



# Metal–organic framework application in wastewater treatment: a review

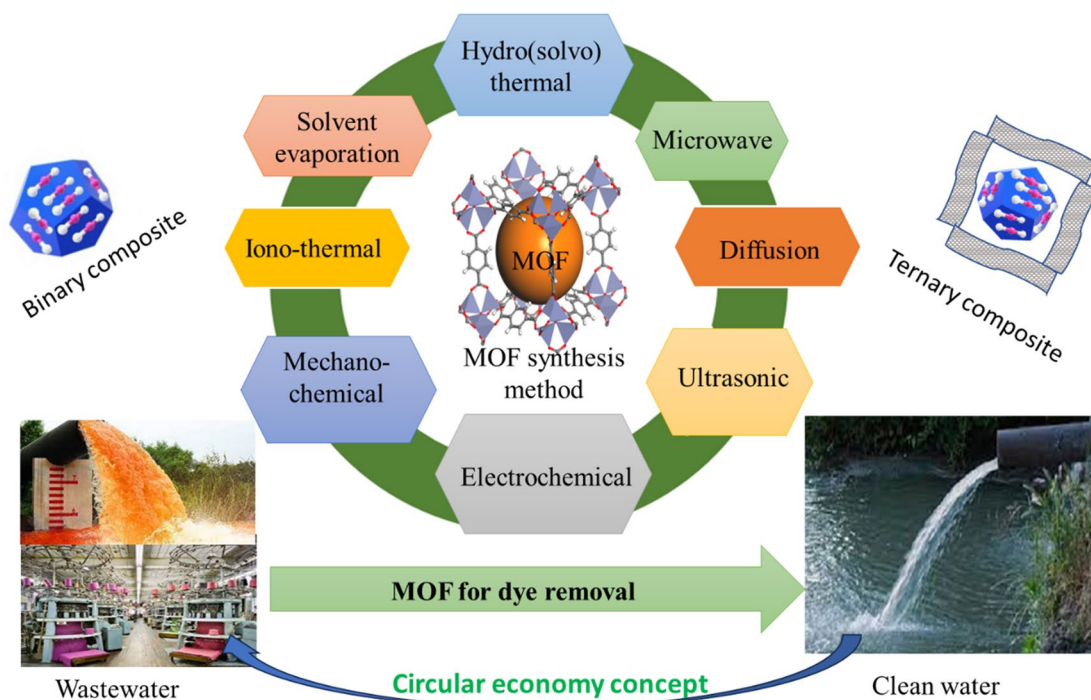
Gerardo Coppola<sup>1</sup> · Saurav Bhattacharyya<sup>1,2</sup> · Valerio Pugliese<sup>1</sup> · Catia Algieri<sup>2</sup> · Francesco Petrosino<sup>1</sup> · Sarah Siciliano<sup>1</sup> · Vincenza Calabro<sup>1</sup>

Received: 7 December 2022 / Accepted: 25 July 2023 / Published online: 26 October 2023  
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## Abstract

Water is an essential component for the survival of living organisms. Wastewater from different industrial activities causes different problems for the aquatic environment. Organic pollutants from textile industries are one of the major contributors to the pollution of surface water. The coloring agents present in the wastewater are mainly produced by the textile (54%) and dyeing (21%) industries. In this review, the different textile wastewater treatment methods and their advantages and disadvantages are discussed. Metal–organic frameworks (MOFs) exhibit interesting wastewater treatment performance. This review describes in detail the synthetic processes of MOF materials. In addition, their application in dye removal is also reported.

## Graphical abstract



**Keywords** Textile wastewater · MOFs · Composite · Adsorption · Degradation

Responsible Editor: Mohamed Ksibi.

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## Introduction

Water scarcity is increasing daily in various parts of the world. Global industrialization has resulted in massive amounts of wastewater production (Ding et al. 2020). The coloring agents present in the wastewater are mainly produced by the textile (54%) and dyeing (21%) industries, as shown in Fig. 1 (De Gisi et al. 2016). Globally, textile industries are located in Asian countries such as India, Bangladesh, China, Sri Lanka, Pakistan, Vietnam, and Indonesia (Masum and Kazuo 2019) and some countries in Africa, such as Morocco and Tunisia (Shan et al. 2020). Textile industries are renowned for being water-consuming sectors, as they require around 200–400 L of water to produce 1 kg of textile product (Erkanlı et al. 2017); on the other hand, the textile industries illegally release a massive volume of wastewater which is not adequately treated and disposed of in the environment. This amount of polluted water not only creates problems for the environment and the soil; it is also harmful to aquatic ecosystems. Textile wastewater contains different pollutants like dyes and organic and inorganic contaminants, which create human and animal health hazards (Gao et al. 2017; Xiong et al. 2021).

For decades, different dye wastewater treatment methods have been used. These methods can be divided into three categories: biological, chemical, and physical (Algieri et al. 2021a). Biological treatment methods are categorized into bacterial, algal, fungal, and enzymatic processes (Holkar et al. 2016; Costa et al. 2018; Ahmad et al. 2015). In these methods, the degradation depends on different factors, such as pH, class of dyes, and concentration. The advantages and drawbacks of the biological methods are summarized in Fig. 2a.

Several chemical processes, such as advanced oxidation processes (AOPs), electrochemical processes, and

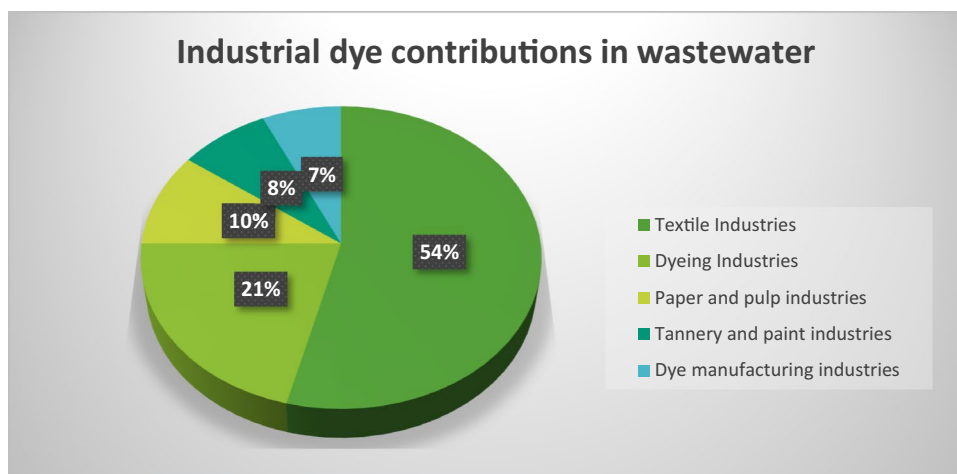
flocculation-coagulation, are used for colorant removal from textile wastewater. The chemical dye elimination process is commercially unattractive because it has a huge energy demand and uses chemicals that generate a relatively big amount of sludge (Crini 2006; dos Santos et al. 2007). To overcome these drawbacks, electrochemical treatment methods are the better option to minimize the production of sludge and toxic by-products (Bhatkhande et al. 2002; Das et al. 2017). In recent years, heterogeneous photocatalysis has gained more attention due to its high chemical stability and non-toxicity. Textile wastewater has been treated with several photocatalytic species, such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdS}$ , and  $\text{Fe}_2\text{O}_3$  (Kumar and Rao 2017; Zheng et al. 2019; Yang et al. 2019). This process is based on the generation of reactive hydroxyl radicals, which are capable of oxidizing a vast range of organic compounds (Molinari et al. 2002; Ljubas 2005; Le-Clech et al. 2006; Das and Saha 2022). A clear view of the benefits and drawbacks of chemical processes is reported in Fig. 2b.

The most used physical methods are membrane processing, ion exchange, and adsorption (see Fig. 2c).

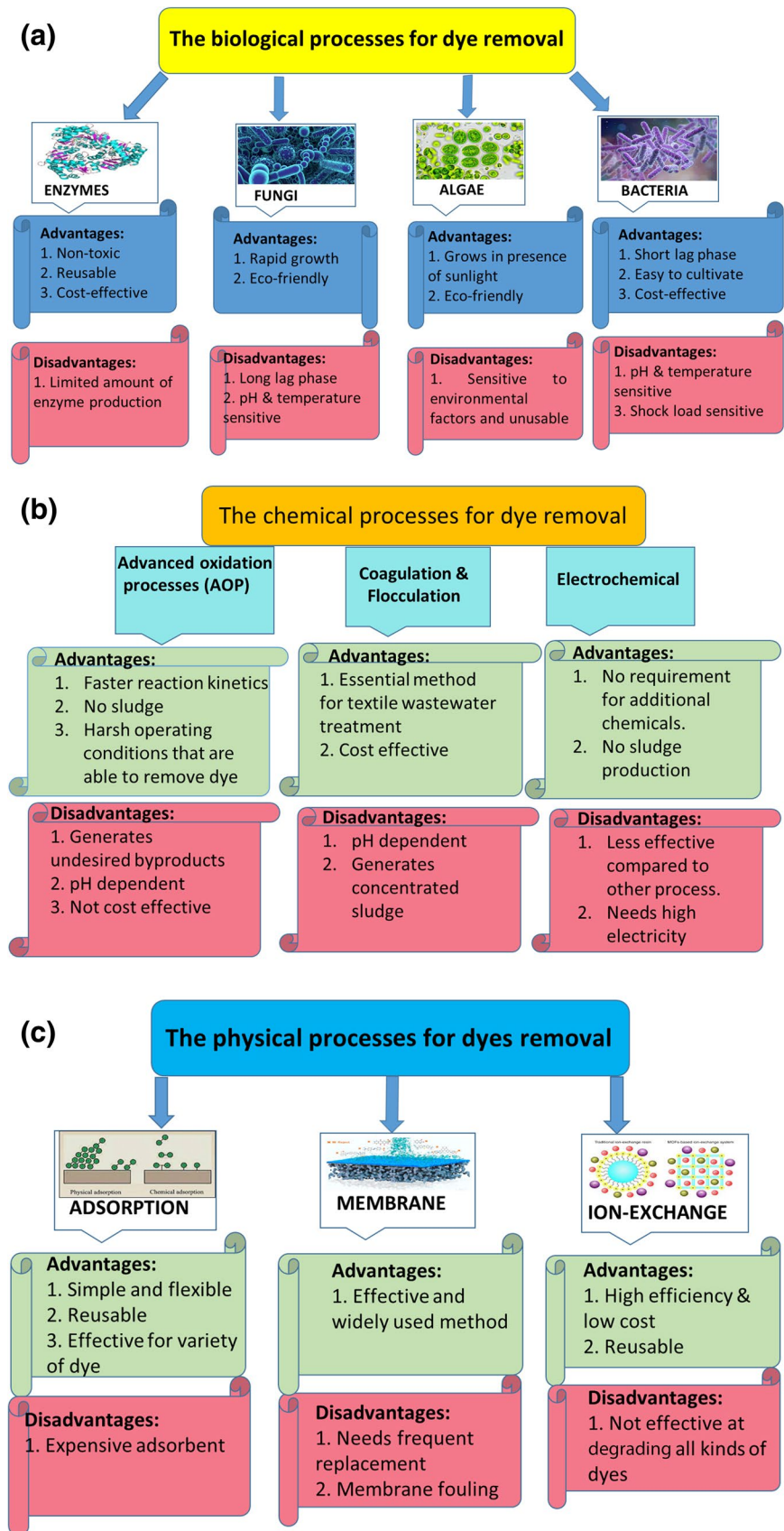
Membrane technology is a highly efficient method for water purification purposes that exhibits excellent qualities such as flexibility in removing various pollutants (Mozia 2010; Lerch et al. 2005; Lowe and Hossain 2008; Algieri et al. 2021b). Among the different pressure-driven membrane processes available, nanofiltration (NF) has recently achieved wide use in textile effluent treatment, especially when coupled with reverse osmosis (RO) (Algieri et al. 2021c; Nataraj et al. 2009). The NF process permits clean water to be obtained when operating at a lower transmembrane pressure than for RO membranes.

The ion exchange resin method removes dyes via electrostatic and intermolecular interactions between the ion-exchange active resins and the functional groups present on the pollutant (Jiang et al. 2021; Piaskowski et al. 2018; Shen and Gondal 2017). The adsorption process is frequently

**Fig. 1** Contributions (%) of various industries to the dyes present in wastewater



**Fig. 2** **a** Advantages and disadvantages of the biological treatment methods (Lund and Jönsson 2003; Katheresan et al. 2018). **b** Benefits and drawbacks of the chemical treatment methods (Solís et al. 2012; Katheresan et al. 2018). **c** Advantages and disadvantages of different physical dye removal techniques



used to remove micropollutants, and its advantages are a low installation cost, high efficiency, and a simple operating design (Rathi and Kumar 2021; Pal 2023). However, when used at a large scale, adsorbing materials for wastewater treatment present a high regeneration cost (Shrestha et al. 2021). In recent years, novel adsorbents have been considered as a way to improve the adsorption capacity, stability, reusability, and production costs (De Gisi et al. 2016; Kyzas and Kostoglou 2014). Metal–organic frameworks (MOFs) offer all these features in the wastewater treatment field. These materials are composed of metal ions or clusters coordinated to organic ligands. They form a unique crystalline structure with a high degree of porosity, creating a network of nanoscale-sized pores and channels.

MOFs with various structural properties are synthesized by using different metal ions and organic ligands (Furukawa et al. 2013). The latter play an important role in the final properties of the MOF, such as its thermal stability and adsorption capability.

In this review, the preparation methods of metal–organic frameworks (MOFs) for pollutant removal are presented. Their application in dye removal is discussed in depth. Finally, the use of modeling and simulation methods to analyze the adsorption phenomena in dye removal by MOFs is considered.

## Synthesis of MOFs

MOFs can be synthesized to have specific explicit shapes, predetermined pore sizes, and surface features via pre-assembly methods and post-synthesis modifications, which

enables them to deliver better performance than other available nanomaterials (Pérez-Cejuela et al. 2020).

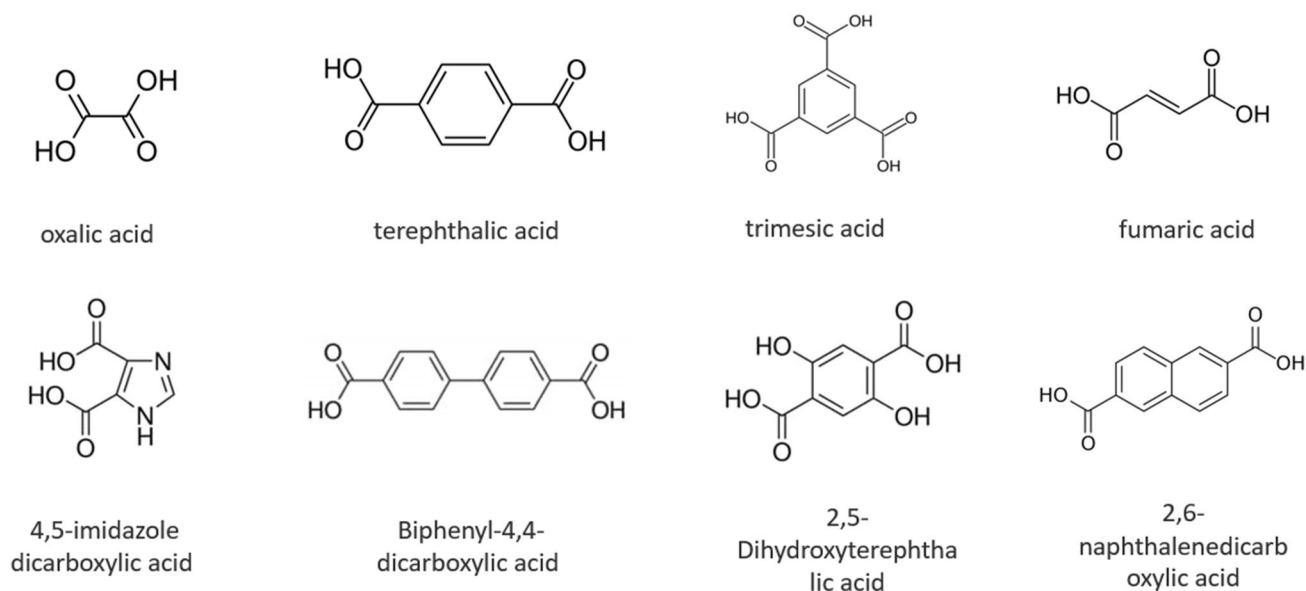
Many metal ions can be exploited to synthesize MOFs. A correct choice of precursor compounds can lead to the synthesis of functional blocks with distinct compositions and features. Both the organic linkers and metal ions chosen play important roles in the final assembly of the material and its features. The most outstanding properties sought for any MOF are a high surface area, tunable chemistry, and uniform porosity (Gangu et al. 2022) at the nanoscale level. Also, the surfaces of these complex compounds can be altered via synthetic methods, allowing the addition of functionalities tailored to precise practical needs (Li et al. 2019).

MOF structures can be synthesized by bonding metal ions (or metal oxides) with polytopic organic linkers. Some of the polytopic organic acids that can be used as linkers are shown in Fig. 3.

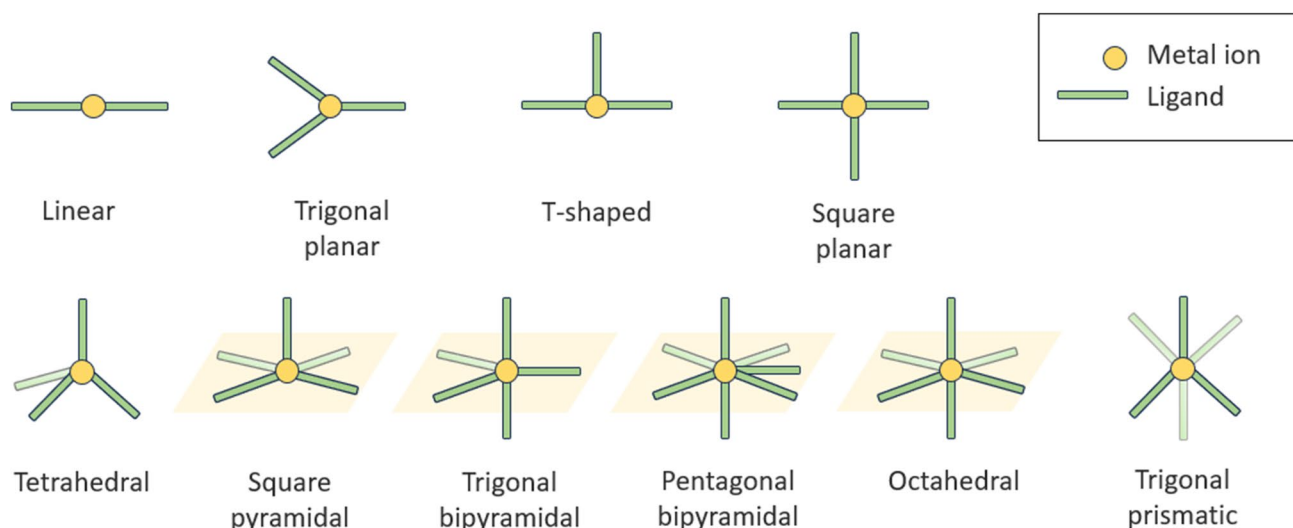
Likewise, even the metal coordination—and consequently the molecular geometry—is critical to achieving the desired structural framework (Fig. 4) (Li et al. 2016).

Picking an appropriate metal and an appropriate linker establishes the network type of the final MOF. The obtainable networks grow in three dimensions by cross-linking individual chains (Furukawa et al. 2013).

While preserving the building units has been the key aim of research efforts in MOF synthesis, there has also been sufficient consideration of the synthesis of new ligands for linkers and the optimization of the relevant variables to achieve satisfactory metal–organic ligand bonds. Aside from trial-and-error synthesis methodologies, some reliable and systematic routes have been successfully tested.



**Fig. 3** Polytopic organic acids used as linkers



**Fig. 4** Transition metal ion coordination geometries

Innovative MOFs can be prepared by considering many important variables. Although the preservation of the framework structure is the most crucial of those variables, lots of research effort has been directed into either new ligands or the optimization of the bond between the metal and the organic ligand itself. Attributes of the ligand—its length, chirality, bulkiness, bond angles, etc.—and those of the metal ions—like the geometries achieved—dramatically impact on the final structure of the MOF.

When designing new MOFs, trial and error is still considered a valid tool, but a plethora of more methodical and yet uncomplicated synthetic methods have been successfully tested, as reported in the literature (Gangu et al. 2022).

Table 1 reports the most important methods of synthesis for MOFs.

This hydrothermal method has usually been employed for metal extractions, but it has recently been applied in crystal engineering. For the synthesis of MOFs, the hydrothermal method is preferred for two main reasons: the minimization of the solubility problem for heavy organic compounds and the speed of nucleation of the complexes (Natarajan et al.

2006). Under the described conditions, the water viscosity lowers, so precursor mobility is favored; as a direct consequence, MOF compounds can be easily isolated.

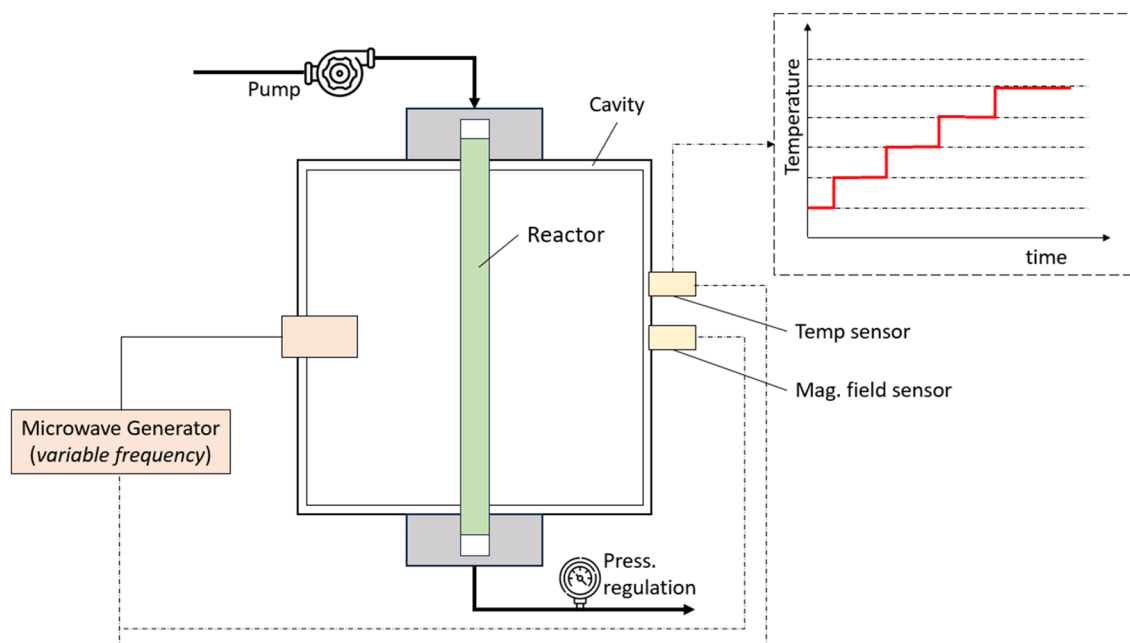
Férey et al. obtained a chromium terephthalate MOF with large pores and high surface area. The structure obtained was a cubic-zeotype-shaped crystal with a very wide cell volume of  $702 \times 10^3 \text{ \AA}^3$ , pore sizes ranging from 30 to 34  $\text{\AA}$ , and a Langmuir surface area (based on  $\text{N}_2$ ) of circa  $6 \times 10^3 \text{ m}^2/\text{g}$  (Férey et al. 2005).

Microwave (MW) MOF synthesis is comparable to the conventional hydrothermal procedure, but it has advantages in that it can reduce crystallization times and it delivers better control over the final morphology and the particle size distribution. However, scalability and energy-efficiency issues and high equipment costs are preventing MW MOF synthesis from becoming one of the most-used methods of synthesis.

The majority of the microwave synthesis practices utilized so far have depended on the use of single-mode MW reactors operated with sealed-vessel processes (Kappe 2008). In Fig. 5, a scheme of a single-mode MW reactor

**Table 1** Principal methods of synthesis for MOFs

Method	Description
Hydro(solvo)thermal	High-temperature, high-pressure heterogeneous reaction
Microwave	Electromagnetic (microwave) radiation-induced reaction
Ultrasonic	Sonochemical (20 kHz–10 MHz) cavitation-induced reaction
Electrochemical	Electrochemical cell: metal ions at the anode, organic linker at cathode
Mechanochemical	Solvent-free mechanical grinding of metal precursors and organic ligands
Diffusion	Diffusion of solvents between layers with the growth of crystals at the interface
Solvent evaporation	Crystal grown by slowly increasing the concentration in the mother solution
Ionothermal	As per hydrothermal, but with ionic liquids as solvents



**Fig. 5** Single-mode MW reactor schematic

presented by Nishioka and coworkers is reported. This reactor generates an electromagnetic field around a quartz tube (the actual reaction zone) through which the reagents are pumped. This tube is 1.5 mm in diameter and 100 mm in length and is situated in the middle of a cylindrical cavity so that the generated field is uniform along all the tube length, while the temperature of the reacting phase in the tube is precisely controlled. This system has proven itself to be very practical for rapidly heating up liquid flows at up to 100 bar. Polar solvent flows—such as those of water, ethanol, and ethylene glycol—have been heated instantly past the boiling point by a positive pressure gradient. Nishioka et al. (2013) experimented with rapid reactions for continuous Cu nanoparticle synthesis by increasing the reaction temperature beyond the boiling point of ethylene glycol at 20 bar.

Ultrasonic (sonochemical) synthesis is a low-cost and efficient method with a low impact on the environment which can lead to MOFs with very clean surfaces (Vaitis et al. 2022). Molecules that are exposed to high-power irradiation—with ultrasonic frequencies of up to 10 MHz—undergo evident physiochemical changes (Akhbari et al. 2013). This technique is a top-down methodology for synthesizing metal–organic coordination polymers, mostly sized within the nano range.

The main phenomenon induced by ultrasound application in a liquid phase is called cavitation. As the ultrasonic perturbation reaches the liquid phase, a periodic variation in pressure develops in the phase itself. This pressure variation causes the formation of bubbles, which first grow before collapsing. During the cavitation, some local hot

spots develop in the liquid; these can reach a temperature of nearly 5000 °C and pressures of around 500 bar, all within a few microseconds (Martos et al. 2001). In these conditions, chemical reactions—like MOF synthesis—result, as they are thermodynamically favored.

To cite some examples, Haque et al. (2010) synthesized MIL-53(Fe) (iron terephthalate) by US, MW, and conventional heating, proving that the rate of crystallization—which involves nucleation and crystal growth—reaches peak values when using US. The study suggested that hot-spot formation effects are far more common than chemical effects in the US and MW syntheses. Jung et al. (2010) synthesized MOF-177 with crystals ranging from 5 to 20 μm by US synthesis: the study proved that a drastic reduction in reaction time—circa 40 min—could be achieved using a fairly low-cost solvent (1-methyl-2-pyrrolidone, NMP). MW synthesis, also using NMP, produced MOFs with lower crystallinity, while the conventional solvothermal method in diethylformamide produced crystals ranging from 0.5 to 1.5 mm in size with a reaction time of 48 h.

Electrochemical synthesis (EC) gives a simple and well-controlled synthetic process, with its key benefit being its rapidity and the purity levels that can be reached. These features are due to the fact that counterions—such as perchlorate, nitrate, and chloride—from metal salts are not present; in fact, metal ions are used instead of metal salts at the anode, while the organic linker is placed on the cathode side. The whole electrochemical cell is then filled with a conducting salt. A Cu-MOF was the first to be synthesized by EC, with copper plates used as the anode and benzene

tricarboxylate as the cathode (in methanol). Cu-MOF was obtained in 150 min with a voltage difference of 12 to 19 V and a current of 1.3 A (Mueller et al. 2006).

Khazalpour et al. (2015) synthesized DMOF-1-Zn by an EC route with short reaction times and under mild conditions with respect to the conventional method, and it was found to be easy to obtain (by tuning the current density) the desired morphology (nanorod-like in this case).

The experiments carried out by Schlesinger et al. (2010) showed how MW is easily the best way to produce  $[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]$  with high purity, high values of specific pore volume (circa  $0.8 \text{ cm}^3/\text{g}$ ), and appreciable yields within short reaction times. It is worth mentioning that, in the same study, a product with a similar specific pore volume ( $0.7 \text{ cm}^3/\text{g}$  circa) was obtained by mechanochemical methods which are described below.

Mechanochemical synthesis has been theorized as a method for preparing porous MOFs to relieve the environmental problems caused by volatile organic solvents. The key factors of this method are the solvent-free conditions used and, again, the short process times (from 10 to 60 min), along with the significant reaction yields obtained. When mechanical force is applied to a mixture, it can induce not only a shift in physical features, but also an increased yield from the desired chemical reactions. It has been shown that mechanochemistry is effective in the synthesis of 1D, 2D, and 3D coordinated MOFs with a marked microporosity (Garay et al. 2007). Nichols et al. (2001) showed that manually grinding metal halides (or nitrates) and phenanthroline allows the formation of  $[\text{M}(\text{phen})_3]^{2+}$  dications (as red  $[\text{Ni}(\text{phen})_3]^{2+}$ ) in short times of around 2 min.

In this context, energetic mixing of solutions of metal salts and organic ligands can yield microcrystals that are incompatible with X-ray diffraction (XRD). To solve the problem of obtaining polycrystalline powder, diffusion methods can often be applied. Continuous diffusion between solvent and liquid phases can generate fairly large crystals that are suitable for single XRD. Crystal growth follows the generation of three layers through diffusion between the two phases. The first layer is composed of the precipitate (solvent); the second contains the product in the solvent; while the separation of those two takes place in the third layer, allowing slow diffusion. During the diffusion process, the crystal growth emerges right at the interface between the layers.

Solvent evaporation is another valuable method for MOF synthesis. In this case, crystal growth is assured by gradually increasing the mother liquor concentration. All reacting compounds are put in solution until complete solubilization occurs, which is practically achieved when a transparent single phase is formed. Once complete solubilization is reached, the mixture is moved to a sealed container. Crystal growth is initiated by either saturating or chilling the

solution or by the elimination of excess solvent (Zhang et al. 2009).

Lastly, the ionothermal method is comparable to hydrothermal synthesis—in which the solvent used is water—but the main difference is that ionic liquids (ILs) are used as solvents. This method relies on their low volatility, good thermal stability and dissolving capacity, low coordination capacity, and extraordinary ionic conductivity. Lin et al. used a mixture of anions in order to obtain ILs with the desired features for ionothermal application; at the end of the procedure, no IL anions were present in the produced MOF (Lin et al. 2007). The use of ILs for synthesis could allow new advances in structure directing, anion control, and even chiral induction, thus advancing MOF design. Once in the reactor, the ionic nature of the system transfers the chiral (or acentric) feature to the solid product compounds.

## Applications of metal–organic frameworks

### Metal–organic framework composites

Metal–organic frameworks (MOFs) are a diverse group of highly active nanostructures with versatile applications, ranging from catalysts to sensors and adsorbents. Their high porosity, large specific area, and remarkable photocatalytic activity make them suitable for the development of a photocatalytic membrane reactor containing immobilized or suspended MOFs (Kökçam-Demir et al. 2020). However, the poor water stability of MOFs currently limits their widespread use. To address this issue, various strategies have been explored to synthesize MOF composites that possess improved water stability, visible light absorption, and reduced recombination between photogenerated species. These aspects will be discussed in detail in the following sections.

### Binary/ternary MOF composites

Noble metal nanoparticles (such as Au, Pd, Ag, and Pt) are high-throughput catalysts for numerous chemical reactions. They are typically characterized by large unsaturated coordinated atoms and a significantly large surface area (Adhikari and Lin 2016). However, they also have some weaknesses, such as aggregation (owing to their high surface energy), which has a detrimental effect on the catalytic efficiency, thus restricting their application (Roduner 2006). Recently, researchers have focused their attention on the production of noble metals embedded in the MOF structure due to the possibility of combining the adjustable porosity of MOFs with the functionality of noble metal nanoparticles used for catalytic activity, sensing, and so forth (Chen et al. 2017). However, MOFs have low stability under different reaction

conditions (such as pH, temperature, and aggressive organic solvents), and these aspects hinder their application at a large scale.

Carbon-based composites, doped carbon materials, and metals/alloys with carbon compounds have been widely employed in catalytic processes for their interesting features. These species present distinctive characteristics such as a lined-up (ordered) structure, functional sites, a homogeneous configuration, and an excellent tendency to interact with other species, which provide the species with electrocatalytic properties (Zhai et al. 2018). Carbon-based compounds show remarkable mechanical strength and conductivity, have significant potential, and are regarded as excellent elements for electrochemical applications (Zhai et al. 2018). Another essential characteristic is their capacity to work as active catalytic materials. Furthermore, these materials represent a favorable approach to improving mass and charge transport and electrocatalytic efficiency (Cong et al. 2021; Tasis et al. 2006).

Quantum dots (QDs) are fluorescent semiconductor nanoparticles with sizes of 1 to 10 nm; they contain approximately 200 to 10,000 atoms (Wildgoose et al. 2006). QDs show interesting properties, but they readily agglomerate, leading to fluorescence quenching, which hinders their application in different fields (Giri et al. 2022). QD/MOF composites avoid such aggregation; at the same time, the presence of the semiconductor nanoparticles improves the physicochemical properties of the MOF. This combination improves dispersion and stability (Xue et al. 2019).

Among the materials employed for ternary composites, graphene is often used to synthesize MOFs (Jayaramulu et al. 2022). Graphene is a single-layer 2D graphite (honeycomb lattice) with remarkable properties such as high thermal and electrical conductivity, a large specific surface area (SSA), and excellent handling and flexibility (Zhang et al. 2017, 2022). It is also characterized by exceptional mechanical resistance and good porosity, which contrast the pulverization phenomena that active materials (e.g., supercapacitors) can undergo. Graphene oxide (GO) and reduced graphene oxide (rGO) are significant byproducts of graphene. rGO is obtained by reducing GO from graphite oxide by ultrasonic exfoliation in a liquid phase. rGO, obtained by removing the oxygen groups present in GO, has distinct characteristics compared to the latter, such as superior chemical stability and better electrical conductivity. In particular, rGO is often used within ternary compounds to improve performance in supercapacitors; e.g., a ternary mixture of ternary polypyrrole/GO/ZO was proposed and successfully synthesized in previous works (Chee et al. 2015; Ishaq et al. 2019). Ternary rGO-based nanocomposites are often employed in photocatalysis since rGO has a higher SSA and a good ability to transport electrons (Gali Anthoni et al. 2022).

Ternary nanocomposites based on rGO are potentially functional in photocatalysis because the high SSA of rGO allows the pollutant to come into contact with a more significant portion of the catalyst's surface. The procedure for incorporating two metal oxides onto rGO is complicated and still under study (Anjaneyulu et al. 2018). However, some studies have been proposed the degradation and treatment of dyes using ternary-compound MOFs; in particular, the ternary composite MIL-101(Cr)/ZnFe<sub>2</sub>O<sub>4</sub>/rGO has been synthesized with the hydrothermal method and used for the sonic degradation of dyes (Nirumand et al. 2018). Catalytic tests have shown that it degrades 80% of methyl orange and 96% of RhB. Methylene blue dye degradation was achieved with Zr-based hybrid MOF materials (UiO-66/g-C<sub>3</sub>N<sub>4</sub>/Ag) synthesized by the sol coating of g-C<sub>3</sub>N<sub>4</sub> protonated powder and photodeposition to charge the Ag (Feng et al. 2019). In other studies, catalytic degradation experiments performed on rhodamine B dye and 2,4-dichlorophenoxy acetic acid showed that the prepared composite exhibits high catalytic activity under the action of visible light. A two-step hydrothermal method produced a hybrid SnO<sub>2</sub>@UiO-66/rGO ternary photocatalyst with a large surface area and high catalytic activity and stability. In particular, this ternary photocatalyst has shown interesting photocatalytic activity in the degradation of RhB (95.5% in 150 min) (Mzimela et al. 2022). This result was due to a combination of adsorption as well as photodegradation mechanisms. A novel composite photocatalyst, MOF-1/GO/Fe<sub>3</sub>O<sub>4</sub>, for efficient MB degradation in aqueous solutions was prepared by Bai et al. (2020). The synthesized nanocomposite was very stable. In addition, it displayed high photocatalytic performance in the degradation of methylene blue (~95% within 80 min) under sunlight irradiation in an aqueous solution. Compared with MOF-1, the photocatalytic efficiency of the composite was improved by 90%, and it operated under solar light irradiation.

Three types of ternary composites are summarized under the three subheadings in Table 2.

### Magnetic MOF composites

Several researchers have added a magnetic species (e.g., ferrosferric oxide: Fe<sub>3</sub>O<sub>4</sub>) as a dopant for MOFs to form a magnetic composite that can be easily separated from the reaction medium by using an external magnetic field (Bai et al. 2020b; Guan et al. 2017; Jin et al. 2016). These composites can be binary or ternary and are synthesized by the solvothermal method (Bai et al. 2020). A novel MOF-magnetic composite (Fe<sub>3</sub>O<sub>4</sub>@ZIF-67) synthesized by Guan et al. (2017) showed excellent photocatalytic activity in Congo red degradation (70%). In addition, the photocatalytic activity did not change after it had been reused five times. A Nd-MOF/GO/Fe<sub>3</sub>O<sub>4</sub> magnetic composite was prepared and used for methylene blue removal. In particular, a degradation of



**Table 2** Different photosensitive ternary composites for the photocatalytic degradation of dyes

Composite	Synthetic method	Pollutant, initial concentration (mg/l)	Light used	Removal (%)	Time (min)	Active species	Comments	References
Metal nanoparticle (MNP)/semiconductor/MOF composites								
ZIF-8/Ag/AgCl	Solution precipitation + photoreduction	RhB, 10	500 W Xe lamp	98	60	$O^{2-}$ , $h^+$	Leaching of Ag from the composite due to small particle size	Liu et al. (2017)
MIL-53(Fe)/Ah/AgCl	Solvothermal	RhB, 10	500 W Xe lamp	100	45	$h^+$	The partial reduction of AgCl to Ag has not been explained	Liu et al. (2018a, b)
UiO-66(Zr)/g-C <sub>3</sub> N <sub>4</sub> /AG	Protonation coating + photodeposition	RhB, 20	350 W Xe lamp	99	180	$OH^-$ , $h^+$	Excellent stability and reusability of the composite	Feng et al. (2019)
MNP/graphene oxide (GO)/MOF composites								
MIL-125(Ti)/Ag/rGO	Photoreduction	RhB, 50	300 W Xe lamp	95	50	$OH$ , $O^{2-}$ , $h^+$	Proper control of the composite's crystallinity	Yuan et al. (2016)
MIL-101(Cr)/Pd/rGO	Solution deposition	Brilliant green (BG), 25	500 W Xe lamp	100	15		High degradation efficiency and reusability of the photocatalyst	Wu et al. (2015)
GO/semiconductor/MOF composites								
MOF-5/GO/BiOBr	Solvothermal	RhB		92	120	$O^{2-}$	The sandwich structure of the composite has high stability and reusability	Chen et al. (2019)
UiO-66(Zr)/rGO/SnO <sub>2</sub>	Solvothermal	RhB, 50	300 W Xe lamp	96	150	$O^{2-}$	Negatively charged surface of the composite facilitates electrostatic adsorption of RhB	Zhao et al. (2016)
Nd-MOF/GO/Fe <sub>3</sub> O <sub>4</sub>	Rotating evaporation + ultrasonication	MB, 10	Sunlight	95	80	$h^+$ , $e^-$	The composite synthesis is time and energy saving	Bai et al. (2020)

95% was obtained within 80 min (Bai et al. 2020). Magnetic composites are very useful for degrading different dye components, as described in Table 3.

Though MOF composites have lots of advantages, most of the techniques used to synthesize them have significant

drawbacks, such as the use of organic solvents that appear to be sensitive and are expensive and the need for multiple steps. As a result, new synthetic approaches are desperately needed to optimize the polymeric phases and thoroughly consider the resulting components.

**Table 3** Different magnetic composites and their characteristics

Composites	Synthesis method	Pollutant, initial concentration (mg/l)	Light used	Removal (%)	Time (min)	Active species	Comments	References
MIL-100(Fe)/Fe <sub>3</sub> O <sub>4</sub>	Solvothermal	MB, 40	500 W Xe lamp	99.7	200	–	High reusability of the photocatalyst	Zhang et al. (2013)
MIL-88B(Fe)/Fe <sub>3</sub> O <sub>4</sub>	Solvothermal	RhB, 0.01 m MB, 0.1 mM	300 W Xe lamp	99.8 99.8	80 30	·OH, e <sup>-</sup>	Hierarchical structure (micro, meso, and macropores) of the composite facilitated charge transfer and hence dye degradation	Jin et al. (2016)
ZIF-67/Fe <sub>3</sub> O <sub>4</sub>	Solvothermal	Crimson red, 0.04 mM	500 W Xe lamp	95	30	h <sup>+</sup> , ·O <sup>2-</sup>	The nanosheet morphology of the composite facilitated charge transfer and hence dye degradation	Guan et al. (2017)
MIL-101(Cr)/Fe <sub>3</sub> O <sub>4</sub>	Solvothermal	Acid red (AR1), 20	500 W Xe lamp Sunlight	90 80	60 10	h <sup>+</sup>	Dye degradation by the composite is increased under sunlight, making the process energy efficient	Zhang et al. (2020)
MIL-53(Fe)/Fe <sub>3</sub> O <sub>4</sub>	Solvothermal	RhB, 10	500 W halogen lamp	99	70	·OH, e <sup>-</sup>	A higher catalyst dose (1 g/L) is required to attain maximum degradation	Zhang et al. (2015)
MIL-53(Fe)/Γ-Fe <sub>2</sub> O <sub>3</sub>	Solvothermal	MB, 10	500 W Xe lamp	72	240	–	One-step, time-saving synthesis of the composite	Feng et al. (2019)
Nd-MOF/GO/Fe <sub>3</sub> O <sub>4</sub>	Rotating evaporation + ultrasonication	MB, 10	Sunlight	95	80	h <sup>+</sup> , e <sup>-</sup>	The composite synthesis is time and energy saving	Bai et al. (2020)

### Modeling and design of dye adsorption with MOF materials

On an industrial scale, MOF-based technologies have proven to be practical and economically attractive in

various processes, e.g., in the recovery of different macromolecules and in separation processes (Bai et al. 2020). As this paper discusses, MOF technologies also represent an essential tool for dye removal due to their very modifiable porous structures. The application of modeling methods

to complex systems for dye removal is currently much appreciated, as these methods can be used to analyze the adsorption phenomena and to predict the effect of process conditions on the recovery rate (Suki et al. 1984). In this regard, multi-scale modeling plays a key role: the different interactions between dyes and MOF structures can be evaluated by different approaches and then incorporated into a nano/microscale model in which the interaction process is simulated (Curcio et al. 2018; Yu et al. 2018; Petrosino et al. 2020). This modeling approach permits the design of a new MOF-based absorbent material.

Dye molecules like direct red (Liu et al. 2018a, b) can be accurately computed by first-principle-based calculations of atom surface partial charges using different quantum mechanics approaches, such as density functional theory (DFT) techniques (Petrosino et al. 2019). DFT is a variational method that is presently one of the most successful approaches to computing the electronic structure of matter. Its applicability ranges from atoms, molecules, and solids to quantum and classical fluids. Geometric and electronic properties of nanostructures can be evaluated faster than using Hartree–Fock methods (Petrosino et al. 2019). A MOF model can be characterized by analogous techniques, and its surface charges computed. The interactions between MOF structures and dye molecules can be calculated using a classical molecular mechanics approach (Slater 1951). Geometry optimizations of a dye molecule on a MOF's surface nanostructures can be performed to build a reliable cluster of interacting structures. In particular, the single-molecule potential describes the potential energy of a single molecule interacting with the MOF surface. Based on Lund and Jonsson, the interaction potential can be split into three main contributions: hard-sphere repulsion, electrostatic interactions, and van der Waals interactions (De Luca et al. 2022).

The information obtained at sub-nanoscale and nanoscale levels through molecular optimization consisted of the adsorption geometries and represented the key link transition to microscale and macroscale optimizations. In this step, chemical and physical parameters are of fundamental importance for the modeling and design of MOF-based materials for dye removal processes.

This approach shows that modeling is a fundamentally important tool which can be indispensable when developing new technologies for wastewater treatment. Quantum simulations based on the well-assessed DFT theory are the basis for complete sub-nanoscale modeling. Ab initio knowledge allowed coarse graining to the nanoscopic scale to simulate adsorption phenomena and finally to the microscopic and macroscopic scale for process simulation. The presented method allowed for a multiphysics description of the analyzed phenomena without resorting to any experimental or empirical parameters, and thus represents a fast and reliable

way of designing new wastewater dye removal methods using MOF-based technologies.

The proposed method allows us to understand and analyze dye adsorptions or the MOF surface during wastewater treatment. On the other hand, this tool permits the design of new MOF-based absorbent materials without the use of any experimental or empirical parameters.

## Conclusions and future perspective

The discharge of wastewater produced by the textile, paper, and food industries causes health problems in both humans and aquatic life. The removal of some dyes with high chemical stability is very difficult with traditional methods. The application of a MOF-based adsorption process represents an alternative route to conventional treatments, and this route can lead to improvements in adsorption capacity, stability, and reusability. In addition, using different metal clusters and/or organic linkers according to the target during the preparation of the MOF permits it to have various features depending on the desired characteristics. This is one of the main elements distinguishing MOFs from other adsorbents. Different efforts are being directed towards simpler preparation methods and reducing costs. The use of MOFs and MOF-based composites with higher efficiency will shorten development times within large-scale applications. However, there is still a long way to go for MOFs to be considered interesting for industrial wastewater treatment, given their price and their structural degradation caused by moisture, oxidizing and reducing agents, altered pH, and radiation. Furthermore, intense research activity is required to solve the critical issues with MOFs and thus enable the large-scale application of them in wastewater treatment processes.

**Acknowledgements** This work has received funding from PRIMA Foundation under grant agreement no. Grant Agreement number: [2024] [TRUST]-Call 2020 Section 1 Water IA.

**Funding** Partnership for Research and Innovation in the Mediterranean Area, 2024 TRUST, Vincenzo Calabrò.

**Data availability** All data generated or analyzed during this study are included in this published article.

## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Ethical approval** Not applicable.

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## Authors and Affiliations

Gerardo Coppola<sup>1</sup> · Saurav Bhattacharyya<sup>1,2</sup> · Valerio Pugliese<sup>1</sup> · Catia Algieri<sup>2</sup>  · Francesco Petrosino<sup>1</sup> · Sarah Siciliano<sup>1</sup> · Vincenza Calabro<sup>1</sup>

✉ Catia Algieri  
c.algieri@itm.cnr.it

<sup>2</sup> Institute on Membrane Technology, National Research Council of Italy (ITM-CNR), Via Pietro Bucci, Cubo 17C, 87036 Rende, CS, Italy

<sup>1</sup> Department of D.I.M.E.S., University of Calabria, Via P. Bucci, Cubo 42-A, 87036 Rende, CS, Italy