Research Journal of Recent Sciences ISSN 2277-2502
Vol. **14(4),** 17-22, October **(2025)** *Res. J. Recent Sci.*

Short Review Paper

Photocatalytic Degradation of Dyes from Industrial Discharge by Metal Oxide Nanoparticles – A Mini Review

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Available online at: www.isca.in, www.isca.me
Received 4th January 2025, revised 29th March 2025, accepted 30th May 2025

Abstract

The rapid growth of industrialization, urbanization, agriculture activities cause the pollution of water. Pollution of water is harmful to living organisms, soil fertility and aquatic organisms. The discharge from dye and textile industries is highly hazardous to living organisms. The various methods have been developed to remove or reduce the dyes contaminants. The photo catalytic degradation is one of the simple and highly efficient methods to degrade the organic pollutant into harmless species like water and CO_2*.To enhance the photo catalytic activity the metal oxide nanoparticles being used instead of its bulk material. In this review article we focus on the photocatalytic degradation of various dyes utilizing metal oxide nanoparticles as photocatalysts.*

Keywords: Photo degradation, Metal oxide nanoparticles, Dopant, Photo catalyst, dyes.

Introduction

In general, Ground water and surface water are main two types of water sources. Groundwater refers to the large volume of water located beneath the water table, while surface water consists of water present in various bodies like lakes, ponds, streams, rivers, canals, and dams. The ground water is less contaminated water as compared to the surface water[1]. The surface water is one of the important resources providing water to industrial activities, agricultural activities and domestic activities and also used for drinking purpose. The discharge of untreated effluent from different industries into water bodies like lakes, ponds, streams, rivers, canals, dams cause the pollution of surface water. Dyes are color substances and toxic used in various industries such as food, textile, paper, cosmetic, leather, pharmaceutical etc**.** was carried out[2].

When such industrial the untreated effluent, industrial dye stuff, textile dyes release into the different water bodies cause the pollution of surface water which is hazardous for aquatic eco system and human being. Treatment of polluted surface water is an essential and serious challenge for the whole world. Textile industry used different dyes which are colored substances. Approximately 10–20% of dye components are present in industrial wastewater contain lot of organic dyes which is directly discharged in natural water resources without any treatment[3].

Industry discharge and wastewater: Due to the diverse range of industrial operations involved in manufacturing. The wastewater or sewage is released from various sectors such as textiles, paper, food, cosmetics, and others into water sources like lakes, ponds, streams, rivers, canals, and dams, resulting in surface water pollution[4]. The discharge of untreated wastewater from these industries can have both positive and negative effects on the environment and ecosystems. The untreated effluent may be rich in nutrients which can benefit the growth of plants and animals representing a positive effect. On the other hand, it may also contain harmful toxins, making it potentially carcinogenic, which reflects the negative aspect[1]. The textile industry is one of the major industries which show the negative impact on environment and ecosystem. During the fabric manufacturing process, various dyes and chemicals—including surfactants, acids, alkalis, electrolytes, chelating agents, leveling agents, promoters, and emulsifying oils—are utilized. The qualitative and quantitative properties of textile wastewater vary depending on the production method employed. Each phase of the manufacturing process generates different types of waste water that may contain organic dyes, heavy metals and other pollutants. The physico-chemical properties of wastewater produced by the textile industry fluctuate at each stage of the process[5].

Green environment and surface water: The surface water is an important resource for providing water to different fields like industrial activities, agricultural activities, domestic activities and drinking purpose. Surface water pollution occurs due to the rapid growth of industrialization, urbanization and agriculture activities. The pollution levels of surface water are significantly elevated due to its geographical location, necessitating the implementation of measures to control and preserve the quality of surface water for the well-being of the environment.

The odour and taste of water get affected by color and turbidity[1]. The chemical reaction between chemical parameters and chemical constituents increases temperature of water and % of nitrogen while it causes low conductivity of water and decreases the amount of oxygen in water bodies which is harmful to the aquatic and plant eco system as well as human health. The existence of the pathogens like bacteria, viruses in the polluted water can infect the health of aquatic ecosystem and human health which causes the nature's biodiversity[1]. To maintain the green environment and ecosystem, it is an important task to maintain the quality of surface water by pollution prevention at the water bodies and precautionary regulations of country.

Water quality standards: The Water Quality Index (WQI) is used for assessing the suitability of water for drinking and other purposes. The evaluation of the WQI involves several parameters including pH (indicating whether the water is acidic or alkaline), total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and ammoniacal nitrogen. Physical changes in polluted water, such as alterations in color, turbidity, temperature, taste, and TSS, are indicative of its condition while variations in BOD and dissolved oxygen reflect the chemical concentrations present. These parameters influencing water quality and serving as the basis for WQI assessment which encompasses chemical, physical, and biological characteristics. To promote environmental health, numerous countries have implemented standard values, practices and national policies aimed at controlling and enhancing water quality. Various regulatory bodies, including the Central Pollution Control Board (CPCB), the World Bank Group, the Federal Environmental Protection Agency (FEPA), and the United States Environmental Protection Agency (EPA), have been established to oversee water quality management.

Classification of dyes: The colored substances have the affinity to color other substrate in such manner that color cannot be removed by rubbing and washing. If the chromogen contains one or more auxochrome then it is known as dye. The auxochrome and chromophore are main two components of dye; the chromophores are responsible for color production while auxochrome just increases the intensity of color and its affinity towards the substrate[2]. It should be noted that the various industries such as leather, plastics, paper, textiles, food, pharmaceutical are used different dyes and considerable quantities of water at different manufacturing steps of the desire product. The wastewater which contains substantial amounts of contaminants and dyes which are released into various water bodies such as lakes, ponds, streams, rivers, canals, and dams[2-6]. Generally, the whole classification of dyes regarding one parameter is quite difficult. The categorization of dyes is conducted by considering various parameters such as the dye's source, chemical composition and applications[7]. On the basic of origin, the two main types are natural dyes and synthetic dyes. The natural dyes derived from natural sources like plants, animals etc. which could not produce on large scale while synthetic dyes are synthesized by man[2]. As demand has escalated, natural dyes have struggled to meet industrial needs. Due to industrialization, urbanization and population growth necessitates the large-scale production of synthetic dyes. Numerous synthetic dyes are utilized across different industries including reactive dyes, direct dyes, vat dyes, acid dyes azo dyes, basic dyes, and disperse dyes[2]. From a chemical structure perspective, dyes are classified into cationic dyes possess functional groups that can dissociate into positively charged ions in aqueous solutions whereas anionic dyes contain functional groups that dissociate into negatively charged ions. These functional groups exhibit solubility in water and are capable of effectively interact with metal oxide nanoparticles which act as photocatalysts characterized by their hydrophilic surfaces[7].

Table-1: A Categorization of Synthetic Dyes and their applications[2].

Dyes	Example of dye	Applications of dyes
Direct dyes	Martins yellow, Direct orange	Cotton, leather
Acid dyes	Acid (blue), Congo red	Nylon, silk,
Vat dye	Indigo	Wool, Rayon
Disperse dyes	Disperse blue	Nylon
Basic dyes	Aniline yellow	Silk, nylon

Surface wastewater treatment strategies: The various methods have been developed to reduce the dye contaminates from surface wastewater. Which are the physical methods like adsorption, the biological method like biodegradation and chemical methods like photo catalytic degradation etc. The biological and physical methods only transform the dye contaminates from one phase to another phase. The photo catalytic degradation of dyes is one of the most effective, suitable and simple method to remove or reduce the dyes or organic pollutants from wastewater[3-6].

Nanoparticles as photo catalyst: Now a day's number of researchers prefers to work on nanotechnology. Nano materials have wide range of applications in various fields. Consequently, researchers are increasingly engaged in the production of nanoscale materials such as nanoparticles, nanowires, nanofilms, nanotubes, and nanosheets. These materials are design at the atomic level and exist in extremely small dimensions ranging from 1 to 100 nanometers exhibiting various crystalline forms, including spherical nanoparticles, nanorods, nanoribbons, and nanoplatelets[8,9]. In this review, we focus on nanoparticles as photo catalyst. They are undetectable by the human eye. Due to the exceptional properties of metal nanoparticles, they show number of applications in various fields such as pharmaceuticals, cosmetics, electronic, environmental, agriculture, textile etc. The small size and large surface area of metal oxide nano particles show good catalytic activity therefore metal oxide nanoparticles being used instead of its bulk material to enhance the photocatalytic activity. The photocatalytic degradation of different dyes by metal oxide nanoparticles as photocatalyst such as ZnO, TiO_2, NiO, α- Fe_2O_3 and dopants like Al doped ZnO, Zn_2SnO_4, Fe-ZnO, $CoFe_2O_4$, has been carried out.

Processing methods: The synthesis of nanomaterials can be carried out by Bottom-up approach and Top-down approach[4]. Bottom-up approach where atoms of nanomaterial form the cluster and then it is converted into the nanomaterial. In contrast, a top-down approach entails the conversion of bulk materials into powder, which is then processed into nanomaterials. Various physical, chemical, and biological methods are employed to synthesize various types of nanomaterials. Physical methods such as mechanical milling, thermal decomposition, chemical methods such as sol-gel method, chemical reduction method and biological methods such as green synthesis using plant extract, micro-organism[2].

Degradation of Dyes: Photo catalytic degradation of organic dyes is the removal of dyes from industrial waste is essential for eco friendly environment. The photocatalytic degradation of dyes utilizing nanoparticles as photocatalysts can be transform the dyes into environmentally friendly products, including water, carbon dioxide, and mineral acids. The photo catalytic degradation of dyes is photon induced reaction which is accelerated in the presence of nanoparticles as catalyst. The photo catalytic reaction takes place through following steps. Photo excitation Charge separation, Migration, Surface redox reactions[10]. i. The absorption of light by photo catalyst. Due to absorption of light excitation of photocatalyst electron from valence band (VB) to conduction band (CB) which generates the e^- (CB) and h+ (VB) pairs. ii. Due to low stability of photo generated electrons, possible recombination of excited electrons and holes may take place and it is not favorable for photo catalytic degradation therefore as much as possible recombination of excited electrons and holes must be prevented. iii. The produced electron (e-) from the conduction band (CB) and the hole (h+) from the valence band (VB) undergoes in oxidation and reduction reactions. The h+ (VB) engages in oxidation reactions with water resulting in the formation of hydroxide ions which are then transformed into hydroxyl radicals. Meanwhile, the e^- (CB) reduces oxygen to form superoxide radicals which are highly effective in the decolorization of dyes. iv. Finally, degradation of dye take place by nano particles as photo catalyst convert the dye (organic complex molecule) into environmentally friendly products such as water, carbon dioxide, mineral acids[10-12].

The photo catalytic degradation of dyes by using the heterogeneous photo catalyst that is doping of photo catalyst enhances the activity of photo catalyst. Doping of photo catalyst increases the activity of photo catalyst in several ways – i. Increase in surface area of photo catalyst, ii. Narrowing of band gap, iii. Oxygen vacancies, iv. Electron trapping, v. Formation of impurity energy levels. Generally, the dopants act as photo catalyst enhances the photo catalytic activity. The dopant prevents the recombination of electrons and holes[7]. Thus, the greater number of e^- (CB) and h^+ (VB) pairs generated by photoexcitation undergoes oxidation and reduction reaction. The h+ (VB) undergoes in oxidation reactions with water resulting in the release of hydroxide ions which subsequently transform into hydroxyl radicals while e- (CB) reduces oxygen into superoxide radical which is powerful species for decolorization of dye. As number of radicals increases the efficiency of degradation of dye increases.

Review Methodology

The keywords such as photocatalysis, metal oxide nanoparticles, wastewater treatment are used to search published articles. The exploration result for the number of peer reviewed journal articles is as summarized. The literature review for this research article was conducted through an examination of peer-reviewed journal articles utilizing keywords such as Photo degradation, Metal oxide nanoparticles are used to identify relevant publications. The findings regarding the quantity of peer-reviewed journal articles are summarized. The research article provided research methodology for synthesis of photocatalyst, dopant and new technology to reduce or degrade the different dyes. The literature review was massive; however, after evaluating and selecting a number of peer-reviewed journal articles, the overall section of the review was systematically organized and analyzed with relevant examples.

Conclusion

If the chromogen contains one or more auxochrome then it is known as dye. Dyes are colored, toxic, non-biodegradable complex organic molecules used in various industries during the number of manufacturing steps. So untreated industrial discharge shows negative impact on environment and ecosystem. Nanomaterials show number of applications in various field; in past few years researcher prefer to work on nanotechnology. The photo catalytic degradation of dye by metal oxide nanoparticles as photo catalyst is most effective, fast, suitable and simple, chemical method that uses the sunlight, water and reusable photocatalyst to remove or reduce the dyes from industrial wastewater discharge. The metal oxide nanoparticles act as photo catalyst activated with UV / visible irradiation promotes the formation of hydroxyl radicals, superoxide radical which in turn completely degrade the dyes to give simple green product such as water, carbon dioxide, mineral acids. Metal doping reduces electron-hole recombination, thereby enhancing the photocatalytic degradation of dyes. Numerous publications have documented the photocatalytic degradation of dyes utilizing metal oxide nanoparticles as photocatalysts, which have been synthesized through various methods.

Table-2: A comparative analysis of the photocatalytic degradation of dyes utilizing metal oxide nanoparticles as photocatalysts.

Synthesis Method	Photocatalyst used	Light source	Dye	Irradiation duration	Degradation efficiency (%)	Ref.
Sol-gel	Ag–CdS@Pr-TiO_2	Visible	Methyl orange	30 min	98%	13
Green synthesis	Iron oxide (α-Fe_2O_3)	Sun light	Remazol yellow RR dye	6 h	76.6%	14
Hydrothermal method	α-Fe_2O_3@ CeO_2 and CeO_2@α-Fe_2O_3	UV light	Rose Bengal	75 min	93%	15
Combustion through microwave technique	Ni-doped copper ferrite spinel Np	Visible	Rhodamine B	Not given	Not given	16
Sol-gel	Cu-doped ZnO	UV light	Methyl orange	Not given	88%	17
Sol-gel	$NiMn_2O_4$	Ultraviolet irradiation	Rhodamine B	80 min	98%	18
Chemical precipitation method	NiO	Solar light	Methylene Blue	Not given	Not given	19
Hydrothermal method	NiO	UV light	Methylene blue	Not given	Not given	20
Green method	NiO	UV light	Rhodamin (RhB)	Not given	92.3%	21
Sol-gel	Zn_2SnO_4	UV light	Methyl orange and Methylene blue	60 min	73% and 62%	22
Coprecipitation technique	Silver doped zinc oxide	Sun light	Methylene blue	Not given	98%	23
Green synthesis	ZnO	Sun-light	Methylene blue and Malachite green	150 min 150 min	94% 92%	24
Green synthesis	ZnO	UV light	Malachite green	180%	89%	25
Mechanical Milling method	Sr-doped ZnO	Visible light	Methylene blue	Not given	97%	26
Sol-gel	Silica nanoparticles	UV light	Methylene blue and Methyl orange	90 min	98% and 95%	27

Acknowledgments

We would like to thank K.T.S.P. Mandal's Hutatma Rajguru Mahavidyalaya, Rajgurunagar, Tal-Khed, Dist-Pune for providing the research facilities**.**

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