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Review

## Advances in metal–organic frameworks as adsorbents, photocatalysts and membranes: a new frontier in water purification

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### Abstract

Water is an essential and irreplaceable necessity for life on earth, sustaining ecosystems, nourishing agriculture and vital for human survival. However, increasing population and industrialization has exacerbated water scarcity and pollution. The Sustainable Development Goal 6 focuses on clean water and sanitation for all; thus, water purification and conservation are key priorities globally. Rampant pollution of water sources by emerging bio-recalcitrant contaminants, often deviant of conventional treatment methods, necessitates new approaches to water treatment. In this regard, metal organic frameworks (MOFs) are gaining prominence and offer solutions in versatile applications due to their unique structural characteristics and tunable properties. This review provides a comprehensive analysis of MOFs, covering their diverse structures, types, synthesis methods and characterization techniques. We explore the application of MOFs in water purification, as adsorbents, photocatalysts, and in membrane separation. The mechanism of operation of MOFs in each application is critically evaluated. The effect of the water treatment methods on energy consumption has also been investigated. We propose that for MOFs application in water treatment to be competitive and sustainable, there is need to address key issues such as synthesis of highly selective MOFs, recovery and reuse, scalability (pilot and industrial scale), and integration with existing water treatment technologies to create synergy. We provide future perspectives on these aspects.

**Keywords** Metal–organic frameworks · Water purification · Adsorption · Photocatalysis · Membrane separation · Reusability

## 1 Introduction

In an era marked by burgeoning populations, industrial expansion, and environmental challenges, the global water crisis has emerged as a formidable threat, demanding innovative solutions. Traditional water treatment methodologies face increasing pressure to meet the escalating demands for clean and potable water. Existing conventional treatment processes including sedimentation, coagulation, filtration, and disinfection, have played crucial roles in safeguarding water quality. However, their efficacy is compromised by drawbacks such as high energy consumption, limited selectivity, and inability to remove emerging bio-recalcitrant contaminants [5]. Recent advancements in

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nanotechnology and the development of novel adsorbents, photocatalytic and membrane separation processes hold a great promise [6–9]. These technologies enhance the elimination of contaminants from wastewater and improve efficiency of desalination process, presenting sustainable strategies to mitigate the global water crisis. Despite their effectiveness, these methods are still limited due to their reliance on primitive materials that have undermined water purification. Amidst these challenges, metal organic frameworks (MOFs) emerge as a captivating prospect, offering a new frontier in water purification technology. Characterized by their crystalline structures, MOFs comprise of metal nodes interconnected by organic linkers which present a versatile platform with tunable properties [10, 11].

The distinctive properties of MOFs not only open avenues for addressing the limitations inherent in traditional water treatment methods but also embrace the principles of sustainability through their recovery and reusability. From the selective adsorption of contaminants [12] to the potential for catalytic degradation of pollutants [13], MOFs exhibit a prowess that holds promise for revolutionizing water purification processes, while concurrently reducing the environmental impact through their repeated utilization. This review explores the unique attributes of MOFs, exploring their exceptional porosity, high surface area, customizable structures, and the pivotal aspect of reusability that sets them apart from conventional materials. Furthermore, we elucidate the specific ways in which MOFs are applied, ushering in a new era of efficiency, sustainability, and innovation in the critical domain of water purification. Emerging trends in MOFs research for water purification and challenges such as scalability, cost, and selectivity have also been extensively discussed.

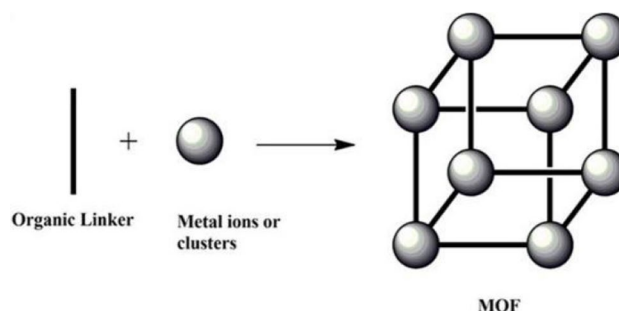
## 2 Historical overview

The MOFs trace their origin to the mid 1990's when Yaghi's group reported the first stable 2D MOF structure synthesized from 1,3,5-Benzene tricarboxylic acid (BTC) [14] and further the synthesis of MOF—1 [15] and MOF—2 in quick succession [16]. A pivotal moment in the history of MOF happened in 1999 when O'Keefe and Yaghi's group synthesized the first true 3D MOF known as MOF—5 using Zinc (II) nitrate and 1,4 Benzene dicarboxylic acid [17] which spurred a surge into MOF's research. As a result, within the same year, Chui and collaborators reported another novel MOF, HKUST -1 (Hong Kong University of Science and Technology) synthesized from copper (II) ions and a trimeric acid [18]. In 2002, G'erald F'erey's group synthesized the MIL—53 (Mat'eriaux de l'Institute Lavoisier) from chromium (II) ions as metal centers and benzene dicarboxylate ligand linkers, acknowledged as the foremost representation of MIL which found application in gas storage, separation, and catalysis [19]. F'erey's group in 2005, they reported another chromium based MOF called MIL—101 which consisted of ultrahigh surface area, large pore size and was thermally and chemically stable [20]. In 2006 another series of MOFs were developed by Yaghi's team, known as zeolitic imidazolate frameworks (ZIFs) particularly the ZIF—1 and ZIF—12 which found applications in gas separation and conversion. Another landmark in MOF research came in 2008, through the synthesis of the UiO 66 (University of Oslo) from zirconium tetrachloride and 1,4 Benzene dicarboxylic acid also known as Zr—MOF by Karl Peter's group [21]. The beginning of the 2010s witnessed an explosion of applications, including gas storage devices, hydrogen fuel cells, and drug delivery systems, alongside the emergence of light-emitting and magnetic MOFs [22–24]. New synthesis methods, such as post-synthetic modification and continuous-flow synthesis, were introduced for large-scale production [25]. Over 90000 MOFs have been reported with continued research done to optimize MOF properties and explore new applications, with a focus on integrating MOFs with other materials for hybrid functionalities [26]. Today, innovative computational tools have revolutionized the creation of novel MOFs with diverse structural and chemical characteristics, enabling the rapid generation of thousands of materials using automation and simulation, highlighting the immense possibilities in realizing a wide range of MOFs [27, 28].

## 3 Structure of metal organic frameworks

Structure of MOFs encompasses nodes and linkers, diverse topologies, and their pore geometry (Fig. 1).

**Fig. 1** General structure of MOFs [1]



### 3.1 Nodes and linkers

The backbone of MOFs consists of metal-containing nodes and organic linkers, which together form the crystalline framework. Nodes typically involve metal ions or clusters, serving as the coordination centers for the assembly process. Common metal ions include zinc, copper, and chromium, among others [29]. The selection of metal nodes significantly influences the MOF's structural stability and properties. Linkers, on the other hand, are organic molecules that bridge the metal nodes, creating robust bonds that contribute to the framework's overall stability. The diversity of available linkers allows for fine-tuning of MOF properties, such as porosity, surface area, and chemical reactivity [13]. Organic ligands like carboxylates [29] are commonly employed as linkers, highlighting the versatility of MOF design. The choice of nodes and linkers is crucial in determining the MOF's functionality.

### 3.2 Topologies

The MOFs exhibit a rich variety of topologies, determined by the spatial arrangement of nodes and linkers. The systematic combination of different nodes and linkers results in an extensive library of MOF structures, each with unique pore sizes, shapes, and functionalities. Some common MOF topologies include cubic, tetragonal, and hexagonal structures, showcasing the diverse architectural possibilities within this class of materials [30].

### 3.3 Pore geometry

The porous nature of MOFs, a defining feature, arises from the carefully designed arrangement of nodes and linkers, creating well-defined channels and void spaces. Pore geometry significantly influences the adsorption capacity and selectivity of MOFs, making them ideal candidates for applications such as gas storage and separation, as well as water purification. Understanding the relationship between pore geometry and adsorption properties is vital for designing MOFs tailored to remove specific contaminants from water sources [31].

## 4 Classification of metal organic frameworks

The MOFs are classified based on their structure and composition as pristine MOFs, MOF derivatives and MOF composites. The pristine MOFs are further categorized into 1D MOFs, 2D MOF nanosheets and 3D micro/nanoscaled MOFs [32].

### 4.1 Pristine MOFs

The pristine MOFs are obtained directly from the synthetic process and their structure and composition are hence well defined. Thus they have not been subjected to any post-synthetic modification [33]. They are further classified into:

#### 4.1.1 The 1D MOFs

One dimensional pristine MOFs have rod like structure and usually grow along a designated direction commonly synthesized via coordination modulation [34]. Examples include MOF-5 which is a zinc-based MOF, 1RMOF-3 which is a zirconium-based MOF and CuBTC which is a copper-based MOF (Benzene tricarboxylate).

#### 4.1.2 The 2D MOF nanosheets

The 2D nanosheet MOFs have a thickness of only few nanometers with a layered and flaky structure. They are synthesized through the top down and bottom down methods [32, 35]. The top-down method involves the exfoliation of bulk MOFs into one or more layer of nanosheets, while the bottom-up method entails the preparation of the nanosheets from metal ions and organic ligands through synthesis strategies such as solvothermal method, template assisted synthesis, among others. Examples of 2D MOF nanosheets include 2D nickel phthalocyanine based MOF and 2D cobalt based MOF (CoMOF).

#### 4.1.3 The 3D micro/nanoscaled MOFs

These include 3D structures containing larger sizes in 3D space [32, 36]. Their exceptional morphologies and structure have made them to widely be used in catalysis and adsorption. Examples include MIL-101 chromium-based MOF and UiO-66 Zirconium based MOF.

### 4.2 MOF composites

The MOF composites are made up of a combination of MOFs and polymers, metals, or even other MOFs. The carrier materials can make MOF even distributed and expose more active sites and become a support surface to enhance their stability [32, 37]. Example of MOF composites include MOF@metals such as the Ce-UiO-66-NH<sub>2</sub>; MOF@metals oxides such as the Fe<sub>3</sub>O<sub>4</sub>@MOF-808; and MOF@carbon materials such as Zn-MOF/PVA (polyvinyl alcohol).

### 4.3 MOF derivatives

The MOF derivatives are materials derived from MOFs by post-synthetic modification, a process of chemically modifying the structure of MOF without destroying their overall structure [32, 36]. Therefore, post treatment methods such as calcination, sulfurization, and chemical etching should preserve the morphology and porous structure of pristine MOFs. They increase the surface area of reactants and improve the transfer efficiency of substances [38]. Examples include the core-shell structure nanoscale zero valent iron@ZIF-67 derivative (NZVI@ZD).

## 5 Synthesis of metal organic frameworks

The MOFs are formed through coordination of metal ions or metal clusters as central connectors and organic ligands as linkers binding them together. The method of synthesis is determined by the reaction time, temperature and pressure, nature of metal ions and organic ligands, solvent used. In addition, structural characteristics, the desired size of nodes, presence of counter ions and kinetics of crystallization also play a key role [39]. Table 1 summarizes the synthesis conditions for some of the mostly used MOFs.

Figure 2 is a schematic representation of synthesis methods for MOFs.

The various synthetic approaches include:

### 5.1 Solvo/hydrothermal method

Solvo/hydrothermal method is widely used for synthesizing MOFs and involves reaction of a solution of metal salts and organic ligands in a closed vessel such as an autoclave under high temperatures and pressures to obtain an insoluble framework [3]. The choice of the solvent and its ratio can significantly influence the final MOF structure. In the autoclave, temperatures of 80–250 °C are maintained for an extended period, and the pressure increases with temperature. The reaction time is a crucial factor in determining the size, structure, and purity of the resulting MOF. After the allotted reaction time, the autoclave is cooled gradually to room temperature and depressurization is done by carefully releasing the pressure from the autoclave. Filtering and washing of MOF crystals is then done to remove any residual solvent or impurities. This method has been used to synthesize highly stable MOFs such as the MOF-74,177, MIL-101, UiO-66 and PCNs

**Table 1** Synthesis conditions of some established MOFs

MOF	Method of synthesis	Temperature/Power	Reaction time	Solvent utilized	Analysis of MOF produced	Ref
MOF-5	Solvothermal	120 °C	16 h	anhydrous dimethylformamide (DMF)	Low yield (25%)	[40]
	Microwave assisted	105 °C	30 min	1-methyl-2-pyrrolidone (NMP)	Relatively low solid phase yield	[41]
	Sonochemical	155 °C, 600W	10 min	1-methyl-2-pyrrolidone (NMP)	Relatively high purity	[42]
	Consecutive combination of Micro-wave and ultrasound	150 °C	2 min	Triethylamine (TEA)	High yield (95%) High purity	[43]
	Electro—chemical	Room temperature	15 min	DMF/H <sub>2</sub> O mixture containing (NBu <sub>4</sub> )PF <sub>6</sub> electrolyte	High purity	[44]
MOF-74	Continuous flow solvothermal	120 °C	3 min	N,N-dimethylformamide	Relatively high yield (84%) Economically scalable	[45]
	Solvothermal	105 °C	24 h	N,N-DMF and water	Moderate yield (57.8%)	[46]
	Microwave assisted	100 °C	90 min	DMF, Ethanol and Water	High yield and purity	[47]
	Sonochemical	500 W	60 min	Triethylamine (TEA)	High purity	[48]
	Mechano—chemical	Room temperature		Liquid assisted grinding (LAG) additive, methanol, water	High yields (87–97%) Phase pure product	[49]
HKUST-1	Solvothermal	120 °C	24 h	Water and ethanol	High yields (99.2%)	[50]
	Microwave assisted	170 °C, 300 W	10 min	Water and ethanol	High yield (92%)	[51]
	Sonochemical	60 W	60 min	DMF and ethanol	Relatively high yield (85.1%)	[52]
	Spray drying	180 °C	4.5 ml/min	DMF, water and ethanol	90% yield 70% purity	[53]
UiO-66	Solvothermal	80 °C	72 h	Acetone	High yield (91%)	[54]
	Mechano—chemical (Extrusion)	Room temperature	60 min	Liquid assisted grinding (LAG) additive	Economically scalable 95% yield	[55]
	Continuous flow—microwave assisted	280 W	7 min	DMF	Good quality 94% yield Economically scalable	[56]
ZIF-8	Continuous flow spray drying	90 °C	90 s 2.4 ml/min	Acetic acid and water	72% yield	[57]
	Solvothermal	150 °C	96 h	N,N-diethylformamide (DEF)	Low yield (25%) High purity	[58]
	Mechano—chemical (extrusion)	Room temperature	<2 min	Ethanol	Economically scalable High yield and purity	[59]
	Hot pressing	200 °C	10 min	Solvent/binder free	Easy scale up High yield	[60]
	Spray drying	180 °C	400 ml/hr	Water	68% conversion Economically scalable	[61]
	Slow evaporation	Room temperature	One month	Methanol and water	70% yield Relatively high purity	[62]

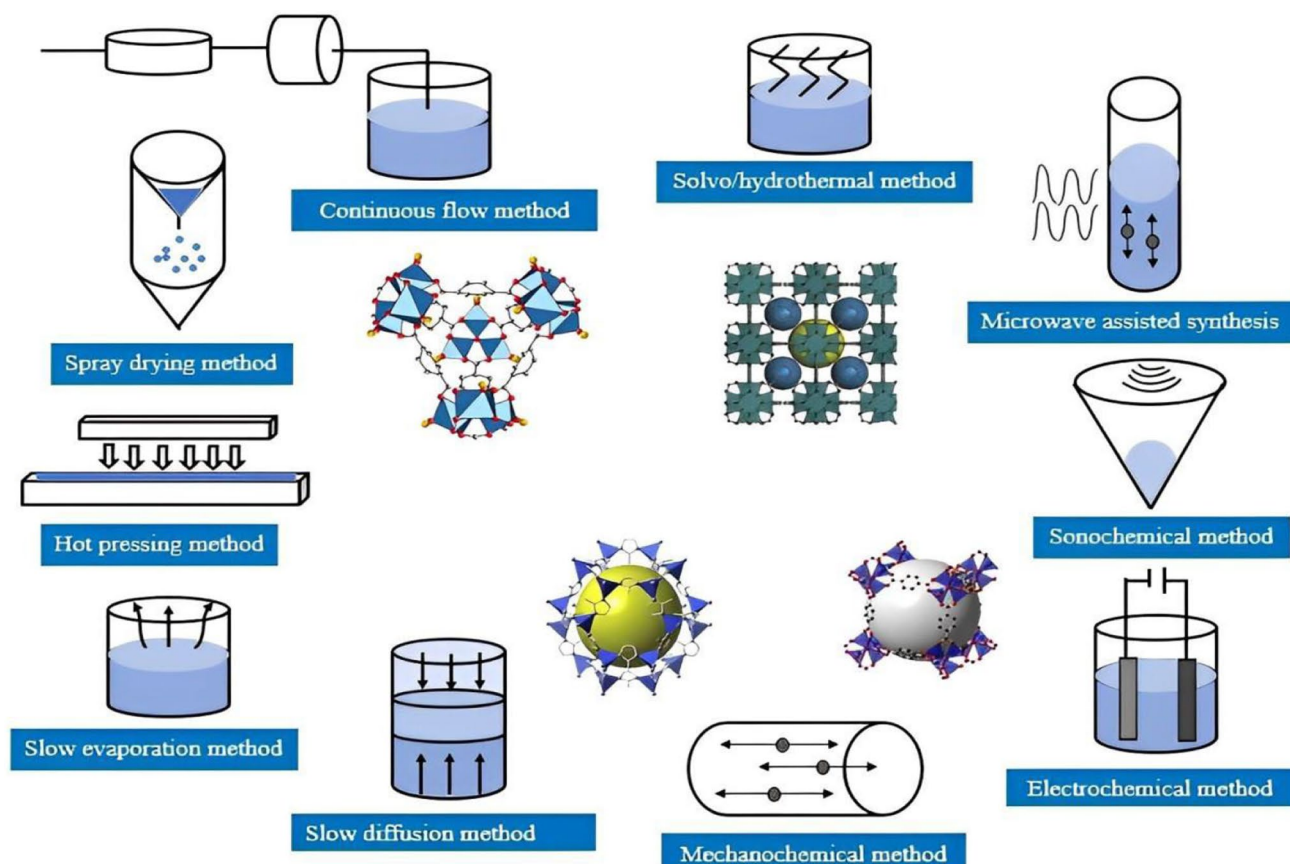


Fig. 2 MOFs synthesis methods, adapted from Ma and co-workers [3]

[3]. Its advantages include high crystallinity and purity of the MOF product, high thermal stability, controllable pore size and functionality through the selection of different organic linkers and easy scalability for large-scale MOF production. Limitations include long reaction times, high energy consumption, harsh synthetic conditions, and solvent consumption.

## 5.2 Microwave assisted synthesis

It involves transferring the mixture of precursor reactants; metal ions and organic ligands and suitable solvents into a sealed Teflon or glass vessel placed in a microwave chamber and heated for an allotted reaction time. Unlike conventional heating that warms the entire reaction vessel, microwaves directly interact with the molecules in the mixture, causing specific internal heating due to dielectric polarization. This leads to faster reaction kinetics, enabling rapid nucleation and growth of MOF crystals within minutes to hours [3]. The method allows tailoring MOFs with specific properties for targeted applications by manipulating the irradiation time, power, and temperature profile, the size, shape, and crystallinity of the MOF crystals which can be controlled precisely. This method been used for rapid synthesis of MIL 100, chromium trimesate, and MIL 53 which took only 4.3 s. Relatively the same crystal yield of the MOF was obtained in 4 h for the microwave assisted synthesis as compared to the conventional hydrothermal synthesis which took 4 days [63]. Despite the advantageous decrease in reaction time, high efficiency, and minimal energy usage; this method is disadvantaged due to limited choice solvents, and it is applicable only to certain MOF species.

## 5.3 Sonochemical method

The sonochemical method utilizes ultrasound in synthesizing MOFs. The precursor reactants, metal ions, organic ligands and suitable solvents are transferred to a horn-like reactor fitted with adaptable ultrasonic power sonicator bar. High-frequency sound waves (ultrasound) are introduced into the reaction mixture containing MOF precursors. The extreme conditions generated by cavitation promote the breakdown of larger molecules into smaller fragments, facilitating

their interaction and self-assembly into the desired MOF structure, generates microturbulence that effectively mixes the reactants, ensuring homogeneity and efficient utilization of precursors, enhancing their reactivity, and promoting faster bonding during MOF formation. Li and co-workers [64] employed sonochemical synthesis to prepare zinc based polymer with flower like structure within 80 min compared to the conventional hydrothermal reaction which took 3 days to obtain a single crystal at 140 °C. Advantages of the method include significantly reduced reaction time, lower energy consumption, improved product purity and enhanced control over crystal morphology. Limitations of the method include limited scalability, potential for solvent degradation and complex equipment is required.

## 5.4 Electrochemical method

Electrochemical method is a novel technique in MOF synthesis that utilizes electricity to drive the formation of MOFs. It involves applying electrical voltage in an electrolytic cell made up of an electrolyte and electrodes consisting of MOF building blocks; organic ligands and metal ions [3]. The metal ions and linkers modified by electrochemical reactions, thus interact, and self-assemble into the desired MOF structure. This process is influenced by various factors like the applied voltage, current density, and electrolyte composition. Once the MOF crystals have formed, the reaction is stopped, and the MOF is collected from the solution. Purification steps may be necessary to remove any remaining impurities or unreacted precursors. There are two types of electrochemical synthesis methods: anodic dilution and cathodic deposition.

### 5.4.1 Anodic dilution

In anodic dilution, the anode is made up of metal ions and the electrolyte solution contains the organic ligand linkers. Applying a specific voltage to the cell triggers electrochemical reactions at the electrodes. At the anode, metal ions are oxidized, losing electrons, and entering the solution. Meanwhile, at the cathode, organic linkers are reduced or undergo other reactions, based on the MOF being synthesized. The metal ions and linkers in the solution, now charged and potentially modified by the electrochemical reactions, interact, and self-assemble into the desired MOF structure. The anodic dilution electrochemical synthesis has been reported by [65], to synthesize rapidly HKUST-1 using a copper plate as the electrode.

### 5.4.2 Cathodic deposition

In cathodic deposition, the electrolyte contains metal ions and organic ligands, the building blocks of MOFs. A classic two-electrode system containing a working electrode and a counter electrode is used to initiate the reaction and the metal ions and organic ligands interact and self-assemble into the desired MOF structure. A three-electrode system with an extra reference electrode is sometimes utilized to measure and control the electrochemical process. The cathodic deposition controlled electrochemical synthesis has been utilized by [66] where they grew 2D  $\text{Cu}_3(\text{HTTP})_2$  (Copper 2,3,6,7,10,11 hexahydrotriphenylene) MOF film on a copper foil. This approach has gained much interest due shorter reaction times, precise control over morphology and environmentally friendly.

## 5.5 Mechanochemical method

Mechanochemical approach to MOF synthesis involves the grinding or milling of MOF precursor reactants; metal ions and organic ligands into smaller fragments thus creating larger surface area for their interaction and subsequent bonding. The grinding creates smaller pieces and generates significant localized pressure due to the collisions. These conditions encourage the fragmented precursors to self-assemble into the desired MOF structure [3]. This method has significantly faster reaction times (minutes to hours). It also eliminates the need for harsh solvents and high temperatures, minimizing environmental impact. By altering the grinding parameters such as pressure, time, and temperature, researchers can fine-tune the size, shape, and even crystallinity of the MOF crystals. However, the method is limited to some synthesizable MOFs since not all MOFs succumb to the grinding approach. Mechanochemical synthesis is divided into ball-milling method and extrusion method.



### 5.5.1 Ball milling method

In ball milling, a mixture of metal salts and organic linkers, the building blocks of MOFs, along with a grinding medium like metal balls or beads is loaded into a grinding jar. The grinding balls relentlessly smash into the mixture, breaking down the precursors into smaller and smaller fragments. This increases their surface area significantly, facilitating easier interaction and bonding. The collisions generate intense localized pressure, further pushing the fragmented precursors closer together. This pressure acts as a driving force for self-assembly. With increased surface area and pressure, the broken-down precursors find their perfect match, snapping together into the desired MOF structure. Ball milling method has been utilized in the manufacture of four well know MOFs; MOF-5, MOF-177, UiO-67 and ZIF-65 [67].

### 5.5.2 Extrusion method

In extrusion, the MOF precursors; metal ions and organic linkers are mixed and fed into a screw extruder. The screws thoroughly mix the precursors, ensuring homogeneity and efficient utilization of materials. This is crucial for consistent MOF formation throughout the process. As the mixture travels through the extruder, it encounters increasing pressure from the screws which compacts the material and promotes self-assembly of the MOF structure. The extruder operates continuously, feeding in precursors and churning out freshly formed MOF material. This allows for high-throughput production, ideal for large-scale applications. By adjusting the screw geometry, pressure, and temperature within the extruder, researchers can influence the properties of the extruded MOF material, such as its density and porosity. The extrusion method was employed for the first time in the synthesis of three typical MOFs; HKUST-1, ZIF-8 and Al (fumarate) OH [59]. This innovative approach utilized twin screw extruders, enabling the production of MOFs with pore volumes and surface areas comparable to those achieved through traditional solvothermal methods.

## 5.6 Slow evaporation method

This is a widely used technique in MOF synthesis at room temperature without the need of an external energy supply. It involves first preparing a solution containing the metal ion precursors and organic linkers, the building blocks of MOFs using a suitable solvent. The prepared solution is then transferred to a sealed container, often a vial or beaker, and left undisturbed at room temperature. As the solvent gradually evaporates, the concentration of the precursors increases within the solution and when it reaches saturation point, the precursors start to self-assemble into tiny MOF crystals, a process known as nucleation. These nuclei then act as seeds for further crystal growth as more precursors become available due to continuous solvent evaporation. Once the desired crystal size or reaction time is reached, the remaining solvent is carefully removed, and the MOF crystals are collected and purification to remove any unreacted precursors or solvent residues. The slow evaporation method has been used in the synthesis of a new supramolecular cobalt MOF [68]. While the method is simple, easy to setup, has a wide range of compatible MOFs and good control over crystal size and morphology over size, its application is often limited due to slow reaction times since crystallization can take hours, days, or even weeks depending on the specific MOF and desired crystal size.

## 5.7 Slow diffusion method

This is a novel technique used to create MOFs with complex interpenetrating structures or core-shell morphologies. Two separate solutions are prepared, one containing metal salts and the other containing organic linkers, both dissolved in suitable solvents. The solutions are carefully layered in a sealed container, one on top of another separated by a layer of solvent. This "sandwich" configuration creates the perfect environment for controlled diffusion. As the precursors slowly diffuse across the solvent barrier, they meet at the interface, triggering MOF nucleation and crystal growth. This process continues as the diffusion front expands. Once the desired crystal size or reaction time is reached, the remaining solutions are carefully removed, and the MOF crystals are collected and purified to remove any remaining solvent and unreacted precursors. The technique was first utilized in the synthesis of MOF-5 by diffusion of  $\text{Et}_3\text{N}$  into a solution containing  $\text{Zn}(\text{NO}_3)_2$  and  $\text{H}_2\text{BDC}$  in a mixture of DMF and chlorobenzene [17]. This method enables access to complex structures as it facilitates the synthesis of MOFs with intricate architectures, including core-shell

structures and interpenetrated frameworks, which are difficult to achieve with other methods. However, it is limited by slower reaction times, making it longer to reach desired crystal sizes.

## 5.8 Continuous flow method

This is an innovative technique that eliminates the stop-start routine and embraces a constant stream of MOF creation, promising faster production, better control, and a greener footprint. The precursor MOFs building blocks are pumped into microfluidic chips or reactor coils. The precursor solutions flow through a microfluidic channel or reactor designed for optimal mixing and reaction conditions. This "highway" allows for precise control of factors like temperature, pressure, and residence time, crucial for tailoring the MOFs. The reactors can be categorized into microfluidic reactors (MRs), where reactant solutions traverse microscale-constrained channels; plug flow reactors (PFRs), where reagents are propelled through pipes or tubes; and stirred tank reactors (CSTRs), where reagents find their way into designated tanks. As the precursors encounter the right conditions, they spontaneously self-assemble into MOF crystals within the reactor. Once the MOF crystals form, they are separated from the remaining solution, often using filters or membranes, and purified. The method was first used to synthesize HKUST-1 MOF in a microscale reactor [69]. The advantages include faster reaction times allowing MOF synthesis in minutes or even seconds, minimizes solvent use and waste generation making MOF synthesis more environmentally friendly and allows for real-time monitoring of the reaction and adjustments to optimize MOF properties. The major drawback includes higher cost in setting up and running continuous flow systems compared to simple batch setups.

## 5.9 Hot pressing method

This is a solvent-free approach that uses a combination of temperature and pressure to fabricate MOF crystals. The MOF precursors: metal ions and organic ligands are first bonded to a substrate with either the functional groups and metal sites and placed between two heated plates made of conductive materials like aluminum or stainless steel. Pressure is applied to the "sandwich" while the plates heat up. Once the stipulated reaction time is achieved the hot press is released and the MOF crystals are collected. Hot pressing method has been used in the synthesis of versatile MOFs including MOF-5, ZIF-8,9,67, Ni-ZIF-8, Co-MOF and Cd-MOF within 10 min under applied temperature and pressure [70]. Advantages include faster reaction times, minutes even seconds, solvent free and environmentally friendly, by manipulating temperature and pressure variety of MOF structure morphologies can be realized and the method works with a diverse range of pre-made MOFs.

### 5.9.1 Spray drying method

Spray drying is a fast, continuous, process for production of MOF powders utilizing rapid evaporation of precursors with a hot gas. A homogeneous solution containing metal ion precursors and organic linkers is first prepared in a suitable solvent and serves as the feedstock for the spray drying process [3]. The feedstock is fed into a spray dryer, where it encounters a hot air stream which rapidly atomizes the solution into fine droplets, creating a mist. As the droplets travel through the drying chamber, the solvent evaporates quickly, concentrating the precursors and triggering MOF nucleation and crystallization. As the solvent evaporates and the concentration increases, MOF nanoparticles start to form within the droplets. These nanoparticles agglomerate into larger spherical micro particles as they collide and dry further. Finally, the dried MOF powder is collected from the outlet of the spray dryer. The advantages include faster reaction time, low cost, and higher throughput. It has been used in green rapid synthesis of two Zirconium based MOFs; UiO-66-NH<sub>2</sub> and MOF-801 with high surface areas [57]. The limitations include delicate frameworks might not withstand the rapid drying conditions or require specific solvent optimization and, in some cases, rapid drying can form amorphous phases alongside crystalline MOFs.

## 6 Characterization of metal organic frameworks

Characterization of MOFs is crucial for assessing their structural, chemical and physical properties that are essential for customizing their properties for specific applications [71]. The major characterization techniques employed are the scanning/transmission electron microscopy to determine MOF morphology, UV-Vis spectrometry to determine the MOF's

distinct absorption spectrum peaks, Fourier transform infrared (FTIR) spectroscopy to study their function groups, nuclear magnetic resonance (NMR) spectroscopy which provides detailed information about specific atoms such as metal ions and organic linkers, X-ray diffraction (XRD) analysis to determine the crystal structure, thermogravimetric analysis (TGA) to determine their thermal stability and Brunauer–Emmett–Teller (BET) and Langmuir methods which measures their specific surface area and pore volumes [72]. This knowledge is vital for optimizing MOF design, tailoring their properties for specific applications, and ultimately unlocking their full potential in various fields. These methods complement each other and enable full characterization of the MOFs to enable matching of material properties and performance. For instance, a higher surface area to volume ratio enhances adsorption; pore size is a key parameter in membrane separation, while UV–Vis light absorption is a key requirement for the use of MOFs as photocatalysts. A summary of MOF characterization methods is presented in Table 2.

### 6.1 Scanning/transmission electron microscopy

The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) offer valuable insights into the morphology, size and nanoscale surface features of MOFs [78, 79]. The SEM reveals the surface texture, particle size, and crystal faceting and provides elemental composition information while TEM peers into the internal structure, showcasing pore arrangement, crystal order, and defects and crystallographic information about the framework. Electron microscopy enables visualization of a diverse range of MOF morphologies; crystals structure cubic, octahedral, rod-shaped, and even intricate flower-like structures; Nanoscale features: pores of varying sizes and shapes (cylindrical, hexagonal, etc.); and Surface texture: roughness, porosity, and presence of secondary phases as shown in Table 2.

### 6.2 UV–Vis spectrometry

UV–Vis spectrometry explores the electronic structure of the MOFs providing insightful perspectives into the energy levels and electronic transitions within the framework. It measures the amount of light absorbed at various wavelengths, creating an absorption spectrum [80]. It unveils sublime features of the MOFs including Metal-to-Ligand Charge Transfer (MLCT) as electrons jump from metal ions to organic linker orbitals they revealing information about metal d-orbital energies and linker functionalities,  $\pi$ - $\pi$  transitions since electrons within conjugated organic linkers absorb light, indicating the presence of these functional groups, band gap which is the difference between the valence and conduction bands hinting at its potential for photocatalytic applications and purity and stability with Impurities or framework defects indicated by additional peaks in the spectrum. The absorption spectrum distinct bands of some of the established MOFs at their respective wavelengths and their band gaps are shown in Table 2.

### 6.3 Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy peers into the vibration of atoms and bonds within the MOF, analyzing functional groups and revealing their chemical fingerprint to determine the MOFs structure, composition, and functionality. FTIR spectroscopy measures the MOF's absorption of infrared light at distinct wavelengths generating the FTIR spectrum [81]. By examining the spectrum, unique functional groups can be identified and confirmed by matching peaks to known linker spectra. Additionally, studying shifts in peak positions allows for the investigation of coordination modes, unveiling the coordination geometry and potential binding sites for guest molecules. Table 2 summarizes the characteristic FTIR bands of some of the established MOFs.

### 6.4 Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy studies the local environment of specific atoms in the MOF by recording how radiofrequency (RF) electromagnetic radiation interacts with the nuclei of molecules in a strong magnetic field [82]. The NMR spectrum provides information about the chemical environment, quantity, and local environment of the nuclei in the sample. Different nuclei experience distinct chemical environments based on their location and interactions within the MOF framework [83, 84]. This allows NMR to determine the connectivity of organic linkers to metal ions, identify defects or disorder in the structure, and even map the positions of guest molecules adsorbed within the pores. Table 2 summarizes the NMR analysis of established MOFs.

**Table 2** Characterization of major Metal Organic Frameworks

MOF	Description	Morphology	UV/VIS analysis	FTIR (cm <sup>-1</sup> )	NMR	Crystal structure	TGA	BET (m <sup>2</sup> /g)	Ref
MOF-5	Made up of [Zn <sub>4</sub> O]6 + clusters linked by 1,4-benzenedicarboxylate (BDC2-) ligands	Cubic	Maximum absorption at 261 nm and wide-band-gap insulator of 8 eV	Peaks at 645, 3597, and 1758, attributed to Zn <sup>4+</sup> O, OH, and C-O bonds	Correspond to carboxylic acid, phenyl or alkyl carbon atoms	Highly ordered cubic structure	Thermal stability up to 400 °C	260–4400	[73]
HKUST-1	Made up Cu (II) clusters connected by benzene-1,3,5-tricarboxylate (BTC-3) linker molecules	Octahedral	Absorption bands at 300 and 700 nm and a band gap of 3–4 eV	1646, 1447 & 1373 are COO-Cu <sub>2</sub> , 728, 760 & 94 are CCO <sub>2</sub> , 1114 is C-O	Probes Cu, benzene-tricarboxylate, BTC, carbonyl and aromatic carbons	Octahedral structure	Thermal stability up to 340 °C	660–1700	[74]
UiO-66	Made up of Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> connected by 1,4-benzenedicarboxylate (BDC) linker	cubic and octahedral	Maximum absorption peak at 300 nm and band gap of 3.82 eV	3419 is OH, 1398 & 1586 is C-O, small 1540 is C=C and 1600 is C=O	Studies terephthalate, carbonyl and aromatic carbons	Cubic structure	Thermal stability up to 450–500 °C	900–1400	[75]
ZIF-8	Made of metallic zinc and 2-methylimidazole ligands	Rhombic dodecahedron	Absorption peaks at around 207 nm and a band gap of 4.34 eV	3455 is N-H, 3135 is C-H, 1635 is C=C, 1146 is C-N and 426 is Zn-N	Probes methyl imidazole, carbonyl and aromatic carbons	Tetrahedral cage structure	Thermal stability up to 210–250 °C	650–1800	[76]
MIL-101	Coordination of Cr <sub>3</sub> O ionic cluster with terephthalic acid (H <sub>2</sub> BDC) Ligand	Octahedral, rod shaped	Absorption peaks at 275, 425, and 610 nm; a band gap of 2.64–2.82 eV	751 is C-H, 1396 & 1583 are -COO- and 1680 is C=O	Identifies terephthalate, carbonyl and aromatic carbons	Hexagonal structure	Thermal stability up to 500 °C	> 3000	[77]

## 6.5 X-ray diffraction (XRD) analysis

XRD analysis is used to determine the atomic and molecular structure of MOFs by studying the diffraction pattern created by interaction of X-rays within the MOF [85]. It involves firing a monochromatic X-ray beam to the MOF sample. As the X-rays strike the MOF crystal lattice planes at various angles, they are scattered in different directions and interfere constructively or destructively, forming a diffraction pattern that contains information about the arrangement of atoms in the crystal lattice. Table 2 summarizes the crystal structure of some of the established MOFs.

## 6.6 Thermogravimetric analysis (TGA)

TGA studies the thermal stability of MOFs [86]. The weight changes are plotted against temperature to give the TGA curve. The derivative thermogravimetry (DTG) provides information about the rate of weight change at different temperatures. The TGA and DTG curves are analyzed to interpret the thermal stability, decomposition pathways, and the presence of different components in the MOF and the temperature at which significant weight loss occurs offer insights into the thermal stability of the framework. Table 2 summarizes the TGA and DTG analysis of some of the established MOFs.

## 6.7 BET and langmuir surface area analyses

The BET (Brunauer–Emmett–Teller) and Langmuir surface area analyses provide understanding of MOFs, surface area, porosity properties and adsorption behavior [87, 88]. The MOF sample is exposed to a gas at various pressure at a particular temperature and the amount of gas adsorbed on the MOF surface is measured as a function of pressure. The data is used to construct an adsorption isotherm. Table 2 summarizes the Langmuir and BET surface areas of some of the established MOFs.

## 7 Applications of metal organic frameworks in water purification

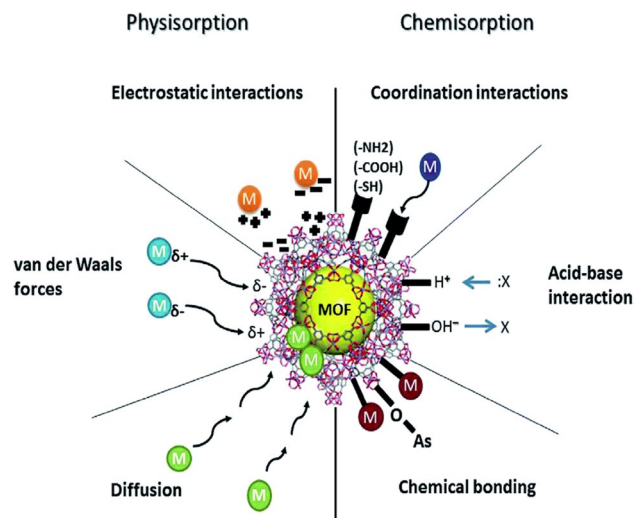
After understanding the synthesis and characterization of MOFs, we now delve into their applications in water purification. Water is fundamental resource for the sustenance of life. Paradoxically, despite the earth's surface being predominantly covered by water, only a meager 0.5% of the planet's total water resources remain readily accessible for human utilization [89]. The escalating challenges we face in securing these limited water sources are predominantly attributed to the compounding factors of rapid population expansion, the pervasive impacts of climate change, and the looming specter of water contamination. This over the years has accumulated to the global water crisis, we are currently facing characterized by increasing water scarcity and deteriorating water quality resources [90]. Approximately 2.2 billion people across the world lack access to safe drinking water, while over 4 billion people experience water scarcity either physical or economic. Water purification thus emerges vital component addressing the crisis with various water treatment technologies being explored globally. The various methods employed constitute the conventional approaches including the sequential primary, secondary and tertiary treatment [91] are summarized in Table 3.

The conventional methods are not effective in the removal of emerging contaminants such as dyes and pharmaceuticals [99]. Advanced water treatment methods such as AOPs, adsorption and membrane separation can greatly benefit from the introduction of MOFs to enhance effectiveness in water treatment [100]. The extremely high surface area extending to over 10000 m<sup>2</sup>/g of MOFs, offers an expansive platform for the exposure of active sites for adsorption and catalysis. Furthermore, the hierarchical porous architecture, encompassing micro- and mesopores, promotes extensive contact between pollutants and these active sites. Remarkably, MOFs exhibit exceptional stability even at high temperatures, withstanding up to 300–600 °C due to the robust nature of the chemical bonds, including C–C, C–H, C–O, and M–O. Owing to these outstanding attributes, MOFs have been applied in wastewater treatment, specifically in adsorption, photocatalysis and membrane separation processes.

**Table 3** Existing water treatment technologies and their limitations

Method	Description	Limitations	Reference
Conventional approaches			
Primary	Preliminary screening to remove larger debris. Includes screening, coagulation, flocculation, and sedimentation	Generate waste by-products in the process	[92]
Secondary	Biological processes use microorganisms break down organic matter and dissolved impurities. Most used methods are activated sludge and trickling filters	Inefficient for some non-biodegradable pollutants	[92]
Tertiary	Final water treatment using filtration and disinfection, to ensure that water is free from remaining contaminants	Generates wastes and ineffective for some pollutants	[92]
Advanced technologies			
Adsorption	Relies on the attractive forces such as Van der Waals forces, hydrogen bonding or chemical bonding between solid adsorbents materials and contaminants; organic compounds, heavy metals, dyes present in water	Generates wastes and requires periodic regeneration of adsorbent for sustained efficacy	[93]
Advanced oxidation processes (AOPs)	Chemical methods used for the removal of organic and inorganic by generating highly reactive chemical species, typically hydroxyl radicals (OH), to break down and eliminate contaminant. They include: <ul style="list-style-type: none"> <li>i. Photo-Fenton process uses iron (<math>Fe^{2+}</math>) as a catalyst and hydrogen peroxide (<math>H_2O_2</math>) as an oxidant</li> <li>ii. Photocatalytic process uses semiconducting materials like titanium dioxide (TiO<sub>2</sub>) to accelerate the degradation of pollutants using light energy, ultraviolet or visible light</li> <li>iii. Catalytic ozonation that harnesses ozone (<math>O_3</math>) as a powerful oxidizing agent to treat wastewater</li> </ul>	Inefficient for some persistent non-biodegradable pollutants	[94–96]
Membrane technology	Employs semi-permeable membranes with tiny pores to selectively separate substances based on size and molecular characteristics	Periodic backwashing is required for high efficiency	[97, 98]

**Fig. 3** MOF's adsorption process reprinted with permission from [4] © RSC 2019



## 7.1 Application of MOFs in adsorption

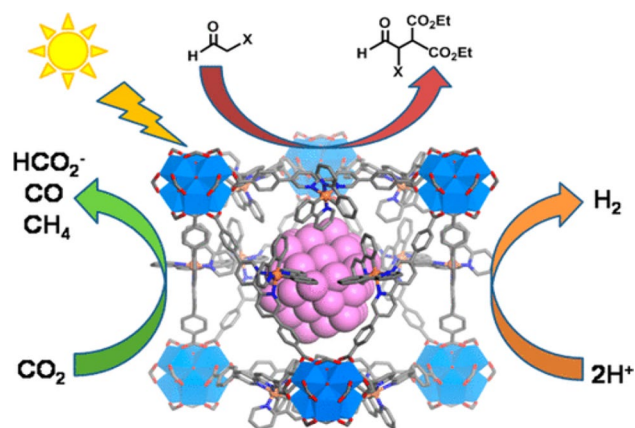
In adsorption, the pollutant is attached on to the surface of the MOF adsorbent by physical or chemical means [4]. Physical adsorption is governed by van der Waals forces between adsorbates and adsorbents and characterized by reversibility due to relatively weak adsorption forces. Chemical adsorption entails chemical interactions between adsorbed molecules and ions and the adsorbent's surface and is hence irreversible in nature. The array of forces underpinning adsorption encompasses van der Waals forces, hydrogen bonding, acid–base interactions, electrostatic attractions, and  $\pi$ - $\pi$  interactions are shown in Fig. 3.

The MOF-808-EDTA, has demonstrated exceptional efficacy in the removal of heavy metals from wastewater [32] exhibiting outstanding single-component adsorption performance for a spectrum of 22 metal ions, including  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Co}^{2+}$ , achieving removal rates exceeding 99%. Even after repeated cycles of use, the MOF-808-EDTA performance exceeded 90% over four consecutive cycles. Table 3 summarized the MOFs utilized, factors affecting MOF performance and the advantages and limitations of the utilization of MOF in adsorptive water treatment processes.  $\text{CeO}_2@ \text{UiO}-66-(\text{SH}_2)$  MOF spherical microbeads prepared by incorporating the organic nanoparticle  $\text{CeO}_2$  into Zr-MOF showed excellent simultaneous removal of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{4+}$ ,  $\text{As}^{3+}$  and  $\text{As}^{5+}$  metal ions in sewage [101]. The aqueous sewage sample containing 100 ppb of the metal ions was continuously passed through a column containing the MOF beads resulting to an impressive 0.25 ppb concentration of metal ions in the residual stream. The diaminomaleonitrile modified MIL-101 MOF synthesized through amidoximation reaction also exhibited exceptional 96% selective removal of uranium in seawater with competing ions such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$  hardly adsorbed [102]. The adsorption capacity maintained its high level even after five adsorption–desorption cycles.  $\text{Fe}_3\text{O}_4@ \text{TMU}-32$  MOF nanocomposite in situ fabricated through encapsulation of  $\text{Fe}_3\text{O}_4$  nanoparticles by TMU 32 ( $[\text{Zn}(\text{OBA})(\text{DPU})] \cdot 2\text{DMF} \cdot \text{H}_2\text{O}$ ) demonstrated efficient adsorption of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  with removal efficiencies only reducing by 10% after three consecutive adsorption–desorption cycles [103].

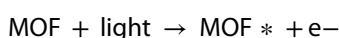
## 7.2 Application of MOFs in photocatalysis

Photocatalysis is a sustainable and environmentally friendly decomposition of organic pollutants into non-toxic compounds or even their complete mineralization into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , using sunlight and other light sources as the driving energy [32]. The composition and structural tunability of MOFs enable them to be engineered to narrower energy band gap as compared to conventional semiconductor photocatalysts. This extends their light absorption properties across a broader spectrum facilitating separation of charges with microsecond decays, rendering them conducive for photocatalytic applications using natural sunlight thus reducing energy costs. Also, the high porosity and open frame structure of MOFs facilitates easy diffusion of degradable substances to the active sites of the catalyst

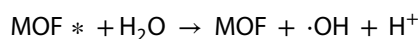
**Fig. 4** MOF's photocatalytic process reprinted with permission from [2] © American Chemical Society 2019



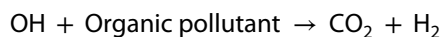
[104]. The photocatalytic degradation mechanism of MOFs has been studied by [105] demonstrating exceptional degradability and recyclability. The mechanism is illustrated in Fig. 4.



The holes then react with water molecules to produce hydroxyl radicals ( $\cdot\text{OH}$ ), which are powerful oxidants while regenerating the MOF photocatalyst.



The hydroxyl radicals then attack the organic pollutant, breaking it down into smaller, less harmful molecules.



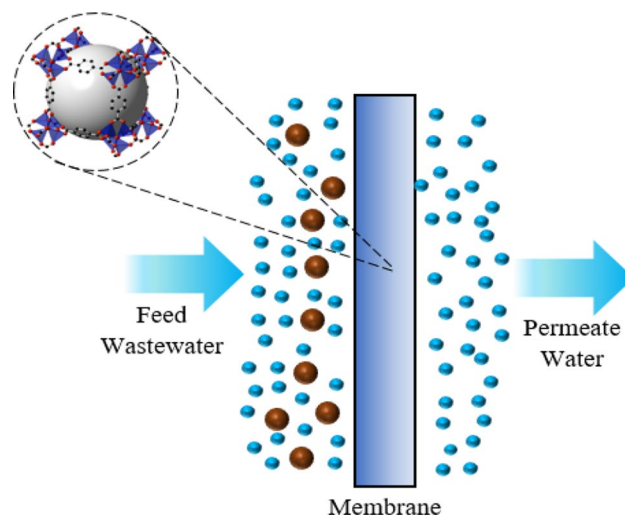
Pristine MOF—5 has a relatively large band gap (3.88 eV) which has limited its photocatalytic performance. However, integrating rGO sheets into the cubic MOF—5 surface showed to improve the photocatalytic performance resulting to strong interfacial attraction enhancing electron transport. The MOF—5/rGO heterostructure exhibited remarkable 95, 97 and 92% efficiency for methylene blue, Rhodamine B and methylene orange respectively after only 20 min [106]. The copper (II) dipyrindyl chloride,  $[\text{Cu}(2,2'\text{-DP})\text{Cl}]_n$  MOF synthesized by the hydrothermal method and utilized for the photocatalytic degradation of methylene blue dye under visible light. The MOF showed good photocatalytic performance which was more enhanced when hydrogen peroxide was added as an electron acceptor resulting to 93.33% dye degradation after only 150 min. Wang and collaborators investigated the photocatalytic performance of two 1,3,5 Benzenetricarboxylate (BTC) MOFs; CuBTC and CuBTC— $\text{NH}_2$  in the removal of reactive blue dye 171 and acid blue from wastewater under sunlight [107]. The MOF showed excellent photocatalytic performance with up to 90 and 70% dye degradation within 24 h for CuBTC— $\text{NH}_2$  and CuBTC respectively. The Zr—based nanosized mixed ligand MOF (nMLM) synthesized using pyrene and porphyrin building blocks and investigated for its photocatalytic performance against Rhodamine B dye in the presence of  $\text{H}_2\text{O}_2$  [107]. The MOF demonstrated remarkable efficiency with complete degradation of the dye within 240 min. UiO/BiFeO<sub>3</sub> MOF nanophotocatalyst fabricated by incorporating the magnetic BiFeO<sub>3</sub> with UiO MOF exhibited excellent photocatalytic degradation performance of 88.7% and 89.35 for Rhodamine B and methyl orange respectively under visible light [108].

### 7.3 Application of MOFs in membrane separation

Membrane separation leverages the selective permeability of membrane pores at the molecular scale to separate pollutants. These membranes effectively function as barriers, permitting the passage of solvents, inorganic ions, and small molecules, while effectively impeding the transit of pollutant particles and macromolecules [109]. The integration of MOF-based thin film composite membranes has exhibited superior performance such as water flux, salt rejection, resistance to foulants, and antibacterial efficacy, as evidenced in applications such as microfiltration, ultrafiltration, nanofiltration, forward osmosis and reverse osmosis, [110]. Figure 5 illustrates membrane separation using MOFs applied in water treatment. Microfiltration (MF) uses pressure difference and 0.1–10  $\mu\text{m}$  pore size membrane to effectively remove particles,



**Fig. 5** MOF membrane separation process



colloidal and microorganisms through membrane screening. The ZIF-8/PTFE composite MF membrane synthesized through modification of the high porosity double layer polytetrafluoroethylene (PTFE) with zeolite imidazole MOF (ZIF-8) was utilized in the decontamination of water from progesterone micro pollutant showing remarkable performance of up to 95% removal efficiency being maintained after three regeneration cycles [111]. Ultrafiltration (UF) utilizes a relatively high-pressure difference and 0.01–0.1  $\mu\text{m}$  pore size membrane to efficiently remove molecular compounds, organic particles and bacteria from wastewater. The amino functionalized Zr-MOFs (UiO-66-NH<sub>2</sub>) combined UF ceramic membranes demonstrated the highest removal of Pb<sup>2+</sup> of 61.4% at the lowest degree of fouling. Nanofiltration (NF) requires a much larger pressure difference and 0.001–0.01  $\mu\text{m}$  pore size membranes to effectively remove ions from wastewater. The MOF 808/Polyamide thin film nanocomposite (TFN) membrane has been investigated in the removal of Na<sub>2</sub>SO<sub>4</sub> salt [112]. The MOF membrane showed superior water permeance and maintained exceptional 97.67% rejection of Na<sub>2</sub>SO<sub>4</sub>. Molecular dynamics indicated that the introduction of MOF 808 filler significantly enhanced the mass transfer of water through the membrane. Forward osmosis (FO) utilizes osmotic pressure gradient and less than 0.001  $\mu\text{m}$  pore size membrane to efficiently remove salts and organic compounds in wastewater. ZIF-8@PDA (PEI/TMC) positively charged nanofunctional selective thin film nanocomposite (TFN) forward osmosis membrane constructed by penetrating the polydopamine (PDA) modified ZIF-8 in the polyethyleneimine (PEI)/1,3,5-benzenetricarboxylic acid chloride (TMC) cross-linked matrix was investigated for the removal of heavy metals in wastewater [113]. The MOF modified membrane demonstrated an exceptional 96% rejection of Cu<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> metal ions. Reverse osmosis (RO) utilizes a high-pressure difference and less than 0.001  $\mu\text{m}$  pore size membrane against an osmotic pressure gradient to efficiently remove dissolved salts, minerals and organic molecules from wastewater. As the global water crisis deepens, desalination of natural saline water particularly seawater and brackish underground water is becoming more prevalent, with reverse osmosis offering the most energy-efficient solution. Duan and collaborators utilized hydrothermal method to synthesize the high compatibility ZIF-8/PA membrane for desalination purposes by incorporating ZIF-8 into thin film nanocomposite (TFN) polyamide (PA) membrane. The MOF modified membrane excellent performance with a remarkable 98% NaCl rejection with brackish water in RO conditions [114]. Table 4 summarizes the MOFs utilized, factors affecting MOF performance and the advantages and limitations of the utilization of MOF in membrane separation processes of water treatment.

## 8 Energy consumption of MOFs in water treatment.

The nearly inextricable interdependence between water and energy known as the water–energy nexus is gaining prominence as the demand for both resources rises. Energy is required for water treatment while energy production demands significant amounts of water. With the continued increase in the global energy demand, it is imperative to investigate the impact of MOFs application in water treatment on the energy consumption. Table 5 gives the description, impact and the amount of energy consumption on the water treatment. As seen, the integration of MOFs in water treatment has significantly reduced the energy consumption compared to conventional approaches.

**Table 4** Application of MOFs in water purification

Method	Summary	Examples of MOFs	Factors	Advantages	Limitations	References
Adsorption	Physical or chemical adsorbing pollutant onto the surface of the MOF	MOF-808-EDTA MOF-5 CeO <sub>2</sub> @UiO-66 MIL-101-OA	Surface area and porosity Temperature pH. Contact time	High surface area. Easy regeneration Good reusability Tailored functionality	Cost Scalability Stability Selectivity	[4, 115, 116]
Photocatalysis	Catalytic decomposition of organic pollutants by MOFs into non-toxic compounds or mineralization into CO <sub>2</sub> and H <sub>2</sub> O, using UV or visible light from sunlight as the driving energy	Copper (II) dipyrindyl chloride UiO-66-NH <sub>2</sub> Ag <sub>3</sub> VO <sub>4</sub> @MIL-125-NH <sub>2</sub> @ cotton composites PCN-222-PW <sub>12</sub> /TiO <sub>2</sub>	Band gap energy Redox potentials Electron/hole recombination rate Surface area and porosity	Tunable bandgap and activity Selective targeting Environmental compatibility Sustainability and reusability	Charge recombination Selectivity Durability Scalability	[105, 117–120]
Membrane separation	MOF thin film semi-permeable membranes to selectively separate pollutants based on size & molecular characteristics	Ag@MOF ZIF-8/PDA/PS membrane PCN-222-TFN membrane PA-ZIF-93-TFN membrane	Porosity and pore size Transmembrane pressure Temperature Chemical stability	Enhanced flux & permeability Tunable pore size Chemically stable Durable and long lasting	Optimization Scalability Selectivity Cost	[109, 121–123]

**Table 5** Energy consumption of MOFs in water treatment

Water treatment	Description of energy consumption	Consumption (Kwh/m <sup>3</sup> )	Reference
Adsorption	MOFs have incredibly high surface areas and tunable pore structures which allows them to capture more contaminants per unit mass compared to conventional adsorbents, thus requiring less frequent regeneration in turn lowering the energy use. And finally, when saturated with contaminants, they demand less energy since they are designed to release the captured contaminants at relatively lower temperatures	0.27–0.32	[124, 125]
Advanced Oxidation processes (AOPs)	Selection of the appropriate metal anodes and organic linkers for the MOF synthesis and subsequent post – synthetic modification tunes the MOF band gap to efficiently absorb visible sunlight. This is more advantageous compared to conventional photocatalysts, which require UV radiation from xenon or mercury lamps that depend on an external electricity source	0.07–0.15	[124, 126]
Membrane separation processes	The highly ordered and tunable pore structures offers both high selectivity and permeability compared to conventional membranes, which allows faster separation of contaminants from wastewater at low pressures translating to low energy consumption from pumps. In addition, the antifouling capabilities of MOFs results to longer lifespans of the membranes which reduces energy costs associated with membrane production and disposal	0.18–0.6	[124, 127]

## 9 Frontiers and opportunities for MOFs in water treatment

The MOFs have the capacity to transform the landscape of water treatment, providing clean and safe drinking water for all. These are summarized as follows:

### 9.1 Selectivity and tunability

The unique properties of MOFs, such as high surface area, tunable pore size, and excellent porosity, make them highly effective in water treatment. However, further research and development is needed to fully realize their full potential. Chemical, water, and thermal stability affect the application of MOFs in water treatment. MOFs need to be robust enough to withstand long-term exposure to water, reactive chemicals of pollutants and high temperatures. Selection of the right organic ligand and metals ions and optimizing their stability and resistance to degradation is thus crucial. Today, innovative computational tools have revolutionized the creation of novel MOFs with diverse structural and chemical characteristics, enabling the rapid generation of thousands of materials using automation and simulation, highlighting the immense possibilities in realizing a wide range of MOFs.

### 9.2 Cost effective synthesis

Cost effectiveness is a major challenge affecting MOFs production and application. Currently, most of the MOFs are expensive to produce on large scale owing to the expensive synthesis methods, and reagents especially the organic ligand linkers. The primary emphasis of research thus lies in the exploration of economical organic ligands, and the development of cost-efficient synthesis techniques. Furthermore, studies on visible light active photocatalytic MOFs that can utilize sunlight can reduce energy costs by eliminating the use of electricity.

### 9.3 Recovery and reuse

Application of MOFs in water treatment is also limited by the low reusability and recovery rate especially for pristine MOFs. The advancement of post-synthetic modification techniques is hence essential to augment the water purification capabilities of the materials. Recovery, regeneration, and reuse of MOFs will enhance their cost effectiveness as well as make them environmentally friendly.

### 9.4 Scalability

Effect of process parameters such as temperature, pressure and pH during pollutant removal requires further research and development based on kinetic and thermodynamic studies to enhance MOF's purification properties. This kinetic data is required to facilitate the design of equipment for MOF applications at pilot and industrial scale. More investigations on the scalability of the MOFs in water treatment will widen the scope of their applications.

### 9.5 Integration with existing water treatment technologies to create synergy

The future of water treatment and remediation lies in development of integrated systems that can operate in a synergistic manner. Integration of MOFs in water treatment as advanced processes for final treatment targeting the removal of bio-recalcitrant pollutants. Process integration can also minimize the overall treatment costs and make it cost effective; hence should be studied further. There is need to develop mathematical models and designs to maximize the synergy among these processes in an economic and environmentally friendly manner.

## 10 Challenges and prospects

The unique properties of MOFs, such as their high surface area, tunable pore size, and excellent porosity, make them highly effective in removing a wide range of contaminants from water sources finding applications in virtually all areas of water cycle, water treatment, wastewater treatment and desalination of seawater or underground brackish

water mainly through adsorption, advanced oxidation and membrane separation processes. However, MOFs applicability in water purification is still faced with challenges that limit their applicability. Chief among these challenges is associated with the method syntheses employ. Scalability and cost effectiveness to meet industrial demands is a major challenge affecting MOF production. Currently, most of the MOFs are expensive to produce on large scale owing to the expensive nature of the synthesis methods used and the high cost of the precursors especially the organic ligand linkers and the solvents particularly the N,N-dimethylformamide (DMF) utilized in most of the production methods. Future research directions should thus focus on enhancing the sustainability of MOF synthesis by developing economical organic ligands and solvents and lower energy processes. Efforts to improve the scalability of methods like microwave-assisted, continuous flow, and mechanochemical synthesis are essential for large-scale production. Hybrid techniques that combine aspects of different methods could offer better control over MOF properties and synthesis efficiency. Automation and advanced process control can further enable high-throughput and reproducible production of MOFs. By addressing these challenges, MOFs have the potential to revolutionize water purification thus addressing the ongoing global water crisis.

## 11 Conclusions

In the face of increasing global water challenges, the continued exploration and advancement of MOF-based water purification technologies hold great promise. This review has provided a compressive overview of these intricate frameworks delving into the structure, classification of MOFs based in their composition and structure, various synthesis methods and characterization techniques which is fundamental for tailoring their properties for specific applications, particularly in water purification. Further, the application of MOFs in adsorption, photocatalysis and membrane separations processes in water treatment have been studied extensively. The MOFs are gaining attention as an appropriate response to the emerging bio-recalcitrant pollutants in water. However, they applicability is still in the early stages and hence needs to be accelerated. With advancements in material synthesis and characterization technologies, it is possible to close the gap between laboratory application, pilot scale and eventually industrial application. The unique characteristics of MOFs open new frontiers in water purification and probably many other related areas. Further studies are required to improve selectivity, recovery and reuse, cost-effectiveness, scalability, and integrated systems. With continued research and development, these versatile materials can shape a future where water scarcity is no longer a threat.

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**Data availability** No datasets were generated or analysed during the current study.

## Declarations

**Ethics approval** No human or animal subjects were used in this study.

**Consent to participate** All authors agree to participate in the research in the current manuscript.

**Consent for publish** All authors have agreed to the submission of this manuscript.

**Competing interests** The authors declare no competing interests.

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