CHAPTER:2

APPLICATIONS OF COPPER-BASED POLYMER NANOCOMPOSITES FOR THE REMOVAL OF ORGANIC DYES FROM WASTEWATER

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Abstract:

The emerging contaminants in water challenge researchers to develop remediation methods that are simple, affordable, and eco-friendly. Dyes are the major pollutant existing in wastewater. The degradation of dyes is seen as a potential technique for the treatment of industrial wastewater owing to its low cost and lack of secondary pollutants. Copper-based nanoparticles are promising semiconductor materials employed for the treatment of dye-containing wastewater. The incorporation of copper-based nanoparticles into the polymer matrix enhanced the properties and applications. This chapter highlights the recent advancement in copper-based polymer nanocomposites as a novel catalyst to treat dye-containing wastewater.

Keywords: Copper-based polymer nanocomposites, dyes, wastewater, adsorbent, photocatalyst

Introduction:

Water pollution is a major problem threatening the living community globally. Industrialization and urbanization are the major contributing source of contaminant discharge in the water bodies. The health of people and aquatic life is put at risk when poisonous substances are released into the water bodies. If we consume industrial effluents in excessive amounts, they might cause various diseases like cancer, heart stroke, gastrointestinal problems, jaundice, etc. [1]. According to World Health Organization (WHO), over 2 billion people live in water-stressed countries, and approximately 2 billion drink contaminated water. This contaminated drinking water can spread diseases like typhoid, diarrhoea, dysentery, polio, and cholera and is anticipated to cause 485000 diarrheal deaths each year [2]. The contaminated water includes metals, pesticides, chromium salts, and dyes. Colour is typically the first wastewater contaminant to be recognized [3], [4]. Over one lakh different dyes are known worldwide and used for colouring purposes in various industries

[5]. The solubility, classification, examples, and application associated with common industrial dyes are represented in Table 1 [6]. The various pollutants produced by these different dyes are colour, organic acids, salts, surfactants, defoamer, phosphates, lubricants, dispersants, alkali, etc..

Table 1. The solubility, types, examples, and application of dyes.

S. No.	Solubility	Type	Examples	Applications
1.	Water soluble	Acidic	Acid blue 25, Acid yellow 36, Acid brown 14, Acid yellow 42, and Acid blue 83	Nylon, Silk, Wool, and Modified acrylic fibers
2.		Basic	Methylene blue, Crystal violet, Rhodamine B, and Amido black 10B	Jute and Acrylic
3.		Direct	Direct red 28, Martius yellow, Congo red, and Direct black 38	Cotton, Rayon, Silk, Linen, Wool, and Nylon
4.		Reactive	Reactive blue 4, Reactive blue 19, and Reactive brilliant red X-3B	Cotton, Rayon, Silk, Viscose, and Nylon
5.	Water insoluble	Dispersive	Disperse red 9, Disperse orange 1, Disperse yellow 26, and Disperse violet 1	Nylon, Polyester, and Acetate and Triacetate fibers
6.		Sulphur	Sulfur blue, Sulfur Black 1, and Phthalic anhydride	Acrylic fibers, Polyamide, and Polyester
7.		Vat	Vat blue 1 and Vat acid blue 74	Cotton, Rayon, Silk, Linen, Wool, and Nylon

The elimination of pollutants from the wastewater is done by various methods, including membrane filtration [7], coagulation-flocculation [8], ion-exchange [9], ozonation [10], electrochemical method [11], adsorption [12], and advanced oxidation processes [13], as shown in Figure 1. Most of these methods are expensive, require long operational time, and produce harmful by-products. However, in the past ten years, much research has been done on adsorption and advanced oxidation processes (AOPs) to treat wastewater. AOPs are the processes that produce reactive active species (ROS) like superoxide ($O_2^{-\bullet}$) and hydroxyl ($OH^{\bullet}$) radicals, which act as strong oxidants to break down contaminants [13]. Nanomaterials are the potential contender for the removal of toxic compounds from wastewater. The different types of nanocatalysts utilized in the elimination of harmful compounds, metals, pesticides, and dyes from the wastewater are represented in Figure 2.

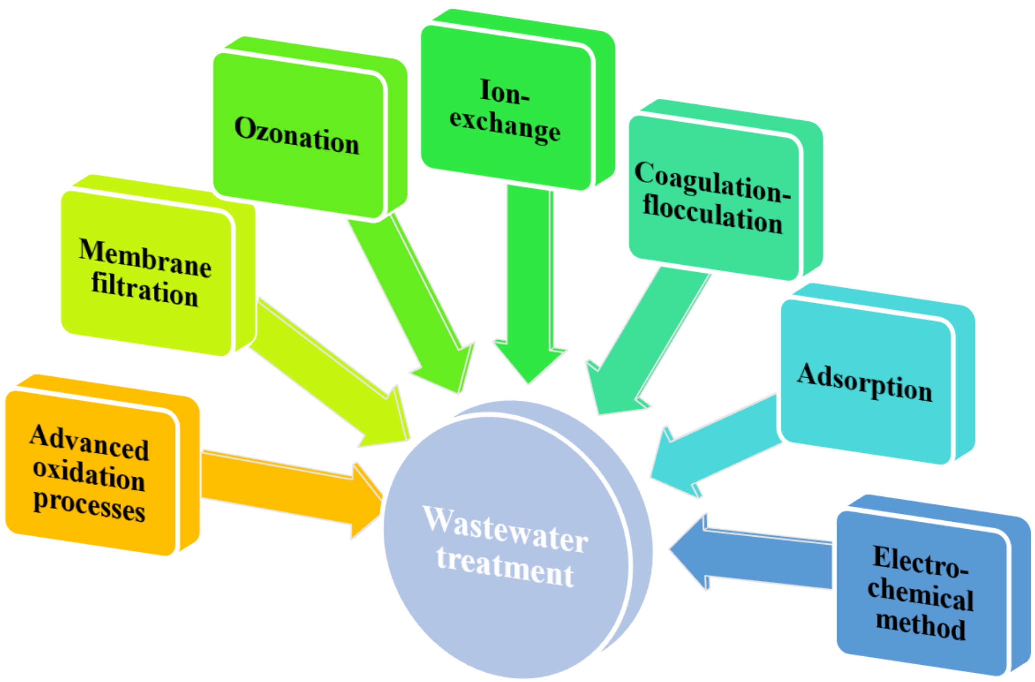

Figure 1. Various methods for the treatment of wastewater.

An ideal catalyst or adsorbent for the removal of organic dye must be affordable, safe, and visible or solar light activated. Copper (Cu) is widely utilized in numerous applications owing to its exceptional physicochemical characteristics, for example, abundance, inexpensive, stability, and less toxicity [14]. The band gap value of copper oxide (CuO) p-type semiconductor is 1.2 eV [15]. Cu or CuO nanoparticles are suitable materials as a photocatalyst because they get easily activated by visible or solar light. To improve the properties of copper-based nanoparticles, they are incorporated with a polymer matrix. The combination of copper-based nanoparticles with polymers prevents the accumulation of nanoparticles and improves the dispersion of nanoparticles in organic media. The copper-based polymer nanocomposites (NCs) have applications in diverse areas such as sensors [16], antibacterial agents [17], solar cells [18], and dye degradation [19].

This current chapter focuses on the removal of toxic dyes from contaminated water using copper-based polymer nanocomposites.

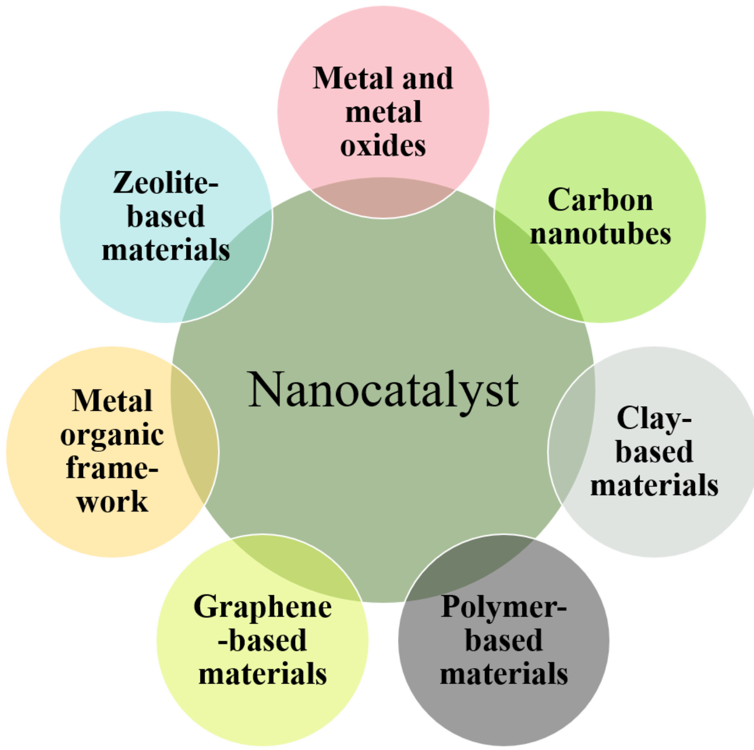

Figure 2. Various types of nanocatalysts are used in wastewater treatment.

Degradation of dyes by copper-based polymer nanocomposites

Different polymers, including chitosan (CS), carboxy methyl cellulose (CMC), polyvinyl alcohol (PVA), etc., were used to improve the adhesion of NPs. These polymers provide support to the metallic copper-based nanoparticles and enhance the surface area and adsorption capacity. Furthermore, nanoparticles embedded with polymers allow the easy and quick recovery of the catalyst from reaction media after the dye elimination process. Copper-based polymer nanocomposites have exceptional optical, electrical, chemical, thermal, and catalytic properties [20]. The narrow band gap, low recombination rate, large surface area, and fast redox capability make it a suitable component for the dilapidation of dyes. The scientific community utilized copper-based polymer nanocomposites in the removal of various toxic dyes from industrial wastewater.

In 2008, Zhou and co-workers synthesized a Cu_2O/chitosan nanocomposite (Cu_2O/CS NCs) using the electrochemical decomposition method. The synthesized Cu_2O/CS NCs were investigated for the decolourization of reactive brilliant red X-3B (BR X-3B) dye in the presence of visible light. The outcomes indicated that a 50% mass ratio of Cu_2O in the Cu_2O/CS NCs provided an excellent photocatalytic degradation efficacy [21]. Later, Xiao and his colleagues demonstrated the *in-situ* synthesis of crosslinked nanocomposites (NCs) composed of Cu_2O and chitosan (CS) through a one-step liquid phase precipitation-reduction method. The obtained Cu_2O/CS NCs were spherical or ellipsoidal in shape. The wrapping of chitosan in Cu_2O nanoparticles modified the surface and increase the roughness and porosity of nanocomposites. Under visible light, the decolorization capabilities of Cu_2O/CS NCs were evaluated using reactive brilliant red X-3B (BR X-3B) dye. The effect of various reaction parameters on the degradation behaviour was also analyzed. It was found that the highest decolourization percentage of 99.5% was observed with 50 mg/L initial dye concentration, 1.0 g/L photocatalyst amount, at pH value 5.6 under 20 min illumination of 500 W halogen lamp [22]. Haldorai and Shim reported the synthesis of chitosan-CuO hybrid material using the chemical precipitation method. The synthesized hybrid material was performed on methylene blue (MB) dye as a photocatalyst. The hybrid showed 84% degradation of MB dye under UV-light illumination of 30 min in the presence of H_2O_2. The hydroxyl radical ($OH^\bullet$) was important for the breakdown of MB dye into degraded by-products [19]. In 2015, Karuthapandian and his group synthesized CuO NPs and incorporated these NPs into the chitosan (CS) matrix using a solution casting method. After that, the photocatalytic activity of synthesized CuO/CS nanocomposite thin film (NCF) was assessed for the dilapidation of rhodamine B (RhB), crystal violet (CV), and congo red (CR) dyes. The CuO/CS NCF showed approximately 99% degradation efficiency for RhB dye at 60 min of visible light radiations. While the CV and CR dyes were decolourized after illumination of 50 min under UV light. The CuO/CS NCF showed higher degradation efficacy than CS and CuO NPs alone because of higher adsorption capacity and less recombination rate of photogenerated electrons and holes [23]. In 2016, Kamal *et al*. synthesized an active catalyst composed of copper nanoparticles (Cu NPs) in chitosan (CS) coating layers over cellulose microfibers of filter paper (FP). They studied the decolourization of methyl orange (MO) and congo red (CR) dyes using Cu/CS/FP catalysts with $NaBH_4$. The complete degradation was accomplished within 13 and 17 min for MO and CR dyes, respectively. The advantage of a filter paper-supported catalyst was the separation of the catalyst after reaction completion. The separation of the catalyst was performed easily with the simple pulling of the strip from the reaction solution [24]. Later in the same year, the same group utilized the same catalyst for the degradation of cresyl blue (CB) dye. The rate constant of the reaction for the degradation of CB dye was 0.0780 min^{-1}. The observed degradation efficacy was 75% in 18 min for CB dye removal [25]. Ali *et al*. fabricated the chitosan-coated cotton cloth-supported copper nanoparticles (Cu/CS/CC) for the removal of dyes from wastewater. The CR dye reduction was observed with Cu/CS/CC nanocomposites and $NaBH_4$ reducing agent. The 96% degradation of CR dye was observed within 12 min. The synthesized nanocomposites showed excellent stability and recyclability during the degradation process [26]. Jothivenkatachalam and co-workers reported the simple, facile, and green method for the synthesis of chitosan-copper nanocomposite (CS/Cu NCs) without the addition of any external reducing agent. The prepared CS/Cu NCs applied as a photocatalyst for the elimination of rhodamine B (RhB) and conge red (CR) dyes from wastewater with visible light illumination. The effect of various reaction parameters on degradation efficacy was also analyzed. The RhB dye degradation efficiency was 58% at pH 3, 0.3 g/L catalyst concentration, and 1.04×10^{-5} M dye concentration. The maximum degradation of CR dye was observed to be 97% at pH 11, 0.3 g/L catalyst concentration, and 5.7416×10^{-5} M dye concentration. The rate constant value for RhB and CR dyes were 0.00445 and 0.01056 min^{-1} at optimum reaction conditions [27]. After that, Alzahrani synthesized the CS-ZnO/CuO NCs membrane for the photodegradation of fast green (FCF) dye under solar and UV light irradiations. The degradation study of FCF indicated that CS-ZnO/CuO NCs membrane accomplished 91.21% and 60.23% of degradation efficiency in 110 min for UV and solar light radiations, respectively. While CS-ZnO NCs membrane showed lower degradation efficacy 71.45% and 57.90% in 110 min for UV and solar light radiations, respectively. The results proved that doping of a CuO narrow band gap semiconductor on CS-ZnO NCs played an important role in the photocatalytic efficacy of NCs [28]. In 2020, Ameta and his colleagues synthesized a chitosan-polyaniline-copper (II) oxide nanocomposites (CS-PANI-CuO NCs) using the batch adsorption method. The CS-PANI-CuO NCs were employed for the eradication of methyl orange (MO) dye. The removal efficacy of MO dye was enhanced from 95.1 to 98.9% with an increase in adsorbent dosage from 0.1 to 0.5 g/L. The optimum conditions for maximum removal of MO dye were observed at pH 4, 20 mg/L dye concentration, and 0.5 g/L adsorbent dosage [29]. After that, Pugazhendhi and co-workers reported a biogenic synthesis of chitosan-copper oxide nanocomposites (CS-CuO NCs) using *Psidium guajava* aqueous leaf extract. The degradation percentage of methylene blue (MB) and congo red (CR) dyes by CS-CuO NCs was 91.3% and 90.8%, respectively, within 150 min of sunlight exposure. The hydroxyl ($OH^{\bullet}$) and oxide ($O_2^{-\bullet}$) radicals formed during the dilapidation process were responsible for the breakdown of MB and CR dyes to less harmful by-products [30]. Zayed *et al*. investigated the catalytic activity of chitosan-supported Cu_2O/CuO nanocomposite (Cs/Cu_2O/CuO NC) towards different types of organic dyes such as anionic dye (MO), cationic dye (MB), and reactive dye (RR) with aids of $NaBH_4$. The evaluated rate constant for the degradation of MO, MB, and RR dyes were 0.51, 0.59, and 0.46 min^{-1}. For eight consecutive catalytic cycles, the Cs/Cu_2O/CuO NC was employed again with no discernible loss in the catalytic activity [31]. Khan and co-authors reported the synthesis of carboxymethyl cellulose/copper oxide-nickel oxide (CMC/CuO-NiO) nanocomposite. The synthesized NCs beads were analyzed for the catalytic reduction of congo red (CR) and eosin yellow (EY) with $NaBH_4$. The results revealed that 96% and 95% reductions were observed within 120 s for CR and EY dyes, respectively. The calculated rate constants for CR was 1.89 x 10^{-2} s^{-1} and for EY was 2.43 x 10^{-2} s^{-1} [32]. Spiridonov *et al*. discovered a one-stage synthesis of Cu_2O nanoparticles embedded in the CMC matrix. The synthesized Cu_2O/CMC nanocomposites showed excellent degradation potential, approximately up to 100% for methyl orange (MO) dye, in the presence of an H_2O_2 oxidizing agent. In the oxidation process, hydroxyl radicals ($OH^{\bullet}$) played a noteworthy role in the degradation mechanism of dyes [33]. In 2021, Feng and co-authors designed a matrix composed of chitosan (CS), filter paper (FP), and titanium dioxide (TiO_2). The zero-valent copper (Cu) nanoparticles were loaded in this matrix. The synthesized nanocatalyst (Cu/CSTiO_2/FP) was investigated to remove four different textile dyes, i.e., bromocresol green (BCG), eriochrome black T (EBT), methyl orange (MO), and rhodamine B (RhB) in the existence of $NaBH_4$. The addition of Cu NPs on the surface of the heterogeneous matrix (CSTiO_2/FP) boosted the photocatalytic activity of the catalyst owing to the electron relay system of Cu NPs assisting to accelerate electron transfer from the donor BH_4^- to the acceptor dye molecule. The results showed that degradation of BCG, EBT, MO, and RhB dyes were achieved in a short span of time 5, 9, 13, and 5 min, respectively, at optimum reaction conditions Cu/CSTiO_2/FP catalyst, 0.5 mL of $NaBH_4$, pH 3, 0.05 mM dye concentration, and at 25 ^oC temperature [34]. Later, Jabli, Ltaief, and Abdessalem synthesized CuO NPs using the *pistacia vera* hull extract. The synthesized CuO NPs were incorporated into chitosan (CS) polymer. The CS/CuO NCs were used for the degradation of naphthol blue-black (NB) with the aid of H_2O_2. The highest degradation percentage of 86% was reached under the optimized reaction conditions at pH 6, 8 mL/L concentration of H_2O_2, 20 ^{o}C temperature, and 30 mg/L of initial dye concentration in 10 min [35]. Zayed *et al*. fabricated a film made up of polyvinyl alcohol (PVA) and cuprous oxide (Cu_2O) nanoparticles. The gallic acid was utilized as a reducing and cross-linking agent in the *in-situ* synthesis of PVA/Cu_2O NCs. The catalytic oxidation of MB dye on PVA/Cu_2O NCs was assessed in the presence of H_2O_2 (Fenton- like reaction). The PVA/Cu_2O nanocomposite film displayed both catalytic oxidation and reduction for MB, MG, and RR dyes. The evaluated rate constants for MB, MG, and RR dyes were 3.85 x 10^{-3}, 2.57 x 10^{-3} sec^{-1}, and 6.23 x 10^{-3} sec^{-1}, respectively. The film showed excellent reusability and could be effectively used in the wastewater treatment [36]. Gouda and his research team synthesized copper oxide/carboxymethyl cellulose nanocomposites (CuO/CMC NCs) using the co-precipitation method in the presence of $NaBH_4$ as a reducing agent. The TEM analysis revealed that the CuO/CMC NCs have a size in the range of 3-10 nm with a random shape and less agglomeration. The NCs were applied for the adsorption of methylene blue (MB) dye at various initial concentrations of MB, contact time, pH, and adsorbent concentration. The 100% removal efficiency was observed at 3 mg/L MB concentration, 2.5 mg adsorbent dosage after 48 h [37]. Recently, Azharudeen *et al*. sonochemically synthesized the polyvinylalcohol (PVA)-modified Mg-doped CuO nanocomposite (PVA/Mg-CuO NCs) by a chemical impregnation method. The synthesized NCs were applied to the degradation of MB dye. The 95.7% elimination of dye was achieved within 180 min of solar light irradiation [38]. Table 2 shows the comparative study of the degradation rate constant of some previously reported copper-based polymer nanocomposites over different dyes.

Table 2. Comparative study of the degradation rate constant of some previously reported copper-based polymer nanocomposites over different dyes.

S. No.	Catalyst	Dyes	Rate constant (k) (min^{-1})	References
1.	Cu_2O/CS NCs	BR X-3B	–	[21]
2.	Cu_2O/CS NCs	BR X-3B	0.265	[22]
3.	CS-CuO hybrid	MB	0.059	[19]
4.	CuO/CS NCF	RhB, CV, and CR	–	[23]
5.	Cu/CS/FP	MO and CR	0.2683 and 0.1655	[24]

6.	Cu/CS/FP	CB	0.0780	[25]
7.	Cu/CS/CC	CR	–	[26]
8.	CS/Cu NCs	RhB and CR	0.00445 and 0.01056	[27]
9.	CS-ZnO/CuO	FCF	–	[28]
10.	CS-PANI-CuO NCs	MO	–	[29]
11.	CS-CuO NCs	CR and MB	–	[30]
12.	Cs/Cu_2O/CuO NC	MO, MB, and RR	0.51, 0.59, and 0.46	[31]
13.	CMC/CuO-NiO	CR and EY	1.134 and 1.458	[32]
14.	CMC-Cu_2O NCs	MO	–	[33]
15.	Cu/CSTiO_2/FP	RhB, EBT, BCG, and MO	0.4843, 0.3612, 0.3605, and 0.4511	[34]
16.	CS/CuO NCs	NB	0.1217	[35]
17.	PVA/Cu_2O NCs film	MB, MG, and RR	0.231, 0.1542, and 0.3738	[36]
18.	CuO/CMC NCs	MB	–	[37]
19.	PVA/Mg-CuO NCs	MB	0.0732	[38]

Abbreviations: CS– chitosan, NCs– nanocomposites, BR X-3B– brilliant red X-3B, NCF– nanocomposite thin film, FP– filter paper, RhB– rhodamine B, CV– crystal violet, CR– congo red, CC– cotton cloth, MO– methyl orange, CB– cresyl blue, FCF– fast green, PANI– polyaniline, RR– reactive red, CMC– carboxy methyl cellulose, EY– eosin yellow, BCG– bromocresol green, EBT– eriochrome black T, NB– naphthol blue-black, and PVA– polyvinyl alcohol

A plausible mechanism involved in the photocatalytic degradation of dyes by copper-based polymer nanocomposites is represented in Figure 3. When copper-based polymer nanocomposites are illuminated by the light source, both metal or metal oxide and polymer absorb light and produce electrons (e^-) and holes (h^+). Both synergically enhanced the photocatalytic activity of each other. The holes (h^+) generated on the metal surface valence band directly transferred to the highest occupied molecular orbital (HOMO) of the polymer, and simultaneously, photogenerated electrons (e^-) transferred from the lowest occupied molecular orbital (LUMO) of the polymer to the metal conduction band. Therefore, the rate of recombination of electrons (e^-) and holes (h^+) was reduced, and photocatalytic activity was enhanced. The reactive oxygen species (ROS) such as hydroxyl ($OH^•$) and superoxide ($O_2^{-•}$) radicals generated by the reaction of water and oxygen molecules present in the solution help in the degradation of dyes and produce safe secondary by-products like H_2O, CO_2, and mineralized products.

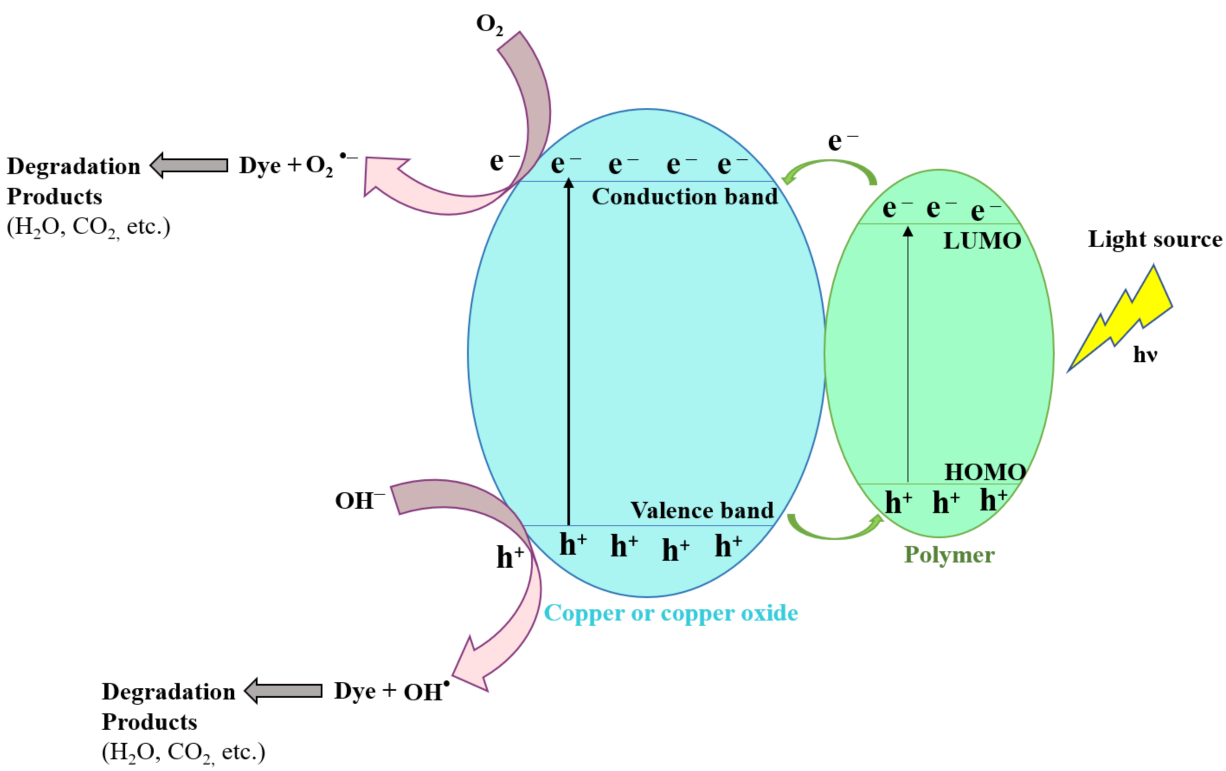

Figure 3. A plausible dye photodegradation mechanism by copper-based polymer nanocomposites.

Conclusion

The elimination of contaminants from wastewater is the demand of the current scenario. This chapter summarizes the classification and applications of various types of dyes. Various wastewater treatment methods were also disclosed. The recent development in the degradation of dyes using copper-based polymer nanocomposites was discussed in detail. Further, the mechanism of dye degradation using copper-polymer nanocomposites was explained. Thus, this chapter focused on comprehensive research on dye degradation using copper-based polymer nanocomposites, which help scientists further understand the study of these nanocomposites.

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