Photocatalytic activity of Metal Oxide Based Nanocomposites of Tranisition elements with reference to dyes removal.

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Abstract –

The elimination of dyes discharged from industrial wastewater into water bodies is crucial due to its detrimental effects on aquatic organisms and potential carcinogenic impact on human health. Various methods are employed for dye removal, but they often fall short in completely degrading the dyes and generating large amounts of suspended solids. Hence, there is a critical need for an efficient process that can achieve complete dye degradation with minimal waste emission. Among traditional water treatment approaches, photocatalysis stands out as a promising method for degrading diverse toxic and organic pollutants present in wastewater.

The variety of methods for their characterization and widespread applications for the degradation of dyes and pollutants are discussed. Structure/activity relationships and methods of improving on some of the recognized short comings of Metal oxide based nanomaterial catalysts are also presented. The enhanced photocatalytic property was also discussed based on the synergistic effects of doped matel oxide based nanocomposite and explained by possible mechanisms. This may be low cost and very helpful for the degradation of different dyes from aqueous solutions under suitable visible light irradiations.

Keywords : nanocomposite ; photocataliyic absorption; visible light irradiation ; dyes degradation

1. Introduction

The rapid expansion of textile, dyeing, and finishing industries has led to the large-scale discharge of dye-laden wastewater into natural water bodies. Textile dyes are chemically stable, highly soluble in water, and resistant to biodegradation due to their complex aromatic and heterocyclic molecular structures. Even at very low concentrations, these dyes impart intense color to water, significantly reducing light penetration and disrupting aquatic photosynthesis, thereby affecting the ecological balance of aquatic environments [1].

Textile dyes are one of the most persistent organic pollutants discharged into aquatic systems. Common dyes such as methylene blue, methyl orange, rhodamine B, congo red, reactive red, direct blue, and malachite green possess complex aromatic structures and high chemical stability, making them resistant to conventional wastewater treatment methods. These dyes reduce light penetration in water bodies, inhibit photosynthesis, and many are toxic, mutagenic, and carcinogenic to aquatic life and humans.

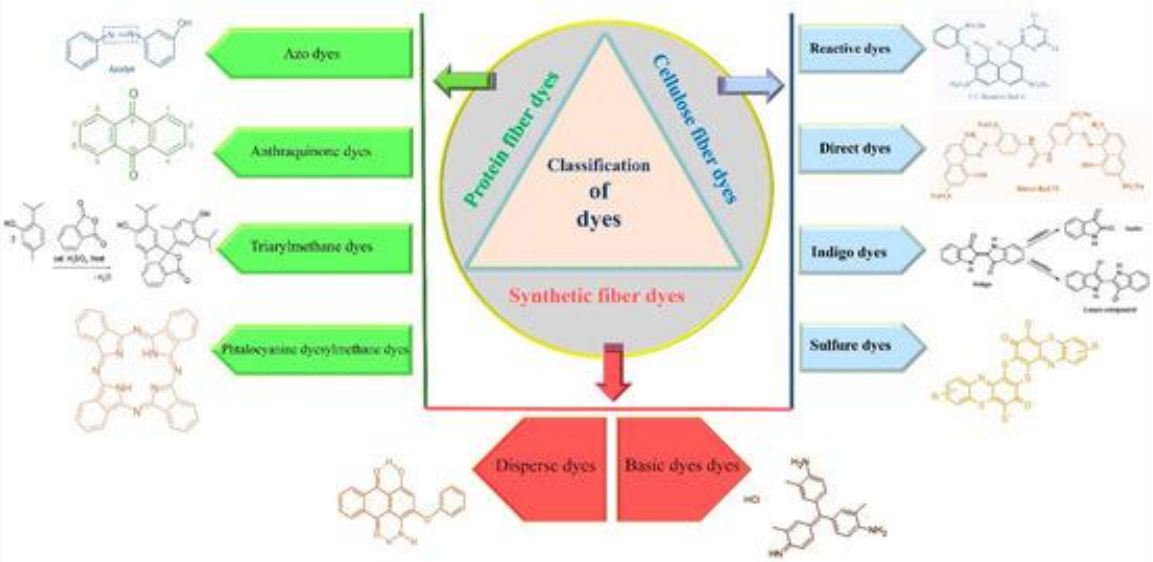

Fig. 1 : Classification of Dyes

Conventional wastewater treatment techniques such as coagulation–flocculation, adsorption, membrane filtration, and biological treatment often exhibit limited efficiency in completely removing textile dyes. These methods mainly transfer pollutants from one phase to another rather than achieving complete mineralization and frequently generate secondary waste or sludge disposal issues. Moreover, many textile dyes and their degradation intermediates are toxic, mutagenic, or carcinogenic, posing serious risks to human health and aquatic organisms. In this context, photocatalytic degradation has emerged as an advanced[2,3].

Photocatalytic degradation has emerged as a promising advanced oxidation process (AOP) capable of complete mineralization of textile dyes into non-toxic end products such as CO_2, H_2O, and inorganic ions using semiconductor catalysts and light energy. During the photocatalysis, the source of light and catalysts are used to accelerate the process of the degradation of organic pollutants. According to the source data, photocatalysis can remove 70–80% of pigments from industrial effluent. Several researchers are working on the heterogeneous photocatalysts such as ZnO, TiO2, Cds, and WO3 for dye degradation [4].

2. General Mechanism of Photocatalysis for Dye Degradation

Photocatalysis is a process where a photocatalyst (TiO_2) absorbs photons (typically ultraviolet light) to generate electron–hole pairs, which then participate in redox reactions with adsorbed species on the catalyst surface, leading to the degradation of synthetic dyes in wastewater [5-7].

The general mechanism of photocatalysis involves three steps :

1. Generation of electron–hole pairs: When the photocatalyst absorbs photons with energy greater than its bandgap, electrons are excited from the valence band to the conduction band, leaving behind positively charged holes in the valence band.

2. Redox reactions: The electrons in the conduction band and the holes in the valence band are highly reactive and can participate in redox reactions with adsorbed species on the catalyst surface, such as water and oxygen, or organic pollutants.
3. Degradation of pollutants: The reactive species, such as hydroxyl radicals (OH•–) formed from water molecules, can react with organic pollutants adsorbed on the catalyst surface, leading to their degradation into smaller, less harmful byproducts.

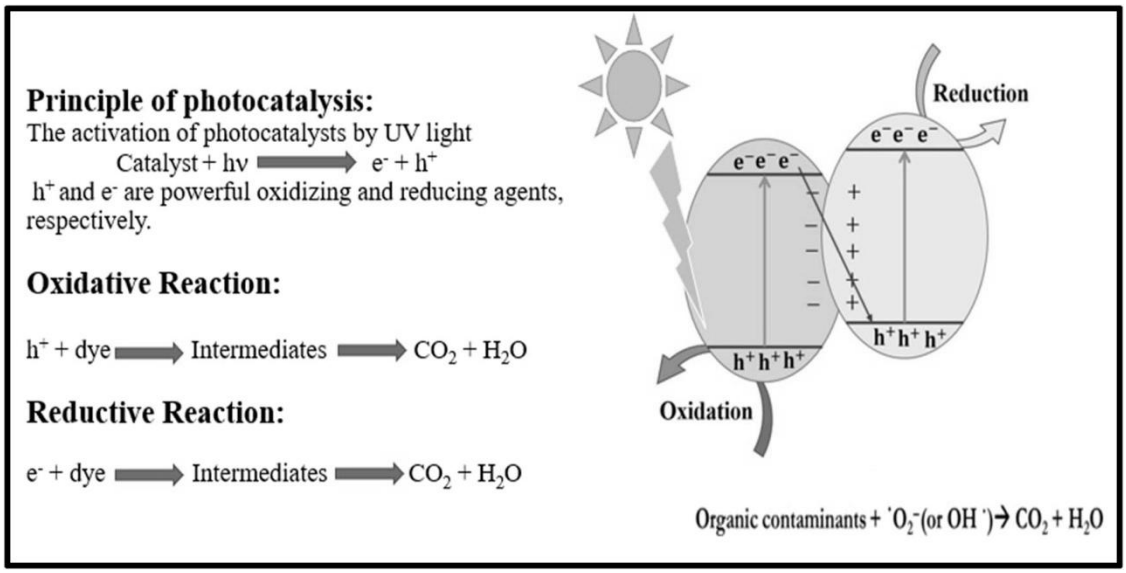

Fig. 2 : Principle of photocatalysis of organic dyes.

3. Nanocomposites of Transition Elements for Photocatalytic Dye Degradation

In recent decades, the application of polymers for the treatment of environmental samples has become authentic. On their basis, ecological materials with various properties have been created such as films, sorbents, membranes, filters for nano- and ultra-filtration, and functional composite materials. Some biopolymer materials with nano-dispersed TiO_2 are used to improve the functional properties of nanocomposites and increase the photocatalytic activity of TiO_2.

One of the prospective biopolymers for solving such tasks is chitosan (CS), which is the product of chitin deacetylation . CS matrices present a high sorption capacity and are effective sorbents of such compounds as PAHs, dyes, heavy metal ions, etc. CS has a high ability to chemical modification due to the presence of reactive hydroxyl and amino groups. This allows one to select the different characteristics of polymeric sorbent according to the tasks. CS is the most studied natural polymer to prepare different nanocomposites. [8-9]

The ZnO/SnO_2 quantum dot (3-5 nm in diameter) heterojunction immobilized on cross-linked CS films (ZnO/SnO_2/CS films) were successfully synthesized.The photocatalytic properties come from semiconductor components and light irradiation. In other applications, pH adjustment, ultrasonic resources and H_2O_2 are required for applying or preparing nanocomposites . Other used polymer materials include polyethersulfone, polysulfone, cellulose acetate and nitrates, polypropylene, polytetrafluoroethylene, polyimide, polyvinylidene fluoride, polyvinyl alcohol and polyacrylonitrile are the most extensively used organic membrane materials. [10-14]

Polymer nanocomposites have many advantages :

(1) Excellent flammability properties.

(2) Increased biodegradability of biodegradable polymers.

(3) Barrier properties are improved compared with the neat polymer.

(4) Mechanical and hermal properties are potentially superior.

(5) These are lighter than conventional composites.

(6) High degrees of stiffness and strength.

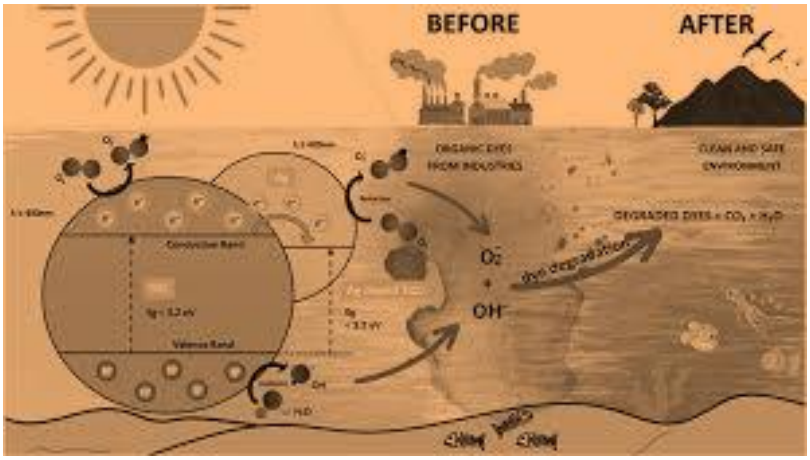

Fig 3 : Progress in Photocatalytic Degradation of industrial organic dye

Chemical reactions in the water system are greatly influenced by the light (visible and UV light). Most of the semiconductors can strongly interact with the photons' wavelengths as their band gaps lie in the same range. In addition to this, the large bandgap of these materials results in the absorption of UV light limiting their practical application because UV light only constitutes 5% of the solar spectrum. Besides suitable bandgap, potential adsorbents should be easy to produce, cost-effective, photostable and non-toxic for the environment. The researchers have also explored numerous other techniques to extend the optical absorption of these transition metal oxides involving dye sensitization, metal doping, semiconductor coupling and non-metal deposition[15-16].

The transition metals and their oxides have been used in different catalytic activities. They show many special properties and industrial applications. They can also behave as superconducting materials, ceramics, crystalline lasers, photoactive materials, photosensitizers, sensors, etc. Metal oxides have played a significant role in the areas of physical, chemical and materials sciences. The metal oxides can easily be synthesized and are multifunctional . Metal oxides have also been potentially utilized in environmental remediation, energy production, storage, and conversion. They exhibit advanced and different functional properties due to crystalline structure, morphology, doping, intrinsic defects, and composition. In general, when metal oxide nanoparticles having wide-bandgap are irradiated with light energy, the positive hole-electron pairs are formed; substrates may adsorb on the surface of photocatalyst and react directly or indirectly with the generated holes and electrons . Metal oxide nanoparticles have been reported to degrade the organic pollutants and toxic inorganic substrates into readily degradable compounds even mineralize them into less harmful carbon dioxide and water [17-18].

Nanocomposites combine different materials in which at least one of the materials has particle sizes 1-100 nm. Nanocomposite materials have gained a lot of attention due to their improved physical and chemical characteristics. Such materials are suitable for different functional and structural applications in science and technology due to their improved properties, i.e., good mechanical strength, porosity, toughness, electrical and thermal conductivities, dispersibility, and high mobility . They have been used to remediation inorganic and organic pollutants, gas sensing, electronic devices, biomedical fields, photocatalytic degradation of organic dyes, etc. The metal oxide-based nanocomposites with advanced surface features, stability, controlled structural and surface features are feasible in the photochemical degradation of organic pollutants. Due to high photodegradation capabilities, controlled bandgap, and efficient synthetic approaches, these materials have been potentially utilized in the photochemical degradation of organic dyes [19-20].

4. Mechanism of Photocatalytic Dye Degradation

Metal oxide nanoparticles utilize diverse mechanisms in the degradation of dyes, among which photocatalytic degradation stands out prominently. In this process, nanoparticles absorb light energy and generate electron-hole pairs, which trigger the production of reactive species such as hydroxyl radicals. These radicals play a crucial role in breaking down dye molecules. Furthermore, adsorption-desorption processes occur, where dye molecules physically bind to the nanoparticle surface, facilitating their removal from the solution. The efficient separation of electron-hole pairs enables swift charge transfer, thereby boosting redox reactions responsible for dye degradation. These multifaceted mechanisms collectively contribute to the highly effective removal of dye pollutants, rendering metal oxide nanoparticles invaluable in environmental remediation and wastewater treatment.[21-22]

In Photocatalytic degradation Metal oxide nanoparticles, are highly efficient in removing organic contaminants like dyes from aqueous solutions and the atmosphere, primarily through their remarkable photocatalytic characteristics. These nanoparticles possess the ability to absorb and utilize light energy to initiate chemical reactions, constituting the essence of their photocatalytic behavior. When subjected to ultraviolet (UV) or visible light, metal oxide nanoparticles generate electron-hole pairs, which form the fundamental basis of photocatalysis. Photon absorption elevates electrons to higher energy levels, creating excited electron-hole pairs within the material. These excited electrons move from the valence band to the conduction band, leaving behind positively charged holes. The degradation of dyes heavily relies on these electron-hole pairs.The bandgap energy of metal oxide nanoparticles, determining the light wavelengths they can absorb, significantly influences the efficiency of photocatalytic degradation. Some metal oxides efficiently utilizes both UV and visible light, broad bandgap metal oxide predominantly absorbs UV light. [23-25

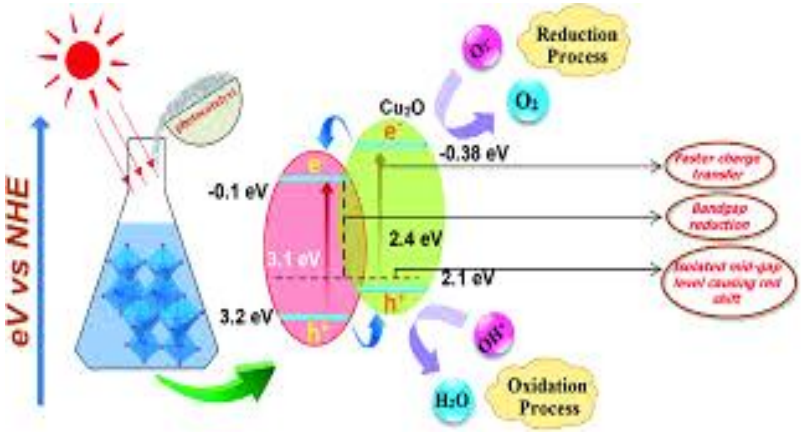

Fig 4 : Photocatalytic mechanism of dye degradation

5. Conclusions and Perspectives

Dye removal from wastewater is imperative to preventing detrimental impacts on ecosystems and human health. Various techniques are employed for wastewater treatment, including biological treatment, physiochemical treatment, membrane filtering, advanced oxidation processes (AOPs), and photocatalytic treatment. However, conventional methods have limitations such as an inability to remove a wide range of impurities, reliance on external chemicals, production of slurry and sludge, and the need for routine maintenance. In contrast, the photocatalytic treatment of wastewater offers several advantages. It results in the complete breakdown of pollutants into simpler compounds without the use of external chemicals. Additionally, photocatalysts can be regenerated and reused for further processing. Photocatalysis has shown significant potential for decomposing dyes, hydrocarbons, insecticides, germs, and microorganisms and reducing dangerous metal ions in wastewater. During photocatalysis, up to 80–90% of pigments can be removed from wastewater without the use of chemicals. However, the performance of photocatalysts depends on various factors such as catalytic morphology, electron–hole pair generation and recombination rate, pH, temperature, and light intensity, among others. Photocatalysis is an imperative route for greener decipher of energy and environmental issues of modern era. Catalytic efficiency of various photocatalysts has been altered by employing different techniques by the researchers. This review has given stress over different adsorbents based on transition metal oxides, bimetallic oxides and their carbon composites for photocatalysis. Different approaches regarding synthetic technique, heterostructure, etc. led to augmented adsorptivity, light absorption intensity, electron/hole pair lifetime with extended light adsorption range which may unlock various breaks for the next generation photocatalysts. Optimization of these parameters is crucial to achieving better results.

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