the probability of electron-hole recombination, making more carriers available for reactions (Liang et al., 2024). Biochar can act as an electron transfer medium, efficiently shuttling photogenerated electrons and channeling them to other components, creating

an extended electron transport path (Javanmard et al., 2024).

Specific charge transfer mechanisms, such as Z-scheme pathways or the transfer of electrons to metal or biochar components in systems like $NiFe_2O_4/ZnIn_2S_4$, further enhance spatial charge separation (Xu et al., 2024). The presence of surface functional groups and defect sites on biochar also promotes rapid electron transfer. This facilitated charge transfer process ultimately drives the generation of reactive oxygen species (ROS) or enables direct redox reactions with adsorbed dye molecules, thereby leading to efficient dye degradation in real wastewater environments (Takhar and Singh, 2025). Experimental evidence from techniques like Electrochemical Impedance Spectroscopy (Mutlu et al.) and photocurrent measurements supports these improved charge transfer dynamics in biochar metal oxide NCs, which shows lower resistance and stronger photocurrents, indicative of faster charge transfer and better carrier separation (Damahe et al., 2024).

The photocatalytic degradation of dyes in engineered BMO-NCs fundamentally relies on ROS generation, yet mechanistic validation remains critically underdeveloped (Damahe et al., 2024). In turn, hydroxyl radicals ($\cdot OH$) and superoxide anions ($\cdot O_2^-$) are frequently considered as primary reactive species. Figure 5 shows the combined adsorption–photocatalytic pathway of ZnO–biochar nanocomposites. Cationic and anionic dyes are first adsorbed onto the biochar surface through electrostatic interactions, while ZnO activates under light to generate reactive oxygen species ($\cdot OH$, $\cdot O_2^-$). Previous studies highlighted that, electron spin resonance (ESR) spectroscopy

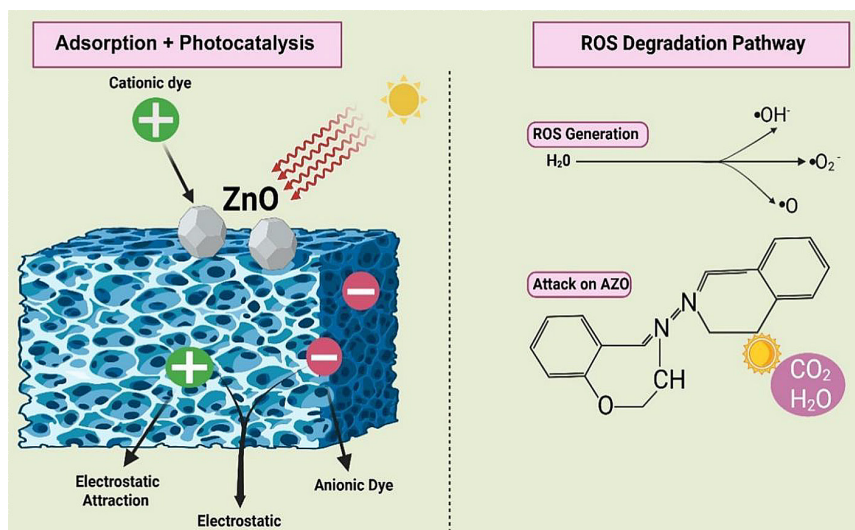


Figure 5. Integrated adsorption–photocatalytic dye removal on metal oxide biochar composites, showing electrostatic adsorption of cationic and anionic dyes followed by ROS-mediated azo-bond cleavage and mineralization into CO_2 and H_2O

with spin-trapping agents (e.g., DMPO) can be used to detect diagnostic signatures of $\text{DMPO}\cdot\text{OH}$ (1:2:2:1 quartet) or $\text{DMPO}\cdot\text{O}_2$ adducts (Jiang et al., 2021). In their absence, mechanistic claims rest on circumstantial correlations rather than spectroscopic proof. Quantitative ROS metrics are often missing, especially in the H_2O_2 -assisted systems where gains are vaguely linked to increased $\cdot\text{OH}$ without mechanistic insight (Brandes et al., 2018). The sustained generation of reactive oxygen species (ROS) in BMO-NCs is critically dependent on the efficient redox cycling of the incorporated metal centers (e.g., $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Cu}^+/\text{Cu}^{2+}$, $\text{Mn}^{3+}/\text{Mn}^{4+}$). This cycling acts as a catalytic engine for ROS regeneration. For instance, in a Fenton-like system, a surface-bound Fe^{2+} site activates H_2O_2 to yield a hydroxyl radical ($\cdot\text{OH}$) and Fe^{3+} ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$) (Zhang et al., 2024). The photocatalytic role of the composite is crucial here: photogenerated electrons from the metal oxide or conductive biochar matrix subsequently reduce Fe^{3+} back to Fe^{2+} ($\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$), closing the loop and allowing the catalytic consumption of H_2O_2 to continue (Xue et al., 2025). Similarly, $\text{Cu}^+/\text{Cu}^{2+}$ pairs facilitate the $\cdot\text{OH}$ production from H_2O_2 or peroxy-monosulfate (PMS), while their interconversion is driven by electron transfer processes that prevent the active sites from being passivated in a higher oxidation state. This continuous electron shuttling is fundamental to maintaining a high flux of radicals for the degradation of pre-concentrated

dye molecules (Feng et al., 2024; Wang et al., 2024). In reality, H_2O_2 amplifies ROS through three distinct pathways: (i) as an electron acceptor facilitating O_2 reduction to $\cdot\text{O}_2^-$ ($\text{O}_2 + \text{e}^- \rightarrow \cdot\text{O}_2^-$); (Rubangakene et al.) via Fenton-like reactions at metal sites ($\text{M}^{n+} + \text{H}_2\text{O}_2 \rightarrow \text{M}^{(n+1)+} + \cdot\text{OH} + \text{OH}^-$); and (iii) through Haber cycles, where $\cdot\text{O}_2^-$ disproportionate H_2O_2 ($\cdot\text{O}_2^- + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2$) (Rangarajan et al., 2022). Kinetic validation of these pathways is rare, and literature employs radical scavengers (isopropanol for $\cdot\text{OH}$, p-benzoquinone for $\cdot\text{O}_2^-$, EDTA for h^+) to deconvolute their contributions.

In addition to well-known reactive species such as $\cdot\text{OH}/\cdot\text{OH}/\cdot\text{OH}/\cdot\text{OH}/\cdot\text{O}_2^-$, other high-potential oxidants are systematically overlooked. Photogenerated h^+ directly oxidizes dyes via surface bound reactions ($\text{dye} + \text{h}^+ \rightarrow \text{dye}^+\cdot \rightarrow \text{fragmentation}$), while singlet oxygen ($^1\text{O}_2$), generated through energy transfer to dissolved O_2 , cleaves electron-rich azo bonds ($-\text{N}=\text{N}-$) (Li et al., 2024). Despite the established detection methods, these reactive species are rarely characterized experimentally, notably using furfuryl alcohol as a selective $^1\text{O}_2$ probe ($k = 1.2 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$) or ammonium oxalate for hole (h^+) scavenging (Shawky et al., 2024). In persulfate activated systems ($\text{S}_2\text{O}_8^{2-}/\text{HSO}_5^-$), sulfate radicals ($\text{SO}_4\cdot^-$, $E^\circ = 2.5\text{--}3.1 \text{ V}$) likely dominate degradation due to superior selectivity toward conjugated systems, yet their role in biochar metal oxide NCs remains uninvestigated (Sutar et al., 2022).

Mechanistic validation: ROS quantification and degradation pathways

Connecting lab research to industry requires thorough mechanistic validation. While various studies highlight the role of reactive oxygen species (ROS), such as $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ in dye degradation, experimental evidence is scarce. Electron spin resonance (ESR) and in situ spectroscopy should help understand reactive species. Liquid chromatography mass spectrometry (LC-MS) can also track dye breakdown paths, identify intermediates, and verify that the degradation process is complete and safe. Degradation pathway mapping suffers from inadequate resolution (Xie et al., 2022). While azo bond cleavage is universally acknowledged, intermediate speciation is rarely tracked (Mutlu et al., 2018). Liquid chromatography mass spectrometry (LC-MS) could reveal sequential transformations: initial (-N=N-) scission generating anilines/naphthylamines, followed by aromatic ring hydroxylation, desulfonation (-SO₃H loss), and ultimate mineralization to aliphatic acids (e.g., oxalate, formate). In the absence of comprehensive carbon tracking, claims of complete mineralization based solely on chemical oxygen demand (COD) reduction remain problematic, since COD quantifies oxidizable species, rather than verifies complete carbon conversion to CO₂ (Oliveira et al., 2023). Total organic carbon (TOC) analyses reported in a study reveal significant shortfalls. Toxicity assessments (e.g., ECOSAR) without structural confirmation of intermediates risk underestimating ecological hazards from residual by-products (Shi et al., 2023).

Biochar itself may act as a ROS sink, its graphitic domains and redox active quinones competitively consume radicals. Consequently, ROS fluxes measured in synthetic dye solutions overestimate real-system performance by 2–5 fold (Xie et al., 2024). Bridging this lab-field divide demands ESR validation of ROS identities/yields, scavenger studies to quantify pathway contributions, LC-MS elucidation of degradation cascades, and TOC based mineralization tracking in complex effluents. Only through such mechanistic rigor can NCs progress from promising concepts to deployable technologies.

Performance challenges in industrial effluents

Industrial effluents contain complex matrices comprising mixed dyes, co-contaminants (including heavy metals and ionic species), and dynamic

physicochemical conditions (pH fluctuations, variable salinity), all of which critically influence nanocomposite performance and treatment efficacy (Omoriegbe et al., 2023). The presence of other organic and inorganic species, including ionic species, can compete with targeted pollutants for active adsorption sites, thereby reducing adsorption capacities (Zhao et al., 2021). Increasing ionic strength, for instance, has been observed to decrease the adsorption of pollutants (Zhang et al., 2019). The wastewater from industries like textiles is particularly complex, containing a diverse array of hazardous organic and inorganic chemicals, often at high temperatures with varying pH, high conductivity, and significant organic matter. Addressing multiple dyes and competing pollutants is key to improving reliability and scalability. Most studies, however, still rely on synthetic dye solutions under ideal laboratory conditions, which limits validation in real industrial effluents (Catarino et al., 2025; Tsauria et al., 2025; Yaseen and Scholz, 2019).

Despite these challenges, some materials have demonstrated potential when tested in complex matrices or real water samples. For instance, Mn-CuO@BC NCs retained approximately 75% CR removal efficiency in textile wastewater, despite competing organics, highlighting their resilience in complex matrices. CuO@BSS, when evaluated using real water samples (agricultural water, Nile River water, and industrial wastewater), achieved high MB removal efficiencies, including 99% photodegradation for 10 mg/L MB in agricultural water (Gomaa et al., 2022). The reduced MB removal efficiency observed in these real samples was attributed to the competition from other co-existing organic and inorganic species for surface active sites. Moreover, ZnO/peanut shell biochar removed more than 50% of chemical oxygen demand (COD) and 82.2% turbidity from real textile wastewater, significantly improving water quality and support achievement SDG 6 targets (Attiqa Ahmad et al., 2024).

Mineralization, indicated by total organic carbon (TOC)/COD decline, is a crucial metric beyond simple color removal (Kovo et al., 2023). Despite the successes in color and turbidity removal, significant gaps persist in thoroughly evaluating material performance under realistic conditions. Real industrial wastewater, with its complex mixtures, fluctuating pH, high salinity, and competing co-contaminants, can drastically reduce efficacy compared to laboratory tests

(Sibhatu et al., 2022). Future research must therefore prioritize testing adsorbents under diverse and dynamic conditions on real industrial wastewater to ensure efficacy, exploring competitive adsorption in actual complex pollutant systems (Selim et al., 2024). While some materials show insensitivity to pH fluctuations, further investigation into the impact of ionic strength and competing pollutants is necessary (Zhang et al., 2019).

Biochar-metal oxide and polymer nanocomposites for dye remediation

BMOs-NCs utilize waste biomass such as agricultural residues or municipal waste, enabling cost-effective synthesis aligned with circular economy principles (Akhtar et al., 2024). These materials demonstrate superior adsorption capacities for diverse dyes while enhancing sustainability through resource valorization. Conversely, PNCs leverage tunable synthetic matrices like PMMA/OMMT or cellulose/polyaniline, offering advantages in cost efficiency and process scalability (Antony Jose et al., 2025). However, PNCs raise environmental concerns due to fossil-derived monomers (Ciardelli et al., 2019). Both material classes show promising reusability across multiple regeneration cycles, yet scalability remains constrained by minimal industrial pilot validation (Singh et al., 2025). Critical research gaps persist in three areas: rigorous economic assessments of synthesis costs, comprehensive lifecycle evaluations of environmental footprints, and compliance validation against international regulatory standards (Pucciarelli, 2023). Industrial metrics, like reactor throughput and energy consumption remain severely underreported in real effluents. Neither technology currently employs AI/ML for design optimization nor adapts to regional variables, such as biomass availability. To advance these materials beyond lab-scale promise, future work must prioritize standardized economic benchmarks, industrial pilot demonstrations in complex wastewater, and regulatory integration frameworks (Akhrame et al., 2018; Kumar et al., 2024).

DISCUSSION

Addressing the persistent challenge of dye-contaminated wastewater treatment necessitates a clear vision toward future advancements, overcoming existing barriers, and ensuring practical,

safe, and policy-aligned implementation of novel technologies such as PNCs and metal oxide-biochar nanoparticles.

Limitations of current research

A primary limitation in current research is the predominant use of synthetic dye solutions in laboratory settings, which often fails to capture the complexity of real industrial effluents containing intricate dye mixtures, fluctuating pH levels, and various co-existing contaminants (Amdeha, 2024). While materials like gelatin NCs have demonstrated high adsorption capacities (e.g., 950.5 mg/g), their efficacy in realistic wastewater scenarios remains largely unproven (Elella et al., 2022).

Technical challenges in material synthesis and performance

Key challenges requiring technical solutions include issues inherent in material synthesis and performance. Batch variability is a notable concern, particularly for biochar production, where the heterogeneous nature of biochar feedstocks or varying preparation conditions can yield materials with inconsistent properties. While green synthesis routes using plant extracts are promising from an eco-friendly perspective, they may contribute to this variability, making standardized production difficult (El-Hussein et al., 2024; Hano and Abbasi, 2022). Another critical challenge, especially concerning MBOs-NCs, is the potential for metal leaching from the nanoparticles into the treated water or environment (Dey and Ahmaruz-zaman, 2023). Although the sources highlight the toxicity of heavy metals found in some dyes and the need to minimize secondary pollution from catalyst precursors, they do not explicitly detail silica encapsulation as a mitigation strategy; however, the general need to assess and mitigate environmental risks and toxicity is recognized. Beyond synthesis, performance challenges include the decrease in removal efficiency after multiple reuse cycles due to the blockage of active sites on the adsorbent surface, necessitating enhanced surface modifications for improved regeneration capabilities (Abdullah et al., 2025; Tripathy et al., 2024). The toxic phenomenon of nanoparticle re-agglomeration in NC materials, driven by strong Van der Waals interactions and, electrostatic also poses a challenge, which might be addressed by creating long-chain carbon materials in the structure of NCs (Jose et al., 2025).

Future opportunities for advanced materials

Future research must decisively shift focus from single synthetic dyes to the treatment of complex dye cocktails and real industrial wastewater under diverse and dynamic conditions to ensure reliability and scalability. This necessitates the development of tailored materials, engineered explicitly for selectivity and efficiency in treating such intricate pollutant mixtures, potentially also targeting the degradation of multiple pollutants simultaneously. Furthermore, comprehensive cost analyses, encompassing material synthesis, regeneration potential, long term feasibility, and lifecycle impact assessments, are important for evaluating the economic feasibility of these technologies. The reusability of materials is vital for cost-effectiveness in large-scale applications.

Policy and regulatory frameworks for sustainable implementation

The successful adoption and impact of these wastewater treatment technologies are inextricably linked to supporting policy and regulatory frameworks. Literature does not specifically detail incentives like eco certification or tax credits; they strongly advocate for developing sustainable, eco-friendly, and cost-effective solutions for dye removal. Promoting closed-loop textile processing, where treated water is potentially reused, aligns with the broader goals of environmental protection and resource conservation. Aligning these research and development efforts with international initiatives like the United Nations Sustainable Development Goal 6 (SDG 6) concerning clean water and sanitation, and the principles of the EU Circular Economy Action Plan.

Finally, there is a pressing need for standardization within the field. This includes developing standardized synthesis protocols and comprehensive characterization techniques for novel materials. The establishment of standardized protocols for dye testing in real wastewater, potentially through international bodies like ISO or ASTM, is critical to ensure data reproducibility, comparability, and reliable evaluation of different treatment technologies across various studies and applications. By addressing these challenges and embracing future opportunities, the research community can contribute significantly to the development and deployment of effective, scalable, and ecological solutions for industrialized dyes discharge treatment, safeguarding water resources and environmental health.

CONCLUSIONS

Biochar metal oxide nanocomposites (BMO-NCs) represent a highly promising class of dual-functional materials capable of delivering sustainable and efficient treatment of textile wastewater. Their synergistic combination of high-surface-area adsorption and photocatalytic degradation enables the removal of complex dye structures while minimizing chemical inputs and energy consumption. However, the substantial performance gap between laboratory conditions and real industrial effluents characterized by variable pH, high salinity, and competing contaminants underscores the need for more rigorous mechanistic understanding and realistic evaluation frameworks. Advancing this field will require in-situ ESR verification of reactive oxygen species, LC-MS tracking of degradation intermediates, long-term regeneration and leaching studies, and standardized testing protocols tailored for complex waste streams. Equally important is the development of scalable, low-energy synthesis routes and the integration of BMO-NCs into pilot and continuous-flow treatment systems. With these scientific and engineering advancements, BMO-NCs have the potential to mature into robust, ecologically safe, and scalable technologies, offering a transformative pathway toward sustainable wastewater management and meaningful progress toward Sustainable Development Goal 6.

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