

Progress in the Application of UiO-66 Metal–Organic Framework Materials for the Removal of Pollutants from Aquatic Environments

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Abstract. Water pollution caused by heavy metal ions, organic dyes, pharmaceutical and personal care products, and oily wastewater has created an urgent demand for stable and efficient treatment materials. This review summarizes recent progress in the application of UiO-66, a zirconium-based metal–organic framework, for aquatic pollutant removal. Owing to its $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters, terephthalate linkers, high porosity, and strong Zr–O coordination bonds, UiO-66 exhibits remarkable hydrolytic, thermal, and chemical stability compared with many conventional MOFs. The paper first discusses its structural characteristics and major synthesis routes, including solvothermal, microwave-assisted, mechanochemical, and diffusion methods, with emphasis on how preparation conditions influence particle size, porosity, defects, and removal performance. It then reviews the use of pristine, functionalized, defective, and composite UiO-66 materials in heavy metal adsorption, dye removal, PPCP adsorption and photocatalytic degradation, and membrane-based separation. Key mechanisms include coordination exchange, electrostatic attraction, hydrogen bonding, π – π interactions, defect-assisted adsorption, heterojunction-driven charge separation, and size-selective membrane transport. Finally, the review highlights remaining challenges, including greener low-cost synthesis, improved stability in complex water matrices, interference resistance, regeneration, and control of potential secondary pollution. Overall, UiO-66-based materials offer a versatile platform for advanced water remediation and show strong promise for future practical engineering applications.

Keywords: UiO-66, Metal–organic frameworks, Water pollution remediation, Adsorption, Photocatalysis

1. Introduction

At the current stage of social development, severe water scarcity and widespread contamination of aquatic environments—two deeply intertwined issues—have jointly evolved into one of the most pressing challenges confronting human society. Industrial wastewater, agricultural runoff, and domestic sewage carry a wide variety of hazardous substances with significant toxicity. These hazardous substances include heavy metal ions, synthetic organic dyes, pesticides, and emerging contaminants that have attracted extensive attention from both academia and society in recent years,

such as pharmaceuticals and personal care products (PPCPs) [1]. Of particular concern is that even when such pollutants occur at extremely trace concentrations, they may still have the potential to cause irreversible damage to the structure and function of aquatic ecosystems as well as to human health. Against this severe practical backdrop, the development and application of water-treatment technologies and materials that combine high treatment efficiency, reasonable economic cost, and favorable environmental compatibility have become an urgent and pressing task.

Among the diverse material systems used for water treatment, metal–organic frameworks (MOFs) have stood out and attracted widespread attention owing to their unique structural advantages. However, most MOFs developed and reported at early stages, such as MOF-5 and HKUST-1, are highly susceptible to framework collapse once exposed to aqueous environments, particularly under operating conditions involving extreme pH values. This intrinsic structural fragility has severely constrained the practical feasibility of applying such materials in the field of water treatment [2]. In 2008, a research team from the University of Oslo, Norway, successfully synthesized for the first time a zirconium (Zr)-based metal–organic framework material, which was designated UiO-66. This landmark achievement fundamentally transformed the previously unfavorable situation in which MOF materials generally suffered from insufficient water stability. UiO-66 retains the typical advantages of MOF materials, such as a large specific surface area and a well-developed porous framework. More importantly, the strong Zr–O coordination bonds within its structure endow UiO-66 with outstanding hydrolytic and chemical stability, which is rarely observed in many comparable MOF systems [3]. Relying precisely on this breakthrough in stability, UiO-66 rapidly emerged within a very short period of time and has evolved into a highly prominent and frontier research hotspot in the field of aquatic environmental remediation.

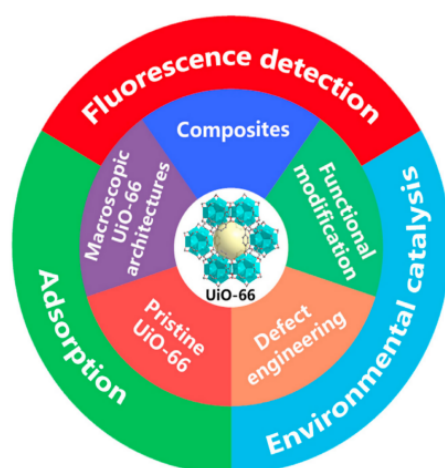


Figure 1. Design, fabrication, and water remediation applications of UiO-66-derived functional materials [4]

2. Basic properties and synthesis methods of UiO-66

2.1. Structural characteristics and stability

The prototypical structure of UiO-66 employs hexanuclear zirconium clusters, with the chemical composition $\text{Zr}_6\text{O}_4(\text{OH})_4$, as secondary building units (SBUs). These clusters are interconnected by 1,4-benzenedicarboxylate (BDC) organic ligands, thereby constructing a three-dimensional network [4]. This three-dimensional network possesses a face-centered cubic (FCC) crystal structure. Within

the ideal crystal framework, each zirconium ion forms coordination bonds with eight oxygen atoms, giving rise to a highly connected 12-coordinated structure. It is precisely this high coordination number, combined with the exceptionally strong affinity between tetravalent zirconium ions (Zr(IV)) and oxygen-containing ligands, that collectively endows UiO-66 with outstanding thermal stability, as evidenced by its ability to withstand temperatures as high as 500°C . At the same time, UiO-66 is also endowed with exceptional chemical stability. Existing studies have systematically demonstrated that UiO-66 can not only maintain the integrity of its crystalline structure over extended periods in aqueous environments, but also effectively resist erosion by various organic solvents [5], such as benzene, acetone, and chloroform. In addition, this material also exhibits reliable tolerance in both acidic and alkaline environments within a certain pH range. The excellent overall stability exhibited under multiple harsh chemical conditions constitutes a fundamental prerequisite for the application of such materials in complex real-world water-treatment environments.

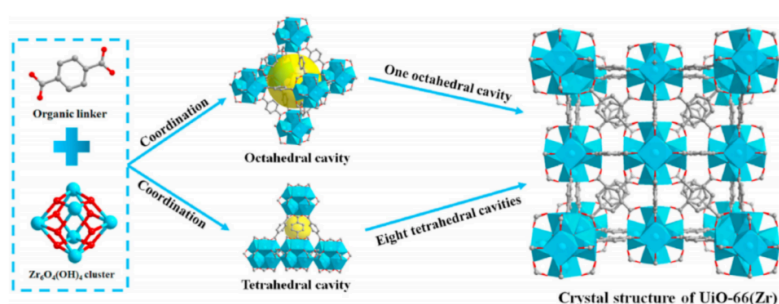


Figure 2. Crystal structure of UiO-66(Zr), where blue represents Zr atoms in the $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters and red denotes O atoms derived from the $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters and H_2BDC ligands. The primrose-yellow spheres correspond to the pore cavities within the structural cages [4]

2.2. Synthesis methods

The synthetic method selected for UiO-66 materials exerts a direct and profound influence on the microscopic size, external morphology, internal porosity, and degree of structural defect formation of the crystals, thereby further affecting the material's pollutant-removal performance. At present, the major synthetic methods widely recognized in this research field can be summarized as follows:

2.2.1. Solvothermal method

This method is regarded as the most classical and widely applied synthetic strategy. Its specific procedure is as follows: Zirconium oxychloride octahydrate (3.900 g) and terephthalic acid (2.001 g) were first accurately weighed and individually dispersed in 50 mL of N,N-dimethylformamide (DMF). The resulting mixtures were stirred for 30 min, respectively, until the solid reagents were fully dissolved and clear, uniform solutions were obtained. Next, under continuous stirring, the metal salt-containing solution is slowly added to the organic ligand-containing solution, and the resulting mixed system is further stirred at room temperature for 24 h. The purpose of this prolonged stirring step is to ensure sufficient pre-coordination between the metal ions and the organic ligands, as well as a high degree of homogeneous mixing. After the above steps are completed, the homogeneous mixed solution is transferred to an oven and subjected to a solvothermal reaction at a constant temperature of 120°C for 24 h. During this process, a white precipitated product gradually forms within the system. After the reaction is completed and the system is allowed to cool naturally, the resulting precipitate is collected by centrifugation and repeatedly washed several times with N,N-

dimethylformamide and methanol in sequence. The primary objective of this washing procedure is to thoroughly remove residual unreacted impurities from the product while simultaneously completing the solvent-exchange process. Finally, the washed product is placed in an air atmosphere at room temperature and allowed to dry naturally, thereby yielding the target product, UiO-66 [6].

2.2.2. Microwave-assisted method

Microwave-assisted synthesis can be regarded as an efficient alternative to the conventional solvothermal method. For instance, in the synthesis of some MOF materials, conventional hydrothermal routes generally require reaction conditions of 180 °C for approximately 16 h. In contrast, microwave-assisted synthesis can markedly reduce the required reaction duration. Specifically, in the preparation of UiO-66, the advantages of the microwave-assisted method are even more pronounced: it not only substantially reduces the 24 h synthesis time required by the conventional solvothermal method to only 0.5 h, but also enables effective regulation of crystal size. The microwave-assisted route produces UiO-66 crystals with a size of about 100 nm, approximately one-quarter of the size of those synthesized by conventional heating methods, which are around 400 nm. The pronounced decrease in particle size is mainly ascribed to the enhanced nucleation rate induced by microwave heating. This process facilitates the generation of a greater number of crystal nuclei within the reaction system, thereby limiting subsequent crystal growth. In addition, UiO-66 synthesized by the microwave-assisted method also exhibits a notably narrower pore-size distribution [7].

2.2.3. Mechanochemical method

Mechanochemical synthesis, often described as a grinding-based method, is an effective strategy for fabricating MOF materials by inducing reactions through mechanical agitation, shear, or impact forces among the reactants. Owing to its ability to markedly shorten reaction duration, avoid harsh thermal conditions, and minimize or even eliminate the consumption of organic solvents, this approach has been widely regarded as a green and sustainable synthetic technique. Based on differences in operation, mechanochemical synthesis is generally classified into three categories. The first is neat grinding, in which the reaction proceeds without the addition of any solvent. The second is liquid-assisted grinding, where a small amount of solvent is introduced to facilitate the reaction and improve molecular-level contact and reactivity. The third is ion- and liquid-assisted grinding, in which salt ions are incorporated together with a limited amount of solvent, further promoting the formation of MOF structures [8].

2.2.4. Diffusion synthesis method

The diffusion method is a class of MOF synthesis approaches that can be carried out under relatively mild conditions; however, a notable characteristic of this type of method is its extremely long reaction duration. Depending on the specific implementation pathway, it can be further classified into three types: gel diffusion, liquid-phase diffusion, and vapor-phase diffusion. The key operational feature of the gel diffusion method lies in pre-dispersing and immobilizing the organic ligands within a gel medium. Subsequently, through prolonged co-mixing and mass-transport processes, MOF crystals are induced to gradually undergo nucleation and growth along the branched network structure within the gel. In contrast, the liquid-phase diffusion method skillfully exploits two mutually immiscible solvents, in which metal ions and organic ligands are separately dissolved in

two independent liquid phases. When the two solutions come into contact, mutual diffusion occurs at their interface, thereby driving the formation of MOF crystals. The vapor-phase diffusion method employs a volatile organic ligand solution as the diffusion source, allowing its vapor to come into contact and interact with the metal ion solution. MOF synthesis is thereby achieved through chemical reactions occurring at the gas–liquid interface. Although diffusion methods are generally carried out under relatively mild temperature and pressure conditions, they are simultaneously constrained by the pronounced limitation of an extremely long preparation cycle. For instance, transparent UiO-66 crystals have been successfully synthesized through a diffusion-based approach in previous studies; however, to achieve this result, the entire reaction process had to be maintained at 100 °C for as long as two full weeks [9].

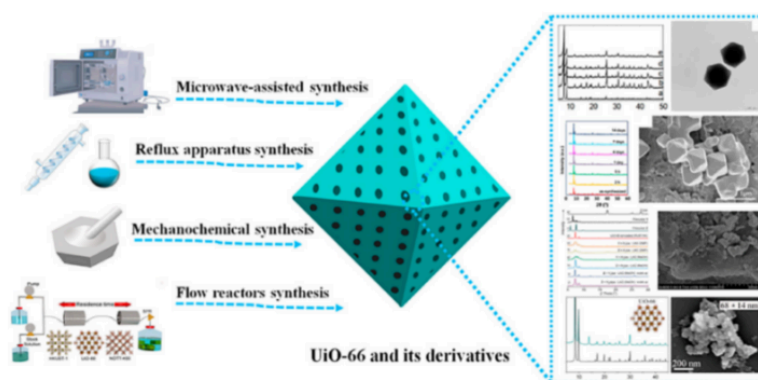


Figure 3. Schematic illustration of different synthetic routes for UiO-66 [4]

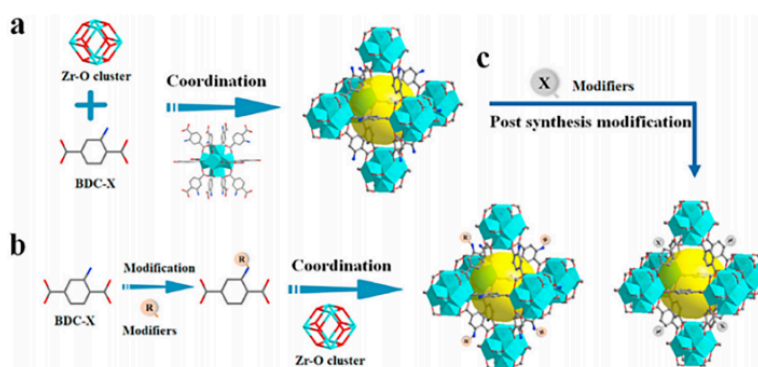


Figure 4. Illustration of the construction strategies involving (a) functional group modification, (b) ligand modification prior to synthesis, and (c) post-synthetic modification [4]

3. Applications of UiO-66 in the removal of water pollutants

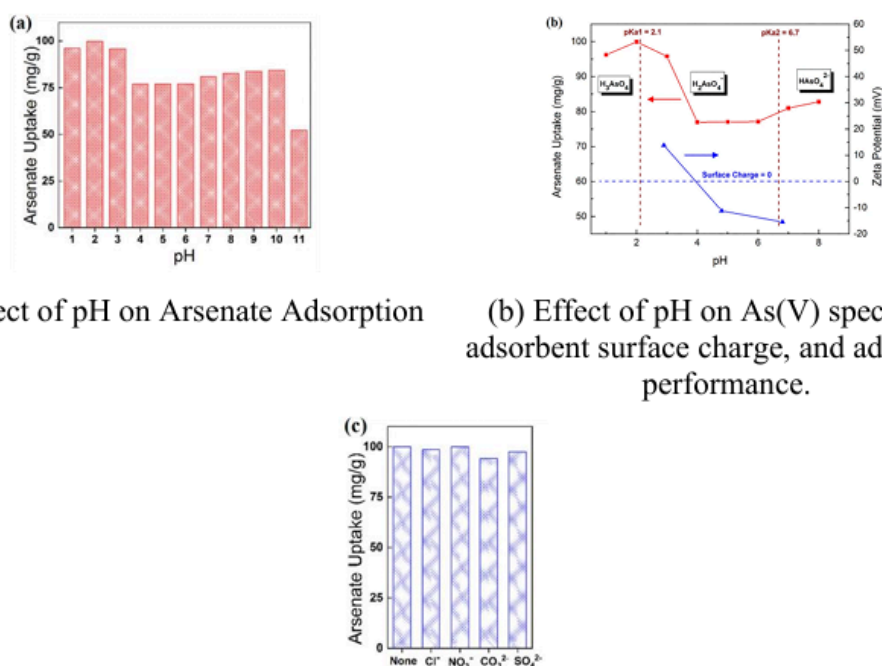
The application of UiO-66 materials in the field of water treatment mainly proceeds along three representative technical pathways: adsorption, photocatalytic degradation, and membrane separation.

3.1. Adsorptive removal of heavy metal ions

Heavy metal ions, such as As, Pb, Cd, and Hg, have become one of the most hazardous classes of pollutants in various aquatic environments because of their inherent high toxicity and strong

bioaccumulative characteristics in living organisms. To meet the demand for adsorptive removal of such heavy metal ions, UiO-66 and its derivative materials modified through different strategies have demonstrated excellent adsorption performance.

Wang et al. first reported the excellent adsorptive removal performance of the water-stable zirconium-based metal–organic framework UiO-66 toward arsenate (As(V)) in aqueous systems. Under the optimal pH condition, namely pH = 2, the adsorption capacity of this adsorbent for arsenate reached as high as 303.34 mg/g according to fitting results based on the Langmuir adsorption isotherm model. Among all arsenic adsorbents reported at that time, including both commercial adsorbents and various synthetic adsorbents, adsorption capacities generally ranged from 5 to 280 mg/g, with the vast majority below 100 mg/g. Therefore, the adsorption capacity achieved by UiO-66 represented one of the highest known As(V) adsorption capacities among the materials available at that time [10]. Regarding the adsorption mechanism, studies have confirmed that this process is not governed solely by electrostatic interactions, but is mainly attributable to strong coordination-exchange interactions between arsenate species and two types of active sites within the UiO-66 framework. Specifically, the first type of active site is the hydroxyl group (Zr–OH) on the $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters, with which arsenate species such as H_3AsO_4 can undergo acid–base-like coordination. The second type of active site is the terephthalate (BDC) ligand that links the Zr clusters, where arsenate can replace part of the BDC ligands through a ligand-exchange process. Through both mechanisms, arsenic can be effectively immobilized in the adsorbent framework via the formation of stable Zr–O–As coordination linkages, thereby endowing the material with superior arsenic removal efficiency.



(a) Effect of pH on Arsenate Adsorption (b) Effect of pH on As(V) speciation, adsorbent surface charge, and adsorption performance.

(c) Effects of coexisting anions on arsenate adsorption at pH 2. Experimental conditions: [UiO-66] = 0.5 g/L, initial [As(V)] = 50 mg/L, [coexisting anions] = 1 g/L, and $T = 25 \pm 1$ °C.

Figure 5. Adsorption performance of UiO-66 toward arsenate under different pH conditions [10]

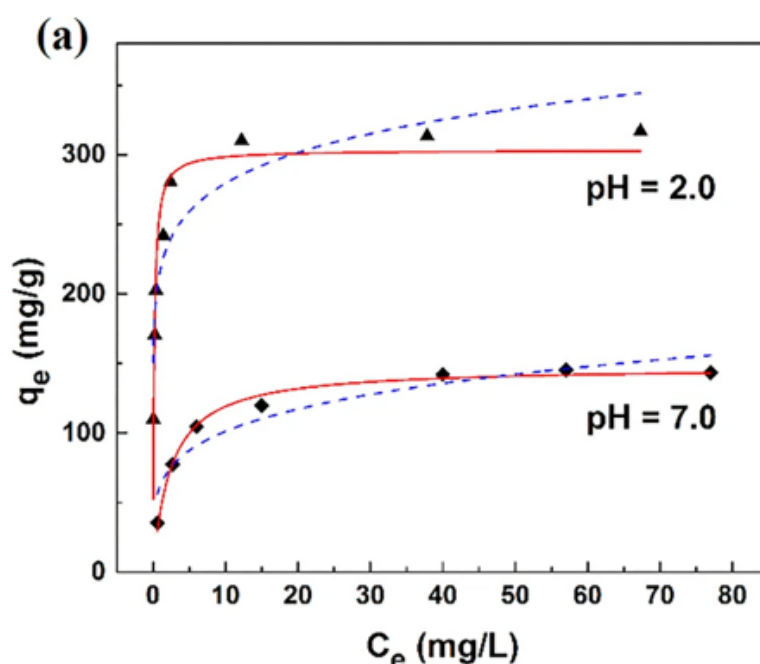


Figure 6. Arsenate adsorption isotherms on the UiO-66 adsorbent at pH 2 and pH 7. The red solid lines represent the Langmuir model fitting, and the blue dashed lines indicate the Freundlich model fitting. adsorption conditions: [UiO-66] = 0.5 g/L and temperature = 25 ± 1 °C [10]

To selectively enhance the affinity of metal–organic framework materials toward specific heavy metal ions, researchers have developed a variety of functionalization strategies. Taking zirconium-based UiO-66 as an example, after thiol groups (–SH) are introduced onto the organic ligands through post-synthetic modification, the material exhibits significantly enhanced selective adsorption toward divalent mercury ions, Hg(II). Experimental measurements show that its adsorption capacity is nearly three times higher than that of the pristine framework. Notably, when the ligand was further modified with N-methylthiourea (NMeTU) groups, its mercury-capture capacity increased substantially to 769 mg g^{-1} . This excellent experimental capacity was further elucidated at the electronic-structure level through subsequent density functional theory calculations. Theoretical studies indicate that the degree of charge transfer and coordination configuration between Hg(II) and functional groups containing soft Lewis base sites, such as sulfur and nitrogen, are key factors governing adsorption performance. Among them, the NMeTU group enables efficient binding with heavy metal ions by virtue of its pronounced charge-donating ability and shorter interaction distance. These computational investigations not only successfully supported the experimentally observed results but also further clarified the interaction mechanism within the bidentate 2,5-dimercapto-1,3,4-thiadiazole (DMTD)-modified system. Specifically, the calculations indicated that nitrogen atoms exhibited a stronger stabilizing effect toward metal ions than sulfur atoms. This insight offers a valuable theoretical basis for the rational design and optimization of functional ligands in subsequent studies [11].

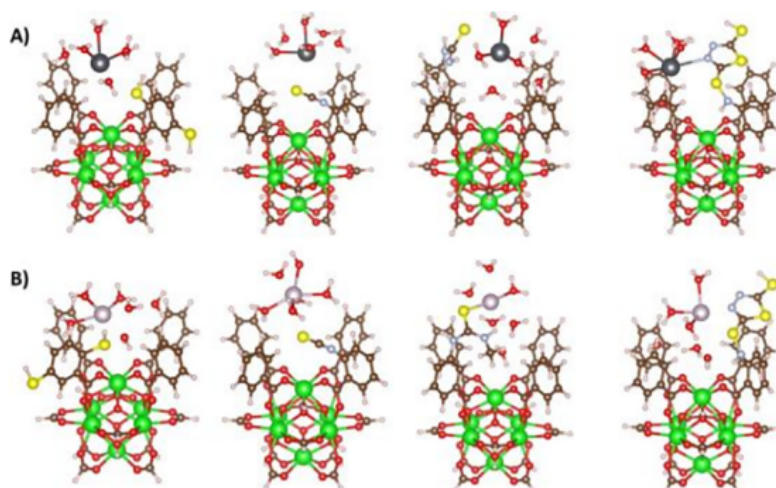


Figure 7. (Color online) optimized adsorption configurations of lead (A) and mercury (B). for both metals, the modified structures are arranged from left to right in the following order: SH, NCS, NMeTU, and DMTD [11]

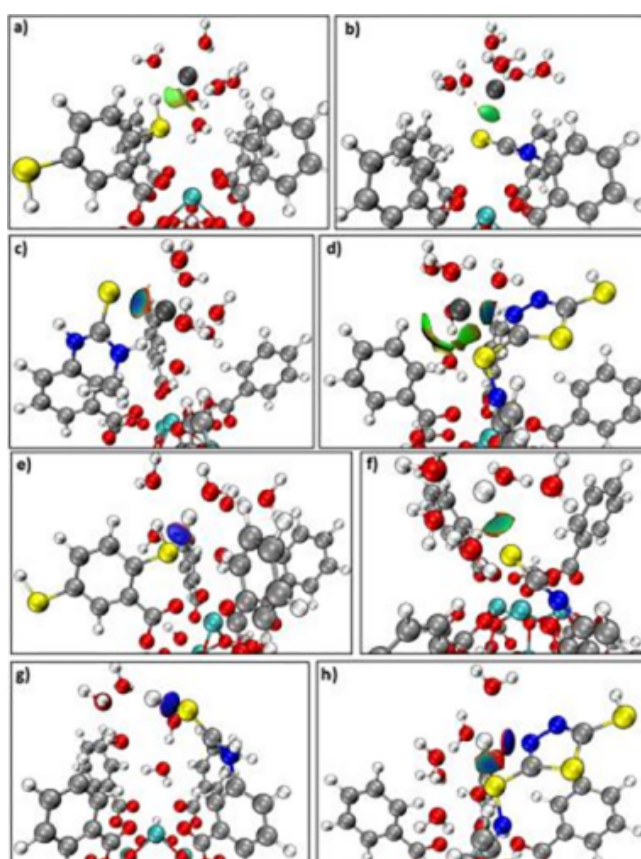


Figure 8. (Color online) RDG isosurfaces between the adsorbed heavy metals and the nearest atoms of the modifiers. panels (a)–(d) represent Pb adsorption on SH, NCS, NMeTU, and DMTD modifications, respectively, and panels (e)–(h) show the same corresponding cases for Hg adsorption [11]

In addition, etched UiO-66 was composited with chitosan to successfully prepare an etched UiO-66/CTS composite aerogel. This material effectively overcomes the prominent difficulties associated

with the recovery and separation of powdered adsorbents in practical applications. Meanwhile, the composite aerogel exhibits excellent adsorption performance toward Pb(II), with a maximum adsorption capacity as high as 654.9 mg/g [12].

3.2. Eand adsorptive removal of organic dye pollutants

Synthetic organic dyes are extensively employed in a wide range of industrial processes, such as textile manufacturing, leather processing, and paper production. Once discharged into aquatic systems, these dye contaminants can markedly decrease water transparency and may also pose potential carcinogenic hazards. Owing to their porous structure and tunable surface properties, UiO-66-based materials have demonstrated excellent adsorption capabilities toward various organic dyes with different molecular configurations.

Pristine UiO-66, as a typical zirconium-based metal–organic framework material, possesses a highly ordered microporous network in its crystal structure, which is generally constructed from Zr_6 clusters and terephthalic acid linkers. This structural feature enables pristine UiO-66 to exhibit favorable adsorption affinity toward negatively charged anionic dyes, such as methyl orange (MO). This is because the framework surface of pristine UiO-66 typically contains partially positively charged or polarizable sites, which can interact with anionic dyes through electrostatic attraction or π – π stacking interactions. However, the relatively small pore size of pristine UiO-66, typically below 1.0 nm, limits its adsorption efficiency toward larger cationic dyes. In particular, dye molecules such as crystal violet (CV), with molecular dimensions of approximately 1.3–1.5 nm, have difficulty entering its internal pore channels. To address this limitation, researchers structurally modified UiO-66 through a defect-engineering strategy and successfully prepared defective UiO-66 (dUiO-66) materials with missing-linker defects. As described in this study, dUiO-66 was synthesized using benzoic acid as a modulator and introducing HCl under solvothermal conditions, thereby generating approximately 0.65 missing-linker defects around each Zr_6 cluster. This defective structure significantly altered the pore characteristics of the material. Compared with pristine UiO-66, dUiO-66 exhibits a typical type-I microporous profile in its Ar adsorption isotherm, while its BET specific surface area reaches as high as 1915 m²/g, far exceeding that of defect-free UiO-66 reported in many studies. More importantly, the pore-size distribution of dUiO-66 exhibits relatively wide micropores of approximately 1.56 nm, while its external surface exposes more coordinatively unsaturated sites as a result of defect formation. Such modifications significantly enlarge the pore volume of the material while increasing the exposure of active adsorption sites. Consequently, the adsorption capacity of dUiO-66 for cationic dye molecules, such as methylene blue (MB) and crystal violet (CV), is greatly improved. Experimental data show that the maximum adsorption capacity of dUiO-66 for MB, as fitted by the Sips model, reaches 366 mg/g, while that for CV is as high as 561 mg/g; these values far exceed those of commercial powdered activated carbon, which are 214 mg/g and 87.2 mg/g, respectively. The fundamental mechanism underlying this enhancement is twofold. On the one hand, the enlarged pore channels allow smaller MB molecules (0.68 nm) to readily enter the framework and undergo effective confined adsorption within the pores. On the other hand, the additional negatively charged surface generated by defect sites—contributed by deprotonated μ_3 -OH, Zr–OH, and Zr–O[–] groups—strengthens the electrostatic attraction between the material and cationic dyes. Meanwhile, XPS and SERS analyses confirmed that the defect sites in dUiO-66 also promote the formation of hydrogen-bonding and π – π interactions. In particular, for CV molecules with substantial steric hindrance, although they have difficulty entering the internal micropores, they can preferentially anchor onto the larger vacancies or external surface defect regions generated by defect engineering, thereby still achieving an exceptionally high adsorption

capacity. In summary, structural regulation of pristine UiO-66 through defect engineering not only effectively addresses its insufficient adsorption capacity toward large-sized cationic dyes, but also provides an ideal structural platform for achieving efficient, rapid, and selective dye removal [13].

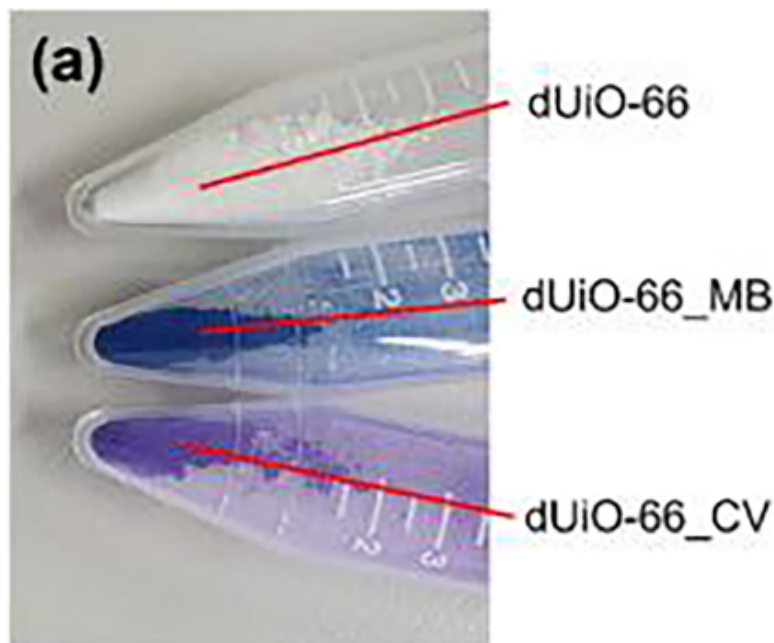


Figure 9. Photographs showing the actual samples before and after the adsorption of organic dyes [13]

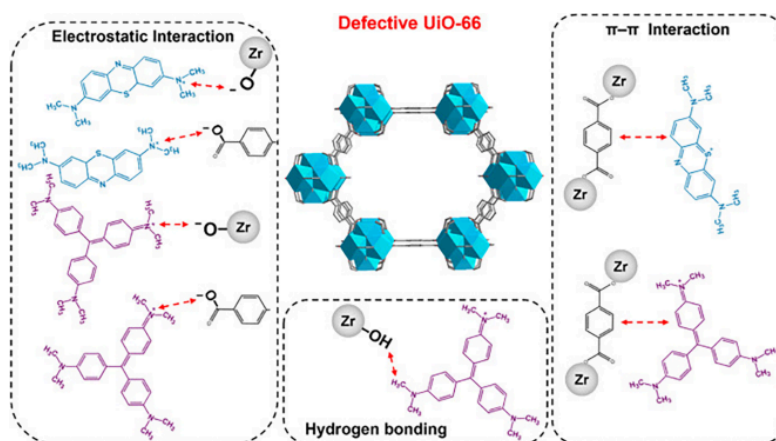


Figure 10. Proposed adsorption mechanisms for methylene blue (MB) and crystal violet (CV) on dUiO-66 [13]

3.3. Removal of emerging contaminants: pharmaceuticals and personal care products (PPCPs)

In recent years, the frequent detection of pharmaceutical compounds, typically represented by antibiotics and anti-inflammatory drugs, as well as personal care products (PPCPs), in aquatic environments has become a serious phenomenon attracting widespread and considerable attention. Such emerging contaminants generally possess complex and variable molecular structures, and it is precisely this structural specificity that often prevents conventional water-treatment processes from achieving highly efficient removal.

In terms of adsorption, as a zirconium-containing metal–organic framework, UiO-66 exhibits highly efficient removal capability toward antibiotics such as doxycycline. Experimental data show that, under neutral conditions at room temperature, 5 mg of UiO-66 can remove nearly 90% to almost 100% of doxycycline from 5 mL of a solution with an initial concentration of 100 μM within 30 min. Its efficiency is comparable to that of activated carbon and significantly superior to that of zeolite. Equilibrium adsorption studies further revealed that this adsorption process fits the Langmuir isotherm model extremely well, with a fitted correlation coefficient (R^2) as high as 0.98. This indicates that doxycycline undergoes monolayer adsorption on the surface of UiO-66, with energetically homogeneous adsorption sites. The theoretical maximum adsorption capacity, Q_m , was approximately 156.25 mg/g, comparable to that of polymer-based adsorbent materials. Moreover, the calculated dimensionless separation factor (R_L) was 0.244, which lies within the range of 0–1, suggesting that the adsorption process was thermodynamically favorable. The kinetic fitting results further demonstrated that the adsorption behavior followed a pseudo-second-order kinetic model, indicating that chemisorption played a predominant role in the overall adsorption mechanism [14]. UiO-66-NH₂, constructed through amino (–NH₂) functionalization, possesses a more suitable and narrower pore size compared with commercial activated carbon. Meanwhile, the amino groups on its framework form significantly enhanced hydrogen-bonding interactions with the target molecules, essentially acid–base interactions, together with multiple affinity mechanisms such as π – π stacking, thereby enabling UiO-66-NH₂ to exhibit an adsorption capacity for PPCPs far higher than that of commercial activated carbon [15].

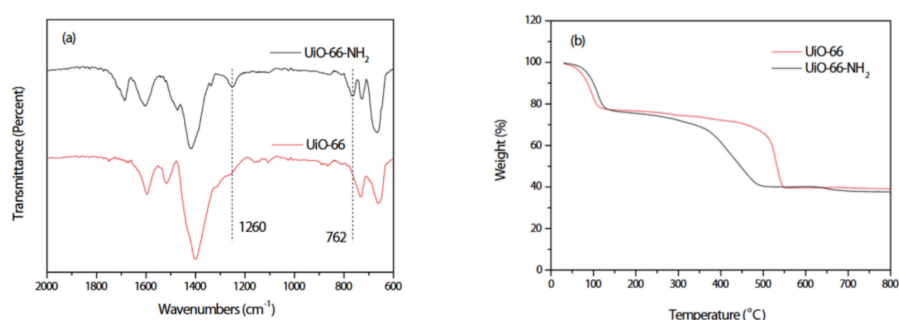


Figure 11. Characterization of UiO-66 samples: (a) FTIR spectra and (b) TGA curves [15]

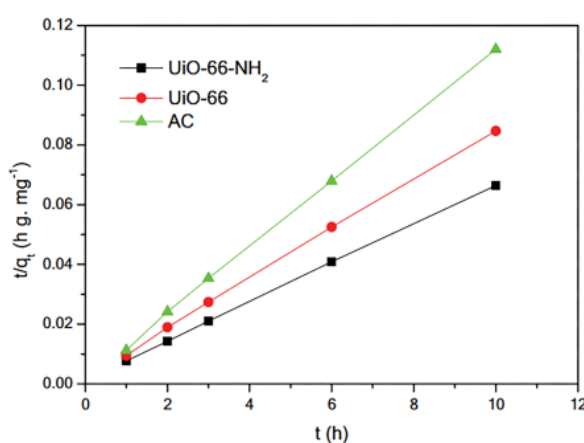


Figure 12. Pseudo-second-order kinetic fitting for diflunisal adsorption on three different adsorbents [15]

Relying solely on physical adsorption cannot achieve the complete mineralization of pollutants. In contrast, photocatalytic degradation technology is regarded as a more ideal pathway capable of completely eliminating pharmaceutical and personal care product pollutants (PPCPs). The zirconium-based metal–organic framework UiO-66 exhibits typical semiconductor-like band-structure characteristics, with a band gap of approximately 3.06 eV. Under ultraviolet irradiation, this material can be photoexcited to produce electron–hole pairs with strong redox capabilities. To extend its photoresponse range and improve quantum efficiency, researchers commonly employ modification strategies such as metal doping, for example through the introduction of Fe or Co, or heterostructure construction, such as UiO-66/p-BN and ZnO@NH₂-UiO-66 composite systems. Through these approaches, the spectral absorption range of the material can be effectively broadened from the ultraviolet region to the visible-light region, while the bulk and surface recombination of photogenerated charge carriers during migration is greatly suppressed. Taking the UiO-66/p-BN composite photocatalytic system as an example, a type-II band alignment is formed between UiO-66 and porous hexagonal boron nitride within this heterojunction, promoting the spontaneous transfer of photogenerated electrons from the conduction band of UiO-66 to that of p-BN, while holes migrate in the opposite direction and accumulate within the valence band of UiO-66, thereby achieving efficient spatial separation of charge carriers. Experimental data show that the prepared UiO-66/p-BN composite, with the optimal composition denoted as UBN-6, exhibits excellent photocatalytic activity. After 180 min of irradiation under visible light with a wavelength greater than 420 nm, it achieves a tetracycline (TC) degradation efficiency of 93.8%, with a pseudo-first-order reaction rate constant 2.46 times that of pristine UiO-66 [16]. According to electron paramagnetic resonance analysis, hydroxyl radicals ($\cdot\text{OH}$) were verified to be the dominant reactive oxygen species throughout the entire photocatalytic degradation process [17].

3.4. Applications in membrane separation technology

Introducing UiO-66 nanoparticles as fillers into polymer matrices to fabricate mixed matrix membranes (MMMs) or thin-film nanocomposite (TFN) membranes has become another crucial application direction for this material in the field of water treatment. Practical evidence indicates that the incorporation of UiO-66 into membrane structures produces beneficial effects that are not limited to effectively enhancing membrane water flux, but also include significantly strengthening the intrinsic antifouling performance of the membrane materials and substantially improving their rejection of target pollutants. In the field of seawater desalination, continuous intergrown polycrystalline membranes fabricated by loading the Zr-based metal–organic framework UiO-66 as a functional layer onto the outer surface of porous alumina hollow fibers via an in situ solvothermal synthesis method have systematically demonstrated excellent desalination performance and outstanding long-term operational stability in aqueous environments.

Experimental characterization results showed that the membrane achieved high rejection rates for divalent salt ions such as hydrated magnesium ions. Moreover, after continuous desalination testing, no obvious changes were observed in its X-ray diffraction patterns or micromorphological structure, fully confirming its structural integrity required for long-term water-filtration applications [18]. In the treatment of dye-containing wastewater, the amino-functionalized UiO-66-based nanofiltration membrane developed and investigated in this study, namely the DETA-UiO-66/PPSU mixed matrix membrane, demonstrated excellent separation performance. Specifically, this membrane achieved rejection efficiencies exceeding 99% for various organic dyes with different structural types. For example, the rejection rate reached 99.3% for Reactive Orange 16 (RO-16), increased to 99.6% for Brilliant Blue G (G250), and was as high as 99.7% for Rose Bengal (RB). These data fully

demonstrate that the membrane possesses an almost complete rejection capability toward macromolecular anionic dyes. Meanwhile, while maintaining high dye-rejection performance, the membrane does not achieve this at the expense of salt permeability. In contrast, it still maintains extremely high salt/dye separation selectivity. According to the research results, its salt/dye separation factor can reach 184.6. This value is significantly higher than that of many conventional nanofiltration membrane materials, indicating that the membrane possesses an excellent ability to distinguish between dye molecules and inorganic salt ions. In the practical treatment of saline dye wastewater, this high separation factor facilitates the effective recovery of dye molecules while enabling the smooth permeation of small salt ions, such as NaCl, through the membrane, thereby enabling subsequent salt treatment or reuse. In summary, this amino-functionalized UiO-66-based mixed matrix membrane exhibits significant application potential in the field of highly selective dye/salt separation [19]. In addition, the composite membrane formed by coating the prepared UiO-66 crystals onto the surface of a stainless-steel mesh exhibited pronounced underwater superoleophobicity, with an underwater oil contact angle reaching 150°. Based on this special wettability, the mesh membrane can achieve an oil–water separation efficiency of over 99.99%, with the residual oil content in the treated water reduced to below 4 ppm. Meanwhile, the membrane also exhibits an extremely high water permeation flux, reaching up to $12.7 \times 10^4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ [20].

Table 1. Material types, performance characteristics, and underlying mechanisms employed for different target pollutants

Application area	Target contaminant	Material type	Performance	Proposed mechanism
Heavy-metal removal	As(V)	pristine UiO-66	Adsorption capacity: 303.34 mg g ⁻¹	Coordination exchange (Zr–O–As)
Heavy-metal removal	Pb(II)	etched UiO-66/chitosan (CTS) aerogel	Adsorption capacity: 654.9 mg g ⁻¹	Electrostatic attraction and coordination interactions
Dye removal	Oil Orange SS	pristine UiO-66	Adsorption capacity: 2062.1 mg g ⁻¹	π – π stacking and hydrogen bonding
Antibiotic degradation	tetracycline	UiO-66/p-BN composite	Visible-light degradation efficiency: 93.8%	Radical oxidation ($\cdot\text{O}_2^-$ and $\cdot\text{OH}$)
Membrane separation	mixed dyes	UiO-66-NH ₂ nanofiltration membrane	Dye rejection: >99%	Size exclusion and electrostatic repulsion

4. Sodification strategies and performance optimization

Given the inherent limitations of pristine UiO-66 in terms of adsorption capacity, photoresponse wavelength range, and target selectivity, researchers have developed and systematically explored various modification strategies to effectively overcome these performance bottlenecks. These strategies can be summarized as follows.

4.1. Functional group modification

The core implementation pathway of this strategy lies in selecting organic ligands bearing specific functional groups, such as –NH₂, –OH, –COOH, and –SH, and chemically tailoring the material in a targeted manner either through direct participation in the synthesis process or through subsequent post-synthetic modification. Through the introduction of the aforementioned functional groups, a series of key interfacial chemical properties of the material, including surface charge distribution, hydrophilicity, and acid–base characteristics, can be purposefully regulated. The precise regulation of

these surface physicochemical properties can further significantly enhance specific intermolecular interactions between the material and targeted pollutants, typically manifested in the form of hydrogen bonding and acid–base interactions.

4.2. Defect engineering

During the synthesis of metal–organic framework materials, modulators such as acetic acid can be introduced to deliberately induce partial missing-linker or missing-cluster defects through competitive coordination with the organic ligands. This controlled defect construction can not only significantly enlarge the original pore dimensions, transforming the material from a purely microporous structure into an open framework containing mesopores and thereby increasing its specific surface area, but also expose zirconium metal nodes that were originally occupied by ligands, generating abundant coordinatively unsaturated zirconium sites. These coordinatively unsaturated zirconium sites are essentially Lewis acidic active centers and can serve as strong adsorption and catalytic sites. Therefore, defect engineering can greatly enhance the adsorption activity of the material toward pharmaceutical pollutants. As observed for defective UiO-66, its adsorption capacity for diclofenac sodium is nearly six times higher than that of nearly defect-free UiO-66, while the adsorption equilibrium time is shortened and the adsorption selectivity is also markedly improved [21].

4.3. Metal doping

In the structural modification of UiO-66 metal–organic framework materials, introducing transition metal ions such as Ti, Fe, and Co into the zirconium–oxygen (Zr–O) cluster nodes represents an effective metal-doping strategy. This process enables fine regulation of the intrinsic electronic band structure of the material, specifically by significantly reducing the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, that is, by effectively narrowing the band gap of the material. The resulting band-gap narrowing fundamentally alters the material's response characteristics to excitation light, successfully extending its originally inert photoresponse—activated only in the ultraviolet region—into the visible-light range. The core of this transformation lies in the new energy levels or hybridized orbitals generated by doping, which substantially lower the energy threshold required for electronic transitions. Consequently, the modified material can efficiently generate highly oxidative reactive species under visible-light irradiation, thereby enabling visible-light-driven photocatalytic degradation. For example, in the treatment of recalcitrant tetracycline antibiotic pollutants in aquatic environments, iron-doped UiO-66 (Fe-UiO-66) not only exhibits significantly enhanced visible-light absorption, but also thereby acquires the ability to rapidly photocatalytically decompose target pollutants under visible-light conditions [22].

4.4. Composite construction

The integration of UiO-66 with materials such as graphene oxide (GO), titanium dioxide (TiO₂), and magnetic nanoparticles (Fe₃O₄) can achieve functional complementarity among different components. Taking magnetic composite systems as an example, the construction of this type of material fundamentally addresses the prominent technical challenge that powdered adsorbents are difficult to efficiently separate and recycle in real aquatic environments.

5. Challenges and future perspectives

UiO-66 has shown significant potential for removing pollutants from aquatic environments. However, its transition from laboratory-scale research to large-scale industrial application still faces several critical challenges. First, scalable production and economic cost remain major bottlenecks. Current UiO-66 synthesis still largely depends on toxic and expensive organic solvents, especially N,N-dimethylformamide (DMF), which increases manufacturing costs while causing environmental burdens and safety risks. Therefore, future research should prioritize greener synthetic strategies using water as the main reaction medium and promote the practical application of continuous fluidized-bed synthesis technologies.

Second, the complexity of real water matrices may greatly affect the removal performance of UiO-66. Laboratory studies usually employ simulated wastewater containing a single target pollutant, whereas natural waters and practical treatment systems contain various coexisting ions, such as Cl^- , SO_4^{2-} , and HCO_3^- , as well as natural organic matter (NOM) with diverse structures and molecular weights. These components can competitively occupy the limited active adsorption sites on UiO-66, thereby reducing its adsorption efficiency and selectivity. Accordingly, improving the anti-interference ability, molecular recognition capacity, and selective capture performance of UiO-66 under complex aqueous conditions remains an important research direction.

Finally, the long-term operational stability of zirconium-based MOFs and their potential secondary pollution risks require careful evaluation. Although UiO-66 exhibits excellent structural stability in pure water and can maintain its crystalline framework over extended periods, its integrity may be challenged under strongly alkaline conditions or in the presence of strongly coordinating anions. For example, phosphate species can attack the zirconium–oxo cluster nodes and replace the original organic linkers, inducing gradual framework degradation through a competitive-coordination-driven digestion mechanism. This process may destroy the periodic network structure, reduce porosity and functionality, and release zirconium species or organic linker fragments into the surrounding environment [23]. Therefore, the leaching risks of Zr ions and organic ligands must be systematically assessed and controlled before long-term practical application.

6. Conclusions

As a metal–organic framework material with exceptionally high hydrolytic stability, UiO-66 provides a multifunctional and efficient platform for the removal of pollutants from aquatic environments. Through rational structural design, defect regulation, and composite modification, UiO-66 has achieved remarkable progress in heavy metal adsorption, organic dye elimination, photocatalytic degradation of emerging contaminants, and the construction of high-performance separation membranes. With breakthroughs in green synthesis processes and a deeper understanding of its interaction mechanisms in complex water bodies, UiO-66-based materials are expected to play an increasingly important role in practical water-treatment engineering in the future.

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