



Photocatalytic Degradation of Organic Dyes Using Zif-67-Based Heterojunction Photocatalysts: A Review

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Abstract

Semiconductor photocatalytic technology has become an area of extensive research due to the extensive environmental contamination. Zeolitic imidazolate frameworks (ZIFs) are a distinct class of metal-organic frameworks that exhibit promise in the field of photocatalysis. This is attributed to their inherent porosity structure, versatile functionalities, rapid electron transfer rate, and excellent chemical-thermal stability are exhibited by this material. In addition, the photocatalytic performance of ZIFs and their derivatives can be greatly increased with the incorporation of active metals or semiconductor materials that act as light collecting centers or electronic mediators. Lately, there has been a growing focus on producing and utilizing materials under consideration are derived from the Co-zeolitic imidazolate framework (ZIF-67)., due to their remarkably great surface area, controllable pore diameter, and outstanding responsively to visible light. This article provides an exhaustive review of the use of ZIF-67-based heterojunctions in visible light-promoted photo-catalytic breakdown of organic dye contaminants. The review discusses and summarizes representative works, with particular emphasis given to the synergistic impacts and proposed mechanisms of the ZIF-67 composite photocatalysts in boosting photocatalysis process. Finally, the recent achievements and challenges in this discipline are discussed, and potential avenues for future investigation are suggested

Keywords: Zeolitic Imidazolate Frameworks; ZIF-67; Heterojunctions; Organic Dye Degradation; Photocatalysis

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1. Introduction

In recent decades, due to urbanization, a significant amount of wastewater effluents have been produced from several agricultural and industrial activities. This wastewater contains many dangerous pollutants such as heavy toxic metals, organic dyes, hazardous substances, and antibiotics, which are released into the aqueous systems without appropriate treatment [1]. This results in serious destruction to the ecological environments, and leading to public health issues [2]. Therefore, it is necessary to treat wastewater effectively before discharging dangerous pollutants into the environment [3].

Organic dyes refer to a class of compounds that are industrially used as colorants in textiles, printing, and plastics industries. Organic dyes are often released into the environment as wastewater from manufacturing processes, and they can have harmful effects on the ecosystem and human health [4].

There are various available approaches for eliminating pollutants from water, including ion exchange, adsorption, membrane separation, coagulation, and advanced oxidation. Among these, photocatalytic method is highly efficient and environmentally friendly, as it can practically completely degrade organic pollutants [5]. This technology involves using photocatalysts in the presence of light to generate reactive oxygen species (ROS), which can then

undergo strong redox reactions with pollutants to produce degradation products and/or CO₂ and H₂O. However, most photocatalysts have limitations, such as inadequate response to visible light, fast recombination rate of photogenerated carriers, and insufficient contact with contaminant molecules. However, several modifications, including doping morphology modification, plasmonic, and composite approaches have been documented for photocatalysts. These modifications aim to improve the photocatalytic capabilities in breaking down organic pollutants and deactivating bacteria in wastewater [6].

2. Organic Dyes and Environmental Concerns

Survival of living things is primarily dependent on water. Additionally, maintaining a verdant environment is essential. Unfortunately, water is becoming increasingly polluted due to increased industrialization and the disposal of waste products from daily human activities. Nevertheless, given the effects of climate change, population growth, industrialization, agriculture, and erratic weather, water scarcity also poses significant dangers to humans [7]. Based on the essential role of wastewater in the water cycle, it is necessary to effectively manage it at every stage of the water management cycle. Despite the fact that there are practically no statistics on the generation, collection, or treatment of wastewater, the vast majority of the wastewater that is produced on a global scale

is neither collected nor treated. There is a significant amount of variance in the treatment of wastewater throughout the various nations as a direct effect of the varying levels of wealth that each nation possesses. The percentage of wastewater that is treated is normally over 70% in countries with high incomes, but it ranges from approximately 38-28% in countries with intermediate incomes to only 8% in countries with low incomes [8]. Multiple chemicals are considered to be water pollutants. Dye compounds are regarded as environmentally hazardous and carcinogenic. [7]. Essentially, Dye substances are organic compounds that may adhere to the surfaces or textiles to give colour. A significant number of dyes are composed of chemically complicated compounds and should be resistant to numerous substances, such as detergents. In several domains of sophisticated technology, for example textiles, paper, leather tanning, food manufacturing, plastics, products for cosmetics, rubber, printing, and dye production, artificial dyes are widely used. Due to their recalcitrant character, their emissions into the hydrosphere constitutes a significant source of contamination. The presence of this substance will result in a visually unappealing hue in the water, hence restricting the extent to which sunlight may penetrate. and the aquatic life's ability to fend off chemical and biological attacks[9]. Furthermore, dye pollution in water pose a cancer risk and are acutely toxic. Numerous infectious diseases, including typhoid, cholera, polio, dysentery, and diarrhea, are attributed to harmful microorganisms transmitted through water, notably *Escherichia coli* (*E. coli*) and continue to be the primary cause of death[10]. More than a hundred thousand different dyes are used in industry today, and their yearly output exceeds 7×10^5 tons/year. The global textile sector consumes annually, a quantity exceeding 10,000 tons of dyes and approximately 100 tons per year into water streams. Yet, the discharge of significant quantities of artificial dyes into the natural environment has presented environmental scientists with concerns [9]. The removal of colours from effluent involves several processes, including adsorption, coagulation, advanced oxidation, and membrane separation [9], ultrafiltration, reverse osmosis (RO), biodegradation, chlorination, and ozone treatment processes [5]. There are several methods to classify commercial dyes. It may be categorized by structure, color, and mode of application. Moreover, dyes can be classified as either cationic (all basic dyes), anionic (direct, acid, and reactive dyes), or non-ionic (dispersed colors) depending on the charge of their particles when dissolved in water. [9]. During the wet processing steps, the textile industry uses a lot of water and chemicals and supplies a lot of colorants and other chemicals. Because of their toxicity to aquatic life and mutagenicity for human beings, the presence of these compounds in industrial wastewaters can lead to severe environmental problems. Color is still a factor that the US Environmental Protection Agency is concerned about. Currently, no restrictions on colour levels, and information is being collected for future consideration. Generally, the criteria addressed for textile operations include biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), sulfides, total chromium, pH, and phenol, and discharges must satisfy must comply with Best Available Technology. Given these facts, attempts have been undertaken to achieve total mineralization of dyes in order to generate oxidation end products, namely carbon dioxide (CO₂)

and water (H₂O), with the aim of effectively removing colour from wastewater generated by the textile industry [11].

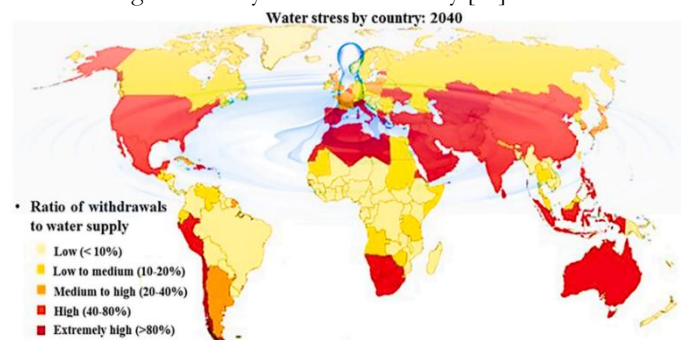


Figure 1. The projected global water stress levels by the year 2040 in terms of percentage, according to the World Resources Institute, this figure indicates that the majority of nations will face a significant water problem within the next few decades. [7]. Open Access Article.

2.1 Classification of Industrial Dyes

Industrial dyes show significant variation in their structure and are often categorized in multiple ways. These categorizations can be based on their color, solubility, structural features, their charge in an aqueous medium, and the way of using onto the principle substrate. Fig. 2 shows some of the common classification methods. Table 1 lists the categorization of dyes according to chemical type and primary substrates.

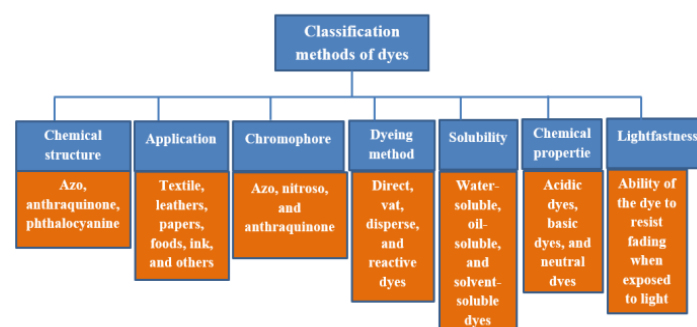


Figure 2. Some of the common dye classification methods

Table 1. Classification of chemical dyes based on their chemical structures and primary substrates.

Class	Chemical structures	Field of application
Acidic	Azo, triphenylmethane, anthraquinone, nitro and nitroso, xanthene, and azine	Leather, wools, papers, silks, and plastics
Cationic (basic)	Azo, Cyanine, azine, diazahemicyanine, hemicyanine, anthraquinone, diphenylmethane, xanthene, acridine, triarylmethane, and oxazine	Inks, plastic and nylon, papers, and polyesters
Azoic	Azo dyes	Rayon, cotton, fibers and plastics
Substantive (direct)	Azo, stilbene, oxazine, and phthalocyanine	Papers, rayon, leather, nylon and cotton
Disperse	Azos, nitro, styryl, benzodifuranone, anthraquinone	Plastics, polyesters and hydrophobic fibers, plastic, and acrylic
Solvent	Azos, anthraquinone, triphenylmethane	Inks, gasoline fuels, oils, wax, and plastic,

Reactive	Anthraquinone, Azos, formazan, phthalocyanine, basic, oxazine	varnishes, and lacquers.
Vat	Indigo, anthraquinone derivatives	Wool, cotton, nylon, and silk.
Mordant	Azos and anthraquinone derivatives	Wool, cotton, cellulosic fibers and rayon.
Oxidation colors	Aniline black and indeterminate	Leather and wool.
Sulfur dyes	Indeterminate constructions	Hair, viscose, cotton, and fur.
Fluorescent brighteners (white dyes)	Pyrazoles, stilbene, naphthalimide, and coumarin	Rayon and cottons
		Detergents and soaps, plastic, paints, and oils

Accordingly, several common methods have been used widely by the researchers to eliminate industrial dyes from water or wastewater, which can be categorized into three groups: physical techniques (e.g., membrane filtration by reverse osmosis and nano-filtration, electrodialysis, sorption techniques, irradiation, ion exchange, electrocoagulation), chemical approaches (e.g., oxidative processes like ozonation, Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), photocatalysis and electrochemical degradation), and biological approaches (e.g., decolorization by fungi, adsorption onto microbial biomass, anaerobic bioremediation, and mixed bacterial cultures).

Table 2. Summaries about treatment technologies [12].

Treatment Method	Advantages	Disadvantages
Physical Methods		
a) Wood chips	Effective removal of cationic, mordant and acid dyes	Expensive. 10-15% loss of the sorbent during reactivation.
b) Silica gel		
c) Activated carbon	Good sorption capacity for acid dyes due to their hardness.	Long retention times and huge quantities are required
	Effective for basic dye removal	Possibility of side reactions
d) Irradiation	Effective oxidation at lab scale.	Requires a lot of dissolved oxygen
Chemical Methods		
a) Fenton's reagent	Possesses the ability to decolorize dyes that are both soluble and insoluble.	Sludge generation.
b) Cucurbituril	An excellent sorption capacity for various dyes.	High cost.
c) Sodium hypochlorite	Accelerates and initiates azo bond cleavage.	Release of aromatic amines.
Biological methods		
Single-cell (Fungal, Algal, and Bacterial)	Highly effective at removing small amounts of pollutants at low concentrations. Highly efficient in removing specific colorants.	Enzyme thermal stability is low.
Advanced Oxidation Process		
a) Ozonation	When applied in the gaseous state, there is no noticeable change in volume..	Short half-life (20 min)

b) H_2O_2 and ozone	No sludge is produced. Foul odors are greatly reduced.	Highly expensive.
c) H_2O_2 and Sonication	Simple method. Very effective in integrated systems	Method that is relatively novel and awaiting widespread application

3. Photocatalysis Process

Photocatalysis is a potential approach for treating organic wastewater. Toxic organic and inorganic substances dissolved in water may be broken down by solar light. As a result of its cheap cost, room-temperature. In recent years, scientists have concentrated on heterogeneous photocatalysis operability, and lack of toxicity, this eco-friendly method has gained in favor [5]. The basis for the photocatalysis process is the interaction of organic contaminants with potent oxidising and reducing agents (h^+ and e^-) produced by UV or visible light on photocatalyst surfaces. Photocatalysts are fundamental to photocatalysis process. Consequently, semiconductor photocatalysts are extensively used in the photocatalysis process [6]. Photocatalysis utilising semiconductors represents an environmentally friendly methodology for the separation of water into hydrogen and oxygen, hence inhibiting the reproduction of bacteria and viruses, and/or eliminating other contaminants. The current trend is the advancement of visible light-driven (VLD) photocatalysts to effectively use the visible portion (wavelength > 400 nm) of the solar spectrum. Nevertheless, a number of drawbacks still exist, such as limited visible light absorption and brief photogenerated electron-hole pair lifetimes, which restrict their practical use [5]. In contrast to semiconductor photomineralization as a technique of water purification, the destructive methods now in use in the water industry, such as chlorination and ozonation, all involve very dangerous and hence unwanted powerful oxidants. Air-stripping and carbon absorption, the two most prevalent non-destructive procedures now in use, are not devoid of issues. The removal of volatile pollutants by air-stripping, for instance, transforms a liquid contamination issue into an air pollution concern, while carbon absorption creates a hazardous solid that must be disposed of [13].

3.1. Photocatalytic mechanism

Organic contaminants were often degraded via photocatalytic reactions. In fact, photocatalytic reaction is an oxidation - reduction reaction, and photocatalysis is significant redox reaction. [6]. Advanced oxidation processes (AOPs) are commonly employed for the purpose of oxidising organic compounds that pose challenges in terms of their conversion into physiologically safer end products. In a broad sense, (AOPs) encompasses the generation of hydroxyl radical ($\bullet\text{OH}$), an extremely reactive, nonselective chemical oxidants. The hydroxyl radical has a comparatively greater level of oxidation activity in relation to widely recognized oxidising agents such as ozone and hydrogen peroxide [14]. The photocatalytic reaction can be categorized into three distinct phases. Initially, the activation of a photocatalyst occurs when it is exposed to photo energy that is equal to or above its band gap energy. This activation process leads to the generation of photoinduced electrons (e^-) and holes (h^+). The process of valence band transition involves the movement of an electron from the valence band (VB) to the conduction band (CB),

and the vacant electron then generates holes (h^+). Hence, the generation of photoinduced electrons occurs within the conduction band (CB), while the generation of photoinduced holes takes place within the valence band (VB). Furthermore, the process involves the interaction of photoinduced electrons (e^-) and holes (h^+) with O_2 and H_2O , resulting in the production of hydroxyl and superoxide radicals, which are known for their high reactivity. The O_2 adsorbed to the photocatalyst surface captured e^- to form superoxide radicals, while h^+ oxidized the H_2O or OH^- adsorbed to the photocatalyst surface in order to create hydroxyl radicals ($OH^\cdot$). These extremely reactive hydroxyl and superoxide radicals effectively transformed organic pollutants into carbon dioxide (CO_2) and water (H_2O), hence reducing the occurrence of secondary pollution. [6].

The following reactions are suggested for the photocatalysis process: [15]–[17].

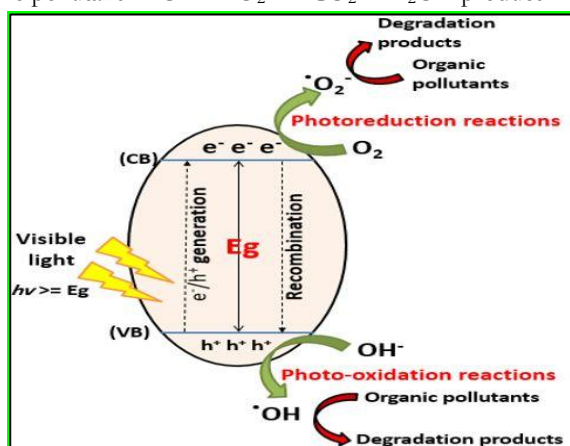
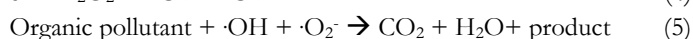


Figure 3. The mechanism of photocatalytic degradation of (Ops) [18]. Open Access Article.

3.2. Photocatalytic Heterojunctions

The construction of heterojunctions is regarded as a promising and efficient way for enhancing photocatalytic performance. Due to the numerous exceptional benefits that 1D semiconductor photocatalysts provide, including their one-of-a-kind structure, a significantly increased surface area, a large quantity of active sites, and a direct pathway for the transfer of charge carriers, these photocatalysts are considered to be an important basic unit that can be combined with another semiconductor [19]. Heterojunctions are, in conclusion, the interface that exists among two semiconductors characterised by differing band structures. Among photocatalyst modification and design strategies, heterogeneous junction system construction is among the most frequently used techniques for photocatalyst production. This is as a result of the heterojunction system's applicability, a strong responsiveness to visible light, a high level of activity, and efficient spatial separation of electron/hole pairs, all while retaining a low rate of recombination [15].

3.2.1. Semiconductors Composites

Despite the fact that photocatalysis research has made significant advances over the past decade, there are still significant obstacles to overcome before photocatalysis can become a practical, efficient, and widely acknowledged technology, specifically for industrial applications. Fundamental characteristics of photocatalyst materials must be enhanced: 1) the electronic structure, 2) the surface structure, and 3) the crystal structure are fundamental design parameters that significantly impact photocatalytic performance. In terms of electronic structure, the two significant obstacles for investigators are the general enhancement of light absorption and the expansion of semiconductor light absorption encompass the visible region of the solar spectrum. In conclusion, increased light absorption, heightened crystallinity, expansive surface areas, and efficient charge carrier separation are the most significant factors in enhancing photocatalytic activity. Also highly desired is a semiconductor material with high chemical stability, ideal band locations, and low cost. By integrating multiple photocatalysts into a composite photo-catalyst system, a number of these issues may be simultaneously addressed [20].

3.2.2. Types of Photocatalytic Heterojunctions

Different photogenerated carrier transfer mechanisms can be seen in heterojunction photocatalysts because of the wide variety of preparation techniques, band energies, morphological characteristics, and topologies used in their construction. In respect to this, heterojunctions are typically divided into the following categories: heterojunction I-type, heterojunction II-type, p-n heterogeneous junction, Schottky heterogeneous junction, Z-type heterogeneous junction, and S-type heterogeneous junction [19].

3.2.2.1. Heterojunction I- Type

In heterojunction I-type, VB of semiconductor 1 is more positively charged than the CB of semiconductor 2. The transport of electrons and holes from semiconductor 1 to semiconductor 2 occurs as a result of the buildup of all charge carriers on semiconductor 2, electron-hole recombination may occur, resulting in a decrease in photocatalytic performance [21].

3.2.2.2. Heterojunction II- Type

The transfer of photogenerated electrons from CB of semiconductor 1 to the conduction band of semiconductor 2, and the migration of photogenerated holes from VB of semiconductor 2 to the valence band of semiconductor 1, occur in this process. The successful separation of photogenerated electron-hole pairs can be attributed to the presence of an internal electric field (IEF) that is generated at the contact point between the two semiconductors. This phenomenon contributes to an increase in the photocatalytic activity [19].

3.2.2.3 p-n Heterojunction

Despite the Type II heterojunction has the potential to effectively separate charge pairs, e^- - h^+ recombination rate in the semiconductor remains high, limiting the extent of electron-hole separation achieved through the Type II heterogeneous junction. In order to boost the photocatalytic performance, here the concept of building a p-n heterogeneous junction photocatalyst is introduced. This approach aims to supply an extra electric field that can facilitate the transmission of e^- - h^+ pairs. The separation efficiency of electron-hole pairs in p-n heterojunctions is significantly higher compared to Type II heterojunctions, this could potentially result in

an improvement in the photocatalytic activity. The synthesis of an appropriate p-n heterogeneous junction photocatalyst can be accomplished [22]. When visible light interacts with semiconductors, electrons that are created by the light are transported from the conduction band of a p-type semiconductor to the conduction band of an n-type semiconductor. The photo-generated holes, however, will be relocated from the valence band of the n-type semiconductor to the valence band of the p-type semiconductor. As a result, the oxidation process will occur in the valence band of the p-type material, whereas the reaction of reduction will occur in the conduction band of the n-type material, resulting in the generation of a significant number of reactive oxygen species (ROS) [15].

3.2.2.4. Z-Type Heterojunction

Although the heterojunction photocatalysts discussed above have the potential to optimize the effectiveness of electron-hole separation, It is necessary to acknowledge that the composite's redox capacity is restricted because of the occurrence of oxidation and reduction reactions on semiconductors with comparatively lower oxidation and reduction potentials, respectively. In 1979, Bard et al. introduced a pioneering endeavour aimed the progression of a Z-scheme photocatalytic system as a means to tackle these aforementioned issues.[23]. The utilization of an artificial Z-scheme photocatalyst, drawing inspiration from the intricate mechanisms of photosynthesis in nature, presents a promising avenue for improving the efficiency of photocatalytic processes. The conventional configuration of an artificial Z-scheme photocatalyst typically comprises 2 interconnected semiconductor photocatalysts, including an oxidation photocatalyst and a reduction photocatalyst [24]. Direct scheme heterogeneous junction refers to the direct flow of photogenerated electrons from the lower CB of semiconductor 2 to VB of semiconductor 1 [23]. Direct Z-scheme photocatalyst comprised of a binary system comprising two semiconductors that are in direct contact at their interface. The direct Z-scheme photocatalyst does not need electron or holes mediators. As a result, the Z-scheme photocatalytic system's building costs may be significantly decreased [25]. In indirect Z-scheme photocatalyst heterogeneous junction, a conductive solid substance serves as an electron mediator [23].

3.2.2.5. Heterojunction S-Type

Yu et al. have suggested an exceptional step scheme (S-scheme) system heterogeneous junction. Similar to the Z-scheme, it may facilitate the separation and transfer of photoexcited carriers and provide enhanced redox capability. S-scheme heterogeneous junction comprise of 2 n-type semiconductors, specifically 1 and 2. Semiconductor 1 exhibits a substantial work function and a relatively low Fermi energy level, in contrast, semiconductor 2 has a reduced work function and a greater Fermi energy level.

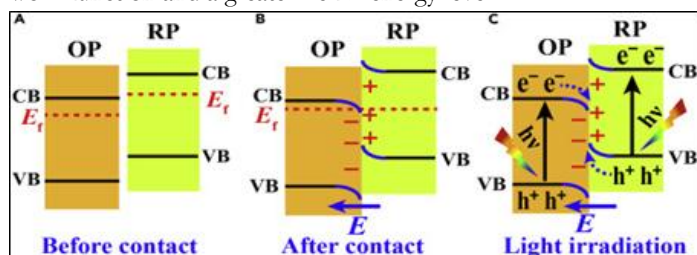


Figure 4. Diagram showing the charge-transfer in an S-type heterogeneous junction [26]. Open Access Article.

In S-scheme heterojunctions, the transfer pathway of photoexcited charge more closely resembles a step or N, meaning that the electrons originating from the conduction band of semiconductor 1 interact with the holes present in the valence band of semiconductor 2. This leads to the spatial segregation of electrons and holes, resulting in an enhanced reduction and oxidation reaction capabilities. In addition, when a heterojunction is formed, electrons from semiconductor 1 will continue to migrate to between these 2 semiconductors, an IEF forms, which consider semiconductor 2 until both semiconductors' Fermi energy levels reach equilibrium. At the boundary as the primary driving force for the movement of photogenerated carriers [19].

3.2.2.6. Schottky Junction

Schottky junctions are heterogeneous junction produced by coupling photocatalysts with cocatalysts such as gold (Au), silver (Ag), platinum (Pt), molybdenum disulfide (MoS₂), and graphene. When type-n semiconductor or type-p semiconductor form Schottky junctions with cocatalysts, the cocatalysts may facilitate the rapid transmission of light-induced electrons in the CB or photogenerated holes in the VB to the cocatalyst, resulting in spatial segregation of light-induced electrons and holes [19].

4. Metal Organic Frameworks (MOFs)

4.1. Introduction

As a bridge between inorganic and organic chemistry, MOFs are of great interest. scientists in several fields. MOFs are Porous coordination polymers (PCPs) consisting of metallic nodes and organic ligands that stretch in 2 or 3 dimensions. Due to its vast surface area, high porosity, geometry, size, and chemical activity, MOFs are used in many disciplines such as electronics, drug delivery, catalysis, drug storage, and chemical separations. Microscale or nanoscale crystalline powders or thin films are essential for most of these applications. Their large surface area, abundance of exposed active sites and rapid guest molecule diffusion make them attractive, nanocrystals are of interest. In addition, nanoparticles are required for efficient transport through the blood system and cellular absorption in biomedicine [27]. The framework integrity of MOFs must be ensured when they are utilized for specific applications in order to keep the desired functions and characteristics. In reality, industrial processes often include water or moisture, and applications like catalysis frequently need for stability in the presence of either aqueous acid/base solutions or coordinating anions. The use and commercialization of many Metal Organic Frameworks (MOFs) have been severely constrained by their instability in water or other hostile environments. As a result, during the last five years, the chemical stability of MOFs has drawn increasing interest.

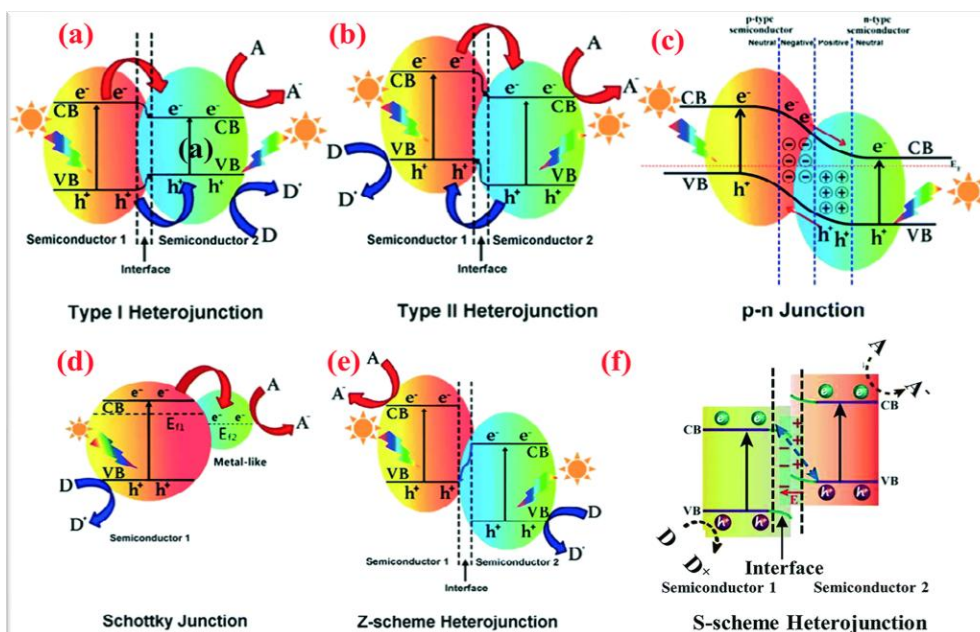


Figure 5. Types of photocatalytic heterojunctions [19]. Open Access Article.

Researchers are striving to create more stable framework structures, understanding the potential breakdown mechanisms, and addressing the stability of MOFs in various conditions. Chemical stability is the capacity of metal-organic frameworks (MOFs) to achieve their ordered long-range structure in specific chemical environments. The stability of MOFs can be influenced by various aspects, such as the conditions of the operating environment, the presence of metal ions, the presence of organic ligands, the coordination geometry between the metal and ligand, and the hydrophobic nature of the surface within the pore [28]. It is believed that the comparatively weak coordination bonds that maintain the framework structures of MOFs are accountable for their fragile stability. Stability of MOF structures requires robust coordination bonds or steric hindrance to prevent guest molecules from accessing the metal nodes in order to withstand the assault of guest molecules [29]. To replace zeolites, aluminosilicates, and other materials now in use, the next generation of catalysts and adsorbents may consist of porous crystalline MOFs with one, two, or three-dimensional structural stability [30]. High demand exists for MOF-based materials in water treatment applications due to their many desirable properties, like their large surface area (more than 7000 m²/g), high porosity (pore volume above four cm³ /g), simple synthesis, active metal surface, ordered and varied porous structures, high crystalline content, remarkable thermal endurance, high removal efficiency, high adsorption capacity, exceptional selectivity, high regeneration, and excellent reproducibility. As a result, MOF-based compounds are considered to be the most favorable solutions for removing hazardous dyes [7]

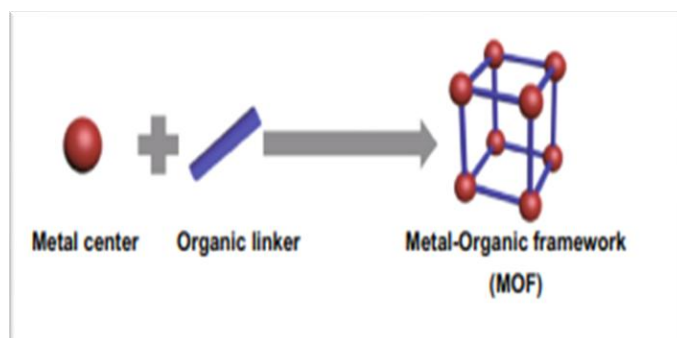


Figure 6. Demonstrates the MOF's structure in schematic form [31]. Open Access Article.

4.2 Zeolitic Imidazolate Frameworks (ZIFs)

As hybrid frameworks, a number of metal organic frameworks with zeolitic structures have been successfully synthesised. The introduction of Zeolitic Imidazole Frameworks (ZIFs) has recently attracted considerable consideration. ZIFs are a subfamily of (mofs) that self-assemble from M-Im-M (M representing Zn, Co cation, and Im representing imidazolate linker). The varied structures of Zeolitic Imidazole Frameworks are comparable to those of traditional Aluminosilicate Zeolites, where silicon is commonly represented by Zn²⁺ ions, and oxygen is represented by imidazolate anions in bridges with M-Im-M (a metal-imidazole-metal) angle of around 145°. Thus, ZIFs often adopt topologies that are structurally analogous to those of zeolites [32]. This framework formula applies to all ZIF types, and hence ZIFs with identical components but different framework topologies may be considered polymorphs [33]. Figure 7 compares the metal-imidazolate bond angle in ZIFs to that of Si-O in zeolites.

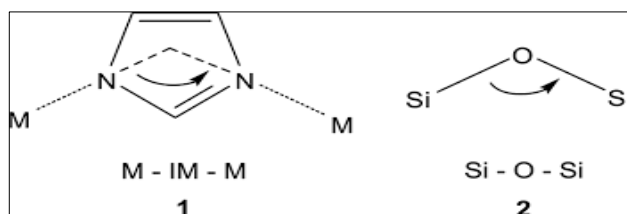


Figure 7. The angles of bridging in ZIFs (1) and zeolites (2)[34].

Open Access Article.

Controlling the size and morphology of ZIFs crystals is crucial since the variations in morphology and size will affect a number of ZIFs applications. The concentration, solvent, temperature, molar ratio of the reactants, time, and mixing are only a few of the variables that might affect the size of the ZIFs crystal. For instance, by increasing the ligand-to-metal molar ratio, the crystal seeds will be coated with an excessive quantity of ligand to prevent further association with metal ions, leading to the formation of smaller particles during crystal growth [35]. ZIFs materials may have topological structures like those of ordinary zeolites, like Sod, rho, gme, lta, and ana, but with a distinct imidazolate ligand, as shown in Figure 8. They can also have configurations that were not known to exist in zeolites. A high-throughput synthesis method was used to isolate a considerable number of novel ZIFs structures, and around 105 ZIFs materials with various chemical compositions or structures were found [36].

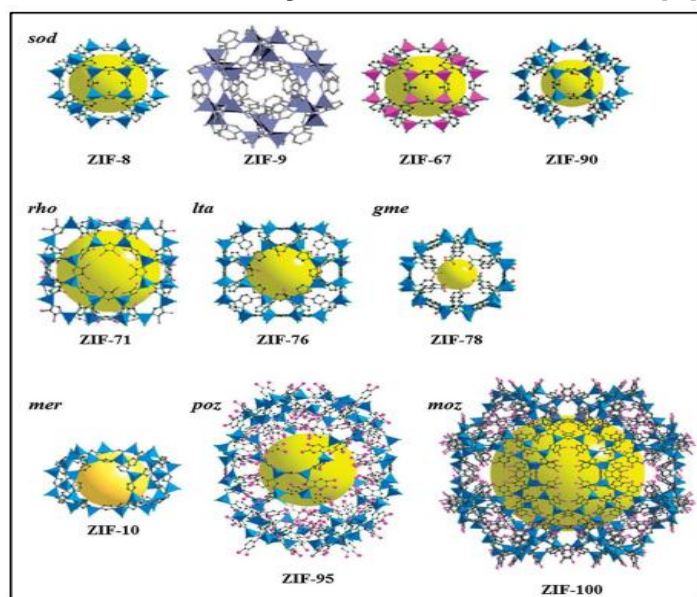


Figure 8. Shows number of novel ZIFs structures [37]. Copyright 2010 Elsevier

In comparison to other forms of MOFs, ZIFs exhibit greater porosity, high specific surface area, crystallinity, functional diversity, adsorption potential, thermal and chemical stability. As a result of these characteristics, ZIFs offer a large deal of industrial application potential in electronic devices, gas separation, sensing, medication delivery, and catalysts [38].

4.3 ZIF-67-Based Composite Photocatalysts

ZIF-67 is a well-known zeolite imidazole framework (ZIF). It is composed of Co metal ions that are tetrahedrally coordinated and anionic imidazolate ligands. Due to its 1) high surface area; 2) small band gap $E_g = 1.98$ eV; 3) high thermal stability (> 550 °C under N₂) and chemical stability; 4) good ability to absorb light and photocatalytic activity, it may be a very promising and exceptional

photocatalyst. when exposed to visible light;5) easy to self-assemble into a regular structure on a large scale under normal conditions [39]. The nanomaterials derived from ZIFs exhibit greater control over particle shape and size than MOFs containing carboxylate ligands such as benzene tricarboxylic acid. (BTC)[40]. The majority of research efforts have concentrated on its large surface area and appropriate band gap width, which can be combined with other materials to enhance its photocatalytic performance and are primarily employed for the oxidative degradation of organic matter [39]. ZIF-67 has been exhaustively investigated for applications involving aqueous phase adsorption [41]. ZIF-67 is a powerful adsorption eliminator of perfluorinated substances, heavy metal ions, and organic dyes [42]. The phenomenon of adsorption has the potential to take place within the internal pores of ZIF-67 in addition to the external surface adsorption due to diffusion. However, because ZIF-67 is microporous, slow diffusion of adsorbate molecules within micropores impedes adsorption. ZIF-67's applications in adsorption, catalysis, and separations are severely constrained due to its limited opening size (1.16 nanometer $\times$ 0.34 nanometer). This problem may worsen if the adsorbate molecules are the same size or larger than the micropore aperture. To overcome the sluggish diffusion restriction in ZIF-67 applications, innovative ZIF-67-based composites with enhanced functionality and porosity are needed. It is essential to introduce bigger holes (such as mesopores) into the ZIF microporous network in order to enhance mass transfer within it. The presence of large mesopores is expected to promote transport of adsorbates from solution to micropore active sites, thereby enhancing adsorption capacity [41]. In contrast to photocatalysts composed of a single component, which have a tendency for rapid electron and hole recombination, the coupling process (heterojunction construction) combines the physical and chemical characteristics of MOFs for instance, ZIF-67, which is one of the different kinds of MOF materials) and semiconductors to increase photocatalytic efficiency for the degradation of contaminants in wastewater [43].

4.3.1. Synthesis Methods of ZIF-67-Based Composites

4.3.1.1. The Solvothermal method

The Solvothermal synthesis process is commonly employed for the production of ZIF-67. In general, it is customary to subject reactants which are dissolved in solvents, for instance. cobalt sources and 2-methylimidazole (Hmim), to a temperature range of 50 to 200 degrees Celsius. in autoclaves for 12–72 hours to produce crystals. In general, three crucial processes are involved: hydrolysis, coordination, and deprotonation.[44]. ZIF-67 materials were synthesized in dimethyl-formamide (DMF) and methanol separately for four hours at 60 degrees Celsius using Co(NO₃)₂·6H₂O and Hmim, by Jayashree et al. experiments involving SEM and nitrogen adsorption-desorption demonstrated that the solvent plays a significant role in the process of crystallization, as ZIF-67 synthesized in methanol possessed a microporous structure while products synthesized in DMF displayed a hierarchical structure [45]. Similar to this, in their study, Qin et al. successfully achieved the synthesis of ZIF-67 in methanol at room temperature, with a reaction duration of 24 hours. [44]. The utilization of novel methodologies in the synthesis of zeolitic imidazolate frameworks (ZIFs) yields advantageous outcomes for environmental

sustainability, due to the adverse environmental impact caused by the detrimental effects of pollution and significant levels of energy usage associated with current synthesis processes. For instance, Using water as a solvent is one of the greenest ways to synthesize ZIFs [46].

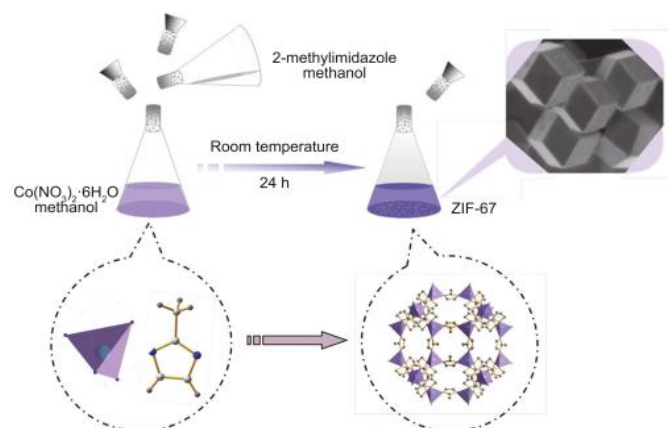


Figure 9. Solvothermal technique for the synthesis of ZIF-67[44]. Open Access Article.

4.3.1.2. Sol-Gel Method

The Sol-Gel synthesis has evolved as a method of regulating the composition of molecules and frameworks at different scales of length [47]. Typically, MOF precursors and coagulants interact via hydrolysis and condensation reactions. Create a colloidal suspension with particulates smaller than one micron. The gels possessing a distinct spatial configuration are then converted into solid particles via a thermal treatment [44]. Subsequently, Fe₃O₄/ZIF-67@WA (WA refers to wood aerogel) was created by Xu et al. by in-situ incorporating magnetic Fe₃O₄/ZIF-67 materials directly into a lightweight natural wood aerogel, creating a hierarchically porous aerogel. Before being placed on the wood aerogel laminate's surface, Fe₃O₄ NPs (NP = nanoparticle) were coated with a Co+2 solution containing PVP (Polyvinylpyrrolidone). ZIF-67 crystal growth on wood aerogel by the presence of Hmim and the strong electrostatic attraction and hydrogen bond formed by the multiple oxygen containing groups on the lengthy chain of cellulose Fe₃O₄ and ZIF-67 NP stick to the outside surface of wood aerogel (WA) instead of penetrating it [48].

4.3.1.3. Surfactant method

The surfactant-assisted method involved adding surfactants to a precursor solution in order to facilitate dissolution and dispersion. [44]. Additionally, the morphology and structure of the samples can be manipulated through the modification of surfactant kinds or quantities [49]. To prepare ZIF-67 materials, for instance, combining a cobalt source with an aqueous solution of Hmim containing CTAB (Cetyltrimethylammonium Bromide) on time (5 minutes). During the crystallization process, cetyltrimethylammonium bromide (CTAB) may be used as a particle-size-modifying capping agent within the range of 50–320 nm. [50]. In recent research, Li et al. immersed Fe₂O₃ nanorods in dimethylformamide containing a specific amount of PVP (PolyVinyl Pyrrolidone), followed by the addition of 2-Methylimidazole (Hmim) and Co(NO₃)₂·6H₂O, produced Fe₂O₃@ZIF-67 composites after 12 hours of drying at 80 degrees Celsius. In a typical procedure, PVP served two purposes: (i) as a capping agent in order to control product size, and (ii) as a linker in order to increase the affinity between Fe₂O₃ nanorods and ZIF-67 through the coordination of Co+2 and pyrrolidone rings (C = O) [51].

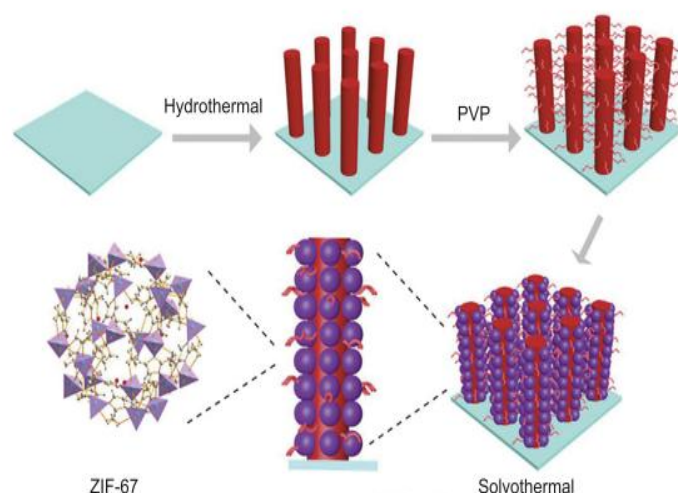


Figure 11. Schematic of the composite Fe₂O₃@ZIF-67 manufacturing procedure [51]. Copyright 2019 Elsevier.

4.3.1.4. Microwave Method

In recent years, interest in the microwave- or ultrasound-assisted synthesis of ZIF-67 has grown. During the processes, enormous magnitudes of local temperature and pressure can be created, which facilitates small particle size contribution, enhances the purity of the phase, and shortens the time of the reaction [52], [53]. Niyaz et al. introduced a straightforward and efficient technique involving ultrasonic assistance to synthesize the composite ZIF-67@Fe₃O₄@ESM, where ESM denotes eggshell membrane. The cobalt nitrate solution suffered sonication, combined with previously synthesized Fe₃O₄@ESM in the water phase, and subjected to sonication once more in the Hmim solution. On the densely interwoven, cross-linked eggshell membrane (ESM) protein fibers, ZIF-67 crystals have grown. The ultrasound-assisted technology increased the local turbulence and microcirculation of liquid within the reaction system and decreased the coordination time from six hours (stirring method) to three hours Copper cation (Cu+2) capture and dye (Basic Red 18: BR18) adsorption processes have been designed and thoroughly investigated using the prepared adsorbents.

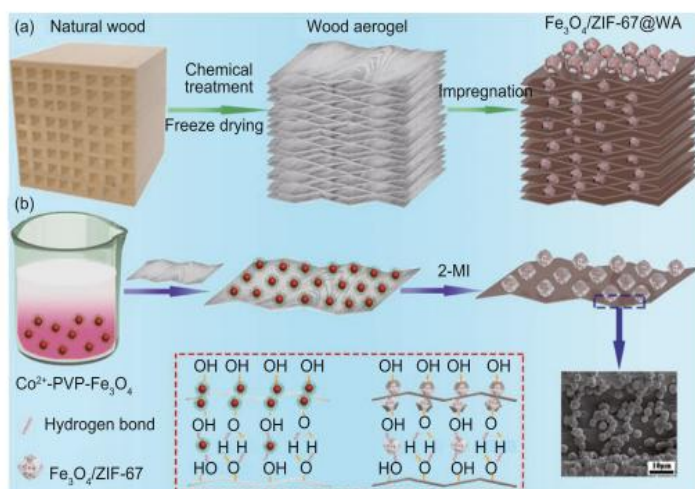


Figure 10. Production scheme for the manufacture of Fe₃O₄/ZIF-67@WA.[48]. Copyright 2019 Elsevier

In experiments carried out with the ZIF-67@Fe₃O₄@ESM composite it has been determined that the adsorption rate and elimination percentage for both categories of pollutants are significantly higher and more rapid compared to those seen for pure ZIF-67[54].

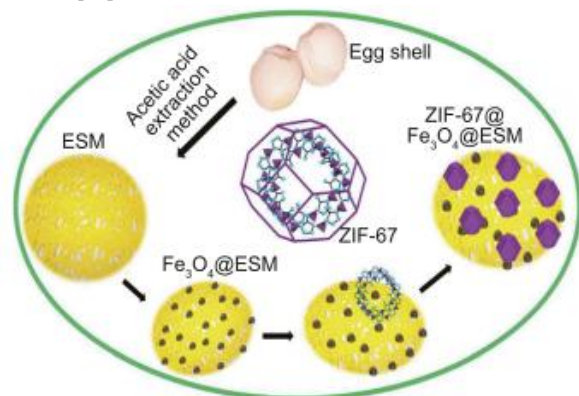


Figure 12. Schematic of the ZIF-67@Fe₃O₄ synthesis [54].

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5. Previous Works

K.C. Devarayapalli et al (2020). researchers fabricated g-C₃N₄/ZIF-67 nanocomposite by a facile microwave method. The photocatalytic properties of the g-C₃N₄/ZIF-67 photocatalyst were evaluated by photocatalytic dye degradation of crystal violet (CV), 4-chlorophenol (4-CP), and photocatalytic hydrogen (H₂) production from H₂O decomposition under visible light illumination. The photocatalytic dye results showed 95% CV degradation and 53% 4-CP degradation within 80 min. The H₂ production of the g-C₃N₄/ZIF-67 composite was 2084 μmol/g, which is 3.84 times greater than that of bare g-C₃N₄ (541 μmol/g)[55].

Ruiqiang Zhong et al. (2022).prepared a novel composite photocatalyst, BiOBr/ZIF-67, by the one-pot method. They prepared a series of BiOBr/ZIF-67 composite photocatalysts by changing the ratio of ZIF-67. The photocatalytic activity of the prepared composite BiOBr/ZIF-67 was evaluated by degrading RhB

under visible [1] light irradiation of a 400W Xe lamp, 20.0 mg of the prepared sample, and a (20.0 mg/L) initial concentration of RhB. The degradation rate of RhB reached 95.2% after 120 min of visible light irradiation using BiOBr/ZIF-67 (30%); compared with pure BiOBr, the photocatalytic efficiency increased by 50%[56].

Yuanyuan Li et al.(2022). reported a novel nanocomposite catalyst (CC@Co₃O₄) derived from Metal organic frameworks-Covalent organic frameworks (MOFs-COFs) (COF@ZIF-67) was prepared and carbonized successfully for peroxymonosulfate (PMS) activation to degrade organic pollutants in water. The required nano-catalyst of CC@Co₃O₄-X was obtained by the carbonization of COF@ZIF-67-X (X is the dosage of COF, and it is equal to 0.05/0.10/0.15 gm). The results showed that the CC@Co₃O₄-0.10/PMS system could degrade 93.8% BPA and 98.2% RhB, which obtained great potential in the treatment of actual water. The degree of mineralization was determined through TOC analysis, and it was found to be 22.3% and 82.5% for BPA and RhB, respectively [57].

Marwa A. Lafta et al. (2022) constructed a ternary visible-light-driven g-C₃N₄/ZIF-67/phosphotungstic acid (PTA) composite. The photocatalytic activity of this composite was evaluated by degradation of methyl violet dye (MV) under visible light irradiation at fixed conditions of 100 ml of dye solution, MV dye concentration = 10 ppm, photocatalyst dose = 0.5 g/l, and initial pH = 6.8. One 50-watt LED lamp was used as a light source. Excellent photodegradation efficiency (98%) within 90 minutes was achieved compared with other photocatalyst components. A recyclability study showed that g-C₃N₄/ZIF-67/PTA exhibited good photocatalytic stability for five consecutive cycles[58].

Fan Wu et al. (2023). Synthesized ZIF-67/BiOCl heterojunction photocatalyst successfully . The photocatalysis ability of the as-prepared photocatalyst was examined by degrading of rhodamine B (RhB) and tetracycline (TC) under visible light irradiation .The obtained ZIF-67/BiOCl heterojunction had the best photocatalytic performance and it had good cyclic stability. The photodegradation rate toward RhB reached 97.38% in 60 min and 78.16% toward TC in 120 min[59].

Table 3. Summary of the ZIF-67-based photocatalysts for organic dye photocatalytic degradation.

Photocatalyst system	Targeted dye	Degradation removal %	Conditions	Refs.
g-C ₃ N ₄ /ZIF-67/PTA	Methylviolet (MV)	98% (in 90 min)	catalyst dose = 1 g/l, pH of the solution = 6.8, [MV]. = 10 ppm, LED lamp of 50 W	[60]
H-ZIF67@PDA@TiO ₂	Acid Fuchsin (AF) Congo red (CR) Erythrosin B (EB) Rose bengal (RB) Methyl orange (MO) crystal violet (CV)	100% (in 40 min) For both (AF) and (CR) 99% (in 150 min) For both (EB) and(RB) 61% (in 150 min)	Photocatalyst dose=50 mg, solution pH = 7 and conc, for all dyes = 10 ppm Xe lamp of 600 W	[61]
ZnO/Mn _{0.5} -ZIF-67	Bismarck brown R (BBR)	94% (in 150 min) 89.5% (in 100 min)	Photocatalyst dose= 10 mg and [BBR] conc. = 50 ppm ultraviolet light	[43]
Fe ₃ O ₄ @ZIF-67	Congo red (CR)	More than 70% in (30 min)	Photocatalyst dose = 10 mg [CR]= 4* 10 ⁻⁵ mol / L Xe High-pressure lamp of 500 W	[62]

Cu/ZIF-67	Methyl orange (MO)	Almost disappeared after (25 min)	Photocatalyst dose=0.05 g [MO]= (16.35 mg/L) pH value of MO-H ₂ O ₂ solution = 6.7 at room temperature. Hydrogen peroxide solution=10ml (H ₂ O ₂ , 30%) Daylight lamp of 500W	[63]
Zn _{0.2} Cd _{0.8} S@ZIF-67	Rhodamine B (RhB)	98.40% (in 2 hr)	Photocatalyst dose = 50 mg [RhB]= 10 ppm Xe lamp= 500 W	[64]
BiO- Ag(0)/C ₃ N ₄ @ ZIF-67	Methylene blue (MB)	For (MB) (96.5% in 120 min)	Photocatalyst loads= 1g/L [MB] equal to 10 ppm [CR] = 10 ppm For MB ,pH=9 And for CR ,pH=2.5 The degradation were Under natural sunlight irradiation	[65]
ZIF- 67@Cd _{0.5} Zn _{0.5} S	Methyl violet (MV)	96.6% (in 60 min)	catalyst dose =1 grammes per litre, [MV] =10 ppm unmodified solution of pH equal to 6.7, 50 W LED lamps	[66]
ZIF- 67@CoWO ₄ @CoS	(MB)	100% (in 10 min)	[MB] =40 parts per million (ppm), catalyst dose =1 g L ⁻¹ , the time of reaction equal to 10 min , pH =6.5, LED lamps (50 W)	[5]
BiOBr/ZIF- 67	Rhodamine B (RhB)	95.2% (in 120 min)	Photocatalyst dose=20 mg [RhB]=20 mg/L a 400W Xe lamp ((light density was 80 mW·cm ⁻²)	[56]
PbS/ZIF-67	Basic Yellow 28	91% (in 180 min)	Photocatalyst dose=20 mg The initial concentration of dyes is equal to 10 ppm PH=11	[67]
	Direct Blue 199	94 % (in 180 min)	400W Metal halide lamp	
ZIF-8@ZIF-6 7	Methylene blue (MB)	≥ 90% (in 50 min)	Photocatalyst dose=25 mg [MB]=(5 × 10 ⁻⁵ mol/L) energy intensity of the Xenon lamp used =140 W/m ²	[68]

6. Conclusions and outlook

The present review concentrates on the current synthesis and developments of ZIF-67-based composites heterojunctions as photocatalysts. The ease of fabrication, suitable bandgap structure, effective charge separations, and high optical-surface properties make the ZIF-67-heterojunctions composites ideal candidates for use in the context of the photocatalytic breakdown of organic dyes, over the past decade. Moreover, the places of commercial applications of ZIF-67-based photocatalysts for dye degradation is that they can be fabricated through low-cost and simple routs, meeting the requirements of being inexpensive and ecofriendly. Hence, the following conclusions may be boosted in future to achieve the industrial manufacturing and photocatalytic request of ZIF-67-based composites.

- Most reports in photocatalysis area focus on ZIF-67-based composites including metals and semiconductors. Thus, the other types of ZIF-67-based composites for photocatalytic dye degradation should be extended in the direction of conductive polymers.

- The photocatalytic recyclability is very crucial for practical applications. Even though these ZIF-67 based composites have good stability in contaminated solutions, they are hard to be separated from the solutions because of their highly dispersive ability. Therefore, it is imperative to suggest an efficient synthesis

approaches for fabrication of ZIF-67 composites with high separation ability. For instance, fabrication or shaping of ZIF-67 composites or derivatives in the form of membranes. Magnetic ZIF-67 based composites may also be benefited for that purpose.

- The combination of semiconductors/conductors in the creation of ZIF-67 photocatalyst composites has demonstrated numerous benefits for the destruction of organic dye contaminants. However, the specific structure of many of these composite materials remains indistinct, posing a significant obstacle to understanding the relationship between structure and photocatalysis. Therefore, future research should focus on elucidating factors like the composition, morphology, construction of each constituent, and the interface between them, as these factors can influence the photodegradation activity of such composite. Such investigations are crucial not only for a comprehensive understanding of the materials but also in order to facilitate the advancement of integrated engineering processes, that include optimizing interface engineering and controlling the structure and morphology of each constituent.

- Furthermore, it is essential to thoroughly investigate and understand the mechanisms involved in photocatalysis. Many aspects remain unclear and require detailed elucidation. For instance, the present comprehension of the photocatalytic mechanism. For certain prepared materials is equivocal, particularly with regards to the efficient separation of light -induced electron-hole pairs, charge

transfer in multicomponent systems and the relationship between structure and activity. Undoubtedly, gaining a better understanding of the photocatalytic mechanism holds significant importance in the design of new photocatalysts with exceptional photocatalytic activities. Achieving this goal may necessitate the utilisation of in situ characterisation techniques and theoretical simulations is employed to explain the complexities inherent in the photocatalytic mechanism.

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