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DYE DEGRADATION APPLICATIONS OF METAL-METAL OXIDE NANOPARTICLES

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Abstract- The industrial growth of sectors such as paper, textiles, medicine, rubber, and plastics has led to an increase in pollution from organic dyes. The release of hazardous dyes into water bodies poses serious health risks due to their carcinogenic and mutagenic properties. Finding effective treatment methods for these harmful effluents is essential. One promising solution is the use of nanoparticles as photocatalysts, which has shown significant potential. Nanoparticles can be synthesized through various methods and are effective in decontaminating dyes from polluted water. Metal and metal oxide nanoparticles, along with their nanocomposites, provide strong solutions for the photocatalytic degradation of hazardous dyes. This paper reviews the types of dyes, metal nanoparticles, the photocatalytic degradation process, and the mechanisms involved in dye degradation.

Keywords- Photocatalysis, Nanoparticles, Dye Degradation, Metal Oxides, Wastewater Treatment.

I. CLASSIFICATION OF DYES

Dyes are intricate chemical compounds that can significantly contribute to the contamination of water bodies. Addressing their impact is important for maintaining water quality and ecosystem health. There are two main types of dyes: (I) Natural dyes and (II) Synthetic dyes. Natural dyes are derived from plant parts like flowers, leaves, roots, and stems, as well as from animal sources and minerals. Typically, they are non-hazardous. Synthetic dyes, produced through chemical processes, are harmful and difficult to degrade. They are categorized into cationic, anionic, and nonionic dyes, with cationic dyes being the most toxic [1-3].

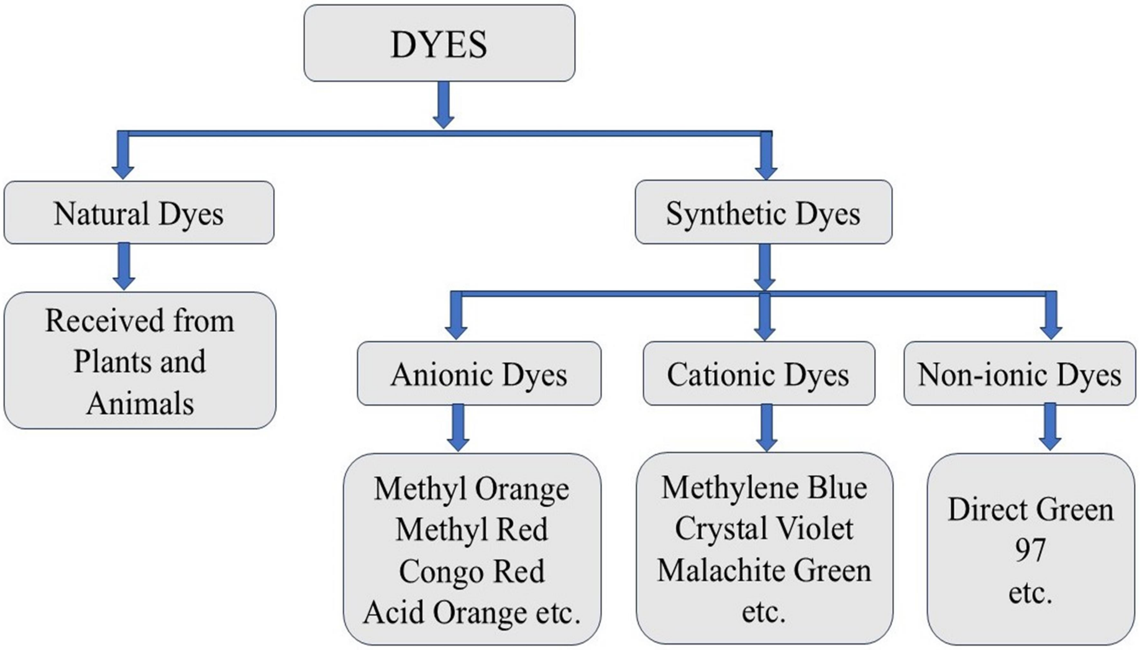

Figure 1: Various types of Dyes

Common dye contaminants and difficulties related to dye contaminants

Common dyes released from various industries such as plastics, rubber, textiles, printing, pharmaceuticals, food processing, and cosmetics include Malachite Green, Eosin Y, Methyl Orange, Phenol Red, Orange G, Bromothymol Blue, Crystal Violet, 4-Nitrophenol, Rhodamine B, Congo Red, and Methylene Blue, among others. Synthetic dyes are used to add color to various substrates and are highly soluble in water, contributing significantly to water pollution. Degrading these dyes is challenging, with concentrations of 1 ppm or higher being harmful to the environment. Levels exceeding 2% pose even greater risks. These dyes can negatively impact the human immune system and health, reduce sunlight penetration in water sources, affecting aquatic life, and degrade soil quality, leading to agricultural issues. Exposure to dyes through contact or inhalation can cause various respiratory and skin-related issues, including sneezing, coughing, breathlessness, itching, eye infections, skin infections, cancer, and hyperactivity [4-5].

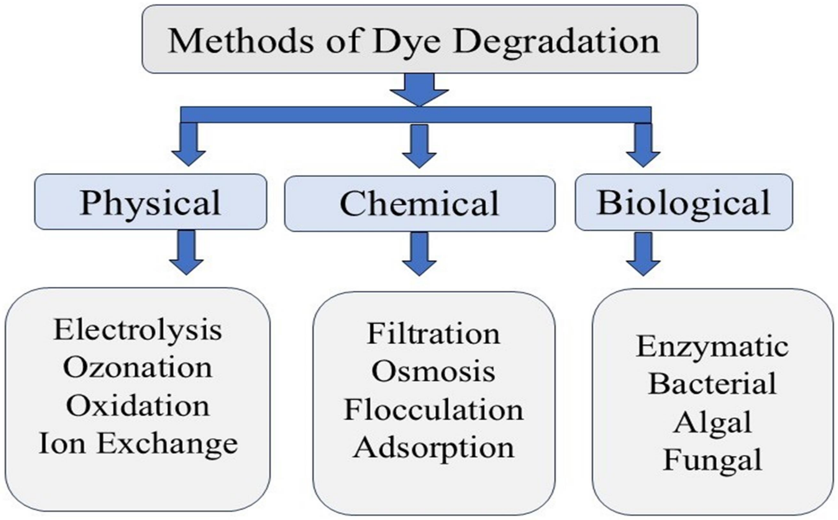

Figure 2: Methods of dye removal

Dye Degradation through Nanoparticles Produced from Plants

The photocatalytic removal of dyes and other contaminants with nanoparticles is a cutting-edge technique for environmental restoration. This method significantly reduces the use of harmful chemicals. Green-synthesized nanoparticles are preferred in modern remediation techniques due to their synthesis benefits, as they do not require high temperatures and pressures and produce non-toxic byproducts. While both catalytic and photocatalytic degradation of chemical dyes have been studied, photocatalytic degradation is more advantageous because it is eco-friendly and cost-effective, utilizing solar light without generating secondary pollutants [6-7].

II. VARIOUS METAL AND METAL OXIDE NANOPARTICLES

Metal NPs are solid, colloidal particles composed of metal, typically ranging in size from 10 to 100 nm. These nanoparticles can have various shapes and sizes, which are produced through a variety of synthesis methods. They are widely used in numerous applications. Commonly utilized metal and metal-oxide nanoparticles in catalytic environmental remediation include gold, silver, titanium, tin, copper, manganese, iron, zinc, cerium, and zirconium, among others.

Gold nanoparticles, which are tiny particles of the noble metal gold (Au NPs), are known for their low toxicity and flexibility in biological systems. These synthesized gold nanoparticles typically have a quasi-spherical shape and display a ruby-red color due to light scattering. Modifications to environmental parameters can alter the optical properties of these colloids. Gold nanoparticles have shown impressive results in the remediation of various dyes [8-9].

Silver nanoparticles (Ag NPs)

Silver nanoparticles can be synthesized through both biological and chemical methods. However, the biological methods are often faster, simpler, and produce non-toxic byproducts. Additionally, these methods can lead to well-defined sizes and desired morphologies under optimized conditions. Silver nanoparticles (Ag NPs) possess unique thermal, electrical, optical, and biological properties, making them suitable for various applications in the medical, healthcare, and food industries [10,11].

Titanium oxide nanoparticles (TiO_2 NPs)

Titanium dioxide nanoparticles (TiO_2 NPs) are synthesized for various applications, including photocatalysis, wastewater treatment, solar cells, and antibacterial agents. These nanoparticles are easy to produce, cost-effective, and exhibit low toxicity. TiO_2 NPs are particularly effective as photocatalysts due to their unique optical and electronic properties, chemical stability, and suitable bandgap. As a result, they can effectively degrade both inorganic and organic pollutants. As an example, the degradation of methylene blue in the presence of TiO_2 NPs was found to be 88% [12-13].

Tin oxide nanoparticles (SnO_2 NPs)

Tin oxide is an N-type semiconductor with a bandgap of 3.6 eV at room temperature. Tin oxide nanoparticles (SnO_2 NPs) exhibit excellent electrical and optical properties, low resistivity, and effective photocatalytic activity at room temperature. These nanoparticles are utilized in various applications, including photovoltaics, coatings, gas sensors, and photo-sensors. Research has shown that biologically synthesized SnO_2 NPs, with a particle size of 21 nm, serve as outstanding photocatalysts for degrading methylene blue (MB). Rod-shaped and smaller-sized SnO_2 NPs demonstrate a higher degradation rate, achieving over 90% degradation of methylene blue under UV light irradiation within 30 minutes [14-15].

Iron and iron oxide nanoparticles

Iron nanoparticles (Fe NPs) exhibit enhanced reactivity with oxygen compared to bulk iron particles and are available in extreme purity. They possess remarkable magnetic properties, a large surface area, and good thermal conductivity. The higher surface area of iron nanoparticles, which enables them to store a substantial amount of energy as surface energy, is responsible for their increased reactivity. This makes iron nanoparticles particularly effective in non-oxidizing environments, batteries, and glassmaking etc. In addition to iron NPs, iron oxide nanoparticles (FeO NPs) are also important. They are widely used in various fields, including biomedicine, catalysis, water treatment, and magnetic materials [16-17].

Copper and copper oxide nanoparticles

Copper nanoparticles (Cu NPs) have garnered significant interest due to their lower cost compared to gold and silver. These nanoparticles have a wide range of applications across various fields, including industrial engineering, agriculture, and technology. A variety of techniques, including chemical reduction, vapor deposition, thermal deposition, and radiolysis reduction of copper salts, can be used to create Cu nanoparticles. Copper oxide (CuO) has the potential to degrade synthetic dyes and other environmental pollutants due to its high surface conductivity, which makes it a perfect material for gas sensor applications. Copper (II) oxide nanoparticles (CuO NPs) typically have a narrow bandgap and a monoclinic structure. They possess several interesting properties, including high stability, good thermal conductivity, photovoltaic capabilities, selectivity, and antimicrobial activities.

Copper oxide (CuO) nanoparticles have a variety of applications, including use in gas sensors, ceramics, advanced superconductors, and magnetic storage media. Recently, green-synthesized CuO nanoparticles were tested for their effectiveness in the photodegradation of dyes, specifically Nile Blue and Yellow 60. The results showed that within 120 minutes, 93% of Nile Blue and 81% of Yellow 60 were successfully degraded [18-20].

Zinc oxide nanoparticles

Zinc oxide stands out among all the metal oxides as a multipurpose semiconductor material because of its distinct chemical and physical characteristics. Since zinc oxide nanoparticles are semiconductors by nature, they can be used in solar cells, gas sensors, catalysts, ceramics, and cosmetics. Various shaped morphologies of zinc oxide nanoparticles, like nanorods, nanoplates, tripods, tetrapods, hexagonal, etc. ZnO NPs are utilized in various environmental applications, including dye degradation and wastewater treatment [21-23].

Manganese dioxide nanoparticles (MnO_2 NPs)

Manganese dioxide is used in ceramic industries under visible light, and found that after 90 minutes, the degradation of CV was achieved 97% while 98.53% of CR degraded in 5 minutes. MnO_2 NPs normally possess a 2D structure and are used in fluorescence sensing, biomedicine, magnetic resonance imaging, and in the functionality of cargo-loading. MnO_2 NPs were used to degrade crystal violet and Congo red (CR) dye from wastewater [24].

Nickel nanoparticles

Nickel nanoparticles (Ni NPs) are currently being intensively explored according to their multiple potential applications and exceptional ferromagnetic properties, such as high coercive forces, chemical stability, and magneto-crystalline anisotropy [25-26]. In experiments involving the degradation of Crystal Violet dye, these nickel nanoparticles achieved a remarkable degradation yield of 99.5%.

Zirconium oxide nanoparticles (ZrO_2 NPs)

Zirconium nanoparticles (ZrO_2 NPs) exhibit a range of advanced properties, including high chemical stability, strong corrosion resistance, and excellent resistance to color changes, chemicals, and microorganisms. ZrO_2 NPs can exist in several crystal structures: cubic, monoclinic, and tetragonal phases, depending on the temperature and pressure conditions. The monoclinic phase of ZrO_2 NPs is stable up to 1100 °C, while the tetragonal phase is stable between 1100 °C and 2370 °C. The cubic phase occurs at temperatures above 2370 °C.

An investigation on photocatalytic breakdown of methyl orange (MO) dye using ZrO2 NPs under UV light found a stunning 97% destruction of the dye within 80 minutes.

Cerium oxide nanoparticles (CeO_2 NPs)

Cerium dioxide (CeO_2) is the most stable oxide of cerium, primarily due to its +4 oxidation state. Cerium oxide nanoparticles (CeO_2 NPs) are commonly used in various fields, including biomedicine, bio scaffolding, drug delivery, and environmental applications. A study conducted by Ravishankar et al. demonstrated that the photodegradation of trypan blue in the presence of CeO_2 NPs and UV light resulted in nearly 100% degradation of the dye from the aqueous solution within 135 minutes [28-29].

III. PHOTO-CATALYSIS ACTIVITY BY NANOPARTICLES AND ITS MECHANISM

When exposed to light energy, metal oxide nanoparticles with wide band gaps generate electron-hole pairs. These interact with substrates on the photocatalyst's surface, effectively degrading organic and inorganic pollutants into less hazardous compounds like carbon dioxide and water. Photocatalysts accelerate chemical reactions under UV and visible light, and effective processes are characterized by stability, an adequate bandgap, high surface area, proper morphology, and reusability. Photocatalytic reactions can be categorized into two types: homogeneous and heterogeneous. The main applications of photocatalytic reagents involve degrading hazardous materials into carbon dioxide and water, destroying or deactivating microorganisms, degrading waste plastics, and decomposing environmental pollutants. Metal oxide nanoparticles and nanocomposites are recognized for having photocatalytic activity in the ultraviolet and solar light spectrum.

Photocatalysis occurs on the surface of metal oxide nanoparticles or nanocomposites, facilitated by conduction and valence bands. Light absorption motivates electrons from the valence band to the conduction band, resulting in oxidation and reduction reactions that produce reactive oxygen species (ROS), which are responsible for dye degradation. This process generates holes (h^+) and electrons (e^-) and accelerates the formation of highly reactive hydroxyl radicals (OH−) from moisture and atmospheric oxygen. These reactive species effectively oxidize and decompose organic materials and can destroy bacteria in the environment.

IV. PHOTOCATALYTIC MECHANISM OF DYE DEGRADATION BY NANOPARTICLES

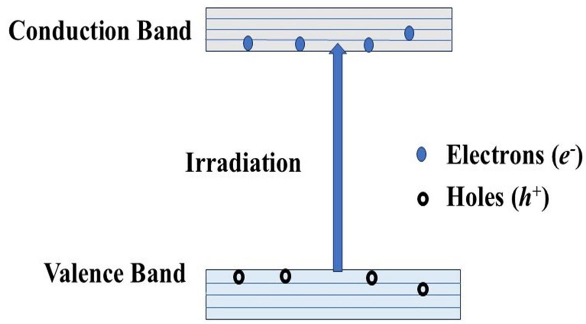

Figure 3: Electron transfer from Valence to Conduction Band

Dye degradation using different metal and metal oxide nanoparticles [30]

nanoparticle	Size	Shape	Name of Dye	Chemical formula of Dye	% Degradation	Reference
Gold	21.52	-	Rhodamine B	$C_{28}H_{31}ClN_2O_3$	87.64	[31]
		-	Eosin Y	$C_{20}H_6Br_4Na_2O_5$	83%	[32]
	24.7	Spherical	4- Nitrophenol	$C_6H_5NO_3$	-	[33]
	10.5	Spherical	Congo red	$C_{32}H_{22}N_6Na_2O_6S_2$	-	[34]
	20	Spherical	Methylene blue	$C_{16}H_{18}ClN_3S$	-	[35]
Silver	6.18	Spherical	Methylene blue	$C_{16}H_{18}ClN_3S$	99.6%	[36]
	6	Spherical	Rhodamine B	$C_{28}H_{31}ClN_2O_3$	85.9%	[37]
	12–25	Spherical	Eosin Y	$C_{20}H_6Br_4Na_2O_5$	97%	[38]
	25–45	Spherical	Rhodamine B	$C_{28}H_{31}ClN_2O_3$	85%	[39]
	2–60	Spherical	Crystal violet	$C_{25}N_3H_{30}Cl$	85%	[40]
	8–32	Spherical	Methylene blue	$C_{16}H_{18}ClN_3S$	100%	[41]
	20	Spherical	Congo red	$C_{32}H_{22}N_6Na_2O_6S_2$	80%	[42]
	10–12	Spherical	Congo red	$C_{32}H_{22}N_6Na_2O_6S_2$	98.5%	[43]
	30	Spherical	Methylene blue	$C_{16}H_{18}ClN_3S$	70.2%	[44]
Copper	61	Spherical	Alizarin yellow R	$C_{13}H_9N_3O_5$	89.71%	[45]
	2–10	Spherical	Methylene blue	$C_{16}H_{18}ClN_3S$	90%	[46]
Nickel	43– 49	Spherical	Crystal violet	$C_{25}N_3H_{30}Cl$	99.5%	[47]
Maganese	<100 nm	Spherical	Congo red	$C_{32}H_{22}N_6Na_2O_6S_2$	78.5%	[48]
Iron	19	-	Methyl orange	$C_{14}H_{14}N_3NaO_3S$	95%	[49]
Zinc oxide	120	Cauliflower	Rhodamine B	$C_{28}H_{31}ClN_2O_3$	75%	[50]

	-	-	Methylene blue	$C_{16}H_{18}ClN_3S$	99.6%	[51]
	19.45	Nanoflower	Methylene blue	$C_{16}H_{18}ClN_3S$	88%	[52]
	13.33	Nanoflower	Rhodamine B	C28H31ClN2O3	98%	[53]
	10.15	-	Methylene Blue	$C_{16}H_{18}ClN_3S$	97%	[54]
	30	-	Methylene blue	$C_{16}H_{18}ClN_3S$	90%	[55]
Iron oxide	21.59	-	Reactive yellow RR	$C_{22}H_{20}N_6Na_4O_{18}S_6$	76.6%	[56]
	9.2	Spherical	Methyl orange	$C_{14}H_{14}N_3NaO_3S$	81%	[57]
	25–55	Semi spherical	Reactive blue	-	95.08%	[58]
Copper oxide	10–50	Circular and hexagonal	Reactive red 120	$C_{44}H_{30}Cl_2N_{14}O_{20}S_6$	78%	[59]
	21.6	Spherical	Methylene blue	$C_{16}H_{18}ClN_3S$	80.5%	[60]
	25	Spherical	Congo red	$C_{32}H_{22}N_6Na_2O_6S_2$	-	[61]

V. BENEFITS AND DRAWBACKS OF NANOPARTICLES FOR DYE DEGRADATION

Metal and metal oxide nanoparticles offer a wide range of applications, and there is a strong interest in exploring and creating novel approaches to address environmental issues such as dye contamination. Various methods exist for synthesizing nanoparticles, with phytogenic synthesis offering several advantages. These advantages include easier management, large-scale production, eco-friendly processing, and a range of applications. However, the synthesis procedures for nanoparticles are currently limited to a small number of metals, oxides, and some sulfides. There is a critical need to discover novel ways for manufacturing nanoparticles from metal oxides, nitrides, carbides, and other substances. Improved experimental techniques are required to better understand the mechanisms included in the nanoparticle manufacturing process. Although plant-mediated techniques have some advantages, they confront limitations when used in industrial settings. The size and shape of nanoparticles depend on the specific plant used and the concentration of metal ions present. Furthermore, the methods for extraction, isolation, and purification are not very effective, which leads to difficulties and results in lower recovery rates.

VI. CONCLUSIONS

Nowadays, a large amount of pollutants is released by industries into water sources and the environment, making environmental pollution a serious problem that is increasing day by day. The primary consideration for remediation methods is that the processes should not negatively impact the environment. The use of harmful chemicals and toxic materials should be avoided, and the methods must be cost-effective. For an eco-friendly and cost-effective remediation strategy, phytoremediation and bioremediation should be prioritized. Utilizing plants and microorganisms in remediation technologies is better for our environment. One significant advancement in synthetic dye degradation is nanoparticle-assisted phytoremediation. Nanotechnology has been rapidly advancing due to the unique properties of nanoparticles, which are often superior to those of bulk materials. Green-synthesized nanoparticles from plants have been established as a promising alternative for environmental remediation. They are effective for the degradation of dyes and offer an eco-friendly, quick, and efficient process for nanoparticle synthesis. In this article, we discuss the method of photocatalysis, including the use of various efficient metals, metal oxides, and their composites as photocatalysts for the degradation of different dyes from aqueous solutions under suitable irradiation. For large-scale wastewater treatment processes, it is essential to design stable, cost-effective, and eco-friendly metal oxides and their composite-based photocatalysts. These photocatalysts should prioritize safety and high efficiency, particularly under visible light. Additionally, they should be reusable and easy to recover.

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