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Vanadium-Based Materials as Photocatalysts for the Degradation of Methylene Blue

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Submitted in fulfilment of the requirements for the
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Declaration

This thesis has been written and compiled by the author, WenXuan Yan, who carried out the research at the University of Glasgow between 2024 and 2026 in the School of Chemistry, under the supervision of Professor Ross Forgan. Where collaborative results have been included in this thesis, the contributions of others have been appropriately acknowledged.

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I do not yet know whether I will continue in chemical research, but the person who has seen the sea is no longer the same as the person who had not. I am grateful for this experience and to everyone who offered me guidance, friendship, and support along the way.

Abstract

The performance of metal-organic framework (MOF) photocatalysts cannot be assessed from surface area alone, because dye removal in aqueous media also depends on molecular accessibility, mass transfer, light-source-dependent response, and framework stability. Three vanadium-based MOFs constructed from distinct tetratopic carboxylate ligands V-MOF-10, V-TBAPy, and V-TCPB were synthesized solvothermally and evaluated using methylene blue (MB) as a model pollutant. Their structural and physicochemical properties were characterized by PXRD, SEM, FT-IR, nitrogen sorption, TGA, and V K-edge XAS. Dark adsorption followed by light-induced removal was investigated at different catalyst dosages under ultraviolet and AM 1.5G simulated solar irradiation.

All three materials formed crystalline vanadium–carboxylate frameworks, but their accessible porosity differed markedly. The BET surface areas of V-MOF-10, V-TCPB, and V-TBAPy were 1300, 485, and 314 m² g⁻¹, respectively, but this order was not reproduced in aqueous adsorption of MB. V-MOF-10 showed slower site utilization, consistent with diffusion limitations within its narrow micropores; V-TBAPy exhibited the fastest initial adsorption response; and V-TCPB provided a more favourable balance between accessible sites and mass transfer. At a catalyst dosage of 5 mg, total MB removal after dark adsorption and subsequent ultraviolet irradiation was approximately 37%, 57%, and 95% for V-MOF-10, V-TBAPy, and V-TCPB, respectively. Under simulated solar irradiation, the corresponding values were 99%, 94%, and 97%, shifting the performance order in favor of the porphyrin-based V-MOF-10. This reversal may reflect a better match between the light-response characteristics of its TCPP-based framework and the broader spectral distribution of the simulated solar source. PXRD comparison of the fresh, post-adsorption, and post-UV-photocatalysis samples showed that the principal framework reflections were retained after treatment, with V-TCPB exhibiting the strongest structural retention.

Ligand selection therefore regulates the combined effects of pollutant pre-enrichment, pore

accessibility, light-source-dependent performance, and structural persistence. Under the

tested conditions, the most effective framework depended on the irradiation environment rather than on porosity alone. Because the two light sources were not photon-flux matched, their comparison reflects overall performance under the applied irradiation conditions rather than intrinsic spectral efficiency. These structure–function relationships provide a basis for designing vanadium-based MOFs for integrated adsorption–photocatalytic treatment of dye-contaminated water.

Keywords: vanadium-based metal–organic frameworks; ligand structure; methylene blue; adsorption–photocatalysis; wastewater treatment

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Chapter 1 Introduction

1.1 Research Background and Significance

1.1.1 Background of Dye Wastewater Pollution

Since the textile, printing, dyeing, pharmaceutical, leather, and dye industries are rapidly developing, large quantities of dye-containing wastewater are pumped into natural bodies of water, becoming an important source of global environmental pollution.^{1,2} According to statistics, more than 700000 tons of synthetic dyes are produced annually globally, and 10% to 20% are pumped into water systems during manufacturing and use process,³ causing significant water pollution. Dye wastewater not only causes obvious visual pollution to water bodies, but more importantly, it poses a serious threat to aquatic ecosystems and human health. Dyes usually have high chemical stability and complex aromatic ring structures, which makes them extremely difficult to degrade in water bodies and become persistent organic pollutants (POPs).⁴

The impact of dye wastewater on the water environment is multifaceted. Firstly, the high coloration in the wastewater significantly reduces the light transmittance of the water body, inhibiting the photosynthesis of aquatic plants, thereby disrupting the primary productivity and ecological balance of the water body. Secondly, many dyes and their degradation products are toxic, mutagenic, and potentially carcinogenic. Long-term exposure of aquatic organisms to these pollutants may be affected, and these harmful substances are transmitted through the food chain, ultimately potentially affecting human health.

Therefore, how to effectively treat dye wastewater and reduce its impact on the environment and ecosystem has become a key issue that urgently needs to be addressed in the current water environment governance field.⁴

1.1.2 Structure and Characteristics of Dyes

The structural characteristics of dye molecules are key factors influencing their environmental persistence, degradability, and treatment difficulty. Dyes typically consist of multiple aromatic rings or similar conjugated structures. These structures not only endow dyes with vivid colors but also give them high chemical stability and low biodegradability, making it difficult for dye molecules to be decomposed by microorganisms in the natural environment.^{5,6}

As an exemplar dye, Methylene Blue is a widely used organic dye whose functionalized phenothiazine skeleton contains an extended planar π -conjugated system.⁷ This structure promotes electron delocalization, contributing to the optical/electrochemical activity and chemical stability of MB in aqueous environments. In addition, nitrogen-containing sites may facilitate interactions with surrounding aqueous species, further hindering its degradation.⁸ Consequently, MB exhibits poor biodegradability and can persist in water for extended periods, particularly under low-temperature or acidic conditions, making it a representative persistent organic pollutant in dye-contaminated wastewater.⁹

Rhodamine B is another common dye. Its molecular structure contains xanthene-based chromophore with multiple nitrogen and oxygen atoms. This rigid, conjugated structure contributes to its chemical stability in water, while the nitrogen and oxygen atoms facilitate interactions with aqueous species. However, Rhodamine B undergoes dynamic equilibrium in solution, so its stability is relative rather than absolute, and its degradation can still occur under certain conditions.^{9–11}

Methyl Orange differs in structure from Methyl Blue and Rhodamine B. Its molecule contains a strongly acidic sulfonic acid group and two aromatic rings connected by an azo bond ($-\text{N}=\text{N}-$).^{12,13} The azo bond allows Methyl Orange to be degraded under reducing conditions, but in the oxidative natural environment, this bond has relatively high stability, making the degradation of Methyl Orange rather difficult.¹⁴ Notably, the degradation of

Methyl Orange is closely related to the pH value of the water body: it has stronger stability in an acidic environment and is more easily degraded in an alkaline environment.¹³

Congo Red is a typical azo dye with two azo groups in its molecule, and its structure is more complex. The molecular structure of Congo Red is composed of multiple aromatic rings and azo groups, forming a longer conjugated system, which makes it highly stable in water and difficult to remove through biodegradation. Even during partial degradation, Congo Red may produce toxic aromatic amine intermediates, further increasing the difficulty of its treatment.^{14–16} The molecular structures of the four representative dyes discussed above are shown in Figure 1.1.

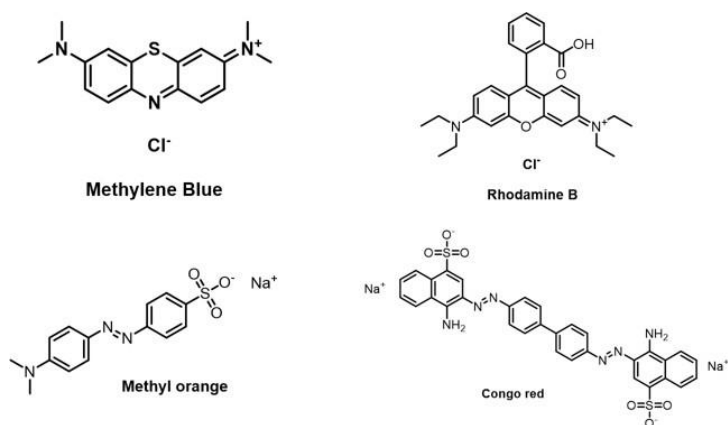


Figure 1.1 Schematic diagrams of the molecular structures of four common organic dyes

Overall, these dyes possess extended conjugated aromatic systems with key functional groups such as azo bonds, nitrogen, and sulfur, which confer high chemical stability and low biodegradability. Consequently, they persist in water, acting as typical refractory pollutants and posing significant challenges for wastewater treatment. Developing efficient treatment strategies to mitigate their environmental impact thus remains a critical research focus.^{17,18}

1.1.3 Limitations of Dye Wastewater Treatment Technologies

Currently, the common methods for treating dye wastewater mainly include physical adsorption, chemical oxidation, and biodegradation. Although these technologies play an important role in wastewater treatment, they still have significant limitations when dealing with dye wastewater.¹⁹ Figure 1.2 shows the classification of common water/wastewater treatment technologies, with common treatment techniques listed under each method, providing a framework for the subsequent discussion of the limitations of dye wastewater treatment technologies.

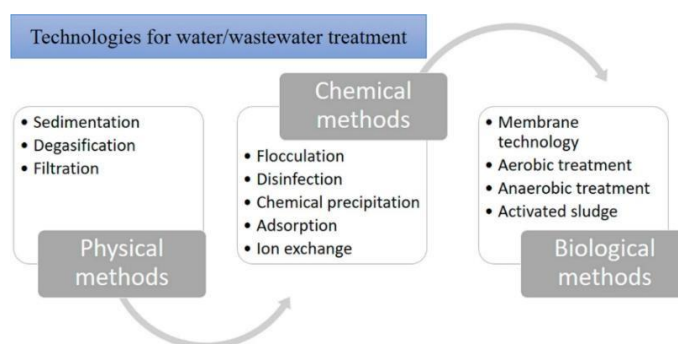


Figure 1.2 Schematic diagram of the classification of water/wastewater treatment technologies. Adapted from Ref.²⁰

Physical adsorption technology, especially the use of activated carbon, is widely applied for its simple operation and good initial removal effect, which can effectively remove various dyes.^{21,22} The high porosity and large surface area of activated carbon enable it to effectively adsorb dye molecules in aqueous solutions.^{23,24} For instance, Ullah et al. reported that boric acid-functionalized activated carbon prepared from *Sesbania sesban* stems could effectively remove methylene blue from aqueous solution, achieving a maximum uptake capacity of 1380 mg g^{-1} under optimized conditions.^{25,26} However, in practical applications, activated carbon adsorption faces the problems of high regeneration cost and low selectivity.²² Activated carbon is prone to saturation during use and requires regular replacement or regeneration, which not only increases the operating cost but may also lead to secondary pollution if mismanaged.²² Moreover, the limited selectivity of

activated carbon means that its adsorption capacity for different dye molecules is relatively limited, and it often fails to efficiently remove a wide spectrum of dyes, resulting in low treatment efficiency.^{21,27}

Chemical oxidation technologies, such as Fenton reaction, ozone oxidation, degrade organic pollutants through the generation of highly reactive species. In the classical Fenton process, Fe^{2+} activates H_2O_2 to generate hydroxyl radicals, while the subsequent $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycle contributes to continued reactive-species generation. As illustrated in Figure 1.3, hydroxyl radicals oxidize organic pollutants, although competing recombination and radical-scavenging reactions may reduce the effective utilization of H_2O_2 . These methods can achieve high removal efficiencies, particularly for refractory dyes.¹⁹

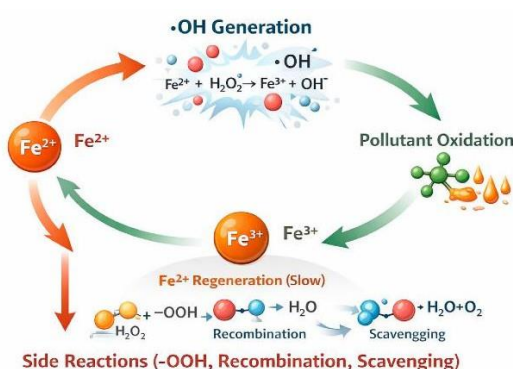


Figure 1.3 Simplified mechanistic scheme of the classical Fenton reaction, illustrating $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycling, H_2O_2 activation, hydroxyl-radical generation, pollutant oxidation, and competing side reactions. Reproduced from Ref.²⁸

For example, Slama et al. investigated the decolorization of reactive dyes using the Fenton reaction, in which Fe^{2+} catalytically activates H_2O_2 to generate highly oxidative hydroxyl radicals ($\cdot\text{OH}$) that attack the chromophoric structures of dye molecules. As shown in Figure 1.4, under acidic conditions ($\text{pH} = 3$) with a dye/ Fe^{2+} / H_2O_2 ratio of 1:3.9:50, the color removal efficiencies of Reactive Yellow 176, Reactive Blue 4, and Reactive Red dye increased progressively with reaction time and reached 92.47%, 96.64%, and 73.27%, respectively, after 120 min of treatment. These results demonstrate the high efficiency of the Fenton process for the decolorization of reactive dye solutions.²⁹ However, chemical

oxidation methods generally require high energy consumption and long reaction times, and may produce toxic intermediate products, leading to secondary pollution. The recovery efficiency of catalysts in many chemical oxidation processes is low, requiring frequent replacement or regeneration, which results in a significant increase in operating costs.³⁰

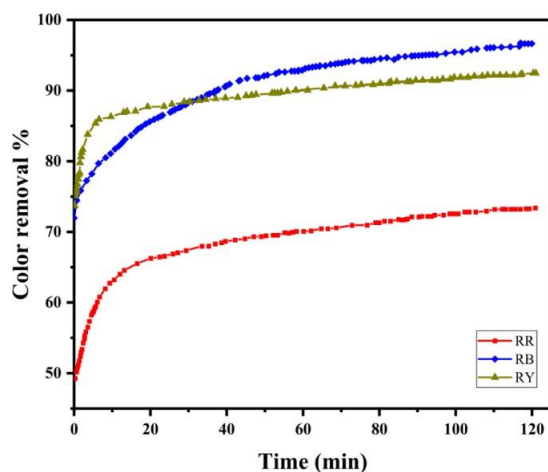


Figure 1.4 Color removal of Reactive Yellow 176 (RY), Reactive Red 239 (RR), and Reactive Blue 4 (RB) textile dyes during Fenton treatment at pH = 3 and [dye]:[Fe²⁺]:[H₂O₂] = 1:3.9:50. Reproduced from Ref.²⁹

Biodegradation offers an environmentally friendly alternative by utilizing microorganisms to decompose dyes. This method is favored for its potential for sustainability and low environmental impact.^{31,32} For example, the inoculation of white-rot fungi (such as *Pleurotus ostreatus*) on solid substrates like sorghum has demonstrated the ability to effectively degrade organic dyes.³³ However, the efficiency of biodegradation is generally low, especially when dealing with complex dye molecules that have aromatic ring structures and poor biodegradability. Azo dyes, commonly found in textile wastewater, are particularly difficult to decompose due to their resistance to microbial degradation.³² The rate of this process is slow, and it has poor efficiencies with high-concentration and toxic dyes. Additionally, the biodegradation method is significantly affected by environmental conditions such as pH, temperature, and dissolved oxygen, which can easily cause changes in microbial activity and thus impact the treatment efficiency.²⁵

Although certain progress has been made in existing dye wastewater treatment technologies, there are still many deficiencies in terms of efficiency, sustainability, and cost-effectiveness. Therefore, it is urgently necessary to explore more efficient, green, and low-cost treatment technologies to address the challenges faced in dye wastewater treatment.³⁴

1.2 Photocatalytic degradation of dyes

1.2.1 Working principle of photocatalysis

Photocatalysis is a process that utilizes light energy to excite catalysts and generate reactive oxygen species (ROS) which can induce chemical transformations, such as the degradation of pollutants. The basic principle of the photocatalytic reaction is as shown Figure 1.5. The catalyst is typically a semiconductor material. When it absorbs photons, the electrons in the catalyst will transition from the valence band to the conduction band, forming electron (e^-) and hole (h^+) pairs. The photo-generated electrons and holes react with water and oxygen in the surrounding environment to produce highly oxidizing reactive oxygen species, such as hydroxyl radicals ($\cdot OH$) and superoxide anions ($\cdot O_2^-$). These reactive oxygen species can efficiently degrade the organic structure of dye molecules and mineralize them into harmless substances, such as carbon dioxide and water.³⁵⁻³⁸

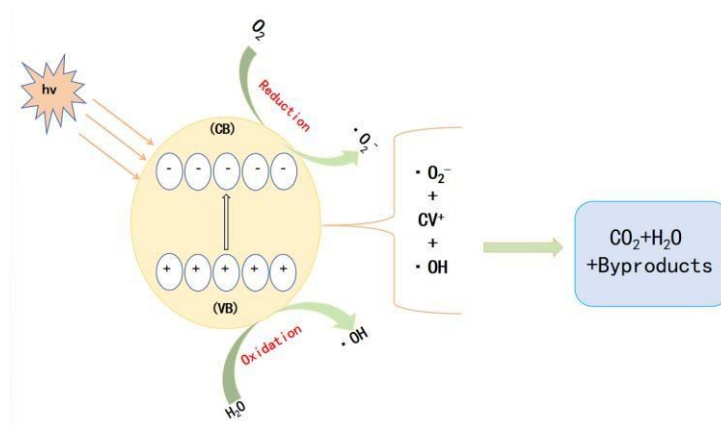


Figure 1.5 Working principle of photocatalysts: The catalyst absorbs light to excite electrons and holes, generating reactive oxygen species (ROS) that degrade dye molecules.

The rutile phase of titanium dioxide (TiO_2) is a widely studied photocatalyst with a band gap of approximately 3.2 eV, which means it primarily absorbs ultraviolet (UV) light.³⁹ Once generated, charge carriers migrate to the catalyst surface. Titanium dioxide (TiO_2) is a representative semiconductor photocatalyst that follows the above mechanism. Upon suitable light irradiation, TiO_2 generates electron–hole pairs, which drive surface redox reactions and produce reactive oxygen species capable of attacking dye molecules. Therefore, TiO_2 has been widely investigated for photocatalytic dye degradation. Nevertheless, its overall performance depends strongly on light absorption, charge-carrier separation, surface area, and reaction conditions.^{35,38}

The efficiency of this process is significantly influenced by, amongst other factors: the light absorption ability of the catalyst; the generation rate of reactive oxygen species; the surface area of the catalyst; and various reaction conditions. A larger surface area helps to increase the adsorption of pollutant molecules, which is crucial for efficient photocatalysis because these highly reactive free radicals have a short lifespan and mainly react on the catalyst surface.³⁵ Therefore, photocatalytic performance can be more scientifically evaluated using measurable indicators such as optical absorption, band-gap energy, ROS generation, and degradation kinetics. In particular, dye degradation activity is commonly quantified by the removal efficiency and the apparent pseudo-first-order rate constant

(k_{app}), rather than by qualitative descriptions alone. The degradation kinetics are commonly described by Equation 1.1:

$$\ln(C_0/C_t) = k_{app}t$$

Equation 1.1

where C_0 and C_t represent the dye concentrations at the initial time and reaction time t , respectively. The value of k_{app} is obtained from the slope of the linear plot of $\ln(C_0/C_t)$ against t .

1.2.2 Advantages of photocatalytic degradation of dyes

Photocatalytic degradation of dyes has several distinct advantages over traditional wastewater treatment methods. First, it generally has a relatively high reaction rate, especially when carried out under sunlight, which can significantly reduce energy consumption. In contrast, traditional chemical oxidation methods, such as ozonation and chlorination, often require high energy input and have a slower reaction rate. Second, photocatalytic reactions usually occur under mild conditions without the need for high temperatures or pressures. This makes photocatalytic technology not only energy-efficient but also safer to operate, and it is particularly suitable for large-scale sewage treatment.^{35,40}

Another significant advantage of photocatalysis is its environmental friendliness. Compared with traditional chemical methods, photocatalytic reactions generate less secondary pollution. Traditional chemical degradation methods often produce toxic by-products or secondary pollutants, which usually incur additional treatment costs during subsequent processing. In contrast, photocatalytic oxidation can degrade dye molecules rather than merely transferring them from water to an adsorbent surface. During this process, dyes are usually degraded through intermediate products and, under sufficient oxidation conditions, may be further mineralized into CO_2 , H_2O , and inorganic ions; therefore, decolorization should not be regarded as complete mineralization.^{35,40}

Moreover, the ability to utilize solar energy makes the application of photocatalysis in wastewater treatment more sustainable. Traditional chemical degradation methods consume a large amount of energy, while photocatalysis can use natural sunlight as an energy source, which not only reduces operating costs but also decreases the dependence on traditional energy sources.^{35,40}

1.2.3 Current Challenges in Photocatalysis Technology

Although photocatalytic degradation of dyes offers numerous advantages in wastewater treatment, the application of current technologies still faces some challenges, necessitating continuous research and optimization.

First of all, the stability of catalysts poses a critical challenge in the application of photocatalytic technology. Many photocatalytic materials are prone to degradation or deactivation during the reaction process. Especially when exposed to an aqueous environment for an extended period, the activity of the catalyst will significantly decline. For example, although TiO_2 is generally considered a stable photocatalyst, Yang et al. reported that P25 TiO_2 showed significant deactivation in the presence of humic acid during photocatalytic water treatment. This deactivation was attributed to the formation of surface complexes between oxidized humic-acid by-products and TiO_2 , which blocked active sites and reduced charge-transfer efficiency.⁴¹ Therefore, improving the operational stability and anti-fouling ability of photocatalysts remains important for practical wastewater treatment.³⁴

Secondly, many traditional photocatalysts have a narrow light absorption range. For instance, titanium dioxide (TiO_2) mainly responds to ultraviolet light. The ultraviolet part accounts for only about 5% of the solar spectrum, which greatly limits the overall efficiency of photocatalytic reactions under natural sunlight.^{36,37} To address this issue, researchers are attempting to expand the light absorption range of photocatalysts through modifications such as synthesizing new photocatalytic materials, doping with metal ions or

non-metallic elements, forming heterojunctions, or introducing photosensitizers, thereby enhancing the photocatalytic performance of the catalysts.³⁸ For example, nitrogen or silver doping can shift the absorption spectrum of TiO₂-based photocatalysts towards the visible-light region. Ag-G-TiO₂ is a representative TiO₂-based nanocomposite in which Ag species and graphene/graphene oxide can enhance visible-light absorption and facilitate interfacial charge transfer, thereby suppressing the recombination of photogenerated electron–hole pairs.⁴² This heterojunction can promote charge separation and improve the generation of reactive oxygen species for dye degradation under visible-light or H₂O₂-assisted visible-light conditions.⁴³ These examples indicate that doping, conductive carbon supports, and heterojunction construction are effective strategies for improving the visible-light photocatalytic activity of semiconductor photocatalysts, as illustrated in Figure 1.6.

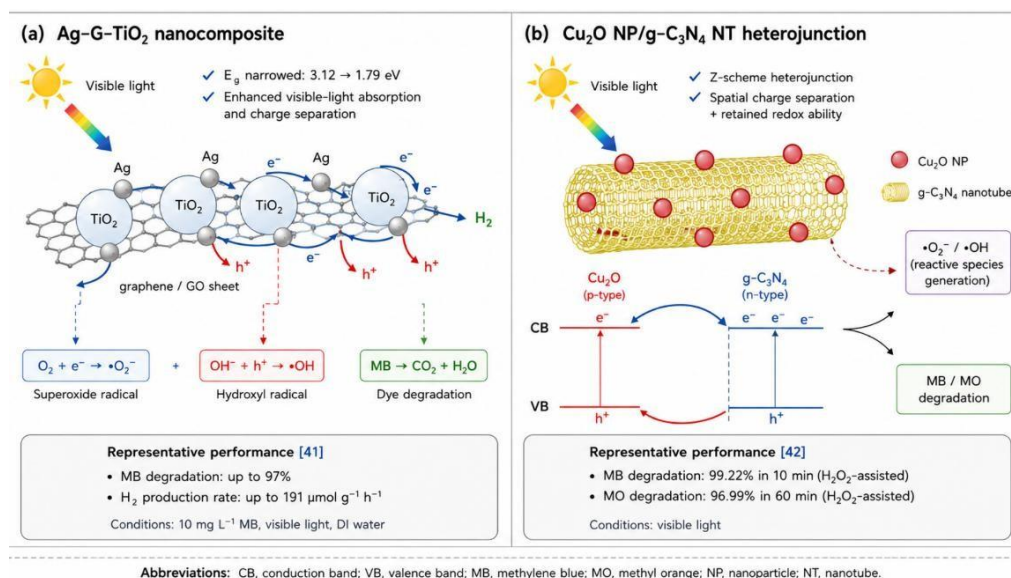


Figure 1.6 Representative visible-light-responsive photocatalytic nanocomposites for dye degradation: (a) Ag-G-TiO₂ and (b) Cu₂O NP/g-C₃N₄ NT. These systems improve photocatalytic performance by enhancing visible-light absorption, promoting charge separation, and facilitating reactive oxygen species generation. Adapted from Refs.^{42,43}

In addition, the degradation kinetics of photocatalytic reactions may be limited in dilute dye wastewater. At low dye concentrations, the reduced collision frequency between pollutant molecules and reactive oxygen species, together with adsorption–diffusion limitations on the catalyst surface, can decrease the apparent degradation rate. Therefore,

photocatalytic activity should be assessed using kinetic parameters such as the apparent pseudo-first-order rate constant (k_{app}), rather than only the final removal efficiency. Enhancing charge separation, reactive oxygen species generation, and pollutant adsorption near active sites is essential for improving degradation efficiency within a shorter reaction time.³⁵

1.2.4 Summary

Photocatalytic degradation of dyes, as an effective wastewater treatment method, utilizes catalysts to absorb light energy and generate reactive oxygen species for degrading dye molecules. Compared with traditional water treatment methods, photocatalysis offers advantages such as a higher reaction rate, environmental friendliness, and solar energy utilization. However, current photocatalytic technologies still face challenges such as poor catalyst stability, a narrow light absorption range, and a slow reaction rate, necessitating further research and optimization. Future development directions include enhancing the stability of catalysts, extending the light absorption range of photocatalysts, and optimizing the rate of photocatalytic reactions.³⁵

1.3 Metal-Organic Frameworks (MOFs) as Photocatalytic Materials

1.3.1 Definition and Structural Characteristics of MOFs

MOFs are crystalline porous materials formed by the self-assembly of metal ions or metal clusters with polydentate organic ligands through coordination bonds.⁴⁴ As illustrated in Figure 1.7, metal ions or clusters and organic linkers into an extended framework. MOFs typically possess a highly ordered three-dimensional network structure, and their pore size, pore volume, and surface chemical properties can be precisely controlled by adjusting the types of metal nodes and organic ligands.^{44,45} This framework structure composed of inorganic metal units and organic ligands enables MOFs to combine the structural

characteristics of both organic and inorganic materials and exhibit excellent structural designability.^{44,46}

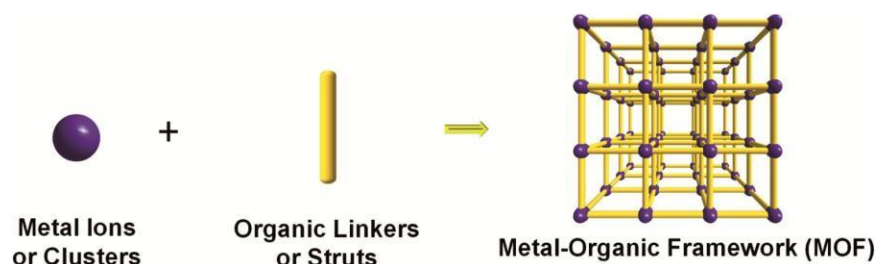


Figure 1.7 Schematic representation of the construction of metal–organic frameworks from metal ions or clusters and organic linkers. Adapted from Ref.⁴⁷

MOFs are constructed from metal nodes or clusters connected by organic linkers through coordination bonds, forming ordered porous three-dimensional frameworks with well-defined pores and channels.

The modular structure of MOFs provides an important foundation for the rational design of materials.⁴⁴ Metal nodes not only play a role in connecting and supporting the framework but also can influence the chemical reaction activity of materials through their specific coordination environments and redox properties.^{46,48} Common metal ions used in MOFs include Zn, Cu, Fe, Zr, and various lanthanide ions. Typical metal clusters and representative organic linkers used in MOF construction are illustrated in Figure 1.8. Organic ligands form regular pore structures by connecting metal nodes and can regulate the chemical environment inside the pores by introducing different functional groups.^{44,49} Many ligands contain functional groups such as carboxylates, phosphates, or nitrogen-containing heterocycles, which coordinate with metal centers and further tailor the internal pore chemistry. By changing the structures of metal centers or organic ligands, the topological structure, pore size, and chemical properties of materials can be regulated at the molecular level, thus achieving the precise design of material functions.^{44–46}

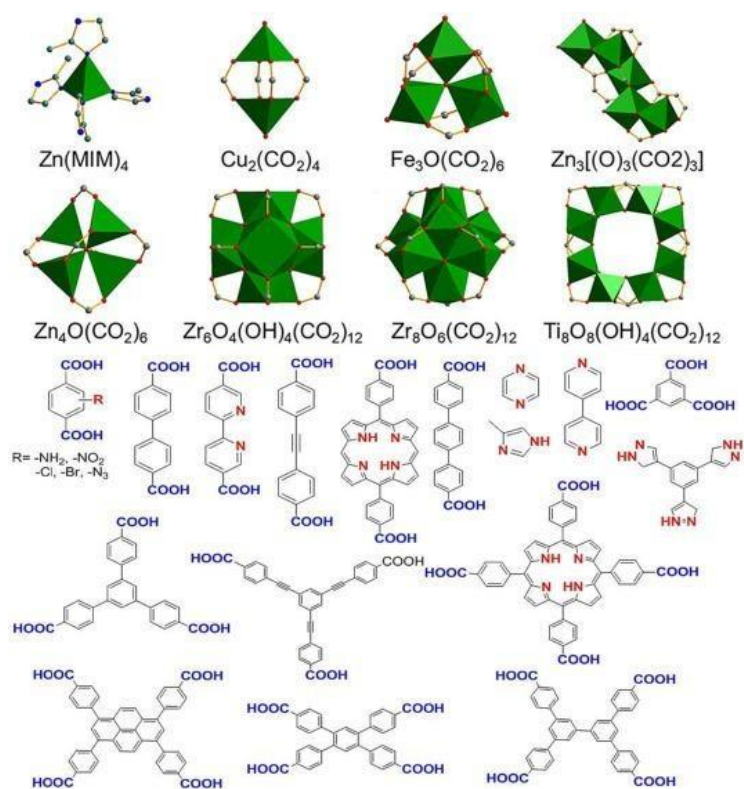


Figure 1.8 Representative metal clusters and organic linkers commonly used for the construction of metal–organic frameworks (MOFs). Typical metal-based secondary building units (SBUs) are shown in the upper panel, while representative organic ligands are shown in the lower panel. Adapted from Ref.⁵⁰

Due to their highly developed pore structures and large specific surface areas, MOFs can provide abundant adsorption sites for guest molecules and form specific host-guest interactions inside the pores. Therefore, MOFs show broad application prospects in fields such as gas storage and separation, sensing, drug delivery, and catalysis.^{44,51,52} In recent years, with the continuous deepening of the understanding of their structures and functions, MOFs have gradually been regarded as a class of environmental functional materials with significant potential, and have attracted extensive attention in environmental governance fields such as pollutant adsorption and photocatalytic degradation.^{53–55}

1.3.2 Advantages of MOFs in photocatalysis

The advantages of MOFs in photocatalysis arise from their high specific surface area, ordered porosity, tunable metal–ligand coordination environments, and modular electronic structures. These structural characteristics allow MOFs to function not only as adsorbents

for pollutant enrichment, but also as photoactive platforms for light harvesting, charge separation, and surface redox reactions. In photocatalytic wastewater treatment, the advantages of MOFs can therefore be understood through several closely related structure–property relationships, including adsorption pre-enrichment, metal-node and ligand cooperation, band-gap engineering, and defect or composite design.^{56–58}

1.3.2.1 Ordered porosity and adsorption pre-enrichment of dye pollutants

One of the most important advantages of MOFs in photocatalytic wastewater treatment is their ability to enrich dye pollutants near catalytic sites within their internal porosity before photodegradation occurs. This pre-enrichment effect is mainly associated with their high specific surface area, ordered pore structure, and tunable surface chemistry. Through non-covalent interactions such as electrostatic attraction, hydrogen bonding, and π - π interactions, dye molecules can be adsorbed within or near the MOF framework, thereby increasing the local pollutant concentration around photoactive sites and enhancing the probability of reaction with photogenerated charge carriers and reactive oxygen species.^{56–}

58

The role of these non-covalent interactions has been systematically discussed by Luo et al., who summarized previous studies showing that pore confinement, electrostatic interactions, hydrogen bonding, and π - π stacking all contribute to dye adsorption by porous materials such as MOFs.⁵⁹ This provides a structural basis for understanding why MOFs can serve as effective adsorption–photocatalysis platforms rather than simple photocatalysts. Experimental studies on defective Fe-MOFs further support this mechanism. In these materials, structural defects enhanced both visible-light utilization and adsorption capacity, leading to a synergistic effect in which adsorbed methylene blue molecules were more efficiently degraded by photogenerated reactive species.⁶⁰

The contribution of specific host-guest interactions has also been demonstrated in zirconium-based mixed-ligand MOFs, where efficient dye adsorption was attributed to the combined effects of electrostatic attraction, hydrogen bonding, and π - π stacking between dye molecules and the functionalized MOF.⁶¹ A similar mechanism was reported by Deng et al. for the adsorption of Congo red (CR) using the water-stable aluminium-based MOF CAU-23. In this system, the suitable pore environment and surface chemistry of CAU-23 promoted CR adsorption through electrostatic attraction, hydrogen bonding between μ -OH groups and CR functional groups, and π - π interactions between thiophene linkers and the aromatic rings of CR.⁶² The proposed adsorption configuration between CAU-23 and CR was further supported by DFT calculations, as shown in Figure 1.9.

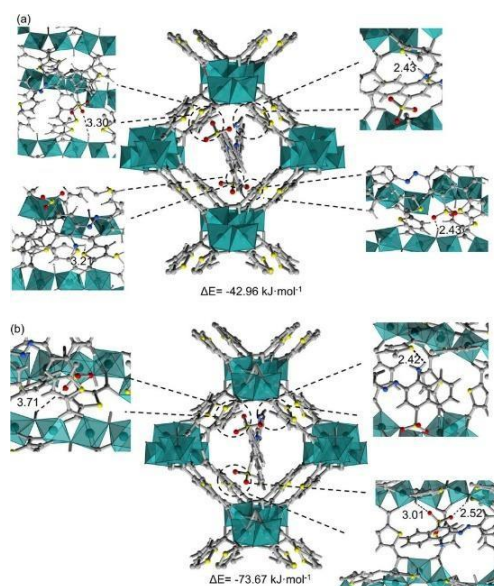


Figure 1.9 DFT-calculated adsorption configurations of Congo red within the CAU-23 framework, showing favourable interaction between CR and the CAU-23 pore environment. Adapted with permission from Ref.⁶²

Therefore, adsorption pre-enrichment should not be regarded as a passive capture process only. Instead, it is an active contributor to photocatalytic efficiency because it concentrates organic pollutants close to photoactive sites and facilitates subsequent oxidative degradation. This principle has also been emphasized in reviews on MOF-based composites and MOF surface engineering, where the adsorption capacity, pore structure,

and surface interactions of MOFs are identified as key factors governing photocatalytic dye removal.^{63–65}

1.3.2.2 Metal-node and ligand cooperation in charge separation and surface redox reactions

Another important advantage of MOFs is the cooperative role of metal nodes and organic ligands in photocatalytic charge generation, charge separation, and surface redox reactions. Unlike conventional adsorbents, MOFs contain periodically arranged inorganic and organic components, both of which can participate in photocatalytic processes. Metal nodes often act as redox-active centres or adsorption sites, while organic ligands can function as light-harvesting units, electron donors, or electron acceptors.^{66–68}

For metal nodes, Fe-based MOFs provide representative examples. As illustrated in Figure 1.10, pristine MIL-100(Fe) can undergo visible-light-assisted photocatalytic or photo-Fenton-like degradation of organic pollutants. Upon light irradiation, photogenerated electrons and holes are produced within the framework. The electrons can migrate to Fe-based active sites and promote the Fe(III)/Fe(II) redox cycle, thereby facilitating the activation of dissolved O₂ or H₂O₂ to generate reactive oxygen species such as O₂•[−] and •OH. These reactive species subsequently oxidize organic pollutants into smaller intermediates and eventually into CO₂ and H₂O. This mechanism highlights the intrinsic role of Fe nodes in promoting charge transfer and ROS generation, without necessarily relying on additional noble-metal nanoparticles.^{69–71}

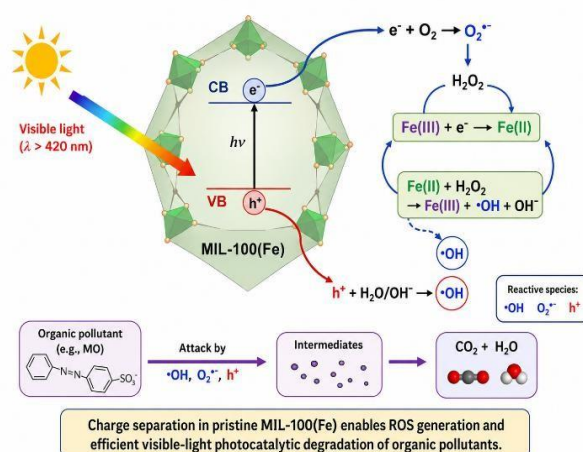


Figure 1.10 Schematic illustration of the proposed visible-light-assisted photocatalytic/photo-Fenton-like degradation mechanism of organic pollutants over pristine MIL-100(Fe). Adapted based on the mechanisms reported in Refs.^{69–71}

The redox activity of metal nodes is therefore central to many MOF-based photocatalytic systems. For example, MIL-100(Fe) has been investigated as an Fe-based photocatalyst for the degradation of organic pollutants.⁷⁰ Thermally activated MIL-100(Fe) containing mixed-valence coordinatively unsaturated Fe sites can accelerate Fe(III)/Fe(II) cycling through visible-light photoreduction, thereby enhancing the synergistic photocatalytic and Fenton-like degradation of organic pollutants.⁷¹ More generally, coordinatively unsaturated metal sites, also known as open metal sites, can function as Lewis acid centres and facilitate the adsorption and catalytic activation of guest molecules.⁷² Other representative systems include MIL-53(Fe) for persulfate-assisted photocatalytic degradation under visible LED irradiation,⁷³ the Zr-based UiO-66-NH₂ for the solar photocatalytic degradation of parabens,⁷⁴ and the Ti-based NH₂-MIL-125(Ti) for the solar photocatalytic degradation of aqueous emerging pollutants.⁷⁵

Organic ligands also play a crucial role in light harvesting and charge separation. Porphyrin-based ligands are particularly important because they exhibit strong visible-light absorption and can be tuned to act as electron donors or acceptors depending on their peripheral substituents and central metal ions.^{76,77} A clear example is the mixed-ligand Zr-MOF constructed from electron-donating meso-tetrakis(4-carboxyphenyl)porphyrin (TCPP) ligands and electron-accepting naphthalene diimide (NDI) ligands. As shown in

Figure 1.11, the ordered arrangement of TCPP donor units and NDI acceptor units within the Zr-MOF framework creates a donor–acceptor system that promotes spatial separation of photogenerated electrons and holes. This internal charge-separation pathway resulted in improved performance in both oxidation and reduction half-reactions.⁷⁸ A similar donor–acceptor design in UiO-type MOFs has also been reported to enhance photocatalytic aerobic oxidation.⁷⁹

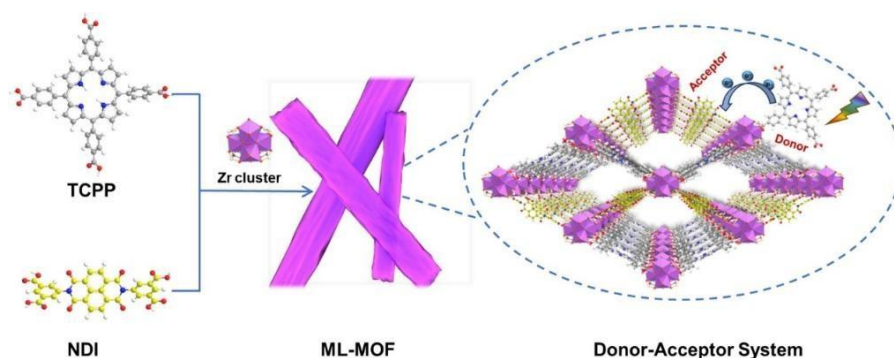


Figure 1.11 Schematic illustration of the donor–acceptor mixed-ligand Zr-MOF constructed from TCPP donor units, NDI acceptor units, and Zr clusters, showing the ordered spatial arrangement that facilitates internal charge separation. Adapted with permission from Ref.⁷⁸

The cooperation between metal nodes and ligands is mainly enabled by directional charge-transfer pathways, including ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT). LMCT is particularly important because it can inject photogenerated electrons from the ligand into the metal node, where reduction reactions or ROS generation may occur.⁶⁷ Conversely, MLCT can lead to longer-lived charges on the ligand, which may benefit oxidation reactions, as observed in ferrocene-based MOFs.⁸⁰

The efficiency of these charge-transfer processes can be further tuned by ligand modification, which may also alter the band gap, as discussed in the following section. For example, introducing electron-donating groups such as $-\text{NH}_2$ or electron-withdrawing groups such as $-\text{NO}_2$ near the carboxylate anchoring group of terephthalic acid ligands was shown to regulate charge separation on FeCo-MOF surfaces and affect tetracycline photodegradation.⁸¹

Overall, these examples indicate that the photocatalytic activity of MOFs can originate from the redox-active metal nodes, photoresponsive organic linkers, and internal charge-transfer pathways within the framework.⁸² The periodic arrangement of metal nodes and organic ligands provides built-in pathways for charge migration and separation, which can reduce charge-carrier recombination and direct electrons and holes towards reactive sites on pore surfaces.^{83,84} Therefore, metal–ligand cooperation is a key mechanism by which MOFs achieve photocatalytic activity beyond simple adsorption.

1.3.2.3 Band-gap engineering and visible-light response

The modular structure of MOFs also provides significant advantages for band-gap engineering and visible-light photocatalysis. Because MOFs are constructed from metal clusters and organic linkers, their electronic structures can be adjusted through rational selection or modification of these components. This design flexibility enables the absorption edge of MOFs to be extended from the ultraviolet region into the visible-light region, thereby improving solar energy utilization compared with conventional wide-band-gap semiconductors.^{85–87}

In many MOFs, the metal-oxo clusters strongly influence the conduction band minimum, whereas the highest occupied molecular orbital of the organic linker contributes to the valence band maximum. By selecting metal nodes with suitable redox potentials and organic ligands with extended conjugation or appropriate electron-donating/electron-withdrawing substituents, the band gap of MOFs can be systematically regulated.⁸⁸ This molecular-level tunability represents an important distinction from traditional photocatalysts such as TiO₂, whose electronic structure is largely constrained by its crystal lattice.

Several strategies have been developed to improve the visible-light response of MOFs. The incorporation of extended π -conjugated ligands, including pyrazino quinoxaline derivatives and other photoactive linkers, can enhance photon absorption and facilitate electron

transport within the framework.⁸⁹ Similar principles have been applied to titanium-based MOFs, which retain some advantages of Ti-based inorganic photocatalysts while offering improved visible-light absorption through ligand modification.⁹⁰ Recent studies further demonstrate that linker design can tune the band structure. For example, extending the length and conjugation of the organic linker in Zr-based MOFs decreased the band gap from 3.97 eV for UiO-66 to 3.63 eV for UiO-67 and 2.28 eV for VNU-1.⁹¹

Charge-transfer processes are closely associated with band-gap engineering. In particular, LMCT can promote photoinduced charge separation by transferring electrons from photoexcited ligands to metal nodes.⁶⁷ Optimizing LMCT through careful selection of metal-ligand combinations ensures that photogenerated electrons and holes can migrate to the surface to drive redox reactions before recombination occurs. In MOFs containing metal-oxo clusters, electron transfer from the photoexcited organic linker to the inorganic cluster is often described more specifically as linker-to-cluster charge transfer (LCCT). As illustrated in Figure 1.12, photoexcitation of the 2-aminoterephthalate linker in NH₂-UiO-66(Zr) induces electron transfer to the Zr-oxo cluster, generating Zr³⁺ species that subsequently participate in the reduction of CO₂ to HCOO⁻.

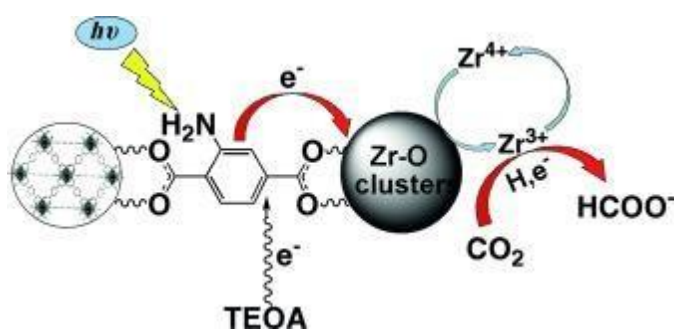


Figure 1.12 Proposed mechanism for visible-light-driven photocatalytic CO₂ reduction over NH₂-UiO-66(Zr), involving photoinduced linker-to-cluster charge transfer, formation of Zr³⁺ species, and subsequent reduction of CO₂ to HCOO⁻. Reproduced from Ref.⁹²

Multivariate MOFs further extend this design strategy by incorporating multiple linkers within a single framework. This approach allows simultaneous regulation of porosity, composition, light absorption, and charge-transfer behavior.⁹³ Therefore, the band structure and visible-light response of MOFs can be tuned at the molecular design stage

through the selection of metal nodes, linkers, and framework topology, rather than only through post-synthetic modification.

1.3.2.4 Defect engineering and composite strategies for enhanced photocatalysis

Although pristine MOFs possess intrinsic advantages in adsorption enrichment, light harvesting, charge separation, and surface redox reactions, they may still suffer from limited stability, insufficient visible-light absorption, or rapid charge-carrier recombination. Defect engineering and MOF-based composite construction have therefore been developed as complementary strategies to overcome these limitations.

Defect engineering is an effective approach for enhancing photocatalytic activity because defects can create additional active sites, modify the local coordination environment, and regulate the electronic structure of MOFs. For example, fluoride inclusion in Ti-based MOFs has been reported to significantly improve photocatalytic hydrogen evolution activity.⁹⁴ This result indicates that controlled defects can provide additional structural and electronic flexibility beyond conventional metal–ligand selection. As a structural example of defect engineering, the formation of missing-linker defects in UiO-66 is illustrated in Figure 1.13, showing how a defect-free MOF framework can be transformed into a defective structure with additional accessible sites.

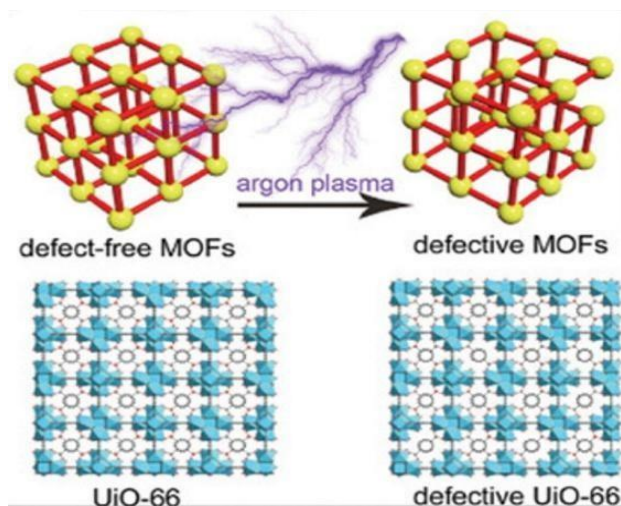


Figure 1.13 Representative illustration of defect engineering in a UiO-66-type MOF. The transformation from defect-free UiO-66 to defective UiO-66 demonstrates how missing-linker-type defects can alter the local coordination environment and generate additional accessible sites. Adapted from Ref.⁹⁵

Composite construction is another important strategy for improving MOF-based photocatalysts. By coupling MOFs with carbon materials, semiconductors, metal compounds, or MOF-derived phases, it is possible to enhance charge transport, improve structural stability, and introduce additional active sites. For example, bimetallic MOFs anchored on corncob-derived porous carbon combine the adsorption capacity of porous carbon with the catalytic activity of MOFs, forming a synergistic system for pollutant capture and degradation.⁹⁶ MOF-derived materials, such as MOF(Fe)/FeS_x composites, have also shown enhanced photocatalytic activity for tetracycline degradation, where the derived structure preserves beneficial porosity while introducing new reactive sites.⁹⁷

Heterojunction construction further improves photocatalytic efficiency by promoting interfacial charge separation. In particular, S-scheme heterojunctions based on MOFs and other semiconductors have been designed to retain strong redox ability while accelerating the separation of photogenerated electrons and holes. This strategy is especially useful for photocatalytic wastewater treatment because improved charge separation directly enhances ROS generation and pollutant degradation. More broadly, reviews on MOF-based environmental remediation have emphasized that the combination of adsorption capacity, pore structure, light response, and interfacial charge transfer is essential for efficient degradation of persistent organic pollutants.⁶⁴

1.3.3 Photocatalytic mechanism of MOFs

Similar to conventional semiconductor photocatalysts, MOFs can generate photogenerated electrons and holes under suitable light irradiation. When the energy of incident light is equal to or greater than the optical band gap of the material, electrons are excited from occupied electronic states to unoccupied electronic states, thereby producing electron–hole pairs. However, unlike traditional inorganic semiconductors with relatively continuous band structures, the electronic structures of MOFs are usually associated with both organic ligands and metal nodes.⁹⁸

In MOFs, the frontier orbitals are often distributed over different framework components. The highest occupied molecular orbital (HOMO), which plays a role similar to the valence band, is commonly related to the π orbitals of organic ligands. In contrast, the lowest unoccupied molecular orbital (LUMO), which plays a role similar to the conduction band, may be located on the d orbitals of metal nodes or on the π^* orbitals of ligands, depending on the electronic structure and energy-level alignment of the specific MOF. Therefore, the charge-transfer process in MOFs is not fixed, but may involve ligand-centred excitation, metal-centred excitation, ligand-to-metal charge transfer (LMCT), metal-to-ligand charge transfer (MLCT), or ligand-to-ligand charge transfer.⁹⁸

Among these possible pathways, LMCT is a representative charge-transfer mechanism in many photoactive MOFs. In an LMCT-type process, photoexcited electrons are transferred from ligand-centred orbitals to metal-cluster-centred orbitals, leaving holes on the organic ligands. This spatial separation of electrons and holes can facilitate charge separation and provide different sites for reduction and oxidation reactions. However, this mechanism should not be regarded as universal for all MOF photocatalysts, because the dominant charge-transfer pathway depends on the specific metal nodes, organic ligands, defect structures, and orbital energy alignment of each MOF system.⁹⁹ As illustrated in Figure 1.14, the metal cluster may act as the electron-accepting site for reduction reactions, while

the ligand may retain photogenerated holes for oxidation reactions in a representative LMCT-type MOF photocatalyst.

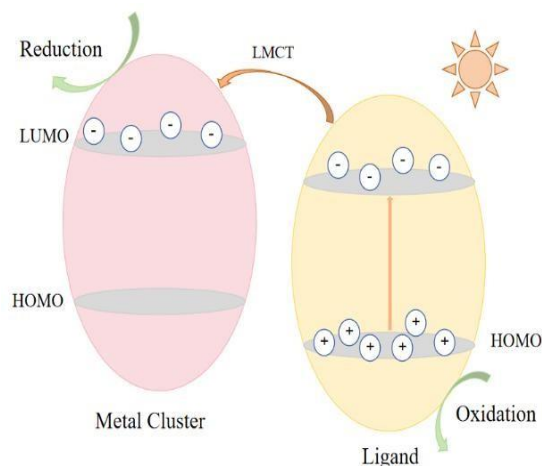


Figure 1.14 Schematic illustration of photogenerated electron–hole separation in a representative LMCT-type MOF photocatalyst. This figure illustrates one possible charge-transfer pathway, in which photoexcited electrons are transferred from ligand-centred orbitals to metal-cluster-centred orbitals, enabling reduction reactions at metal nodes and oxidation reactions at ligands. The dominant charge-transfer pathway may vary among different MOF photocatalytic systems depending on the metal nodes, ligands, defects, and energy-level alignment.⁹⁹

After charge separation and migration, the photogenerated electrons and holes can participate in surface redox reactions. Electrons can react with dissolved oxygen to generate superoxide radicals ($\text{O}_2^{\bullet-}$), while holes can directly oxidize adsorbed pollutants or react with water or hydroxide ions to produce hydroxyl radicals ($\bullet\text{OH}$). These reactive oxygen species, together with photogenerated holes, can attack the chromophoric groups and conjugated structures of dye molecules, resulting in decolorization, molecular fragmentation, and further mineralization under sufficient reaction conditions.^{100–102}

Overall, MOF photocatalysis involves a coupled process of light absorption, charge transfer, charge separation, surface redox reactions, and pollutant adsorption. The defect engineering, composite construction, and heterojunction strategies discussed in Section 1.3.2.4 can be understood as structural approaches for regulating these mechanistic steps

rather than as separate mechanisms. In particular, the missing-linker defect example illustrated in Figure 1.13 shows how defect engineering can modify the local coordination environment and create additional accessible sites, thereby influencing charge separation and surface redox reactions. By adjusting electronic structure, active-site accessibility, and interfacial charge migration, these modification strategies can improve the photocatalytic performance of MOFs in wastewater treatment.

1.3.4 Limitations of Photocatalytic Research on MOFs

Although the considerable progress of MOF-based photocatalysts in pollutant degradation, their practical application in wastewater treatment and environmental remediation remains limited by several unresolved challenges. These limitations are mainly associated with framework stability, charge transport, visible-light utilization, and the gap between laboratory studies and real wastewater conditions.

The structural stability of MOFs under aqueous and photocatalytic reaction conditions remains a major concern. During long-term operation in water, some MOFs may undergo hydrolysis, ligand dissociation, or metal-node dissolution, leading to partial structural degradation or framework collapse.^{103,104} For example, iron-based MOFs such as Fe-MIL-101 have been reported to suffer from photocorrosion in aqueous systems, which can reduce catalytic activity and recyclability.¹⁰⁵ In addition, the release of metal ions during framework degradation may introduce secondary pollution risks.¹⁰⁶ Therefore, improving the hydrolytic and photochemical stability of MOFs is essential for their use in practical wastewater treatment.

Most MOF materials generally suffer from the problem of low electrical conductivity. MOFs are composed of metal nodes and organic ligands, and many organic ligands themselves have insulating properties, which can limit the migration efficiency of photogenerated carriers within the material. When electron–hole pairs are generated by light irradiation, due to the restricted carrier migration, rapid recombination is likely to

occur, thereby reducing the quantum efficiency of the photocatalytic reaction.¹⁰⁷ Compared with traditional inorganic semiconductor photocatalytic materials (such as TiO₂ or g-C₃N₄), MOFs usually exhibit weaker charge transport capabilities.¹⁰⁸ To address this issue, in recent years, researchers have attempted to construct composite photocatalytic systems or heterojunction structures to promote charge separation and improve interfacial electron transport efficiency, thus enhancing the overall photocatalytic performance.¹⁰⁹

In addition, many unmodified MOF materials exhibit strong absorption mainly in the ultraviolet region, while their photoresponse in the visible light region is weak.¹¹⁰ Since visible light accounts for a major proportion in the solar spectrum, this characteristic limits the application potential of MOFs in solar-driven photocatalytic systems to some extent. In recent years, bandgap engineering through ligand functionalization has been proven to be an effective strategy. For example, compared with the parent MIL-125(Ti), which is mainly UV-responsive, amino-functionalized NH₂-MIL-125(Ti) exhibits an extended absorption edge in the visible-light region and a narrower optical band gap, decreasing from approximately 3.6 eV for MIL-125(Ti) to about 2.6 eV for NH₂-MIL-125(Ti).^{111,112} This visible-light response enables NH₂-MIL-125(Ti) to be excited under visible-light irradiation and to participate in photocatalytic redox reactions, thereby improving pollutant degradation or reduction performance.

Although the above studies have improved the performance of MOF photocatalytic materials to some extent, how to simultaneously achieve the synergistic optimization of structural stability, charge transfer efficiency, and light absorption ability remains an important challenge. Many modification strategies often only improve one aspect of the performance and may have an adverse impact on other properties.¹¹³ Therefore, rationally designing the structures of metal nodes and organic ligands and constructing functional composite systems have become important development directions in current MOF photocatalysis research. Solving these problems not only helps to enhance the practical application performance of MOF photocatalytic materials but also provides important

theoretical basis and technical support for the development of new and efficient photocatalytic systems.

1.4 Vanadium-based metal-organic frameworks (V-MOFs)

After discussing the platform advantages of MOFs as adsorption and photocatalytic materials in the previous text, a natural further focus is on vanadium-based metal-organic frameworks (V-MOFs). V-MOFs combine the structural designability of MOFs with the intrinsic redox activity of vanadium centers, thus showing greater research potential in environmental remediation, especially in the treatment of dye wastewater. Vanadium can stably exist in multiple valence states such as V^{3+} , V^{4+} , and V^{5+} , making it easier to participate in electron transfer during catalytic and photocatalytic processes.¹¹⁴ Meanwhile, the flexible coordination chemistry of vanadium enables the construction of diverse vanadium–oxygen secondary building units (SBUs), particularly infinite $\{V-O-V\}_{\infty}$ chains and oxido-centered vanadium trimers. As illustrated in Figure 1.15, these V–O SBUs can be connected with different organic ligands to generate diverse framework topologies and pore architectures. Therefore, the structural diversity of V-MOFs provides abundant opportunities for regulating framework topology, pore environment, accessible active sites, and charge-transfer pathways, offering rich space for structure–property optimization.¹¹⁵

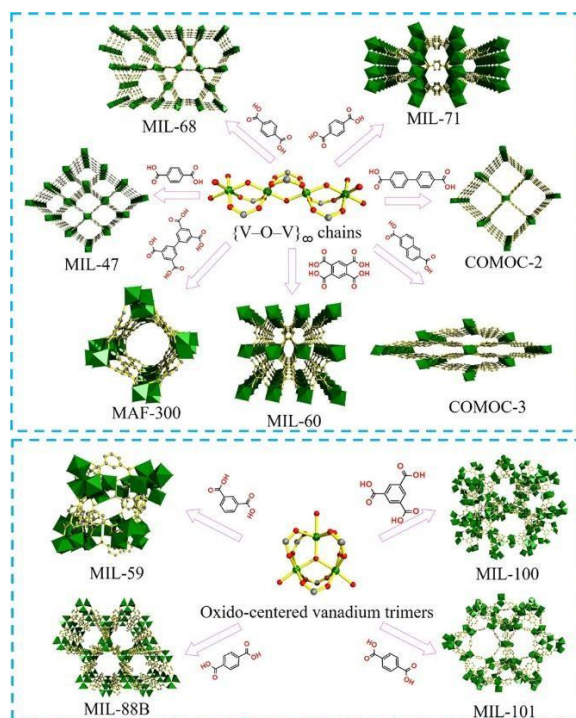


Figure 1.15 Representative vanadium–oxygen secondary building units in V-MOFs, including infinite $\{V-O-V\}_{\infty}$ chains and oxido-centered vanadium trimers. These V–O SBUs represent important structural origins of the diversity of V-MOFs. Reproduced from Ref.¹¹⁶

For dye wastewater treatment, the distinctive feature of V-MOFs is the coupling of ligand-regulated pore environments with redox-active vanadium–oxygen sites. This coupling allows the framework structure to influence both pollutant adsorption and subsequent light-driven degradation.^{114,117}

A structurally well-defined example is MIL-47(V), a vanadium (IV) terephthalate with the framework formula $[V^{IV}O(BDC)]_n$, where BDC denotes benzene-1,4-dicarboxylate. The framework consists of infinite chains of corner-sharing $V^{IV}O_6$ octahedra linked by BDC ligands to form a three-dimensional porous structure with one-dimensional diamond-shaped channels. MIL-47(V) has also been evaluated for the photocatalytic decolourisation of methylene blue under UV irradiation, demonstrating the relevance of structurally defined V-MOFs to dye treatment.¹¹⁸

Zhang et al. subsequently reported one-pot-synthesized V-based organic frameworks for the combined adsorption and solar-driven photocatalytic removal of di(2-ethylhexyl)

phthalate (DEHP). The optimized system achieved a total DEHP removal efficiency of 98%, demonstrating the potential of V-based frameworks for combined adsorption and light-driven pollutant removal.¹¹⁹

More importantly, the removal experiment included an initial dark period followed by solar irradiation, as shown in Figure 1.16. Here, C/C_0 represents the normalized DEHP concentration, where C is the concentration measured at a given time and C_0 is the initial concentration before treatment. The decrease in C/C_0 during the dark period was attributed primarily to adsorption. After irradiation began, the further decrease indicated an additional photocatalytic contribution, although adsorption may have continued during this stage. The nearly unchanged blank curve showed that spontaneous DEHP loss under the same experimental conditions was negligible.¹¹⁹

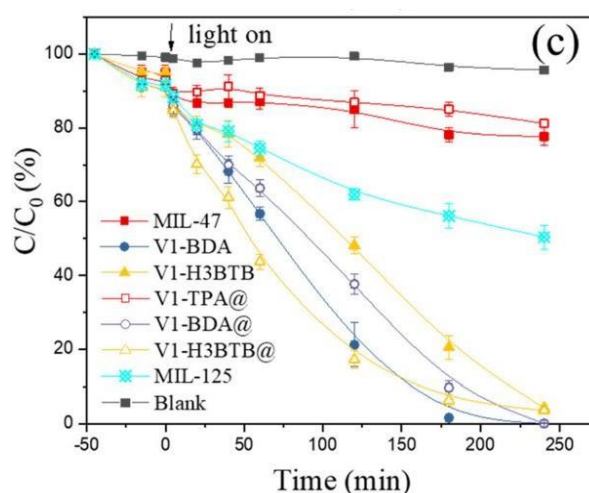


Figure 1.16 Time-dependent normalized DEHP concentration during an initial dark adsorption period followed by solar irradiation over the V-based frameworks reported by Zhang et al. The vertical dashed line marks the onset of irradiation. Adapted from Ref.¹¹⁹

Beyond overall pollutant-removal performance, BIT-66 provides complementary mechanistic evidence for light-induced charge generation and radical-mediated oxidation in V-MOFs. BIT-66 is a hydrolytically stable V(IV) MOF with the composition $V_3(O)_3(H_2O)(BTB)_2$, where BTB denotes 1,3,5-tris(4-carboxyphenyl) benzene. Its porous framework is constructed from V(IV)-oxo inorganic units connected by the carboxylate groups of the BTB ligands, as illustrated in Figure 1.17.¹²⁰

EPR spin-trapping measurements showed that radical species were generated under visible-light irradiation, whereas no obvious signal was detected in the dark (Figure 1.18).¹²¹ BIT-66 was originally reported for photocatalytic bacteriostatic activity and was subsequently applied to the visible-light-driven selective oxidation of amines and sulfides. Although these reactions are not dye-degradation reactions, they demonstrate that a structurally defined V-MOF can generate reactive species and mediate oxidation under visible-light irradiation.^{120,121}

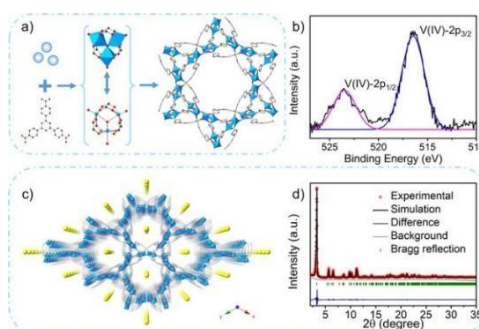


Figure 1.17 Structural representation of BIT-66, showing V(IV)-oxo inorganic units connected by BTB ligands to form its porous coordination framework. Adapted from Ref.¹²⁰

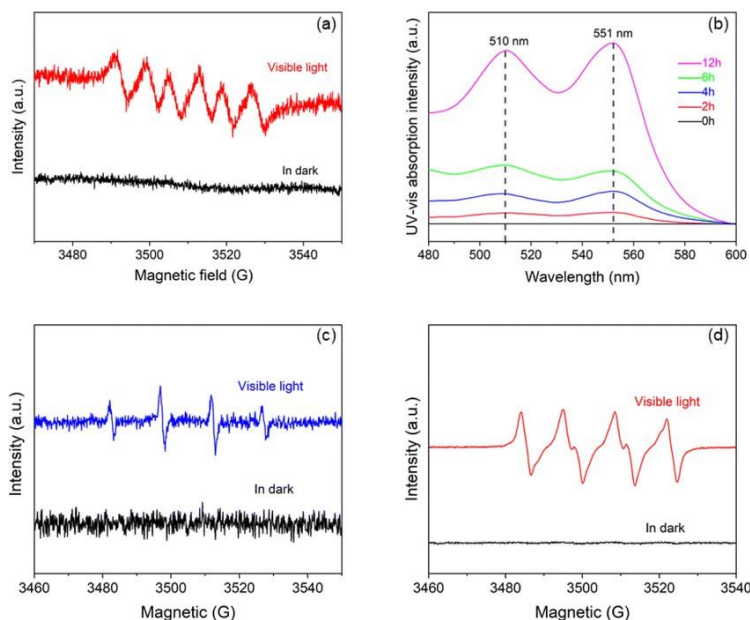


Figure 1.18 EPR spin-trapping spectra of BIT-66 recorded in the dark and under visible-light irradiation, showing light-induced radical generation. Adapted from Ref.¹²¹

Beyond light-induced radical chemistry, vanadium centers in V-MOFs may also participate directly in guest adsorption and redox conversion. For instance, Jaramillo et al. reported a

porous vanadium (II) MOF, $V_2C_{2.8}(\text{btdd})$, where $H_2\text{btdd}$ denotes bis(1H-1,2,3-triazolo[4,5-b], [4',5'-i]) dibenzo [1,4] dioxin and btdd^{2-} is its dianionic linker. Its exposed V(II) sites that can back-donate electron density to weak π -acidic gases such as N_2 , enabling highly selective N_2 adsorption over CH_4 through specific metal–guest orbital interactions rather than simple physisorption.¹²² More directly, Han et al. further reported the reactive adsorption of NO_2 in MFM-300(V), a redox-active V(III) MOF with the composition $[V_2(OH)_2(L)]$, where H_4L is biphenyl-3,3',5,5'-tetracarboxylic acid; its framework consists of chains of corner-sharing $[VO_4(OH)_2]$ octahedra bridged by L^{4-} ligands. During adsorption, V(III) centers in the framework were oxidized to V(IV), while adsorbed NO_2 was reduced to NO, accompanied by deprotonation of framework hydroxyl groups.¹²³ These examples indicate that the adsorption behavior of V-MOFs may be coupled with redox changes at vanadium centers, providing a mechanistic basis for their potential in integrated adsorption–conversion processes.

Overall, existing studies have demonstrated that V-MOFs possess a designable porous framework, tunable ligand structures, and redox-active vanadium coordination centers. However, most existing studies focus on the synthesis and performance demonstration of individual materials, while systematic comparisons of the relationship among ligand structure, framework properties, adsorption behavior, and photocatalytic performance remain limited. Since organic ligands can regulate pore size, pore aperture, surface polarity, host–guest interactions, and pollutant diffusion within the framework, they are expected to strongly influence both dark adsorption capacity and light-induced degradation efficiency.

Against this background, this thesis selects V-MOFs constructed with different organic ligands as the research objects. It not only focuses on whether they can achieve dye removal, but also pays more attention to how the change of ligands affects the framework properties and how these property changes are further reflected in the adsorption behavior and photocatalytic degradation performance. Through such a comparative study, it is

expected to establish a clearer correlation among "ligand structure/material properties/functional performance", providing a basis for the rational design of vanadium-based MOFs in the treatment of dye wastewater.

1.5 Research objectives of this thesis

Based on the previous analysis of the demand for dye wastewater treatment, the development of photocatalytic technology, the characteristics of the MOFs material platform, and the research status of V-MOFs, this thesis takes vanadium-based metal-organic framework materials constructed with different organic ligands as the research object, and conducts research on their adsorption and photocatalytic behaviors during the dye removal process, focusing on investigating the influence of ligand structure changes on the framework properties and their functional performance. In the overall research idea, this thesis not only focuses on whether the materials can achieve dye removal, but also pays more attention to how the structural differences caused by different ligands further affect the material's adsorption and enrichment ability, the degradation behavior under light conditions, and the synergistic relationship between the two.

The specific research objectives of this thesis include the following aspects. First, the synthesis of V-MOFs constructed with different organic ligands, and systematic characterization of their crystal structures, morphological features, pore structures, and relevant physicochemical properties to clarify the influence of different ligands on the basic structural features of the materials. Second, investigation into the adsorption behavior of each material towards the target dyes in the dark, to compare their adsorption rates, adsorption capacities, and equilibrium characteristics, so as to analyze the differences in the pollutant enrichment capabilities of different frameworks. Third, on the basis of clearly distinguishing the contribution of dark adsorption, further study of the degradation performance of each material towards the target dyes under light conditions, and comparison of the differences in degradation efficiency and reaction behavior among different systems. Finally, combining the structural features and performance results of the

materials to analyze how the changes in framework properties caused by different ligands affect the synergistic effect of adsorption and photocatalysis, and establish the relationship among "ligand structure/framework property in dye removal performance", providing a basis for the rational design of vanadium-based MOFs in dye wastewater treatment.

Chapter 2 Experimental Section

2.1 Experimental Reagents and Instruments

All the chemical reagents used in this study were commercially available analytical grade or higher, and were used directly without further purification. The water used in the experiments was ultrapure water with a resistivity of no less than 18.2 MΩ·cm. The main experimental reagents and instruments are shown in Table 2.1 and Table 2.2, respectively

Table 2.1 Main experimental reagents

Reagent Name	Chemical Formula	Purity	Purpose
Vanadium(III) chloride	VCl_3	98%	Synthesis of V-MOF-10
Vanadyl sulfate hydrate	$\text{VOSO}_4 \cdot x\text{H}_2\text{O}$	99.9%	Synthesis of V-TCPB/V-TBAPy
meso-Tetra(4-carboxyphenyl)porphyrin	$\text{C}_{48}\text{H}_{30}\text{N}_4\text{O}_8$	99%	Synthesis of V-MOF-10
1,3,6,8-Tetrakis(p-benzoic acid)pyrene	$\text{C}_{48}\text{H}_{26}\text{O}_8$	98%	Synthesis of V-TBAPy
1,2,4,5-Tetrakis(4-carboxyphenyl)benzene	$\text{C}_{46}\text{H}_{26}\text{O}_8$	98%	Synthesis of V-TCPB
Hydrochloric acid	HCl	37%	Solvent
N,N-Dimethylformamide (DMF)	$\text{C}_3\text{H}_7\text{NO}$	99.8%	Solvent
Acetic acid	CH_3COOH	99.7%	Solvent
Acetone	$\text{C}_3\text{H}_6\text{O}$	99.5%	Washing, Solvent exchange
Methylene Blue	$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$	Indicator grade	Adsorption model pollutant

Table 2.2 Main experimental instruments

Instrument Name	Model	Purpose
Electronic Analytical Balance		Precise weighing
Teflon-Lined Stainless Steel Autoclave	45, 100 mL	Solvothermal synthesis
Vacuum Drying		Sample drying
High-Speed Centrifuge		Solid-liquid separation
UV Lamp System	Arimed B6 ($\lambda_{\text{max}} = 320 \text{ nm} \pm 30 \text{ nm}$, 36 W)	UV light photocatalytic experiments
Solar Simulator	SunLife series	Simulated sunlight photocatalytic experiments
Ultraviolet-Visible Spectrophotometer	UV-1800	Solution concentration analysis
Powder X-Ray Diffractometer (PXRD)	D8 Advance	Phase and structural analysis
Field Emission Scanning Electron Microscope (FE-SEM)	SU8010	Microscopic morphology observation
Surface Area and Porosity Analyzer	3Flex	N ₂ adsorption analysis
Fourier Transform Infrared Spectrometer (FT-IR)	Vertex 70	Chemical bond and functional group analysis
Thermogravimetric Analyzer (TGA)	TA Instruments TGA 5500	Thermal stability analysis
Laboratory X-ray Absorption Spectrometer	EasyXAFS300+	V K-edge XAS/XANES analysis and determination of vanadium oxidation states

2.2 Synthesis of Vanadium-based MOFs

Three vanadium-based metal–organic frameworks, namely V-MOF-10, V-TBAPy, and V-TCPB, were synthesized via solvothermal methods. The detailed synthesis procedures are described in the following sections.

2.2.1 Synthesis of V-MOF-10

V-MOF-10 was synthesized according to a previously reported method with minor modifications.¹²⁴ Vanadium(III) chloride (0.15 g, 0.952 mmol) and meso-tetra(4-carboxyphenyl)porphyrin (0.34 g, 0.430 mmol), were added to into *N,N*-dimethylformamide (DMF, 50 mL) and glacial acetic acid (150 μ L). The mixture was dispersed by ultrasonic treatment for 5 min to form a uniform suspension. Subsequently, the obtained suspension was transferred to a 100 mL stainless-steel autoclave lined with polytetrafluoroethylene and reacted at 150 °C for 24 h.

After the reaction was completed, the reaction system was naturally cooled to room temperature, and the obtained dark red-brown solid was collected by centrifugation. The product was first subjected to solvent exchange in DMF (10 mL each) and then further exchanged in acetone (10 mL each) to remove the residual guest molecules in the pores. Finally, the sample was vacuum-dried and activated at 100 °C for 24 h to obtain the activated V-MOF-10 powder, which was stored in a desiccator for later use. The PXRD pattern of the obtained V-MOF-10 was in good agreement with the simulated PXRD pattern derived from the reported Al-PMOF structural analogue.^{124,125}

2.2.2 Synthesis of V-TBAPy

V-TBAPy was synthesized according to a previously reported method with minor modifications.¹²⁶ Vanadyl sulfate hydrate (0.0327 g) and 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (TBAPy, 0.0546 g) were added to *N,N*-dimethylformamide (DMF, 19.6 mL),

followed by the addition of concentrated hydrochloric acid (14.9 μ L) as a modulator. The mixture was sonicated for 5 min to obtain a homogeneous suspension. The resulting suspension was transferred to a 45 mL Teflon-lined stainless-steel autoclave and heated at 180 $^{\circ}$ C for 72 h.

After the reaction, the autoclave was allowed to cool naturally to room temperature. The resulting solid was collected by centrifugation, washed three times with DMF (10 mL each), and subsequently washed twice with acetone (10 mL each) to remove unreacted precursors and residual solvent molecules. The product was then activated under vacuum at 100 $^{\circ}$ C for 24 h and stored in a desiccator until further use. The PXRD pattern of the obtained V-TBAPy was compared with the literature-predicted pattern, and the main diffraction peaks showed good agreement, confirming the formation of the target framework.¹²⁶ To obtain sufficient material for structural characterization and photocatalytic experiments, ten identical reactions were conducted in parallel using ten 45 mL Teflon-lined stainless-steel autoclaves under the same reaction conditions.

2.2.3 Synthesis of V-TCPB

V-TCPB was synthesized according to a previously reported method with minor modifications.¹²⁶ Vanadyl sulfate hydrate (0.0327 g) and 1,2,4,5-tetrakis(4-carboxyphenyl) benzene (TCPB, 0.0460 g) were added to *N,N*-dimethylformamide (DMF, 19.6 mL), followed by the addition of concentrated hydrochloric acid (14.9 μ L) as a modulator. The mixture was sonicated for 5 min to obtain a homogeneous suspension. The resulting suspension was transferred to a 45 mL Teflon-lined stainless-steel autoclave and heated at 180 $^{\circ}$ C for 72 h.

After the reaction, the autoclave was allowed to cool naturally to room temperature. The resulting solid was collected by centrifugation, washed three times with DMF (10 mL each), and subsequently washed twice with acetone (10 mL each) to remove unreacted precursors and residual solvent molecules. The product was then activated under vacuum

at 100 °C for 24 h and stored in a desiccator until further use. The PXRD pattern of the obtained V-TCPB was compared with the literature-predicted pattern, and the main diffraction peaks showed good agreement, confirming the formation of the target framework.¹²⁶ To obtain sufficient material for structural characterization and photocatalytic experiments, ten identical reactions were conducted in parallel using ten 45 mL Teflon-lined stainless-steel autoclaves under the same reaction conditions.

2.3 Material characterization methods

To systematically evaluate the physicochemical properties of the synthesized V-MOFs materials, multiple characterization techniques were employed in this study.

The phase analysis of the samples was performed using a Bruker D8 Advance powder X-ray diffractometer (PXRD) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a nickel filter. The test range was 3°-50° (2 θ), with a step size of 0.02° and an integration time of 1 s per step. Before the test, the samples were evenly spread in a glass sample holder. The crystallinity, phase purity, and structural stability of the samples were analyzed by comparing the experimental diffraction patterns with the patterns simulated by Mercury software from reported crystal structures or the results reported in the literature.

The microscopic morphology of the samples was observed using a Hitachi SU8010 cold field emission scanning electron microscope, and the elemental distribution was analyzed in combination with energy dispersive X-ray spectroscopy (EDS). Before testing, a small amount of powder samples was evenly spread on the surface of the conductive adhesive and sputtered with gold for about 10 nm to improve conductivity. The test voltage was 5 kV. The EDS analysis used an Oxford Instruments X-MaxN 80 mm² silicon drift detector to characterize the distribution and relative content of elements such as V, C, O, and N in the samples.

The specific surface area and pore structure of the samples were characterized by nitrogen adsorption–desorption tests using a Micromeritics 3Flex surface area and pore size

analyzer at 77 K. Prior to the tests, the samples were degassed in an external degassing station at 150 °C under a vacuum of less than 10^{-3} Pa for at least 12 h to remove adsorbed water and residual solvent molecules in the pores. The relative pressure (P/P_0) ranged from 10^{-6} to 0.995. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.30; the total pore volume was calculated from the adsorption amount at $P/P_0 = 0.995$; the pore size distribution was analyzed using the non-local density functional theory (NLDFT) model based on the nitrogen adsorption data at 77 K.

Fourier transform infrared spectroscopy (FT-IR) testing was performed using a Bruker Vertex 70 infrared spectrometer equipped with a diamond attenuated total reflection (ATR) accessory. The scanning range was 4000–400 cm^{-1} , the resolution was 4 cm^{-1} , and each sample was scanned 32 times in total. By analyzing the position and intensity changes of characteristic absorption peaks, the characteristics of functional groups in organic ligands were determined, and the coordination interaction between them and vanadium ions was analyzed through the changes of symmetric and asymmetric stretching vibration peaks of carboxylate groups.

Thermogravimetric analysis (TGA) was conducted using a TA Instruments TGA 5500 thermogravimetric analyzer under a high-purity nitrogen atmosphere with a gas flow rate of 50 $\text{mL} \cdot \text{min}^{-1}$. A 5–10 mg sample was weighed and placed in a platinum crucible, and then heated from room temperature to 800 °C at a heating rate of 10 °C·min⁻¹. Based on the weight loss behavior of the sample with temperature, the thermal stability of the material, the framework decomposition temperature, and the presence of guest molecules in the pores were analyzed.

Vanadium K-edge X-ray absorption spectroscopy (XAS) measurements were performed at the Durham X-Ray Absorption Facility using an EasyXAFS300+ laboratory-scale spectrometer (EasyXAFS, WA, USA) operating in a Rowland-circle optical

geometry.^{127,128} V K-edge XAFS were acquired using a Ge (442) spherically bent crystal analyser (SBCA) and a Ag anode X-ray tube (20260AGT19019) at 40 kV. The X-ray current was varied depending on the sample to maintain a collection deadtime of < 30%.

Data collection and processing incorporate a deadtime correction, which is performed by the silicon drift detector (SSD) with a 6 x 15 mm aperture and multiple component analyser (MCA) within the instrument. Background correction, using I_0 and I_t to obtain $\mu(E)$, and energy shifts were conducted using the EasyXAFS software. Sample energies were calibrated using a V foil standard. The processing of XANES data for visualization was conducted with the Demeter package (Athena).¹²⁹

V-MOF-10, V-TBAPy, and V-TCPB were analyzed together with V foil, VOSO_4 , V_2O_5 , and NH_4VO_3 as reference materials representing vanadium oxidation states of 0, +4, and +5. A single 50 min scan was collected for each MOF sample and reference material.

2.4 Experiments on adsorption and photocatalytic performance

2.4.1 Dye Adsorption Experiments

Using methylene blue (MB) as a model pollutant, the adsorption performance of V-MOFs was preliminarily evaluated.

In the adsorption kinetics experiment, 3 mg of V-MOFs adsorbent was added to 100 mL of MB solution with a concentration of $30 \text{ mg}\cdot\text{L}^{-1}$ in a 250 mL conical flask, and magnetically stirred at 270 rpm in the dark. Samples were taken at set time intervals (0, 5, 10, 30, 60, 120, 180 min) and filtered through a $0.22 \text{ }\mu\text{m}$ membrane filter. The absorbance of the filtrate was measured using a Shimadzu UV-1800 UV-Vis spectrophotometer at the maximum absorption wavelength of MB (664 nm), and the remaining concentration of MB in the solution was calculated according to the pre-drawn standard curve.

The adsorption capacity is calculated according to Equation 2.1:

$$qt = \frac{(C_0 - C_t)V}{m}$$

Equation 2.1

Among them, C_0 is the initial concentration (mg/L), C_t represents the solution concentration at time t (mg/L), V is the solution volume (L) and m is the adsorbent mass (g).

2.4.2 Photocatalytic Degradation Experiment

2.4.2.1 Light Source System

To investigate the photocatalytic performance of the materials, two different light source systems, namely an ultraviolet light source and a simulated solar light source, were employed in this experiment.

The ultraviolet light source was an Arimed B6 low-pressure ultraviolet lamp, which emits light at a wavelength of 320 ± 30 nm and has a power of 36 W. The light source is installed in a light-tight reaction chamber and equipped with a magnetic stirring device.

The simulated solar light source uses the SunLite series solar simulator from Abet Technologies, which employs a xenon lamp as the light source and is equipped with an AM 1.5G filter. The light intensity on the surface of the reaction solution is $100 \text{ mW} \cdot \text{cm}^{-2}$, which can effectively simulate the solar spectrum at the Earth's surface.

2.4.2.2 Experimental Setup and Photocatalytic Degradation Steps

The photocatalytic degradation experiment of methylene blue was conducted in a self-made photochemical reaction device. To ensure good light transmission, a glass reactor was used as the reaction vessel. By performing experiments under ultraviolet light and simulated

sunlight conditions respectively, the photocatalytic performance of the materials within different spectral ranges was evaluated. During the entire reaction process, magnetic stirring was employed to ensure the uniform dispersion of the catalyst in the solution, and the reaction was carried out at room temperature.

In the specific experiment, different masses (1, 3, 5, or 10 mg) of V-MOFs catalysts were added to 50 mL of methylene blue (MB) solution with a concentration of $30 \text{ mg} \cdot \text{L}^{-1}$. First, the solution was magnetically stirred in the dark for 2 h to establish an adsorption-desorption equilibrium, and then the light source was turned on to initiate the degradation reaction.

To distinguish the contributions of adsorption, uncatalysed photodegradation, and photocatalytic degradation to the removal of MB, two control experiments were conducted. In the light control experiment, the MB solution was irradiated under the same conditions as those used in the photocatalytic experiment, but without the addition of a catalyst, to evaluate the uncatalysed photodegradation of MB. In the dark adsorption control experiment, the catalyst was added to the MB solution, and the suspension was stirred in the dark to evaluate the removal of MB by adsorption. Both control experiments were performed using the same initial MB concentration, solution volume, sampling intervals, and stirring conditions as those used in the photocatalytic experiment. The results of the control experiments were compared with those of the photocatalytic experiment to distinguish the effects of adsorption and uncatalysed photodegradation from the photocatalytic activity of the V-MOFs.

During the reaction process, approximately 2 mL of the suspension sample was taken at 0, 10, 20, 30, 45, 60, 90, and 120 min respectively. After centrifuging to remove the solid catalyst, the supernatant was taken, and its absorbance was measured using a UV-1800 UV-Vis spectrophotometer to obtain the variation of MB concentration with time.

2.4.2.3 Data Analysis and Performance Evaluation Methods

The change in the concentration of the MB solution was quantitatively analyzed using ultraviolet-visible absorption spectroscopy. The absorbance at its maximum absorption wavelength was used as the basis for quantification, and it was assumed that the absorbance and concentration conformed to the Lambert–Beer law within the experimental range. The concentration of the solution at dark adsorption equilibrium was the initial concentration C_0 , and the concentration at any time C_t during illumination.

The photocatalytic degradation efficiency η is calculated according to Equation 2.2:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$

Equation 2.2

In this context, C_0 denotes the concentration of methyl blue once dark adsorption equilibrium is achieved, while C_t indicates the concentration of methyl blue at a given irradiation time t .

To investigate the reaction kinetics, we employed a quasi-first-order kinetic model to fit the experimental data. The model's expression is given in Equation 2.3:

$$\ln \frac{C_0}{C_t} = kt$$

Equation 2.3

In this context, k denotes the apparent reaction rate constant (min^{-1}). It is determined by performing a linear fit of $\ln(C_0/C_t)$ against time (t).

Additionally, to assess the material's adsorption performance for MB, the adsorption amount per unit mass of the catalyst is determined based on the concentration change during the dark adsorption phase, using Equation 2.4:

$$q_t = \frac{(C_0 - C_t)V}{m}$$

Equation 2.4

In this context, V denotes the solution's volume in litres, while m signifies the catalyst's mass in grams. C_0 and C_t represent the initial concentration and the concentration at a given time t , respectively. The adsorption capacity at equilibrium is indicated by q_t .

The photocatalytic activity and adsorption performance of V-MOFs materials were systematically assessed by examining degradation efficiency, kinetic constants, and adsorption capacity across varying catalyst dosages and light source conditions.

Chapter 3 **Structural Characterization and Adsorption-Photocatalytic Performance of Vanadium-Based MOFs towards Methylene Blue**

3.1 Structural Characterization and Physicochemical Properties of Vanadium-Based MOFs

V-MOF-10, V-TBAPy, and V-TCPB were selected to compare vanadium-based MOFs derived from tetratopic carboxylic acid ligand precursors with distinct aromatic cores. V-MOF-10 was prepared from the porphyrin-based meso-tetrakis(4-carboxyphenyl)porphyrin (H_6TCPP) precursor, whereas V-TBAPy and V-TCPB were prepared from the pyrene-based 1,3,6,8-tetrakis(4-carboxyphenyl)pyrene (H_4TBAPy) and benzene-based 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (H_4TCPB) precursors, respectively.^{124,126} Their chemical structures are shown in Figure 3.1. Differences in linker size, conjugation, and geometry produce distinct framework and pore environments, providing a basis for comparing their adsorption and photocatalytic behavior towards methylene blue. Because the three MOFs are not strictly isostructural, the comparison is intended to identify broader structure–property relationships rather than the effect of a single structural variable. As shown in Figure 3.1, V-TBAPy contains rod secondary building units composed of infinite chains of corner-sharing vanadium–oxygen octahedra, which are connected by $TBAPy^{4-}$ linkers to form one-dimensional rhombohedral channels along the $[100]$ direction.¹²⁶

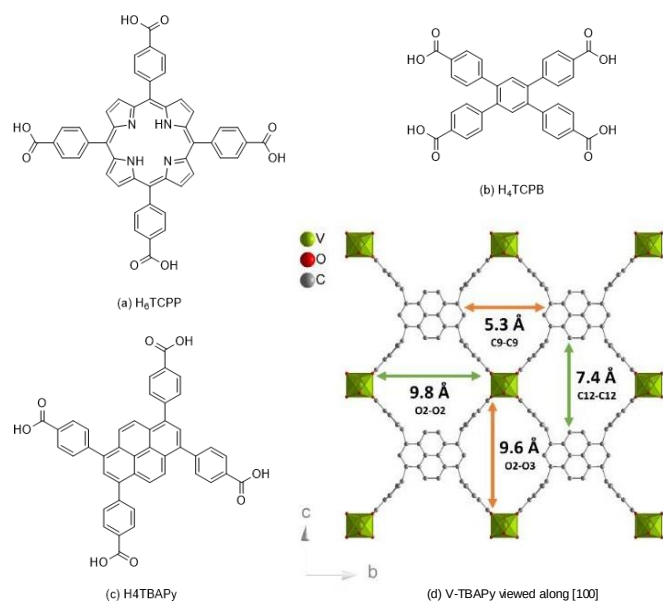


Figure 3.1 Chemical structures of the tetratopic carboxylic acid ligand precursors: (a) meso-tetra(4-carboxyphenyl) porphyrin (H₆TCPP), (b) 1,2,4,5-tetrakis(4-carboxyphenyl) benzene (H₄TCPB), and (c) 1,3,6,8-tetrakis(4-carboxyphenyl) pyrene (H₄TBAPy), together with (d) the crystal structure of V-TBAPy viewed along the [100] direction, showing its one-dimensional rhombohedral channels and estimated pore dimensions. Panels (a–c) were drawn using ChemDraw. Panel (d) was adapted from Figure S10 of Ref.¹²⁶ V, O, and C atoms are shown in green, red, and grey, respectively.

All three MOFs were prepared using solvothermal methods adapted from previously reported procedures, as detailed in Section 2.2.^{124,126} Briefly, V-MOF-10 was synthesized from VCl₃ and H₆TCPP in DMF containing acetic acid at 150 °C for 24 h. V-TBAPy and V-TCPB were synthesized from VOSO₄·xH₂O and H₄TBAPy or H₄TCPB, respectively, in DMF containing HCl at 180 °C for 72 h. The products were subsequently collected, washed, solvent-exchanged, and vacuum-activated.

To elucidate the structural and morphological characteristics of the synthesized vanadium-based metal-organic framework materials, V-MOF-10, V-TBAPy, and V-TCPB were systematically characterized using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR), N₂ adsorption-desorption porosimetry and X-ray absorption spectroscopy (XAS). These results provide the necessary structural information for the subsequent discussion of the adsorption and photocatalytic degradation behavior of methylene blue.

3.1.1 Powder X-ray Diffraction Analysis

Powder X-ray diffraction (PXRD) was employed to characterize the crystallinity and phase purity of the three synthesized vanadium-based MOF powder samples. For MOF materials, good crystallinity and high phase purity are crucial for maintaining the integrity of the framework and the accessibility of the pores, which are closely related to the adsorption and photocatalytic behaviors of the materials.^{130,131} Therefore, PXRD tests were conducted on V-MOF-10, V-TBAPy, and V-TCPB to analyze their diffraction characteristics and verify the successful construction of the crystalline frameworks.

3.1.1.1 PXRD of V-MOF-10

The crystallinity and phase purity of the synthesized V-MOF-10 powder were characterized by PXRD. As shown in Figure 3.2, the sample exhibits several distinct diffraction peaks in the low-angle region, with representative peaks at approximately $2\theta = 5.23^\circ, 7.43^\circ, 10.56^\circ, 11.85^\circ, 13.07^\circ, 15.03^\circ, 16.46^\circ, 19.22^\circ,$ and 22.68° . The intense peak at 7.43° and the presence of multiple well-defined low-angle reflections indicate good crystallinity and a periodically ordered framework. No obvious impurity peaks are observed within the measured range, suggesting relatively high phase purity.

Since no deposited single-crystal CIF file or standard PXRD reference pattern is available for V-MOF-10, the simulated pattern based on the reported Al-PMOF structural analogue was used as a reference.¹²⁵ The main diffraction peaks of the synthesized V-MOF-10 agree well with the reference pattern, particularly in the low-angle region, supporting the formation of the crystalline V-MOF-10 framework. Minor intensity differences may arise from metal substitution, preferred orientation, and powder packing effects.

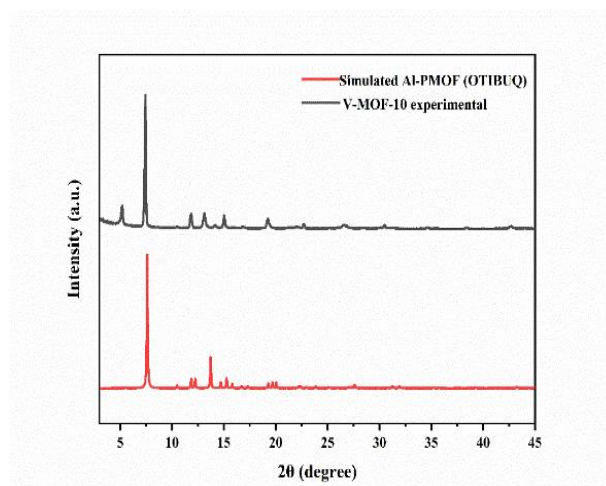


Figure 3.2 PXRD pattern of synthesized V-MOF-10 and the reference pattern based on the reported Al-PMOF structural analogue. The main diffraction peaks show good positional agreement, indicating the formation of a crystalline V-MOF-10 framework with relatively high phase purity.

3.1.1.2 PXRD of V-TBAPy

The PXRD pattern of the synthesized V-TBAPy is shown in Figure 3.3. In the experimental diffractogram, clear and sharp diffraction peaks appear, with representative peak positions at approximately $2\theta = 3.57^\circ, 5.54^\circ, 7.99^\circ, 13.32^\circ, 16.11^\circ$, and 20.52° , indicating that the sample has good crystallinity. No obvious impurity-related diffraction peaks are observed in the pattern, suggesting that the sample has relatively high phase purity.

As shown in Figure 3.3, the experimental XRD pattern is generally consistent with that predicted from the published single crystal structure in terms of the main peak positions, especially in the low-angle region where the corresponding relationship of the main characteristic peaks is relatively good.¹²⁶ This indicates that the synthesized sample retains the expected V-TBAPy crystal framework structure. There are slight differences in the relative peak intensities between the experimental and reference patterns, which can usually be attributed to preferred orientation, grain size effects, and differences in the sample packing mode during testing. However, these differences do not affect the overall judgment of the successful construction of the target framework.

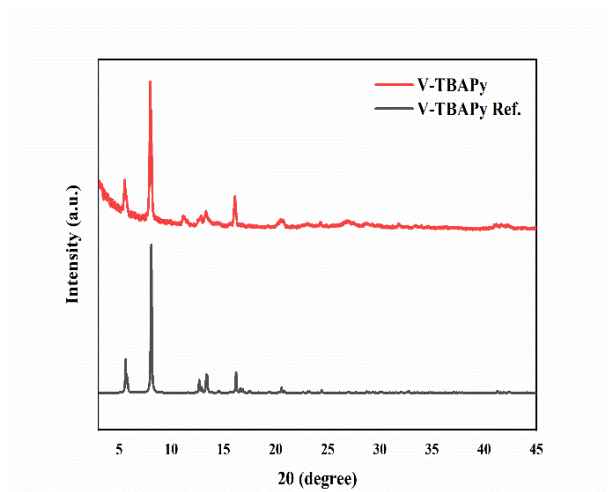


Figure 3.3 Experimental PXRD pattern and reference pattern of V-TBAPy. The characteristic diffraction peaks of the experimental pattern are approximately located at $2\theta = 5.54^\circ$, 7.99° , and 16.11° , and are generally consistent with the reference pattern, indicating that the target crystal framework is successfully formed and has good phase purity.

3.1.1.3 PXRD of V-TCPB

The PXRD pattern of V-TCPB is shown in Figure 3.4. Multiple clear and well-resolved diffraction peaks can be observed in the figure. The representative peak positions are approximately at $2\theta = 5.48^\circ$, 8.06° , 9.78° , 11.06° , 13.75° , and 19.72° , indicating that the sample has good crystallinity. Meanwhile, no obvious additional impurity peaks are observed in the pattern, suggesting that the sample has high phase purity.

As further shown in Figure 3.4, the experimental diffractogram and the diffractogram predicted from the published single crystal structure exhibit good consistency in the main peak positions, which supports the successful synthesis of the target V-TCPB framework.¹²⁶ The small differences in peak intensities between the experimental diffractogram and the reference may stem from preferred orientation or differences in grain morphology. However, the overall consistency between the two diffractograms fully demonstrates the successful construction of the target framework.

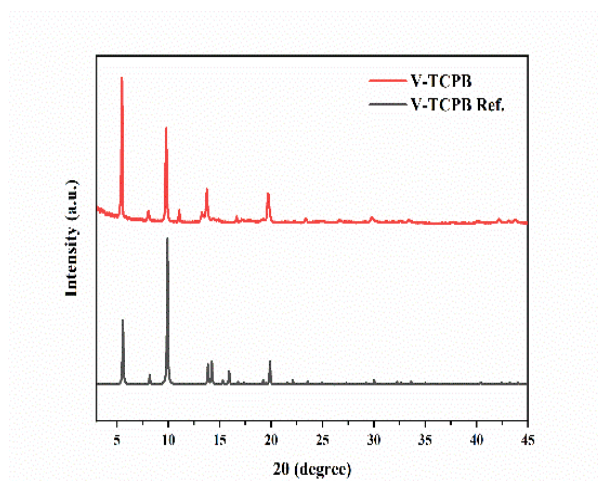


Figure 3.4 shows the experimental PXRD pattern and the reference pattern of V-TCPB. The characteristic diffraction peaks of the experimental pattern are located at approximately $2\theta = 5.48^\circ$, 9.78° , 13.75° and 19.72° . The positions of the main peaks are in good agreement with those in the reference pattern, indicating the successful construction of the target crystal phase.

3.1.2 Scanning Electron Microscopy Analysis

Based on the crystallographic information obtained from PXRD, scanning electron microscopy (SEM) was further employed to examine the morphology of the synthesized vanadium-based MOFs. SEM observation provides information on particle shape, surface texture, and aggregation state, which is useful for understanding the contact between the materials and methylene blue molecules.^{119,124}

As shown in Figure 3.5, V-MOF-10 mainly exhibits flower-like lamellar microcrystals with relatively uniform particle distribution. At low magnification, the particles are distributed in the micrometer scale and are assembled from layered plate-like units. At higher magnification, the lamellar stacking becomes more evident, and the particles show wrinkled surfaces with relatively clear edges. This morphology indicates that V-MOF-10 forms a well-defined layered microcrystalline structure under the present synthesis conditions.

In contrast, V-TBAPy, shown in Figure 3.5, presents irregular aggregated particles with a relatively compact morphology. The particles are composed of closely packed

microcrystalline units, and the surface is rough rather than smooth. Compared with V-MOF-10, the layered feature is less obvious, while particle aggregation is more pronounced. This compact morphology suggests that V-TBAPy has a lower degree of external surface exposure.

V-TCPB exhibits a different morphology, as shown in Figure 3.5, with irregular plate-like or block-like aggregates with obvious stacking. At higher magnification, folded lamellar textures and rough surfaces can be observed. Some small fragments are also attached to the particle surface, indicating that the sample is composed of stacked microcrystalline units rather than smooth isolated crystals.

Overall, the three vanadium-based MOFs show different external morphologies. V-MOF-10 displays relatively uniform flower-like lamellar particles, V-TBAPy forms compact aggregated particles, while V-TCPB exhibits irregular stacked plate-like aggregates. These differences may influence the surface exposure and diffusion path of methylene blue molecules during adsorption and photocatalytic degradation. Together with the PXRD results, the SEM observations further support the formation of the three crystalline MOF materials.

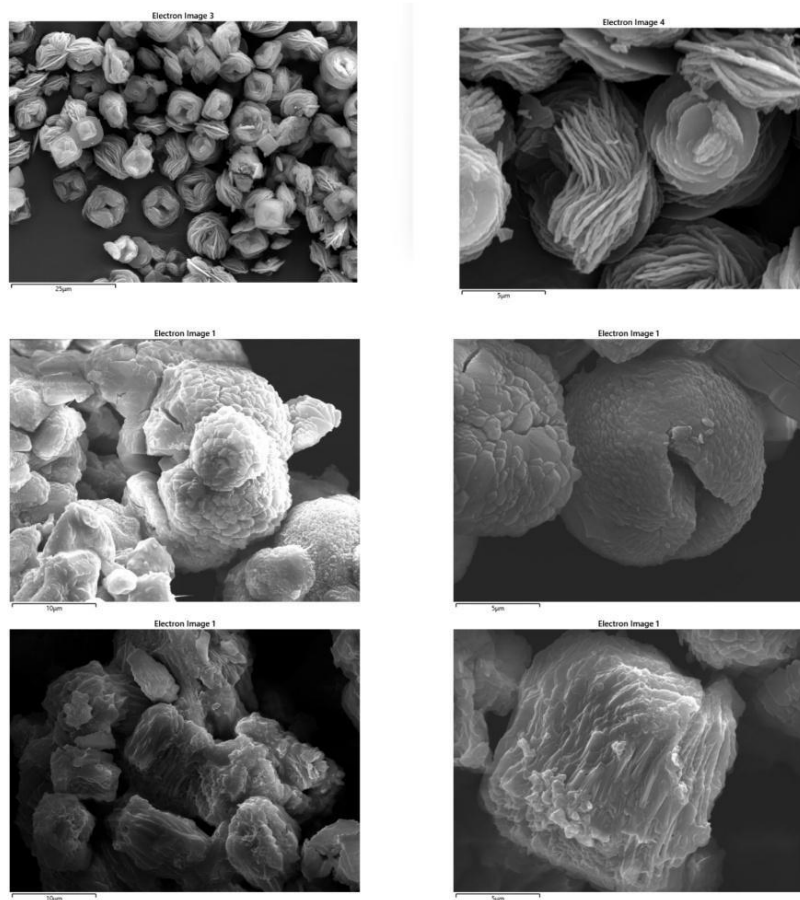


Figure 3.5 SEM images of the synthesized vanadium-based MOFs: (a,b) V-MOF-10, showing flower-like lamellar microcrystals; (c,d) V-TBAPy, showing compact aggregated particles with rough surfaces; and (e,f) V-TCPB, showing irregular plate-like aggregates with folded lamellar textures. Scale bars: (a) 25 μm ; (c, e) 10 μm ; and (b, d, f) 5 μm

3.1.3 Fourier Transform Infrared Spectroscopy Analysis

Fourier transform infrared spectroscopy (FT-IR) was employed to examine the coordination environment and functional group characteristics of the three vanadium-based MOFs. The comparative FT-IR spectra of V-MOF-10, V-TBAPy, and V-TCPB are shown in Figure 3.6.

The three samples exhibit characteristic absorption bands in the 1600–1400 cm^{-1} region, which can be assigned to the asymmetric and symmetric stretching vibrations of coordinated carboxylates. This indicates that the carboxylate groups in the organic ligands

are involved in coordination with vanadium centers. In addition, absorption features below 1000 cm^{-1} are observed in the three spectra and can be tentatively related to V–O and framework vibrations. These common features support the formation of vanadium–carboxylate coordination frameworks in V-MOF-10, V-TBAPy, and V-TCPB.

Although the main coordination-related bands are similar, differences in relative intensity and peak position are observed in the ligand-related vibration regions. These differences are likely associated with the different organic linker structures, including the porphyrinic framework in V-MOF-10 and the aromatic skeletons in V-TBAPy and V-TCPB. The retention of these ligand-related vibrations suggests that the organic skeletons remain largely intact after coordination.

Overall, the FT-IR results support the formation of the three vanadium-based MOFs, while the spectral differences reflect the distinct ligand environments within the respective frameworks. However, FT-IR alone cannot provide a reliable assignment of the oxidation states of the vanadium centers. Therefore, V K-edge XANES was further employed to examine their local electronic states.

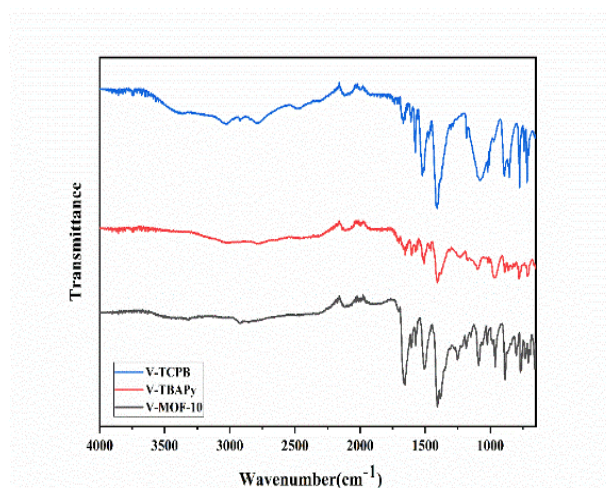


Figure 3.6 Comparative FT-IR spectra of V-MOF-10, V-TBAPy, and V-TCPB. The spectra are vertically offset for clarity. The three samples show similar absorption features in the 1600–1400 cm^{-1} region, corresponding to coordinated carboxylate vibrations, as well as low-wavenumber bands below 1000 cm^{-1} related to V–O/framework vibrations.

3.1.4 V K-edge X-ray Absorption Spectroscopy Analysis

V K-edge XAS was used to further investigate the vanadium electronic states in V-MOF-10, V-TBAPy, and V-TCPB. As shown in Figure 3.7, the XANES spectra of the three MOFs were compared with those of V foil, VOSO_4 , V_2O_5 , and NH_4VO_3 reference compounds. V-MOF-10 and V-TBAPy show absorption-edge positions close to that of VOSO_4 , suggesting that their vanadium centers are mainly in a V(IV)-like state. In contrast, V-TCPB exhibits a noticeable edge shift towards lower energy compared with V-MOF-10, V-TBAPy, and VOSO_4 , indicating a more reduced vanadium environment. This result suggests that lower-valent vanadium species, possibly V(III), may be present in V-TCPB.¹³² However, because no quantitative fitting analysis was performed due to time limitations, this assignment should be regarded as preliminary.

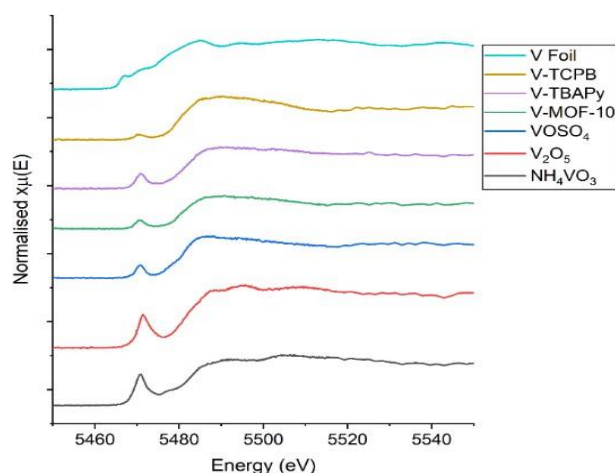


Figure 3.7 Normalized V K-edge XANES spectra of V-MOF-10, V-TBAPy, and V-TCPB together with V foil, VOSO₄, V₂O₅, and NH₄VO₃ reference compounds. The spectra are vertically offset for clarity.

3.1.5 Physicochemical Properties Analysis

After the successful construction of three vanadium-based MOFs was confirmed by PXRD, SEM, FT-IR, and XAS, characterization, their physicochemical properties were further investigated to understand the structural factors that might influence the adsorption and photocatalytic behavior of methylene blue. In particular, N₂ adsorption-desorption tests at 77 K were employed to analyze the pore structures and specific surface area characteristics of V-MOF-10, V-TBAPy, and V-TCPB. These results provide important information for understanding the accessible specific surface area, pore volume, and pore size distribution of the materials, which are closely related to the number of adsorption sites and mass transfer behavior in the aqueous phase system.

3.1.5.1 BET Specific Surface Area and Pore Structure Analysis

The nitrogen adsorption-desorption isotherms and pore size distribution curves of three vanadium-based MOFs are shown in Figure 3.8 to Figure 3.11. Since the specific surface area, pore volume, and pore size distribution of MOF materials can significantly affect the accessibility of dye molecules into the interior of the framework, these parameters are of great significance for evaluating their potential adsorption and photocatalytic properties.

3.1.5.1.1 Analysis of the pore structure characteristics of V-MOF-10

The N₂ adsorption-desorption isotherm of V-MOF-10 at 77 K is shown in Figure 3.8. The isotherm exhibits a distinct and rapid adsorption increase in the low relative pressure region, followed by a slow increase in the higher relative pressure range, and there is almost no obvious hysteresis loop between the adsorption and desorption branches. This behavior is characteristic of a typical Type I isotherm, indicating that V-MOF-10 mainly has a microporous structure.

Quantitative analysis further supports this judgment. The BET specific surface area of V-MOF-10 is 1300 m²/g, among which the t-plot micropore area is 963 m²/g and the external surface area is 336 m²/g, indicating that most of its accessible specific surface area comes from the internal micropores of the framework rather than the external surface of the particles. Meanwhile, its micropore volume reaches 0.38 cm³/g, and the cumulative pore volumes of BJH adsorption and desorption are 0.22 cm³/g and 0.21 cm³/g, respectively. These results suggest that the pore filling of V-MOF-10 is mainly contributed by the internal micropores of the framework.

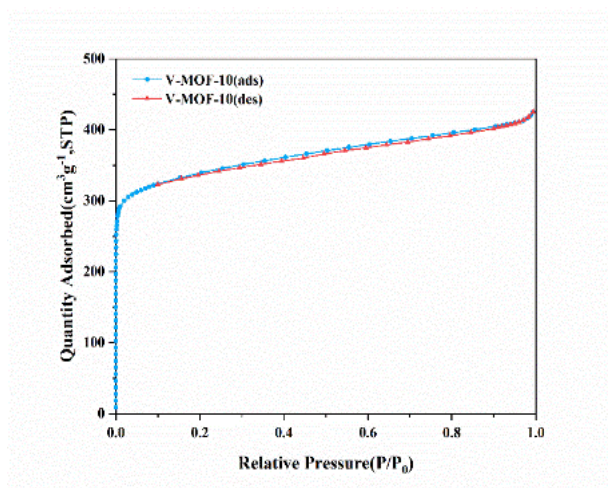


Figure 3.8 N₂ adsorption-desorption isotherms of V-MOF-10 at 77 K. The isotherm exhibits typical Type I characteristics, rising rapidly in the low relative pressure region, indicating that the material is predominantly microporous.

The pore size distribution curve shown in Figure 3.9 exhibits two main micropore peaks at approximately 5.93 Å and 6.65 Å, with weaker contributions at around 5.22 Å and 7.36 Å. The presence of two main pore-size maxima indicates that V-MOF-10 contains two distinct microporous environments rather than a single uniform pore system. This feature can be consistent with the reported dual-pore crystal structure of V-MOF-10, in which two types of framework pores with dimensions of 5.2×11.9 Å and 3.5×11.9 Å are formed along the y and z axes, respectively.¹²⁴ Therefore, the observed micropore distribution can be mainly attributed to the intrinsic pore channels of the crystalline V-MOF-10 framework. In contrast, the weak distribution observed in the larger pore-size region is more likely associated with secondary pores or interparticle voids formed by particle stacking rather than the primary framework micropores.

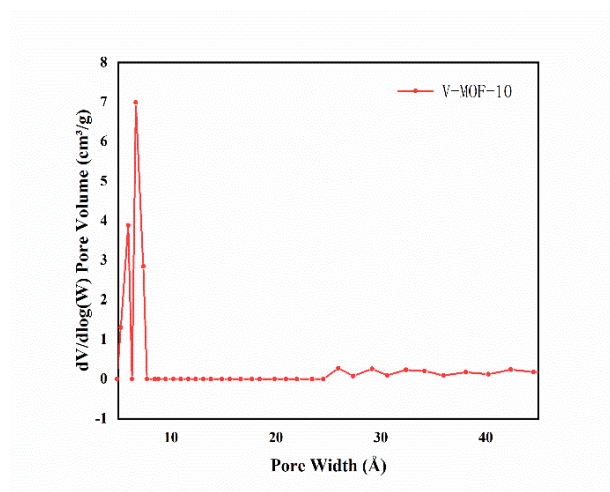


Figure 3.9 shows the pore size distribution curve of V-MOF-10. The material exhibits a dominant pore distribution within the sub-nanometer pore size range, and there are also a small number of wider pore structures in the larger pore size region.

From an application perspective, the high specific surface area, remarkable microporous characteristics, and large micropore volume make V-MOF-10 promising to exhibit good methylene blue adsorption capacity. This pore structure can not only provide abundant adsorption sites but also help shorten the diffusion distance between dye molecules and subsequent photocatalytic active sites.

3.1.5.1.2 Pore structure characteristic analysis of V-TBAPy

The N₂ adsorption-desorption isotherm of V-TBAPy at 77 K is shown in Figure 3.10. Compared with V-MOF-10, V-TBAPy has significantly lower nitrogen adsorption in the low relative pressure region, indicating that the contribution of micropores is limited. Meanwhile, the gradual increase in adsorption over a wide range of relative pressures should be interpreted with caution. This behavior may be related to weak textural porosity or interparticle voids, but it could also be affected by uncertainty in the free-space measurement during the isotherm collection.

The BET specific surface area of V-TBAPy was 314 m²/g, and the single-point specific surface area was 302 m²/g, both of which are substantially lower than those of V-MOF-10. Together with the weak nitrogen uptake in the low relative pressure region, these results

indicate that V-TBAPy has limited accessible microporosity after activation. Therefore, under the present activation and measurement conditions, V-TBAPy is more appropriately interpreted as a material with limited accessible porosity, rather than a fully preserved porous framework comparable to V-MOF-10.

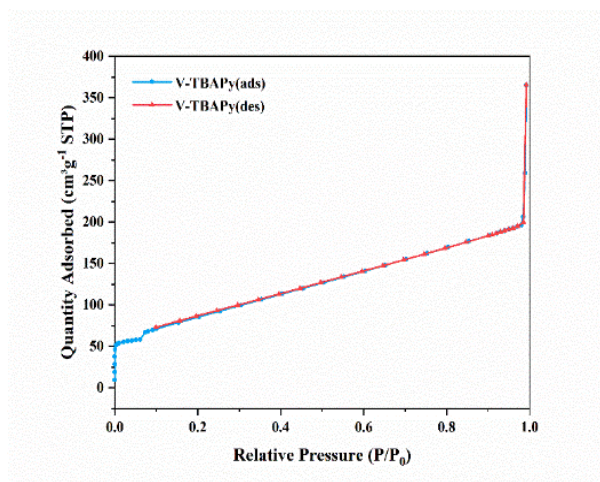


Figure 3.10 N₂ adsorption - desorption isotherms of V - TBAPy at 77 K. The material exhibits limited adsorption capacity in the low relative pressure region, and the overall adsorption behavior is relatively gentle, indicating that its pore structure is not dominated by significant micropores.

3.1.5.1.3 Analysis of the pore structure characteristics of V-TCPB

The N₂ adsorption-desorption isotherm of V-TCPB at 77 K is shown in Figure 3.11. V-TCPB exhibits a clear nitrogen uptake in the low relative pressure region, indicating the presence of accessible microporosity. However, its overall adsorption capacity is lower than that of V-MOF-10, suggesting that the total accessible pore volume and specific surface area of V-TCPB are more limited.

Quantitative analysis further supports this judgment. The BET specific surface area of V-TCPB is 485 m²/g, and the single-point specific surface area is 480 m²/g. Its t-plot micropore area is 332 m²/g, while the external surface area is 153 m²/g. The corresponding micropore volume is 0.13 cm³ g⁻¹. These results indicate that micropores still make a meaningful contribution to the accessible surface area and pore volume of V-TCPB, although the degree of porosity is substantially lower than that of V-MOF-10.

Therefore, V-TCPB can be interpreted as a material that retains partial accessible microporosity after activation. Compared with V-MOF-10, however, its lower nitrogen uptake and lower BET surface area indicate a less developed accessible porous framework. This more limited pore structure may reduce the number of available adsorption sites for methylene blue, while still allowing some contribution from framework-accessible micropores during adsorption and subsequent photocatalytic processes.

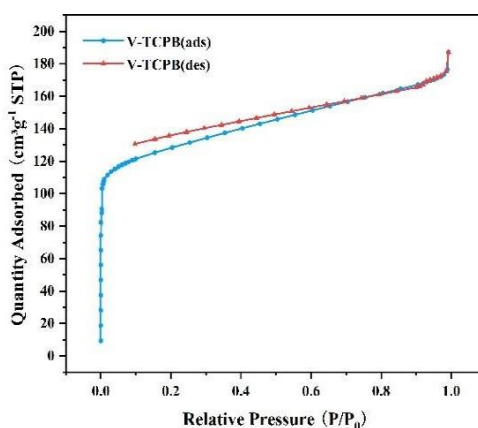


Figure 3.11 N₂ adsorption - desorption isotherms of V-TCPB at 77 K. The material shows a significant adsorption increase in the low relative pressure region and continues to increase slowly in the higher relative pressure region, indicating that it has a significant microporous contribution and at the same time exhibits characteristics of a wide pore structure.

3.1.5.1.4 Comparative Discussion

Nitrogen adsorption-desorption results reveal clear differences in the accessible porosity of the three vanadium-based MOFs. V-MOF-10 shows the most developed microporous structure, with the highest BET specific surface area of 1300 m²/g and the largest micropore volume of 0.38 cm³/g. In contrast, V-TBAPy exhibits a much lower BET surface area of 314 m²/g and limited accessible microporosity after activation. V-TCPB shows intermediate porosity, with a BET surface area of 485 m²/g and a micropore volume of 0.13 cm³/g.

Overall, the accessible surface area and microporosity follow the order V-MOF-10 > V-TCPB > V-TBAPy. This difference is expected to influence the number of available

adsorption sites and the diffusion of methylene blue molecules within the frameworks. Therefore, the adsorption performance of the three materials was further investigated to clarify how these pore-structure differences affect their interaction with methylene blue.

3.1.5.2 Thermogravimetric Analysis

To evaluate the thermal stability of three vanadium-based MOFs, thermogravimetric analysis (TGA) was conducted. The TGA curves of V-MOF-10, V-TBAPy, and V-TCPB are shown in Figure 3.12 to Figure 3.14, respectively. All three samples show an initial mass loss at low temperature, which can be mainly attributed to the removal of adsorbed water and residual solvent molecules. The following major weight loss at higher temperature corresponds to decomposition of the organic framework, leaving vanadium oxide as the final inorganic residue.

For the residue analysis, the final inorganic product after heating in air was assumed to be V_2O_5 . The theoretical V_2O_5 residue was calculated from the proposed framework formulae, and the experimental final residue was normalised by taking the mass remaining at 200 °C as the solvent-free MOF mass. The calculated and experimental values are summarized in Table 3.1.

For V-MOF-10, the formula $V_2(OH)_2(C_{48}H_{26}N_4O_8)$ gives an expected V_2O_5 residue of 19.7%. After normalisation using the mass at 200 °C, the experimental final residue is 19.0%, which is close to the calculated value. This indicates that, after correction for solvent loss, the inorganic residue is consistent with the proposed V-MOF-10 composition. Together with its highest BET surface area and micropore volume among the three samples, this close agreement suggests that V-MOF-10 is the most compositionally consistent and structurally well-preserved material examined in this study. This result is also in agreement with the reported V-MOF-10 structure and residue analysis in the literature.¹²⁴

For V-TBAPy and V-TCPB, the framework formulae were taken as $V_2O_2(TBAPy)$ and $V_2O_2(TCPB)$, respectively, according to the reported vanadium-based TBAPy and TCPB frameworks.¹²⁶ The calculated V_2O_5 residues are 22.4% for V-TBAPy and 26.4% for V-TCPB. After solvent correction, the normalised residue of V-TBAPy is higher than the theoretical value, while that of V-TCPB is lower. The higher residue of V-TBAPy may indicate the presence of excess inorganic vanadium oxide or other vanadium-rich species, which could partially block the pore channels. This interpretation is consistent with its low N_2 uptake and limited accessible porosity. In contrast, the lower residue of V-TCPB may reflect retained unreacted linker or other organic-rich species, which would reduce the apparent inorganic residue and could also restrict pore accessibility. This is consistent with the lower N_2 uptake of V-TCPB relative to V-MOF-10. However, these interpretations remain tentative because TGA alone cannot definitively identify the residual or pore-blocking species.

Overall, the TGA results show that the three samples contain different amounts of residual solvent before framework decomposition. The solvent-corrected residue analysis, together with the well-developed porosity of V-MOF-10, supports its proposed composition and suggests that it has the best-preserved framework among the three samples. The larger deviations observed for V-TBAPy and V-TCPB, together with their lower N_2 uptakes, may reflect pore blockage by inorganic and organic residual species, respectively. Their residue values should therefore be interpreted as approximate indications of sample composition rather than definitive evidence of phase purity.

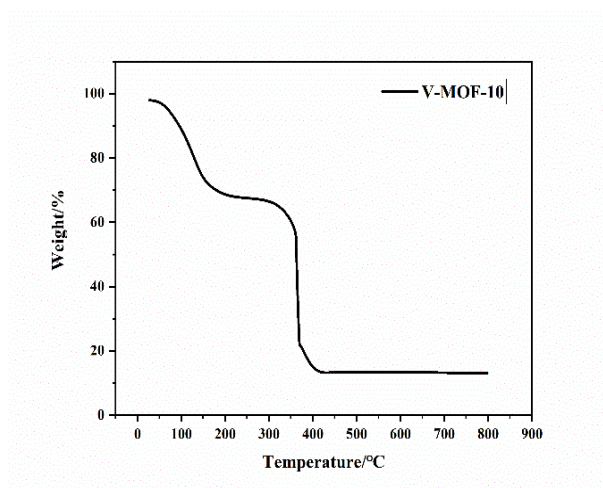


Figure 3.12 Thermogravimetric (TGA) curve of V-MOF-10 measured from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. The curve shows multistep weight-loss behavior, including low-temperature removal of guest species and high-temperature framework decomposition.

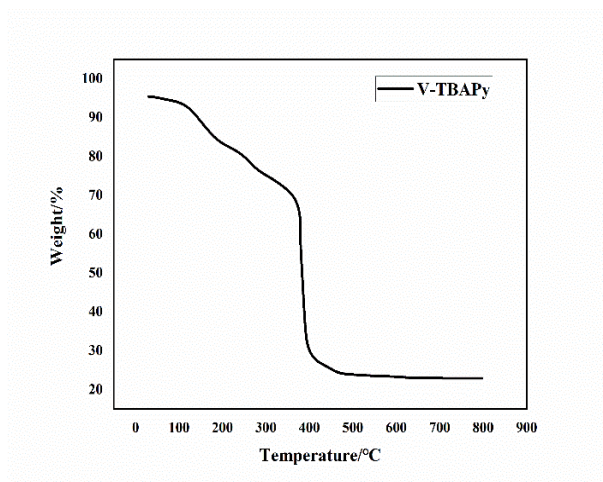


Figure 3.13 Thermogravimetric (TGA) curve of V-TBAPy measured from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. The material exhibits typical multistep thermal decomposition behavior, with minor low-temperature mass loss and major framework decomposition behavior, with minor low-temperature mass loss and major framework decomposition at higher temperature.

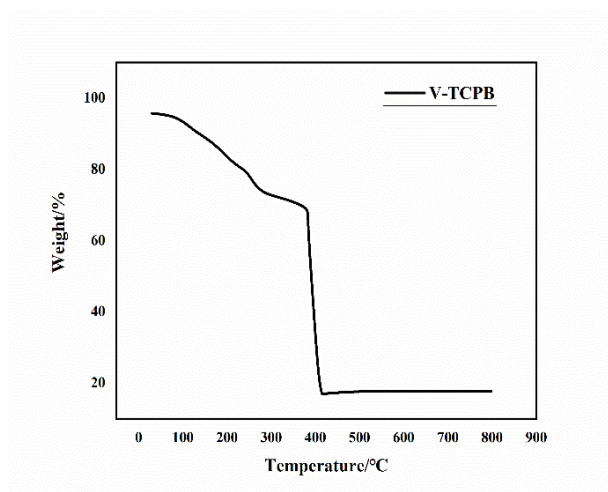


Figure 3.14 Thermogravimetric (TGA) curve of V-TCPB measured from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. The material shows multistep weight-loss behavior corresponding to guest removal and subsequent framework decomposition.

Table 3.1 Comparison of theoretical and experimental V₂O₅ residues after solvent correction.

Sample	Formula used for calculation	Theoretical V ₂ O ₅ residue / %	Mass at 200 °C / %	Final residue / %	Normalised final residue / %
V-MOF-10	V ₂ (OH) ₂ (C ₄₈ H ₂₆ N ₄ O ₈)	19.7	68.7	13.1	19.0
V-TBAPy	V ₂ O ₂ (C ₄₄ H ₂₂ O ₈)	22.4	83.4	22.9	27.5
V-TCPB	V ₂ O ₂ (C ₃₄ H ₁₈ O ₈)	26.4	83.6	17.7	21.2

3.2 Adsorption Behavior of Vanadium-Based MOFs towards Methylene Blue

3.2.1 Adsorption Kinetic Behavior

To compare the dark adsorption behaviors of the three vanadium-based MOF materials towards methylene blue (MB), the time-dependent MB removal efficiencies at different MOF dosages were investigated in a 50 mL system by monitoring the absorbance at 664 nm using UV–Vis spectroscopy. The initial MB concentration was adjusted for each material to obtain well-resolved kinetic curves, as specified in the corresponding figure captions. Therefore, the following comparison focuses primarily on the adsorption kinetic trends rather than a strict ranking based solely on the final removal efficiencies. Overall, all three materials exhibited rapid adsorption during the initial stage, followed by a slower approach to equilibrium.

The dark adsorption curve of V-MOF-10 towards MB is shown in Figure 3.15. Generally, its MB removal rate gradually increases with time. However, there are certain fluctuations in the early stages under the condition of low MOF dosage, indicating that this material is more susceptible to the mixing state of the system and test errors in a short time and at a low dosage. As the MOF dosage increases, the change pattern of the curve becomes clearer. The removal rate increases within the first 10 minutes, then continues to rise slowly, and gradually stabilizes in the later stage. This shows that V-MOF-10 has a certain adsorption capacity, but its adsorption process is relatively slow, to the point that the system may not have reached equilibrium on these timescales. In addition to surface adsorption, the mass transfer process inside the pores may also have an important impact on its adsorption behavior.

The removal rate-time curve of V-TBAPy is shown in Figure 3.16. Compared with V-MOF-10, V-TBAPy exhibits a faster adsorption response in the early stages, with

significant adsorption before the first measurement can even be taken. Especially under the condition of a higher dosage, the removal rate increases most significantly within the first 10 minutes, and then enters a relatively static stage. Overall, V-TBAPy also undergoes a process of transition from rapid adsorption to equilibrium adsorption, but the slope of its early curve is larger, indicating that the adsorption sites on the material surface or in the easily accessible pores capture MB molecules at a faster rate.

The dark adsorption curve of V-TCPB is shown in Figure 3.17. It can be seen that the adsorption response of V-TCPB is more prominent in the initial stage. The MB removal rate rises rapidly in a short time, followed by reaching equilibrium quite quickly in a concentration dependent manner. Compared with the other two materials, V-TCPB exhibits intermediate adsorption kinetics under the tested conditions, being faster than V-MOF-10 but slower than V-TBAPy. This indicates that its structural features are still conducive to the diffusion of MB molecules and the effective utilization of adsorption sites.

Overall, all three materials showed a transition from rapid initial adsorption to a gradual approach to equilibrium during the dark adsorption process, but their kinetic behaviors differed. V-MOF-10 exhibited a relatively slow and continuous adsorption process, indicating that equilibrium was not fully reached within the tested period. V-TBAPy showed the fastest initial response, with substantial MB uptake occurring before the first measurement, while V-TCPB displayed intermediate adsorption kinetics, being faster than V-MOF-10 but slower than V-TBAPy. As the initial MB concentrations were not identical, the final removal efficiencies are used here only as supporting indicators of the adsorption trends, rather than as a strict basis for performance ranking.

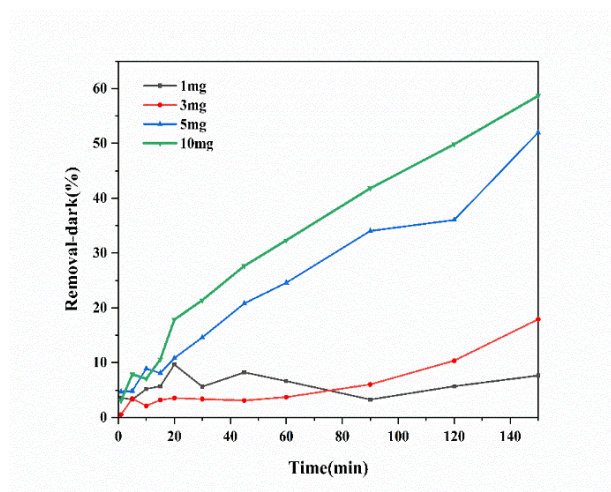


Figure 3.15 Removal efficiency of methylene blue during dark adsorption by V-MOF-10 as a function of time at different MOF dosages. The initial MB concentration and solution volume were 30 mg L⁻¹ and 50 mL, respectively

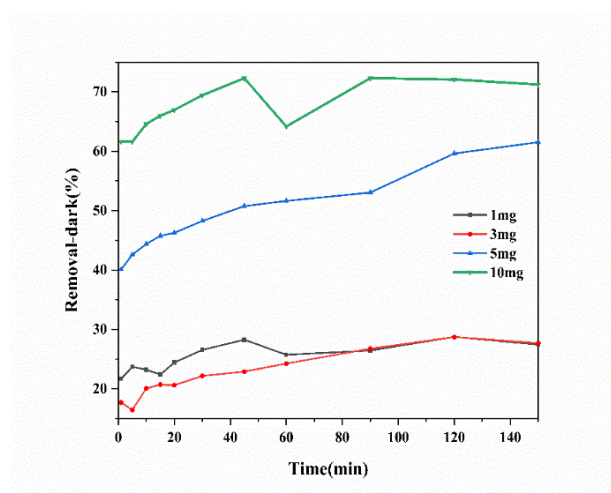


Figure 3.16 Removal efficiency of methylene blue during dark adsorption by V-TBAPy as a function of time at different MOF dosages. The initial MB concentration and solution volume were 50 mg L⁻¹ and 50 mL, respectively

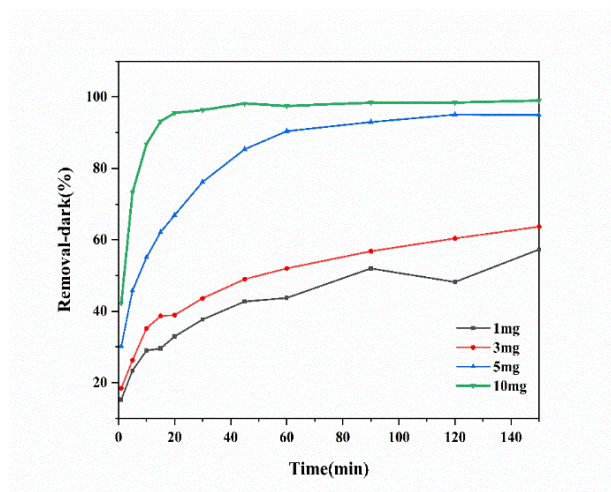


Figure 3.17 Removal efficiency of methylene blue during dark adsorption by V-TCPB as a function of time at different MOF dosages. The initial MB concentration and solution volume were 30 mg L^{-1} and 50 mL, respectively.

3.2.2 Analysis of the Change in Adsorption Capacity (qt)

Figure 3.18 to Figure 3.20 show that the adsorption capacity per unit mass of the three materials gradually increases with adsorption time during the dark adsorption process, although some fluctuations were observed. The rate of increase gradually decreased as the systems approached equilibrium. The comparatively smoother V-TCPB curves may also be partly attributed to the higher initial MB concentration, which produced larger absorbance changes and adsorption-capacity values, thereby reducing the relative influence of experimental error.

In terms of the influence of dosage, different materials all exhibit to some extent the phenomenon that an increase in MOF dosage is beneficial for improving the overall removal rate, as would be expected, but the adsorption capacity per unit mass decreases instead. The main reason is that when the dosage of the adsorbent increases, the total number of adsorption sites in the system increases significantly, while the total amount of MB does not increase synchronously. As a result, some adsorption sites are not fully utilized, leading to a decrease in the adsorption capacity of the adsorbent per unit mass. In addition, under the condition of a relatively high dosage, local accumulation may occur

between particles, which will also affect the exposure and utilization of adsorption sites to some extent.

For V-TBAPy (and possibly V-TCPB), this pattern is even more evident. That is, under the condition of low dosage, their adsorption capacity per unit mass is higher and continues to increase over time, indicating that their adsorption process is still ongoing within the experimental time frame. In contrast, the overall adsorption capacity per unit mass of V-MOF-10 is relatively low, but its growth trend in the later stage is relatively more continuous, suggesting that the utilization of some of its adsorption sites may depend on the pore diffusion process on a longer time scale.

Overall, under the present experimental conditions, V-TCPB exhibited the highest adsorption capacity per unit mass, followed by V-TBAPy, whereas V-MOF-10 showed lower values but continued to increase at longer adsorption times, suggesting that equilibrium had not yet been reached. This order differs from the BET surface-area trend of V-MOF-10 ($1300 \text{ m}^2 \text{ g}^{-1}$) > V-TCPB ($485 \text{ m}^2 \text{ g}^{-1}$) > V-TBAPy ($314 \text{ m}^2 \text{ g}^{-1}$). The discrepancy suggests that aqueous MB adsorption is governed not only by total surface area but also by pore accessibility and diffusion limitations. The relatively large fluctuations observed for V-MOF-10 may also reflect amplified experimental error at low adsorption quantities.

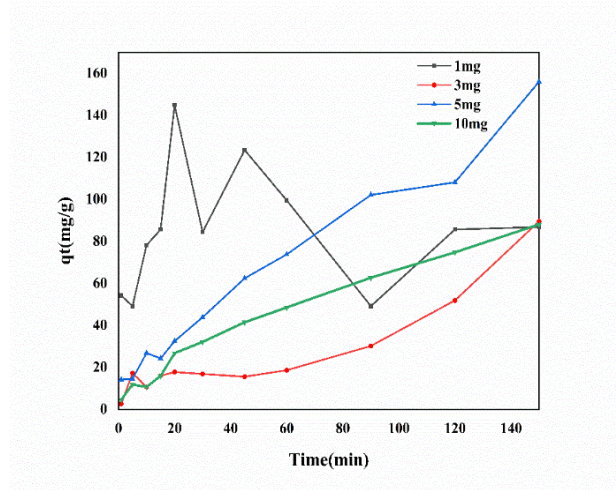


Figure 3.18 Time-dependent adsorption capacity (q_t) of V-MOF-10 for methylene blue under dark adsorption at different dosages.

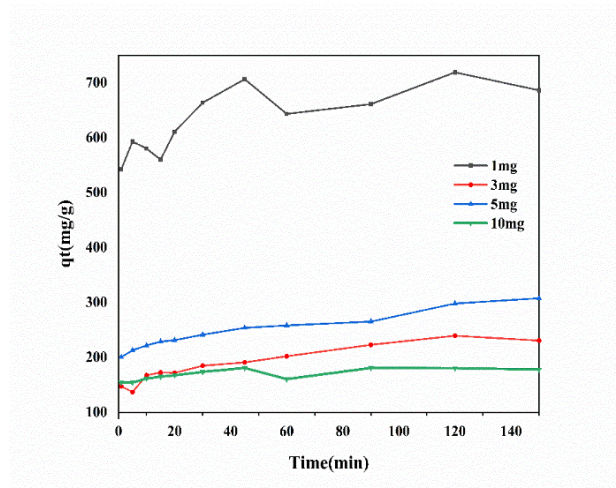


Figure 3.19 Time-dependent adsorption capacity (q_t) of V-TBAPy for methylene blue under dark adsorption at different dosages.

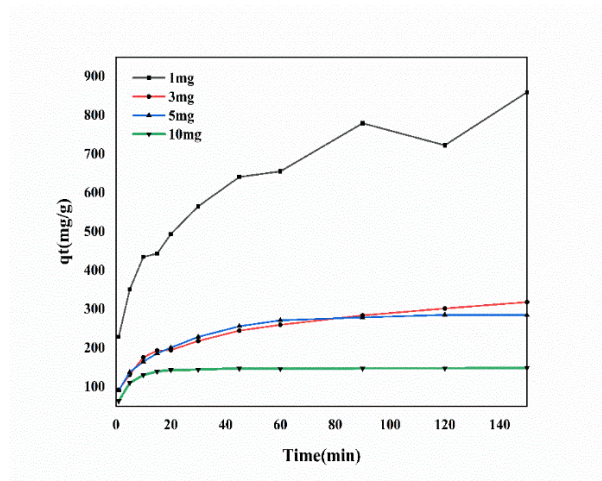


Figure 3.20 Time-dependent adsorption capacity (q_t) of V-TCPB for methylene blue under dark adsorption at different dosages.

3.2.3 Comparison of Adsorption Behavior and Structure–Performance Relationship

To compare the adsorption behavior of the three materials under the same adsorbent dosage, Figure 3.21 and Figure 3.22 show the MB removal efficiencies within the first 10 min and over the full adsorption period, respectively, at a MOF dosage of 3 mg. Figure 3.23 further compares the corresponding time-dependent adsorption capacities (q_t) at the same dosage. Because different initial MB concentrations were used for the three materials, the following comparison focuses on kinetic trends and structure–performance relationships rather than establishing a strict performance ranking.

During the first 10 min, V-TBAPy showed substantial MB uptake before the first measurement, indicating the fastest immediate adsorption response. V-TCPB exhibited the clearest continued increase in removal efficiency during this period, whereas V-MOF-10 showed only a limited initial change. Over the full adsorption period, V-TCPB maintained a pronounced increase in MB removal, while V-TBAPy changed more gradually after its rapid initial uptake. V-MOF-10 showed slower but more continuous adsorption at longer times, suggesting that equilibrium had not been reached within the tested period.

At the fixed dosage of 3 mg, the apparent adsorption capacity followed the order V-TCPB > V-TBAPy > V-MOF-10 under the respective experimental conditions. However, because q_t depends on the initial MB concentration and different concentrations were used, this order should not be interpreted as an intrinsic adsorption-capacity ranking.

These adsorption trends do not follow the BET surface-area order of V-MOF-10 (1300 m² g⁻¹) > V-TCPB (485 m² g⁻¹) > V-TBAPy (314 m² g⁻¹). Although V-MOF-10 possesses the most developed microporous structure, diffusion of MB into its narrow internal pores may limit the initial adsorption rate. The rapid immediate response of V-TBAPy may be

associated with readily accessible external or shallow adsorption sites, while the intermediate porosity and stacked plate-like morphology of V-TCPB may provide a favourable balance between site availability and diffusion accessibility. Because BET surface areas were measured by N₂ adsorption under dry conditions, the aqueous MB adsorption behavior is better interpreted by considering pore accessibility, particle morphology, and mass-transfer limitations together with the total surface area.

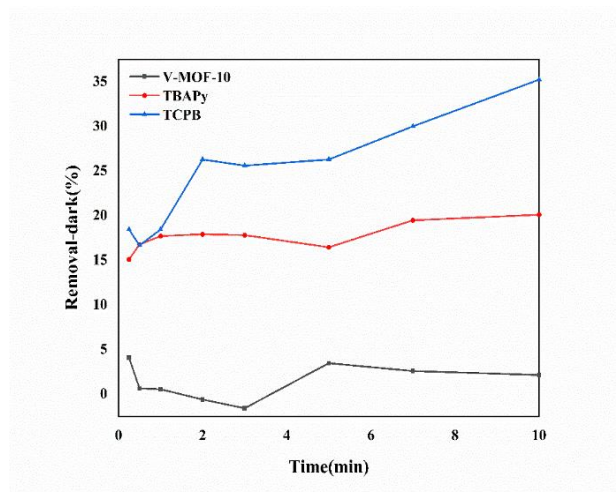


Figure 3.21 Comparison of methylene blue removal efficiency during the first 10 min of dark adsorption by the three vanadium-based MOFs at a fixed MOF dosage of 3 mg. Initial MB concentrations: 30 mg L⁻¹ for V-MOF-10 and V-TCPB, and 50 mg L⁻¹ for V-TBAPy; solution volume: 50 mL.

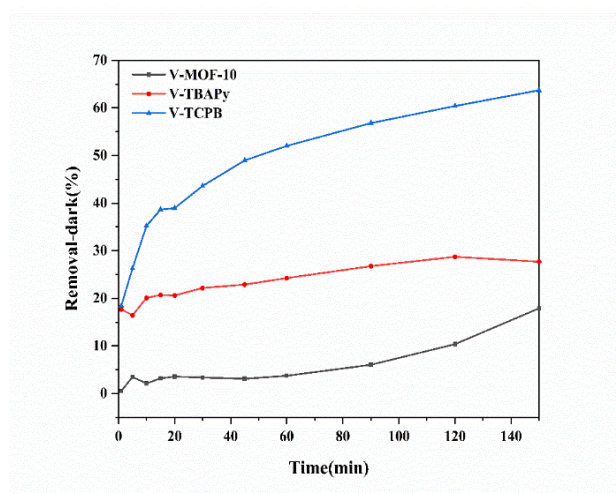


Figure 3.22 Comparison of the time-dependent removal efficiency of methylene blue during dark adsorption by the three vanadium-based MOFs at a fixed MOF dosage of 3 mg. Initial MB concentrations: 30 mg L⁻¹ for V-MOF-10 and V-TCPB, and 50 mg L⁻¹ for V-TBAPy; solution volume: 50 mL.

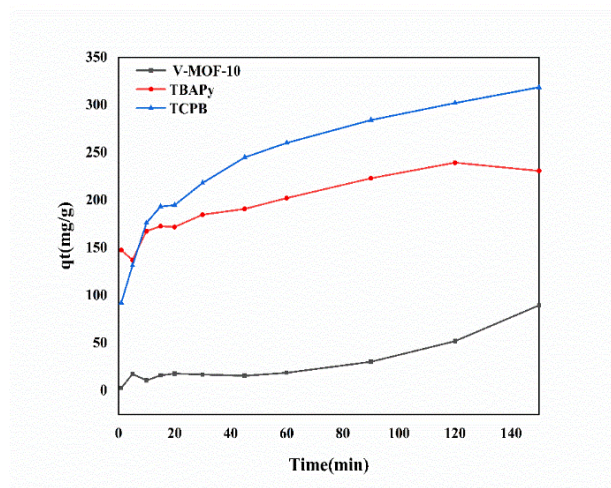


Figure 3.23 Comparison of the time-dependent adsorption capacity (q_t) of the three vanadium-based MOFs for methylene blue during dark adsorption at a fixed MOF dosage of 3 mg. Initial MB concentrations: 30 mg L⁻¹ for V-MOF-10 and V-TCPB, and 50 mg L⁻¹ for V-TBAPy; solution volume: 50 mL.

3.3 Photocatalytic Degradation Performance under Ultraviolet Light Conditions

Based on the experimental methods described in Chapter 2, the photocatalytic removal MB by three vanadium-based metal-organic frameworks, namely V-MOF-10, V-TBAPy, and V-TCPB, was evaluated. The photocatalytic tests were conducted under UV irradiation and simulated solar-light irradiation, which is hereafter denoted as VL for clarity. Before irradiation, all suspensions were kept in the dark to reach adsorption equilibrium, allowing the dark-adsorption contribution to be distinguished from the light-induced removal process. The total removal efficiency was calculated based on the initial MB concentration before dark adsorption, whereas the pseudo-first-order kinetic analysis used the MB concentration after dark adsorption equilibrium as C_0 . Therefore, the fitted rate constant mainly reflects the apparent removal rate during the irradiation stage rather than the overall adsorption–photocatalysis process.

3.3.1 Blank Control Experiment

To describe the variation in MB concentration during irradiation, the normalized concentration is expressed in Equation 3.1:

$$\frac{C}{C_0} = \frac{C_t}{C_0}$$

Equation 3.1

where C_0 is the initial concentration of MB before irradiation, and C_t is the MB concentration at irradiation time t . A lower C/C_0 value indicates a greater decrease in MB concentration.

As shown in Figure 3.24, in the absence of a catalyst, the C/C_0 value of the MB solution remained close to 1.0 during the 180 min of UV irradiation, with only minor fluctuations and no continuous downward trend. This indicates that, under the UV irradiation conditions used in this study, the self-photolysis of MB was negligible. Therefore, the concentration decrease observed after adding the catalysts can mainly be attributed to dark adsorption and light-induced photocatalytic degradation, rather than uncatalysed decomposition of MB. This blank experiment provides the reference for evaluating the photocatalytic activity of the three V-MOFs under UV irradiation.

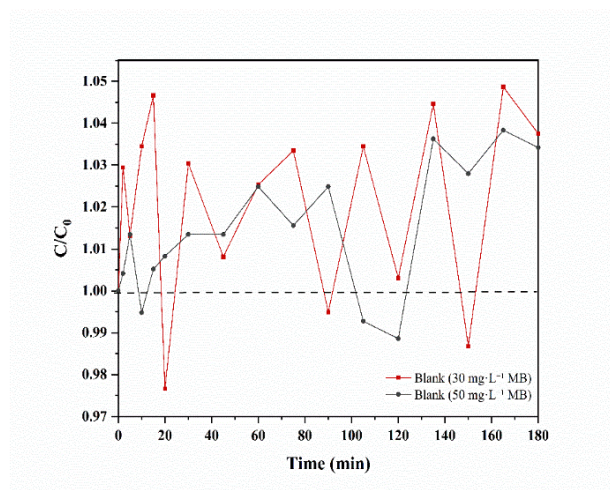


Figure 3.24 Blank control curve of MB under UV irradiation in the absence of catalyst.

3.3.2 Comparison of the Overall Removal Behaviors and Stage Contributions at a Catalyst Dosage of 5 mg

As shown in Figure 3.25, at a catalyst dosage of 5 mg, all three vanadium-based MOFs exhibited two-stage MB removal, consisting of dark adsorption followed by further removal under UV irradiation. V-TCPB reached the lowest final normalized MB concentration, followed by V-TBAPy and V-MOF-10. Therefore, the overall removal performance under UV irradiation followed the order V-TCPB > V-TBAPy > V-MOF-10.

The observed performance order does not directly follow the BET surface-area order of V-MOF-10 ($1298 \text{ m}^2 \text{ g}^{-1}$) > V-TCPB ($485 \text{ m}^2 \text{ g}^{-1}$) > V-TBAPy ($313 \text{ m}^2 \text{ g}^{-1}$). Although V-MOF-10 possesses the most developed microporous structure, diffusion into its internal micropores may limit the accessibility of adsorption and photocatalytic sites within the experimental period. V-TBAPy may provide more readily accessible external or shallow sites but has a smaller reserve of accessible internal sites. In contrast, V-TCPB appears to provide a more favourable balance between site availability and diffusion accessibility, supporting both MB pre-enrichment and subsequent UV-driven removal.

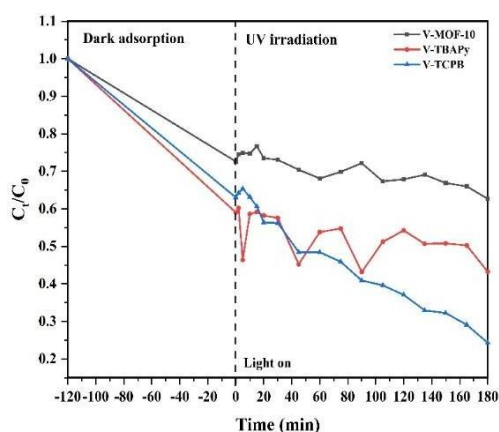


Figure 3.25 Comparison of normalized MB concentration (C_t/C_0) for the three vanadium-based MOFs during dark adsorption and subsequent UV irradiation at a catalyst dosage of 5 mg. Only the initial and equilibrium points are shown for the 120 min dark-adsorption stage. The initial MB concentration and solution volume were 30 mg L⁻¹ and 50 mL, respectively. UV irradiation was provided by an Arimed B6 low-pressure ultraviolet lamp with an emission wavelength of 320 ± 30 nm and a power of 36 W.

Figure 3.26 further separates the contributions of dark adsorption and UV-light-induced removal. At a catalyst dosage of 5 mg, the total MB removal efficiencies of V-MOF-10, V-TBAPy, and V-TCPB were approximately 37%, 57%, and 95%, respectively. V-MOF-10 showed limited contributions from both stages, whereas V-TBAPy exhibited a greater dark-adsorption contribution than V-MOF-10 but only moderate additional removal under UV irradiation. In contrast, V-TCPB showed substantial contributions from both stages. This result indicates that its high overall performance arose from the combination of effective MB pre-enrichment and subsequent UV-driven removal, rather than from either stage alone.

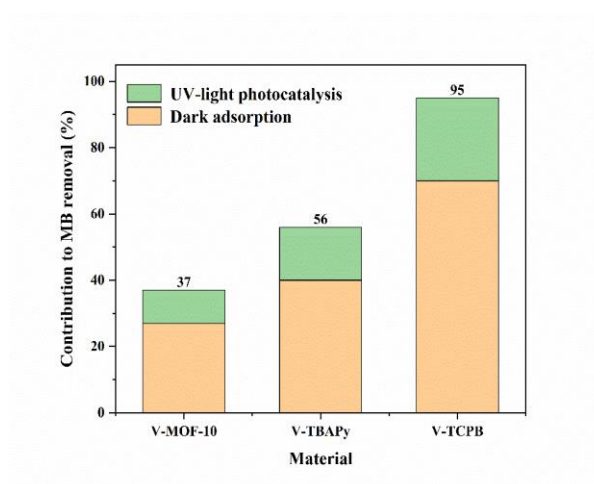


Figure 3.26 Comparison of the contributions of dark adsorption and UV-light-induced removal to the total MB removal by the three vanadium-based MOFs at a catalyst dosage of 5 mg. The initial MB concentration and solution volume were 30 mg L⁻¹ and 50 mL, respectively.

3.3.3 Effect of Dosage on the Removal Behavior by Ultraviolet Light

As shown in Figure 3.27, the removal efficiency of V-MOF-10 under UV conditions gradually improves with the increase of dosage. At a dosage of 1 mg, the system only shows a limited decline after irradiation, indicating that the number of effective sites provided by the material at a low dosage is insufficient to support significant removal. As the catalyst dosage increases to 3 mg, 5 mg, and 10 mg, the overall curve gradually moves downward, suggesting that after more catalysts are introduced into the system, the total number of sites capable of participating in adsorption and light response increases, resulting in a higher final removal rate. However, it is worth noting that even at a dosage of 10 mg, the improvement of the removal efficiency of V-MOF-10 is achieved gradually rather than suddenly at the initial stage of light irradiation, indicating that the utilization of its internal sites still has certain diffusion control characteristics.

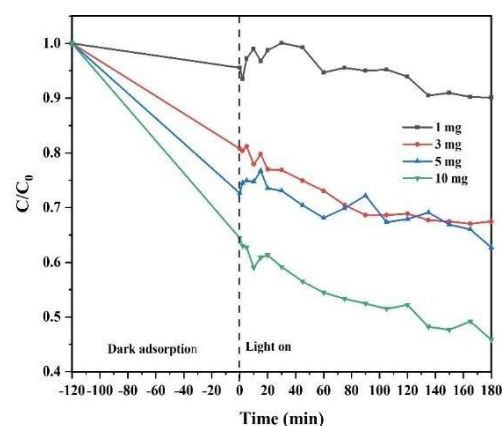


Figure 3.27 C/C_0 variation curves of MB over V-MOF-10 during dark adsorption and subsequent UV irradiation at different catalyst dosages.

As shown in Figure 3.28, V-TBAPy is more sensitive to the change in dosage. As the catalyst dosage increases from 1 mg to 10 mg, the decline of C/C_0 during the entire reaction process is significantly greater, indicating that the limitation of this material at low dosages is more prominently reflected in the insufficient total number of sites. Since the internal effective surface area of V-TBAPy is relatively low, increasing the dosage actually directly increases the density of accessible sites per unit volume of the system, so its response is more obvious.

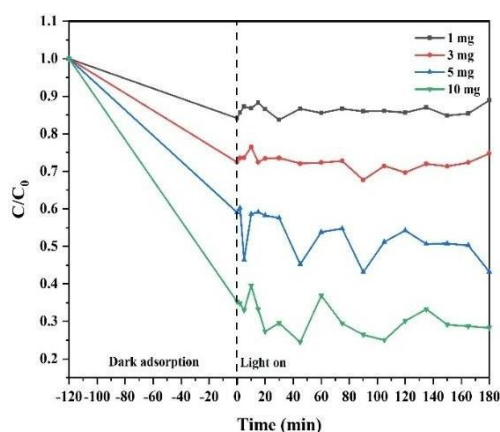


Figure 3.28 C/C_0 variation curves of MB over V-TBAPy during dark adsorption and subsequent UV irradiation at different catalyst dosages.

As shown in Figure 3.29, V-TCPB already exhibits obvious advantages at a relatively low dosage. Especially under the conditions of 3 mg and 5 mg, its C/C_0 rapidly drops to a relatively low level after the light is turned on, indicating that this material has a high unit mass utilization efficiency in the UV system. Figure 3.30 summarizes the relationship between the final removal rate and the dosage. It can be seen that the final removal rates of all three materials increase with the increase of the dosage, but the growth amplitudes and growth modes are different. The improvement of V-MOF-10 and V-TBAPy is more gradual, while V-TCPB can achieve significant removal at a relatively low dosage. This further indicates that in the UV light system, the key to determining the performance is not only how much is added, but more importantly, whether the intrinsic pore structure of the material can efficiently convert these sites into actually available interfaces.

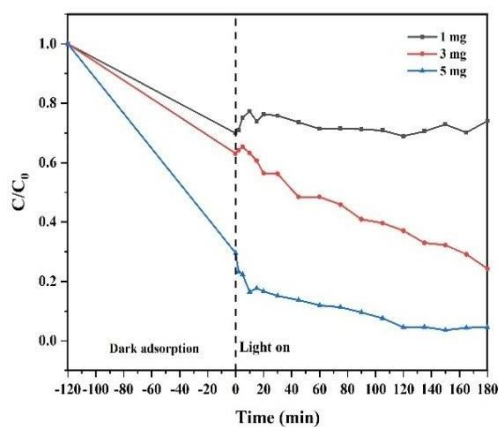


Figure 3.29 C/C_0 variation curves of MB over V-TCPB under UV irradiation at different catalyst dosages.

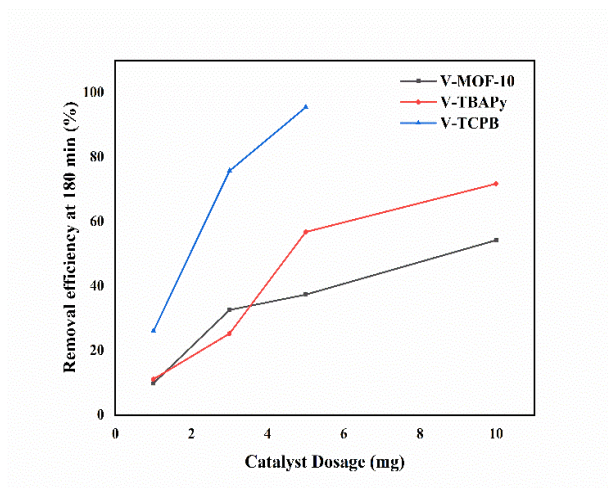


Figure 3.30 Relationship between catalyst dosage and MB removal efficiency at 180 min under UV irradiation for three vanadium-based MOFs.

3.3.4 Degradation Kinetics Analysis under Ultraviolet Light

To further compare the reaction rates of the three materials under UV irradiation, the data obtained at a catalyst dosage of 5 mg were fitted using the pseudo-first-order kinetic model. According to the definition in Chapter 2, C_0 in the kinetic fitting represents the MB concentration after dark adsorption equilibrium. Therefore, the fitted k value represents the apparent photocatalytic rate constant during the irradiation stage, rather than the overall removal rate including dark adsorption.

As shown in Figure 3.31 to Figure 3.33 , the apparent pseudo-first-order rate constants (k_{app}) of V-MOF-10, V-TBAPy, and V-TCPB were 8.00×10^{-4} , 1.01×10^{-3} , and $1.05 \times 10^{-2} \text{min}^{-1}$, respectively. The corresponding R^2 values were 0.816, 0.309, and 0.937. V-TCPB exhibited a substantially higher k_{app} and a better linear fit than the other two materials, indicating a higher apparent UV-light-induced removal rate and behavior more consistent with the pseudo-first-order kinetic model.

In contrast, V-MOF-10 and V-TBAPy showed much lower apparent rate constants. In particular, the low R^2 value of V-TBAPy is mainly attributed to its weak photocatalytic contribution under UV irradiation and the relatively large fluctuation of the concentration data, rather than to a clearly defined complex reaction pathway. These results suggest that V-TCPB has the highest apparent reaction rate under UV irradiation, consistent with its superior removal efficiency discussed above. To reduce experimental uncertainty, future kinetic measurements should be performed in triplicate.

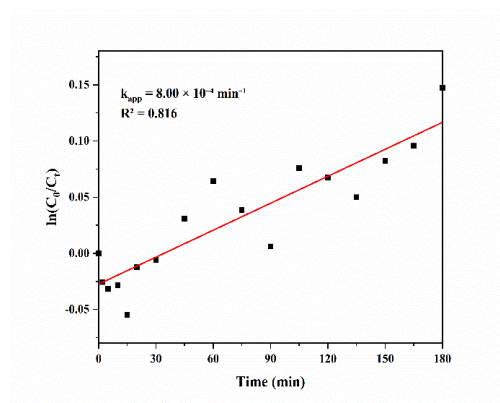


Figure 3.31 Apparent pseudo-first-order kinetic fitting of MB removal over V-MOF-10 under UV irradiation at a catalyst dosage of 5 mg.

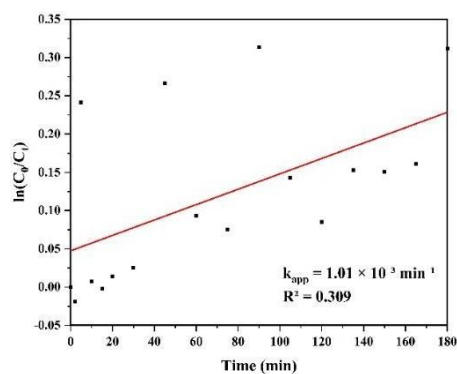


Figure 3.32 Apparent pseudo-first-order kinetic fitting of MB removal over V-TBAPy under UV irradiation at a catalyst dosage of 5 mg.

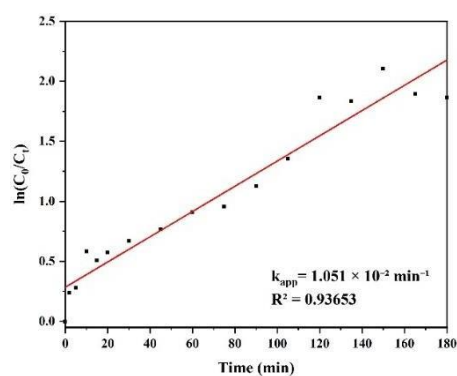


Figure 3.33 Apparent pseudo-first-order kinetic fitting of MB removal over V-TCPB under UV irradiation at a catalyst dosage of 5 mg.

3.4 Photocatalytic Degradation Performance under Simulated Visible Light (VL) Conditions

The simulated visible-light photocatalytic experiments were carried out using a SunLite series solar simulator (Abet Technologies, USA). The system uses a xenon lamp equipped with an AM 1.5G filter, and the irradiation intensity at the surface of the reaction solution was adjusted to $100 \text{ mW} \cdot \text{cm}^{-2}$. This condition was used to approximate the terrestrial solar spectrum. Before irradiation, the catalyst/MB suspension was stirred in the dark for 2 h to reach adsorption–desorption equilibrium, after which the simulated solar light was turned on to initiate the reaction.

3.4.1 Blank Control Experiment

As shown in Figure 3.34, in the absence of a catalyst, the MB solution also showed only slight fluctuations during 180 min of simulated sunlight irradiation, and C/C_0 remained basically around 1.0. This indicates that under the conditions of the solar simulator used in this study, the uncatalysed photolysis of MB can also be neglected. Therefore, the subsequent decrease in concentration in the system can still be mainly attributed to the dark adsorption and light - response processes of the material. In other words, the blank control results under simulated sunlight conditions are consistent with those under UV conditions, which makes the comparison of the material performance under the two light sources more comparable.

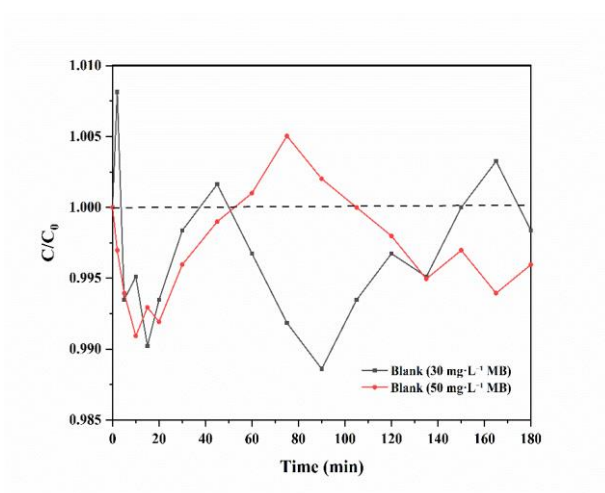


Figure 3.34 Blank control curve of MB under simulated solar-light irradiation in the absence of catalyst.

3.4.2 Comparison of the Overall Removal Behaviors of the Three Materials under the Condition of 5 mg

As shown in Figure 3.35, at a dosage of 5 mg, the three materials exhibited significantly different ranking relationships under simulated sunlight irradiation compared to those under UV conditions: the curve of V-MOF-10 was the lowest, followed by that of V-TCPB, and V-TBAPy had the highest curve, i.e., V-MOF-10 > V-TCPB > V-TBAPy. This result is one of the most noteworthy phenomena to be discussed in this chapter, as it indicates that the performance superiority or inferiority among materials is not fixed but can shift with the change of the light source spectral region.

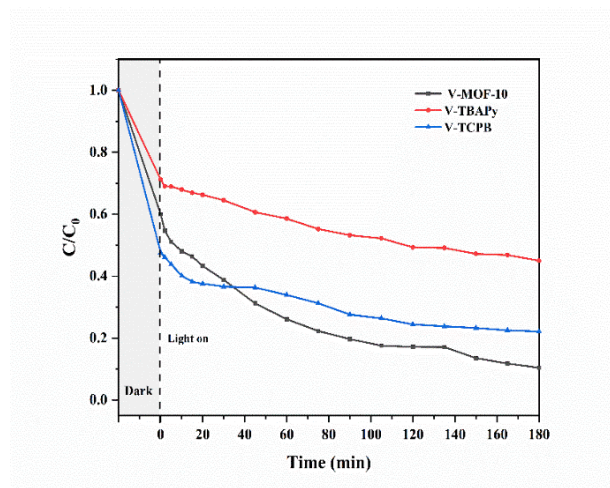


Figure 3.35 Comparison of C/C_0 changes of MB over three vanadium-based MOFs under simulated solar-light irradiation at a catalyst dosage of 5 mg.

If only based on the basis of dark adsorption, V-MOF-10 is not the most favourable material. As shown in Section 3.2, its initial adsorption response is relatively slow, indicating that the high proportion of microporous structure does not endow it with the fastest pre-enrichment ability. According to conventional intuition, such a material may not be optimal after entering the photocatalytic stage. However, the results in Figure 3.35 show that under simulated sunlight conditions, V-MOF-10 instead becomes the material with the best comprehensive performance. This change indicates that in the environment of wide-spectrum irradiation, the dominant factor controlling the reaction performance is no longer just the pore accessibility, but whether a stronger synergy can be formed between the spectral response ability of the material itself and the storage capacity of the pore structure.

The synthesis section in Chapter 2 indicates that V-MOF-10 uses the meso-tetra(4-carboxyphenyl)porphyrin (TCPP) ligand, while V-TBAPy and V-TCPB are derived from the TBAPy and TCPB ligands, respectively. Porphyrin ligands themselves have a stronger potential for broad-spectrum absorption, which is an important characteristic distinguishing them from common aromatic carboxylic acid ligands.^{133–135} Therefore, under simulated sunlight conditions, V-MOF-10 not only provides a large potential enrichment capacity through its well-developed microporous network but is also more likely to enhance the response intensity during the illumination stage by absorbing photons in a wider

wavelength range via the ligand itself. In other words, the "advantage of high storage capacity" that was not fully realised under UV conditions is more prominently manifested under simulated sunlight conditions due to the better-matched light absorption conditions.

In contrast, V-TCPB still maintains a relatively high level under simulated sunlight, but its advantage is no longer as prominent as under UV conditions. This indicates that the core advantage of V-TCPB lies more in pore accessibility, site balance, and pre-enrichment efficiency, rather than the strongest broad-spectrum response ability. That is to say, when the reaction conditions mainly test whether the sites can be quickly utilized by the substrate, V-TCPB has a greater advantage. However, when the light source is extended to an environment closer to the real solar spectrum, the ligand electronic structure and light absorption ability of the material itself begin to play a more important role, and the structural advantage of V-TCPB is no longer sufficient to outperform V-MOF-10.

V-TBAPy still ranks last under simulated sunlight, indicating that although this material has a certain light response ability, its overall performance is still limited by the insufficient reserve of internal sites. Its relatively open pore structure is indeed conducive to the rapid approach of substrate molecules to the outer surface in the solution. However, if the number of effective active interfaces that can be continuously provided in the unit volume system is small, it is difficult to convert this open - structure advantage into the highest total removal rate during long-term light irradiation. The lowest specific surface area and the insignificant microporous contribution of V-TBAPy in Section 3.1 are in line with this result.

3.4.3 Analysis of the Contributions of Dark Adsorption and Simulated Sunlight Irradiation

As shown in Figure 3.36, under the condition of 5 mg, the total removal rates of V-MOF-10, V-TBAPy, and V-TCPB were 99%, 94%, and 97%, respectively. Compared with the UV results, the most significant change is that the ranking of V-MOF-10 has risen from the

lowest to the highest, indicating that its advantage in light response under simulated sunlight conditions is fully demonstrated.

If the total removal is further divided into the contributions of dark adsorption and light irradiation, it can be found that the removal patterns of the three materials under VL conditions are not entirely the same. The high total removal rate of V-MOF-10 is not solely determined by dark adsorption. Instead, on the basis of the existing enrichment, the light irradiation stage continues to provide a strong incremental removal. This indicates that its high specific surface area and broad-spectrum absorption ability achieve true synergy under simulated sunlight conditions. The proportion of the light irradiation contribution of V-TBAPy is relatively large, suggesting that its removal process is more dependent on the light irradiation stage itself. However, due to the relatively low pre-stage enrichment degree and overall rate, its total removal rate is still lower than those of V-MOF-10 and V-TCPB. V-TCPB shows a certain light irradiation gain superimposed on the basis of strong dark adsorption, so its overall performance is still relatively good. It can be seen that the differences among the three materials under simulated sunlight conditions essentially reflect the different synergy modes between establishing a local concentration advantage through dark adsorption and continuously consuming the enriched substrates during the light irradiation stage, rather than a simple addition of single adsorption or single photocatalytic behavior.

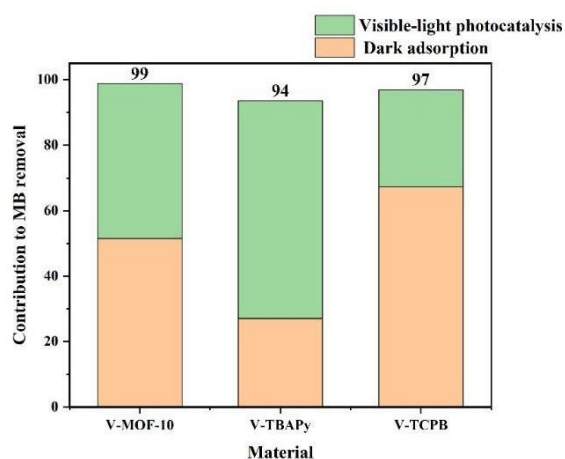


Figure 3.36 Comparison of dark-adsorption and light-induced contributions to MB removal over three vanadium-based MOFs under simulated solar-light irradiation at a dosage of 5 mg.

3.4.4 Effect of Dosage on the Removal Behavior under Simulated Sunlight

The existing simulated sunlight data mainly focus on two representative MOF dosages of 5 mg and 10 mg. As shown in Figure 3.37, after the dosage of V-MOF-10 increased from 5 mg to 10 mg under simulated sunlight conditions, the C/C_0 decreased more rapidly after the light was turned on and approached a lower level in the later stage, indicating that increasing the dosage further enhanced its overall removal ability. Compared with the UV condition, V-MOF-10 responded more fully to the increase in dosage under the VL condition, further demonstrating that its structural advantages can be more completely transformed into actual reaction capabilities only when combined with more suitable spectral conditions.

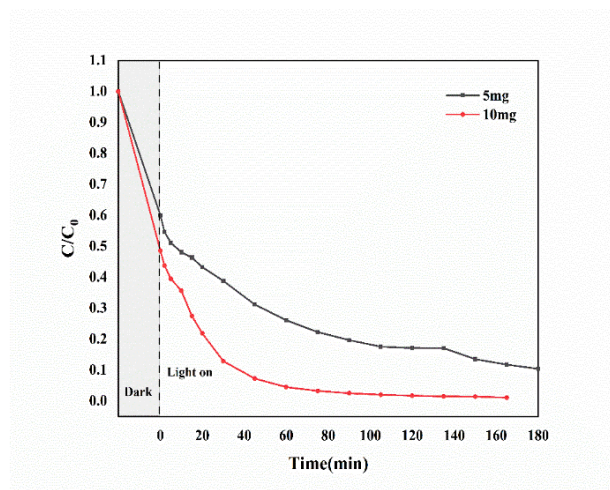


Figure 3.37 C/C_0 variation curves of MB over V-MOF-10 under simulated solar-light irradiation at different catalyst dosages.

As shown in Figure 3.38, the curve of V-TBAPy at a dosage of 10 mg is significantly lower than that at 5 mg, indicating that increasing the dosage significantly improves its performance. This suggests that the material is more likely to be restricted by the insufficient active sites at lower dosages, and increasing the dosage can, to some extent, compensate for this deficiency by increasing the interfacial density.

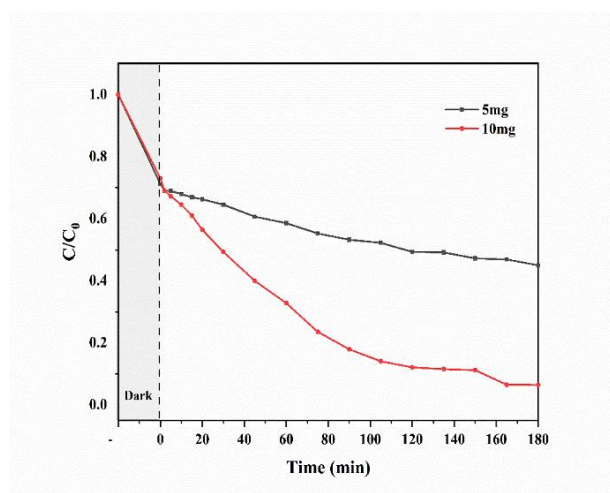


Figure 3.38 C/C_0 variation curves of MB over V-TBAPy under simulated solar-light irradiation at different catalyst dosages.

As shown in Figure 3.39, V-TCPB already exhibits high efficiency at a dosage of 5 mg, and the curve further shifts downward at 10 mg, indicating that in the simulated sunlight

system, its final removal effect can still be improved by increasing the dosage. Figure 3.40 summarizes the final removal rates of the three materials at 180 min under the conditions of 5 mg and 10 mg. It can be seen that the removal rates of all three materials at 10 mg are higher than those at 5 mg. Among them, V-MOF-10 is closest to complete removal at the high dosage, V-TCPB still maintains a high level, and the improvement of V-TBAPy is also relatively obvious.

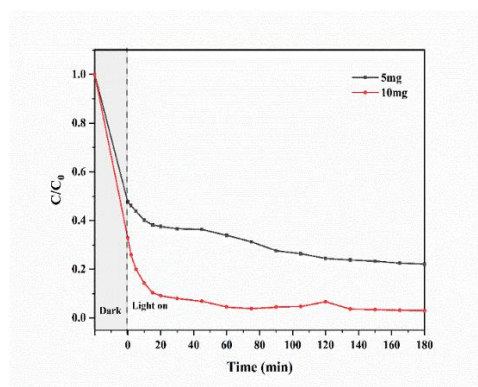


Figure 3.39 C/C_0 variation curves of MB over V-TCPB under simulated solar-light irradiation at different catalyst dosages.

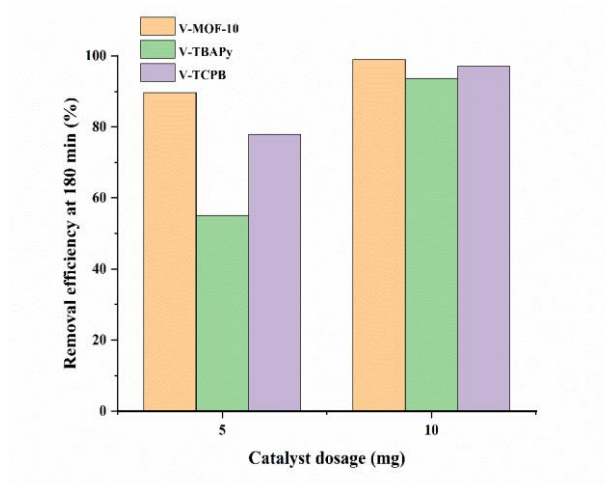


Figure 3.40 Relationship between catalyst dosage and MB removal efficiency at 180 min under simulated solar-light irradiation for three vanadium-based MOFs.

Overall, increasing the dosage has a promoting effect on all three materials under simulated sunlight conditions, but the promotion mechanisms are not entirely the same. For V-MOF-10, increasing the dosage means that more light absorption centers and internal

storage sites are simultaneously introduced into the system; for V-TBAPy, it is more likely compensating for the shortage of its internal storage sites by increasing the density of externally accessible sites; while for V-TCPB, it is manifested as further enhancing the conversion efficiency during the illumination stage on the basis of its existing strong enrichment ability.

3.4.5 Degradation Kinetics Analysis under Simulated Sunlight

From a kinetic perspective, the differences among the three materials under simulated sunlight conditions can better reflect their apparent reaction characteristics than the endpoint removal rates alone. As shown in Figure 3.41 to Figure 3.43, the MB removal processes over V-MOF-10, V-TBAPy, and V-TCPB were well described by the pseudo-first-order kinetic model, with corresponding R^2 values of 0.961, 0.970, and 0.952, respectively. The apparent pseudo-first-order rate constants (k_{app}) were calculated to be $(9.62 \pm 0.50) \times 10^{-3}$, $(2.68 \pm 0.12) \times 10^{-3}$, and $(4.32 \pm 0.25) \times 10^{-3} \text{ min}^{-1}$ for V-MOF-10, V-TBAPy, and V-TCPB, respectively. The reported uncertainties are the standard errors obtained from the linear fittings and therefore represent fitting uncertainty rather than the standard deviation of repeated experiments.

Although the apparent rate constants of V-TBAPy and V-TCPB are relatively close compared with the difference between them and V-MOF-10, their fitted confidence intervals do not overlap, supporting that V-TCPB has a higher apparent degradation rate than V-TBAPy under simulated sunlight. More importantly, V-MOF-10 shows the highest k_{app} value among the three materials, indicating that under simulated sunlight it not only achieves a high final removal rate but also maintains the fastest apparent MB consumption rate during irradiation. This result is consistent with its lowest final C/C_0 under the 5 mg condition, suggesting that the performance reversal is not caused by an individual endpoint but reflects a kinetic advantage throughout the illumination process.

The k_{app} value of V-TCPB is intermediate between those of V-MOF-10 and V-TBAPy, indicating that it still possesses a relatively good reaction rate under simulated sunlight, but no longer dominates the degradation process. Considering its clear advantage under UV irradiation, V-TCPB appears to be more favourable under high-energy UV illumination combined with efficient mass transfer, whereas its advantage is weakened when the light source is changed to simulated sunlight. In contrast, the improved kinetic performance of V-MOF-10 under simulated sunlight suggests that its ligand-centered light absorption and porous structure are better matched with the broader spectral distribution of the light source.

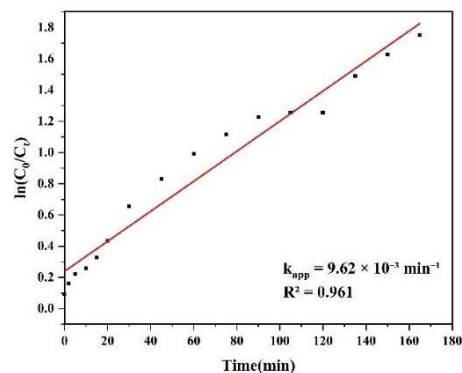


Figure 3.41 Apparent pseudo-first-order kinetic fitting of MB removal over V-MOF-10 under simulated sunlight irradiation at a catalyst dosage of 5 mg.

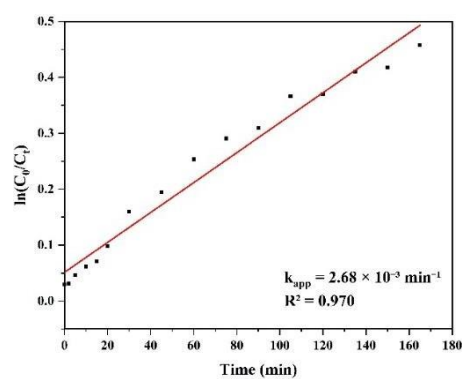


Figure 3.42 Apparent pseudo-first-order kinetic fitting of MB removal over V-TBAPy under simulated sunlight irradiation at a catalyst dosage of 5 mg.

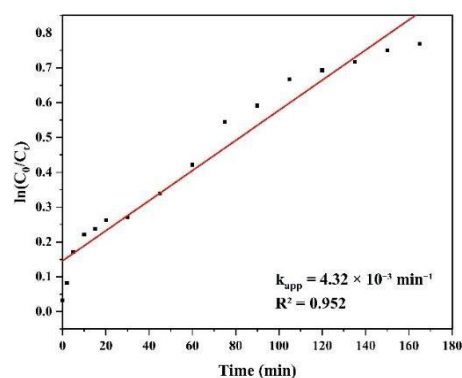


Figure 3.43 Apparent pseudo-first-order kinetic fitting of MB removal over V-TCPB under simulated sunlight irradiation at a catalyst dosage of 5 mg.

3.5 Analysis of the Changes in the Framework Structure before and after the Reaction

In this section, PXRD patterns of the fresh samples, the samples after dark adsorption, and the samples after UV photocatalysis are compared. The purpose is to evaluate whether the crystalline frameworks remain preserved after the aqueous adsorption–photocatalysis process, rather than simply to judge whether framework collapse occurs. As demonstrated in Section 3.1, all three materials exhibit good crystallinity and high phase purity in the initial state. Therefore, the PXRD results in this section are used to assess the structural retention of these ordered frameworks under the UV-driven MB removal conditions.

As shown in Figure 3.44, the fresh V-MOF-10 sample shows sharp diffraction peaks, confirming its ordered crystalline structure. After dark adsorption and UV photocatalysis, the main low-angle reflections are still detectable, indicating that the framework is not completely amorphized. However, the markedly reduced peak intensity and weakened high-angle reflections suggest a partial loss of crystallinity and long-range order. Therefore, the PXRD results support partial structural disorder rather than complete framework collapse.

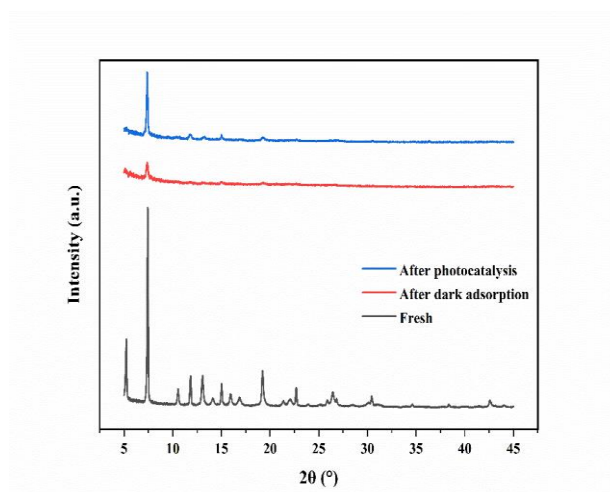


Figure 3.44 Comparative PXRD patterns of fresh V-MOF-10, the sample after dark adsorption, and the sample after UV photocatalysis.

As shown in Figure 3.45, V-TBAPy also retained the main characteristic peaks after the reaction, but the overall peak intensity decreased significantly, and the background was relatively elevated, indicating that the framework order was also weakened to a certain extent. Considering that this material is more dominated by relatively open pores or intergranular pores, this decrease in crystallinity may not immediately lead to the complete inactivation of the outer surface sites, but it still shows that its real reaction state is not completely consistent with the initial crystal state.

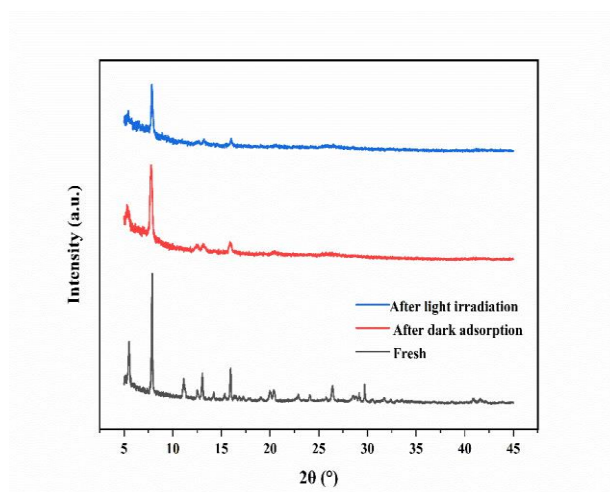


Figure 3.45 Comparative PXRD patterns of fresh V-TBAPy, the sample after dark adsorption, and the sample after UV photocatalysis.

As shown in Figure 3.46, multiple sets of major diffraction peaks of V-TCPB are still clearly retained after dark adsorption and photocatalysis, and the peak positions basically correspond to those of the fresh sample, indicating that its main framework remains relatively intact after the reaction. Compared with the other two materials, V-TCPB shows a better retention of characteristic peaks, suggesting that it has relatively superior structure retention ability under the conditions of this study.

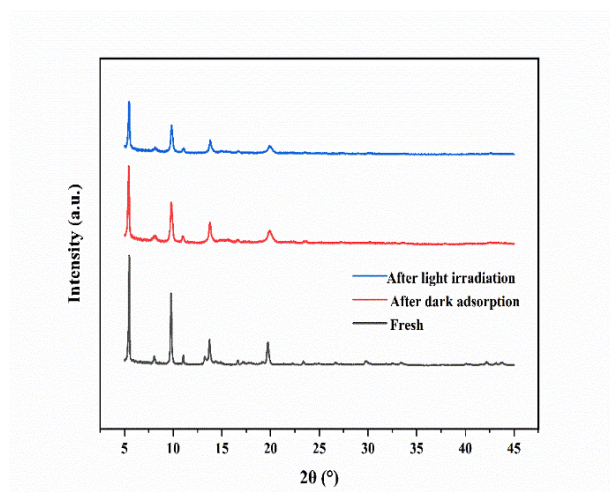


Figure 3.46 Comparative PXRD patterns of fresh V-TCPB, the sample after dark adsorption, and the sample after UV photocatalysis.

Overall, all three V-MOFs retained their main diffraction features after a single adsorption–UV photocatalysis cycle, indicating basic framework stability under the present reaction conditions. Nevertheless, their crystallinity decreased to different degrees, with V-TCPB showing the best structural retention. This structural stability may contribute to its superior UV photocatalytic performance..

3.6 Comprehensive Analysis of Structure-Activity Relationships under Two Irradiation Condition

The combined results indicate that MB removal by the three V-MOFs is governed by the interaction of pore accessibility, substrate enrichment, light response, and framework stability. Under the present experimental conditions, all three materials achieved higher total MB removal under simulated solar-light irradiation than under UV irradiation, although the extent of improvement differed. Because the two light sources were not photon-flux matched, this difference should be interpreted as a comparison of overall performance under the applied irradiation conditions rather than as direct evidence of intrinsic spectral efficiency.

The performance order changed from V-TCPB > V-TBAPy > V-MOF-10 under UV irradiation to V-MOF-10 > V-TCPB > V-TBAPy under simulated solar-light irradiation. Under UV irradiation, V-TCPB benefited from its balance of pore accessibility, effective site utilisation, and structural retention. Under simulated solar-light irradiation, the stronger performance of V-MOF-10 may reflect a better match between the light-response characteristics of its TCPP-based framework and its developed microporous structure. V-TBAPy remained limited by its lower reserve of accessible internal sites. Post-reaction PXRD showed that all three frameworks retained their main crystalline features after one adsorption–photocatalysis cycle, with V-TCPB showing the best structural retention. Overall, these results indicate that effective MOF design requires a balance between molecular accessibility, light response, and framework stability rather than optimisation of surface area alone.

Chapter 4 Conclusions and Outlook

4.1 Conclusions

This thesis focuses on the construction of vanadium-based metal–organic frameworks with different organic ligands and their application in the adsorption–photocatalytic removal of methylene blue. Three representative vanadium-based MOF materials, V-MOF-10, V-TBAPy, and V-TCPB, were successfully synthesized, and the influence of ligand structures on framework characteristics, adsorption behavior, photocatalytic response, and structure–activity relationships were systematically investigated. The study was developed around the relationship between framework construction, structural regulation, and functional performance, providing insights into how ligand design governs the adsorption–photocatalytic behavior of MOF materials.

The results reveal that the organic ligand plays a critical role in determining not only the formation of the MOF framework but also the accessibility of functional sites, pore structure characteristics, and reaction adaptability. Although V-MOF-10 exhibited a highly developed porous structure, the utilization of its internal sites was limited by diffusion constraints. In contrast, V-TBAPy benefited from more accessible adsorption regions but showed limitations in maintaining sufficient active site availability. V-TCPB achieved a more favourable balance between pore accessibility and mass transfer, leading to improved overall performance in the adsorption–photocatalytic process. These findings indicate that the effectiveness of MOF-based materials cannot be simply evaluated by specific surface area alone, while the matching between pore structure and molecular transport behavior is equally important.

The photocatalytic studies further demonstrate that the dominant factors controlling catalytic performance are closely associated with the irradiation conditions. Under ultraviolet irradiation, efficient substrate enrichment and accessible active sites were key factors governing the removal efficiency, whereas under simulated solar-light irradiation,

the photoresponsive characteristics of the organic ligands became increasingly important. The different performance trends under various light sources highlight the importance of balancing adsorption capability, light absorption properties, and structural features during the design of multifunctional photocatalytic materials.

The investigation of structural evolution after reaction further confirms that framework stability is an essential factor affecting the practical application of MOF-based materials. Maintaining structural integrity during adsorption–photocatalytic operation is necessary for preserving active sites and ensuring long-term performance. Overall, this work demonstrates that the adsorption–photocatalytic behavior of vanadium-based MOFs is governed by the synergistic contribution of pore architecture, molecular accessibility, photoresponse ability, and framework stability. The findings provide a useful structure–function relationship for the rational design of MOF-based materials towards efficient wastewater treatment applications.

4.2 Outlook

Although this work establishes the relationship between ligand-regulated structures and adsorption–photocatalytic performance of vanadium-based MOFs, further investigations are still required before practical applications can be realized.

The current evaluation was mainly performed using methylene blue as a representative organic pollutant under controlled laboratory conditions. Since real wastewater contains various organic contaminants, inorganic ions, and complex environmental factors, future studies should focus on evaluating the performance of these materials in more realistic wastewater systems and exploring their resistance to potential interference.

A deeper understanding of the photocatalytic mechanism is also necessary. Although the present results reveal connections between structural characteristics and catalytic performance, the detailed processes involving charge generation, separation, migration, and reactive species formation remain to be clarified. In particular, the fate of MB

adsorbed during the dark-equilibration stage should be determined. It remains unclear whether the adsorbed MB is subsequently degraded under irradiation or remains within the framework and blocks accessible pores. Future studies should therefore combine solution-phase concentration measurements with desorption tests, total organic carbon analysis, identification of degradation intermediates, and post-reaction porosity characterization to distinguish adsorption from actual degradation. In situ characterization, electrochemical analysis, and theoretical calculations may provide further insight into the intrinsic catalytic processes.

In addition, long-term stability and regeneration behavior should be systematically investigated. Continuous operation, repeated adsorption–photocatalytic cycles, and structural evolution during extended use are important factors for assessing the practical feasibility of MOF-based treatment systems. Further optimization of ligand structures and framework architectures may provide opportunities to enhance visible-light utilization, improve mass-transfer efficiency, and maintain structural stability simultaneously.

Overall, future development of MOF-based wastewater treatment materials should focus on achieving a balanced integration of adsorption capacity, molecular accessibility, photocatalytic activity, and operational stability. The design strategy established in this thesis may provide a foundation for developing multifunctional MOF systems with improved efficiency and practical applicability.

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