

# **ADVANCES IN DYE DEGRADATION**

**Editors:**

**Paulpandian Muthu Mareeswaran  
Jegathalaprathaban Rajesh**

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# **Advances in Dye Degradation**

***(Volume 2)***

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## FOREWORD

Regarding the environmental aspects, dye removal is more crucial. The “process” of eliminating dyes is just as significant because it has various economic and chemical effects. Degrading or removing dyes needs to be low-energy and safe for the environment. Once more, the process of chemical degradation will result in environmental hazards. High energy consumption will also result in environmental issues since there will be a greater energy demand. For this reason, the best method for meaningful dye degradation or removal will be to use reusable, effective materials that require less energy.

The editors in volume I have already covered basic aspects of dye degradation. In volume II, the editors address efficient degradation through light, a benign and sustainable energy source, and absorption for removing dyes. Given that the energy required for photochemical dye degradation is found in nature, this is an intriguing aspect of dye degradation. Numerous kinds of photocatalysts for dye degradation are covered in this book. Various materials for effective photodegradation are discussed in this volume. The relevant chapters justify the materials' suitability and go into great detail about their inherent qualities.

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## PREFACE

The environmental and economic perspectives create a need for dye degradation techniques. The fundamentals and importance of the dye degradation process were covered in “Advances in Dye Degradation,” volume I. In this volume, we have covered advanced oxidation techniques for degrading dyes. The Fenton process, a radical reaction, is used in Chapter 1 to degrade dyes. Radical production can break the dye materials into a safe byproduct when iron is present. The Fenton process can be combined with other processes, such as photochemical and electrochemical ones because it can be adjusted to produce a chain reaction that produces radicals. As a result, the Fenton process is among the most effective methods for degrading dyes.

The application of metal-organic frameworks to dye degradation is covered in Chapter 2. Metal-organic frameworks are porous materials whose synthetic pore modification allows for tuning the selectivity of these compounds. One of the key elements in the field of dye degradation is the application of electrocatalytic or photocatalytic degradation of these materials.

The photocatalytic materials active in the visible light and near-infrared regions of the electromagnetic spectrum are covered in Chapter 3. The band gap is the crucial factor for a successful photocatalyst. The ultimate goal of photocatalysis will be the utilization of solar light. As a result, the materials must absorb the entire spectrum of solar light's wavelengths. Nonetheless, there are several benefits to using NIR and the red region. This chapter provides a detailed discussion of the NIR active materials.

The photocatalytic degradation of transition metal dichalcogenides (TMDs) is covered in Chapter 4. The back combination of electrons and holes is the main element that lowers the degradation reaction's efficiency. Chalcogenides can, therefore, be used to create hybrid composites that inhibit the back combination process and yield beneficial outcomes in the degradation of dyes. The mechanism underlying each of these dye degradation processes is covered in this chapter.

The synthesis of photocatalysts for dye degradation is covered in Chapter 5. This chapter discusses the green synthetic approach of photocatalytic materials and their efficiency towards dye degradation since the production of photocatalysts should be benign. The use of metal oxide nanoparticles in dye degradation is covered in Chapter 6. The latest developments and trends regarding metal oxide nanoparticles and dye degradation are covered in this chapter.

The photocatalytic dye degradation employing graphene oxide composite materials is covered in Chapter 7. Effective conductive materials, such as graphene oxide, can control their electron injection by mixing it with materials that receive electron injection and synthetic modification to create composites. Because of these materials' high reusability, this chapter discusses their recent advantages. We hope that this volume will be helpful to both those working in the field and students who are about to enter it, as it starts with basic methods and provides information about advanced techniques.

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**CHAPTER 1****Fenton and Fenton-Like Processes for the Degradation of Dye in Aqueous Solution****R. Liju<sup>1</sup> and Eswaran Rajkumar<sup>1,\*</sup>**

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**Abstract:** Water is necessary for the growth of humans and all other living things. Water is becoming scarce due to industrialization and its rapid growth, and the water ecosystem is negatively impacted by the direct release of wastewater into the environment. The textile, tanning, coating, plastics, paint, printing, and other industries, discharge dyes and pigments into the environment. One major problem is to remove dyes and pigments from industrial wastewater in a inexpensive and environmentally friendly way. Before they are released into the environment, there are several ways to mitigate the situation, including chemical, biological, and chemical oxidation processes. The advanced oxidation process (AOP) is a widely employed technique for eliminating contaminants from water and wastewater. The dye molecules are broken down by a Fenton and Fenton-like mechanism, in which the breakdown of hydrogen peroxide produces hydroxyl radicals. This chapter focuses on the most current advancements and various strategies used in the Fenton and/or Fenton-like processes used to degrade the dye molecules.

**Keywords:** Decolourization, Dye degradation, Fenton process, Hybrid Fenton processes.

**INTRODUCTION**

According to Business Fortunes Insights, the global market for dyes and pigments is anticipated to expand at a compound annual growth rate (CAGR) of 4% from \$40.7 billion in 2022 to \$56.91 billion by 2029. Pollutants (dye molecules, which can be entirely organic, inorganic, or organometallic) pose a serious risk to human health and that of animals, plants, and aquatic life forms.

These substances also linger in water bodies for extended periods, deteriorating the ecosystem. Typically, the textile, tanning, coating, plastics, paint, printing, and

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other industries discharge dyes and pigments into the environment; because of this, scientists, environmentalists, and academics are very interested in policies that can regulate and improve water quality. The Environment Protection Agency (EPA) categorizes these waste from industries as harmful under the Property, Conservation, and Recovery Act (RCRA). The production waste of the product is designated as EPA hazardous waste K181. When dyes and pigments are made and processed on-site, waste is produced at the manufacturing facilities. The only way to lessen the harmful effects of pollutants (like dyes) is to break down the dye molecules into innocuous compounds, which requires technological innovation to monitor the discharge levels of the pollutants. It would be quite challenging to control the amount of dye released into the environment due to the speed at which the industry is developing. However, dissolving these dangerous chemicals into safe, non-toxic compounds gives us a workable way to lessen the adverse effects. Before the dye molecules are released into the environment, they can be broken down or degraded by using various techniques, such as chemical treatment, biological treatment, and chemical oxidation.

Compared to other dye degradation techniques, chemical oxidation methods have several advantages. For example, biological treatment is more expensive and selective towards certain pollutants. In contrast, chemical treatment frequently risks becoming a pollutant in and of itself, making it unsuitable for the environment. On the other hand, chemical oxidation techniques are low-cost, efficient, and safe for the environment. The effluents of industrial dyes, notably textile dyes, have recently been shown to negatively affect the ecosystem's health and environment [1]. They have provided a concrete solution for the bioremediation process using microorganisms and enzymes and a summary of the many methods of reducing and eliminating pollutants. Nevertheless, there are several practical and sustainable constraints to these bioremediation techniques. By using extremely reactive hydroxyl radicals to break down organic pollutants (dye), the advanced oxidation process (AOP) produces carbon dioxide, water, and inorganic salts that are environmentally benign and do not endanger the environment [2]. Fenton/ Fenton-like processes, which are based on the breakdown of hydrogen peroxide to produce hydroxyl free radicals, have been studied and used more than other AOPs because of their straightforward operation, mild operating conditions, higher rate of  $\bullet\text{OH}$  production, and redox potential of roughly 2.73 eV, which is sufficient to break down even resistant dyes.

Three types of Fenton processes can be distinguished: the hybrid Fenton process, the heterogeneous Fenton process, and the homogenous Fenton process [3]. Homogenous Fenton is the term for the conventional method of conducting Fenton reactions, in which the oxidizing agent (hydrogen peroxide), catalyst

(metal ion), and reactant (organic dye) are all present in the liquid phase. On the other hand, reusable solid catalysts are utilized in heterogeneous Fenton reactions, including iron oxides, nano zero-valent iron, iron-loaded zeolites, and iron-immobilized clays. This makes oxidation reactions possible at neutral pH values and simplifies the separation of the liquid and solid components. Bi/tri metallic iron catalysts like  $\text{NiFeMnO}_4$  and copper-iron bimetallic  $\text{CuFeO}_2$  are also utilized in the heterogeneous system. Several review articles and book chapters are available to treat water and wastewater or to remove contaminants based on Fenton and Fenton-like processes. This chapter focuses on current advancements and the many strategies used for dye molecule degradation by Fenton and/or Fenton-like reactions.

### CONVENTIONAL FENTON PROCESS

The Fenton process, a sophisticated oxidation method that uses hydrogen peroxide as an oxidant and ferrous ions as a catalyst to produce extremely reactive hydroxyl radicals in an acidic medium, is extensively researched for dye degradation. Below is a list of the reactions that comprise the Fenton process (Fig. 1).

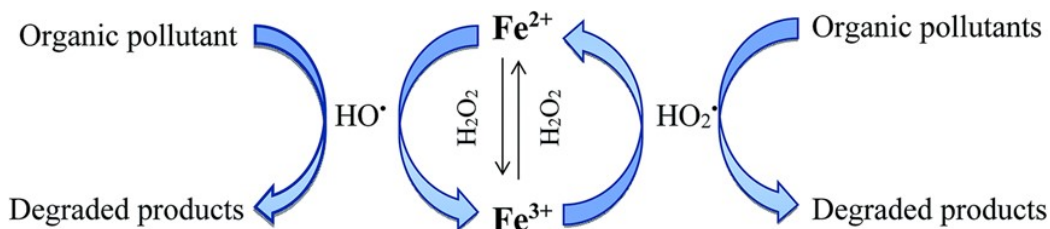
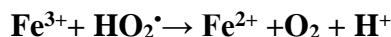
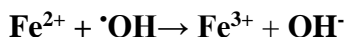
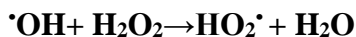


Fig. (1). Schematic mechanism of conventional fenton process [4].

# Photocatalytic Dye Degradation Using Metal-Organic Frameworks

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**Abstract:** This chapter deals with degrading dyes using Metal-Organic Frameworks as a heterogeneous catalyst. Metal-Organic Frameworks (MOFs) are an excellent material for dye degradation due to their multifunctionalities, such as semiconducting properties, ease of use with controllable structures, high surface area, and enormous active sites. MOFs exhibit a promising photocatalytic activity under UV–visible light irradiation due to band gap presence. Several MOFs show an excellent reusability performance even after a few consecutive cycles. The MOFs used to degrade dyes are classified as bare MOFs (Lewis acid MOF, Brønsted Base MOF), MOFs@SiO<sub>2</sub>, magnetic MOFs, MOF nanocomposites, ionic MOFs, bimetallic MOFs, nanoparticles doped MOFs, *etc.*, The mechanism of dye removal and photocatalytic degradation of organic dyes using MOFs and the detailed pros and cons of these materials are discussed in detail.

**Keywords:** Bare MOF, Bimetallic MOF, Ionic MOF, Magnetic MOF, Nanocomposite MOF, Silica supported MOF.

## INTRODUCTION

In the 19<sup>th</sup> century, Alfred Werner laid the foundation for assigning the metal ions' coordination number and oxidation states [1]. The first synthetic coordination polymer was the Prussian Blue compound, where the inorganic CN<sup>-</sup> ions connect the metal centers [2]. In 1965, Tomic described a new form of metal complexes as Metal-Organic Frameworks (MOFs) or supramolecular structures and described their properties [3]. In 1989, the first Metal-Organic Framework [Cu(tctp)(BF<sub>4</sub>)]

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(tctp = 4,4',4'',4'''-tetracyanotetraphenylmethane) was realized that the structure resembled the structural arrangement of a diamond [4]. After a long break, the name Metal-Organic first gave Metal-Organic Frameworks (MOFs). M. Yaghi [5 - 7], to the coordination type of polymeric materials, is one of the pioneers in this field. Metal-Organic Frameworks (MOFs) Porous Coordination Polymers (PCPs) or hybrid organic-inorganic materials are formed by linking metal ions or cluster nodes with multi-functionalized linear or nonlinear organic molecules, which act as linkers, giving rise to some extendable frameworks with various dimensional porous or non-porous networks (0D, 1D, 2D and 3D) through self-assembly process (Fig. 1) [8 - 11].

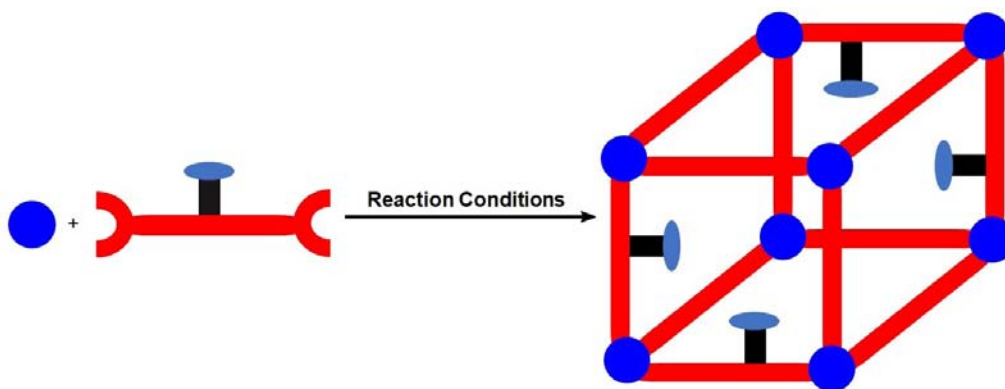


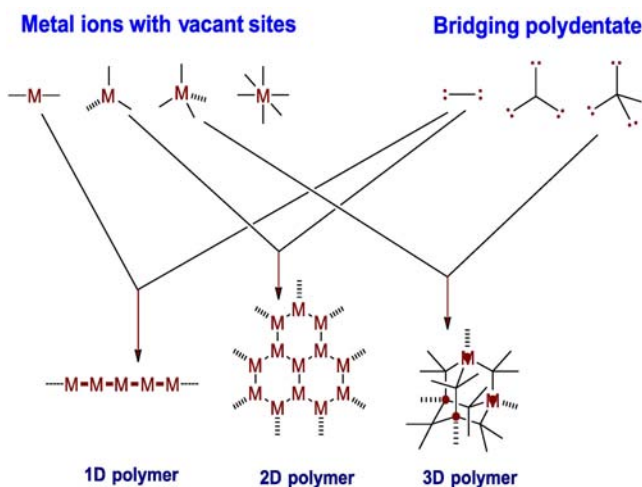
Fig. (1). General schematic representation building scheme for the MOFs.

Metal-organic interactions occur between metal and hetero-atoms, such as nitrogen, oxygen, sulfur, and phosphorus. Depending on the size of organic linkers, inorganic connecting points, and network connectivity, the porosity of MOFs can be readily tuned to afford open channels and pores with various dimensions of several angstroms (Å) to several nanometers. MOFs' pores, open spaces, or voids can hold "guest molecules," leading to various functionalities. This void space helps to incorporate reactive functional groups or nanoparticles into the MOFs, making them excellent materials for heterogeneous catalysis [12 - 17]. The diameter of the pore size classifies the porous nature of the materials. According to IUPAC nomenclature, the materials are distinguished as microporous (< 2 nm), mesoporous (2-50 nm), and macroporous (> 50 nm) [18].

During the last two decades, MOFs have attracted numerous research interests due to their potential applications in various fields such as gas storage, separation process, luminescence, sensors, nonlinear optics, magnetic materials, membranes, drug storage and delivery, biomedical imaging, and catalysis. Unlike other porous materials such as zeolites, activated carbon, and metal complexes, MOFs have

unique features such as stability, tunable pore size, reusability, high surface areas, porosity, and potentially active unsaturated metal sites. MOF-based catalysis finds broad applications, from basic synthetic transformations to large-scale industrial applications [19].

MOFs are built by inorganic metals and organic linkers, which might possess ionic, coordinate, and orbital directing properties. The well-defined pores and channels in MOFs have a unique property for size- and shape-selective catalysis, the best alternative for zeolites and Covalent Organic Frameworks (COFs). Because zeolites have ionic bonds while COFs have covalent bonds, MOFs have both these properties at a single site. Metal-Organic Frameworks have a geometrically well-defined structure through strong covalent or coordinated bonding between the metals and ligands. It also has functional units for post-synthetic modifications [20, 21]. MOFs can be classified into different families according to the dimensionality of the inorganic frameworks (Fig. 2) [22].



**Fig. (2).** The assembly of nodes and spacers to form polymer structures (obtained using the building block principle).

The number of studies including various kinds of MOFs used for the degradation of organic pollutants has increased in the last decade, as shown in Fig. (3). Recent studies have focused on enhancing the degradation of dyes using salient features of MOFs. Fig. (4) shows the photocatalytic degradation of organic molecules (dyes) using the Metal-Organic Framework as a photocatalyst. This chapter reveals how MOFs' unique textural and chemical properties are useful for dye degradation [23].

## UV, Visible, and Near-Infrared Responsive Photocatalyst for Dye Degradation

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**Abstract:** Environmental contamination has long been a big problem for the planet. One of the greatest ways to harness the massive amounts of sunshine available is photocatalysis, which may be used to remove dangerous organic pollutants from water and the air. Due to its large band gap (3.2 eV), the golden standard TiO<sub>2</sub> catalyst only uses the UV area of the sun, or 5% of it, and cannot absorb all of the solar energy. To attain optimal photocatalytic effectiveness, the photocatalytic materials must efficiently harvest photons from sunlight's visible, NIR, and ultraviolet energies to form photocarriers. Several methods for efficiently forming and separating light-induced charge carriers and absorbing visible and near-infrared light photons from sunlight are compiled in this chapter to provide increased photocatalytic efficiency. Effective tactics, including doping and the fabrication of composite materials, are highlighted to emphasize the distinct physicochemical qualities and photocatalytic enhancement of changed materials that are impacted by band alignment, shape, and defect structures. Despite the discussion of an up-conversion method for NIR light absorption, multiphoton emission, continuous luminescence, photo carrier multiplication, and/or plasmonic processes, in addition to the control of photo-thermo effects, make it difficult to use NIR effectively. To fully use the solar spectrum for enhanced photocatalytic pollutant degradation, the chapter provides an overview of UV, Visible, and/or NIR active catalytic materials based on design, synthesis, and interface engineering.

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**Keywords:** Dye degradation, NIR photocatalyst, Plasmonic nanoparticle, Visible photocatalyst, Z – scheme composites.

## INTRODUCTION

The growing rate of environmental contamination is startling, posing a serious risk to human health and natural ecosystems' long-term viability. Resolving these crucial issues requires environmentally friendly and green processes for environmental remediation and energy conversion [1 - 3]. Among the different strategies, photocatalysis is advantageous for protecting the environment and treating pollutants since it can efficiently use artificial or solar light sources, creating a limitless global energy supply. Toxic compounds, including dyes and heavy metals, have been extensively photo-oxidized and photo-degraded using semiconductor photocatalysts like ZnO and TiO<sub>2</sub> [7 - 9]. Semiconductor photocatalysis saw a turning point with Fujishima and Honda's invention of the n-type TiO<sub>2</sub> electrode in 1972 [10]. In the 1980s, TiO<sub>2</sub>-based semiconductors gained new momentum in the fight against pollution when Carey and Bard published the first report on TiO<sub>2</sub> catalyst for the photodegradation of cyanide and polychlorinated biphenyl [11, 12].

Solar energy utilization is an exciting development that has attracted much attention to photocatalysis. TiO<sub>2</sub> photocatalyst forms electron-hole pairs under light energy ( $> 3.2$  eV), which is responsible for photocatalytic reactions of pollutant degradation. However, pristine TiO<sub>2</sub> activity is limited to UV light and inactive in visible and NIR light due to their wide band gap (3.2 eV) [2, 13]. As a result, other photocatalytic materials have been thoroughly studied; nonetheless, commercial photocatalytic applications have been scarce due to the limited absorption of solar energy and the rapid photocarrier recombination [14]. The low photocatalytic activity of TiO<sub>2</sub> is typically correlated with the lack of commercial applications.

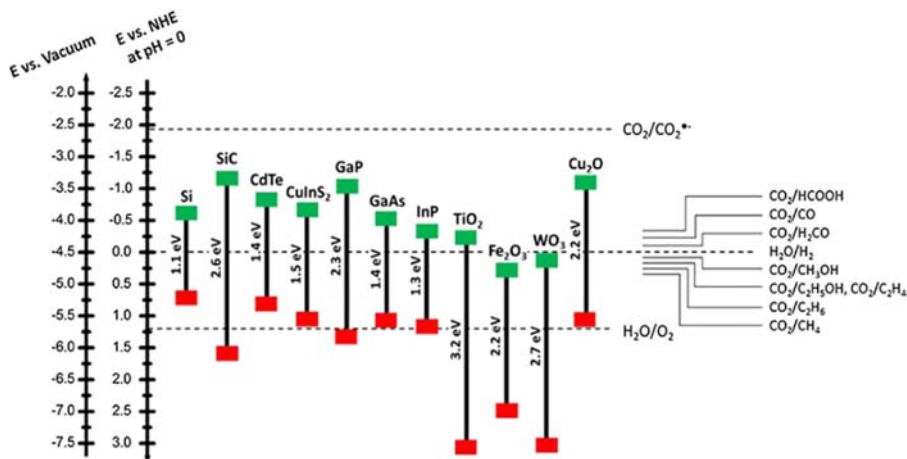
Numerous techniques have been reported for fine-tuning TiO<sub>2</sub> surfaces to absorb large amounts of solar radiation and extend the duration of light-produced charge carriers [6, 15]. These techniques entail the insertion of noble metals, metal cations, non-metals, and metal oxides into the TiO<sub>2</sub> lattice through appropriate synthesis techniques, such as hydrothermal, wet chemical synthesis, and physical ion-implantation, among others [16]. The alteration of the TiO<sub>2</sub> structure enhances light absorption to some degree and permits it to absorb long wavelength regions of solar radiation [17]. Nevertheless, not all the solar energy photons will be captured by the resulting TiO<sub>2</sub>. If the photocatalyst absorbs the entire solar energy region (UV, visible, and NIR) with maximal quantum efficiency, a significant amount of sunlight might be captured [17]. Consequently, the photocatalyst might

produce energy from solar cells, clean water, and air and employ solar energy for other cutting-edge uses.

### Principle of Semiconductor Photocatalysis

A semiconductor material has a band gap and electrical conductivity between conductors and insulators. Applications for metal oxides and sulfide semiconductors include biomedicine, electronics, photonics, sensors, and catalysis [18, 19]. New semiconductors' creation, synthesis, and use in nanomaterials research are hot topics. When exposed to enough light energy, semiconductors' specific band structures determine how active they are in photocatalysis. A photon equal to or larger than the semiconductor's band gap can excite the semiconductor and move an electron from the valence band into the conduction band [5, 20].

The semiconductor's band gap and band edge positions are used to calculate its optical absorption and photocatalytic potential. As a result, band gap and band edge are essential to semiconductor photocatalytic efficiency. Fig. (1) displays the band positions of popular semiconductor photocatalysts. The semiconductor-based photocatalysis was first shown by Professors Fujishima and Honda using UV light-active  $\text{TiO}_2$  to split water. This phenomenon is well-known as the "Honda-Fujishima effect" [10]. Consequently, the method for degrading contaminants in contaminated water has evolved. Fig. (2) shows an illustrative diagram showing the production and separation of photocarriers and the degradation of contaminants.



**Fig. (1).** Valence band and conduction band positions of some of the common semiconductors [21] (*Catalysis today* 317 (2018) 56–75).



## CHAPTER 4

# Transition Metal Dichalcogenide Hybrids for Visible-light-driven Photocatalytic Dye Degradation

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**Abstract:** The 21<sup>st</sup> century has seen tremendous industrialization in many countries worldwide, making environmental protection and energy conversion important issues. As such, investigations on the decomposition of dye molecules in water for environmental protection and clean energy construction are challenging yet impressive. It is still difficult to create a photocatalyst with a sensible design that is affordable and extremely effective for degrading organic dye contaminants. Our work showcases an incredibly effective “interfacial connection and suitable band gap matching” method to create nano-architecture hybrid catalysts based on Transition metal dichalcogenides (TMDs) built using hydrothermal processes. With its large surface area, colossal energetic sites, and interfacial charge assignment, the TMDs-based nano-hybrid catalyst significantly enhances the catalytic degradation of dye pollutants. This demonstration could provide a new hybrid catalyst that degrades dye molecules more effectively and sustainably when exposed to visible light. Lastly, certain recommendations are emphasized for advancing hybrid catalysts based on transition metal dichalcogenides in the future.

**Keywords:** Dye degradation, Interfacial connection, Nano-architecture, Suitable band gap matching, Transition metal dichalcogenide.

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## INTRODUCTION

Transition metal dichalcogenides (TMDs) are two-dimensional layer structures composed of sandwich layers of atomic metal layers layered on top of chalcogen sheets.

The isolated chalcogen-metal-chalcogen layers only slightly interact with one another. Because the weak van der Waals force between the layers can easily flow through the bulk and result in some monolayer sheets, TMDs are still considered the inorganic conducting materials of graphene [1 - 5]. As typical examples of TMDs, tungsten disulfide ( $WS_2$ ) and molybdenum disulfide ( $MoS_2$ ) are exfoliated from the bulk using various wet chemical methods *via* sonication *via* a top-down technique. Transition metal dichalcogenide exfoliation exhibits distinct properties from aggregate materials, and their unique electrical and physical properties suit photochemical energy applications [6 - 11].

Due to their intriguing photocatalytic behavior and improved photocatalytic efficiency, transition metal dichalcogenides have recently shown promise as a very effective component for photocatalytic degradation. Unlike the photocatalytically inert point, the photocatalytic action of transition metal dichalcogenides is directly correlated with visible edges [12]. As a result, the active sites of transition metal dichalcogenide can be enhanced to increase its photocatalytic activity. This can be achieved through defect or edge engineering, which builds on the unsaturated chalcogen atoms at the edges and/or increases the efficiency between the photocatalyst surface and the semiconducting material's surface [13].

Furthermore, the occupants of imperfection sites can be utilized using an artificial bottom-up technique of transition metal dichalcogenide in conjunction with a constituent acting as a photocatalyst [14]. In particular, employing highly conductivity materials supports, including carbon nanotubes, graphene oxide, and graphene, the inclusion of transition metal dichalcogenide into a broad surface area can supply the highly active places for photosynthesis; quicker electron transport is ensured [15 - 18].

Our current effort aims to achieve the photodegradation of contaminants by visible light irradiance through hydrothermal stages in a  $g\text{-CN@TiO}_2$  nanostructure-based transition metal dichalcogenides ( $MoS_2$ ) nano-hybrid. The objectives of this research are as follows: (i) create transition metal dichalcogenide hybrids that exhibit a satisfactory visible light response; (ii) assess the impact of varying ratios of transition metal dichalcogenide hybrids on the degradation of organic compounds; (iii) look at the stability and reusability of catalytic materials to explore their potential for practical use; and (iv) propose a

mechanism for this catalyst's degradation and reveal the likely degradation of organic pollutants.

## TRANSITION METAL DICHALCOGENIDE HYBRIDS

A useful method for increasing the photocatalytic activity of hybrid photocatalysts is the design of g-C<sub>3</sub>N<sub>4</sub>@TiO<sub>2</sub>-based transition metal dichalcogenide hybrids. This is achieved through the hybrids' distinctive morphology structure, large specific surface area, suitable band gap matching, interfacial connections, and promotion of the charge separation of photoinduced holes and electrons. As previously mentioned, graphitic carbon nitride's chemical structure is malleable due to its polymeric activity. This property is particularly useful for creating hybrid structures because graphitic carbon nitride and different semiconductors (such as TiO<sub>2</sub> and MoS<sub>2</sub>), metal oxides, and metal disulfides are closely interconnected. As a result, semiconductors and graphitic carbon nitride have been combined to create metal-free transition metal dichalcogenide hybrid photocatalysts. Examples include g-C<sub>3</sub>N<sub>4</sub>-based transition metal dichalcogenide hybrids, TiO<sub>2</sub>-based transition metal dichalcogenide hybrids, and g-C<sub>3</sub>N<sub>4</sub>@TiO<sub>2</sub>-based hybrids. Moreover, thorough research and reporting were done on the optical, structural, surface area, and compositional aspects [19 - 23].

### TiO<sub>2</sub>-based Transition Metal Dichalcogenide Hybrids

According to Yuanqing Sun *et al.* [24], TiO<sub>2</sub>@MoS<sub>2</sub> hybrids have a morphological structure-controlled nanostructure thanks to their enhanced photocatalytic activity in visible light. The unique two-dimensional (2D) layered TMDs, which can detect electrons and offer active sites for catalytic processes, are responsible for the TiO<sub>2</sub>@MoS<sub>2</sub> nano-hybrids photocatalyst (Fig. 1).

They gave the TEM picture of the as-synthesized TiO<sub>2</sub> microspheres and a 180 nm-diameter smooth surface. Then, the (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> and MoS<sub>2</sub> nanosheets can form on the surface of TiO<sub>2</sub>, and the core-shell structure of TiO<sub>2</sub>@MoS<sub>2</sub> is created using the solvent-thermal method. As a result, the final core-shell structure showed a consistently spherical morphological form, and it was discovered that the particle size was superior to TiO<sub>2</sub> microspheres. Moreover, the MoS<sub>2</sub> nanosheets that can be coated on the surface of the TiO<sub>2</sub> microsphere resemble flowers in such core-shell configurations.

### g-C<sub>3</sub>N<sub>4</sub>-based Transition Metal Dichalcogenide Hybrids

Yong-Jun Yuan *et al.* [22] reported liquid exfoliation of graphitic carbon nitride nanosheets to create a 2D-2D MoS<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> hybrid catalyst for enhanced photocatalytic activity. The high surface area and carefully crafted 2D interfaces

## Photocatalytic Degradation of Dyes Using Green Synthesized Metal Nanoparticles

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**Abstract:** Environmentally hazardous, synthetic organic substances with a complex structure are known as dyes. A major environmental issue is the removal of dyes from the environment, and many techniques are often employed to break down colors. One thought to be a good replacement for dye degradation is photocatalysis. Various photocatalysts carry out the complete mineralization of colors without generating hazardous by-products. When exposed to UV or visible light, metal nanoparticles' promising catalytic ability allows them to break down dangerous synthetic dyes. Compared to traditional methods, green production of metal nanoparticles is more economical and environmentally benign. This book chapter focuses on using different green synthesized metal nanoparticles to degrade synthetic colors. The photodegradation mechanism presented in this chapter could clarify future uses for dye degradation.

**Keywords:** Green synthesis, Metal nanoparticles, Photocatalytic degradation, Synthetic dyes.

### INTRODUCTION

Water contamination is the main form of pollution that receives much attention worldwide. The effluents dumped by numerous companies seriously threaten the ecosystem and poison water supplies. Dyes and other chemicals that are possibly harmful endocrine-disrupting chemicals (EDCs) for humans and aquatic life can be found in the wastewater discharged by the textile industry [1 - 3]. According to Konstantinou and Albanis [4], dyes are one of the biggest categories of intricate organic compounds that impact the environment. During dyeing, textile effluents leak roughly 20% of the color into the water resources and create hazardous by-products through chemical reactions [5]. In addition to having harmful consequences, these colors and their by-products reduce light penetration in contaminated waterways [6]. Industrial dye waste can kill mammals and have

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detrimental impacts on microorganisms. The amount of dye present and the length of exposure determine how an organism responds to it. Therefore, it is imperative to eliminate the hazardous dye components from water.

Sources. Synthetic dyes can be degraded using various techniques, most of which are labor-intensive and provide disposal issues.

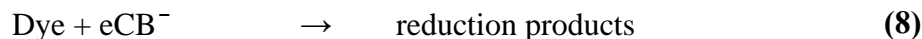
### PHOTOCATALYTIC DEGRADATION

Organic contaminants and colors are removed from water using various physical and chemical techniques, including ion exchange, adsorption, flocculation, reverse osmosis, coagulation, biodegradation, accelerated oxidation process, and photocatalytic degradation [7 - 10]. Among them, photocatalytic degradation can effectively remove contaminants and artificial dyes from industrial effluents and aquatic bodies. Using this method, light interacts with the photocatalyst and transfers charges. Reactive oxygen species are created during this charge transfer process and are used in the oxidation and mineralization of organic contaminants and pigments [11]. Because of their photocatalytic properties and stability, transition metal oxides are regarded as a great catalyst for degrading dyes [12, 13]. Semiconductor photocatalysts are one type of metal-oxide catalyst frequently used to remove colors from water sources. Due to its stability, great oxidation efficiency, adaptability, non-toxicity, and chemical inertness, titanium dioxide is the most utilized photocatalyst for removing pollutants and dyes [14, 15].

The fundamental idea behind photocatalytic degradation is that the catalyst undergoes redox processes and produces an electron-hole pair when exposed to UV or visible light. The photocatalysts' redox process is started by the electron-hole pair that is thereby created [16]. The holes produced in an aqueous medium are absorbed by the -OH groups, transforming them into hydroxyl radicals (OH•). The resulting OH• radical interacts quickly with synthetic dyes, causing the colors to become mineralized [17]. The whole process of employing TiO<sub>2</sub> photocatalyst to photodegrade dyes is given below:







where  $h\nu$  is the energy of the photon required to transfer the electron of  $\text{TiO}_2$  from the valence band (VB) to the conduction band (CB).

$\text{TiO}_2$  is one of many metal-oxide photocatalysts used recently for the photocatalytic degradation of dyes. The primary disadvantage of  $\text{TiO}_2$  photocatalyst is that it absorbs more UV light than the visible spectrum. UV radiation comprises less than 10% of the total solar radiation, while visible light accounts for 50% [18]. As a result, many researchers are working to add metals and non-metals to  $\text{TiO}_2$  to increase its catalytic effectiveness [19].

### **GREEN SYNTHESIS OF METAL NANOPARTICLES**

The study of nanotechnology is a young field of study that links the material sciences, chemistry, and physics departments. Usually, top-down or bottom-up methods are used to create nanoparticles [20]. The physio-chemical and biological characteristics of metal nanoparticles differ from those of bulk materials. The shape, surface energy, and size of nanoparticles affect their characteristics [21]. Nanomaterials are building blocks for creating optical, chemical, and biosensors, which are synthesized due to recent advancements in nanotechnology [22]. Nanoparticles are widely utilized in various fields, including electronics, photonics, photocatalysis, and medicines.

Expensive and dangerous physical and chemical processes typically synthesize nanoparticles [23, 24]. Harmful compounds like poly-N-vinyl pyrrolidone, sodium borohydride, hydroxylamine, and tetrakis(hydroxymethyl)-phosphonium chloride are employed in old wet techniques. These hazardous substances restrict the use of nanoparticles in the medical field. Researchers are working to create biocompatible, non-toxic, and ecologically benign nanoparticles because, aside from these, UV irradiation and lithography techniques are not thought to be environmentally friendly [25]. Because it is less expensive and more environmentally benign than traditional approaches, green synthesis of nanoparticles offers a breakthrough. Because it is easy, affordable, and safe for the environment, synthesizing metal nanoparticles utilizing bioactive agents, that is, plant materials, microbes, and different biowastes is receiving a lot of interest (Fig. 1). Aqueous plant extracts are used to synthesize metal nanoparticles; the nanoparticles are formed by the bioactive chemicals present in the plant extracts.

## CHAPTER 6

# Recent Developments and Perspectives in Photocatalytic Degradation of Dyes Employing Metal Oxide Nanoparticles

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**Abstract:** Among the  $7 \times 10^5$  tonnes of synthetic dye manufacturing, 1,000 tonnes of non-biodegradable textile dyes are disposed each year into natural streams and water bodies. Due to rising environmental concerns and awareness, it is necessary to remove dyes (pollutants) from municipal and industrial water effluents using a method that is both efficient and affordable. In this regard, photocatalysis has proven to be a safe, long-lasting, and effective wastewater treatment method with a high potential for color removal. Due to their excellent potential as a photocatalyst to degrade various organic dyes, metal oxide nanoparticles have been hailed as promising materials throughout the past two decades. The fundamentals of photocatalysis, drawbacks of traditional water purification techniques, and strategies for dye decolorization and degradation are all briefly covered in this book chapter. It focuses on the mechanisms in relatively well-understood metal oxide photocatalysts. It summarizes recent developments to improve metal oxide NPs photocatalytic efficiency, shape and structural modifications of metal oxide, and immobilization of metal oxide by using various supports to make it a versatile and financially successful dye treatment technology. Then, the conclusion and the outlook for the future were considered and hypothesized, releasing the field for advanced study to be granted for developing a photocatalytic system that can be widely employed for various pollutants.

**Keywords:** Composites, Degradation, Nanoparticles, Photocatalytic Degradation, Photocatalysis, Pollutants.

## INTRODUCTION

Environmental remediation, industrialization, and rapid urbanization are widely accepted ideas for creating a sustainable ecosystem. Organic and inorganic waste is discharged into water systems by businesses and households. These wastes contain pollutants that are harmful to the environment. As a result, a suitable wastewater treatment technology is urgently required for the efficient cleaning of our water systems. One promising strategy is using metal oxide nanoparticles as photocatalysts to degrade these water contaminants. In addition to having good

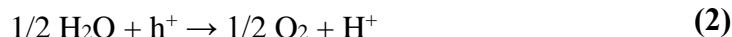
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photocatalytic activity, metal oxides and their composites also have favorable lateral properties like stability and non-toxicity that make them valuable in various applications. Here, we cover a variety of metal oxides, including TiO<sub>2</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>, ZnO, NiO, WO<sub>3</sub>, CuO, and Cu<sub>2</sub>O, which are the most prevalent and widely acknowledged to be economical, stable, effective, and, most importantly, ecologically friendly for a long-term method of environmental remediation.

The photocatalytic functions of these metal oxides are highlighted in this chapter, along with current advancements, difficulties, and adjustments made to get around their limitations and maximize their effectiveness in the photodegradation of pollutants.

## PHOTOCATALYSIS

In the 1970s, Fujishima and Honda initially introduced photocatalysis, which came to be known as the “Honda-Fujishima Effect” [1].



The term “photocatalysis” describes the quickening of a chemical reaction when light and a catalyst are present. With its reliance on solar energy and lack of chemical input, photocatalysis is seen as a green and sustainable process. Indirect and direct photocatalysis methods for pollutant degradation are possible; indirect mechanisms are more frequently used. The photoexcitation step is the first step in the indirect reaction process. The semiconductor will be made active by light irradiation.

The creation of holes (h<sup>+</sup>) in the valence band (VB) and photogenerated electrons (e<sup>-</sup>) in the conduction band (CB) is caused by the excitation of the electron from the valence band (VB) to the conduction band (CB) by the photon energy from the light source. An ion is created as the e<sup>-</sup> in CB reacts with dissolved oxygen. This ion then reacts with water to create OH radicals. The h<sup>+</sup> will combine with the water in the VB to create OH radicals. Since they are the primary radicals engaged in the breakdown of contaminants, OH radicals are particularly important [2, 3]. Fig. (1) depicts a schematic illustration of photocatalytic pollutant degradation.

An essential component of environmental preservation is the eradication of organic contaminants from wastewater [4]. Electron-hole pairs are produced when

a photon with energy equal to or greater than the semiconductor's band gap absorbs the photon, which starts the photodecomposition process over semiconductor oxides [5]. Photocatalysts are required to remove or transform water-soluble coloring dyes into innocuous molecules. One of the most promising techniques for leftover water treatment is photocatalysis using metal oxide semiconductors. Doping transition metal oxides and using quantum dots, which need high band gap energy ( $>3.0$  eV), and recombining photogenerated electrons and holes in the semiconductor for electron excitation from VB to CB are two ways to solve this issue.

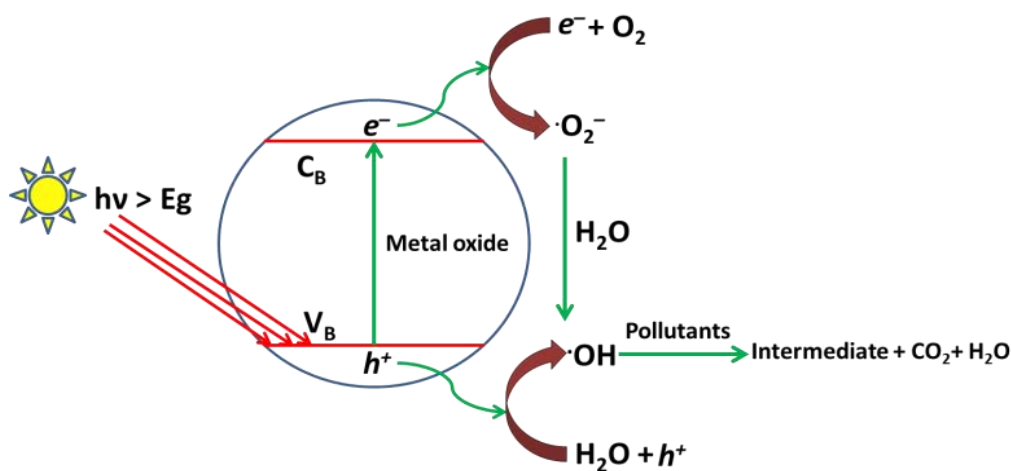


Fig. (1). Photocatalytic pollutant degradation by using metal oxide as a catalyst.

On the semiconductor surface, avoiding chemical reactions with electron-designated products is essential. It has been proven that several semiconductors can break down many resistant materials in aqueous systems by UV-vis irradiation. One of the main issues that scientists, technicians, and researchers worldwide face is the decomposition of dyes into tiny trashes of less hazardous chemical substances. The primary objective is to create catalysts that can interact with sunlight to break down harmful dyes into small, colorless, benign particles that may be disposed of in water bodies without altering their physicochemical qualities. The favored method is photocatalytic degradation utilizing solar light since it is straightforward and economical.

The degradation of various reactive dyes has been extensively studied [6 - 15] using a variety of photocatalysts, including perovskites, titanates, zinc oxide, niobates, calcium oxide, nanoparticle-nickel oxide composites, and semiconductors. Since the substances are broadband gap semiconductors or

## CHAPTER 7

## Graphene Oxide Nanocomposites: Photocatalytic Dye Degradation Investigations

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**Abstract:** This chapter presents research on using novel dye-degrading processes in the chemical process industries to prevent the increasing water demand caused by the overuse of water in businesses near farmland. This chapter also describes the dye degradation processes used to treat industrial effluents contaminated with dyes and the associated chemical reactions, benefits, and drawbacks. Commonly employed chemical techniques for treating industrial effluents contaminated with dyes demand more costly chemicals and reagents for dye degradation. Solid precipitates or emulsions are created when the additional chemicals interact or react with the contaminants in the industrial effluents that are contaminated with dye. These products could harm our ecological creatures in a variety of ways. Physiological techniques like membrane filtration, nanofiltration, ultrafiltration, and microfiltration have their membrane pores closed by different pollutants, shortening their lifespan. The primary focus of this chapter is on the dye degradation characteristics of graphene oxide nanocomposite materials that have been mixed or doped with different metal oxides and metal nanoparticles. These days, there is increased interest in carbon-based compounds such as graphene and graphene oxides due to their potential environmental benefits when used in the oil and organic gas industry to purify water. The water purification activity of graphene oxide filters is further increased when combined with photochemical active metal oxide. Another benefit is that they don't require extra chemicals or reagents, which also indirectly control other pollutants, and they use solar energy rather than electrical energy. These graphene oxide nanocomposites are unique because they can regenerate without chemicals once they run out of resources. Its physical and chemical characteristics don't change over many cycles.

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**Keywords:** Dye degradation, Dye-contaminated industrial effluents treatment, Graphene oxide, Nanocomposites.

## INTRODUCTION

Contamination of water occurs when there are changes to its chemical, biological, and physical properties. Stated differently, water pollution is the loss of water purity brought about by human activity in lakes, rivers, seas, groundwater, *etc.*, as well as the unstable nature of a given ecosystem. Natural occurrences like earthquakes, storms, droughts, and volcanic eruptions alter the ecological conditions and water quality. Nevertheless, much human activity also contributes to water pollution, rendering the water unfit for human consumption. Soil and groundwater are significantly impacted by dye-contaminated industrial effluents from the chemical processing of oil and gas (Fig. 1). This impacts agricultural land and raises the possibility of food crop poisoning. As a result, there is a good chance that future drinking water shortages, groundwater pollution, and soil scarcity will occur. The effluent contains a lot of hazardous chemicals and heavy metals. Another source of soil and water pollution is the incorrect disposal of industrial effluent contaminated with dyes.



**Fig. (1).** Sequence of industrial dye-contaminated wastewater flowed through canals and contaminated the land resources.

## Background of Dye-contaminated Industrial Effluents

Due to commercialization, the world is concentrating on advancing industrialization and urbanization. Due to inadequate treatment of industrial effluents contaminated with dye and solid waste management, domestic and commercial managements continuously generate enormous volumes of solid and liquid waste that contaminate the environment, including soil, air, and water. The problem of getting rid of effluents that contain both organic and inorganic wastes affects petrochemical companies and petroleum refineries. The industrial effluents contaminated with dyes, which are discharged by the petrol industry, contain a variety of pollutants, both carbon and non-carbon, as well as sulfides,

hydrocarbons, phenol, and heavy metal ions. The process of producing oil, transportation, oil refineries, petrochemical products, garages, and distribution all contribute to the increased amount of toxic pollutants that are leaving the petroleum and oil industry. These toxic chemical-containing effluents pose a serious threat to all environmental biological systems.

### **Treatment Methods for Dye-contaminated Industrial Effluents**

These days, with water shortages, stricter environmental regulations, and ever-increasing demands, it has become imperative to utilize dye-contaminated industrial effluents better. Because dye-contaminated water has a high concentration of organic salt and oil, it's critical to devise a specific decontamination solution. Municipal dye-contaminated industrial effluents, for instance, are known to contain high levels of various impurities, including minerals, radioactive materials, dissolved gases, wax, microorganisms, and dissolved oxygen, as well as aromatic hydrocarbons like benzene, toluene, ethylbenzene, xylene, naphthalene, and phenanthrene-di-benzothiophene polycyclic aromatic compounds. There are methods available for biological, physical, and chemical removal of hydrocarbon components from produced water. Due to space restrictions, offshore extraction centers prefer compact physical and chemical remedy technologies, photo-electro catalytic processes, flocculation, and coagulation.

### **Graphene Oxide Composite Dye Removal**

Graphene oxide composites are made from graphene oxide and mixed, embedded, or doped with other inorganic or organic materials [1]. The graphene oxide composite's attached functionality includes eliminating inorganic salts, heavy metal ions, and organic dyes. Moreover, biological disinfection employs them. The process of purifying water is accelerated by the absorption site between the graphene oxide layers, which attracts and binds with the adsorbate [2]. When used for water purification, graphene oxide embedded with titanium oxide produces a composite material with good photochemical activity and lower energy consumption [3]. The exhausted graphene oxide composites can readily and affordably regenerate after water purification. Thus, researchers are greatly interested in the search for effective graphene oxide-based composites to meet water purification needs using graphene [4, 5].

### **Advantages of Graphene Oxide Composites in Dye-contaminated Industrial Effluents Treatment**

Many organic and inorganic compounds that increase the chemical behavior of graphene oxides can be used to modify their surface and functionality easily.

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