

# Zinc Oxide Nanophotocatalysts in Textile Dye Degradation: A Mini Review

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**Abstract-** Water is the essence of the universe. In recent years, Industrialization have put adverse impacts on our environment especially aquatic ecosystem. Industrial dyes are one of the main waste pollutants [1]. Dyes contaminate water ecosystem and this effects aquatic habitat. These dyes also have severe impacts on human health. So, this is alarming to treat wastewater containing hazardous coloring agents(dyes) specially belonging to the textile industry. The textile industry is of the biggest contributors for water pollution, due to large amounts of synthetic dyes released into water bodies and enhance pollution. These dyes can cause serious health and environmental issues because they resist natural degradation. The best solution to this problem is photocatalytic degradation in which nanomaterials help to the breakdown of these dyes which are basically pollutants. Zinc oxide nanoparticles have gained a lot of attention among various photo catalysts due to their strong photocatalytic activity, cost-effectiveness and environment friendliness. This review explores how the zinc oxide nanoparticles break down the dyes, the factors that influence their efficiency, and recent developments in improving their performance. In this review we also highlight future directions, which include green synthesis methods and integration of zinc oxide with renewable energy sources for applications that are more environmentally friendly.

**Keywords -** Photo catalysis, Zinc Oxide Nanoparticles, Textile wastewater, Dye removal, Environmental sustainability.

## I. INTRODUCTION

Water is the most valuable compound on earth. The 70% of the earth space is cover up by water [1]. Two-thirds of ours is water. Water has an equal importance in environment[2]. However, water pollution is alarming threat to our environment. Industrialization is one of its major cause and due to this source of pollution, water pollution is increasing day by day[3]. Different kinds of pollutants excrete from these industrial units as waste products. These pollutants include heavy metals, organic dyes, hydrocarbons, toxic ions.

One of the major waste products are dyes. These are the effluents which can be visualized by human eye and 1ppm of dye is enough to produce

saturation[5]. All dyes and additives used up to the end of the eighteenth century were mostly made on a small scale using natural ingredients such as bugs, plants, and snails. Only after Perkin's groundbreaking discovery of Mauveine in 1856 of the first inorganic dye, were colors produced synthetically on a wide scale[6]. Various industries such as plastics, leather, rubber, pharmaceuticals, textile and cosmetics use dyes as coloring agents to color their products[7]. Synthetic dyes are the major group belonging to the organic compounds used in our daily life[8].

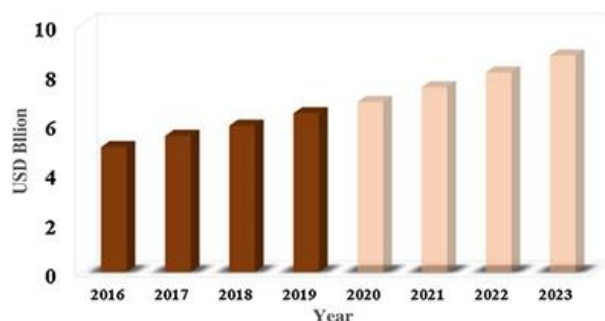


Fig 1: Global textile dyes market over the period of 2016-23

Textile dyeing accounts for approximately 20% of global industrial pollution. According to World Bank Reports, nearly 17%-20% water pollution comes from textile industry during tanning and coloring process [9]. Dyes are the major waste product of these textile industries. About 10,000 types of the commercially synthesized dyes are available [10]. These are considered as micro-pollutant due to their low concentration in aquatic environment [11]. Even in low concentration, these dyes have harmful impacts on environment especially aquatic ecosystem. Dumping dyes decreases the sunlight passage into the water [12]. Total dissolved solids (TDS), total suspended solids (TSS), pH, and chemical and biological oxygen demand (BOD and COD) are all impacted by the effluent's discharge into the aquatic reservoir [13].

The polluted water from textile industry contains high concentration of hazardous chemicals, salts and dye residues, which are discharged in their raw forms can contaminate rivers, lakes and groundwater. This pollution affects aquatic life [14]. Dyes and their by-products are subjected to reductive processes which convert them into carcinogenic compounds that are dangerous for the survival of life that are present in water bodies and also soil [15]. These pollutants are introduced in human body through intake of polluted water and food stuff. The drinking of contaminated water can cause broad spectrum of immune-problems, central nervous, allergy, eye infections [16]. The water that are polluted with dyes specially textile dyes can cause serious health complications like formation of DNA

and protein adducts at the sub cellular level and also have capacity to induce oxidative stress [17].

Methods of treatment of wastewater that are very basic, such as biological degradation, flocculation, and coagulation are unable to completely remove these toxic dyes [18]. Physical and biological processes have their own disadvantages. In aerobic treatment method, there is disposal of large amount of waste, while in case of an anaerobic method, there is no proper lower down of pollutants to the safe level [19]. The transformation of toxic substances from one medium to another medium is not a long term way to get rid and better management of hazardous materials. Nowadays, an alternative method is introduced to conventional physical and biological methods, that is "advanced oxidative process" (AOPs) which is basically an in situ generation of non-selective and reactive species like superoxide anion radicals, hydroxyl radicals and hydrogen peroxide which are the starter of oxidative degradation reactions [20, 21]. In advanced oxidative process, heterogeneous photocatalysis is the best method as it is suitable for degradation of pollutants, including dyes. Heterogeneous photocatalysis is a method in which degradation of dyes is done by semiconductor catalyst, oxidizing agent and emitted light. The semiconductor catalyst are more advanced than conventional chemical oxidation process because semiconductor catalyst are cheap and less toxic [22].

The synthesis of an effective semiconductor-based photocatalyst is challenging because this type of semiconductor photocatalyst should have to work in visible and solar light [23]. Among the different types of semiconductor photocatalysts, Zinc oxide (ZnO) gained a lot of attention due to its valuable characteristics, which include a band gap of (3.37 eV) that is wide, chemical stability, non-toxic behaviour, excitation binding energy, and cost effectiveness [24]. Zinc oxide is a hexagonal and has wurtzite-type structure. Zinc oxide has a band gap energy near that of titanium dioxide (TiO<sub>2</sub>) [25].

As we know that Zinc Oxide based nanoparticles, contain physicochemical properties and also have high surface area-to-volume ratio, so due to these

unique properties, No metal based nanoparticles shows much better performance in breaking down dyes as compared to their bulk counterparts[26].

In this review, a comprehensive overview of ZnO-based nanoparticles will be discussed, that how it is synthesized, modified, and its applications as photo catalyst for textile dyes degradation. The review also discusses the mechanisms involved, factors affecting the degradation process, and current challenges and future aspects in this field. This review describes the importance of modification in material design and processes to control the challenges and enhance the applicability of ZnO based photo catalyst in dye degradation of dyes.

### Mechanism of photocatalytic degradation using ZnO based nanoparticles

Photocatalytic degradation using Zinc oxide nanoparticles consists of redox reactions that are activated by light radiation, generally in the UV spectrum. As we know that, Zinc oxide becomes activated when it absorbs photon with equal or greater energy than its band gap (3.37 eV). This excitation creates an electron-hole-pairs, which are very important for initiation of photocatalytic process[27].

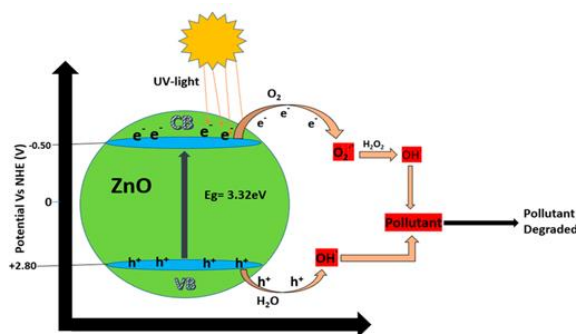
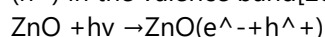


Fig:2 Mechanism of photocatalytic degradation using ZnO nanoparticles

### Photoexcitation

Zinc oxide nanoparticles are exposed to UV light of energy with equal or exceeding energy then their bandgap, electrons present in the valence bond are excited and transitions to the conduction band, this process leaves behind positively charged holes as ( $h^+$ ) in the valence band[28].



### Reactive oxygen species formation

The holes and electrons produced by photocatalytic activity move to the surface of Zinc oxide nanoparticles, where they will take part in redox reaction. The electrons in the conduction band react molecular oxygen and formed the product as superoxide radicals[29].

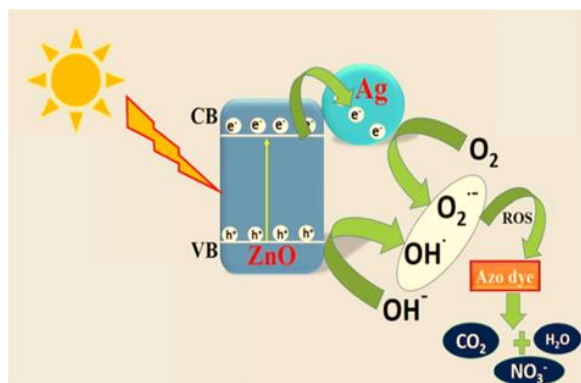


Fig:3 Formation of oxygen reactive species

While the electrons that are present in valence band holes react with oxidize hydroxide ions and water molecules to produce product as hydroxyl radicals( $\cdot OH$ ) [30].

### Dyes Molecule degradation

The reduced oxygen specie attack the molecule of dye, leading to degradation of the macromolecules into smaller and less toxic products[31].

Tuning ZnO nanoparticles for enhanced photo catalysis

The Physical-chemical characteristics of Zinc Oxide Nanoparticles greatly depend on the methods of their synthesis. These methods include the sol-gel method, hydrothermal and Solvothermal process, co-precipitation and combustion synthesis.

### Sol-gel method

This is basically a low temperature process which provides a refined and size optimization of particles and its structure. In Sol-gel method, zinc is taken as precursor such as zinc acetate which undergoes hydrolysis and dehydration synthesis to form a gel, then further drying and calcination to fabricate Zinc oxide nanoparticles [32].

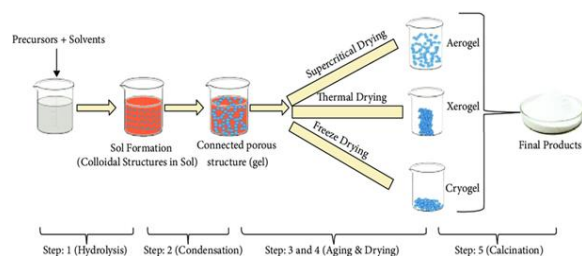


Fig:5 Different stages of Sol-gel process

### Solvothermal and hydrothermal methods

This includes crystallization of zinc oxide under high temperature and pressure from organic or aqueous solutions. By using these methods for preparation of nanoparticles we get highly crystalline nanoparticles with controlled shapes as spheres, rods and flower like structure[33].

### Co-precipitation method

This is a simple method which includes precipitation of ZnO from the solution that contains base and zinc salt. To achieve crystallinity that we want and for the removal of impurities, this method needs post-synthesis heat treatment[34].

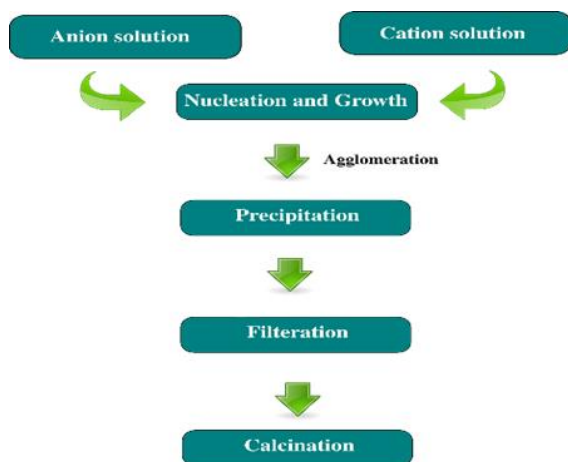


Fig:6 Co-precipitation method

### Combustion synthesis

This method is for nanoparticles includes a redox reaction between oxidizer (zinc nitrate) and fuel like (glycerin or urea), which leads to the rapid growth of ZnO nanoparticles. This process is cheapest and can be used for large industrial scale production[35].

### Alternation strategies

The Zinc Oxide nanoparticles are limited to optical absorption and speedy riposte of electron-hole pairs, that are produced by photocatalytic activity, So, to conquer these obstacles, various rotation techniques have been utilized:

#### Metal ion Dopants:

The combination of transition or noble metal ions like  $Ag^+$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$  and  $Co^{2+}$  into Zinc oxide crystal lattice, termed as metal ions doping. This doping of metal ions introduced localized energy states within bandgap and provides better charge separation. For example, Silver doping increases the photocatalytic degradation of zinc oxide nanoparticles for degradation of dyes by acting as electron trap, and also increases the combination phenomenon of electron-hole pairs[36].

#### Non-Metal ion Dopants:

Elements of the periodic table such as nitrogen (N), carbon(C), phosphorus(P), and Sulphur (S) are non-metals ions, that are doped into Zinc oxide material to enhance its visible light absorption, due to strong hybridization between non-metal orbitals and oxygen orbitals in ZnO. Among non-metal doped ions, nitrogen(N) is regarded as most effective element due to its capacity to form shallow acceptor states above the valence band and its compatible atomic size with oxygen[37].

#### Performance of ZnO in textile dye degradation:

Textile industries are a major contributor to water pollution due to the release of toxic dyes that are resistant to simple treatment methods. Among all the materials that are used for dye degradation, Zinc oxide nanoparticles have strong photocatalytic activity and low cost[38].

As we know, ZnO is a broad bandgap semiconductor (3.37eV) with high binding energy, which helps to create electron-hole pairs, when bring to UV irradiation. These charged species act with water and oxygen to generate reactive oxygen species (ROS), which are highly efficient in breaking of macromolecule into less toxic product[39].

#### Degradation of Dyestuff

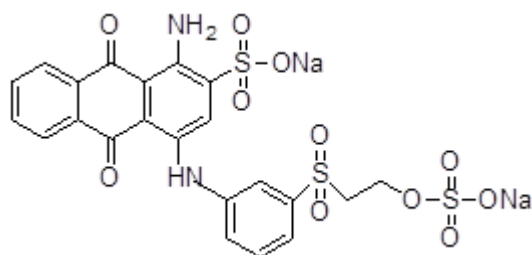
Dyestuff is classified based on their chemical structure. Here are some basic dyes described below:

### Anthraquinone dyes

Reactive blue 19(RB19) is classified as class of anthraquinone dyes. ZnO oxidizes the anthraquinone ring through generation of hydroxyl radicals. Its efficiency is about 85-92% in 90-150 minutes[40].

### Remazol Brilliant blue

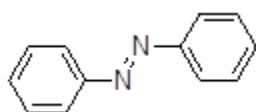
This dye is degraded when spray-pyrolyzed ZnO thin film showed performance in the presence of UV light and achieved about 92% decolorization. Moreover, the thin films retained their performance activity over 20 cycles that can be reused[41].



Chemical structure of Remazol Brilliant blue dye  
Azo dyes

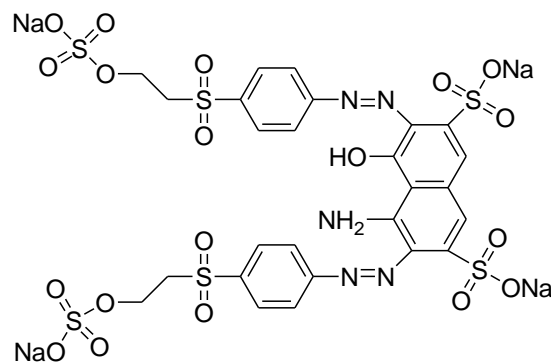
Azo dyes include methyl orange, rb5 and Congo red. Azo bond (-N=N-) present in methyl orange and Congo red is broken by ZnO nanoparticles under UV/Visible light, and converted them into aromatic amines such as CO<sub>2</sub> and H<sub>2</sub>O. Its efficiency is about 90-98% in 60 to 120 minutes[42].

### Chemical structure of Azo dye



### Reactive black 5(rb5)

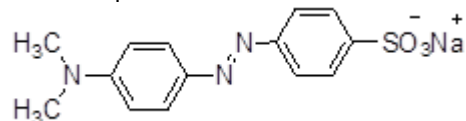
Reactive black 5 is an azo dye and has a very complex structure and it is very hard to degrade it. But, ZnO nanoparticles have ability to degrade it up to 90% under visible light, which improves electron-hole separation and increases the light adsorption[43].



Chemical structure of Rb5 dye

### Methylene orange

ZnO nanoparticles facilitates the procreation of reactive oxygen species which breaks down the azo bond present in methylene blue and cause formation of less harmful products such as CO<sub>2</sub> and H<sub>2</sub>O[44].



### Chemical structure of methylene orange

Challenges and limitations of ZnO based photocatalyst

Zinc oxide photo catalyst due to its favorable and unique properties, including a suitable band gap, cost-effectiveness and high electron affinity, has gained a lot of attention. However, some challenges limit their practical applications as photo catalyst.

### Photo corrosion of ZnO-Based photo catalysts

The one of the significant hurdles that limits the prolonged efficiency of ZnO-based photo catalyst is photo corrosion that occurs when under light irradiation, mostly when in aqueous environment. This limits the reusability of ZnO based on photocatalytic applications.

Photo corrosion basically occurs when the hole generated by photocatalytic process(h<sup>+</sup>) oxidizes the ZnO itself, rather than the oxidation of target material, it causes the dissolution of Zn<sup>2+</sup> into solution. This self-decomposition is accelerated when exposed to UV irradiation which results in the degradation of ZnO lattice and reduce its photocatalytic activity[45].

For the mitigation of photo corrosion, researchers have explored many methods including:

Surface coating: Coating of ZnO with protective layers such as TiO<sub>2</sub>, carbon materials and SiO<sub>2</sub> can act as barrier against photo corrosion [46].

Protective coating: Carbon layers like graphene and carbon dots are used as protective coatings that protects zinc oxide from photo corrosion and also improving transfer of charge [47, 48]. The inert oxides like TiO<sub>2</sub> form core-shell structures with ZnO that helps in protection of surface from degradation [49].

Doping of Metal and Non-Metals: Doping of elements like Al, Ag and N facilitate the charge carrier separation, and causing the hole density at the ZnO surface and lowering the photo corrosion rate [50].

pH optimization: pH optimization has property to inhibit the dissolution of ZnO by maintain pH (pH>10),it helps to prevent the photo corrosion of ZnO [51].

Dye	Dye type	Toxicity	Origin	ZnO Modification	Light Source	Degradation time (min)	Degradation mechanism	Degradation efficiency	Reference
Methylene Blue	Cationic	Carcinogenic, mutagenic	Paper, textile, medical	ZnO particles (Pure)	UV	120	Attack by •OH radical	95%	[52]
Methyl orange	Azo	Irritant	Food, textile	ZnO/TiO <sub>2</sub>	UV-Vis	150	N=N bond breakage, Hydroxylation	88%	[53]
Reactive black 5	Reactive azo dye	Hazardous, mutagenic	Textile, paper industry	Fe doped ZnO nanorods	Visible light	200	Attack by radical, Electron-hole separation	85%	[54]
Reactive blue 19	Reactive azo dye	Aquatic toxicity, mutagenic	Textile dyeing	ZnO/Fe <sub>2</sub> O <sub>3</sub>	UV	120	•OH, radical attack, azo bond breakage	94%	[55]
Alizarin Red S	Anthraquinone	carcinogenic	medical	Pure ZnO particles	UV/visible	180	•OH, radical attack on ring	70-80%	[56]

### **Development of Visible-light-Active ZnO photocatalyst for dye degradation of textile**

Zinc oxide photo catalyst referred as promising photo catalyst due to its chemical durability, harmless behavior and high photosensitivity. ZnO based photo catalyst has a broad band gap of about (3.37 eV), which limits or less its activity to the UV region, and absorbs only about 5% of solar radiation. To enhance the efficiency of photo catalyst under UV light, we must made efforts to enhance the activity of photo catalyst and develop visible-light –active photo catalyst for dye degradation of industrial dyes.

#### **Doping strategies:**

The common strategy to develop visible-light-activity in ZnO photo catalyst is through the doping of transition metals like (Fe, Mn, Co) and non-metals like (S, C, N). The introduction of these dopants produces high energy within bandgaps, which facilitate electron excitation when under the visible light. Fe-doped ZnO nanoparticles developed to showed boost photocatalytic activity as after doping charge separation improved and also optical light absorption[24].

#### **Surface sensitization and modification**

Surface modification by using noble metal nanoparticles and organic dyes enhance the ZnO sensitize activity towards optical light. Dye sensitized enhances the light absorption range of ZnO photo catalyst, by injecting electrons from the dye and putting it in the conduction band of ZnO when irradiated with UV light. For example, Ag nanoparticles deposited on the top of ZnO and enhance its photocatalytic activity and improved its charged activity[57].

#### **Application in Textile dye degradation**

Textile industry brings about a large volume of wastewater that carry synthetic dyes that are resistant to conventional methods of removing or treatment of wastewater. ZnO photo catalysts have potential to degrade the toxic dyes even azo dyes in the presence of solar light, when surface modifications are done. These methods of treating wastewater offers an effective alternative to traditional methods ,that cause the breakdown of

complex molecules of dyes into non-toxic products[58].

#### **Future Perspective and research direction**

Future research expected to focus on enhancing the photo catalytic venture of ZnO-based nanoparticles for textile dye breakdown under visible light irradiation, major limitation of pure ZnO due to its wide bandgap[59]. Modifications such as coupling with semiconductors like TiO<sub>2</sub> and metal and non-metal doping, are the strategies to refine the separation of charges and extend light absorption in the visible region[60]. The synthesis of nanostructured ZnO composites that has uniform morphology and high surface area is another way to improve the photocatalytic efficiency and dye degradation[61]. For the industrial application of ZnO nanoparticles based photocatalyst, attention must be given to the stability of catalyst , reusability and degradation of toxic dyes to provide safe environment[62].

The future research should concentrate on optimization of reactor designs like fixed-bed system or fluidized-bed, for the purpose of achieving industrial scale dye wastewater treatment, because scalability is one of the biggest critical challenges. To comparing the economic viability and environment friendly behavior of the metal-enhanced ZnO system with conventional treatment methods, the essential methods of analysis are lifecycle and techno-economic analysis.

Finally, if academia and industry work with collaboration, then it is very important to real-world implementation, like making of practical solution of ZnO based advanced oxidation for dye degradation remains a critical challenge, and future studies should focus on optimizing reactor designs (e.g.,

## **II. CONCLUSION**

Zinc oxide nanoparticles are utilized for the breakdown of toxic dyes of textile industry, and it served as a productive and sustainable method for the curing of wastewater. As we know that ZnO has a wide bandgap, high stability and are cost effective that will help for degradation of toxic dyes in UV

region [63]. The doping of metal-based catalyst enhances the photocatalytic activity of ZnO by improving charge separation, bringing down electron hole recombination and enhancing light absorption. Regardless of these advantages, the performance of ZnO photo catalyst is diminished by photo corrosion, which reduces the stability and usability of ZnO photo catalyst.

Various mitigation strategies, such as surface coating, protective coating, doping of metal and non-metals and pH optimization, have been explored to increase the ZnO photo catalyst activity. More ever, the development of cost-effective methods like use of waste-derive materials, ensure the cost friendly methods for dye degradation for use on large industrial scale. Future research should focus on increasing the ZnO composite activity and adaptation of methods, that enhance its stability and reusability to perform on larger industrial scale. Ultimately, ZnO based advanced oxidative possesses properties that have ability or performance for sustainable wastewater treatment in the textile industry.

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