



# An overview of advanced oxidation processes using copper-based catalytic degradation of organic pollutants in water

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## ABSTRACT

Organic pollutants are harmful to the environment due to their bio-accumulative and long-persistent nature, causing adverse effects on plants, animals, and humans. Their rapid spread beyond target applications in the ecosystem could be responsible for various fatal diseases and eco imbalances. Conventional techniques for removing these pollutants are ineffective because of their high solubility in water and nonbiodegradability. In contemporary times, we have witnessed a notable surge in interest in advanced oxidation processes (AOPs) for water treatment processes. This heightened attention is attributed to their exceptional degradation efficiency for recalcitrant organic pollutants. This review, therefore, focuses on copper-based homogeneous and heterogeneous catalysts for AOPs that offer both cost-effectiveness and high performance. Emphasis is placed on the use of copper-based catalysts in photocatalysis, Fenton-like process (including photo-Fenton ( $\text{Fe}^{2+}/\text{UV}/\text{H}_2\text{O}_2$ )), persulfates activation, and ultrasonic irradiation. The catalytic performance, mechanism, and pathway for the abatement of the target pollutants by the copper-based catalysts in each AOP are described in detail. The reusability, stability, and factors affecting the AOPs are briefly highlighted. We further provide perspectives on the key opportunities and challenges associated with copper-based catalysts in AOPs, recommending further exploration for enhanced applications in future studies.

## 1. Introduction

The rapid growth witnessed in population and industrialization has led to a significant global challenge – the contamination of water with organic pollutants. This issue poses a critical threat to public health and safety [1–4]. Wastewaters release various refractory organic compounds, including pharmaceuticals and personal care products (PPCPs), dyes, pesticides, and pharmaceuticals, into freshwater bodies [5–10]. It is recognised that these compounds are mostly persistent organic pollutants (POPs), which pose various threats to living organisms and humans [11–15]. Various biological and physical treatment techniques have emerged to address the elimination of organic contaminants from water, including methods such as coagulation, ultrafiltration, and adsorption [16–23]. Nevertheless, the implementation of these in practical scenarios are often set back by inefficient removal of trace organic pollutants resulting from the phase transfer of organic pollutants.

Additionally, there is a possibility of generating toxic by-products and wastes that could cause secondary pollution. Therefore, economic, eco-friendly, and highly effective treatment processes have become crucial for the removal of POPs in water. The advanced oxidation processes (AOPs) have fuelled great interest among researchers globally, sequel to their high efficacy in the degradation and even mineralization of aqueous organic pollutants [24–27,28]. Moreover, the AOPs demonstrate greater eco-friendliness compared to biological and physical treatment methods, as they involve reduced sludge generation or do not require diversion of organic pollutants from one phase to the other [29–31]. The AOPs support the degradation and mineralization of most organic pollutants into intermediate  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , or other smaller intermediate products [32]. The unique activity and adaptability of the AOPs are incident on the generation of highly reactive oxygen species (ROS) such as  $\text{O}_2^{\bullet-}$ ,  $^1\text{O}_2$ ,  $\text{SO}_4^{\bullet-}$ , and  $^{\bullet}\text{OH}$ , which effectively attack the organic pollutants resulting in their decomposition [33–35].

In general, numerous AOPs exist, including photochemical

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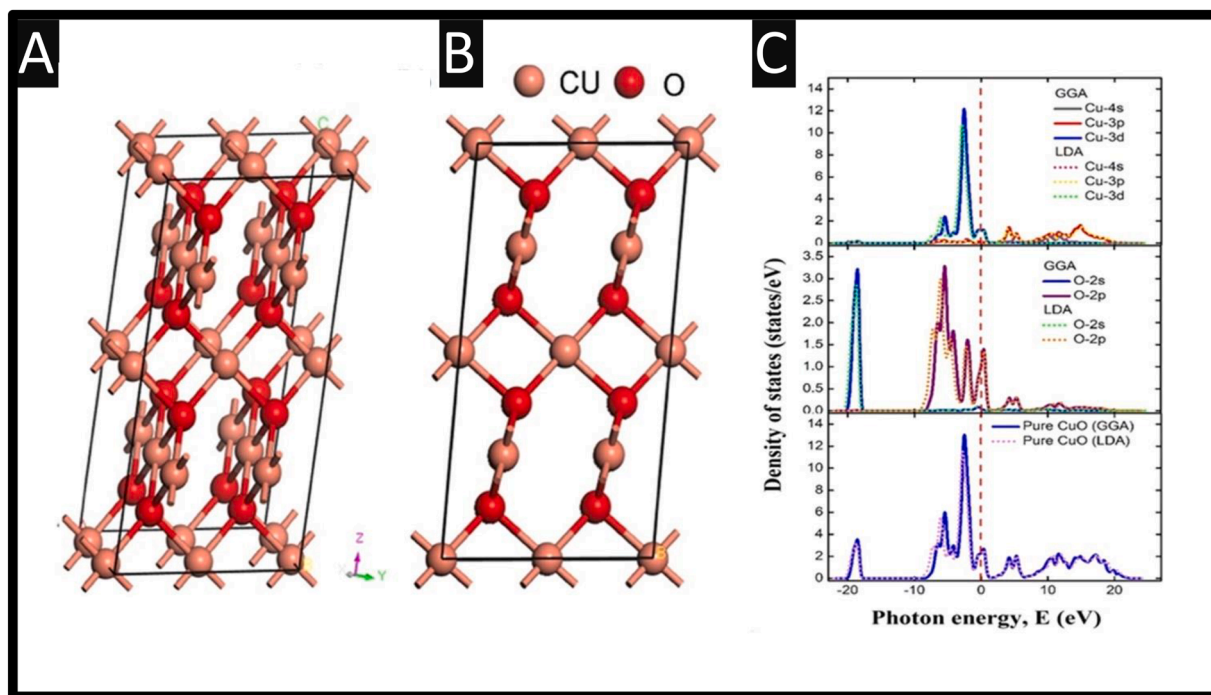
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**Fig. 1.** The crystal structure of (A) 3D CuO and (B) 2D CuO and (C) the partial and total density of states (DOS) of CuO supercell. Figure reproduced from reference [47]. Copyright 2020 Elsevier.

oxidation, ozone oxidation, electrochemical oxidation, Fenton and Fenton-like oxidation [36]. Typically, AOPs consist of homogeneous AOPs (homAOPs) and heterogeneous AOPs (hetAOPs). The hetAOPs commonly employ solid in conjunction with other systems (light, ozone ( $O_3$ ), persulfates (PS),  $H_2O_2$ ,  $Cl^-$ , etc) to decompose organic contaminants [37–39]. Relative to the homAOPs catalysts, the primary benefit of their heterogeneous counterparts lies in the ease of recovering and reusing the catalyst. In real-world water treatment applications, it is expected that heterogeneous catalysts meet certain criteria, including chemical and physical stability, as well as sustainability [32]. Consequently, various endeavours have been dedicated to the exploration of durable and efficient heterogeneous catalysts for AOPs with particular emphasis on copper-based catalysts (CBC). Copper (Cu) has been recognised as an efficient activator for initiating AOPs, leading to the generation of strong oxidants. Given the presence of Cu ions in many water/wastewater samples, exploring CBC holds potential for water remediation. In this review, we summarise the use of copper-based catalytic degradation of organic pollutants in water using AOPs, reporting on opportunities and challenges with emphasis on enhanced applications for researchers to pursue.

## 2. Copper-based catalysts for AOPs

Copper-based catalysts (CBC) have in recent years emerged as auspicious catalysts in AOPs owing to their earth abundance, easy preparation, minimal toxicity, good stability, cost-effectiveness, and unique electronic configurations. A variety of CBC have been synthesized and applied in AOPs to efficiently degrade and mineralize organic pollutants in water with high efficiency, reusability, stability, and low toxicity of intermediate products.

### 2.1. CuO/Cu<sub>2</sub>O homogeneous structures in AOPs

Cupric oxide has piqued research interest due to its unique characteristics as a p-type semiconductor featuring a narrow band gap (1.2–2.0 eV). It serves as the basis for huge magnetoresistance and finds application in numerous high-temperature semiconductor devices [40,41].

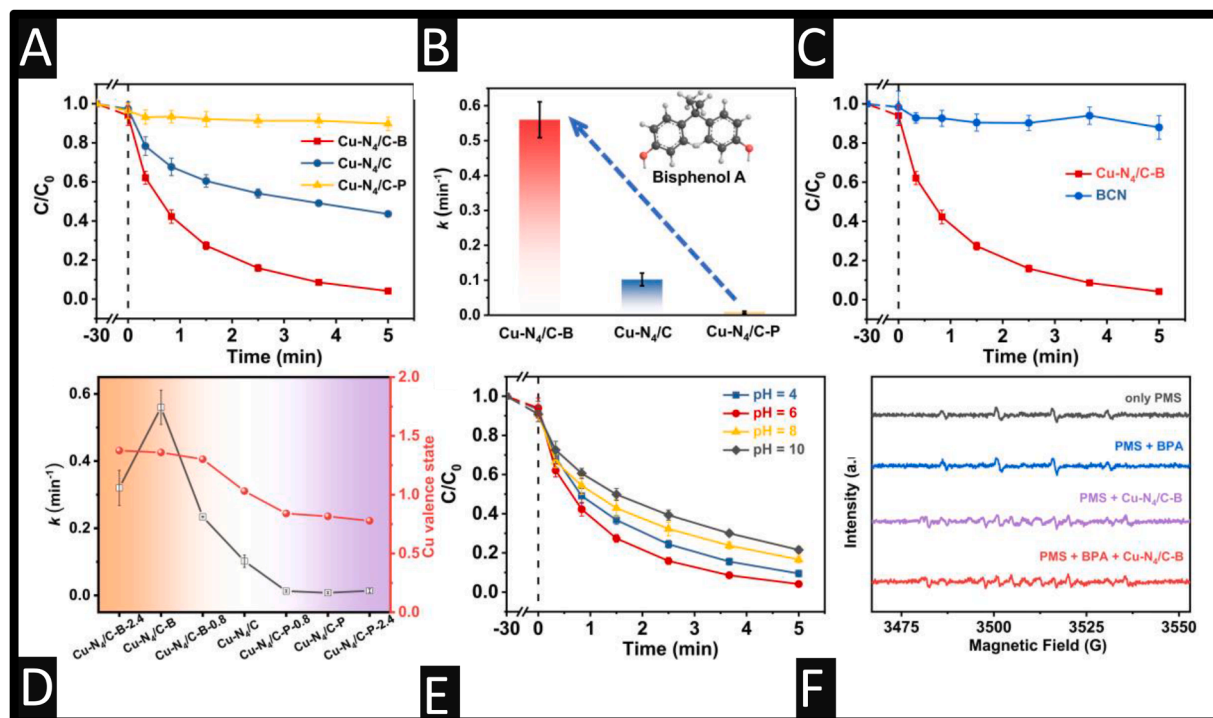
Cupric oxide monoclinic crystal architecture, Fig. 1, exhibits exceptional chemical and physical properties such as favourable electrochemical performance, appropriate redox potential, super thermal conductivity, exceptional stability in solution and large surface area [42,43]. CuO is made up of 3d and O 2p shells occupied by conduction band (CB) and valence band (VB) edges having lower energy gap ( $E_g$ ) leading to the optimal generation of ROS. Additionally, its visible light (VL) wavelength of maximum absorbance ( $\lambda_{max}$ ) extends up to the infrared region [44,45]. For instance, a CuO photocatalyst with an  $E_g$  of 1.7 eV has a CB of 0.46 V and a VB of 2.16 V potential, which represents a potential greater than the standard redox potential and appropriate also for  $\cdot OH$  and  $O_2^{\cdot -}$  radical release, needed for photodegradation [46].

### 2.2. Cu-O based heterostructures in AOPs

Pure CuO transition metal oxides are not very effective in degrading organic pollutants because of rapid charge recombination in photocatalysis, and sluggish  $Cu^+/Cu^{2+}$  redox cycle in Fenton-like process and PS activation. Consequently, numerous strategies are required to augment the catalytic efficiency, improve stability, and achieve recyclability. These strategies include doping with transition and rare earth metals, constructing binary, ternary, and even quaternary heterojunctions, forming Z-scheme heterojunctions, and incorporating carbonaceous materials [48].

### 2.3. Cu-S based heterostructures in AOPs

Generally, transition metal sulfides (TMS) are some of the most abundant and widely distributed semiconductor materials on Earth. In these materials, a combination of sulfur anion with a metal/semi metal cation occurs leading to the formation of  $M_xS_y$  compounds with diverse stoichiometries [49] or bimetallic sulfides described as  $A_{1-x}B_xS_y$  (A and B representing different metals, while x and y are integers) [50,51]. Contrary to other popular transition metal catalysts, the TMS exhibit rich redox sites, higher electrical conductivity, superior optical properties, a tuneable band gap, excellent thermal and mechanical stabilities, in addition to high catalytic activity [52,53]. For instance, a 2D  $CuCo_2S_4$



**Fig. 2.** Fenton-like activity of Cu-N<sub>4</sub> catalysts. (A) Kinetics of the bisphenol A (BPA) degradation in Cu-N<sub>4</sub>/C-B/PMS system, Cu-N<sub>4</sub>/C/PMS system, and Cu-N<sub>4</sub>/C-P/PMS within 5 mins. (B) Comparing the *k* value of BPA decomposition using different Cu-N<sub>4</sub> catalysts. (C) Kinetics of BPA degradation in Cu-N<sub>4</sub>/C-B/PMS system and BCN/PMS system. (D) The relationship between *k* and the Cu valence state in the as-prepared Cu-N<sub>4</sub> catalysts. (E) Effect of pH on BPA degradation in the Cu-N<sub>4</sub>/C-B/PMS system. (F) EPR spectra of the PMS activation in the presence of Cu-N<sub>4</sub>/C-B catalyst. (Reaction condition: [BPA] 20 ppm, [PMS] 200 ppm, [catalyst] 100 ppm, T = 298 K, [pH]<sub>0</sub> = 6.0. Figure reproduced from reference [57] Copyright 2022 National Academy of Sciences.

nanosheet ( $E_g = 2.24$  eV) facilitated the generation of a well-opened 3D hierarchical structure, exposing greater portion of the surface. As a result, the nanosheet was enriched with capacities to absorb the whole visible light spectrum for water splitting reactions, with probable apparent quantum yield reaching 2.48%. The indirect band gap of the nanosheet limited the rapid recombination of charges. In addition, the CuCo<sub>2</sub>S<sub>4</sub> nanosheet possessed a high surface area of 62.9 m<sup>2</sup> g<sup>-1</sup> and donor concentration of  $7.22 \times 10^{18}$  cm<sup>-3</sup> alongside a richly filled DOS at the Fermi level, which supports H<sup>+</sup> adsorption on S-sites, thus making it a promising photocatalyst [54].

#### 2.4. Cu-N<sub>x</sub> heterostructures in AOPs

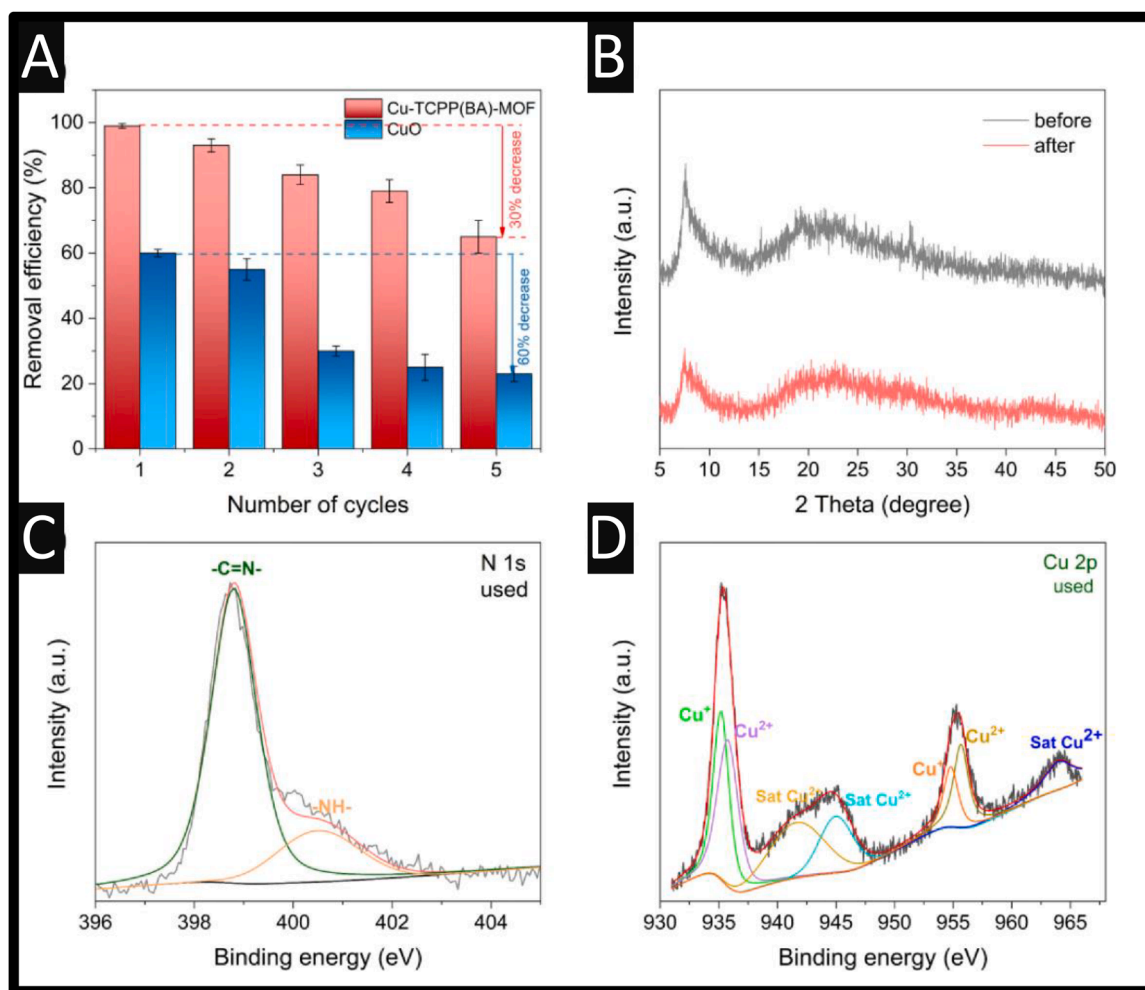
Developing hetAOPs with atomically dispersed active sites is crucial to enhance oxidant activation in Fenton-like processes. However, effectively manipulating the electronic configuration of metal centres to boost the activation kinetics is still difficult. Recent research has shown that the abundance of Cu-N<sub>x</sub> species demonstrates the potential to enhance the decomposition of H<sub>2</sub>O<sub>2</sub> to generate <sup>•</sup>OH radicals [55]. However, decorating g-C<sub>3</sub>N<sub>4</sub> with metals in the form of single-atoms and ultra-small clusters has emerged as a hot research area due to the exceptional performance of high atom-utilization [56]. Zhou *et al.* [57] successfully configured the electronic structure of Cu-N<sub>4</sub> sites by incorporating electron-deficient Boron (B) or electron-rich phosphorous (P) into a carbon substrate towards the activation of peroxymonosulfate (PMS) in a Fenton-like reaction. Interestingly, the electron-deficient Cu-N<sub>4</sub>/C-B presented the most active oxidation activity than Cu-N<sub>4</sub>/C-P and Cu-N<sub>4</sub>/C (Fig. 2). In contrast, Cu-N<sub>4</sub>/C-P decreased PMS activation, attributed to the decrease in the electronic density of active sites of Cu, and the downshifts of the d-band centre due to long interaction with B atoms. Thus, this increased the energy of absorption required for the activation of PMS.

#### 2.5. Cu-C heterojunction in AOPs

Cu metal has been used to dope carbonaceous materials and increase the quantity of active sites contained in the carbon material. This involves the formation of Cu-C sites that boost the interaction with PS. For example, Yu and co-workers [58] fabricated a Cu-doped sludge biochar (CSBC) by simple impregnation-pyrolysis technique. The loaded Cu<sup>2+</sup> in the sewage sludge was transformed into Cu<sup>0</sup>/Cu<sup>I</sup> species following pyrolysis, which significantly amplified the removal efficiency of bisphenol A (BPA) and increased the pH window.

#### 2.6. Copper metal oxides (Cu-MO) heterostructure in AOPs

Copper metal oxides (Cu-MO) exist in two different forms, cupric oxide (CuO) and cuprous oxide (Cu<sub>2</sub>O). To ensure the total oxidation of pollutants while minimizing the quantity of leached active metal into the solution, it is imperative to optimize reaction conditions such as oxidant concentration (H<sub>2</sub>O<sub>2</sub>, PDS, etc.), catalyst loading, and pH [59]. For a Fenton-like process, Fang *et al.* reported that the use of pure CuO nanosheets revealed that a concentration of 20.3, 13.6 and 10.5 ppm Cu leached into the solution at pH levels of 3, 6 and 9, respectively [60]. A similar observation was made in a CuO/CeO<sub>2</sub> heterostructure, where 9% of the Cu loading leached into the solution at pH 5, which limited the reusability of the catalyst [61]. However, doping metal oxide semiconductors with Cu reduced the leaching of the Cu metal into the solution. Silva *et al.* [62] demonstrated the effectiveness of Cu-MgO nanoparticles (NPs) in Fenton-like catalysis for the degradation of pharmaceutical pollutants in wastewater. Under ideal circumstances, they achieved complete oxidation of salicylic acid (SAA) within 60 mins. The dissolution of MgO at the surface led to an increase in the pH of the solution, which completely prevented the leaching out of Cu, while maintaining high catalytic performance. Note that even after five cycles, the catalyst's reusability remained satisfactory.



**Fig. 3.** A: Cu-TCPP(BA)-MOF and stability activity test of CuO; B: Comparing the XRD pattern of the applied catalyst and fresh catalyst; C: XPS spectra N1s of applied Cu-TCPP(BA)-MOF; D: XPS Cu 2p spectra of applied Cu-TCPP(BA)-MOF. Figure reproduced from reference [67]. Copyright 2022 Elsevier.

## 2.7. Copper metal organic frameworks (Cu-MOF) heterostructures in AOPs

In recent years, metal-organic frameworks (MOF) have attracted huge development potential due to their distinctive structural features such as large specific surface area (SSA), adjustable structure and high porosity [63]. They have seen notable advances in modern material science. Additionally, the arrangements of organic ligands, clusters, or metal ions provide a pellucid directionality in MOFs to generate diverse framework pore structures, resulting in different adsorption [64], optical [65], and electromagnetic [66] properties. Bai *et al.* [67] employed Cu porphyrin and Cu as ligand and metal node, respectively, in designing an ultra-thin MOF enriched with Cu<sup>2+</sup> active sites for the degradation of refractory rhodamine B (RhB) in water, in a PMS system. The Cu-modified MOF exhibited superior catalytic removal efficiency, and lower ion leaching compared to pure CuO in the degradation of RhB (Fig. 3).

## 2.8. Zero valent copper

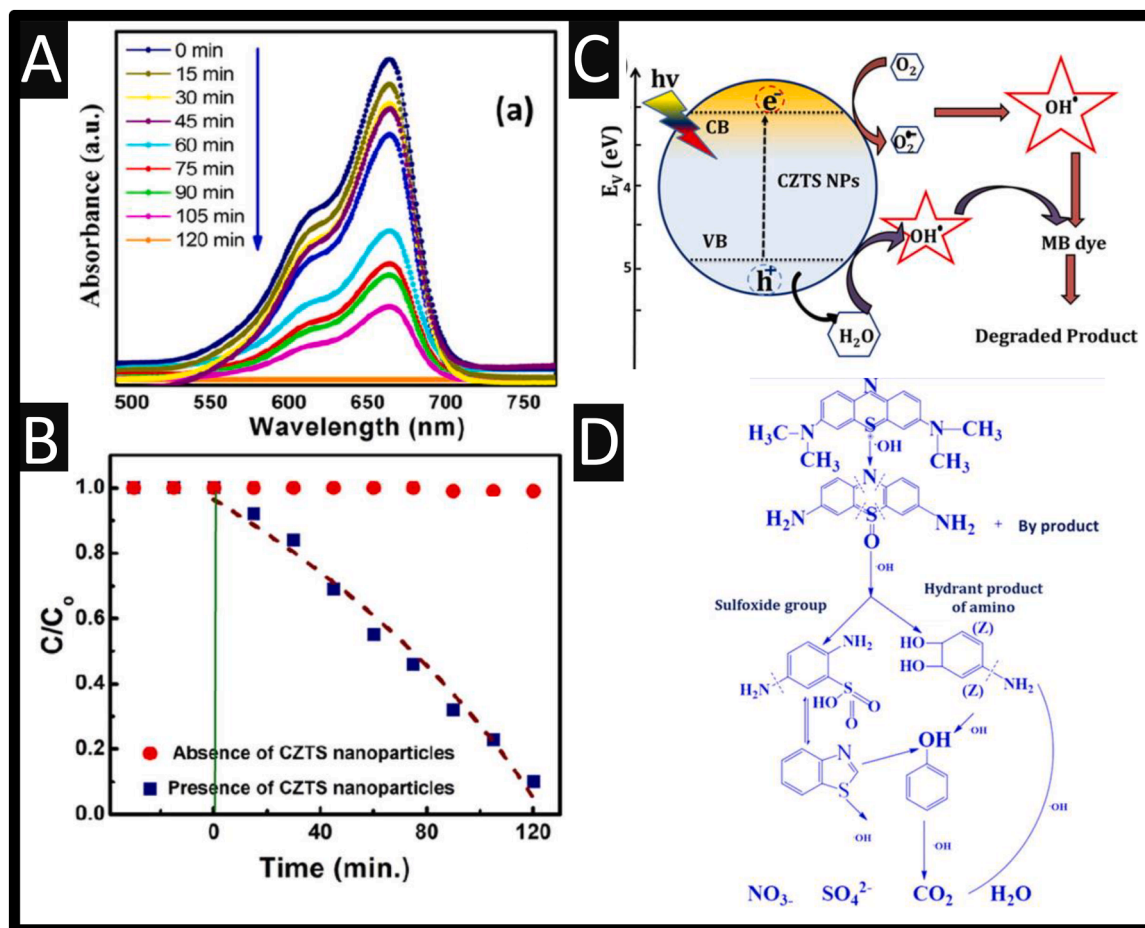
Zero valent copper systems are promising in the area of environmental remediation and have been used with ultrasonic irradiation to activate oxidants for various applications. For instance, it has been used with PS for the degradation of bisphenol AF, [68] H<sub>2</sub>O<sub>2</sub> for the oxidative degradation of norfloxacin, [69] and for acetaminophen (ACT) [70]. A further report suggests that the injection of Cl<sup>-</sup> significantly enhances

the remediation of ACT, where the generation of <sup>•</sup>OH and reactive chlorine species is attributed to play dominant roles [71]. Other approaches have used zero valent copper to activate PS via ultrasound for the degradation of p-chlorophenol [72].

## 2.9. Copper layered double hydroxide (Cu-LDH)

Layered double hydroxides as catalysts for AOPs have been extensively studied. The use of Cu-LDH involves layer structures that can be tuned in terms of morphology, composition, surface defect structure and particle size through various synthetic methods and exfoliation approaches. This allows for the creation of low-coordinated steps, edges, and/or corner atoms, which facilitate heterogeneous catalysis. Moreover, strong electrostatic interactions between layers and interlayer anions contribute to an ordered arrangement of interlayer species and an orientation of active sites [27]. For example, Cu-Co-Fe-LDH was synthesized to activate PMS for nitrobenzene (NB) degradation, resulting in the generation of <sup>•</sup>OH and achieving the degradation of 16 μM in 6 mins [73]. Another notable work has reported the use of LDH-MoS<sub>4</sub> with Cu (II) ions in conjunction with PS to improve the efficiency by 10-20 times in the removal of atrazine (ATZ) over that of previously related structures, where the authors report that the role of Cu(II) ions are continuously supplying electrons from the unsaturated S<sup>2-</sup> and Mo<sup>4+</sup> of the LDH-MoS<sub>4</sub> [74].





**Fig. 4.** A: The UV-vis spectrum of the degraded pollutant, B: comparison between the kinetics in the presence and absence of the catalyst, C: the schematic representation of energy level diagram revealing the band structure and separation of  $h^+$  and  $e^-$  at the catalyst interface and D: the mechanism of the degradation of MB. Figure reproduced from reference [88]. Copyright 2017 Elsevier.

### 3. Application of copper-based catalysts in AOPs

#### 3.1. Photocatalysis

Photocatalysis is an environmentally benign, sustainable, and energy-saving technology that utilizes solar energy to degrade organic pollutants. With the advent of semiconductor-based photoelectrochemical water-splitting reactions, photocatalysis, as an AOP has attracted huge research attention in recent years. It has gained wide applications in the degradation of contaminants characterized with low biodegradation, high complexity and high concentration [75]. Furthermore, there is an increasing usage of metal oxides such as  $TiO_2$  and  $ZnO$  as semiconductor photocatalysts, for the generation of photo-induced electron ( $e^-$ ) and hole ( $h^+$ ) that react with the  $OH$  group,  $O_2$ , and  $H_2O$  to form ROS, such as hydroxyl radical ( $^{\bullet}OH$ ) and superoxide radical anion ( $O_2^{\bullet-}$ ) with strong oxidation activities [52,76–78]. In a typical photocatalysis, when a light with the appropriate wavelength (adequate energy) falls on a photocatalyst, the photon energy is absorbed by a VB  $e^-$ , and it is excited to the CB. Herein, a  $h^+$  is generated in the VB. The outcome of this process is the generation of photoexcitation, and  $e^-$  and  $h^+$  pair. The excited electron is employed in the reduction of an acceptor in which a  $h^+$  is utilised for oxidation of donor molecules where the fate of  $e^-$  and  $h^+$  is determined by the relative positions of the valence and conduction bands in a semiconductor system and the redox substrate levels [79]. Based on band gap, materials are divided into three main types: *insulator*, *conductor* and *semi-conductor*. Therefore, the applicability of photocatalysis in the abatement of organic contaminants

in water could be limited by high  $E_g$ , rapid recombination rates of the photoinduced  $e^-$  and  $h^+$ , and weak light absorption capacities [80,81]. Large  $E_g$  values necessitate the absorption of more light (energies) to reach the separation of charge carriers [82]. In addition, the  $e^-$  and  $h^+$  can easily recombine without taking part in the reaction. This spontaneous  $e^-h^+$  recombination can result in reduced amount of photoinduced ROS present on reaction sites to undergo photoreduction.

Since most semiconductor metal oxides used in photocatalysis have high  $E_g$  values, several research directions have shifted towards modification of photocatalysts to overcome the limitations concomitant to their applications in photocatalysis. The evaluation of different hybrid nanocomposites for their lower  $E_g$  values [83], tuneable morphology [84,85], and reduced charge recombination capacities have been conducted [86]. With regards to degradation of organic contaminants via photocatalysis, Cu-based nanomaterials have demonstrated appreciable catalytic properties on account of their good stability and reusability [87]. For example, Ansari *et al.* [88], fabricated a low-cost single phase quaternary semiconducting copper zinc tin sulfide ( $Cu_2ZnSnS_4$ ) NPs, with low band gap (1.72 eV), and a high degree of absorption coefficient ( $\sim 10^4 \text{ cm}^{-1}$ ) for a VL irradiation of methylene blue (MB) dye. A total decomposition of the MB dye was realized in 120 mins with small amount of the catalyst (Fig. 4A,B). Empirical data obtained in the study aligned with a pseudo-first order kinetics with a rate constant ( $k$ ) value of  $0.0144 \text{ min}^{-1}$ . The exceptional performance observed in the degradation of the MB was attributed to small and uniform distribution size of the  $Cu_2ZnSnS_4$  NPs ( $\sim 7 \text{ nm}$ ), and even dispersion without agglomeration; the photocatalysis and mechanism of the degradation is

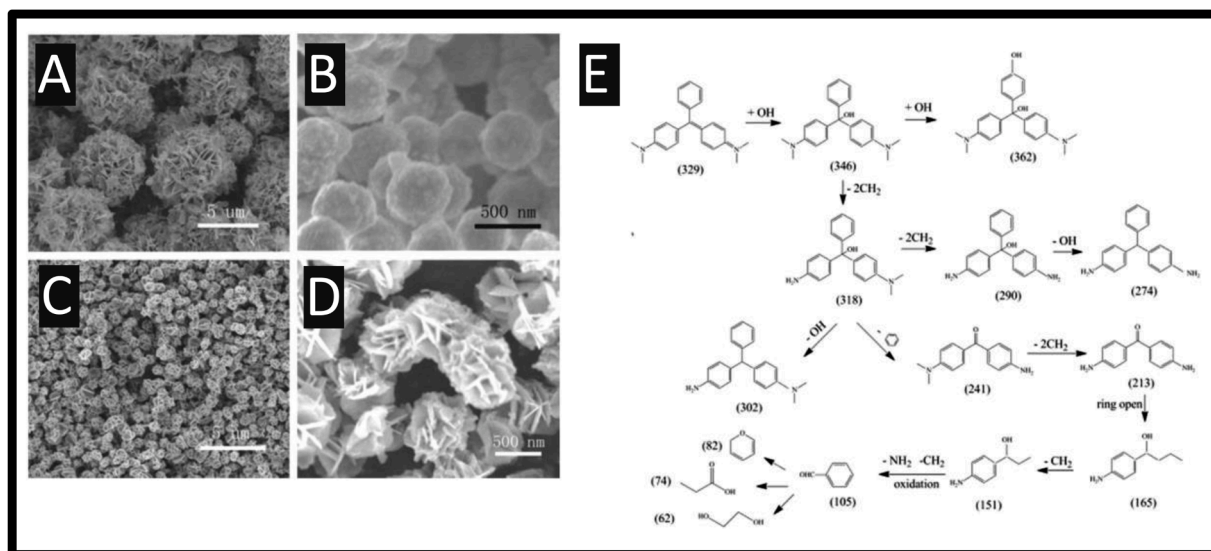
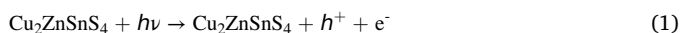


Fig. 5. Morphological characterizations of Cu<sub>2</sub>CdSnS<sub>4</sub> nanoflowers (A–D), mechanistic pathway of the degradation of MG using Cu<sub>2</sub>CdSnS<sub>4</sub> nanoflowers (E). Figure reproduced from reference [93]. Copyright 2022 Elsevier.

schematically represented in Fig. 4C and D.

From equation 1, the irradiation of the VL (from 0.15 kW halogen lamp) with  $h\nu > E_g$  on the catalyst formed  $e^-$  and  $h^+$  in the Cu<sub>2</sub>ZnSnS<sub>4</sub> nano architecture, which acted as a strong redox agent.



Consequently, water adhered onto the surface of Cu<sub>2</sub>ZnSnS<sub>4</sub> NPs, enters the  $h^+$ , and is oxidized to form OH radical. The  $e^-$  at the CB was taken by the O<sub>2</sub>, to form anionic O<sub>2</sub><sup>•-</sup> radical, which partakes further in the oxidation activity. The O<sub>2</sub><sup>•-</sup> radical reacts with H<sup>+</sup> to form OOH<sup>•</sup> which generates H<sub>2</sub>O<sub>2</sub> that subsequently turns into an aggressive •OH. The •OH thus formed attacks the aromatic ring of the MB, ripping open the hydroxylated ring and azo bond to produce H<sub>2</sub>O, CO<sub>2</sub>, NO<sub>3</sub>, NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ions [89]. Other related works in the degradation of MB using quaternary Cu<sub>2</sub>ZnSnS<sub>4</sub> were described in the one-step synthesis by Zhou *et al.* [90] and two-step synthesis by Phaltane *et al.* [91]. Quaternary Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) thin films were also useful in their phase dependent photocatalytic degradation of RhB dyes [92] with the highest  $k$  value achieved in the pure phase.

To forestall Sn<sub>Cu</sub> and Cu<sub>Sn</sub> defects, achieve lower  $E_g$  value, reduce  $e^-$ - $h^+$  recombination, enhance light absorption efficiency and increase the SSA and improve crystallinity, Xu and co-workers [93], substituted Zn with Cd in hierarchical Cu<sub>2</sub>CdSnS<sub>4</sub> nanoflowers (Fig. 5A–D) for the irradiation of malachite green (MG). The degradation obeyed a pseudo-first-order kinetics ( $k = 5.68 \times 10^{-3}$ ), and more than 90% degradation of MG was achieved in 120 mins. The mechanism (Fig. 5E) indicated that the degradation of MG originated from  $N$ -demethylation, elimination of benzene ring and subsequent ring-open reactions.

The synthesis and applications of magnetic and biocompatible NPs have become a popular part of the growing scientific explorations in modern times [94,95]. The use of magnetic compounds has become known as a competitive substitute to heterogeneous catalysts due to their ease of separation [96–98]. Diverse compounds such as zeolites [99,

100], polysaccharides [101], lignin [102], magnetic compounds [103], and graphene [104] have been applied in the dispersion and prevention of agglomeration of metal NPs. The use of biological polymers has become common because of their environmental friendliness, accessibility, unique physical properties, and low cost of preparation [101, 102]. Lignin is the second most abundant biopolymer with active sites such as hydroxyl, carbonyl, aldehyde, phenolic and methoxy moieties [102]. Herein, Orooji *et al.* [105], valorised liginosulfonate (sulfonic acid-based lignin) into a Cu-containing magnetically recyclable photocatalyst (FLN-Cu complex) for the degradation of Congo red (CR), RhB, and MB, depending on the reaction time, temperature and catalyst load. At optimal conditions, 95% of the MB was removed in 60 mins.

To further enhance the activity of CBC in the irradiation of organic pollutants, carbonaceous materials with high SSA (theoretical SSA of 2.63 km<sup>2</sup> kg<sup>-1</sup>) [106], excellent electronic attributes (mobility of charge carriers 20 m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at ambient temperature) [107], optical and mechanical characteristics (mechanical strength of 1.06 Tpa) [108–110] and thermal properties (thermal conductivity of 5.3 kWm<sup>-1</sup> K<sup>-1</sup>) [111] were conjugated with Cu. For example, the graphitized Cu-P25 (Cu-P25-graphene) nanocomposite was prepared by Jin *et al.* [112]. The synergistic impacts of Cu<sup>2+</sup> ions and graphene not only enhanced better charge separation capacity but presented extended light absorption (by Ti–O–C bonds) in the VL and narrowed the band gap of TiO<sub>2</sub>, which played a huge role in the degradation of MB. Benefiting from the charge separation, Cu-P25-graphene nanocomposite demonstrated high activity for MB degradation under VL irradiation, obtaining 98% within 100 mins. Copper in the composite behaves as the capture centre for the  $e^-$  that reduces the charge recombination rate. Consequently, the production of O<sub>2</sub><sup>•-</sup> and •OH radicals at the catalyst surface was amplified, which resulted in the faster abatement of the dye. Additionally, the excellent absorption ability of graphene boosted  $\pi$ - $\pi$  driven complexation between the aromatic regions of graphene and MB [113]. Good stability of the designed catalyst is attributed to strong chemisorption on the surface of TiO<sub>2</sub> promoted by the interaction between P25 and graphene, making it difficult to be removed after 5 repeated cycles.

Rare earth-based copper oxide Ln<sub>2</sub>CuO<sub>4</sub> (Ln = Eu, Tb, Sm, Pm, Nd, etc.) nanostructures are distinct for their unique attributes that position them for industrial relevance in applications such as magnetocaloric materials, sensors, and superconductors [114,115]. In recent years, this group of photocatalysts have gained extensive usage in photocatalysis. In one of such cases, Yousefzadeh *et al.* [116], synthesized a pure phase Sm<sub>2</sub>CuO<sub>4</sub> nanostructures using the sonochemical approach (power 10%

**Table 1**

Reaction conditions and efficiencies of Cu-based catalysts as photocatalysts towards the removal of organic contaminants in water

| Reaction conditions                                                                                           |                |           |                     |                                            | Efficiency of catalyst                            |                      |                          |                                                         |           |
|---------------------------------------------------------------------------------------------------------------|----------------|-----------|---------------------|--------------------------------------------|---------------------------------------------------|----------------------|--------------------------|---------------------------------------------------------|-----------|
| Catalyst                                                                                                      | Contaminant    | [C]       | [Cu]                | Irradiation                                | $E_g$ (eV)                                        | [EoD] (min)          | $k$ (min <sup>-1</sup> ) | KRS                                                     | Reference |
| Cu <sub>2</sub> ZnSnS <sub>4</sub> NPs                                                                        | MB             | 10 ppm    | 10 mg               | 0.15 kW THL                                | 1.72                                              | >99 % (120)          | 0.0144                   | <sup>•</sup> OH                                         | [88]      |
| Cu <sub>2</sub> ZnSnS <sub>4</sub> NPs-H <sub>2</sub> O <sub>2</sub>                                          | MB             | 10 ppm    | 20 g                | 0.1 kW XLS                                 |                                                   | 100% (90)            | 0.04                     | <sup>•</sup> OH                                         | [90]      |
| Cu <sub>2</sub> ZnSnS <sub>4</sub>                                                                            | RhB            | -         | -                   | VL                                         | 2.05 – 1.45                                       | 79% (240)            | 0.0065                   | O <sub>2</sub> <sup>•-</sup> and <sup>•</sup> OH        | [119]     |
| Cu <sub>2</sub> ZnSnS <sub>4</sub>                                                                            | BB 41          |           |                     | VL                                         | 1.90                                              | 90% (120)            |                          |                                                         | [120]     |
| Cu-P25-graphene                                                                                               | AO 8           |           |                     |                                            |                                                   |                      |                          |                                                         |           |
|                                                                                                               | MB             | 10 ppm    | 100 mg              | 0.25 kW XLS                                | -                                                 | 98% (100)            | 0.0387                   | O <sub>2</sub> <sup>•-</sup> and <sup>•</sup> OH        | [112]     |
| Cu <sub>2</sub> ZnSnS <sub>4</sub>                                                                            | MB             | 70 ppm    | 25 mg               | VL                                         | 1.53                                              | 50% (45)             | 0.018                    | <sup>•</sup> OH                                         | [91]      |
| CuO-NPs                                                                                                       | MB             | 200 mg    | 0.005 M             | VL                                         | 3.24                                              | 97% (50)             | 0.01                     | <sup>•</sup> OH                                         | [121]     |
| TiO <sub>2</sub> /CuO                                                                                         | MO             | -         | -                   | 6 W UV lamp                                | 2.53                                              | 95% (210)            | 0.0151                   | <sup>•</sup> OH                                         |           |
| TiO <sub>2</sub> /CuO/U/CN nanocomposite                                                                      | DR 16          | -         | -                   | 0.05 kW LED lamp                           | 1.5                                               | 100% (120)           | -                        | <sup>•</sup> OH, and O <sub>2</sub> <sup>•-</sup>       | [122]     |
| CuO/Cu(OH) <sub>2</sub> nanostructure                                                                         | RG 19A         | 50 ppm    | 200 mg/L            | Vilber Lourmat Multilamp                   | 2.39                                              | 98% (12)             | 0.0033                   | <sup>•</sup> OH O <sub>2</sub> <sup>•-</sup> and $h^+$  | [123]     |
| CuO/Cu <sub>2</sub> O                                                                                         | MO             | 20 µM     | 15 mg               | 0.3 kW XLS                                 | -                                                 | 90% (30)             |                          | <sup>•</sup> OH and O <sub>2</sub> <sup>•-</sup>        | [124]     |
| Nano TiO <sub>2</sub> /CuO                                                                                    | MB             | 10 ppm    | 100 mg              | 0.3 kW XLS                                 | -                                                 | 99% (300)            | -                        | O <sub>2</sub> <sup>•-</sup>                            | [125]     |
| Co <sub>3</sub> O <sub>4</sub> /CuO                                                                           | MB             | 10 ppm    | -                   | 0.5 kW XLS                                 | Co <sub>3</sub> O <sub>4</sub> = 1.7<br>CuO= 1.4  | 56% (180)            | -                        | <sup>•</sup> OH and O <sub>2</sub> <sup>•-</sup>        | [126]     |
| ZnO/CuO                                                                                                       | O-II           | 12 ppm    | -                   | XLS                                        | 2.77                                              | 41.8% (300)          | ≈ 0.01                   | <sup>•</sup> OH and O <sub>2</sub> <sup>•-</sup>        | [127]     |
| ZnO/CuO                                                                                                       | DB 71          | 20.34 ppm | 1.85 g/L            | Sunlight                                   | -                                                 | 89.58% (177.13)      | -                        | <sup>•</sup> OH                                         | [128]     |
| N <sub>3</sub> Cu-TiO <sub>2</sub>                                                                            | MB             | 10 µM     | -                   | Sunlight                                   | -                                                 | > 95% (360)          | 0.007                    | O <sub>2</sub> <sup>•-</sup> and <sup>•</sup> OH        | [129]     |
| CuCr <sub>2</sub> O <sub>4</sub> /CuO                                                                         | MO/MB          | 15 ppm    | 50 mg               | 0.3 kW XLS                                 | 1.23                                              | 97.16%/98.16%        | 0.01550/<br>0.01161      | <sup>•</sup> OH and O <sub>2</sub> <sup>•-</sup>        | [130]     |
| Chitosan/ZnO/CuO                                                                                              | FG             | 30 ppm    | -                   | 0.1 kW HPML                                | -                                                 | 91.21% (110)         | -                        | <sup>•</sup> OH and O <sub>2</sub> <sup>•-</sup>        | [131]     |
| Graphene/CuO NC                                                                                               | MB             | 20 ppm    | 0.3g/L              | Sunlight                                   | 1.39 ± 0.09                                       | 99.44% (80)          | 0.06                     | <sup>•</sup> OH, O <sub>2</sub> <sup>•-</sup> and $h^+$ | [132]     |
| CuO/Cu <sub>2</sub> O/Cu                                                                                      | MB             | 10 ppm    | 0.3 g/L             | Blue LED lamp                              | 1.42                                              | 91.91% (90)          |                          | <sup>•</sup> OH, O <sub>2</sub> <sup>•-</sup> and $h^+$ | [133]     |
| Fe <sub>3</sub> O <sub>4</sub> /rGO/CuO/H <sub>2</sub> O <sub>2</sub>                                         | MB             | 30 ppm    | 10 mg               | 0.5 kW XLS                                 | 1.5                                               | 98.70% (150)         | 0.0175                   | <sup>•</sup> OH, O <sub>2</sub> <sup>•-</sup> and $h^+$ | [134]     |
| BiVO <sub>4</sub> /CuO (e 0.75Cu/BVO)                                                                         | BPA            | 210 ppb   | 0-1000 mg/L         | 0.1 kW XLS                                 | 2.30                                              | 95% (5)              | -                        | <sup>•</sup> OH and CO <sub>3</sub> <sup>-</sup>        | [135]     |
| ZnAl LDH/g-C <sub>3</sub> N <sub>4</sub> /CuO NPs                                                             | Phenol         | 20 ppm    | 1.0 g/L             | 0.125 kW UV lamp/VL                        | 3.10                                              | 85% (60)             | 0.0330<br>/0.00083/h     | <sup>•</sup> OH, and O <sub>2</sub> <sup>•-</sup>       | [136]     |
| Fe <sub>3</sub> O <sub>4</sub> /CuO                                                                           | p-ASA          | 133 ppb   | 10 mg               | 0.3 kW XLS                                 | 1.69                                              | 100% (32)            | 0.1056                   | <sup>•</sup> OH, and O <sub>2</sub> <sup>•-</sup>       | [137]     |
| CuO-CP                                                                                                        | PAP            | 20 ppm    | 2.0 g/L             | -                                          | -                                                 | ≈ 60% (120)          | 0.0054                   | <sup>•</sup> OH                                         | [138]     |
| Ag <sub>3</sub> PO <sub>4</sub> /CuO                                                                          | Phenol         | -         | -                   | 0.125 kW, UV lamp                          | CuO-1.7;<br>Ag <sub>3</sub> PO <sub>4</sub> -2.45 | -                    | -                        | <sup>•</sup> OH                                         | [139]     |
| g-C <sub>3</sub> N <sub>4</sub> /CuO                                                                          | RhB            |           |                     | 0.3 kW XLS                                 |                                                   | 100% (5)             |                          | O <sub>2</sub> <sup>•-</sup>                            | [140]     |
| WO <sub>3</sub> /CdS/ CuO                                                                                     | MB             | 10 ppm    | 5 mg                | 0.3 kW Xe lamp                             | CuO-1.76,<br>WO <sub>3</sub> -2.87,<br>CdS-2.33   | 87.11% (240)         | -                        | e <sup>-</sup> and $h^+$                                | [141]     |
| CuS/Cu/CuO                                                                                                    | MB             | 10 ppm    |                     | 0.5 kW Xe lamp                             | 1.63                                              | 98.6% (40)           | 0.1092                   | <sup>•</sup> OH                                         | [142]     |
| Pb <sub>2</sub> O <sub>3</sub> /CuO                                                                           | RBD            | -         | -                   | 0.3 kW Xe lamp                             | 1.28                                              | 99% (90)             | 0.092                    | <sup>•</sup> OH and O <sub>2</sub> <sup>•-</sup>        | [143]     |
| Li <sub>3</sub> BO <sub>3</sub> /CuO                                                                          | AV 7           | 10 ppm    | 50 mg               | 0.4 kW Osram lamp                          | 3.11                                              | 80% (150)            |                          | <sup>•</sup> OH, O <sub>2</sub> <sup>•-</sup> and $h^+$ | [144]     |
| Li <sub>3</sub> BO <sub>3</sub> /Cu <sub>2</sub> O                                                            |                |           |                     |                                            | 3.05                                              | 85% (150)            | -                        |                                                         |           |
| Dy <sub>2</sub> Cu <sub>2</sub> O <sub>5</sub>                                                                | PR             | 10 ppm    | 100 mg              | 150 W VL                                   | 3.20                                              | 96.4% (120)          | 0.029                    | <sup>•</sup> OH                                         | [145]     |
| Cu <sub>3</sub> B <sub>2</sub> O <sub>6</sub>                                                                 | AV 7           | 25g/L     | 15 mg/L             | GYZ-250                                    | -                                                 | 86% (90)             | 0.0182                   | -                                                       | [146]     |
| g-C <sub>3</sub> N <sub>4</sub> /Cu <sub>3</sub> B <sub>2</sub> O <sub>6</sub> -H <sub>2</sub> O <sub>2</sub> | MB             | 10 mg/L   | 50 mg (60 wt. %)    | 300W Xe-lamp                               | ≈ 2.6                                             | 100% (60)            | 0.0474                   | <sup>•</sup> OH                                         | [147]     |
| Cu-WO <sub>3</sub>                                                                                            | TC             | 50 mg/L   | 0.05 g              | A 300 W Xe lamp                            | 2.69                                              | 96.8%                | -                        | <sup>•</sup> OH                                         | [148]     |
| CuCo <sub>2</sub> O <sub>4</sub>                                                                              | AB 14<br>AR 88 | 25g/L     | 15 mg/L             | 250 W high pressure mercury lamp (GYZ-250) | 1.74                                              | 79% (90)<br>89% (90) | 0.0116<br>0.0159         | <sup>•</sup> OH                                         | [149]     |
| [Cu(SCN) <sub>2</sub> (phen) <sub>2</sub> ]@CuI                                                               | AR 1           | 0.8 mM    | 1 g/dm <sup>3</sup> | LED illuminator                            |                                                   | >50% (60)            | 0.017.6                  | O <sub>2</sub> <sup>•-</sup>                            | [150]     |
| La <sub>2</sub> Cu <sub>2</sub> O <sub>5</sub>                                                                | AB             | 10 ppm    | 30 mg               | 150 W VL                                   | 3.25                                              | 80.1% (120)          | 0.01332                  | <sup>•</sup> OH                                         | [151]     |
| Cu-ZnO/g-C <sub>3</sub> N <sub>4</sub>                                                                        | ATZ            | 100 ppm.  | 0.5 g               | VL                                         | 2.45                                              | 90% (120)            | -                        | <sup>•</sup> OH, e <sup>-</sup> , and $h^+$             | [152]     |

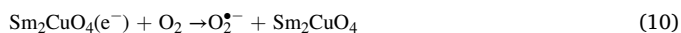
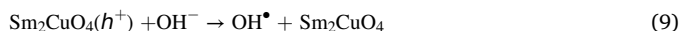
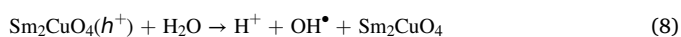
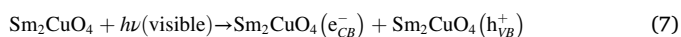
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Table 1 (continued)

| Reaction conditions                                                            |                           |          |                |                                           | Efficiency of catalyst |                                      |                          |                                                |           |
|--------------------------------------------------------------------------------|---------------------------|----------|----------------|-------------------------------------------|------------------------|--------------------------------------|--------------------------|------------------------------------------------|-----------|
| Catalyst                                                                       | Contaminant               | [C]      | [Cu]           | Irradiation                               | $E_g$ (eV)             | [EoD] (min)                          | $k$ (min <sup>-1</sup> ) | KRS                                            | Reference |
| 3D NP-Cu+H <sub>2</sub> O <sub>2</sub>                                         | MO, CR, MB, AO II and RhB | 20 mg/L  | 27.2 g/L       | Fluorescent lamp                          | 2.0–2.2 eV             | 100% (10) (MO)                       | 0.147                    | *OH                                            | [153]     |
| Lu <sub>2</sub> Cu <sub>2</sub> O <sub>5</sub> /Lu <sub>2</sub> O <sub>3</sub> | TB                        | 10 ppm   | 50 mg          | 400 W mercury lamp                        | 3.20                   | 98.5% (120)                          |                          | *OH                                            | [154]     |
| RGO/Cu                                                                         | RhB and MB                | 10 ppm   |                |                                           | 2.85                   | RhB = 91.0% (60) and MB = 72.0% (60) | RhB = 0.0409 MB = 0.0221 | *OH or O <sub>2</sub> <sup>-</sup>             | [155]     |
| CuO/C                                                                          | MO and MV                 | 1 μM     | 15 mg          | Mercury lamp                              | ~ 3.5                  | MV = 100% (10) MO = 100% (15)        | -                        | *OH                                            | [156]     |
| TNCuPc                                                                         | RhB                       | 10 mg/L  | 0.05 g         | 0.15 kW xenon lamp                        | -                      | 91% (300)                            | -                        | *OH                                            | [157]     |
| ZnO/CuO (8:1)/Pd                                                               | RhB and TCP               | 10 ppm   | 0.10 g /150 ml | 0.125 kW, low pressure mercury vapor lamp | -                      | RhB = 97.58% (60) TCP: 92.99%        | RhB: 0.184 TCP: 0.405    | *OH                                            | [158]     |
| Cu <sub>x</sub> Zn(1-x)O NPs/H <sub>2</sub> O <sub>2</sub>                     | MB                        | 10 μM    | 0.01 g         | 400W metal halide lamps                   | 2.70                   | 100% (120)                           | -                        | *OH                                            | [159]     |
| Ag <sub>3</sub> VO <sub>4</sub> /Cu-MOF/rGO                                    | AB 92                     | 10 mg/L  | 10 mg/L        | VL                                        | -                      | 95% (120)                            | 0.008                    | O <sub>2</sub> <sup>-</sup>                    | [160]     |
| ZnFe <sub>2</sub> O <sub>4</sub> @TiO <sub>2</sub> /Cu                         | NPX                       | 10 mg/L  | 5 mg/L         | Sunlight                                  | 2.62                   | 80.73% (120)                         | 0.0166                   | *OH                                            | [161]     |
| CuO NPs                                                                        | BV 3                      | 100 mg/L | 0.05 g         | Fluorescent lamp                          | -                      | 86% (150)                            | 0.0128                   | *OH                                            | [162]     |
| Cu <sub>2</sub> MoS <sub>4</sub> -Fe <sub>3</sub> O <sub>4</sub> @PPy-Ag       | MG                        | 10 mg/L  | 0.05 g         | 300 W XLS                                 | -                      | 94.8% (60)                           | 0.0333                   | O <sub>2</sub> <sup>-</sup> and *OH            | [163]     |
| FLN-Cu                                                                         | MB                        | 10 mg/L  |                | UV                                        |                        | 95% (60)                             | -                        | *OH                                            | [105]     |
| Cu-doped ZnO                                                                   | MCP                       | -        | 0.5 g          | -                                         | 2.88                   | 90% (120)                            | -                        | *OH                                            | [164]     |
| ZnO <sub>0.80</sub> -CuO <sub>0.18</sub> /NCP                                  | BP                        | 30 mg/L  | 0.12 g/L       | Medium-pressure mercury-vapor lamp        | 2.6                    | -                                    | 0.0012                   | *OH,                                           | [165]     |
| ZnS <sub>1.39</sub> -CuS <sub>2.88</sub> /NCP                                  |                           |          |                | (0.035 kW)                                | 2.8                    |                                      | 0.0011                   | O <sub>2</sub> <sup>-</sup> and h <sup>+</sup> |           |

**Key:** NPs: Nanoparticles; THL: Tungsten halogen lamp; XLS: Xenon light source; VL: Visible light; HPML: High pressure mercury lamp; U: Urea; CN: L-Asparagine; NC: Nanocomposite; [Cu(SCN)<sub>2</sub>(phen)<sub>2</sub>]: Diisothiocyanatobis (1,10-phenanthroline)copper(II) complex; CuO-CP: CuO supported Clinoptilolite; TNCuPc: Tetranitro copper phthalocyanine; Cu<sub>2</sub>MoS<sub>4</sub>-Fe<sub>3</sub>O<sub>4</sub>@PPy: Polypyrrole-functionalized Cu<sub>2</sub>MoS<sub>4</sub> magnetic composites modified with Ag NPs; FLN-Cu: Fe<sub>3</sub>O<sub>4</sub>@LS@naphthalene-1,5-diamine@copper complex; FLN-Cu: MCP: monocrotophos pesticide; NCP: clinoptilolite NPs; BP: benzophenone; [C]: Pollutant concentration; [Cu]: Copper catalyst concentration; EoD: Degradation efficiency; Methyl blue; MB; BPA: bisphenol A; BB 41: Basic blue 41; AO 8: Acid orange 8; PAP: p-aminophenol; DR 16: Direct red 16; RG 19A: Reactive green 19A; O II: Orange II; AV 7: Acid violet 7; DB 71: Direct blue 71; FG: Fast green; p-ASA: p-arsanilic acid; AR 88: Acid red 88; AB 14: Acid brown 14; BV 3: Basic violet 3; PR: Phenol red; TC: Tetracycline; AR 1: Acid red 1; AB: Acid black; AO II: Acid orange II; TB: Toluidine blue; MV: Methyl violet; TCP: Tricopyr; AB 92: Acid blue 92; MCP: Monocrotophos pesticide; NPX: Naproxen.

and time 15 mins) for the photocatalytic degradation of methyl orange (MO) in water medium ( $E_g = 1.62$  eV). With a catalyst load of 30 mg, 20 mg/L of the MO was degraded under a VL by 91.4% in 100 mins, the mechanism of the degradation follows the equation (7-17).



The utilization of ZnO semiconductor in the photocatalytic removal of organic contaminants has been immensely limited by its wide  $E_g$  (3.30 eV) [117]. The addition of perovskite-type metal oxides to ZnO showed enhanced photocatalytic property for the elimination of organic pollutants under VL. Therefore, Yulizar *et al.* [118] decorated ZnO with La<sub>2</sub>CuO<sub>4</sub> and achieved improved photo-degradation of MG under VL. Within 120 mins, 91.0% degradation of the MG dye was achieved using VL irradiation. Similar reports involved the use of two phase

Lu<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>/Lu<sub>2</sub>O<sub>3</sub> for the removal of thymol blue (TB), with 98.5% removal efficiency within 120 mins. Table 1 shows the extensive use of CBC as photocatalysts in the abatement of organic contaminants in water and the ROS involved in the development.

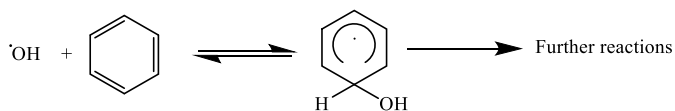
Another way of reducing the high possibility of charge recombination associated with the use of pure copper oxide semiconductor catalysts is the introduction of other semiconductors with suitable CB and VB to form heterostructures (e.g. Ag<sub>3</sub>VO<sub>4</sub>/TiO<sub>2</sub>/graphene [166], CeO<sub>2</sub>/TiO<sub>2</sub> [167], N,S-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> [168]) with improved photocatalysis of organic pollutants. Luo *et al.* [147] prepared g-C<sub>3</sub>N<sub>4</sub>/Cu<sub>3</sub>B<sub>2</sub>O<sub>6</sub> hybrid photocatalysts using liquid chemisorption and thermal post-treatment technique and investigated the photocatalytic activity of the g-C<sub>3</sub>N<sub>4</sub>/Cu<sub>3</sub>B<sub>2</sub>O<sub>6</sub> as an oxidant under VL irradiation. The results demonstrated that the well-matched band edge structure between Cu<sub>3</sub>B<sub>2</sub>O<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub> in the as-prepared g-C<sub>3</sub>N<sub>4</sub>/Cu<sub>3</sub>B<sub>2</sub>O<sub>6</sub> significantly supported separation and transfer of charge carriers when compared with individual Cu<sub>3</sub>B<sub>2</sub>O<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub>. The 60% g-C<sub>3</sub>N<sub>4</sub>/Cu<sub>3</sub>B<sub>2</sub>O<sub>6</sub> showed maximum  $k$  value of 0.0474 min<sup>-1</sup>, which was 2.14 and 3.16 times higher than the Cu<sub>3</sub>B<sub>2</sub>O<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub>, respectively. The observed improvement in the photocatalytic performance was attributed to the boost in the separation efficiency of photogenerated  $e^-$ - $h^+$  pairs with the combination of Cu<sub>3</sub>B<sub>2</sub>O<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub>, thus improving the activation of H<sub>2</sub>O<sub>2</sub> for decolorization of MB under VL. After four cycles, the catalysts lost a slight degradation activity on the target pollutant. The degradation efficiency of Cu<sub>2</sub>O and CuO-doped with Li<sub>3</sub>BO<sub>3</sub> (Li<sub>3</sub>BO<sub>3</sub>/Cu<sub>2</sub>O and Li<sub>3</sub>BO<sub>3</sub>/CuO, respectively) were investigated on the photocatalytic degradation of AV 7 by Ranjeh and co-workers [144]. Differences in the morphology and band gaps accounted for 5% difference in the photocatalytic degradation of the AV 7 by the two copper-oxide based catalysts. With lower crystalline size and  $E_g$ , the Li<sub>3</sub>BO<sub>3</sub>/Cu<sub>2</sub>O demonstrated higher catalytic efficiency than the Li<sub>3</sub>BO<sub>3</sub>/CuO counterpart. Another



strategy is the use of plasmonic nano-metals to boost the photocatalytic property of copper oxides [124,169–171].

### 3.2. Fenton-like processes

Fenton reaction is renowned for its outstanding performance in the abatement of organic contaminants in water media [172–174]. In an ideal Fenton reaction, Fe(II) catalyses the decomposition of  $\text{H}_2\text{O}_2$  to form  $\cdot\text{OH}$  (Eqs. (18–24)) [174]. The spontaneously generated  $\cdot\text{OH}$  destroys the structure of the pollutant due to its strong oxidation potential. More significantly, the generated Fe(III) can be reduced to Fe(II) through a similar reaction as represented in Eq. (2) [175], which guarantees steady generation of the  $\cdot\text{OH}$ . In the case of an organic pollutant, the  $\cdot\text{OH}$  reacts with the organic compound to generate carbon-centred radicals. The  $\cdot\text{OH}$  although present in vanishing trace concentration reacts in well-defined ways with the organic pollutants, typically by abstraction of the H in O–H, N–H, or C–H bonds, in addition to the aromatic rings (Eqs. (25–27) [176,177]. Nevertheless, the use of the traditional Fenton reaction is commonly limited by its intrinsic limitations such as poor recyclability/reusability, accumulation of Fe-dense sludge, and slim working pH range. To circumvent these challenges, diverse heterogenous Fenton-like catalysts were devised as substitutes to the homogeneous processes [178–180].

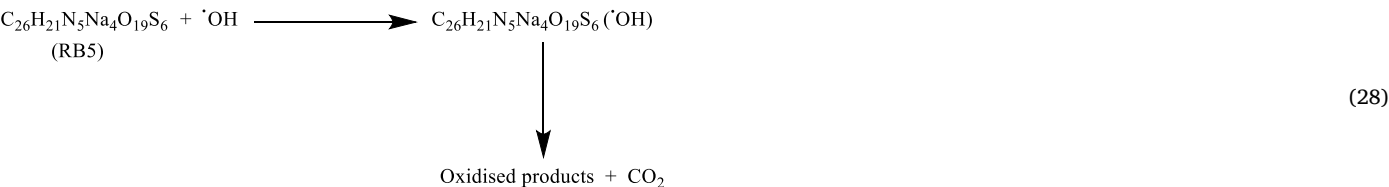


Nowadays, Cu-based materials have been widely used as catalysts in Fenton-like reactions for the effective elimination of organic contaminants in water, owing to their outstanding characteristics such as eco-friendliness, cost-effectiveness, high stability, high natural abundance and efficient catalytic activity [181]. Table 2 summarises the reaction conditions and performance of Cu-based catalysts in Fenton-like reactions towards the removal of organic contaminants in water. In addition, owing to its broad range of existence in various oxidation states ( $\text{Cu}^0$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Cu}^{3+}$ ), CBC can participate and promote Fenton-like reactions [182]. The rate of reduction of  $\text{Cu}^{2+}$  by  $\text{H}_2\text{O}_2$  is fast ( $4.6 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ ) and  $\text{Cu}^+$  can efficiently react with  $\text{H}_2\text{O}_2$  to generate  $\cdot\text{OH}$  radical with a high reaction rate ( $1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ ) [183]. Contemporary research has revealed that organic contaminants can form bonds with Cu catalysts species, generating orbital interactions that involve the

mobility of electrons in the form of  $\pi \rightarrow \text{Cu}^{2+}$ . This process leads to the decrease of high oxidation state Cu and accelerates the decomposition of  $\text{H}_2\text{O}_2$  into more  $\cdot\text{OH}$  [184,185]. Moreso, in Fenton-like reactions, electron distribution tuning has been shown to be an effective strategy for enhancing catalytic performance [186]. The negative and the positive areas in the distribution of electrostatic potential are anticipated to be favourable reactive sites for redox reactions of  $\text{H}_2\text{O}_2$  [187]. Lyu *et al.* applied phenoxyphenol functionalized reduced graphene oxide nano-sheets (POP-rGO NSs) in Fenton-like process catalysis and realized that the surface complexation of POP with rGO via C–O–C bridges enhanced the uneven dispersal of electrons in the catalyst, resulting in efficient  $\text{H}_2\text{O}_2$  decomposition on the electron-poor and electron-rich centres around the C and O atoms, respectively [188]. Furthermore, the charge redistribution in some materials polarized the related orbits and atoms to generate an internal electric field (IEF) [189]. Effects such as promotion of charge transfer, reduction of diffusion and improvement of accessibility of charge to reactants are reported to be driven by the IEF [190]. These effects are also reported for semiconductor catalysts like copper oxides [191–193]. For example, Li *et al.* [193] prepared a framework of Cu-doped boron nitride nanobelts (Cu-BN, Fig. 6) with an IEF arising from the uneven dispersion of electrons with electropositive Cu sites and electronegative N sites. This was used for the oxidative decomposition of BPA in a Fenton-like process. The unique architecture enhanced the oxidation of  $\text{H}_2\text{O}$  on the electropositive Cu sites and the reduction of  $\text{H}_2\text{O}_2$  molecules on the electronegative N sites, generating highly reactive  $\cdot\text{OH}$ . This acceleration facilitated the abatement of BPA adsorbed on Cu-BN system. Typically, the electron paramagnetic resonance (EPR) results confirmed that BPA donated electrons to Cu through the  $\pi \rightarrow \text{Cu}^{2+}$  interaction in the  $\sigma$ -Cu–ligand complexes between the Cu surface and phenolic groups, followed by the oxidation of the pollutant.

Gong *et al.* [194] utilized artificially designed Cu-Schiff bases nanozyme ( $\text{Cu}@\text{SB}$ ) to realize efficient activation of  $\text{H}_2\text{O}_2$  for the degradation of amlodipine (AD), achieving 100% degradation within 90 mins at a temperature of  $45^\circ\text{C}$ . Schiff bases were used as special donor ligands that efficiently stabilized the active copper ion. The removal complied with a pseudo first-order kinetic model, while  $\cdot\text{OH}$  and singlet oxygen ( $^1\text{O}_2$ ) were the key reactive species in the degradation process. The Fenton-like activity was driven by the redox reactions between  $\text{Cu}^+/\text{Cu}^{2+}$ . The  $k$  value of the AD degradation increased with increasing

catalyst,  $\text{H}_2\text{O}_2$  concentrations, pH, and temperature. Naz and team [197], also prepared and analyzed a silica-based  $\text{Cu}^{2+}$  organic-inorganic hybrid compound, achieved by grafting of Schiff base onto silica surface and complexation of the base by  $\text{CuCl}_2$ . The as-prepared metal complex hybrid heterogeneous catalyst was effective in the oxidative degradation of a non-biodegradable RB5 azo dye in the presence of  $\text{H}_2\text{O}_2$  to generate  $\cdot\text{OH}$  free radicals. At the best reaction parameters for optimal degradation of RB5, 91% of the recalcitrant dye was removed in 100 mins, at a  $k$  degradation rate of  $0.017 \text{ min}^{-1}$ . The possible mechanism indicates that the molecules of  $\text{H}_2\text{O}_2$  were activated first by the  $\text{Cu}^{2+}$  hybrid catalyst to form the  $\cdot\text{OH}$  radical. The generated  $\cdot\text{OH}$  radical attacks the organic substrate, bringing about the chemical decomposition of the substrates through abstraction of H and addition to the  $\text{C}=\text{C}$  bonds [206]. Therefore, the generated  $\cdot\text{OH}$  radicals reacts with the RB5 and is transformed to dye-radical products as shown in Eq. 28:



2

Ma and co-workers [181] incorporated Cu<sup>+</sup> into g-C<sub>3</sub>N<sub>4</sub> towards the removal of various contaminants. When g-C<sub>3</sub>N<sub>4</sub> is generated, the Cu<sup>2+</sup> is reduced to Cu<sup>+</sup> by the release of nitride and carbon fragments, thereby fostering Fenton-like activation of H<sub>2</sub>O<sub>2</sub>. The removal efficiencies of 84.4%, 94.6%, 96.0% and 99.2% were recorded for TC, BPA, AR 73 and RhB, respectively, positing that the Cu(I)-doped g-C<sub>3</sub>N<sub>4</sub> (Cu(I)-g-C<sub>3</sub>N<sub>4</sub>) was an efficient Fenton-like catalyst to remove various organic pollutants. Interestingly, the narrow pH window associated with the Fenton process was overcome by this Fenton-like process as the degradation of RhB enjoyed a broad pH window of 3-11. Increasing the Cu metal load on the g-C<sub>3</sub>N<sub>4</sub> was reported by Zhu *et al.* [61] to increase the amount of Cu-N<sub>x</sub> species which accelerated the H<sub>2</sub>O<sub>2</sub> decomposition to generate <sup>•</sup>OH. Consequently, the Cu-g-C<sub>3</sub>N<sub>4</sub> demonstrated superior catalytic properties for the removal of MB, MO, and RhB (Table 1). Copper-iron

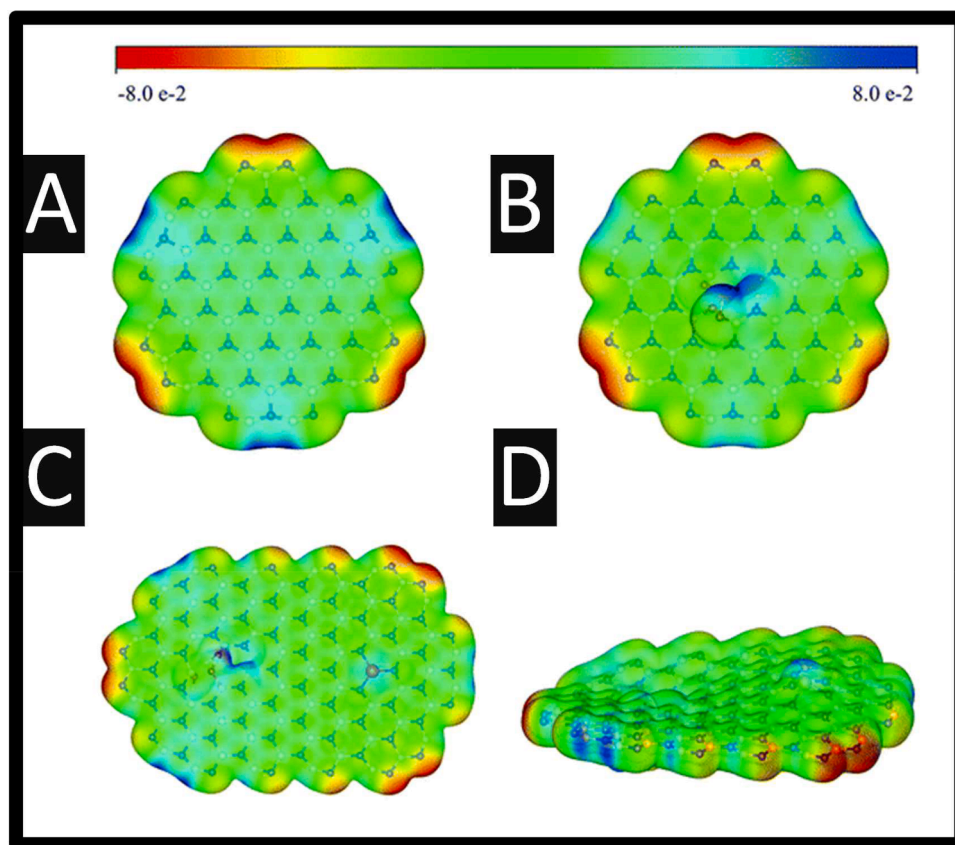
based bimetallic systems have demonstrated a broad range of heterogeneous catalysis including oxidation of phenol [207] and toluene [208], and heterogeneous Fenton degradation of phenolics [209,210], RhB [211], DPD [203], SA [202], and SMX [200]. Fig. 7A portrays a probable mechanism of reaction of SMX degradation using Fe<sub>0.75</sub>Cu<sub>0.25</sub> (BDC).

In a report by Gao *et al.* [198], the efficiency of a coupled Fenton-like and photocatalytic process using Cu<sub>2</sub>O/BiOBr with S-scheme heterojunction in the decomposition of organic solvents such as CR, MB, MV, RhB, TC, and a mixture of the contaminants was described. The reduction of glucose remarkably restored the photocatalysis of the Cu<sub>2</sub>O/BiOBr catalyst to ~90% from ~60% (after 4 cycles). Here, a Fenton-like Cu<sub>2</sub>O and stable BiOBr were employed to generate the IEF (Fig. 7B), which functioned as the driving potential for the migration of photo-induced charge. This configuration supported the separation of

**Table 2**  
Reaction conditions and performance of Cu-based catalysts in Fenton-like reactions towards the removal of organic contaminants in water

| Reaction conditions                                              |                     |             |            |                                  |         | Efficiency of catalyst                                                         |                                       |             |                                                                                  |           |
|------------------------------------------------------------------|---------------------|-------------|------------|----------------------------------|---------|--------------------------------------------------------------------------------|---------------------------------------|-------------|----------------------------------------------------------------------------------|-----------|
| Catalyst                                                         | Contaminant         | [C]         | [Cu]       | [H <sub>2</sub> O <sub>2</sub> ] | pH      | [EoD](min)                                                                     | k <sub>abs</sub> (min <sup>-1</sup> ) | [TOC] (min) | KRS                                                                              | Reference |
| Cu@SB                                                            | AD                  | 10 μM       | 10 -50 ppm | 0.5 mM -2.0 mM                   | 5-9.0   | 100% (90)                                                                      | 0.0168 @ 35 °C                        | -           | <sup>•</sup> OH and O <sub>2</sub> <sup>•-</sup>                                 | [194]     |
| Cu-doped MgO                                                     | SA                  | 50 ppm      | 500 ppm    | 20 mM                            | 10.8-11 | 100% (45)                                                                      | 0.042                                 | 100% (45)   | <sup>•</sup> OH or <sup>•</sup> HO <sub>2</sub> /O <sub>2</sub> <sup>•-</sup>    | [62]      |
| Cu(I)-g-C <sub>3</sub> N <sub>4</sub>                            | RhB                 | 50 ppm      | 80 ppm     | 40 mM                            | 7       | 99.2% (60)                                                                     | -                                     | 22.8% (60)  | <sup>•</sup> OH, and O <sub>2</sub> <sup>•-</sup>                                | [181]     |
| Cu-g-C <sub>3</sub> N <sub>4</sub>                               | RhB                 | 10 ppm      | 20 ppm     | 300 mM                           | 7       | 92.3% (15)                                                                     | -                                     | 42% (60)    | <sup>1</sup> O <sub>2</sub> , O <sub>2</sub> <sup>•-</sup> , and <sup>•</sup> OH | [61]      |
| Cu-doped Fe@Fe <sub>2</sub> O <sub>3</sub> /CNT/Ni               | TC                  | 20 ppm      | -          | -                                | 3       | 98.1% (120)                                                                    | -                                     | 89.8% (6 h) | <sup>•</sup> OH                                                                  | [195]     |
| Cu-Zn-Fe-LDH                                                     | ACT                 | 0.1 mmol/L  | 0.5 g/L    | 30 mmol/L                        | 7       | 100% (24h)                                                                     | -                                     | -           | <sup>•</sup> OH                                                                  | [196]     |
| Cu (II)-hybrid                                                   | RB 5                | 45 ppm      | 17.6 mM    | 0.8 g/L                          | 4-10    | 91% (100)                                                                      | 0.017                                 | -           | <sup>•</sup> OH                                                                  | [197]     |
| Cu <sub>2</sub> O/BiOBr S-scheme                                 | MB, RhB, CR, MV, TC | 100 ppm     | 50 mg      | 0.5 mL                           |         | MB: 98% (50)<br>RhB: 82% (50)<br>CR: 95% (50)<br>MV: 86% (50)<br>TC: 100% (50) | 0.0787 @MB                            | -           | <sup>•</sup> OH                                                                  | [198]     |
| Ni <sub>(2-x)</sub> Cu <sub>(x)</sub> Al-LDH                     | SPRW                | 80 ppm      | 0.4 g/L    | -                                |         | 100% (90)                                                                      | 0.0316                                | 74.8% (90)  | <sup>•</sup> OH                                                                  | [199]     |
| Fe <sub>0.75</sub> Cu <sub>0.25</sub> (BDC)                      | SMX                 | 20 ppm      | 6 mM       | 0.5 g/L                          |         | 100% (120)                                                                     | -                                     | -           | <sup>•</sup> OH                                                                  | [200]     |
| 5Fe2.5Cu-Al <sub>2</sub> O <sub>3</sub>                          | NB                  | 100 ppm     | 0.5 g/L    | 300 μL                           |         | 100% (60)                                                                      | -                                     | -           | <sup>•</sup> OH                                                                  | [201]     |
| Cu-BN(2.84 wt% Cu)                                               | BPA                 | 25 ppm      | 1.0 g/L    | 5 mM                             | 3-11    | 100% (30)                                                                      | 0.198                                 | 64.2% (120) | <sup>•</sup> OH                                                                  | [141]     |
| Fe/Cu/Al-pillared clays                                          | SA                  | 0.29 mmol/L | 2.0 g/L    | 5.23 mmol/L                      | 3.5     | 98% (240)                                                                      | -                                     | -           | <sup>•</sup> OH                                                                  | [202]     |
| CuFe/SBA-15 bimetallic                                           | DPD                 | 0.1 g/L     | 0.1 g/L    | 8 mM                             | 4       | 90% (120)                                                                      | -                                     | 70% (120)   | <sup>•</sup> OH                                                                  | [203]     |
| Cu <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> /Cl <sup>-</sup> | CMZ                 | -           | 1 μM       | 10 mM                            | 7       | 96% (120)                                                                      | 0.028                                 | -           | <sup>•</sup> OH, and O <sub>2</sub> <sup>•-</sup>                                | [204]     |
| CuO NPs/H <sub>2</sub> O <sub>2</sub>                            | Alachlor            | 30 ppm      | 0.2 g      | 2 mL                             | 4-9     | 100% (30)                                                                      | 0.292                                 | -           | <sup>•</sup> OH, or <sup>•</sup> HO <sub>2</sub> <sup>•</sup>                    | [205]     |
|                                                                  | Ph                  | 0.5 ppm     | 0.1 g      | -                                | -       | -                                                                              | -                                     | -           | -                                                                                | -         |

**Key:** LDH: Layered double hydroxide; Cu (II)-hybrid: SiO<sub>2</sub>\*NH<sub>2</sub>\*QC\*Cu; QC: 2-Quinolinecarboxaldehyde; x = 0.0; 0.5; 1.5; and 2.0; SPRW: synthetic petroleum wastewater; Fe<sub>0.75</sub>Cu<sub>0.25</sub> (BDC): Iron and copper bimetallic MOF material; Cu-doped boron nitride nanobelts; DPD: N, N-diethyl-p-phenyl diamine; SA: Sulfanilamide; CMZ: Carbamazepine; SMX: Sulfamethoxazole; Ph: Phenanthrene; AD: Amlodipine; RB 5: Reactive black 5; NB: Nitrobenzene.



**Fig. 6.** A framework of Cu-doped boron nitride nanobelts (Cu-BN) showing ESP distribution for (A) perfect BN, (B) the as-prepared BN, (C) the plan map of ESP and (D) 3D-map for Cu-doped BN. (orange, red, pink, blue, and white circles represent Cu, O, B, N, and H atoms respectively). Reproduced from reference [193]. Copyright 2019 The Royal Society of Chemistry.

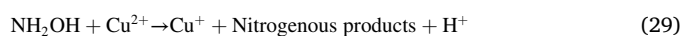
photoinduced carriers and generation of the  $\cdot\text{OH}$  by  $\text{H}_2\text{O}_2$  and  $\text{Cu}^+$ , leading to successful photocatalytic decomposition of organic contaminants. Interestingly, during irradiation by light, the prevalence of the in-built electric field can result in the photoinduced  $\text{e}^-$  in the BiOBr CB combining with the  $h^+$  in the  $\text{Cu}_2\text{O}$  VB. Simultaneously, the  $h^+$  in the BiOBr VB and the  $\text{e}^-$  of the  $\text{Cu}_2\text{O}$  CB are preserved for photo-redox reactions (Fig. 7C). This path of charge transfer demonstrates that the prepared heterojunction between  $\text{Cu}_2\text{O}$  and BiOBr is S-scheme heterojunction. This heterojunction promoted the aggressive oxidation and reduction qualities of the 15% $\text{Cu}_2\text{O}$ /BiOBr, thereby promoting the efficient degradation of pollutants through coupled Fenton-like and photocatalytic processes.

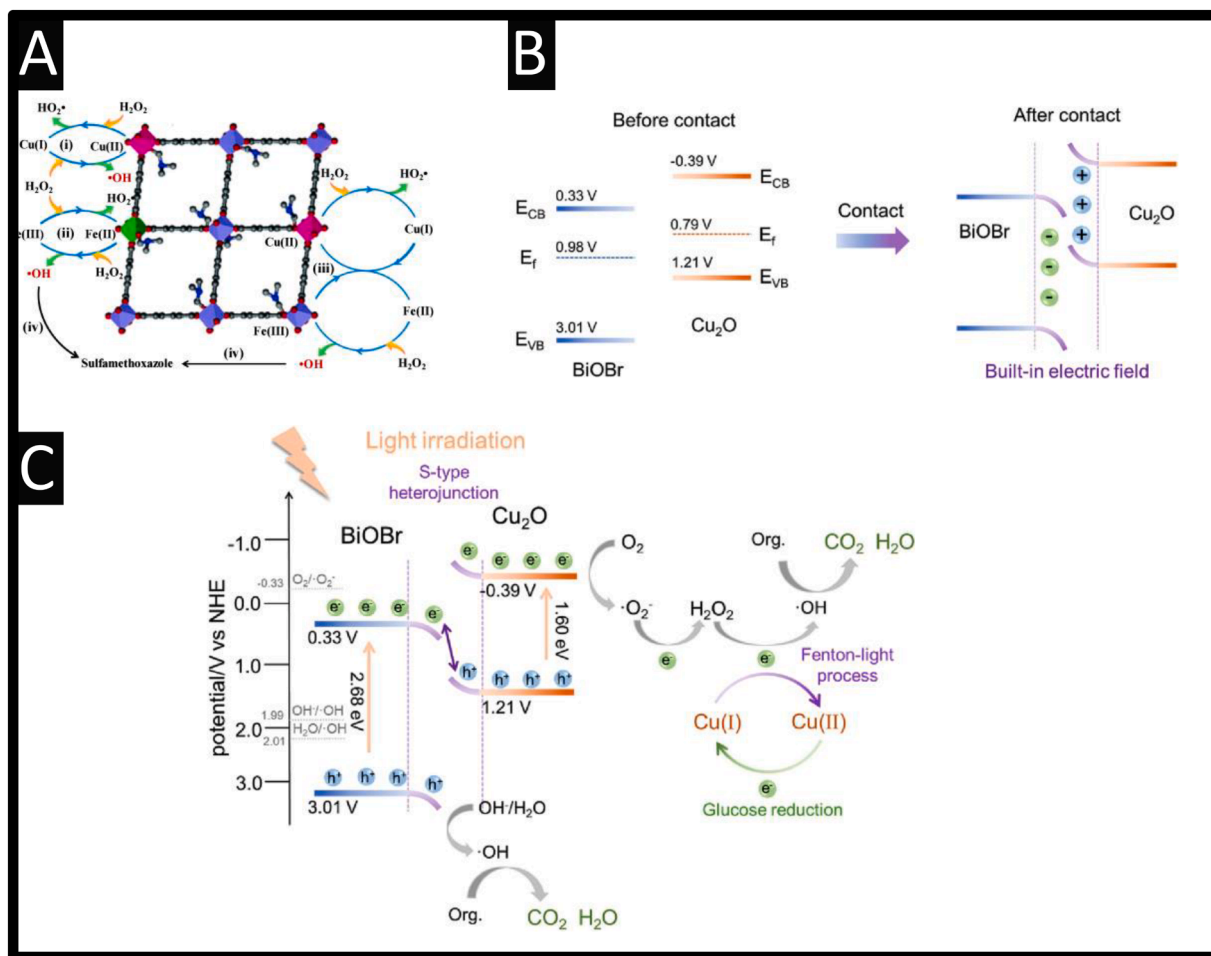
### 3.3. Persulfates activation

The AOPs based on PS such as peroxydisulfate (PDS,  $\text{S}_2\text{O}_8^{2-}$ ) or peroxymonosulfate (PMS,  $\text{HSO}_5^-$ ) as efficient and auspicious methods for the abatement of organic pollutants in water have attracted a growing popularity in the last decade [18,212,213]. The activation of PMS or PDS generates powerful single-electron  $\text{SO}_4^{\cdot-}$  [214,215] with advantages of higher redox potentials (2500–3000 mV) than that of  $\cdot\text{OH}$  (1800–2700 mV) [216], long half-life (0.03–0.04 ms) [217], and high selectivity [218]. In addition,  $\text{SO}_4^{\cdot-}$  radicals can efficiently react with target contaminants over a wider window of pH values (2–8) [219,220]. The sulfate radicals can decompose recalcitrant organic pollutants in water and generate inorganic salt,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and other lower molecular substances [221,222]. Many scientific reports have demonstrated that PS-based AOPs can effectively degrade refractory organic contaminants including PPCPs, antibiotics, dyes, chlorinated organic contaminants, phenolics, and endocrine-disrupting chemicals (EDCs) [216,223–227]. The PMS and PDS are typified by the presence of O–O bonds [215], and

O–O bonds can generate reactive radicals that degrade pollutants [228]. Relative to other oxidants, such as  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , the PS are more convenient to transport and store because of their existence as solid powder.

Nonetheless, the direct activation of the PMS and PDS to generate the sulfate radicals for the abatement of most organic contaminants are terribly slow, which demands additional physical or chemical stimulation for practical application. In a review by Tian *et al.* [216], the activation of the PMS and PDS to generate reactive radicals were achieved with various strategies such as conventional (thermal, alkaline, UV, and transition metal ions activations), and modern (microwave, metal oxide, and carbon activation). Among these strategies, the interest in the use of heterogeneous catalysts have peaked because of their high catalytic activity, exceptional reusability, and less energy requirement [39,229]. Hence, huge attention has been given to investigating heterogeneous catalysts for PS activation and CBC have enjoyed such attention for their effectiveness in the abatement of organic contaminants in water. Table 3 presents an overview of the reaction conditions and performance of PMS-based catalysts in the abatement of organic contaminants. For instance, Wang *et al.* [230] showed that adding  $\text{Cu}^{2+}$  not only enhanced the effectiveness of degradation of  $\text{Fe}^{2+}$ /hydroxylamine (HA)/PS platforms, but also widened the pH window of  $\text{Fe}^{2+}$ /HA/PS decomposition of O II (pH; 2–10). Scavenger reactions reveal that  $\text{SO}_4^{\cdot-}$  is the main ROS. The degradation followed different pathways in the acidic and basic medium, both favourable by the introduction of the  $\text{Cu}^{2+}$  ion. In the acidic range,  $\text{Cu}^+$  was oxidized to  $\text{Cu}^{2+}$  by  $\text{Fe}^{2+}$ , while in the basic environment, HA reduced  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  to produce the  $\text{SO}_4^{\cdot-}$  (Eqs. 29–30) by activating PS, which extended the pH to the alkaline range in the use of the  $\text{Fe}^{2+}$ /HA/PS for the elimination of O II.





**Fig. 7.** A: Probable mechanism of reaction of SMX degradation using Fe<sub>0.75</sub>Cu<sub>0.25</sub> (BDC). Figure reproduced from reference [200]. Copyright 2020 Elsevier. B: The band structure of Cu<sub>2</sub>O and BiOBr; C: Schematic diagram of synergism between Fenton-like process and S-scheme heterojunction. Figure reproduced from reference [198]. Copyright 2023 Elsevier.



### 3.3.1. Peroxymonosulfate (PMS)

Lei and co-workers [238] revealed that copper ferrite-graphite oxide hybrid (CuFe<sub>2</sub>O<sub>4</sub>@GO) catalyst could activate PMS for the abatement of MB in solution. A removal efficiency of 93.3% was realized when 0.8 mmol/L PMS and 200 ppm CuFe<sub>2</sub>O<sub>4</sub>@GO were applied on 20 ppm of MB at room temperature condition. The CuFe<sub>2</sub>O<sub>4</sub>@GO catalyst presented outstanding stability and reusability. Additional investigation on the mechanism of oxidation of MB showed that the Cu<sup>2+</sup>/Cu<sup>+</sup> redox couple on CuFe<sub>2</sub>O<sub>4</sub>@GO performed the key role in the activation of PMS, where both sulfate and hydroxyl radicals were produced and led to the decomposition of the targeted contaminants. Although the use of Cu<sup>2+</sup>/Cu<sup>+</sup> redox cycles have been very significant in the activation of PMS in the Fenton-like processes, the conversion of Cu<sup>2+</sup> to Cu<sup>+</sup> is characteristically very slow [262], especially in acidic or neutral conditions [263]. Huang *et al.* [257] demonstrated that the addition of Cl<sup>-</sup> makes it possible for the Cu<sup>2+</sup>/PMS system to oxidize acid orange (AO7) in neutral, acidic, and alkaline solution (pH range of 4–9). This result demonstrates the significance of Cl<sup>-</sup> concentration in accelerating the efficiency of oxidation of the Cu<sup>2+</sup>/PMS system under different pH values, which is hardly employed in the trace Cu(II) supported PMS system in saline wastewater. The degradation of AO7 followed a pseudo first-order with *k* that was linearly correlated with increasing Cl<sup>-</sup> concentration (0–300 mM). The AO7 was completely abated in the presence of 100 mM of Cl<sup>-</sup> in 60 mins. The scavenger experiments and EPR

measurements showed that <sup>1</sup>O<sub>2</sub> was the ROS in the Cu<sup>2+</sup>/PMS system. Nonetheless, some undesirable by-products were identified in the degradation pathway of the AO7, thus signalling a need to be cautious in the evaluation of the use of Cu<sup>2+</sup>/PMS system in chloride-containing solutions.

Yang *et al.* [240] synthesized diverse crystalline MnO<sub>2</sub> (C-MnO<sub>2</sub>) and single and bimetallic-doped amorphous MnO<sub>2</sub> described as M-AMO, where M represents Cu, Co, Fe and Ni for organic oxidation with PMS. The result showed that at a concentration of 1 mol%, the M-AMO demonstrated higher catalytic activities than C-MnO<sub>2</sub>, while the Cu-AMO catalysed PMS system presented *k* value that is at 3.5 times more than that of Co-AMO, Fe-AMO, and Ni-AMO. The non-radical degradation of target pollutant phenol followed two pathways (Fig. 8). The first pathway (pathway 1) is the overall PMS activation mechanism through a direct transfer-electron process (DTP) and the second pathway (pathway 2) is the oxidation of phenol. In pathway 1 detailing the DTP mechanism for both AMO/PMS and Cu-AMO/PMS platforms, the PMS bonds firstly with the surface of the catalysts to generate an aggressive Mn<sub>(s)</sub><sup>3+</sup>-(HO)OSO<sub>3</sub><sup>-</sup> intermediate, attacking phenol through inner-sphere interactions with the transfer of one-electron over the AMO/PMS and Cu-AMO/PMS surface. With the generation of Mn<sub>(s)</sub><sup>3+</sup>-(HO)OSO<sub>3</sub><sup>-</sup> intermediate, Mn<sub>(s)</sub><sup>3+</sup> is oxidized to Mn<sub>(s)</sub><sup>4+</sup>, meanwhile transferring the lost one-electron to HSO<sub>5</sub><sup>-</sup>. Phenol is consequently oxidized by losing one electron to the activated PMS. As a result, the surface adsorbed PMS gains two electrons from phenol and Mn<sub>(s)</sub><sup>3+</sup> and decomposes to OH<sup>-</sup> and to SO<sub>4</sub><sup>2-</sup>, resulting in the simultaneous oxidation of phenol and Mn<sub>(s)</sub><sup>3+</sup>.

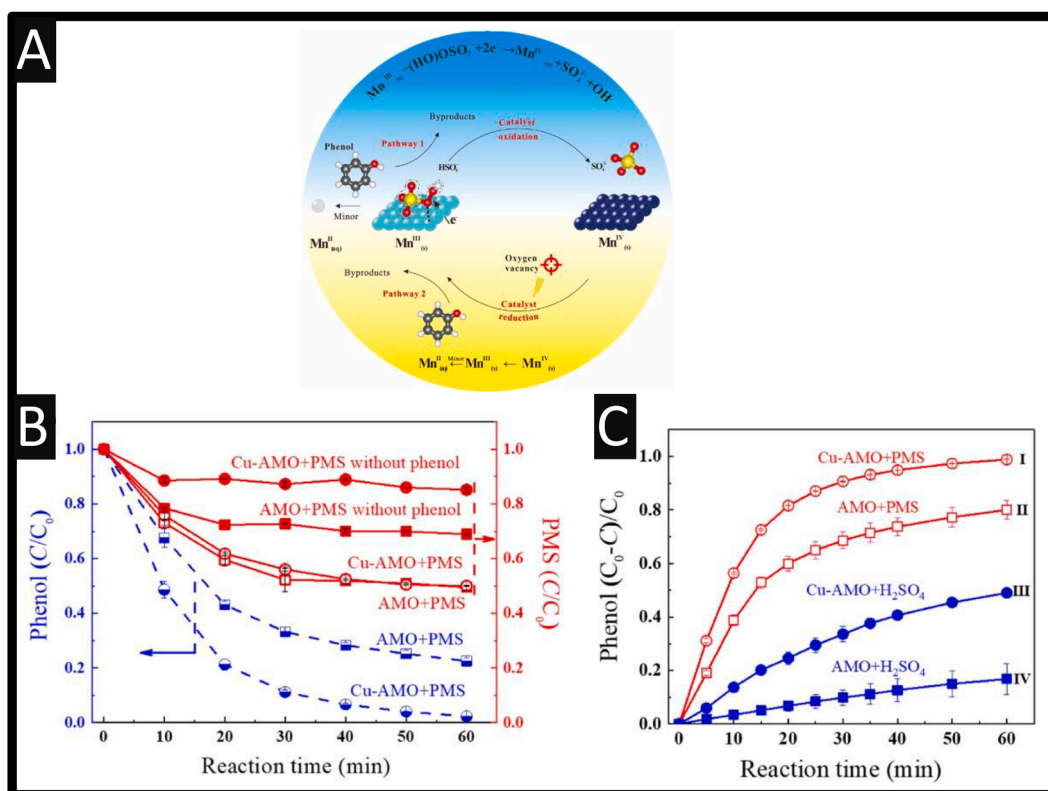


**Table 3**

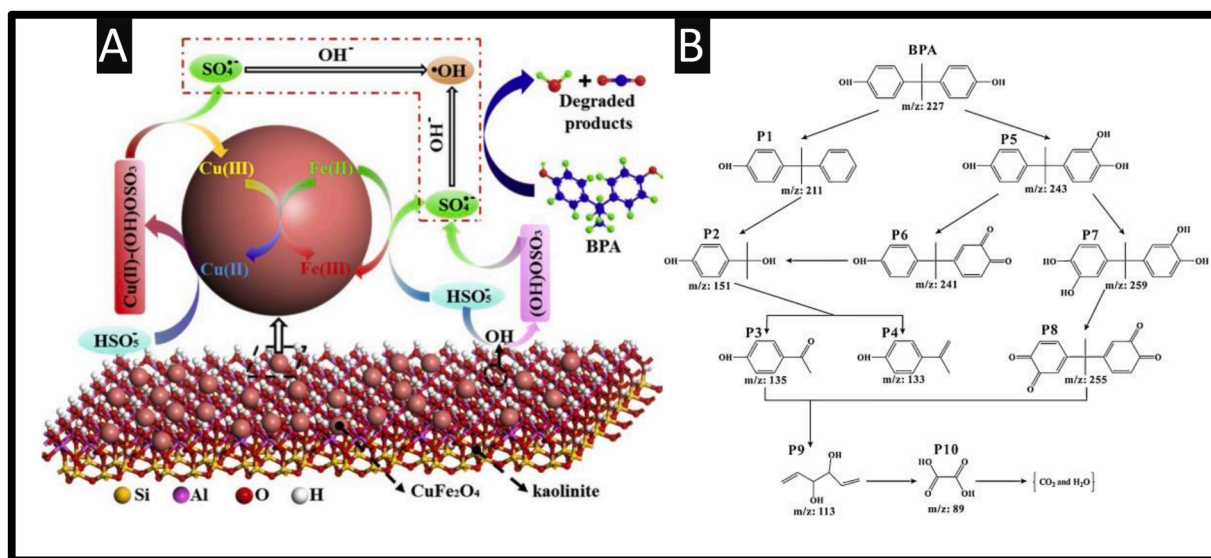
Reaction conditions and performance of PMS-based catalysts in the abatement of organic contaminants

| Reaction conditions                                                                              |                                  |                           |                  |                   |                  | Efficiency of catalyst                                              |                                           |                |                                                                                                                              |           |
|--------------------------------------------------------------------------------------------------|----------------------------------|---------------------------|------------------|-------------------|------------------|---------------------------------------------------------------------|-------------------------------------------|----------------|------------------------------------------------------------------------------------------------------------------------------|-----------|
| Catalyst system                                                                                  | Contaminant                      | [C]                       | [Cu]             | [PMS]             | pH               | [EoD](min)                                                          | $k_{\text{abs}}$<br>( $\text{min}^{-1}$ ) | TOC(min)       | KRS                                                                                                                          | Reference |
| Fe(III)/ Cu <sup>2+</sup> /HA/PMS<br>CT/HA/PS                                                    | AO7                              | -                         | 1 $\mu\text{M}$  | 1 mM              | 3-10             | 100% (5)                                                            | 0.569                                     | -              | •OH, and SO <sub>4</sub> <sup>•-</sup>                                                                                       | [231]     |
|                                                                                                  | AO7                              | 0.06 mM                   | 0.1 g/L          | 0.5 mM            | 3-5              | 99.69%<br>(20)                                                      | 0.128 @<br>0.5 mM HA                      | 68.26%         | SO <sub>4</sub> <sup>•-</sup>                                                                                                | [232]     |
| Cu-doped (110)/PMS/<br>Light                                                                     | BPA                              | 50 mg/L                   | 10 mg            | 15                | 3–9              | 84.79%                                                              | 0.059                                     | 95%            | <sup>1</sup> O <sub>2</sub> and O <sub>2</sub> <sup>•-</sup>                                                                 | [233]     |
| HA/Cu <sup>2+</sup> /PMS                                                                         | RhB                              | 10 $\mu\text{M}$          | 50 $\mu\text{M}$ | 0.4 mM            | 5.0              | 91.1% (30)                                                          | -                                         | -              | •OH and SO <sub>4</sub> <sup>•-</sup>                                                                                        | [234]     |
| CuOx/OMS-2                                                                                       | RhB                              | 2.5 ×<br>10 <sup>-4</sup> | 5 mg             | 0.83<br>mmol/L    | -                | 98% (3.73)                                                          | -                                         | -              | •OH and SO <sub>4</sub> <sup>•-</sup>                                                                                        | [235]     |
| Cu (II)/PMS                                                                                      | 2,4-DCP; BTA; 1,4-D; and toluene | 10 $\mu\text{M}$          | 10 $\mu\text{M}$ | 400 $\mu\text{M}$ | 8                | 2,4-DCP =<br>93%<br>BTA = 88%<br>1,4-D =<br>79%<br>Toluene =<br>68% | 0.1707 for<br>2,4-DCP                     | -              | Cu (III) and •OH                                                                                                             | [236]     |
| PMS/CuO                                                                                          | BPA                              | 5 mg/L                    | 10               | 1.0 mM            | 3.2–9.4          | 100% (60)                                                           | 0.0979                                    | 50%            | <sup>1</sup> O <sub>2</sub>                                                                                                  | [237]     |
| CuFe <sub>2</sub> O <sub>4</sub> @GO                                                             | MB, RRD, AO7 and<br>RhB          | 20 mg/L                   | 200 mg/<br>L     | 0.8<br>mmol/L     | 11               | 93.3% (30)<br>for MB                                                | -                                         | -              | SO <sub>4</sub> <sup>•-</sup> and •OH                                                                                        | [238]     |
| Cu <sub>3</sub> P                                                                                | SMX                              | 0.5–4.1<br>mg/L           | 20–80<br>mg/L    | 0.05–1<br>g/L     | -                | 100% (20)                                                           | 0.200                                     | -              | SO <sub>4</sub> <sup>•-</sup>                                                                                                | [239]     |
| Cu-AMO–PMS<br>complex-based                                                                      | Phenol                           | 0.22 mM                   | 0.1 g/L          | 0.65 mM           | 3.0 to 8.0       | 100% (60)                                                           | 0.087                                     | -              | SO <sub>4</sub> <sup>•-</sup> and •OH                                                                                        | [240]     |
| CuFe <sub>2</sub> O <sub>4</sub> /PMS                                                            | p-ASA                            | 10 ppm                    | 0.2 g/L          | 1 mM              | 4.26             | 85% (60)                                                            | 0.0311                                    | -              | SO <sub>4</sub> <sup>•-</sup> , •OH and<br>O <sub>2</sub> <sup>•-</sup>                                                      | [241]     |
| CuS/PS                                                                                           | ATZ                              | 25<br>mmol/L              | 35<br>mmol/L     | 4 mmol/<br>L      | 2.5              | 91.5% (40)                                                          | 0.808                                     | -              | •OH and SO <sub>4</sub> <sup>•-</sup>                                                                                        | [242]     |
| CuO/Fe <sub>2</sub> O <sub>3</sub> /CuFe <sub>2</sub> O <sub>4</sub>                             | LEF                              | 10 ppm                    | 50 mg            | 1.5 g/L           | 4.33 to<br>9.37  | 75.5%<br>(120)                                                      | -                                         | 64.5%<br>(120) | SO <sub>4</sub> <sup>•-</sup> , •OH and<br>O <sub>2</sub> <sup>•-</sup>                                                      | [243]     |
| Boric acid/Cu/PMS                                                                                | RhB                              | 10 ppm                    | 10 $\mu\text{M}$ | 0.4 mM            | 10               | 100% (5)                                                            | -                                         | -              | SO <sub>4</sub> <sup>•-</sup> and Cu(III)                                                                                    | [244]     |
| CuOx@Co-LDH                                                                                      | Phenol                           | 0.1 mM                    | 0.3 g/L          | 54 mM             | 5.0–12.0         | 100% (40)                                                           | 0.170                                     | -              | SO <sub>4</sub> <sup>•-</sup> , •OH and<br>O <sub>2</sub> <sup>•-</sup>                                                      | [245]     |
| Cu@C/SiO <sub>2</sub> NFMs                                                                       | TCH                              | 10 ppm                    | 0.3 g/L          | 5 mg/L            | 4-10             | 95% (40)                                                            | 0.054                                     | -              | •OH and SO <sub>4</sub> <sup>•-</sup>                                                                                        | [246]     |
| Cu <sup>2+</sup> /Fe(VI)                                                                         | SMX                              | 5 $\mu\text{M}$           | 20 $\mu\text{M}$ | -                 | 7.0              | 100% (8)                                                            | 2.41                                      | -              | O <sub>2</sub> <sup>•-</sup>                                                                                                 | [247]     |
| CoOOH-Cu/PMS                                                                                     | TC                               | 22.5 $\mu\text{M}$        | 0.2 g/L          | 0.2 mM            | 7.0              | 97.7% (10)                                                          | 0.6482                                    | 60.7%<br>(60)  | O <sub>2</sub> <sup>•-</sup>                                                                                                 | [248]     |
| MS-(AgC)/Cu                                                                                      | HEPES                            | 50-200<br>ppm             | 1-2 g/L          | 0.5-2 g/L         | 7.10             | 98.3% (30)                                                          | 0.1138                                    | 61.60%<br>(30) | SO <sub>4</sub> <sup>•-</sup> and •OH                                                                                        | [249]     |
| Cu <sup>+</sup> /g-C <sub>3</sub> N <sub>4</sub> (1:4)/<br>Sunlight                              | RhB                              | 10<br>mmol/L              | 0.5 g/L          | 0.5<br>mmol/L     | 2.0–10.0.        | 95.7% (30)                                                          | -                                         | -              | SO <sub>4</sub> <sup>•-</sup> , •OH, h <sup>+</sup><br>VB, <sup>1</sup> O <sub>2</sub> , and<br>O <sub>2</sub> <sup>•-</sup> | [250]     |
| NBC-Fe-Cu                                                                                        | SMX                              | 15 ppm                    | 0.05 g/L         | 1.2 mM            | 7                | 91.6% (60)                                                          | 0.0403                                    | -              | •OH, O <sub>2</sub> <sup>•-</sup> and<br><sup>1</sup> O <sub>2</sub>                                                         | [251]     |
| UV-vis light/<br>Zn <sub>0.8</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub> /<br>sulfite | ATZ                              | 4.4 $\mu\text{M}$         | 200<br>ppm       | 0.5 mM            | 7.2              | 95% (30)                                                            | 0.2                                       | -              | SO <sub>4</sub> <sup>•-</sup>                                                                                                | [252]     |
| 40%-CuFe <sub>2</sub> O <sub>4</sub> NPS/<br>kaolinite                                           | BPA                              | 50 ppm                    | 0.5 g/L          | 0.5 mM            | 7.0              | -                                                                   | 0.0589                                    | 55% (60)       | SO <sub>4</sub> <sup>•-</sup>                                                                                                | [253]     |
| Fe-Cu@N-C                                                                                        | O II                             | 20 ppm                    | 0.04 g/L         | 20 mg             | -                | 100% (50)                                                           | -                                         | ~66.1%<br>(50) | <sup>1</sup> O <sub>2</sub>                                                                                                  | [254]     |
| CuHNPs-7.5/VL/PMS                                                                                | TC                               | 40 ppm                    | 0.20 g/L         | 0.45 mM           | 2.14 to<br>10.75 | 97.80%<br>(30)                                                      | 0.1254                                    | -              | SO <sub>4</sub> <sup>•-</sup> , •OH O <sub>2</sub> <sup>•-</sup><br>and <sup>1</sup> O <sub>2</sub>                          | [255]     |
| ZCFO/PM                                                                                          | CIP                              | 10 ppm                    | 10 mg            | 2.5 mM            | 7.5              | 96.6% (15)                                                          | 1.90                                      | 70% (60)       | SO <sub>4</sub> <sup>•-</sup> , •OH O <sub>2</sub> <sup>•-</sup><br>and <sup>1</sup> O <sub>2</sub>                          | [256]     |
| Cu <sup>2+</sup> /PMS                                                                            | AO7                              | 0.05 mM                   | 0.08<br>mM       | 3 mM              | 9.0              | 98.6% (60)                                                          | 0.0475                                    | 46% (60)       | <sup>1</sup> O <sub>2</sub>                                                                                                  | [257]     |
| Cu-TCPP(BA)-MOF/VL                                                                               | RhB                              | 10 ppm                    | 0.1 g/L          | 0.1 g/L           | 7                | 100% (40)                                                           | 0.9011                                    | -              | <sup>1</sup> O <sub>2</sub>                                                                                                  | [67]      |
| Zero valent copper                                                                               | 2,4-DCP                          | 5 ppm                     | 1 mM             | 0.5 mM            | 3.1              | 100% (10)                                                           | 0.557                                     | 56.7%<br>(120) | SO <sub>4</sub> <sup>•-</sup> and •OH                                                                                        | [258]     |
| Nano zero valent<br>copper                                                                       | -                                | -                         | -                | -                 | -                | 100% (10)                                                           | 1.122                                     | 45.3%<br>(120) | -                                                                                                                            | -         |
| Cu/PTI(C6N8.7Cu)/<br>VL                                                                          | RhB                              | 10 ppm                    | 0.1 g            | 0.1 nM            | 3–10             | 96.2% (60)                                                          | -                                         | -              | O <sub>2</sub> <sup>•-</sup> , <sup>1</sup> O <sub>2</sub> , h <sup>+</sup> VB,<br>and SO <sub>4</sub> <sup>•-</sup>         | [259]     |
| Cu-NC/PMS (1.85 wt%<br>Cu)/H <sub>2</sub> O <sub>2</sub>                                         | TC                               | 20 ppm                    | 0.2 g/L          | 1 mM              | 5.0              | 91.3% (40)                                                          | 0.0762                                    | -              | •OH                                                                                                                          | [260]     |
| AM/PM                                                                                            | RhB                              | 20 ppm                    | 0.3 g/L          | 0.5 mM            | 3–10             | 100% (13)                                                           | 0.34761                                   | -              | SO <sub>4</sub> <sup>•-</sup> and <sup>1</sup> O <sub>2</sub>                                                                | [261]     |

**Key:** CT/HA/PS: Copper tailings/hydroxylamine/persulfate; OMS-2:  $\alpha$ -MnO<sub>2</sub> octahedral molecular sieves; BTA: Benzotriazole; 2,4-DCP: 2,4-dichlorophenol; MS-(AgC)/Cu: Magnetic-chitosan/amine supported CuNP; NBC: Natural biochar; Fe-Cu@N-C: Fe, Cu-coordinated ZIF-derived bimetal encapsulated N-doped carbon nanotubes; CuHNPs-7.5: Cu-doped hematite nanoplates; ZCFO: copper substituted zinc ferrite; Cu/PTI: poly(triazine imide) (PTI) with intercalation of Cu ion heterogeneous catalysts; Cu-NC/PMS: copper supported polyurethane foam; AM: recycled anode material; 2,4-DCP: 2,4-dichlorophenol; 1,4-D: 1,4-dioxane; LEV: Levofloxacin; HEPES: [4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid]; CIP: Ciprofloxacin; TCH: Tetracycline hydrochloride; RRD: reactive X-3B red dye.



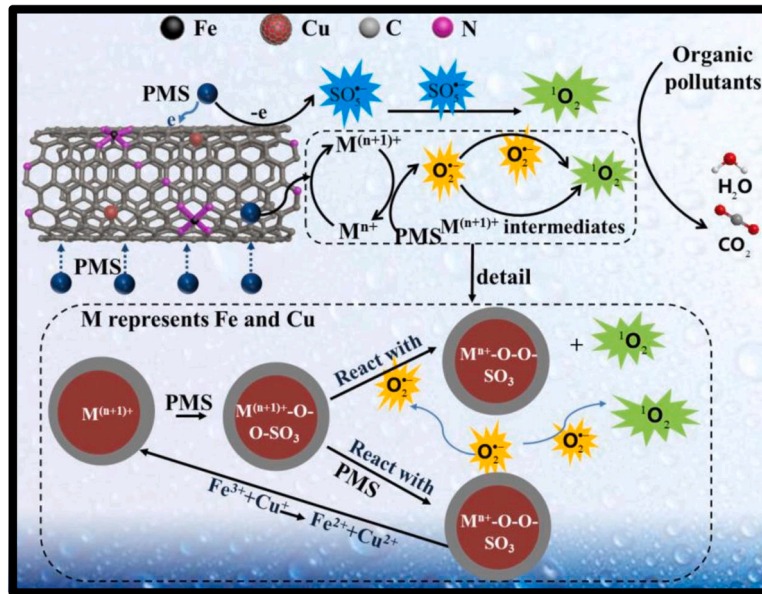
**Fig. 8.** A: The schematic representation of non-radical degradation of Phenol following two pathways; B: Phenol degradation and PMS consumption using AMO and Cu-AMO; C: catalytic degradation of + PMS or H<sub>2</sub>SO<sub>4</sub>. Conditions of experiment: [catalysts]<sub>0</sub> 100 ppm [PMS]<sub>0</sub> 0.65 mM, [phenol]<sub>0</sub> 0.22 mM, pH<sub>0</sub> 3.2 and T 30°C. Figure reproduced with permission from reference [240]. Copyright 2021 Elsevier.



**Fig. 9.** A: The reaction mechanism for the decomposition of BPA in the CuFe<sub>2</sub>O<sub>4</sub>/kaolinite system; B: The probable mechanism for the decomposition of BPA. Figure reproduced from reference [253]. Copyright 2019 Elsevier.

Fig. 8A shows a schematic representation of non-radical degradation of phenol following two pathways and Fig. 8B shows phenol degradation and PMS consumption using Cu-AMO and AMO. The superior performance of Cu-doped AMO in the Cu-AMO/PMS system was attributed to the generation of copious high-valence Mn species, which invariably strengthened direct oxidation process (DOP) mechanism. In addition, doping with Cu had a significant effect on the charge transfer and surface electron through generation of more O<sub>2</sub> species. The lattice

distortion caused by the Cu dopant allowed more K<sup>+</sup>, resulting in the increase of the Mn<sup>4+</sup>/Mn<sup>3+</sup> ratio of the Cu-AMO lattice, which improved DOPs for direct oxidation of phenol by the rich-valence Mn<sup>4+</sup>. Doping with Cu resulted in less leaching of Mn<sub>(aq)</sub><sup>2+</sup>, a better crystallinity of AMO, and higher O<sub>2</sub> vacancies, driving the redox circling between Mn<sub>(s)</sub><sup>4+</sup> and Mn<sub>(s)</sub><sup>3+</sup> in the DTP and DOP mechanisms. Hence, the greater presence of Mn<sub>(s)</sub><sup>4+</sup> in Cu-AMO supported the DOPs; in the interim, the generated Mn<sub>(s)</sub><sup>2+</sup> aids coordination with PMS for the formation of the reactive



**Fig. 10.** Suggested non-radical mechanism of reaction using the Fe-Cu@N-C-950/PMS system. Figure reproduced from reference [254]. Copyright 2021 Elsevier.

complex towards the abatement of phenol through the DTP route. In addition, the possibility of copper leaching will be insignificant to the activation of PMS and decomposition of phenol.

Dong and co-workers [253] reported the preparation of  $CuFe_2O_4$ /kaolinite catalysts via a simple citrate combustion technique. The prepared catalysts were assessed for their capacity to activate PMS towards the oxidative degradation of BPA. Higher SSA, more OH groups, larger pore volume, and more available reactive sites were realized at 40%- $CuFe_2O_4$  NPs/kaolinite catalyst ratio, which resulted in effective activation of the PMS. As seen in Fig. 9A, monodispersed  $CuFe_2O_4$  NPs were evenly hinged on the Fe-O-Al bond, which hinders metal ions leaching and supported exceptional reusability. The degradation of BPA also followed two pathways (Fig. 9B), including the generation and decomposition of  $\equiv Cu^{2+}-(HO)OSO_3-(Cu^{2+}/Cu^{3+}$  and  $Cu^{3+}/Cu^{2+}$  redox reaction) and the oxidation of  $\equiv Fe^{2+}$ .

Yao et al. [254] proposed a new Fe, Cu-coordinated ZIF-based bimetal encapsulated N-doped CNT (Fe-Cu@N-CNT). This material boasts abundant bimetallic active sites (Fe-Nx and Cu-Nx), a large surface area, high levels of N-doping and a conducted porous carbon structure, facilitating rapid electron and mass transport. These attributes collectively contributed to the outstanding and effective organic pollutants degradation in

water (Fig. 10). Wang et al. [233] described a phase-assisted degradation of BPA using  $\alpha$ - $MnO_2$  doped with various facets of Cu in a PMS and full-spectrum light irradiation system. Three different Cu facets i.e. (100), (110), and (310) were prepared and doped on the  $\alpha$ - $MnO_2$  to produce catalysts designated as Cu-doped(100)/PMS/light, Cu-doped(110)/PMS/light, Cu-doped (310)/PMS/light and pristine (110)/PMS/light system, respectively. The Cu-doped (110)/PMS/light system demonstrated the highest degradation efficiency of the BPA, with rich  $^1O_2$  selectivity and generation, that is better than the rest of the phases and the pristine (110)/PMS/light counterpart. The associated pathway revealed that doping of  $\alpha$ - $MnO_2$  with Cu improved light absorption,  $O_2$  vacancies formation and electronic conductivity, in addition to activation of PMS. The Cu-doped(110)/PMS/light mineralized the organic pollutant, with 95% degradation efficiency of the TOC, and limited the harmfulness of the intermediates.

### 3.3.2. Peroxydisulfate (PDS, $S_2O_8^{2-}$ ) and coupled systems

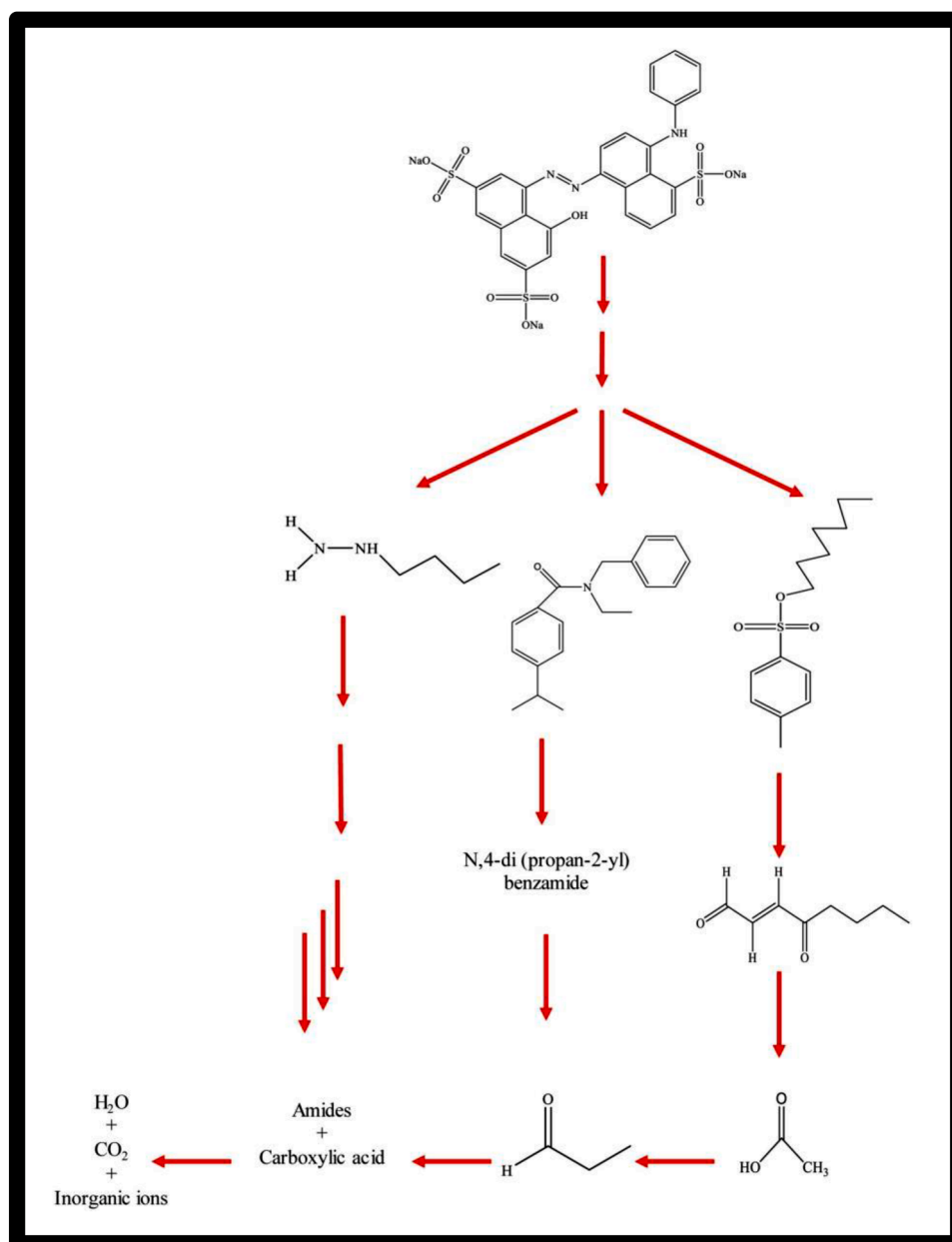
The PDS with a greater redox potential than PMS (2.01 vs 1.82 V) [264] has also been activated with a CBC in AOPs towards the abatement of organic contaminants from water. Ma et al. [265] synthesized a two-metal organic framework (MIL-101(Fe/Cu)) for coupled PS

**Table 4**

Reaction conditions and performance of peroxydisulfate-based catalysts in the degradation of organic pollutants

| Reaction conditions                         |             |         |                                     |          |          | Efficiency of catalyst |                                   |                |                                                                   | Reference |
|---------------------------------------------|-------------|---------|-------------------------------------|----------|----------|------------------------|-----------------------------------|----------------|-------------------------------------------------------------------|-----------|
| Catalyst                                    | Contaminant | [C]     | [Cu]                                | [PDS]    | pH       | [EoD](min)             | $k_{abs}$<br>(min <sup>-1</sup> ) | [TOC]<br>(min) | KRS                                                               |           |
| $CuFe_2O_4$ /PDS NPs                        | p-NP        | 50 ppm  | 30 g/L                              | 8 mmol/L | 7        | 89% (60)               | -                                 | 81%            | $SO_4^{\bullet-}$                                                 | [267]     |
| $Fe_3Cu_2$ @NPC                             | TBBA        | 2.0 ppm | 0.2 g/L                             | 1 mM     | 10       | 100% (20)              | 0.2476                            | 90 %           | $O_2^{\bullet-}$                                                  | [268]     |
| $Cl^{-1}/Fe^{3+}/Cu^0$ /PDS                 | TC          | 5.0 ppm | 1.0 $\mu$ M                         | 0.2 mM   | 3.0–7.0. | >96.5% (8 min)         | 0.406                             | -              | $Cl^{\bullet}$ , $SO_4^{\bullet-}$ , and $^{\bullet}OH$           | [269]     |
| $Fe_2p$ /CuO/PS system                      | ACT         | 100 ppm | CuO: 0.3 g/L<br>$Fe^{2+}$ : 0.07 mM | 0.8 g/L  | 6.5      | 92% (90)               | -                                 | -              | $SO_4^{\bullet-}$ , and $^{\bullet}OH$                            | [270]     |
| $CuFeS_2$ /PS/HA                            | CPF         | 20 ppm  | 0.9 g/L                             | 0.6 mM   | 5        | 99% (80)               | 0.044                             | -              | $^{\bullet}OH$                                                    | [266]     |
| MIL-101(Fe/Cu (Fe to Cu molar ratio of 3:1) | TC          | 50 ppm  | 0.05 g/L.                           | 2 mM     | 5        | 90.5%                  | 0.0242                            | -              | $SO_4^{\bullet-}$ , $O_2^{\bullet-}$ , $^{\bullet}OH$ , and $h^+$ | [271]     |

Keys: p-NP: p-nitrophenol; TBBA: Tetrabromobisphenol A; CPF: Chlorpyrifos.



**Fig. 11.** The degradation pathway of the dye, AB 92, using the Cu<sub>2</sub>O–CuO/HTC in a heterogeneous sonocatalysis. Figure reproduced from reference [292]. Copyright 2021 Elsevier.

oxidation and photocatalytic systems towards TC degradation. A degradation efficiency of 90.5% for 50 mg/L of TC was realized in the (MIL-101(Fe)/Cu)/VL/PDS system; meanwhile 52.0% of equivalent TC concentration was removed in the MIL-101(Fe)/VL/PDS. The improved degradation of TC in the Cu-doped coupled PS oxidation and photocatalysis system can be attributed to several factors. These include the increased availability of stronger absorption energy ( $E_{abs}$ ) to PDS, a reduction in the rate of recombination of  $e^-h^+$  pair due to the capturing of photogenerated electrons by Cu, which limits  $e^-h^+$  recombination. In addition, the improvement in electrical conductivity contributes to enhanced catalytic performance by increasing the catalyst's DOS (1.23 electron/eV). Successful degradation of organic contaminants has been reported for similar coupled systems using magnetic Zn<sub>0.8</sub>Cu<sub>0.2</sub>-Fe<sub>2</sub>O<sub>4</sub>/UV-vis light/PDS system in eco-friendly degradation of ATZ [252], Cu<sup>+</sup>-decorated triazine-based g-C<sub>3</sub>N<sub>4</sub> (Cu<sup>+</sup>/g-C<sub>3</sub>N<sub>4</sub>) nanosheet-activated H<sub>2</sub>O<sub>2</sub> for activation of PMS towards degradation of RhB [250], Cu-doped hematite nanoplates (named as CuHNPs)/PMS/VL

for degradation of TC [255] and ultra-thin MOF (Cu-TCPP(BA)-MOF) with porphyrin/VL/PMS for the removal of RhB [67]; please see Table 4. The application of light was incredibly significant in acceleration of the transfer of electrons in the Cu<sup>2+</sup>/Cu<sup>+</sup> redox circles. The activation of PS by the earth-abundant copper-iron sulfide mineral chalcopyrite (CuFeS<sub>2</sub>) for the degradation of imidacloprid (IMP) and pesticide chlorpyrifos (CPF) in water was promoted by the addition of HA. The introduction of HA accelerated the regeneration of the Fe<sup>3+</sup> and Cu<sup>2+</sup> in the solution for PS decomposition [266].

### 3.3.3. Percarbonate, peroxyacetic acid, and periodate

Sodium percarbonate (SPC) has been used in the elimination of organic pollutants. For example, Liu and co-workers [272] reported the activation of SPC using micro-molar concentration levels of copper (II) towards orange 7 degradation where 97.5% could be removed within 15 mins. Another study has explored the use of CuO activated SPC in the presence of ascorbic acid where they studied the effect of pH on the



elimination of sulfamethazine (SMZ). The research demonstrated that the target pollutant could be degraded up to 86% at pH 9, with both Cu (III) species playing a significant role in the degradation mechanism [273]. Another notable work has reported the one-step hydrothermal synthesis of carrollite ( $\text{CuCo}_2\text{S}_4$ ) for the activation of SPC directed towards bisphenol S (BPS) degradation [274]. The authors diligently studied the critical factors of pH, BPS concentration,  $\text{CuCo}_2\text{S}_4$  dosage, SPC concentration, reaction temperature, water matrices, and inorganic anions. The results indicated that BPS can be degraded up to 88.5% at pH 6.9. The mechanism involved the degradation of BPS by  $\text{CuCo}_2\text{S}_4$  activated by the SPC system, where a multiple ROS process was identified. This process included  $^1\text{O}_2$ ,  $\text{O}_2^{\bullet-}$ ,  $^{\bullet}\text{OH}$ , and carbonate ( $\text{CO}_3^{\bullet-}$ ) radicals. Additionally, the sulfur species, S(-II), expedited rapid redox cycles between Cu(I)/Cu(II) and Co(II)/Co(III). The  $\text{CO}_3^{\bullet-}$  not only directly reacted with BPS molecules, but also acted as a bridge to promote the generation of  $^1\text{O}_2$  and  $\text{O}_2^{\bullet-}$ , thereby accelerating the degradation of BPS [274].

Peroxyacetic acid (PAA) also known as peracetic acid, is an organic peroxide-based colourless liquid with a low pH and a strong, pungent, and vinegar-like odour [275,276]. Zero valent copper has been used for the degradation of diclofenac, where PAA is activated to produce radicals that produce  $^{\bullet}\text{OH}$ ,  $\text{CH}_3\text{COO}^{\bullet}$  and  $\text{CH}_3\text{COOO}^{\bullet}$  which are attributed to its catalytic decomposition [277]. Through the use of nanoparticle copper oxide, the degradation of CMZ has been reported within a neutral pH where the mechanism involves  $\text{CH}_3\text{C}(\text{O})\text{OO}^{\bullet}$  as the main dominant reactive species. [278] The use of PAA has been studied with cobalt, silver and copper ions as a catalyst where cobalt outperformed the use of silver and copper ions for the abatement of phenols [279]. This work suggests that researchers using exclusively CBC should focus on other activations. Periodate exists in different solid forms such as  $\text{NaIO}_4$  (sodium metaperiodate),  $\text{Na}_3\text{H}_2\text{IO}_6$  (sodium triparaperiodate, also named as trisodium dihydrogen orthoperiodate),  $\text{KIO}_4$  (potassium metaperiodate),  $\text{Ba}(\text{IO}_4)_2$  (barium periodate) and  $\text{H}_5\text{IO}_6$  (orthoperiodic acid). Copper (III) periodate has been applied in the oxidation of substances such as glucitol and carbenicillin [280,281]. For a detailed overview, readers are encouraged to refer to the provided references [275,282].

### 3.4. Heterogeneous sonocatalytic degradation

Ultrasonic irradiation has become very significant in wastewater treatment and could be used in the abatement of organic contaminants such as herbicides, insecticides, pharmaceuticals, dyes, etc. [283]. Sonochemical methods employ ultrasound to generate an oxidative system through acoustic cavitation as a result of the rise and corresponding fall of microbubbles from compression/rarefaction induced by acoustical waves [284]. The bubble collapse produces a localized high temperature and pressure (hot-spots) conditions. The gases of a collapsing cavity can reach pressures up to 1000 atm and temperatures more than 5000 K within the collapsing cavity, with temperatures nearly reaching 1900 K in the interfacial area between collapsing bubble of the solution [285–289]. The organic contaminants are decomposed via two mechanisms:

- The POPs within the cavity and around the interfacial regime (cavity-liquid) can go through thermal decomposition, involving combustion or pyrolysis reactions of  $\text{O}_2$  during the implosion [289]. The significance of these hot-spots lies in the cleavage of  $\text{H}_2\text{O}$  molecules (into  $^{\bullet}\text{OH}$  and  $\text{H}^{\bullet}$  atom) and dissolved  $\text{O}_2$  molecules (reactions (31), (32) [285–291]. Through the reactions of  $\text{H}^{\bullet}$ ,  $^{\bullet}\text{OH}$  and  $\text{O}^{\bullet}$  with one another, as well as with  $\text{O}_2$  and  $\text{H}_2\text{O}$  during the quick cooling phase, the  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^{\bullet}$  radicals are generated [291].
- The hydroxyl radical and the homolytic oxygen are generated in the bubble during the rapid collapse [285–291]. These radicals either combine within the bubble (Eqs. 33–35) or leave the bubble, leading to the release of  $\text{H}_2\text{O}_2$  into the system (Eqs. 36–38).



Reports have shown that with ultrasonic irradiation as a source of energy,  $e^-$  of  $\text{M}^{n+}$  can be excited from VB into CB, creating a  $h^+$  by exceeding the  $E_g$  or aligning with the energy requirements of the catalyst. The generated  $h^+$  can dislocate water molecules to form  $^{\bullet}\text{OH}$  radicals, participating in the degradation of POPs in water. However,  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  exhibit a lower quantum yield due to their high recombination rate and poor charge carrier mobility. To address this problem, heterogeneous sonocatalysis has been explored by researchers. For instance, Khataee and team [292] doped a high-yield and environmental friendly sawdust hydrochar, prepared by hydrothermal carbonization with  $\text{Cu}_2\text{O}$ - $\text{CuO}$  ( $\text{Cu}_2\text{O}$ - $\text{CuO}/\text{HTC}$ ) at different carbonization times (2, 6, 12 h). This material demonstrated efficacy in the sonocatalytic decomposition of three dyes, namely, AB92, AR14, and AO7. Under optimal conditions, the  $\text{Cu}_2\text{O}$ - $\text{CuO}/\text{HTC}$ -2h demonstrated the peak removal efficiency of 85.43% after 90 mins with a removal efficiency of 77.77%. Fig. 11 summarizes the decomposition pathway of the dye.

### 4. Factors influencing AOP

It is essential to highlight that the performance of the CBC in AOPs is a function of several factors, including: 1) temperature, since reaction rates in AOPs are often temperature-dependent. Elevated temperatures can enhance reaction kinetics, but excessively high temperatures may also lead to energy inefficiency or decreased stability of the reactants; 2) pH, which can significantly affect the efficiency of AOPs. Some AOPs are more effective under acidic or alkaline conditions and adjusting the pH to the optimal range for a specific AOP is crucial for achieving maximum degradation efficiency; 3) Concentration of reactive species, such as  $^{\bullet}\text{OH}$ ,  $\text{O}_3$ , or other oxidizing agents, plays a critical role where optimizing the generation and concentration of these species is essential for efficient pollutant degradation; 4) type of AOP, which have distinct mechanisms and reactants. Common AOPs include photocatalysis (e.g.,  $\text{TiO}_2$  photocatalysis), ozonation, Fenton's reaction, and sonochemistry. The choice of AOP depends on the specific pollutants, water quality, and treatment objectives; 5) target pollutants, where the nature and concentration of pollutants in the water or air influence the selection of the AOP. Some AOPs may be more effective against certain types of pollutants, such as organic compounds, pathogens, or heavy metals; 6) reaction time, where the duration of exposure to the AOP is a crucial factor. Longer reaction times may lead to increased pollutant removal, but there is a trade-off with the energy consumption and practicality of the treatment process; 7) catalysts, such as semiconductor materials in photocatalysis or iron-based catalysts in Fenton's reaction, can enhance the efficiency of AOPs. Catalysts facilitate the generation of reactive species and promote the degradation of pollutants; 8) matrix effects, where the composition of the water matrix (e.g., presence of organic matter, ions, and other impurities) can influence the performance of AOPs. Some substances may compete for reactive species or scavenge radicals, affecting the overall degradation efficiency; 9) UV light availability, since AOPs like photocatalysis rely on the availability of UV or VL to activate catalysts. The intensity and wavelength of light can impact the effectiveness of the AOP, and consideration must be given to the light

source and its practical application; 9) safety and environmental impact, including the generation of by-products and potential risks, must be considered. Some AOPs may produce secondary pollutants, and their environmental sustainability should be assessed; 10) scale-up considerations where the feasibility of scaling up AOPs for practical applications in water treatment plants or industrial processes is a crucial factor. Factors such as reactor design, energy requirements, and cost-effectiveness need to be considered. In summary, understanding and optimizing these factors are essential for the successful application of AOPs in water and air treatment, helping to address environmental pollution challenges effectively.

## 5. Challenges and perspective

For more than ten decades now, a centralized municipal water purification process has been utilized, in an effort to provide safe water for communal use. However, growing concerns with these conventional water treatment processes necessitate a transition to more decentralized processes where AOPs might be competitive treatment alternatives. The use of heterogeneous catalysts has been pivotal in addressing the fundamental limitations that have constrained the practical application of typical AOPs, such as lowering their energy and chemical input requirements. Recent breakthroughs in the fabrication of advanced functional materials have been of tremendous benefit in engineering heterogeneous catalysts for applications in AOPs. From this perspective, the environmental impact of POPs was elucidated, while the properties and real-world applications of CBC in AOPs previously investigated, as well as reaction mechanisms and degradation pathways, were discussed in detail. The architecture and initial concentration of CBC, the initial dosage of the abated pollutant, the intensity of light, the surface chemistry and number of oxidation agents, the period of treatment, and the wastewater solution composition were all significant aspects of the AOPs. Without a doubt, the CBC exhibited exceptional catalytic performance in photocatalysis, Fenton-like processes, PS activation, and sonocatalytic processes, and could effectively abate organic pollutants from water via these AOPs. However, a few more issues are yet to be resolved, including:

- i. The relatively high operational cost of these processes because of the employment of costly chemicals and higher energy requirements.
- ii. The use of toxic CBC in some processes, which further poses an additional threat to the environment.
- iii. The formation of unknown and in some cases, toxic intermediates that could be more harmful than the target pollutants.
- iv. Scavenging of ROS radicals by non-target compounds.
- v. Hindrances to large-scale production and requirement for highly skilled professional associated costs.
- vi. Difficulties in monitoring and maintaining reaction conditions in addition to monitoring water quality (e.g., chemicals, organic matter, and pH).
- vii. Difficulty of removing  $H_2O_2$ , for example, from treated water.

Consequently, future investigations should involve step-by-step approach to lower resource and energy costs, environmental pollution, and employment of a cross-disciplinary approach involving science, engineering, technology, and artificial intelligence. This holistic approach is essential for addressing the whole challenge surrounding large-scale applications of copper-based heterogeneous catalysts in AOPs.

## CRediT authorship contribution statement

**Enyioma C. Okpara:** Writing – review & editing, Writing – original draft. **Olanrewaju B. Wojuola:** Writing – review & editing, Writing – original draft. **Taiwo W. Quadri:** Writing – review & editing, Writing – original draft. **Craig E. Banks:** Writing – review & editing, Writing –

original draft.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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