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Enhancing Dye Wastewater Treatment: A Review of Organometallic-Based Adsorption, Photocatalysis and Chemical Degradation

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Abstract. Dye waste is difficult to remove using conventional methods due to its high stability and resistance to biodegradation. However, scientific advancements have introduced alternative approaches, such as organometallic compounds, which can serve as catalysts and adsorbents. These compounds, particularly metal-organic frameworks (MOFs), possess a large surface area, flexible structure, high crystallinity, and adjustable pore size, making them highly effective in adsorption and photodegradation processes for dye wastewater treatment. This review discusses organometallic compounds, including Materials of Institut Lavoisier (MIL), Zeolitic Imidazolate Frameworks (ZIFs), and Porous Coordination Networks (PCNs), which have proven effective in absorbing certain dyes from water solutions. These MOFs, either alone or in composites with metal oxides, can significantly reduce dye contaminants in water. This review provides an in-depth exploration of the characteristics of organometallic compounds and analyzes their potential as adsorbents and photodegradation catalysts for the removal of dye contaminants from wastewater. Radicals produced through reactions between the valence and conduction bands of the catalyst material with H₂O₂ can oxidize dye pollutants. This review offers deep insights into the potential of organometallic compounds in dye wastewater treatment

Keywords : Dye waste, organometallic compounds, adsorbents, photodegradation catalysts

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Introduction

Water pollution is one of the critical global environmental issues that requires sustainable and effective solutions. Various human activities, including industry, textiles, agriculture, urban living and households, generate wastewater containing various pollutants, posing a threat to water resources. Organic dyes, in particular, are gaining significant attention due to their toxic properties and detrimental effects on all forms of life [1]. The discharge of dyes into rivers, even in small amounts, can have a negative impact on living organisms.

Conventional wastewater treatment methods, including ultrafiltration, coagulation, oxidation, ozonation, reverse osmosis, sedimentation, flotation, and sedimentation, encounter limitations in treating wastewater from certain sources, particularly industrial and textile wastewater, due to economic considerations [2]. Consequently, efforts to alleviate the negative impacts of wastewater have driven the development of innovative technologies, including the utilization of organometallics as a promising solution. Organometallics, which are metal-containing organic compounds, have gained attention as potential materials for wastewater treatment.

Organometallic compounds play an important role in wastewater treatment, serving as catalysts and adsorbents for contaminant removal. In recent years, the use of adsorbents for wastewater treatment has been popular due to their proven efficiency in converting effluents into stable forms compared to conventional treatment methods [3]. However, adsorbents have limitations, such as the presence of impurities that hinder maximum absorption. Activation is required to optimize the sorption process. Organometallic compounds offer a solution by providing chemical properties that enable chemical reactions to effectively remove contaminants present in wastewater. The incorporation of organometallic compounds is expected to significantly increase the adsorption capacity [4].

The efficiency and sustainability of chemical reactions could be greatly increased by using organometallic catalysts. The customizable structural features allow for more specific tuning of catalyst performance, leading to faster, more selective, and more efficient reactions. As cata-

lysts, organometallics have several advantages, including porosity, high thermal stability, high specific surface area and unique structures. These attributes enhance catalytic performance and minimize by-products during the process.

The dye's resistance to time, sun exposure, and biodegradation due to its chemical structure makes it difficult to remove through conventional wastewater treatment. This has prompted research into the use of organometallic catalysts, which has seen significant advances in recent years, especially in the fields of catalysis and adsorption. This article aims to explore and analyze in depth how organometallic compounds can help in the mitigation of dye wastewater pollution. By understanding the advantages and limitations of each material discussed, new insights into the effectiveness, safety, and efficiency of using organometallic materials for dye wastewater remediation are expected.

Experimental

This review article is based on current research on the application of organometallic complexes for dye wastewater treatment. The research stages include: (1) A comprehensive search of national and international journals published in the past 12 years (2013-2024) was conducted to identify relevant literature on the topic, (2) sorting the important literature related to the predetermined topic, (3) examining the contents of the selected literature to gain a comprehensive understanding of the characteristics of organometallic compounds and analyzing their potential as adsorbents and photodegradation catalysts for the removal of dye contaminants from wastewater.

Result and Discussion

1.1 Metal Organic Framework (MOF)

Through coordination connections between metal clusters and organic ligands, a material known as a metal organic framework (MOF) combines metal and organic components to create one-, two-, or three-dimensional structures. When followed by a numerical identifier, this abbreviation indicates a single metal organic framework structure [5]. A porous crystalline substance called a metal organic framework (MOF) is made up of metal clusters or centers joined by organic metal ions or linkers. For example, nitrogen-containing carboxylic acids are often used to make frameworks with metals such as zinc, copper, chromium, aluminum, zirconium, and other elements [6]. MOFs exhibit large surface area,

flexible structure, high crystallinity, and customizable pore size. In view of these characteristics, MOFs are widely used in a variety of processes, including gas storage, adsorption, separation, and catalysis. Their outstanding performance in various fields has led MOFs to be considered as an important member of the new generation of porous materials in recent years [7], [8]. The following diagram illustrates the formation process of MOFs in general.

1.2 Classification of Metal Organic Framework (MOF)

The assemblable Metal Organic Framework (MOF) exhibits a wide range of functional diversity. These MOFs can be classified into several groups based on their different constituent units [9].

1.2.1 Materials of Institut Lavoisier (MIL)

Dicarboxylic acid ligands and transition metal ions combine to generate compounds known as MIL (Materials of Institut Lavoisier) materials. The ability to modify the pore size configuration in response to external stimuli is what makes MIL materials special. Zhang et al. created a resistive humidity sensor with a high sensitivity and quick response by hydrothermally synthesizing MIL-101(Cr) [10].

1.2.1.1 MIL-100

Chromium with carboxylate trimer clusters are composed of metal-organic frameworks (MOFs). MIL-100(Cr) is a particularly attractive catalytic material because of its high thermal stability (270°C) and huge Langmuir surface area (3100 m²/g). The same as MIL-100(Fe) was produced using hydrothermal methods [11]. Another noteworthy MOF is MIL-101(Cr), which is prepared from chromium ions and terephthalate ligands. With two different groups of mesoporous cages and a three-dimensional porous structure, this material exhibits remarkable stability. Numerous Lewis active sites found in MIL-101(Cr) are crucial for adsorption processes. In addition, there are more active sites accessible for direct contact with pollutants during the adsorption process because to the large Langmuir surface area (2800 m²/g). MIL-100 finds great uses in the field of photocatalysis in addition to having a large specific surface area and robust structural stability.

1.2.1.2 MIL-101

Octahedral chromium (III) trimeric clusters joined by a 1,4-benzendicboxylate ligand [13] make up MIL-101(Cr) (Figure 3) [13]. This material is thermally stable up to 250°C and has a very high Langmuir surface area of 5900 m²/g. The effective adsorption of pollutants from water is made possible by this huge Langmuir surface area. Current research focuses on increasing the material's specific surface area in order to increase its adsorption capacity.

In contrast, MIL-101(Fe) has a low toxicity, an active iron center, and thermal stability up to 300°C. The catalytic performance of MIL-101 has been improved with recent amine modifications. For instance, NH₂-MIL-101(Fe) demonstrated superior organic contaminant degradation than MIL-101(Fe)

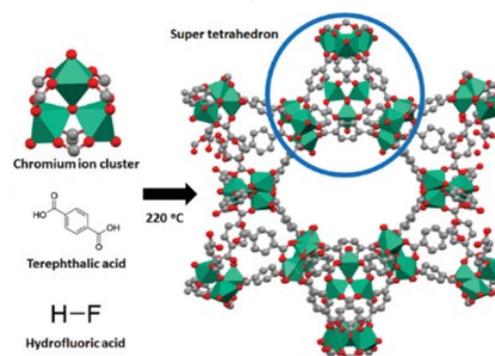


Figure 1. Synthesis of MIL-101 MOF compound [8]

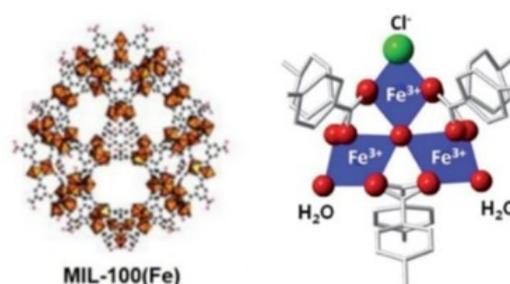


Figure 2. (a) Structure of MIL-100(Fe) [7], (b) Structure of MIL-101(Cr) [12]

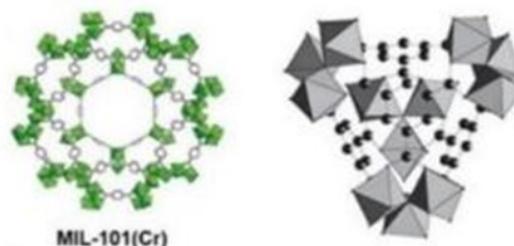


Figure 3. (a) Structure MIL-101(Cr) [8], (b) Structure MIL-101(Fe) [14]

[7].

1.2.2 Zeolitic Imidazolate Frameworks (ZIFs)

ZIF (Zeolitic Imidazolate Frameworks): ZIFs are a subclass of Metal Organic Framework (MOF) characterized by their zeolite-like topology. ZIFs are formed by linking transition metal ions (e.g., Zn, Co, Fe) in a tetrahedral coordination geometry with imidazole-based organic ligands. This specific combination results in several key properties such as regular porous structure, high surface area, and high stability that make ZIFs attractive materials for various applications.

1.2.2.1 ZIP-8

ZIP-8 has an enlarged three-dimensional structure and is a porous crystal. As seen in Figure 4a, it is made up of imidazolate ligands that bridge tetrahedral zinc ions. ZIP-8 has a rapid adsorption rate (achieving adsorption equilibrium in less than an hour) and a high adsorption capacity (highest adsorption capacity of 2500 mg/g) [15]. Additionally, the Zeolitic Imidazolate Framework (ZIF) generally possesses desirable chemical characteristics, a large pore size, and outstanding thermal stability. Because of these characteristics, ZIF is frequently utilized as a matrix to create novel MOF composites.

1.2.2.2 ZIP-67

Metal ions (Zn, Cu), organic ligands, and extra metal ions make up ZIP-67, a Metal-Organic Framework (MOF) material (Figure 4b). The pore size of ZIP-67 is determined by the selection of the constituent metal ion salts. This material was applied as a new adsorbent to remove malachite green (MG) from water because it is stable in water and easy to synthesize. Synthesis and characterization of ZIP-67 were carried out in preparation for use in MG adsorption from water. Lin & Chang's research showed that ZIP-67 has an MG adsorption capacity of up to 2430 mg/g at

20°C. This capacity increases at higher temperatures [16].

1.2.3 Porous Coordination Networks (PCNs)

PCNs are a type of material with a three-dimensional structure built from octahedral stereo and exhibit a "cage-within-a-cage" topology. Some examples of PCN materials include PCN-333, PCN-224, PCN-222, and PCN-57. Among the various PCN materials, PCN-222 is widely used for dye adsorption applications.

1.2.3.1 PCN-222

The highly organized nanoporous crystal PCN-222 is a member of the metal-organic framework (MOF) class. As seen in Figure 5a, this material is made up of metal ions (Mn, Fe, Co, Ni, Cu, Zn, and Pd) joined by organic molecules (ligands) to create a three-dimensional structure. PCN-222 has a maximum adsorption efficiency of 589 mg/g for cationic methyl orange (MO) and 906 mg/g for anionic methylene blue (MB) in a single dye solution, according to research by Li et al. The high adsorption capacity for both cationic and anionic dye types in aqueous solution was facilitated by PCN-222's large pore size and appropriate zeta potential. A high surface area, quick adsorption kinetics, and a simple desorption process are further advantages of PCN-222 [17].

1.2.3.2 PCN/MIL-100 (Fe)

A composite material integrating a PCN layer on the MOF structure was successfully prepared through protonation of graphene carbon nitride (g-C₃N₄) powder followed by sol coating using a porous MIL-100(Fe) framework (Figure 5b). The PCN/MIL composite showed potential in facilitating three different photocatalytic processes, namely rhodamine B (RhB) or methylene blue (MB) dye degradation and pyridine oxidative denitrification, all using visible light as the energy source. The presence of PCN on MIL-100(Fe) adjusts its specific surface area and porous size to the optimal range, thereby in-

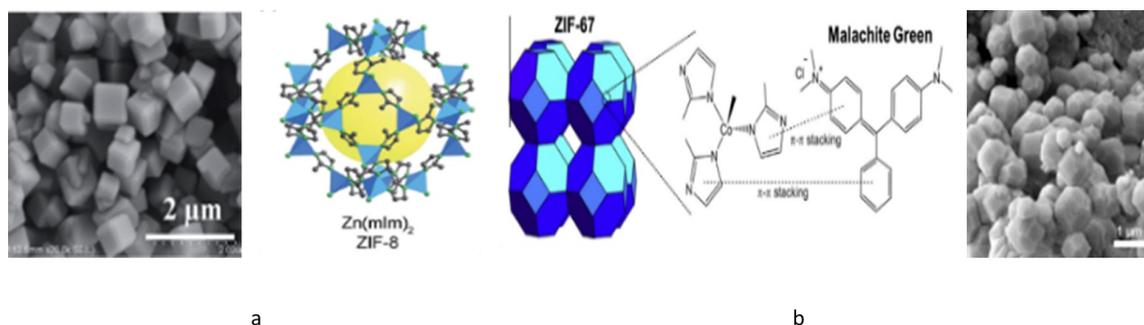


Figure 4. (a) Structure and SEM of ZIP-8 [15], (b) Structure of ZIP-67 [16].

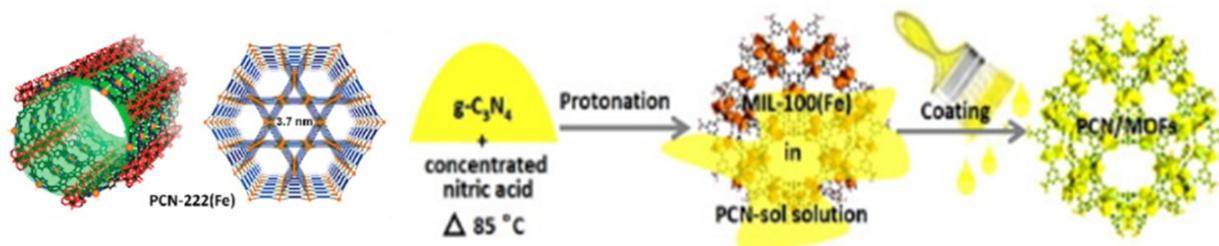


Figure 5. (a) Structure of PCN-222 [19], (b) forming process of PCN/MIL-100 (Fe) zango [18].

creasing the adsorption efficiency for the specified contaminant molecules. In addition, the MIL-100(Fe) framework contributes to the presence of several active species that play an important role in reactions involving RhB and pyridine. The main active species involved in the photocatalytic transformation of RhB, MB, and pyridine are the combined effects of hydroxyl radicals ($-\text{OH}$) and superoxide anions ($-\text{O}_2^-$), along with hydrogen cations ($-\text{H}^+$) and superoxide anions ($-\text{O}_2^-$), as identified by research (Huang et al., 2018)[18].

1.3 Organometallic Compounds as Dye Adsorbent

Adsorption is an efficient alternative method for removing contaminants in wastewater treatment. The process involves the attraction of contaminant molecules to the adsorbent surface through diffusion from the solution to the active pores of the adsorbent [20]. Adsorption mechanisms occur through intermolecular interactions such as chemisorption, which includes ionic interactions, and physisorption, which involves π - π interactions [21]. The effectiveness of adsorption is determined by the intrinsic characteristics of the adsorbent, including high porosity, large surface area, thermal stability, and ease of regeneration, which enable high selectivity to specific contaminants [20].

Among carbonaceous porous materials, activated carbon (AC) is the most commonly used [22], although it is derived from non-renewable sources such as lignite, coal, and petroleum coke. AC has drawbacks in removing pollutants at low concentrations and has an inefficient regeneration process. However, advances in materials science have enabled the development of new adsorbents with increased porosity and surface area, such as mesoporous silica, Molecular Imprint Polymers (MIPs), and Metal Organic Frameworks (MOFs), which offer better selectivity and higher pollutant removal capacity, mainly due to the tunable pore size on the MOF framework [20].

1.3.1 Adsorption of Methyl Orange (MO) Dye

The study examined the ability of MIL-100 (Fe) in removing Methyl Orange (MO) dye. Based on the data in Table 1, MIL-100(Fe) showed better adsorption performance compared to its Cr-based counterpart. This study observed the MO sorption behavior of MIL-100(Fe) and MIL-100(Cr) through the measurement of MO adsorption kinetics. The MO adsorption capacity on MIL-100(Fe) increased rapidly within 3 days, while MIL-100(Cr) showed a slower but sustained increase even after 22 days. At a concentration of 1000 ppm (CO), the MO adsorption capacities of these two solids exceeded those reported for other MOFs, as shown in Figure 6. A thorough comparison was carried out at a con-

Table 1. Use of organometallic compounds as dye adsorbents

Color Substances	Organometallic Compounds	Concentration (mg L^{-1})	Maximum Adsorption Capacity (mg g^{-1})	Recycling (%)	Equilibrium Time	Ref.
Methyl Orange	Mil-100 (Fe)	30	1045.2	85	-	[23]
	Mil-100 (Cr)	30	211.8	8	22 days	[23]
	PCN-222	10	589	70	50 minutes	[24]
Methylen Blue	Mil-100 (Fe)	30	736.2	100	3 days	[23]
	Mil-100 (Cr)	30	645.3	100	-	[23]
	PCN-222	10	906	78	50 minutes	[24]
	ZIF-8	20	2500	99	30 minutes	[25]
Malachite Green	ZIF-67	50	2430	100	2 hours	[26]

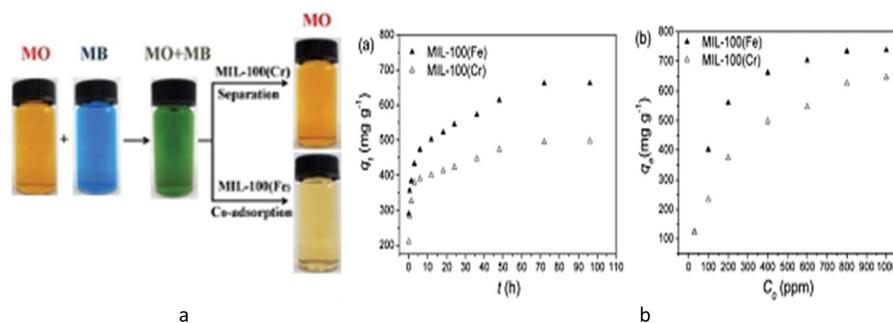


Figure 6. (a) Separation process of MO-MB mixture by MIL-100 (Fe, Cr), (b) Effect of sorption contact time and initial concentration of MB by MIL-100 (Fe, Cr) [27].

tact time of 3 days [27]. The two MOFs showed different behaviors, with MIL-100(Fe) outperforming its Cr counterpart. Moreover, PCN-222 efficiently removed 92.7% of the dye in 60 min equilibrium testing, showing high adsorption capacity of MO at pH 5. In the meantime, when MO and MB were present in solution at the same time, MO's adsorption capability significantly increased [17]. (Li and others, 2017). PCN-222 demonstrated a maximum loading efficiency of 906 mg/g for anionic methylene blue (MB) and 589 mg/g for cationic methyl orange (MO) in a single dye system in comparison to the study that was cited. It's interesting to note that the combined capacity of MB and MO in solution rose by 36.8% (to 1239 mg/g) and 73.5% (to 1022 mg/g) respectively. These findings unequivocally show that PCN-222 preferentially adsorbs MB over MO.

1.3.2 Methylene Blue (MB) Dye Adsorption

The study evaluated the adsorption ability of two materials, MIL-100(Fe) and MIL-100(Cr), which have negatively charged surfaces in water on methylene blue (MB) dye. The results showed that MIL-100(Fe) was able to adsorb 736.2 mg/g MB, while MIL-100(Cr) adsorbed 645.3 mg/g. These values are high compared to other materials. Both materials showed similar MB adsorption patterns, indicating that the type of metal did not have a significant effect. However, the presence of other solutes in water may affect the dye adsorption process. The data obtained fit the second-order pseudo-kinetic model and the Langmuir isotherm model. Adsorption tests using a mixture of two dyes, methyl orange (MO) and MB, showed differences in the behavior of the two materials. MIL-100(Fe) was able to adsorb 85% MO and 100% MB, while MIL-100(Cr) adsorbed only 8% MO but 100% MB [27]. Research by Pasaribu et al. also showed that the

sorption of MO by MIL-100(Fe)@Fe₃O₄ follows second-order pseudo kinetics with a rate constraint value of 3.963×10^{-2} g/mg.min and an adsorption capacity of 151.47 mg/g following the Langmuir isotherm [28]. This indicates that the type of metal in the material can affect the adsorption selectivity towards different dyes. In general, MIL-100(Fe) was able to adsorb MO and MB rapidly, while MIL-100(Cr) was more selective to MB in a mixture of MO and MB.

This study highlights the versatility of Metal Organic Frameworks (MOFs), specifically PCN-222 (MOF-545), in textile wastewater treatment, with emphasis on the effect of metal ion substitution. PCN-222 was synthesized and its structure was confirmed using XRD and FT-IR. Li et al. [17] (Li et al., 2017) studied the adsorption performance of PCN-222 on MB dyes, both individually and in combination with other dyes. They found that the adsorption capacity of PCN-222 increased significantly at pH above 5, removing 95.2% of the dye in 60 minutes (figure 7a). The capacity also [29] increased when MB and MO were simultaneously present in the solution. Another study by Feng et al. [29] used Zeolitic Imidazolate Framework-8 (ZIF-8) as an adsorbent for MB. They found that high surface area alone does not guarantee MB adsorption. Although ZIF-8 has a pore size of about 3.4 Å, the theoretical size of MB is too large to fit into the pore. However, because of the interaction between the positively charged ZnO core (Zn(OH)⁺) and the negatively charged MB functional group (-SO₃⁻), ZIF-8 exhibits great selectivity in MB adsorption. ZIF-8 has a fast adsorption rate (achieving saturation in 30 minutes), 99% purity, and a greater MB adsorption capacity than the majority of the reported adsorbents (maximum capacity of 2500 mg/g).

1.3.3 Adsorption of Malasite Green (MG) Dye

ZIF-67 was synthesized and characterized

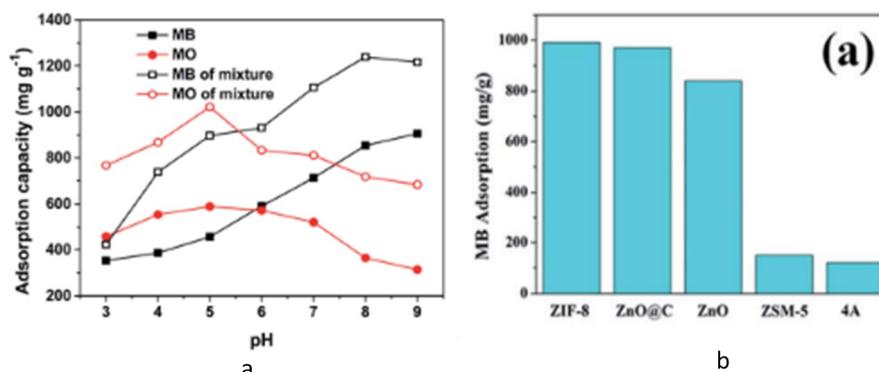


Figure 7. (a) Effect of initial pH on the adsorption capacity of MB and MO in single system and MB-MO mixture [17], (b) adsorption capacity of MB on different adsorbents [29].

for application in the adsorption of green malazite (MG) from water. Fourier transform infrared (FT-IR) analysis showed the ability of ZIF-67 to rapidly remove MG through the adsorption process (Figure 8). Mixing ZIF-67 with MG solution and stirring for 10 minutes resulted in almost complete removal of the dark green color. This shows the potential of ZIF-67 as an effective MG adsorbent. The adsorption capacity of ZIF-67 towards MG reached 2430 mg/g at 20°C and can be increased at higher temperatures. The dye removal quality reached 100% with an equilibrium time of 2 hours. The mechanism underlying this high adsorption capacity is proposed to be related to the π - π overlap interaction between MG and ZIF-67 [16]. This capacity of ZIF-67 is almost 10 times higher than traditional adsorbents such as activated carbon and biopolymers.

1.4 Organometallic Compounds as Photodegradation Catalysts

Photocatalysis refers to a specific set of catalytic reactions triggered by light energy. Photocatalytic degradation is an advanced oxidation process that uses photocatalyst materials to efficiently decompose toxic pollutants from wastewater. In this process, light energy is converted into chemical energy, producing chemical radicals such as hydroxyl radicals that attack pollutants and break them down into non-toxic by-products [20].

The ideal photocatalytic material should be able to tolerate intense light irradiation and be stable in both organic and aqueous solvents, as well as in basic or acidic solutions. Furthermore, photocatalytic degradation should be very porous, economical, simple to use, and readily regenerable. As a result, a variety of porous materials have been found, such as mesoporous and

microporous materials, which are notable for their consistent diameter, pore volume, particle size, and surface morphology. Various mechanically engineered porous materials have been identified for wastewater treatment applications, including organometallic compounds as depicted in Table 2.

1.4.1 Photodegradation of Methylene Blue (MB) dye

Hariganesh et al. conducted photocatalytic activity research using Metal Organic Frameworks (MOFs) and nanocomposites. MOFs, such as MIL-101(Cr) with a surface area of 6000 m²g⁻¹, and nanocomposites such as CuCr₂O₄/CuO, which have a high surface area and porous structure, support photocatalytic activity as shown in Figure 9a. These two materials work together in absorbing light photons, forming electron-hole pairs, and triggering redox reactions that generate hydroxyl radicals (OH⁻) that are highly reactive for decomposing organic pollutants [39].

The synthesis of MIL-101(Cr) was carried out hydrothermally using terephthalic acid, Cr(NO₃)₃·9H₂O, and HF (40%) in deionized (DI) water. Cu-Cr₂O₄/CuO nanocomposites were synthesized using

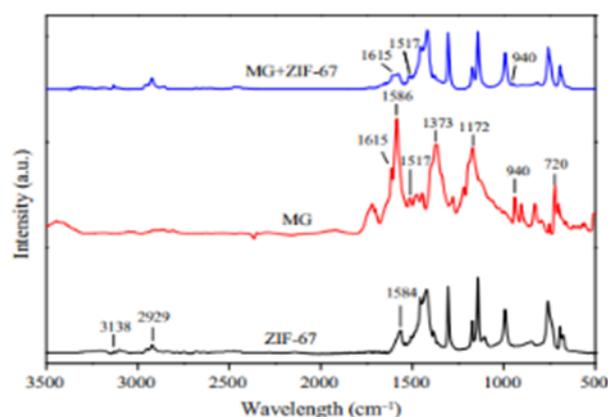


Figure 8. FT-IR spectra of ZIF-67, green malazite and recovered ZIF-67 at room temperature [16].

Table 2. Application of organometallic compounds as dye photodegradation catalysts

Color Substances (Pollutants)	Organometallic Compounds	Surface Area (m ² g ⁻¹)	Light Source	(%) Degradation	Radiation Time	Ref
Methylen Blue	MIL-101(Cr)	2361	Ultraviolette	90	35 minutes	[30]
	TiO ₂ -MIL-101 (Cr)	531	Ultraviolette	100	30 minutes	[31]
	PCN/MIL-100 (Fe)	1252	Visible Light	75	200 minutes	[32]
	CuO-ZnO/ZIF-8	-	Visible Light	59	100 minutes	[33]
Methyl Orange	MOF-199-NH ₂	-	Ultraviolette	98	50 minutes	[34]
Congo Red	Fe ₃ O ₄ @ZIF-67	300,7	Visible Light	70	-	[35]
	ZIF-8/HKUST-1	-	Ultraviolette	91	60 minutes	[36]
Basic Blue 41	MIL-100 (Fe)	5	Ultraviolette	99	180 minutes	[37]
	MOF-199	343	Ultraviolette	99	180 minutes	[38]

MIL-101 by mixing Cu(NO₃)₂·3H₂O with ethanol. In a visible light photoreactor equipped with a 300 W halogen lamp, photocatalytic investigations were conducted. In the process, light attracted electrons in the CuCr₂O₄/CuO valence band (VB) to the conduction band (CB), where they mixed with H₂O₂ to produce hydroxyl radicals (OH·) and hydroxyl ions (OH⁻), which converted contaminants into innocuous chemicals. CuCr₂O₄/CuO nanocomposites shown outstanding photocatalytic activity in the destruction of organic contaminants and were successfully manufactured utilizing a straightforward technique using MIL-101(Cr) as the template. These composites demonstrated a degradation efficiency of roughly 90% for MB solution in 35 minutes and 95% in 60 minutes when H₂O₂ was present.

The TiO₂-MIL-101 composite acts as a photocatalyst in the degradation of MB dye, utilizing the photocatalytic properties of TiO₂. When exposed to UV light, this material triggers a photocatalytic reaction that leads to the degradation

of MB dye molecules in aqueous solution. This process is due to TiO₂'s ability to generate reactive oxygen species (ROS) upon light absorption, which can oxidize and decompose the dye molecules into less harmful substances. Following hydrothermal synthesis and characterization, the composite had a pore volume of 1.2 cm³ g⁻¹ and a BET surface area of 531 m² g⁻¹. When exposed to visible light, it demonstrated increased photocatalytic activity and a greater adsorption affinity for MB, which resulted in nearly 100% destruction of MB in water (figure 9b). The MIL-101 substrate facilitates the composite's high surface area, which supports the photocatalytic process. In conclusion, MB is successfully removed from aqueous solutions by the TiO₂-MIL-101 composite, which combines the adsorption and catalytic activities of MIL-101 and TiO₂. [40].

MIL-100(Fe) serves as a photocatalyst for MB dye degradation through adsorption and photocatalysis processes. This MOF adsorbs dye molecules onto its surface and pores, helping to remove MB from solution. When modified with protonated

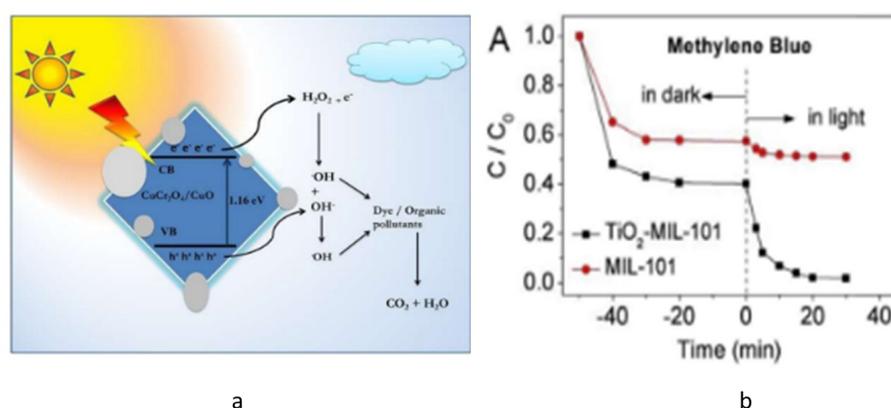


Figure 9. (a) Schematic scheme of organic pollutant degradation mechanism by photocatalytic reaction of H₂O₂ addition of CuCr₂O₄/CuO nanocomposites [39], (b) adsorptive and photocatalytic activities of MIL-101 and TiO₂-MIL-101 for MB adsorption and degradation [40].

g-C₃N₄ (PCN), its photocatalytic activity increases, thus facilitating the separation of light-excited electron-hole pairs. MIL-100(Fe) was hydrothermally synthesized at 150°C for 12 hours. In the photocatalytic degradation process, the catalyst was added to the MB dye solution, and then the suspension was subjected to a 300 W Xe lamp under dark conditions to initiate a photo-reaction, resulting in 53.4% degradation of the MB dye over 200 min (Figure 10). This process involves the formation of highly reactive species such as superoxide radicals ($\cdot\text{O}_2^-$) and the combination of light-excited holes (h^+) with superoxide radicals ($\cdot\text{O}_2^-$) that can oxidize and degrade MB [18]. Overall, the combination of adsorption and photocatalysis on MIL-100(Fe) and PCN/MIL composite is effective in decomposing MB.

The combination of ZIF-8 with semiconductors such as CuO-ZnO can improve the photocatalytic activity and reduce the recombination rate of charge carriers in the photocatalysis process. This combination overcomes the limitations of ZnO and CuO photocatalysts, such as wide band gap and low specific surface area. The addition of ZIF-8 into the CuO-ZnO photocatalyst improves the overall photocatalytic performance. ZIF-8 provides additional active sites for adsorption and degradation of organic dyes such as Methylene Blue (MB). Its high surface area allows efficient contact between the photocatalyst and dye molecules, thus increasing the degradation efficiency. Based on the research of Abdollahi et al. (Abdollahi et al., 2021), CuO-ZnO/ZIF-8 showed photocatalytic activity by removing 59% of MB (10 mg.L⁻¹) in 100 minutes under simulated sunlight. According to the results, the ideal CuO-ZnO/ZIF-8 composition is 20% W/W since it

has superior optical and physico-chemical characteristics. Investigations were also conducted on the effects of a number of operating parameters, including beginning pH, photocatalyst dosage, and pollutant concentration. According to the findings, CuO-ZnO/ZIF-8 exhibited the maximum photocatalytic activity at an initial pH of 7, a photocatalyst load of 1 g/L, and an AO7 concentration of 80 mg/L. Furthermore, under ideal circumstances, the activity dropped by just 16% following four cycles of operation, demonstrating the photocatalyst's remarkable stability. As a result, the novel CuO-ZnO/ZIF-8 photocatalyst may offer a viable way to remove MB dye.

1.4.2 Photodegradation of Methyl Orange (MO) dye

Research by Ayati et al. [41] used MOF-199-NH₂, an organometallic framework modified with amine, and BaWO₄ to enhance the photocatalytic activity in organic dye degradation. BaWO₄ was hydrothermally synthesized and then combined with MOF-199-NH₂ to form nanocomposites. Photocatalysis tests showed that these nanocomposites were effective in degrading methyl orange (MO) and 4-Nitrophenol (4-NP) dyes, reaching peak efficiencies of about 98% and 79% within 50 and 80 minutes irradiation time, respectively (Figure 11). The presence of MOF-199-NH₂ and BaWO₄ forms a heterojunction system that allows the creation of a local electric field at the interface, thus effectively separating electron pairs. This efficiency is higher under UV light conditions compared to dark conditions. The photocatalysis mechanism involves the formation of electron pairs at the MOF-BaWO₄ interface, which then separates the electron pairs and enhances the photocatalytic activity.

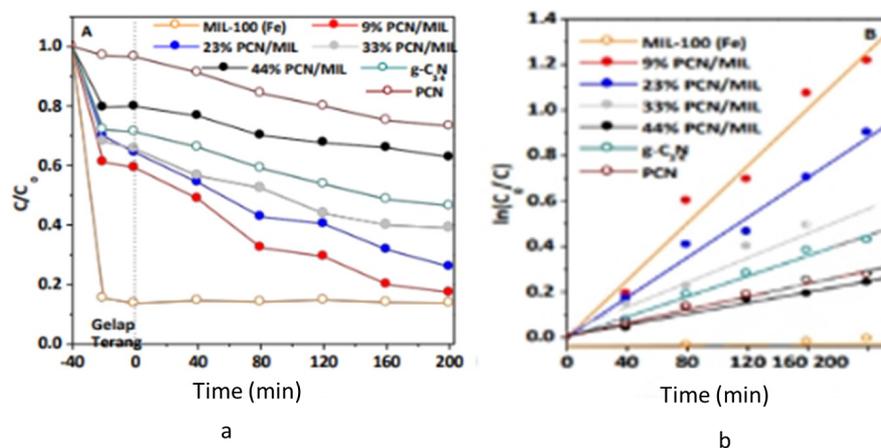


Figure 10. Adsorption and photocatalyst profiles (a) and first-order kinetics plot (b) of MB degradation of MIL-100(Fe)-g-C₃N₄, PCN and X%PCN/MIL [18].

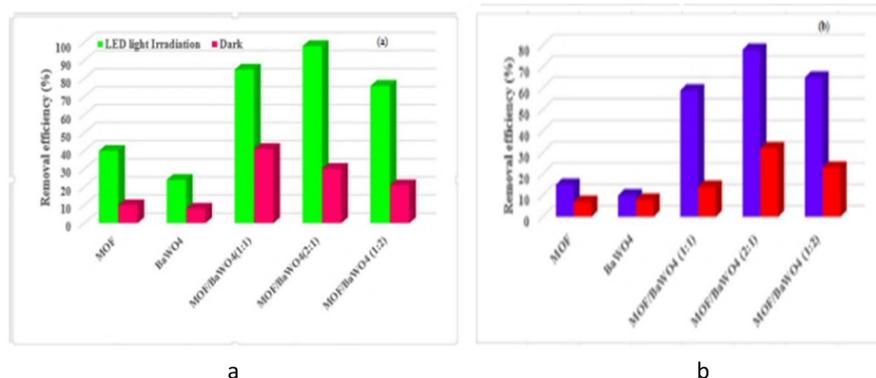


Figure 11. Photocatalytic degradation results for (a) MO and (b) 4-NP contaminants catalyzed with various weight ratios of MOF-199-NH/BaWO₄ composites under UV irradiation and dark conditions [41].

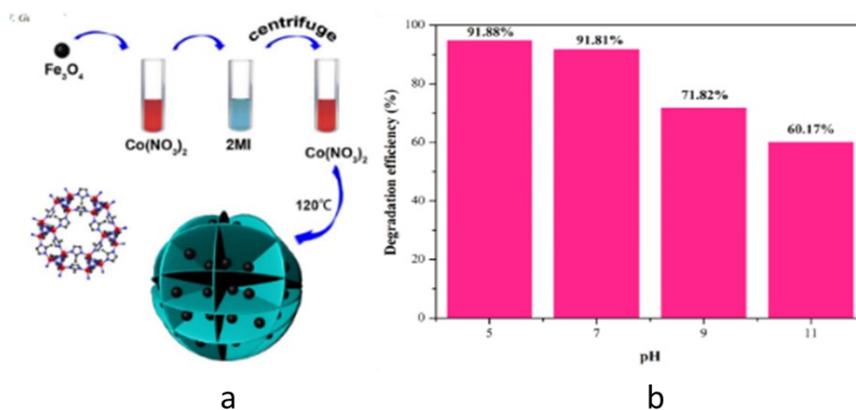


Figure 12. Synthesis of Fe₃O₄@ZIF-67 microspheres [42] (Guan et al., 2017), (b) Effect of pH on CR dye degradation by ZIF-8/HKUST-1 [43].

1.4.3 Photodegradation of Congo Red (CR) dye

The Fe₃O₄@ZIF-67 composite material, which consists of magnetite nanoparticles (Fe₃O₄) and metal organic framework (ZIF-67) as shown in Figure 12a, exhibited significant photocatalytic activity when exposed to visible light. This makes the material a potential solution for the degradation of Congo Red dye in wastewater. The photocatalysis process involves the formation of active species, specifically hydroxyl radicals (-OH) and superoxide radicals (-O₂⁻), which play an important role in degrading congo red dye [42]. This photocatalytic process occurs on the surface of Fe₃O₄@ZIF-67 nanocomposite under visible light irradiation. The composite is magnetically recoverable and retains its high photocatalytic activity even after multiple reuse cycles, demonstrating its potential for dye removal from wastewater.

ZIF-8/HKUST-1 composites, composed of two different metal organic frameworks, were solvothermally synthesized. The addition of graphene oxide (GO) with mass variation produces a

heterojunction structure that has potential for photocatalysis applications. The process involves adsorption and photocatalysis to decompose Congo Red dye. Electron-hole pairs are created in the valence bands of ZIF-8 and HKUST-1 when exposed to UV light. The excited electrons leave holes in the valence band when they migrate from the valence band to the conduction band. Electrons can move more easily from the HKUST-1 conduction band to the ZIF-8 valence band when graphene oxide (GO) is added as an electron mediator. This aids in maintaining substantially oxidized holes in the valence band of HKUST-1 and significantly reduced electrons in the conduction band of ZIF-8 (Figure 13). Through hydrogen bonding, electrostatic contact, and π - π overlap interaction, the active sites on GO/ZIF-8/HKUST-1 contribute to the binding of Congo Red dye. Active species for dye degradation are created by reactions with oxygen and water molecules. The GO(10)/ZIF-8/HKUST-1 composite showed a degradation efficiency of 91.81% in 60 minutes for a Congo Red concentration of 50 mg/L (Figure 12b).

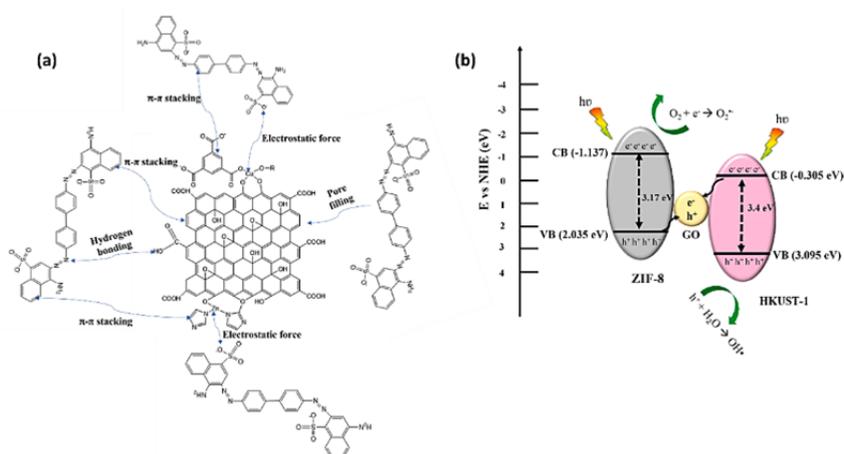


Figure 13. Mechanism of (a) adsorption (b) photocatalytic GO(10)/ZIF-8/HKUST-1 [43].

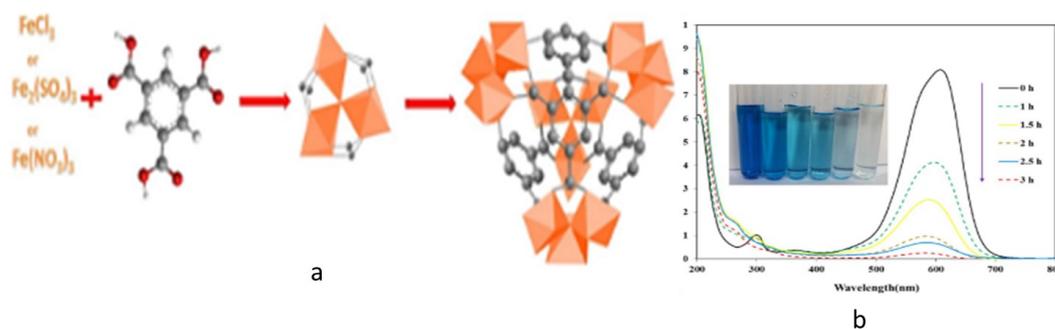


Figure 14. (a) Synthesis of different MILs-100 (Fe) as metal-organic framework [44], (b) UV-Vis spectral changes of dye during photocatalytic degradation of BB41 by MOF-199 [45].

1.4.4 Photodegradation of Basic Blue 41 (BB41) dye

Three iron compounds— FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, and $\text{Fe}_2(\text{SO}_4)_3$ —known as MIL-100-1, MIL-100-2, and MIL-100-3, respectively, were used to create MIL-100(Fe), a metal organic framework. The hydrothermal method was used in the synthesis process, as seen in figure 14, and the solids that were produced were dried and purified. MIL-100(Fe) has the ability to remove dye by acting as a photocatalyst. Its surface produces electron-hole pairs (e^-/h^+) when exposed to UV light. Electrons in MIL-100(Fe) migrate from the valence band (VB) to the conduction band (CB) due to the absorbed energy, leaving holes in the VB. These excited electrons in the conduction band of MIL-100(Fe) can react with organic dye molecules, leading to their degradation. Photocatalytic dye degradation experiments show that the decolorization increases with the increase of MIL-100 dosage and decreases with the increase of dye concentration. This photocatalyst can be recycled and reused several times with high efficiency.

Therefore, MIL-100 had a significant effect on the degradation of BB41 dye.

Hydrothermally synthesized MOF-199 exhibits photocatalytic activity under UV irradiation, promoting the degradation of BB41 dye in wastewater. This degradation process is mediated by the formation of reactive oxygen species (ROS) upon light absorption by the MOF, leading to the formation of electron-hole pairs. These highly reactive species then target organic pollutants, resulting in their breakdown through azo bond cleavage. As shown by Mahmoodi et al. (figure 14b), MOF-199 effectively degraded 99% of BB41 dye under UV light within 3 hours. It should be noted that the efficiency of this decolorization process is affected by factors such as catalyst load, initial concentration of dye, and solution pH. Such results indicate that the synthesized MOF-199 has potential as a photocatalyst for wastewater treatment, specifically for the removal of BB41 dye.

Conclusion

Dye contaminants in water are a serious

problem due to their toxicity and detrimental impact on all forms of life. Conventional wastewater treatment methods are often ineffective in the complete removal of these dyes, due to their low total removal concentration and slow process. However, advances in science have led to alternative solutions, such as the use of Metal-Organic Frameworks (MOFs) as catalysts and adsorbents. MOFs, including Lavoisier Institute Materials (MILs), Zeolitic Imidazolate Frameworks (ZIFs), and Porous Coordination Networks (PCNs), were shown to be effective in adsorbing certain dyes from aqueous solutions, exhibiting high adsorption and catalytic capacities. These MOFs, either singly or in composite form with metal oxides, can significantly reduce dye contaminants in water. Their mechanisms of action include enhancing the interaction between dye molecules and the adsorbent surface, or acting as photocatalytic degraders through the reaction between the valence and conduction bands of the catalyst material with H₂O₂, producing radicals that oxidize dye pollutants. This review article provides a comprehensive understanding of these three aspects, beneficial to readers in this field.

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