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Iron-based metal-organic framework: Synthesis, structure and current technologies for water reclamation with deep insight into framework integrity

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ABSTRACT

Water is a supreme requirement for the existence of life, the contamination from the point and non-point sources are creating a great threat to the water ecosystem. Advance tools and techniques are required to restore the water quality and metal-organic framework (MOFs) with a tunable porous structure, striking physical and chemical properties are an excellent candidate for it. Fe-based MOFs, which developed rapidly in recent years, are foreseen as most promising to overcome the disadvantages of traditional water depolluting practices. Fe-MOFs with low toxicity and preferable stability possess excellent performance potential for almost all water remedying techniques in contrast to other MOF structures, especially visible light photocatalysis, Fenton, and Fenton-like heterogeneous catalysis. Fe-MOFs become essential tool for water treatment due to their high catalytic activity, abundant active site and pollutant-specific adsorption. However, the structural degradation under external chemical, photolytic, mechanical, and thermal stimuli is impeding Fe-MOFs from further improvement in activity and their commercialization. Understanding the shortcomings of structural integrity is crucial for large-scale synthesis and commercial implementation of Fe-MOFs-based water treatment techniques. Herein we summarize the synthesis, structure and recent advancements in water remediation methods using Fe-MOFs in particular more attention is paid for adsorption, heterogeneous catalysis and photocatalysis with clear insight into the mechanisms involved. For ease of analysis, the pollutants have been classified into two major classes; inorganic pollutants and organic pollutants. In this review, we present for the first time a detailed insight into the challenges in employing Fe-MOFs for water remediation due to structural instability.

1. Introduction

In this century, the crucial problem that plagues human survival and development is environmental pollution. The rapid development in the industrial sector to meet the demands of an alarmingly increasing world population generates tons of hazardous waste and toxic gases over desired products (Giusti, 2009; Palmer et al., 2004; Shakoor et al., 2017). Pollutants generated from anthropogenic activities primarily affect the earth's water ecology. Untreated industrial effluents reaching the water bodies and groundwater often contains radioactive species, heavy metal oxyanions/cations, and organic contaminants. These have a high potential to create threat to aquatic life and human health

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(Elzwayie et al., 2017; Tchounwou et al., 2012; Trellu et al., 2016; Yang et al., 2017). Sources of organic contaminants are very vast compared to inorganic contaminants. The common organic pollutants present in water streams are pharmaceuticals and personal care products (PPCPs), dyes, detergents, oils, and polyatomic hydrocarbons (Barbosa et al., 2016; Ghattas et al., 2017; Tsai et al., 2008). Each year 7×10^5 tons of dves are produced worldwide, and 2% of the total production end up in the water stream through industrial effluents (Dongjie Chen et al., 2020). Most of these dyes are carcinogens and disturbs the aquatic life cycles by preventing the penetration of sunlight (Ngulube et al., 2017; Tsai et al., 2007). The increased usage of PPCPs by modern society to improve life expectancy and quality is the most dangerous contaminants of emerging environmental concern. The first detection of PPCPs as a contaminant was reported in 1980s (Rivera-Jiménez and Hernández--Maldonado, 2008). This class of pollutants includes antibiotics, sweeteners, cosmetics, fragrances, veterinary drugs, pesticides, and agrochemicals. These chemicals are highly stable and retain structural and biological activity for a prolonged period causing adverse consequences to microbial species, and may even lead to the formation of new strains of viruses and bacteria (Fatta-Kassinos et al., 2011; Gago-Ferrero et al., 2017; Klatte et al., 2017; Tijani et al., 2016). On the other hand, the indigenous aquatic species are affected by aftereffects of eutrophication caused by excessive utilization of nitrate and phosphate based fertilizers and detergents. (Ansari and Gill, 2014). In comparison to the organic contaminants, the highly soluble nature of inorganic pollutants make them persistent and extremely resistant towards the decontamination. Dominant number of these pollutants are highly toxic or lethal even at ppm or ppb level. The highest risk of these pollutants is their ease to undergo biomagnification and create hazards to higher tropic level organisms in the food web (Mon et al., 2018).

Water remedying techniques has paramount importance as water is indispensable for the existence of life. Conventional decontamination methods include filtration, coagulation, precipitation, adsorption, oxidation, membrane technology, biological process, and disinfection (Esplugas et al., 2007; Remanan et al., 2020; Vieno et al., 2006). The advantages of these methods are nullified by the high operational cost and energy requirement along with the generation of secondary toxic residues or by-products (Gupta et al., 2012; Jeong et al., 2012; Plewa et al., 2008; Sharma et al., 2017; Von Gunten, 2003). Furthermore, most of these methods are proved inefficient to eliminate trace residual contents. The efficient removal of these pollutants could be achieved through adsorption, photocatalysis and advanced oxidation process. Photocatalysis results in completely nontoxic by-products (Khan et al., 2013; Sharma and Feng, 2019; Wang et al., 2020). However, existing adsorbents and photocatalysts are inefficient for exploiting the complete efficiency of these techniques. Typical adsorbents e.g., zeolite, aluminophosphate, carbonaceous materials, and mesoporous clay lacks structural and chemical tunability, inadequacy for pollutant selectivity, inferior adsorption capacity and limited surface area (Ali, 2012; Gao et al., 2019). While considering the photocatalytic degradation, the regular photocatalysts titanium dioxide and metal sulfides exhibit very low quantum efficiencies under the visible light spectrum, besides suffer from photo corrosion (Y. Zhang et al., 2015; Z. Zhang et al., 2013).

To rectify the limitations of existing materials for water treatment, the best alternative is metal-organic frameworks (MOFs). MOFs with very large surface area, tunable porosity, tailorable topology, crystallinity, adjustable functionalities, excellent photoelectronic properties, and high thermal and mechanical stability could eradicate prevailing challenges (Feng et al., 2018; Khan et al., 2013; Subudhi et al., 2018). These porous coordination reticular structures are synthesized by the coordination polymerization reaction between the metal ion/cluster and multi-topic organic ligands (Eddaoudi et al., 2001; Safaei et al., 2019). Metal-organic frameworks for the desired application could be designed by carefully choosing, combine and tuning the synergistic properties of organic struts and inorganic secondary building units (SBUs) (Rubio-Martinez et al., 2017). Currently, MOFs research shows arousing developments in diverse fields such as molecular sensing, gas separation, transport and storage, drug delivery, catalysis, optoelectronics, and magnetism (Achmann et al., 2009; Chaturvedi et al., 2020; Chen et al., 2018; Cunha et al., 2013; Fujie and Kitagawa, 2016; Stavila et al., 2014; Wang et al., 2016).

Research on water remediation techniques using MOFs has been scarce compared to other areas of investigation due to the poor stability of these porous structures in an aqueous medium. The prior members of MOFs, MOF-5 (Zn-O) and HKUST-1 (Cu-O) were proved to be very sensitive to moisture (Feng et al., 2018; Yang et al., 2019). The metal-ligand interactions and bond strengths are the most important criteria determining the stability of the porous structures. The MOFs with the same inorganic counterpart behave differently to moisture depending on the nature of organic ligand. For example, MOF-5 with week Zn-O bond completely lose the structural integrity, while ZIF-8 with Zn-N bond is a best example of water-stable framework structure (Han et al., 2010). Further improvement in structural integrity of the reticular framework could achieve from higher metal-ligand coordination, octahedral Zn-MOF-74 exhibits more stability than the tetrahedral coordinated MOF-5 with the same Zn-O metal-ligand interaction (Avati et al., 2016). Ligand displacement by water and foreign chemical species are the sever threats to structural integrity.(De Toni et al., 2012). However, the number of published works to develop water-stable MOFs are boosting in recent years. These stable MOFs give rise to a new research area for water remediation (Taylor et al., 2012; Wu et al., 2010; Yang et al., 2011). Zr-based MOFs, ZIF-8, MIL-100 (Cr, Fe), MIL 53 (Cr, Al), and MIL-101 (Cr, Fe, Al) are the reported best candidates of water-stable MOFs (Fatta-Kassinos et al., 2011). The investigations on water remediation using different MOFs are listed in Table 1.

Among plentiful MOFs, Fe-MOFs have been extensively investigated for water treatment. The low toxicity and abundant content of iron in the earth's crust facilitate the facile development of Fe-MOFs (Xia et al., 2019). Additional advantageous of Fe-MOFs include enormous unsaturated metal centers with high catalytic activity, this ensures its applicability in advance oxidation process (AOPs), especially in Fenton and Fenton-like pollutant degradation. Fe-MOFs with excellent interfacial electron transfer property and Fe (III)/Fe (II) redox couple is a perfect catalyst. (C. Gao et al., 2017; Sharma and Feng, 2019; Zhang et al., 2019). Compared to other MOFs the photocatalytic degradation of contaminants is economically facile with the Fe–O system, most of the photoactive MOFs reported possesses very large band gaps such as 3.4

Table 1

Different MOFs utilized in the water remediation process.

MOF	Pollutant	Method	Reference
MIL-53(Al)	Methylene blue	Photocatalysis	(Du et al.,
			2011)
ZIF-67	Rhodamine B.	Heterogeneous	(Lin and
		catalysis	Chang, 2015)
NH ₂ -MIL-68(In)	p-Arsanilic acid	Adsorption	(Lv et al.,
			2018)
MIL-101(Cr)	Dimetridazole	Adsorption	(Seo et al.,
			2017)
Fe-Cr-MIL-101,	RR195	Fenton degradation	(Vu et al.,
Cr-MIL-101			2014)
UiO-66(AN)	Methyl orange	Photocatalytic	(Pu et al.,
		degradation	2015)
MIL-101(Cr)-	Perfluorooctanoic	Adsorption	(Liu et al.,
DMEN	acid		2015)
CAU-1	Nitrobenzene	Adsorption	(Xie et al.,
			2014)
β-MnO ₂ @ZIF-8	[As(III)]	Adsorption	(Jian et al.,
			2016)
Pt/ZIF-8/TiO ₂ -	Phenol	Photocatalytic	(Miao et al.,
NTs		degradation	2017)
MIL-53Al	Dimethyl phthalate	Adsorption	(Li et al.,
			2015)
MIL-100(Fe),	Benzene	Photo-Fenton	(Wang et al.,
MIL-68(Fe)		degradation	2015)

eV, 3.9 eV, 3.6 eV for MOF-5, UiO-66(Zr), and MIL-125(Ti), respectively. Wideband gaps restrict the photoexcitation range to short-wavelength UV rays thus reduces the effective usage of solar energy (Alvaro et al., 2007; J.-X. Liu et al., 2016; Shen et al., 2015). On the contrary, Fe -MOFs with a bandgap between 1.88 and 2.88 eV could be directly excited using visible light (Wang et al., 2020). In Fe-MOFs the adsorption, catalytic and photocatalytic activity combinedly acts to degrade the contaminants present in the water samples (Wang et al., 2020).

Utilization of Fe-MOFs for water remediation have been discussed in numerous research articles. Fig. 1 represent the trend of reported researches in this field within last 10 years. From the statistics, it is possible to understand a clear image of rapid boom in the utilization of Fe-MOF for water remediation, especially as adsorbent, catalyst or photocatalyst. So far several review papers have mentioned the utilization of Fe-MOFs for water remediation techniques (Liu et al., 2017; D. Wang et al., 2014; Wang and Li, 2017). But, maximal work reported focus on the activity/performance regardless of their structural stability, a prime prerequisite for its potential utilization in water remediation (Howarth et al., 2016). This knowledge gap is needed to be addressed to avoid unwanted structural degradation by selection of suitable reaction parameters as well as to tackle the bottle neck towards the large-scale industrial applications. Moreover, the toxicity generated from the secondary products derived from organic ligand is an issue of concern, which require further monitoring (Kumar et al., 2019). Therefore, for the first time, we discuss the structural instabilities of Fe-MOFs, which limits its extensive utilization in water treatment. Over and above, we present collective information regarding the latest synthesis techniques, structural diversities present in Fe based MOF family, merits and major applications of various Fe-MOFs in wastewater treatment along with underlying mechanisms. We conclude this review by emphasizing the limitations and outlooks of plausible research directions to rectify the challenges.

2. Different synthesis routes for Fe based MOF structures

Synthesis methods for Fe-MOFs could be generally classified as conventional synthesis routes and non-conventional synthesis routes. Fig. 2 represent a consolidate schematic of important synthesis techniques along with general reaction condition.



2.1. Conventional synthesis routes

Conventional synthesis of MOFs is carried out either by solvothermal or hydrothermal methods (Fig. 3). In this method, the soluble MOF precursors are subjected to a temperature gradient, which in turn leads to a concentration gradient and once the critical concentration is reached self-assembled nucleation and crystal growth are initiated, resulting in the formation of crystalline porous metal-organic framework. Sealed autoclaves are used to heat the reactants under autogenous pressure above or near the solvent boiling point.

Table 2 summarizes the reported Fe-MOFs synthesized by conventional methods. Reaction temperature has a great influence on the morphology of the formed frameworks. Suitable crystalline forms of MOFs are obtained by prolonged heating at very high temperatures. During conventional synthesis crucial temperature control is required to avoid the degradation of reticular networks (Stock and Biswas, 2012). The reported conventional methods are highly energy and time demanding, which reduces its feasibility for large-scale synthesis and practical application.

2.2. Non-conventional synthesis routes

Conventional MOF synthesis methods possess many flaws. Prime issue is the requirement for large amount of solvents, hazardous chemicals and expenditure of enormous energy. Due to these factors conventional synthesis methods are incompatible for large scale industrial applications (Lee et al., 2013). Thus to tackle these stumbling blocks non-conventional MOF synthesis routes are introduced, which includes mechanochemical synthesis, electrochemical synthesis, dry-gel synthesis, diffusion synthesis, and plasma synthesis. The listed methods are new candidates for scalable futuristic preparation of MOF with reduced energy requirements and are recognized for their decisive economic and environmental impact.

2.2.1. Mechanochemical synthesis

The first MOF synthesized mechanochemically was in 2006, and this paved a new pathway for the solvent-free synthesis of MOF (Pichon et al., 2006). This approach with zero waste generation and high yield has a potential for industrial scale-up. In this synthetic route, mechanical energy induce bond breakage and chemical transformations within very short time. Two different approaches are majorly employed, grinding in the absence of solvent (known as neat grinding-NG) and grinding assisted with the feeble amount of solvent (referred to as liquid assisted grinding-LAG). Pilloni et al. reported the synthesis of MIL-100 (Fe) with improved crystallinity and thermal stability through LAG methods utilizing TMAOH (tetramethylammonium hydroxide) as a solvent for hastening the molecular level motion and transformation in the reaction (Pilloni et al., 2015). A three-dimensional superstructural MIL-88 (Fe) was prepared in a solvent-free mechanism using FeCl₃ and sodium fumarate (Jeong and Lee, 2019).

The main advantage of this method is the enhanced reaction kinetics and fast nucleation rates leading to the generation of nano-sized particles. Samal et al. scale-up production of MIL-100(Fe) by using a kitchen grinder which is a facile pathway for industrial production (Samal et al., 2018). Furthermore, He et al. reported the synthesis of highly catalytically active Fe/C by direct pyrolysis of Fe-MOF obtained through cheap and fast mechanochemical synthesis (He et al., 2019). A drawback observed in this method is the formation of defective crystals structure, but this could be rectified by using structural reconstruction agents. Souza et al. reported the role of water as a green structural reconstruction agent (Souza et al., 2020).

In mechanochemical synthesis inexpensive and less hazardous metal precursors such as oxides and carbonates are majorly used which facilitates large-scale generation of MOF structures with minimal generation of waste by-products (Kumar et al., 2020). The potential use of this up-scaled method could be observed during the drastic uptake of



Fig. 2. Synthesis approaches and conditions used for MOFs synthesis.



Fig. 3. Schematic representation of conventional solvothermal synthesis.

arsenate from contaminated water using MIL-88B(Fe). MIL-88B(Fe) synthesis by ethanol assisted ball milling removes 156.7 mg/g of arsenate at a low dosage and from trace arsenate solution ($6.4 \ \mu g \ L^{-1}$) it could remove 32.3 mg/g of trace arsenate. Compared to this the MIL-88B(Fe) prepared by solvothermal method using DMF removed only 90.50 mg/g. This discrepancy in adsorption is due to the high surface and higher concentration of exposed active sites present in mechanochemically synthesized MIL-88B(Fe). In addition to better performance, the main advantage of mechanochemical synthesis is its possibility to scale-up to very high space-time yield without sacrificing the targeted performance (Hou et al., 2018).

2.2.2. Electrochemical synthesis

The first patented MOF synthesis by interconversion of electrical energy to chemical energy reported by BASF paved the way to a new synthesis pathway operating in milder conditions and in a continuous manner (Mueller et al., 2006). Control over the applied current and voltage helped to perform a controlled reaction in a short period. This method allows the industrial scale-up of MOF films and coatings. Compared to the conventional methods, this method is highly advantageous in eliminating the generation of corrosive anions in the reaction system. Anodic dissolution and cathodic deposition are the two classifications of the electrochemical method (Pourfarzad et al., 2020). In the anodic approach, the desired metal is employed as anode and the organic linker is dissolved in the reaction medium. In the cathodic approach reaction medium containing metal ion and the organic link, which interacts with cathode (Rubio-Martinez et al., 2017).

Achman et al. reported the room temperature synthesis of Fe-BTC MOF. In this method, the reaction between steel cathode, 1,3,5-tricarboxylic acid, and methyl tributyl ammonium (MTBS) in methanol resulted in the MOF generation for the sensor application (Achmann et al., 2009). The first electrochemical synthesis of phase characterized MIL-100(Fe) was studied under high temperature and high-pressure. The effect of various parameters like the effect of temperature variation, the presence of conductive compound (MTBS) in the reaction medium, and the effect of adhesion offered by the electrode to MIL-100 (Fe) was investigated. The finding depicted that increment in temperature leads to the formation of smaller crystals and the improved adhesion. In addition, the absence of conductive salt improved the formation of layered MOFs (Campagnol et al., 2013). The proposed utilization of common carbon steel as an electrode for the generation of MOF without compromising the crystal property ensures the industrial application of this method (Pourfarzad et al., 2020).

Electrochemical method is a promising method for the generation of engineering MOF materials such as MOF films for water remedying application. MOF material obtained as insoluble crystalline powder is

Table 2

Various Fe-MOFs synthesized by conventional method.

Fe-MOF	Ligand and point group	Solvent	Conditions	References
MIL-53 SIFSIX-3-Fe [[Fe(pyz) ₂ (SiF ₆)]] PCN-332 (Fe) PCN-333 (Fe) MIL-65	1,4-Benzene dicarboxylic acid, I2/a Pyrazine Benzo-tris-thiophene carboxylate, p6mm 4,4',4″-s-triazine-2,4,6-triyl-tribenzoate, p6mm 1,3,5-benzene tricarboxylate (BTC)	DMF Methanol DMF/DEF DMF/DEF H ₂ O	180 °C, 2 days 85 °C, 3 days 150 °C, 12 h 150 °C, 12 h 150 °C, 12 h 179 °C, 2 days	Whitfield et al. (2005) Elsaidi et al. (2017) (Feng et al., 2014) (Feng et al., 2014) Riou-cavellec and Férey (2002)
MIL-82 [Fe(H ₂ O) ₂ (C ₉ O ₆ H ₄)] ⋅H ₂ O (MIL-67) MIL-88 MIL-89	1,2,4,5-benzenetetracarboxylic acid, C2/c 1,2,4-benzenetricarboxylic P-1 Fumaric acid, P-62c Trans transmuconic acid	H ₂ O H ₂ O H ₂ O, Methanol H ₂ O, Methanol	200 °C, 2 days 200 °C, 2 days 100 °C, 3 days 100 °C 3 days	Sanselme et al. (2004) Riou-Cavellec et al. (2003) Surblé et al. (2006) Surblé et al. (2006)
MIL-05 PCN-53 PCN-600 MIL-141	Tetrakis (4-carboxyphenyl) porphyrin P6/mmm Tetracarboxylate porphyrin (Ni-TCPP), C2/c	DMF DMF DMF	120 °C, 5 days 120 °C, 5 days 150 °C, 12 h 150 °C, 2 days	Yuan et al. (2012) (Wang et al., 2014) Fateeva et al. (2011)
MIL-85 Fe ₄ (µ ₃ O) ₂ (BTB) _{8/3} (DMF) ₂ (H ₂ O) ₂ .(DMF) ₁₀ (H ₂ O) ₂ MIL-100 [Fe ₃ O(H ₂ O) ₃ (1,3-BDC) ₃] [Cl] ·9H ₂ O MIL-62 MIL -62	1,4-dicarboxylic acid, P6 ₁ Benzene-1,3,5-tribenzoate, R (-3) Benzene-1,3,5-tricarboxylate, Fd-3m 1,3-benzenedicarboxylate Pa-3 1,2,4,5-benzenetetracarboxylates, C2/m	Methanol DMF H ₂ O H ₂ O H ₂ O	89 °C, 5 days 130 °C, 1 day 150 °C, 5 days 130 °C, 5 days 200 °C, 3 days	Serre et al. (2004b) (Choi et al., 2007) Horcajada et al. (2007) (Li et al., 2009) Sanselme et al. (2002) Exterve et al. (2010)

hard to process as continuous films. This method allow formation of films at very mild reaction temperature and pressure which avoids the chances for crack formation thus enables the wide application of MOF films as adsorbent and membranes. Electrochemical method performed with metal anode avoiding metal salt pave a way for continuous production of MOFs and industrial expansion (Bedia et al., 2019).

2.2.3. Spray drying synthesis

Spray drying is a proven technique with advantages such as a simple, fast method with minimum waste generation and maximum solvent recovery. In this method, dispersed products are recovered from solutions by a simple evaporation step. The combined effect of evaporation and local heating of atomized droplets could lead to novel chemical reactions. The synthesis of MOF by spray drying was reported by Carne-Sanchez et al. Spray drying consist of three steps, (1) the atomization of MOF precursor solutions by simultaneous injection of compressed nitrogen/air and the reactant, (2) the atomized droplets suspended are evaporated at a certain temperature, and (3) reduction in the solvent concentration results in a surge of reactant concentration in the droplets and as it reaches critical concentration porous MOFs are formed (Carné-Sánchez et al., 2013).

A critical parameter of spray drying is the mode of introduction of the reagent into the reaction system. This determines the morphology and other characteristic properties of the resultant product. Two-fluid nozzle method, three-fluid nozzle method, T-junction, and continuous flow coupled method are the four different modes of solvent introduction. The first three method results in hollow superstructures of MOFs and a compact micrometer MOFs are synthesized in continuous flow assisted spray drying (Troyano et al., 2020).

Carne-Sanchez et al. studied the detailed spray drying synthesis of nano MOFs. Through this research three nozzle syntheses of MIL-88A (Fe₃O(fumarate)₃) and a two-nozzle synthesis of MIL-88B were developed (Fe₃O(NH₂-BDC)₃) (Carné-Sánchez et al., 2013). The mixture of organic ligand and Fe(III) ion precursor was used in a two-fluid nozzle synthesis. In the three-fluid nozzle method, the reactants were mixed just before heating. Within 5 min, the obtained yield was 40% with a purity of 72%. The production of MIL-88A was also patented by Kang et al. (2014).

A continuous flow coupled spray dry technique ensures the synergetic effect of both methods. Fe-BTC/MIL-100 synthesized by the coupled method ensures a yield of 78%. The precursors for the reaction were injected into a flow reactor with a continuous coil maintained at the reaction temperature, followed by direct atomization and instant drying. The enhanced nucleation rate achieved during continuous flow improved the yield. The reduced crystallization and slight reduction in surface area were the major flaws of this method (Garzón-Tovar et al., 2016). Template-assisted spray drying synthesis of the iron trimester is an advanced method to synthesis mesoporous $Fe_3(BTC)_2$ with improved crystallinity and surface area. Cetyltrimethylammonium (CTAB) and non-ionic triblock copolymer Pluronics F-127 were used as a template. In the continuous CTAB assisted one-pot synthesis method, improved surface area and crystallinity were observed (Serre and Boissiere, 2013). The most spectacular advantage of spray drying is that this enables continuous and rapid formation of dry microspherical powder either hollow super structure or beads with minimal fabrication costs within short production time. These structures could enhance the industrial and largescale utilization of MOF especially in adsorption, but currently the studies involved are scarce and further investigations are required (Troyano et al., 2020).

2.2.4. Dry-gel synthesis

Steam assisted conversion of MOF precursors/sols to crystalline porous coordination compound, widely known as dry-gel conversion (DGC) is a rapidly expanding synthesis method. Potential advantages of this method are high concentration of reactants in the reaction medium, minimum waste generation, reduced consumption of the templates, shape-controlled formation of MOFs with reduced size, continuous production and reduction in reaction time. Most striking benefit is the possibility for reusing the solvent for multiple cycles of synthesis without compromising the yield and quality of the crystals formed (Das et al., 2016; Ren et al., 2017).

Ahmed et al. synthesized MIL-100(Fe) using DGC and explored the structure-directing effect of water. Moreover, the reaction was carried out in the absence of mineral acid, salts, or fluorides. In this reported research, steam generated by evaporating water at 165 °C was treated with the dry gel of metallic iron (Fe⁰) and trimesic acid placed separately on a porous holder above the water in the same container. A porous holder of the dry gel allows the perfect contact between the reactants. The perfect crystalline Fe-MOFs were obtained after a reaction period of 4 days and possessed higher pore volume and surface area than the MIL-100(Fe) synthesized by conventional electric heating (10 days) (Ahmed et al., 2012). Following this strategy, Tannert and co-workers presented a microwave-assisted DGC method for the fast and facile synthesis of Fe-MOF in 3 h (Tannert et al., 2018) (Fig. 4a). The obtained MOFs were with reduced surface area and pore size in comparison with MOFs obtained from conventional DGC but with an improved yield. A solvent reuse technique for up to 3 cycles was also performed without sacrificing the yield of the product. DGC in the absence of solvent described by Luo et al. and co-workers, demonstrated the preparation of Fe MOF with improved pore volume and pore size in the absence of high-pressure condition. The experiments were performed in airtight jar at 140 °C and reported highly crystalline MOFs with a higher yield than



Fig. 4. a) Schematic representation of microwave-assisted dry gel process. Reprinted with permission from (Tannert et al., 2018). b) schematic representation of ultrasound assisted synthesis of Fe-MOF.

hydrothermal methods (Luo et al., 2020).

2.2.5. Continuous flow synthesis

Flow chemistry, a proven technique utilized in the synthesis of functional nanomaterials is a promising tool for the large-scale synthesis of metal-organic frameworks (Dunne et al., 2016). The continuous streamflow of reagents through pipes or coils maintained at a reaction temperature with enhanced surface area to volume ratio enable the fast formation of MOF crystallites. This is due to improved heat and mass transfer in contrary to batch reactions (Batten et al., 2015). This method with high reproducibility and precise control over each reaction parameter is the best tool for the optimization of reactions (Kim et al., 2013). The presented possibility of this method operating in harsh conditions with little wastage of solvent makes it an ideal method for scaled-up production (Myers et al., 2014).

The flow chemistry process comprises of three steps, (i) introduction of fluid reagents to the mixing unit (ii) transformation reactions through a flow reactor maintained at a temperature, and (iii) finally the separation of the products. Microfluidic reactor plug flow reactor and stirred flow reactor are the major classification of flow chemistry synthesis (Kim et al., 2013).

In 2013 Paseta et al. and co-workers reported the microfluidic continuous synthesis of MIL-88 B(Fe) and its derivatives. They demonstrated the development of Fe- MIL-88B, Fe-MIL-88B(NH₂), and Fe-MIL-88B(Br). In addition, systematically studied the effect of residence time, input temperature, and slug volume on the crystallite size and size distribution. Size and Size distribution maintains an inverse relationship

with residence time, temperature, and slug volume (Paseta et al., 2013). A bioactive MIL-88A framework was synthesized in a single continuous microfluidic flow system. The method possesses the high potential to synthesize double-shell hollow MOFs, Functional nanoparticles, or enzyme encapsulated single-shell hollow MOF (Jeong et al., 2015). The most fascinating peculiarity of continuous flow chemistry is that it could be adopted to produce MOF in gram scale by maintaining conditions standardized for lab scale reactions through simply supplementing the reactor with further solution of reactants (Rasmussen et al., 2020). By this method, crystalline MOF structures with a space time yield up to 1300 kg m⁻³ d⁻¹ could be produced without sacrificing ultra-high surface area and that too in a short time span of 5-6 min (Bayliss et al., 2014). In addition to conventional continuous flow method microwave assisted continuous flow method was used to synthesize MIL-100(Fe) at a production rate of 771.7 kg m⁻³ d⁻¹. The resulting MOF structure exhibited better crystallinity and porosity in comparison with the structure formed in conventional batch method. These advantages favor the utilization of this method for synthesizing MOF structure for large scale real world applications (Le et al., 2020).

2.2.6. Microwave assisted synthesis

Microwave irradiation-based synthesis techniques are rapid and considered to be environmentally friendly. This technique is highly promising for the synthesis of metal-organic frameworks. Microwaves interact directly with the mobile electric charges in the solvents and the solids, thus facilitates heat energy sufficient for the crystallizations. In contrast to the conventional synthesis methods, here the thermal energy is not transferred to the reaction vessels thus saves energy and reaction time. Phase selectivity, diverse morphology, facile evaluation, and optimization of reaction parameters along with size reduction are the main advantages of microwave synthesis (Babu et al., 2016; Khan and Jhung, 2015).

Chromium-based MIL-100 reported by Sung et al. initiated the utilization of microwave radiation for the synthesis of MOFs (Sung et al., 2005). Pioneer report on synthesis and functionalization of MIL-101(Fe) presented by Taylor-Pashow et al. (2009) utilized microwave radiation as an energy source. The developed product exhibited a crystalline nanostructure with a high surface area (3700 m²/g–4535 m²/g) and unusual octahedron morphology. Likewise, Devic et al. reported MW-assisted gram-scale synthesis of modified MIL-53(Fe) without utilizing HF(Devic et al., 2010). The morphology tuning property of this technique was studied by Guo et al. They demonstrated the variation in porosity and morphologies of MIL-53(Fe) with changes in the irradiation time (Guo et al., 2017).

Recently, Mingyan et al. evaluated the influence of time, temperature, and other reaction parameters on the formation of various phases of Fe MOF. A short time interval of microwave irradiation leads to a less stable phase which transforms into stable phases with prolonged reaction time (Ma et al., 2013). The detailed kinetics of MW-assisted synthesis of MOF was discussed by various groups and verified that the crystal size and crystallinity have a direct correlation with the time and temperature of the radiation (Chalati et al., 2011; Gordon et al., 2012). Kinetic studies conducted by Haque et al. discarded all the hypotheses and proved the importance of physical effects such as hot spot generation in the course of MW assisted reaction rather than chemical effects in the fast reaction rates and depicted the significance of acceleration in crystal growth over the fast nucleation rate. (Haque et al., 2010).

The modulations in the structural and texture property of MOF attained by the influence of microwave irradiation technique greatly alter its removal efficiency. The unique homogeneous heating effect of microwave synthesis results in small sized crystallites with larger pore size (Chalati et al., 2011). For example, MIL-101(Fe) synthesized by microwave irradiation (MW-MIL-101(Fe)) possess average pore diameter 3.1 nm and pore volume 2.9 cm³/g, while the same MOF synthesized by conventional solvothermal (C-MIL-101(Fe)) method shows average pore diameter 2.9 nm and pore volume 2.3 cm³/g. These differences in porous structure highly alter the sorption efficiency. MW-MIL-101(Fe) exhibit a maximum adsorption capacity of 332.7 mg/g of tetracycline, whilst C-MIL-101(Fe) could remove only 163.7 mg/g. Thus, it could infer that the energy efficient microwave synthesis could utilize to synthesize high performance MOF structures in a rapid and bulk scale (Dong et al., 2020).

2.2.7. Sonochemical synthesis

Ultrasound assisted synthesis is an energy-efficient method to perform chemical reactions at a fast pace under ambient conditions with high product selectivity (Fig. 4b). In this treatment cyclic mechanical vibrations with very high wavelength interacts with the liquids and creates spots of alternating pressure variation. The acoustic cavitation of formation, growth, and collapse of bubbles in these points leads to the generation of localized hot spots with temperature and pressure of 5000 K and 1000 atm, respectively. These momentary hotspots of high pressure and high temperature can facilitate chemical reactions in a solution containing precursors (Khan and Jhung, 2015; Vaitsis et al., 2019). The first investigation on the sonochemical-assisted synthesis of metal-organic framework dealt with the synthesis of Zn-based MOF (Zn₃(BTC)₂) (Jung et al., 2010).

The sonochemical Fe-MOF (MIL-88 A (Fe)) synthesis was reported by Chalate et al. In this study variation in particle size, crystallinity, and size distribution of MOF with respect to various reaction parameters was analyzed. A direct correlation between DLS (Dynamic light scattering) particle size with pH and reaction time was observed and a reverse relation with concentration was reported. The lower temperature was preferred for the small-sized monodispersed particles. The major drawback cited is the lower yield obtained (Chalati et al., 2011). The power applied and the type of ultrasound generator, along with the mode of power supply highly affect the properties of the final product. The sonication time highly influenced the nucleation rate and crystal growth. Short sonication time and pulsed probe resulted in highly crystalline particles while in continuous mode and in bath sonication amorphous MOF structures were formed (Amaro-Gahete et al., 2019).

The greatest advantage of ultrasound assisted synthesis of MOF in environmental remediation are, rapid generation of smaller particle size of the obtained adsorbent, phase selectivity favoring the reaction kinetics and shorter requirement of energy. The MOF particles synthesized by sonochemical method are mostly obtained as monodispersed nanometer range particles, which facilitates enhanced pollutant-adsorbent interaction and facilitates tremendous degradation capacity (Vaitsis et al., 2019). But, to utilize this synthetic technique extensively in water remediation we should tackle the obstacle created by poor yield and strict requirements on instruments.

3. Diverse structures of Fe-MOFs with different ligands

The unprecedented application of MOFs such as separation, adsorption, catalysis, storage, etc. depends greatly on the versatile reticular frameworks, metal clusters, ligand functionalities, mode of connections, structural integrity, and porosity. Porous coordination complexes encompassing similar metalcore could exhibit divergent characteristic properties subject to slight variation in organic struts or coordination environment. Knowledge of Fe-metal clusters, ligands, and the chemical environment is required to select or design the perfect candidate to fulfill the requirements.

In this section, different reported structures of Fe-MOFs are analyzed in terms of organic linkers, connectivity, and core cluster building units In Fe MOFs majorly two kinds of secondary building units are reported $[M(OH)(COO)_2]_n$ chain s and $[M_3 (\mu_3-O)(COO_6)]$. (Farha and Hupp, 2010; Mueller et al., 2006). Fig. 5a depicts both the SBUs.

Water remediation applications of Fe-MOFs require high structural stability which is directly correlated to charge density and Pearson's HSAB (hard/soft acid/base) principle (Yuan et al., 2018). Most of the Fe-MOFs are based on Fe^{+3} oxidation state, the perfect ligand for this high valent, hard acid metal ion is carboxylate-based organic linkers (Hard base). Based on the number of separate binding sites these organic struts are divided into ditopic, tritopic, and tetratopic ligands.

3.1. Fe-MOF with ditopic ligands

The linear dicarboxylate i.e. 1,4-benzene dicarboxylate (1,4-BDC) is largely utilized to design flexible frameworks with high breathing effects. A representative framework is MIL-53(Fe) (Fig. 5b), The structural backbone of MIL-53 is formed by the trans corner-sharing FeO₆ octahedral core clusters. The resulting zigzag chains are bridged with 1,4-BDC resulting in a 3D framework with rhombohedral channels and I2/ a space group. Each organic linker binds two distinct FeO₆ clusters in the neighboring chains along with the 2 equatorial Fe-O bonds (Millange et al., 2007; Whitfield et al., 2005). With the same ligand, two more MOFs were reported MIL-68 and MIL-85 (Fateeva et al., 2010; Serre et al., 2004b). Solvent-free MIL- 68 framework is a pseudomorph of MIL-53. In MIL-68 the corner-sharing Fe(OH)₂(O_{car})₄ octahedral chains connect through the 1,4-BDC linkers creating a triangular and hexagonal pored orthorhombic framework with a maximum surface area of 665 m^2/g . The reported surface area of MIL-85 is inferior compared to MIL-68, and the measured BET surface area is $110 \text{ m}^2/\text{g}$. The reported structure consists of trimeric secondary building units connected through μ_3 -O. **MTN** topology-based MIL-101 made from [Fe₃ (μ_3 -O) (COO)₆] SBU and 1,4-BDC linkers exhibit enormous surface area $(2500-4500 \text{ m}^2/\text{g})$ and large pores with diameters 29 and 34 Å (Bauer et al., 2008). Two isoreticular analogs with extra-large pore size by



Fig. 5. a) Most commonly reported Fe-Secondary building units. Reprinted with permission from (Yuan et al., 2018). **b)** Structural illustration of MIL-53(Fe) (Devic et al., 2010). **c)** *MTN* topology of MIL-101, MIL-101(Fe)-NDC, and MIL-101(Fe)-BPDC. Reprinted with permission from (Horcajada et al., 2014). **d)** The arrangement of trigonal prismatic SBUs (blue) and organic linkers (grey) in the **acs** nets of MOF-235 and MOF-236. Reprinted with permission from (Sudik et al., 2005). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

replacing 1,4-BDC with 2,6 naphthalene dicarboxylate (MIL-101 (Fe)-NDC), and 4,4'-biphenyl dicarboxylate (MIL-101(Fe)-BPDC) (Fig. 5c), (MIL-101(Fe)-BPDC) have a pore size 52 and 68 Å with accessible windows of diameter 20 and 26 Å. MIL-101(Fe) series exhibits lesser stability in water and transforms into more stable denser topologies (MIL-53/MIL-88) (Horcajada et al., 2014).

Apart from aromatic linkers aliphatic dicarboxylic acids are also proved to be potential candidates to create 3D porous frameworks (Horcajada et al., 2014). [Fe3 (µ3-O)(COO)6] SBU-based MIL-88 and MIL-89 are built using fumaric acid and trans, trans muconic acid linkers. Despite the similar SBUs, the structure of both frameworks is different (Serre et al., 2004a). MIL-88 is indexed to hexagonal space group P-62c. MIL-89 has a dense structure compared to MIL-88. The framework shows the influence of organic linkers in the final porous structure. A series of isorecticular structures of MIL-88 was prepared by substituting fumaric acid linkers with terephthalic acid (MIL-88B), 2, 6-Naphthalenedicarboxylic acid (MIL-88C), and 4,4'-biphenyl dicarboxylic acid (MIL-88D). All the structures exhibit two types of pores, a small microporous hexagonal channel and a relatively larger bipyramidal cage with strong breathing properties. Pore size strongly depends on the length of the organic linkers (Dhakshinamoorthy et al., 2012; Surblé et al., 2006).

A highly symmetrical *acs* topology is obtained by connecting trigonal prismatic $Fe_3O(CO_2)_6$ with 1,4-BDC and 1,3-BDC to form MOF-235 and MOF-236, respectively. The *acs* framework obtained by the cornersharing trigonal prism (Fig. 5d) is very rare for ditopic binders. Both structures have pores in the micron range, MOF-235 possesses a slightly larger pore (6.7 Å) than MOF-236 (1.9 Å) (Sudik et al., 2005).

3.2. Fe-MOF with tritopic ligands

The stability of MOFs designed with ditopic ligands is susceptible to moisture. The stability of MOFs is augmented by using tritopic ligands, the most commonly used one is trimesic acid (benzene-1,3,5-

tricarboxylic acid). MIL-100(Fe) with *MTN* topology (Fig. 6a) is similarly structured to zeolitic architecture, the super tetrahedral structure is formed from the binding of trimesic acid and [Fe₃ (μ_3 -O)(COO)₆] SBUs (Jeremias et al., 2016). The structure has two types of permanent mesopores with apertures 25 and 29 Å, which are accessible through pentagonal and hexagonal micropores windows (Fig. 6b). The reported surface area is estimated to be > 2800 m²/g (Horcajada et al., 2007).

Isoreticular analogs (MIL-100(Fe)-BTB) of MIL-100(Fe) was reported by Horcajada et al. (2014) using organic strut 1,3,5-tris(4-carboxyphenyl)benzene (BTB) as a replacement. MIL-100(Fe)-BTB have a larger pore size (68 Å), accessible through a large window (20 and 26 Å) and the surface area is up to 4500 m²/g.

Benzo-tris-thiophene carboxylate (BTTC) and 4,4'-s-triazine-2,4,6-triyl-tribenzoate (TATB) are linked with Fe₃ (μ_3 -O)(OH)(H₂O) to form super tetrahedral PCN-332 and PCN-333 MOFs with improved water stability in a wide range of pH (3–9) and enormous surface area (4000 m²/g). These MOFs could consider as extended structures of MIL-100 with very large pores. PCN 333 consists of one microporous tetrahedral cage (11 Å) and two mesoporous cages i.e. a dodecahedral cage (34 Å), and hexacaidecahedral cage (55 Å). PCN-333 is one of the rare MOFs with very large pores and extremely stable towards the activation process. PCN-332 is similar to PCN-333 with a slightly reduced pore size (Feng et al., 2015).

PCN-53 is a mixed valance Fe-MOF with two trivalent and one divalent Fe octahedra bridged by μ_3 -O. SBUs are connected through benzo-tris-thiophane carboxylate. The three different types of pores are present in PCN-53 with diameters spanning from 9.5 to 22.2 Å and the estimated total surface area of 2780 m²/g (Yuan et al., 2012). A non-centrosymmetric monoclinic crystal of MIL-65 i.e. [Fe^{II}₃(H₂O)₅(-C₉O₆H₃)₂·3H₂O] is developed by interlinking Fe(II) in octahedral coordination and the isolated [FeO₄(H₂O)₂] octahedra by 1,3, 5-benzenetricarboxylate (Riou-cavellec and Férey, 2002). A two dimensional MOF MIL-67 i.e. [[Fe (H₂O)₂(C₉O₆H₄)]·H₂O]) is designed using trimellitate organic ligands and exhibits an antiferromagnetic



Fig. 6. a) Structural framework of MIL-100(Fe) with two different pores. Reprinted with permission from (Jeremias et al., 2016). b) Two types of cages in MIL-100 with (I) pentagonal window and (II) hexagonal window. Reprinted with permission from (Horcajada et al., 2007).

behavior (Riou-Cavellec et al., 2003).

3.3. Fe-MOFs with tetratopic ligands

The basicity and number of ligating groups of organic linkers strongly alter the stability of MOFs and thus highly stable structures are reported with tetratopic ligands. These frameworks are stable in both acidic and basic pH. MIL-127(Fe) with *SOC* topology exhibit superior stability in comparison with MIL-100(Fe). The tetratopic ligand present in MIL-127 is 3,3',5,5'-azobenzene-tetracarboxylate (TazBz) and is connected to Fe (III) octahedral trimers sharing one central μ_3O to form a 3D structure with two types of micropores. 1D narrow channel (6 Å) and cages accessible through very narrow windows (3 Å). The structural integrity is maintained in the pH range 2–8 with complete amorphization at basic pH 12 (Chevreau et al., 2016; Wongsakulphasatch et al., 2015). The Fe (III) SBU, ligand TazBz and the SOC topology produced from their combination are depicted in Fig. 7a.

PCN-600(Fe) exhibits very high stability in a wide range of pH, starting from pH 2–11. PCN -600 is the only metalloporphyrin-based MOF which is stable in basic pH. PCN-600 is designed by the preassembly of tetrakis (4-carboxyphenyl) porphyrin (TCPP) with Fe₃O (OOCCH₃)₆ to form a *STP-a* network with mesoporous (3.1 nm) onedimensional channels. When compared to other phorphyrinic MOFs, PCN-600 exhibits very large pore volume (1.8 cm³/g) and BET surface area (2270 m³/g) (K. Wang et al., 2014).

MIL-141 is also a member of iron-based phorphyrinic MOF build from nickel (II) tetracarboxylate porphyrin (Ni-TCPP) and distorted Fe (III) octahedra. Each SBU is connected to 4 neighboring units through 4 distinct Ni-TCPP creating a *PtS* network topology (Fig. 7b). Porphyrin organic struts could be considered as a multifunctional linker, which incorporates unsaturated metal sites to the network. Framework exhibits slight flexibility. Counter cations are also present in the frameworks

(Fateeva et al., 2011).

Sanselme reported two Fe MOFs MIL-62 and MIL-82 utilizing the -ligand, 1,2,4,5-benzene tetracarboxylates (pyromellitic acid) (Sanselme et al, 2002, 2004). MIL-62 consists of ferrous-based edge-sharing octa-hedral chains and MIL-82 consists of trans corner-sharing ferric-based octahedral chains connected by tetratopic organic ligands to the neighboring chains.

Other than carboxylic acid 2,4,6-tris(4-pyridyl)-1,3,5-triazine (TPT) and pyrazine (pyz) are also reported as efficient organic connecters. A Spin crossover Fe- organic 3D framework is formed with NbO topology, formulated [Fe (TPT)_{2/3}{M¹(CN)₂}_]·nG M¹ = Ag/Au, G = guest molecules. In this MOF, Fe (II) is in a rare FeN₆ mode where axial positions are occupied with pyridine and four equatorial positions are connected to cyanide groups of M¹(CN) (Piñeiro-López et al., 2014). SIFSIX-3-M analogs of Fe are formed by Fe (pyz)²⁺₂ type square grids, connected by SiF₆ Pyrazine. The framework with pcu, topology exhibits a BET surface area 358 m²/g with pore diameters 3.5–3.8 Å (Elsaidi et al., 2017).

4. Utilization of Fe-MOFs for water remediation

4.1. Removal of organic contaminants

The extraordinary structural framework and the superior tunable catalytic properties of the metal center present in the MOFs, make them a perfect candidate for the removal of organic contaminants from the aqueous system. The present section deals with the three major classes of organic contaminants such as PPCPs, industrial waste, and dyes (Rojas and Horcajada, 2020).

4.1.1. Removal of PPCPs

The major sources of contaminants of emerging concern (CEC) in



Fig. 7. a) The structural units of MIL-127: (I) Fe(III) octahedra trimers or Fe secondary building unit (SBU), (II) 3,3',5,5'-azobenzenetetracarboxylic acid (H₄-TazBz; ligand-TazBz), and (III) schematic representation of SOC framework. Nitrogen-blue, Oxygen-red, Carbon-grey, Iron-orange, and Hydrogen-white. Reprinted with permission from (Chevreau et al., 2016). b) PtS network structure of MIL-141. Reprinted with permission from (Fateeva et al., 2011). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

aquatic ecosystems are PPCPs (pharmaceuticals and personal care products), herbicides, and veterinary products. With ever-increasing consumption and lack of efficient disposal as well as decontamination protocols, these newly spotted chemicals of synthetic origin are increasing the threat barriers to very dangerous limits. These micropollutants are present at very low concentrations and inadequately removed during routine water treatment procedures. The pseudo persistence of these biologically active pollutants has detrimental effects on aquatic and human health. The presence of pharmaceutical products including antibiotics is highly potent to develop ecotoxicity and evolution of bacteria and pathogens resistant to antibiotics and therapeutic techniques. The current techniques are inadequate for the complete removal of contaminants (Rasheed et al., 2020). Adsorptive removal and photocatalytic degradation using MOF is a feasible alternative for the fast removal of PPCPs (Joseph et al., 2019; Zhang et al., 2020). Fe-based MOFs are superior candidates for various advanced oxidation processes such as heterogeneous Fenton degradation, photocatalytic degradation, photo-Fenton, electro-Fenton degradation of these pollutants.

Very recently, Chaturvedi et al. reported the removal of levofloxacin a fluoroquinolone drug that comprises 17% of global antibiotic consumption using MIL-100(Fe) synthesized by a cost-effective solid-state method with remarkable absorption of 87.34 mg/g (Chaturvedi et al., 2020). Hydrogen bonding and π - π interactions could be considered as major directing forces influencing the adsorptive removal of PPCPs (Fig. 8a&b) (Li et al., 2020). The observed improvement in adsorption with the increase in the pH indicates the enhanced electrostatic interaction between the adsorbate and adsorbent. Hasan et al. and Moradi et al. discussed the effect of surface area and pore size of different MOF structures on the removal efficiency of naproxen, clofibric acid, and ciprofloxacin. The adsorptive removal of ciprofloxacin and surface area of adsorbents followed the same trend i.e. $Fe_3O_4@MIL-100(Fe) > MIL-100(Fe) > Fe_3O_4@MOF-235(Fe) > MOF-235(Fe) > Fe_3O_4 NPs.$ According to this study, the non-porous structure of Fe_3O_4 is least suitable for the removal of PPCPs (Hasan et al., 2012), (Moradi et al., 2016). The adsorptive removal of antibiotics and particle size of the adsorbate greatly depend on the synthesis method and modification. Compared to the convention hydrothermal method, microwave-assisted synthesis results in enhanced performance (Fig. 8c&d) (Dong et al., 2020).

Compared to the pristine MOF, the MOF composites and derived materials possess better adsorption capacities and are found to be more stable in aqueous systems. For example, Xiong et al. proposed the enhanced sorption capacity of multi-walled carbon nanotube (MWCNT) coupled MIL-53(Fe) in comparison to pristine MWCNT. MWCNT/MIL-53(Fe) exhibited 1.25, 8.28, and 3.34 times higher adsorption of tetracycline antibiotics such as tetracycline hydrochloride (TCN), oxytetracycline hydrochloride (OTC), and chlortetracycline (CTC). The presence of MWCNT improved the water stability and thermal stability of the adsorbent, the maximum adsorption capacity reported was 364, 325, and 180 mg/g respectively at pH7 (Xiong et al., 2018a). The same group reported the intensified removal of TCN and CTC using amino-functionalized MWCNT/NH2-MIL-53 due to the introduction of hydrogen bonding between hydroxyl groups of antibiotics and amino-functionalized MIL-53 (Xiong et al., 2018b). Mesoporous carbonaceous materials derived by the pyrolysis of MIL-53 at 800 $^\circ \mathrm{C}$ removes 72 mg/g of ciprofloxacin (CFX), while MIL-53(Fe) removes 60.2 mg/g within 60 min. Recently, remarkable performance of derived Fe-carbon materials is reported in copious number. They are highly stable and suitable for reuse, the reuse of pristine Fe-MOF was restrained, indicates the structural instability of MIL-53 in aqueous solution. Thus derived materials could be employed instead of pristine MOFs (Tran et al.,

J. Joseph et al.



Fig. 8. (a&b) Illustration of adsorptive removal of antibiotics using Fe-MOF and intermolecular interaction existing between MOF and pollutant (tetracycline) (Li et al., 2020). c&d) The dependency of adsorption equilibrium curves and particle Size on modification and synthesis method (Dong et al., 2020).

2019).

Apart from adsorptive depolluting techniques, Fe-MOFs are a promising tool for catalytic degradation. Liang et al. proposed the initiatory utilization of MOFs for the photodegradation of PPCPs from the aqueous phase (Liang et al., 2015). Namely, Pd@MIL-100(Fe), Au@MIL-100(Fe), and Pt@ MIL-100(Fe) prepared by a simple facile alcohol reduction were employed as photocatalyst for the degradation of theophylline, ibuprofen, and bisphenol A (Liang et al., 2015). Pd@MIL-100(Fe) exhibited superior degradation compared to MIL-100 (Fe) and noble metal loaded catalyst. Pd@MIL-100(Fe)/VS/H₂O₂ system successfully removed 99.5% theophylline. Similarly, Wu et al. reported the supreme efficiency of MIL-101 to degrade tetracycline

hydrochloride over a wide pH range and improved catalytic Fe(III)/Fe (II) cycle under visible light irradiation (Fig. 9a) (Wu et al., 2020). Tang and Wang et al. evaluated the importance of coordinatively unsaturated coordination sites in the photocatalytic performance of MOF, MIL-100 (Fe). They reported an improvement in activity with an increase in the unsaturated sites. Specifically, mixed valence Fe(III)/Fe(II) secondary building units were generated by high-temperature thermal treatment and observed that the photocatalytic activity to degrade sulfamethazine enhanced tremendously compared to pristine Fe(III)-MOF (Fig. 9b). Mixed valence Fe(III)/Fe(II) in MIL-100(Fe) (CUS-MIL-100(Fe)) degrades 17.6% sulfamethazine, whereas MIL-100(Fe) degrades only 11.1% sulfamethazine (Tang and Wang, 2018).



Fig. 9. a) Proposed catalytic mechanism of MIL-101/H₂O₂/visible light system for tetracycline hydrochloride (TC–HCl) degradation (Wu et al., 2020). **b**) The FESEM images and schematic representation of MIL-100(Fe) and CUS-MIL-100(Fe). Reprinted with permission from (Tang and Wang, 2018). **c)** Comparison of photoluminescence response and transient photocurrent generated in pristine and modified MIL-100(Fe). Reprinted with permission from (Ahmad et al., 2019).

Fe-MOF composites drastically improve catalytic performance compared to the parent MOF structures. Ahmad et al. (2019) improved the photo-Fenton degradation efficiency of mesoporous MIL-100(Fe) with the addition of ZnO nanoparticles. Mesoporous MIL-100(Fe) @ZnO enhanced the photocatalytic removal of phenol, bisphenol A, and atrazine (Ahmad et al., 2019). MIL-100(Fe)@ZnO/VS/H₂O₂ degraded 43–49% of TOC within 120 min, this is superior in comparison to the conventional MIL-100(Fe) (30% of TOC). The enhanced activity of this system is achieved by the reduction in the recombination of the photogenerated h^+ and e^- in the presence of metal oxide. This is evident from the reduction in photoluminescence response and improvement in the transient photocurrent generated (Fig. 9c). Good reusability up to 5 catalytic cycles was obtained and after each cycle catalyst was regenerated by simply washing with alcohol and water.

A highly photosensitive MIL-53(Fe) composite was synthesized by

coupling it with n-type semiconductor WO₃ (Oladipo, 2018). By this coupling, WO₃/MIL-53 exhibits an exceptional photocatalytic reduction of Cr(VI) and oxidation of organochlorinated herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D). Z-scheme photocatalytic system generated along the heterojunction of WO₃ and MIL-53(Fe) enhance the e^- - h^+ separation. A synergetic effect of photo-reduction and photo-oxidation is observed in the binary pollutant system and resulted in the rapid removal of pollutants compared to the single pollutant system. This indicates the effective separation and utilization of e^- - h^+ pair in the coupled system. Furthermore, persulfate and percarbonate are considered as efficient e^- scavengers to enhance photocatalytic degradation of PPCPs (R. Li et al., 2018; Yin et al., 2020). For instance, Vis/MIL-53(Fe) is inefficient to activate percarbonate and the introduction of ferric ion enhances the photoactivation capability of MIL-53(Fe), Vis/MIL-53 (Fe)/Fe(III)/percarbonate mineralized 90% of sulfamethazine while

Vis/MIL-53(Fe) achieved only 12% degradation. Recently reported studies on the removal of PPCPs using Fe-MOFs are summarized in Table 3.

4.1.2. Removal of industrial organic waste

The rapid growth of industrialization generates tons of industrial residues, which end up in the aquatic ecosystem and create a threat to it. Most of the industrial effluents contain carcinogens with high stability. Appropriate treatment of these hazardous materials is highly required, MOFs with fine-tunable frameworks and catalytic properties are perfect for the annihilation of industrial organic wastes (Dias and Petit, 2015).

Fe-based MOFs are reported to be very successful in the complete removal of phenols and their derivatives compared to the conventional Fe₂O₃, α-FeOOH, and Fe₃O₄. MIL-88B shows 1-3 times higher degradation than the conventional sorbents (C. Gao et al., 2017). In addition to this, terephthalic acid-based Fe-MOFs, Fe(BDC)(DMF), MIL-53(Fe), and NH₂-MIL-53(Fe) could remove 90% of phenol at ambient temperature (35 °C) and at neutral pH 6.2. Similarly, porous carbon derived from the pyrolysis of Fe-MOFs is also a robust adsorbent for phenol. The porous carbon obtained by pyrolysis of MIL-53(Fe) removes 83% of phenol i.e. 4 times higher than MIL-53(Fe) through chemisorption at pH 6.6 (Tran et al., 2020). Beside to this, Fe-MOFs exhibits exceptionally high catalytic degradation and adsorption for nitroaromatics, for example amine-modified MIL-88B(Fe) adsorbs 163.66 mg/g of highly explosive 2,4,6-Trinitrophenol (TNP) from the aqueous phase (Guo et al., 2019), H-bonding between TNP and NH₂-MIL-88B is the major cause for the improved adsorption rate and stability of the framework.

The presence of Fe (II) in Fe(BDC)(DMF), enhances the catalytic activity and results in the complete removal of phenol (Sun et al., 2015). Moreover, the phase and morphology of MOF highly influence catalytic activity, rod-shaped MIL-88A with (100) surface degrades phenol completely in 15 min while the diamond and spindle-like MIL-88A degrade 65% and 81% of initial phenol concentration. This is because, the rod-shaped MIL-88A (100) with a lower energy barrier for generating •OH exhibits a fast degradative Fenton cycle in comparison to reported MIL-88B-Fe, MIL-101-Fe, and MIL-53(Fe) (Liao et al., 2019). Fe-MOF also exhibits exception visible light photocatalytic activity on coupling with suitable systems, ternary BiOI@MIL-88A (Fe)@g-C₃N₄ composites exhibit 70% degradation of phenol within 180 min even in the absence of additional oxidants (Gholizadeh Khasevani and Gholami, 2018). Coupling Fe-MOF (MIL-88A (Fe)) with BiOI a major photoactive particle and C₃N₄ core-shell structure facilitate the separation of generated e⁻ - h⁺ pair, which facilitates faster degradation of the pollutants. Photocatalyst obtained by growing NH2-MIL-53(Fe) on C₃N₄/PDI synthesized by the calcination of pyromellitic dianhydride and melem show excellent degradation of Bisphenol A, Fig. 10 a&b represent detailed synthesis of g-C₃N₄/PDI@NH₂-MIL-53(Fe) and explains the mechanism involved in the degradation of Bisphenol A. g-C₃N₄/PDI@NH₂-MIL-53(Fe) with the equimolar proportion of g-C $_3N_4$ /PDI and NH $_2$ -MIL-53(Fe) shows the highest activity, superior to the individual components (Li et al., 2019).

Magnetite decorated MIL-53-(Fe) exhibits improved photocatalytic degradation of p-nitrophenol compared to conventional photocatalysts Fe_2O_3 and Fe_3O_4 (C. Zhang et al., 2015). This adsorbent-catalytic system is easily removed from the aqueous solution using an external magnetic field which enhances the wide applicability of the magnetic-MIL-53-(Fe). In addition to this the magnetic carbon nanocomposites derived from the pyrolysis of Fe-MOF at 500 °C is reported to be an exceptional heterogeneous Fenton catalyst and degrades 89% of 4-nitrophenol in 75 min (Chen et al., 2017). Modifications enhancing the H-bonding improves the rate of degradation and adsorption of nitroaromatics (Pi et al., 2018). Flame retardants such as tris (2-chloroethyl)-phosphate (TCEP) and hexabromocyclododecane (HBCD) are also degraded completely using Fe-MOFs (Hu et al., 2019b; X. Li et al., 2018). The reported studies on the remediation of industrial organic wastes using Fe-MOFs is tabulated in Table 4.

4.1.3. Removal of dyes

Every year 70,000 tons of dyes are produced worldwide, 2% of this ends up in the aquatic ecosystem. These synthetic compounds with complex aromatic structures are highly toxic and are resistant to most conventional water treatment methods (Khan et al., 2013). Apart from the aesthetic concerns of coloration, organic dyes create threats to the photosynthetic cycles of aquatic plants and thus disturbs the water ecosystem. Many advanced techniques such as adsorption, advanced oxidation, and catalytic degradation have been practiced for the complete removal of dyes (Cheng et al., 2018; Pi et al., 2018). Among them, the technologies using MOFs achieved paramount success, especially with Fe-MOFs due to their superior adsorption capacity and excellent capability to perform Fenton-type catalytic degradation (Zhang et al., 2019).

The overall dye capture efficiency of MOFs majorly depends on the size of the dye, pore size, and structure of the synthesized MOF, together with physical or chemical interactions between dye and MOF. Moreover, it is highly influenced by the nature of the metal ion present in the framework (Martínez et al., 2018). MIL-100(Cr) and MIL-100(Fe) exhibit entirely different behavior towards the adsorption of methyl orange (MO) and methylene blue (MB). MIL-100(Fe) adsorbs similar amount of MO (1045.2 mg/g) and MB (736.2 mg/g) while MIL-100(Cr) adsorb MB (645.3 mg/g) preferentially than MO (211.8 mg/g) (Tong et al., 2013). The sorption capacity of MIL-100(Fe) depends largely on the particle size. Adsorption maxima is directly proportional to particle size whereas, the sorption rate decrease with an increase in particle size (Tan et al., 2015). Modifications on MOFs further influence the sorption characteristics. MIL-101(Fe) adsorbs MB and Basic Blue-41, Phosphotungstic acid (PA) modification on MIL-101(Fe) alters its preference towards MB and selectively adsorbs higher concentration of Basic Blue -41 (Mahmoodi et al., 2020).

The best degradation performance of Fe-MOFs is obtained through catalytic degradation. Heterogeneous photo-Fenton degradation, photo-Fenton degradation, Fenton like AOPs, and catalytic ozonation are the major pathways for dye removal. The catalytic ozonation efficiency of MIL-53(Fe), MIL-88B(Fe), MIL-100(Fe), MIL-101(Fe) for Rhodamine B (RhB) is shown in Fig. 11a. The activity of Fe-MOF/O₃ is 4 times higher than MOF alone (Yu et al., 2019b). The combined effect of UV radiation with ozone further enhances the catalytic activity (Fig. 11b) (Yu et al., 2019a). Surface lewis acid sites (LAS) are the active ozone decomposition spots, MIL-53 with the highest LAS possess the maximum capacity.

Fe-MOFs exhibits fair capacity to activate active oxidants such as persulfate and hydrogen peroxide both in the presence and in the absence of visible light. In the treatment with highly active oxidants, these metal-organic frameworks show high stability with 3–5 cycles of reusability (Andrew Lin et al., 2015; Yaowen Gao et al., 2017; C. Zhang et al., 2015). The leached Fe metal concentration is negligible (Angamuthu et al., 2017; Araya et al., 2017). The photocatalytic activity of Fe-MOF is improved by modifying the basic framework. MOF hybrid catalyst prepared by the self-assembly between positively charged MIL-53(Fe) and negatively charged MIL-100(Fe) broadened the catalytically active visible light bandwidth. This is achieved through the efficient separation of photogenerated $e^- - h + pair through the synergistic effect of bandgap modification (Abdpour et al., 2018).$

Enhanced dye decontamination rates were achieved by biodegradation techniques coupled with Fe-MOF. Fe- MOF is a perfect substrate for bacteria due to the minimal cytotoxicity of Fe, large pores, and huge surface area. Pseudomonas putida cells immobilized on the composite aerogel containing graphene-based aerogel and MIL-100(Fe) could be employed to remove Acid Orange-10 (AO-10) (Fig. 12) (Dong et al., 2019). The degradation takes place in two stages, graphene/MIL-100 (Fe) adsorbs AO-10 and after attaining the adsorption maxima P. putidia starts the cycle of biodegradation, compared to the conventional biodegradation process coupled technique reduces the overall time by 8–9 h with 100% degradation. Fe₃O₄@MIL-100(Fe) core-shell–P. Putidia nanocomposite also shows similar ultrafast kinetics towards the

Table 3

The main PPCP contaminants found in water and removal techniques using Fe-MOF systems.

MOF system	Pollutants	Method	Efficiency	Surface area (m²/g)	Kinetics/adsorption isotherm/stability	Ref
M.MIL-100(Fe)@ZnO/H ₂ O ₂ /VS	Atrazine	Photocatalytic degradation		654	5 cycle	(Ahmad et al., 2019)
MIL-100(Fe)	Naproxene, Clofibric acid	Adsorption	-	1492	Pseudo second-order, Langmuir adsorption isotherm	Hasan et al. (2012)
MIL-100(Fe) MOF-235(Fe) Fe ₃ O ₄ @MIL-100(Fe)	Ciprofoxacin	Adsorption	-		Elovich, pseudo second- order. Langmuir adsorption, 6 cycle	Moradi et al. (2016)
Pd@MIL-100(Fe)/H ₂ O ₂ /VS	Theopylline	Photocatalytic	99.5%	2102	4 cycle	Liang et al. (2015b)
Fe@MesoC (MIL-100(Fe)/H ₂ O ₂	Sulfamethoxazole	Heterogeneous Fenton degradation	100.0%	272.35	3 cycle	Tang and Wang (2018b)
Vis/MIL-53(Fe)/Fe(III)/SPC	Sulfamethazine	Photocatalytic degradation	91.0%			Li et al. (2018)
1TMoS ₂ @ MIL-53(Fe) H-O- /VS	Ibuprofen	Photocatalytic degradation	95.0%	337	5 cycle	N. Liu et al. (2019)
MIL-101(Fe) NH ₂ -/H ₂ O ₂ /UV MIL-101(Fe)/H ₂ O ₂ /UV	Imidacloprid	Photocatalytic degradation	97.0% 89.0%	2865, 1137	3 cycle	(Gecgel et al., 2019)
MIL-100(Fe(III)/Fe(II))/H ₂ O ₂	Sulfamethazine	Heterogeneous degradation	100.0%	568.9	Pseudo first-order	Tang and Wang (2018a)
WO ₃ /MIL-53(Fe)	2,4-dichlorophenoxyacetic acid (2,4-D)	Photocatalytic degradation	100.0%	96.5	5 cycle	Tang and Wang (2018a)
MIL-53(Fe)	Ciprofloxacin	Adsorption	-	199	Pseudo second order Langmuir adsorption isotherm,5 cycle	Tran et al. (2019a)
MWCNT/NH ₂ -MIL-53(Fe)	Tetracycline hydrochloride Chlortetracycline hydrochloride	Adsorption	-	125.5	Pseudo second-order, Langmuir adsorption isotherm, 4 cycle	Xiong et al. (2018b)
MIL-53(Fe)/Ni	Doxycycline	Adsorption	-		Pseudo second-order, Langmuir adsorption isotherm. 5 cycle	(Xiong et al., 2019a)
MIL-100(Fe)	Levofloxacin	Adsorption	-	110.49	Pseudo second-order, Langmuir adsorption isotherm, 4 cycle	Chaturvedi et al. (2020)
MIL-101(Fe) MIL-100(Fe) MIL-52(Fe)	Tetracycline	Adsorption Photocatalytic	96.6% 57.4%	252.59 1203.36 21.42	Pseudo second-order, Langmuir adsorption	(Dongbo Wang et al., 2018)
g-C ₃ N ₄ /PDI@MOF/H ₂ O ₂ /VS	Tetracycline Carbamazepine	Photocatalytic degradation	90.0% 78.0%	-	5 cycle	(Li et al., 2019)
$\alpha\mathchar`-Fe_2O_3@g\mathchar`-C_3N_4 \mathchar`-S3(Fe))/H_2O_2/VS$	Tetracycline	Photocatalytic degradation	92.0%	6.22	5 cycle	(Guo et al., 2019)
MWCNT/MIL-53(Fe)	Tetracycline hydrochloride Oxytetracycline hydrochloride Chlortetracycline hydrochloride	Adsorption	_	60.17	Pseudo second-order, Langmuir adsorption isotherm, 4 cycle	Xiong et al. (2018a)
Fe ₃ O ₄ @MOF-100(Fe)	Diclofenac sodium	Adsorption	-	198.47	Pseudo second-order, Langmuir adsorption isotherm, 5 cycle	(Zheng et al., 2018)
MIL-100(Fe)/PDS/VS	Sulfamethoxazole	Photocatalytic degradation	98.0%	-	Pseudo first-order, 5 Cycle	Yin et al. (2020)
MIL-53(Fe)/H ₂ O ₂ /vis system	Clofibric acid Carbamazepine	Adsorption, Photocatalytic degradation	90.0%	200	Pseudo second-order, Freundlich adsorption isotherm. Pseudo second-order, Langmuir adsorption isotherm. 4 cycle	(Gao et al., 2017)
BiOI/MIL-53(Fe) Fe/Fe-MIL-53(Fe) Fe/Fe-MIL-100(Fe) Fe/Fe-MIL-53(Fe)	Carbamazepine Tetracycline	Photo-Fenton Adsorption	67.0% 46.6% 96.1% 96.6%	25.8 0.8 17.5 10.3	Pseudo first-order, 5 cycle Pseudo first-order, 5 cycle	(Zhang et al., 2021) (W. Li et al., 2020)
Carboxymethyl cellulose/MIL- 101(Fe)/poly (β-cyclodextrin)	Tetracycline	Photocatalytic degradation	85%		3 cycle	(Zhang et al., 2021)
PDINH/MIL-88A(Fe)	Chloroquine phosphate	Photocatalytic, AOP	95.7%		Pseudo first-order, 5 cycle	(Yi et al., 2021)
Ag ₃ PO ₄ /MIL-100(Fe)	Tetracycline	Photocatalytic degradation	91.4%	908.8	Pseudo first-order, 5 cycle	Xu et al. (2020)
MIL-100(Fe)/PANI	Tetracycline		84.0%		5 cycle	(continued on next page)

Table 3 (continued)

MOF system	Pollutants	Method	Efficiency	Surface area (m ² /g)	Kinetics/adsorption isotherm/stability	Ref
Fe-BTC	Diclofenac sodium Ibuprofen	Photocatalytic degradation Adsorption	62.5 mg/g 18.7 mg/g	815.8	Pseudo second-order Freundlich adsorption	(Dan-dan Chen et al., 2020) (Castañeda Ramírez et al., 2021)
	Naproxen sodium		102.7 mg/ g		isotherm	
Fe ₃ O ₄ –FeBTC	Diclofenac sodium Ibuprofen Naproxen sodium	Adsorption	204.1 mg/ g 18.2 mg/g 117.9 mg/ g	217.0	Pseudo second-order Freundlich adsorption isotherm	(Castañeda Ramírez et al., 2021)
MIL-88(Fe)@ TiO ₂ @chitosan	Monocrotophos	Photocatalytic degradation	98.7%		Pseudo first-order, 5 cycle	Vigneshwaran et al. (2021)
MIL-100 MIL-88-A/PS/UVA	Diclofenac sodium Naproxen	Adsorption Heterogeneous catalysis/AOP	773 mg/g 92%		Sips isotherm Zero order, 4 cycle	(Zhang et al., 2019) (El Asmar et al., 2021)

degradation of AO-10 (Fan et al., 2018). A major issue faced in the treatment of wastewater using MOFs is the recyclability of the catalyst. Most of the catalyst are lost in the process of recovery and washing. Magnetic metal-organic composite has great potential to improve the recovery of the used metal organic framework. The improved surface active site during coupling of MOF with magnetic nanoparticle also improves the photocatalytic activity (Edem et al., 2020) Magnetic recyclable Fe_3O_4 @MIL-100(Fe) could remove 99% of MB and could maintain almost similar activity up to 5 cycle (C. F. Zhang et al., 2013) The relevant investigations on the decontamination of dyes using Fe-MOFs are summarized in Table 5.

4.2. Removal of inorganic contaminants

Environmental pollution arising from inorganic contaminants has raised huge concerns because of the induced phytotoxicity in plants and oxidative harm in other species. Inorganic contaminants majorly include heavy metals, oxyanions/cations, radioactive wastes, and inorganic acids (Gao et al., 2019).

The role of MOFs as a catalyst or adsorbent of these contaminants are still less explored. However, the advancements achieved in the utilization of Fe-MOFs for cleanup of these pollutants are highly promising. MIL-88B(Fe) synthesized by a green protocol at ambient temperature has been successfully employed as an adsorbent for the removal of Sb (III) and Sb(V) (Cheng et al., 2020). The maximum adsorption capacities obtained were 243.1 mg/g for Sb(V) and 511.3 mg/g for Sb(III), superior compared to the adsorbents such as graphene, Zn/Fe LDH, Polyamide-graphene, TiO₂, etc. The strong interaction between Fe₃-µ₃-oxo clusters of MIL-88B(Fe) and Sb and the highly active in-situ generated hydrous ferric oxide (HFO) sites enhances the overall adsorption capacity. The traces of arsenic from drinking water could be effectively removed using MIL-88B(Fe) and MIL-88A (Fe), meeting the arsenic threshold for drinking water (Hou et al., 2018; Wu et al., 2018). MIL-100(Fe) is a potential nanoadsorbent for effective phosphate management in real water systems (Fig. 13a) (Nehra et al., 2019). Real water samples with different initial phosphate concentrations behave differently to the treatment, the highest phosphate removal was reported in tap water with the least initial phosphate concentration.

In comparison to pristine Fe-MOFs the Fe-MOF composites exhibit superior performance. MIL-101/GO composite shows a 50% higher adsorption capacity than MIL-101(Fe) (Lu et al., 2019). The ultrahigh surface area and comparatively more active sites lead to the excellent adsorption capacity of 128.6 mg/g for Pb²⁺ within 15 min. However, sometimes the composites exhibit inferior surface area compared to parent MOF but still preserve the adsorption capacity. As an example, incorporation of Al species in Fe-MOF (Al@-Fe-MOF) reduces the surface area from 1641 m²/g to 1368 m²/g, but the adsorption rate for selenite shows an increment by 77%. This indicates the prominence of enhanced adsorption sites in composites and its role in the overall sorption performance (Wang et al., 2019). Further modification of composites augments the stability and capability of Fe-MOFs. For instance, nFe₃O₄@MIL-88A (Fe)/APTMS possess maximum adsorption capacities for cadmium (II)- 693.0 mg/g, lead (II)- 536.22 mg/g, and chromium (VI) -1092.22 mg/g and retained the performance for 5 consecutive test with a reduction of only 3% (Wang et al., 2019). Additionally, MIL-101(Fe)/Fe3O4@morin nanocomposite selectively adsorbs V(V) in the presence of V(IV) without losing sorption capacity and selectivity up to 12 cycles (Esmaeilzadeh, 2019). The metal-organic framework-based filter developed by the in-situ decoration of MIL-100 (Fe) on a commercially available iron mesh simultaneously adsorbs arsenite [As(III)] and oxidase it to a less toxic arsenate [As(V)] (Dawei Wang et al., 2018). The dual function filter purifies groundwater with complete removal of As(III) in a duration of 6 h (Fig. 13b).

Photocatalytic techniques have been also used for the elimination of inorganic contaminants. TiO2@NH2-MIL-88B (Fe) was used in a sunlight-driven catalytic reduction of Cr(VI) to Cr(III) with an efficiency of 98.6% in 35 min (Yuan et al., 2019). The TiO₂ modification on MOF provides an easy pathway for the transfer of photogenerated e⁻ and ends up in the generation of superoxide radicles, thus utilize the sunlight completely. Plasmonic ternary heterostructure Ag/AgCl/NH2-MIL-88B (Fe) exhibit 87% photocatalytic degradation of Cr (VI), point out the further scope for enhancing the catalytic performance through modification (Fig. 13c) (Bao et al., 2021). WO₃/MIL-53(Fe) and SnS/MIL-53 (Fe) composite have been evaluated as efficient photocatalytic reducers of Cr(VI) under visible light irradiation (Oladipo, 2018; Xia et al., 2018). A 70% reduction was obtained in the presence of MIL-53(Fe) and 94% reduction was achieved with WO3/MIL-53(Fe). A slight lower yield was reported for SnS/MIL-53(Fe) in comparison with WO₃/MIL-53(Fe), but superior to MIL-53(Fe). Table 6 summarizes the major studies on the removal of inorganic contaminants using Fe-MOFs.

5. Mechanisms involved in the water treatment process using Fe-MOFs

Wastewater treatment using MOFs proceeds majorly through adsorption and catalysis. Catalysis could proceed in the presence or absence of light. Fenton type catalysis is majorly discussed for Fe-MOFs. A deep understanding of the mechanisms involved in each treatment is essential for enhancing the efficiency of each method through modification and also for developing new methods.

5.1. Mechanisms involved in adsorption

Adsorptive decontamination using MOFs is a fast cost-effective



Fig. 10. a) The synthetic pathway for g-C₃N₄/PDI and g-C₃N₄/PDI@NH₂-MIL-53(Fe); Preparation of g-C₃N₄/PDI: I) The mixing of pyromellitic dianhydride (PMDA) and melem (MA) by grinding in an agate mortar, II) transferring of this mixture into a porcelain crucible and heating to 325 °C for 4 h, III) grounding and washing the obtained yellow product, and IV) filtration and drying the g-C₃N₄/PDI yellow powder. Preparation of g-C₃N₄/PDI@NH₂-MIL-53(Fe): I) Dispersion of g-C₃N₄/PDI powder into dimethylformamide (DMF) by ultrasonication for 30 min, II) the addition of ferric chloride hexahydrate (FeCl₃-6H₂O) and 2-aminoterephthalic acid (NH₂-BDC) to this suspension with vigorous stirring for 60 min, III) the transfer of reaction solution to a Teflon-lined stainless-steel autoclave and heating at 150 °C for 24 h, then cooling to ambient temperature, and IV) the g-C₃N₄/PDI@NH₂-MIL-53(Fe) creation after centrifugation, washing, drying, and grounding. **b)** the possible mechanism for photocatalytic degradation of organic pollutants by using the g-C₃N₄/PDI@NH₂-MIL-53(Fe) under visible light irradiation. Reprinted with permission from (Y. Li et al., 2019). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

method with a simple strategy and high performance. The efficiency of this method is determined by different interactions such as electrostatic interaction, H-bonding, hydrophobic-hydrophilic interactions, pore size, and metal selective interactions (Khan et al., 2013; Mon et al., 2018). Electrostatic interactions dominantly determine the preferential adsorption of hazardous materials from a real water system. The net charge on the MOF surface varies with the pH of the medium and thus interacts with the contaminants with opposite charge favorably than in comparison to the species of similar charge. For example, MIL-53(Fe) selectively adsorbs clofibric acid (CA) over carbamazepine (CBZ), maximum adsorption capacities of CA and CBZ are about 0.80 mmol/g and 0.57 mmol/g at low pH. This could be explained by the variation in surface charge at different pH. pKa value of CA is 3.18 and the isoelectric

point of MIL-53(Fe) is obtained at pH 5, this indicate the higher interaction between the positively charged MIL-53(Fe) and anionic CA at low pH. However, with the increment in the pH, a reduction in CA adsorption rate is observed due to electrostatic repulsion. Contrarily CBZ with pKa 13.9, exhibits consistent adsorption throughout the entire pH range, indicates the possibility of only π - π interaction. Here the inferior selective adsorption could be due to the absence of electrostatic interaction. The interactions present in the system are shown in Fig. 14a and Fig. 14b represent interaction between the adsorbate and adsorbent as well as the influence of pH on adsorption rates of CA and CBZ (Yanxin Gao et al., 2017). The variation in the adsorption of cationic dye MB and anionic dye MO on MOF 235 with pH also validates the importance of electrostatic interaction (Haque et al., 2011).

Table 4

The main industrial organic contaminants found in water and removal techniques using Fe-MOF systems.

MOF system	Pollutant	Method	Efficiency	Surface area (m ² /g)	Kinetics/adsorption isotherm/ stability	References
MIL-101(Fe)/Persulfate/VS	Tris (2-chloroethyl) phosphate	Photocatalytic degradation	90.0%	-	Pseudo first-order, 3 cycle	Hu et al. (2019b)
Fe-Pd@C/H ₂ O ₂ /VS	Phenol	Photocatalytic degradation	95.0%	113.5	Pseudo first-order	He et al. (2019)
MIL-88B (Fe)/H ₂ O ₂ /VS	Phenol	Photocatalytic degradation	99.0%	165.4	Pseudo first-order, 4 cycle	(C. Gao et al., 2017)
NH ₂ -MIL-88B	2,4,6-trinitrophenol	Adsorption	-	414	Pseudo second order, Langmuir adsorption isotherm, 5 cycle	(Hongxu Gao et al., 2019)
Fe–C composite	4-nitrophenol	Heterogeneous catalytic degradation	89.0%	86.68	Pseudo first-order, 4 cycle	Chen et al. (2017)
r-MIL-88A/H ₂ O ₂ s-MIL-88A/H ₂ O ₂ d-MIL-88A/H ₂ O ₂	Phenol	Heterogeneous catalytic degradation	100.0% 81.0% 65.0%	24.3 20.7 12.0	Pseudo first-order, 3 cycle	Liao et al. (2019)
Fe-Pd@C	Phenol	Heterogeneous catalytic degradation	100.0%	113.5	5 cycle	He et al. (2019)
MIL-88B(Fe)	Phenol	Heterogeneous catalytic degradation	99.0%	165.4	Pseudo first order, 4 cycle	(C. Gao et al., 2017)
g-C ₃ N ₄ /PDI@MOF	Bisphenol A p- nitrophenol	Photocatalytic degradation	100.0% 100.0%		5 cycle	(Y. Li et al., 2019)
Magnetic porous carbon	Phenol 4-nitrophenol	Adsorption	83.0% 97.0%	225.3	4 cycle	Tran et al. (2020)
BiOI@MIL-88A(Fe)@g-C ₃ N ₄	Phenol	Photocatalytic degradation	70.0%	70.1	Pseudo first-order	Gholizadeh Khasevani and Gholami (2018)
MIL-88A(Fe)/UV + ozone	4-nitrophenol	Photocatalytic ozonation	100.0%	19.74	Pseudo first-order, 4 cycle	Yu et al. (2019b)
Co ₃ O ₄ @MOFs (Zn, Fe)/PMS	4-chlorophenol	Catalytic degradation	100.0%	196.3	4 cycle	(Zeng et al., 2015)
Fe ₃ O ₄ - MIL-53(Fe)-H ₂ O ₂ /VS	p-nitrophenol	Photocatalytic degradation	60.0%	-	3 cycle	(C. Zhang et al., 2015)
MIL-100(Fe)	Bisphenol A	Adsorption	-	1754	Pseudo second-order, Langmuir adsorption isotherm	(Qin et al., 2015)
Quinone- MIL-101(Fe)/ persulfate	Bisphenol A	Heterogeneous catalysis	94.2%	-	3 cycle	(Huaisu Gao et al., 2019)
MIL-53(Fe)/Bi ₂ WO ₆	Phenol	Photocatalytic degradation	63.0%	34.9	Pseudo first-order, 4 cycle	(Tu et al., 2020)
MIL-88(Fe) NH ₂ -MIL-88(Fe)	Chrysene	Adsorption	98.9% 95.2%	1240 941	Pseudo second-order, Langmuir adsorption isotherm 5 cycle	Uba et al. (2020)
MIL-100(Fe)/CoS	Bisphenol A	Fenton degradation	95.7%		Pseudo first-order 5 cycle	(Wu et al., 2021)
Pd@Fe ₃ O ₄ @MOFs	2-chlorophenol 4-chlorophenol 2,4-chlorophenol 2,4,6-trichlorophenol Phenol	Fenton degradation	100.0% 100.0% 100.0% 75.0% 100.0%	165.3	Pseudo first-order 5 cycle	(Niu et al., 2018)
Fe-MOF@PDI	Phenol	Photo-Fenton	97.0%		3 cycle	(Huang et al., 2021)
BiOI/MIL-53(Fe)	Phenol Bisphenol A	Photo-Fenton	59.0% 90.4%	25.8	Pseudo first-order 5 cycle	(Zhang et al., 2021)
Fe-MOF-74/Molecular imprinted polymer	Dimethyl phthalate	Adsorption, AOP	90.0%	213.8	Pseudo-second-order, Freundlich adsorption isotherm	(Ding et al., 2021a)
g-C ₃ N ₄ /NH ₂ -MIL-101(Fe)	2,6-dichlorophen 2,4,5-trichlorophenol	Photo-Fenton	98.7% 97.3%	266.8	Pseudo first order, 5 cycle	(Su et al., 2021)
Fe-MOF-74@SiO ₂ + PS	Dimethyl phthalate	Heterogeneous Catalytic AOP	99.0%	154.23	Pseudo first-order, 4 cycle	(Ding et al., 2021b)

Further understanding could be achieved from the adsorption behavior of different species of Arsenic by MIL-101(Fe). This reported research demonstrates the effect of chemical structures and the modes of interaction that could enhance the adsorption efficiency. Among the various arsenate forms, MIL-101(Fe) removes 232.98 mg/g of arsenate As(V). Compared to the inorganic As(V) superior adsorption capacities are shown for the aromatic organic forms, i.e. roxarsone (ROX, 507.97 mg/g), p-arsanilic acid (p-ASA, 329.65 mg/g), and inferior capacity for aliphatic organic form, dimethyl arsenate (DMA, 158.94 mg/g). The huge discrepancy in adsorption capacities could be explained by the difference in the interactions between contaminants and the framework structures (Z. Li et al., 2019). The schemes of adsorption of different arsenic chemicals, arsenate (As(V)) and its organic forms such as dimethyl arsenate (DMA), p-arsanilic acid (p-ASA), and roxarsone (ROX) with MIL-101(Fe) are shown in Fig. 14c and Fig. 14d depicts the adsorption capacity based on the kinetic studies. The superior adsorptive removal of tetracycline antibiotics using MWCNT/MIL-53(Fe) than MWCNT could be explained by a simple mechanism of π - π interactions

present between MOF composite and the adsorbents (Xiong et al., 2018a).

In contrast to ionic pollutants, the adsorption of nonionic pollutants is governed by the hydrophobic interactions and Van der Waals interaction between the benzene ring in the framework and the contaminant (X. Li et al., 2018). Pore size and pore size selectivity also influence the adsorption behavior of MOFs. Appropriate correlation between pore and pollutant size is pivotal for ensuring superior adsorption capacity. This could be understood by closely analyzing the behavior of MIL-88 (Fe) and NH₂-MIL-88 (Fe) as an adsorbent for chrysene (CRY). MIL-88 (Fe) with larger pore size, 12.5 nm adsorbs 98.9 \pm 1.83% and NH_2-MIL-88 (Fe) with pore size 8.8 nm remove 95.2 \pm 1.00% of CRY. The discrepancy in adsorption rates could only be explained by the variation in pore size as the non-polar sites on CRY eliminates all the possibilities for typical adsorbate-adsorbent interactions such as H-bonding and other polar interactions (Uba et al., 2020). Similarly pore expanded MIL-100 (Fe) designed with abundant micropores, large mesopores with a size around 40 nm along with macropores are reported to be most promising



Fig. 11. a) The mechanism, degradation capacity and degradation rate of Rhodamine B (RB) by using different Fe-MOFs. Reprinted with permission from (Yu et al., 2019b), **b)** Schematic representation of photocatalytic ozonation of 4-nitrophenol (4-NP) using MIL-88A (Fe) and comparison of 4-NP degradation rate at different reaction conditions (Yu et al., 2019a).

adsorbent compared to conventional MOF structures (Duan et al., 2020). The importance of pore size could be further explained by the high adsorption capacity of cationic MOF CPM-97-Fe towards large sized cationic dye RhB, irrespective of the electrostatic repulsion. CPM-97-Fe exhibits a total adsorption of 306 mg/g of RhB, which is highest compared to 177.8 mg/g reported for the predecessors. This anomaly could be ascribed to the special large open window pores present in the crystal structure (Tian et al., 2019). The pore size of MOFs plays a vital role in the selectivity of preferred pollutant and preferential adsorption. PCN-222(Fe) with very large pores (3 nm) selectively adsorbs larger dyes than smaller MO and MB irrespective of the electrostatic charges (Sarker et al., 2019). The requirement for strong interrelation between pore size and pollutant size could be further verified by the sorption behavior of MIL-100(Fe) with tuned pore size distribution. MIL-100(Fe) with pore size distribution dominates at 1.2, 2.0 and 2.5 assimilated 489 mg/g of MB, which shows perfect mass transfer in the pore size between 1.33 nm and 2.70 nm. However, RhB with a molecular size 1.59 × 1.18 × 0.56 nm finds it difficult to diffuse through the pores of the adsorbent which reduced annihilation (134 mg/g) under similar experimental conditions. Compared to RhB, MIL-100 (Fe) exhibited higher adsorption capacity towards negatively charged, small sized MO despite of electrostatic repulsion (Tan et al., 2015). The decontamination of AO-7 using different Fe-MOFs shows a reduction in the adsorption capacity in the order MIL-101(Fe) > MIL-100(Fe) > MIL-53(Fe) > MIL-88B(Fe)

which can be correlated to the pore size (Ke et al., 2016; Li et al., 2016). These observations reinforce the important role played by pore size in enhancing the sorption capacity of MOFs.

5.2. Mechanisms involved in heterogeneous catalysis

Heterogeneous Fenton-like catalysis using Fe-MOFs has been considered as a highly promising technology for degrading contaminants in water. These catalysts show high stability and reusability with minimal sludge production in comparison with conventional homogeneous catalysts. Fe(II) formed by the reduction of Fe(III) present in the active site of MOF exhibits superior activity towards the degradation of phenols and other organic contaminants in the presence of H₂O₂. The catalytic Fe(III)/Fe(II) cycle activates the H₂O₂ to generate hydroxyl radical, the major oxidative species for pollutant degradation (Fig. 15a) (C. Gao et al., 2017). The crucial step in the degradation mechanism is the contact between H₂O₂ and the active site. Likewise, sulfate radical-based advanced catalytic oxidation using Fe-MOFs are also of high practical importance due to low energy input and cost-effectiveness (Pu et al., 2018). The Fe(III)/Fe(II) transformation possible in the SBU induces the catalytic generation of persulfate radical to degrade organic pollutants. The mechanism involved is that the porous structure of MOF facilitates plenty of active Fe (III) sites to create $S_2O_8^{-\bullet}$ and Fe(II) (Eq (1)). Fe(II) further oxidize persulfate to sulfate radicle, the active species



Fig. 12. Schematic representation of different steps involved in the synthesis of GA/MIL-100/P. Putida. Synthesis of graphene aerogel (GA): I) The mix of graphene oxide (GO) solution with ascorbic acid, heating the mixture in boiling water bath for half an hour, then frozen in the freezer for 30 min, II) the reduced GO formation by thawing the reaction mixture, continuing to boil in a boiling water bath for 8 h, III) the GA creation via washing, freeze-drying and treating of reduced GO at 200 °C for 2 h. Synthesis of GA/MIL-100(Fe): I) GA addition into ethanolic solution containing (3-aminopropyl)triethoxysilane, II) taking out the GA from ethanolic solution after 8 h shaking at room temperature, washing with ethanol, adding to DMF solution containing succinic anhydride, shaking for 8 h, and washing the surface-adhered reagent with ultrapure water, III) the addition of obtained GA into ethanolic solution containing FeCl₃ and 1,3,5-benzenetricarboxylic acid (H₃BTC) for 20 and 40 min, respectively, and IV) preparation of GA/MIL-100(Fe) by treating the obtained product with ethanol, washing with ultra-pure water, and ethanol, finally freezing drying. Immobilization of P. putida cells onto GA/MIL-100(Fe): I) scattering the GA/MIL-100(Fe) and N-hydroxy succinimide (NHS) into DMF solution, II) addition of N,N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) into reaction mixture, and shaking for 24 h, III) washing the mixture with phosphate buffered saline (PBS) solution, IV) dispersion of P. putida bacteria and treated GA/MIL-100(Fe) with PBS solution, and their reaction in the consistent temperature shaking bed at 37 °C during a day, and V) washing the resulted sample with PBS. Reprinted with permission from (Dong et al., 2019).

(Eq (2)). Sulfate radicle will lead to the generation of •OH (Eq (3)). These oxidative species combinedly degrade the pollutant (AO7) completely (Eq (4)) (Li et al., 2016). Fig. 15b represents the schematic pathway involved in the degradation of AO7.

$$Fe(III) + S_2 O_8^{2-} \rightarrow Fe(II) + S_2 O_8^{-}$$
(1)

$$\operatorname{Fe}(\mathrm{II}) + \operatorname{S}_{2}\operatorname{O}_{8}^{2^{-}} \to \operatorname{Fe}(\mathrm{III}) + \operatorname{SO}_{4}^{-^{\bullet}} + \operatorname{SO}_{4}^{2^{-}}$$
(2)

$$SO_4^{-} + H_2O \rightarrow OH + H^+ + SO_4^{2-}$$
(3)

$$SO_4^{-} + OH \longrightarrow SO_4^{2-} + OH$$
 (4)

$$AO7 + SO_4^{-\bullet} OH/O_2^{-\bullet} \to \cdots \to CO_2 + H_2O + \cdots$$
(5)

5.3. Mechanisms involved in photocatalysis

The efficiency of heterogeneous catalytic degradation using Fe-MOFs could be improved by coupling it with photocatalysis. The band gaps of Fe-MOFs are suitable for visible light photoactivation and thus Fe–O clusters could be directly excited to generate e^- and h^+ . The separated e^- - h^+ degrade organic pollutants or further leads to the generation of active species. For example, The photogenerated e^- with strong reductive power boost the Fe(III) reduction to form Fe(II), which further activates PDS to generate •OH and O_2^- radicals to degrade the pollutant (Fig. 16a) (Yin et al., 2020). The efficiency of photocatalytic decontaminations depends greatly on the interval between the e^- - h^+ pair recombination. Different modification methods delay the recombination

rate and thus improves performance.

Modifications on MOFs using nanoparticles improve photocatalytic efficiency through enhancing the separation between the e^- and h^+ . The nanoparticles will form Schottky junctions/heterojunctions which allow the interfacial charge transfer at the interface and act as electron sink. In Fe-MOF composites mainly two kinds of heterojunctions are reported, traditional heterojunctions (Type I and Type II) and Z-scheme heterojunction. Type I and Type II heterojunctions are reported the most and Z-scheme heterojunction in Fe-MOFs are reported recently.(Fig. 16b) (Wang et al., 2020).

Coupling amino-functionalized MIL-88B(Fe) with g-C₃N₄ results in the formation of Type-1 heterojunction. The conduction band (CB) of NH₂-MIL-88B(Fe) and g-C₃N₄ are approximately 0.13 eV and -1.14 eV, respectively. Photogenerated electrons are transferred from g-C₃N₄ effectively to NH₂-MIL-88B(Fe) suppressing the charge recombination and facilitate activation of H₂O₂ to generate •OH to form Fenton type degradation of MB (Fig. 17a) (Wang et al., 2020). Type II heterojunction is formed by MIL-100(Fe)@MIL-53(Fe). MIL-100(Fe) acts as the p-type semiconductor and MIL-53(Fe) acts as the n-type semiconductor. The photoelectron excited from the VB to CB of MIL-100(Fe) is migrated to the CB of MIL-53(Fe) with lower negative potential. Similarly, the h⁺ from the VB of MIL-53(Fe) is migrated to the VB of MIL-100(Fe) with less positive potential. This relative migration of photoactive species facilitates effective electron-hole pair separation. e⁻ in the conduction band and h^+ in the VB reacts with O_2 and H_2O respectively to generate •OH radical to degrade MO as shown in Fig. 17b (Abdpour et al., 2018).

Table 5

Different types of dyes found in water samples and their decontamination techniques using Fe-MOF systems.

MOF system	Pollutant	Method	Efficiency	Surface area (m ² /g)	Kinetics/adsorption isotherm/ stability	Reference
GA/MIL-100/P. Putida	Acid orange-10	Adsorption, Biodegradation	100.0%	-	3 cycle	Dong et al. (2019)
MIL-100(Fe)	Methylene blue	Adsorption	-	2776	Pseudo second-order, Langmuir adsorption isotherm 3 cycle	Tan et al. (2015)
MIL-88A(Fe)/persulfate	Rhodamine B	Heterogeneous catalytic	80.%	-	Pseudo first-order, 4 cycle	Andrew Lin et al.
MIL-53(Fe) persulfate/VS	Acid orange -7	Photocatalytic	100.0%	-	5 cycle	(Yaowen Gao
Fe ₃ O ₄ MIL-53(Fe)/H ₂ O ₂ /VS	Rhodamine B	Photocatalytic	98.7%	-	3 cycle	(C. Zhang et al.,
Fe ₃ O ₄ @MIL-100(Fe)	Methylene blue	Adsorption	73.8%	366.14	Pseudo second-order, 5 cycle	(Shao et al., 2016)
MIL-100(Fe)	Methyl orange	Photocatalytic	100.0%	2,007	Pseudo first-order, 4 cycle	Liang et al.
MIL-88B(Fe)–Ag/TiO ₂ nanotubes/	Methyl orange	Photocatalytic	90.0%	-	Pseudo first order	(Mohaghegh et al.,
NH2-MIL-88B(Fe)/TiO ₂ /VS	Methylene blue	Adsorption Photocatalytic degradation	100.0%	supporting	5 cycle	Li et al. (2018)
Fe-BTC	Rhodamine B Congo Red, Orange II	Adsorption	70.9% 96.9% 88.2%	21.89	Pseudo second-order	(Wu et al., 2018)
MIL101(Fe)/phosphotun-gstic	Basic blue-41, Methylene blue	Adsorption	-	-	Pseudo second- order, Langmuir adsorption isotherm 3 cycle	Mahmoodi et al.
Ni/Fe-MOF-0.3-DMF/H ₂ O ₂ /VS	Rhodamine B	Photocatalytic degradation	90.0%	480	Pseudo first-order	(Nguyen et al., 2018)
MIL-100(Fe)@MIL-53(Fe)	Methyl orange	Photocatalytic degradation	90.0%	315	5 cycle	Abdpour et al. (2018)
MIL-53(Fe)/SiO ₂ /UV	Methylene blue	Photocatalytic degradation	66.3%	149.1	First-order	(Sarkar et al., 2018)
PCN-222(Fe)	Brilliant green Crystal violet Acid red-1 Acid blue-80	Adsorption	-	2476	Langmuir adsorption isotherm, 5 cycle	Sarker et al. (2019)
Fe ₃ O ₄ @MIL-100(Fe)/P.Putida	Acid orange –10	Adsorption Biodegradation	100.0%	305.7	Pseudo first-order Pseudo second-order 3 cycle	Fan et al. (2018)
NH ₂ -MIL-88B(Fe)/H ₂ O ₂	Methylene blue	Heterogeneous catalytic degradation	100.0%	163.9	Pseudo second- order, 5 cycle	(He et al., 2018)
TiO ₂ @MIL-100 (Fe)/H ₂ O ₂ /VS	Methylene blue	Photocatalytic degradation	100.0%	1001	Pseudo first-order, 4 cycle	(Hejazi et al., 2020)
Fe-BTC	Alizarin red S Malachite green	Adsorption	80.0 mg/g 177.0 mg/	443	Pseudo secong-order	(Delpiano et al., 2021)
Fe-BTC	Orange II	Adsorption	₀ 435 mg∕g	877	Pseudo second-order, Langmuir adsorption isotherm.4 cycle	(García et al., 2014)
MIL-53 (Fe)	Methyl orange	Adsorption	77.0%	53	Pseudo second-order Langmuir adsorption isotherm, 3 cycle	(Yılmaz et al., 2016)
MOF-Fe@chitin/VS	Methylene blue	Photocatalytic degradation	65.0%	8	Pseudo second-order, 5 cycle	(Sadjadi et al., 2021)
MoS ₂ @MIL- 88(Fe)	Methylene blue Rhodamine B	Photocatalytic degradation	98.5% 97.4%	94.3	Pseudo first-order, 5 cycle	(Govarthanan et al., 2021)
MIL-53(Fe)/Bi ₂ WO ₆	Rhodamine B	Photocatalytic degradation	98.0%	34.9	Pseudo first order, 4 cycle	(Tu et al., 2020)
FeNi _x -BDC	Methylene blue	Adsorption Photo-Fenton degradation	99.6%	201.80	Pseudo second-order Langmuir adsorption isotherm Pseudo zero order	(Wu et al., 2021)
MIL-53-Fe/biochar/Fe ₃ O ₄	Rhodamine B	Adsorption	75.0%	42.2	Pseudo second-order Langmuir adsorption isotherm	(Navarathna et al., 2020)
NiCuZr layered double hydroxide (LDH)/MIL-101(Fe)–NH ₂	Methylene blue	Photocatalytic degradation	98.2%	180	7 cycle	(Khajeh et al., 2021)
BiOI/MIL-53(Fe)	Methylene blue	Photo Fenton	99.0 %	25.8	Pseudo first order, 5 cycle	(Zhang et al., 2021)
MIL-88A/PS	Orange G	Heterogeneous catalytic degradation	96.4%	31.98	2 cycle	(J.Wang et al., 2016)
CPM-97-Fe	Brilliant Red X–3B Acid orange 7 Congo red Methylene blue Rhodamine B Croscein Scarlet 3B Methyl blue	Adsorption	648 mg/g 468 mg/g 831 mg/g 380 mg/g 306 mg/g 356 mg/g 304 mg/g	1397.0	Pseudo second-order	Tian et al. (2019)

(continued on next page)

Table 5 (continued)

MOF system	Pollutant	Method	Efficiency	Surface area (m²/g)	Kinetics/adsorption isotherm/ stability	Reference
MIL-101(Fe)@PDopa@Fe ₃ O ₄	Acid black 1 New coccine Methyl red Malachite green	Adsorption	325 mg/g 304 mg/g 1250.0 mg/g 833.3.mg/		Pseudo second-order Langmuir adsorption isotherm	(Hamedi et al., 2019)



Fig. 13. a) Phosphate adsorption efficiency of MIL-100(Fe) from real water samples. Reprinted with permission from (Nehra et al., 2019). b) Schematic representation of iron mesh-based MOF filter and the proposed mechanism for arsenic removal. Reprinted with permission from (Wang et al., 2018). c) The presentation of possible mechanism for hexavalent chromium reduction on the Ag/AgCl/NH₂-MIL-88B (Fe). Reprinted with permission from (Bao et al., 2021).

Z-scheme heterojunction have recently gained increased research interest, due to beneficial improvement in catalytic activity. The mechanism involved in Z-scheme heterojunction could be understood by closely investigating the degradation of tetracycline (TC) by $Ag_3PO_4/MIL-100$ (Fe). The VB and CB values of Ag_3PO_4 are estimated to be 2.59 eV and 0.33 eV, while its bandgap energy is 2.26 eV. Further, the

counterpart MIL-100(Fe) has band gap energy 2.42 eV with VB and CB at 1.81 eV and -0.61 eV. According to traditional heterojunction formation, Ag₃PO₄/MIL-100(Fe) could form a Type II heterojunction, which facilitates migration of the photogenerated electrons to the CB of Ag₃PO₄ and photogenerated holes to the VB of MIL-100(Fe). However, with this migration the formation of reactive O₂*⁻ and HO* is not feasible

Table 6

The main inorganic contaminants found in water and removal techniques using Fe-MOF systems.

MOF system	Pollutant	Method	Efficiency	Surface area (m ² /g)	Kinetics/adsorption isotherm/stability	Reference
nFe ₃ O ₄ @MIL-88A(Fe)/ APTMS	Cr(Vl), Cd(II), Pb (II)	Adsorption	-	62.21	Pseudo second-order,5 cycle	(Mahmoud et al., 2020)
Fe/Mg-MIL-88B(n)	As(V)	Adsorption	-	360	Langmuir adsorption isotherm, 5 cycle	(Gu et al., 2019)
MIL-101(Fe)/GO	Pb(II)	Adsorption	-	377	Pseudo second-order, Langmuir isotherm, 4 cycle	Lu et al. (2019)
TiO ₂ @NH ₂ -MIL-88B(Fe)	Cr(VI)	Photocatalytic reduction	98.6%	8.85	Pseudo first order, 4 cycle	Yuan et al. (2019)
MIL-100(Fe)	Phosphate	Adsorption	-	790.5	Pseudo second-order, Langmuir isotherm, 8 cycle	Nehra et al. (2019)
WO ₃ /MIL-53(Fe)	Cr(VI)	Photocatalytic reduction	94	-	-	Oladipo (2018)
MIL-53(Fe)/SnS	Cr(VI)	Photocatalytic	71.7	33.96	5 cycle	Xia et al. (2018)
Fe-BTC/polydopamine (PDA)	Hg, Pb	Adsorption	75.3 mg/g	2324	4 cycle	(Sun et al., 2018)
Al@Fe-MOF	Se (IV)	Adsorption	-	1368	Pseudo second-order, Langmuir adsorption isotherm	Wang et al. (2019)
MIL-101(Fe)/ Fe ₃ O₄@morin	V(IV), V(V)	Adsorption	-	-	12 cycle	Esmaeilzadeh (2019)
MIL-100(Fe)–Na ₂ CO ₃	Cr(VI)	Adsorption	45	1327	Pseudo second-order, Langmuir adsorption isotherm. 4 cycle	(Fang et al., 2018)
MIL-88A(Fe)	Arsenic (V)	Adsorption	_	_	Pseudo second-order, Langmuir	Wu et al. (2018)
MIL-88B (Fe)	Arsenic (V)	Adsorption	-	214	Pseudo second-order, Langmuir adsorption isotherm	Hou et al. (2018)
MIL-88B (Fe)	Sb(III), Sb(V)	Adsorption	-	32.8	Pseudo second-order, Langmuir adsorption isotherm, 4 cycle	Cheng et al. (2020)
Fe-Co MOF-74	Arsenic (V)	Adsorption	292.2 mg/	147.8	Pseudo second-order, Langmuir adsorption	(J. Sun et al., 2018)
	Arsenic (III)	Ĩ	g 266.5 mg/		isotherm	
			g			
MIL-100(Fe)PDA	Pb(II)	Adsorption	99.35%	640	Pseudo second order, 3 cycles	(Zhang et al., 2021)



Fig. 14. a) The adsorbate-adsorbate interactions between MOF and the pharmaceuticals and personal care products (PPCPs). **b)** The pH influence on the adsorption of carbamazepine (CBZ) and clofibric acid (CA) onto MIL-53(Fe) (adsorbents dosage = 0.1 g/L and PPCPs initial concentration = 40 mg/L). Reprinted with permission from (Y. Gao et al., 2017). **c**) Schematic representation of different interactions between arsenate (As(V)) and its organic forms such as dimethyl arsenate (DMA), p-arsanilic acid (p-ASA), and roxarsone (ROX) with MIL-101(Fe). **d)** The adsorption kinetic of arsenic species onto MIL-101(Fe). Reprinted with permission from (Z. Li et al., 2019).

as the redox potential of $O_2/O_2^{\bullet-}$ (-0.33 eV vs. NHE) is more negative than CB edge of Ag_3PO_4 and standard redox potential of $\bullet OH/H_2O$ (+2.40 eV vs NHE) is more positive than the VB edge of MIL-100(Fe). Therefore, Type II heterojunction could not explain strong signals of

both HO• and $O_2^{\bullet-}$ detected in electron spin resonance (ESR) spectroscopy. The formation of reactive species could be better explained by Zscheme mechanism. The photogenerated holes in the VB with higher positive potential than the •OH/H₂O will react directly with H₂O to form



Fig. 15. The schematic representation of mechanism involved in the heterogeneous catalytic degradation of pollutants a) assisted by hydroxyl radical (C. Gao et al., 2017), and b) assisted by sulfate radicle. Reprinted with permission from (Li et al., 2016).



Fig. 16. a) Schematic illustration of the photoactivation of MIL-100(Fe) utilizing visible light followed by the activation of peroxydisulfate (PDS). Reprinted with permission from (Yin et al., 2020). b) Proposed heterojunctions formed in the Fe-MOF composites.

•OH to oxidize TC. Meanwhile the photoelectron accumulated on the CB of MIL-100(Fe) with more negative potential than $O_2/O_2^{\bullet-}$ react with O_2 producing strong $O_2^{\bullet-}$ radicals to degrade TC. In addition, a cross transfer of photo generated electrons from the CB of Ag₃PO₄ to closely situated VB of MIL- 100(Fe) occurs, which leads to effective charge transfer and retards the rate of undesired recombination of electron –hole pair in the MIL-100(Fe)(Xu et al., 2020). Similarly through the

formation of Z-scheme heterojunction the MIL-100(Fe)/PANI composite exhibit outstanding photocatalytic degradation of tetracycline and hexavalent chromium under the irradiation of white light (Dan-dan Chen et al., 2020).

Owing to the porous structure and ultrahigh surface area possessed by MOF structure photocatalytic degradation is mostly accompanied by a combined action of adsorptive removal (Vigneshwaran et al., 2021).



Fig. 17. Schematic representation of heterojunction formation and catalytic pathway in MOF composites: **a)** NH_2 -MIL-88B(Fe)/g-C₃N₄. Reprinted with permission from (Li et al., 2017), and **b)** MIL-100(Fe)@MIL-53(Fe). Reprinted with permission from (Abdpour et al., 2018).

The photocatalytic degradation of tetracycline by Fe based MOFs (Fe-MIL-101, Fe-MIL-100, and Fe-MIL-53) proves the synergistic action of photocatalytic degradation and adsorption. Fe-MIL-53 removes 40.7% of tetracycline in which 10.5% is removed by adsorption and 30.2% during photo irradiation. Likewise, Fe-MIL-100 remove 57.4% of tetracycline through the combined action of adsorption (44.1%) and visible light irradiation (13.3%). Among the three, the most promising integrated photocatalytic adsorbent is Fe-MIL-101. Fe-MIL-101 exhibit a 55.1% adsorptive removal efficiency and 40% photocatalytic degradation efficiency and synergistically remove 96.6% of tetracycline (Dongbo Wang et al., 2018).

6. Structural instability of Fe-MOFs: major challenge in water treatment and possible solutions

Despite the excellent performance and extensive investigation of Fe-MOFs for water treatment. The commercialization and real-world utilization of these porous coordinating frameworks are still in infancy, which is because of the structural instability experienced by Fe-MOFs during harsh experimental conditions, large-scale recurring pollutant treatments, and in the course of regeneration as well as activation. The stability of these reticular structures is governed by Pearson's hard/soft acid/base (HSAB) principle. Fe-MOFs employed for water treatment satisfy the HSAB principle, and are majorly formed from the high-valent hard acid Fe³⁺ metalcore and hard base carboxylate ligands (Yuan et al., 2018). Most of the Fe-MOFs are substantially water stable, however, a serious framework instability such as complete or partial crystal structure destruction, metalcore leaching, exudation of entrapped guest molecules, and protonation followed by decoordination of ligands are reported when exposed to chemical, thermal, mechanical, and photocatalytic stimuli (Yang et al., 2020).

6.1. Chemical instability

The competitive coordination between organic linkers and coordinating species with strong coordinative or redox properties leads to Chemical destruction of MOF. Fe-MOFs are more labile towards hydroxide, acids, coordinative anions, and water molecules present in the reaction system, compared to the isostructural Cr-MOFs. This is due to the dynamic nature of metal-ligand (M-L) bonds in Fe³⁺ complexes with M-L exchange constant ($1.6 \times 10^2 \text{ s}^{-1}$), in contrast for Cr³⁺ it is more inert ($2.4 \times 10^{-6} \text{ s}^{-1}$) (Helm and Merbach, 2005). The reactive species

attack the metal-carboxylate coordinative bond resulting from the leaching of Fe³⁺, this cause obstacles towards their reuse and recycle. The structural arrangement of SBU has a critical role in attenuating structural instability caused by chemical species, infinite 1-D chain MIL-53(Fe) is stable than MIL-88 with Fe₃ (μ_3 -O) Cluster. Mesoporous MIL-101(Fe) is labile and thermodynamically unstable, transforms to relatively denser MIL-53 or MIL-88 crystalline structure in polar solvents (Horcajada et al., 2014).

Koo et al. designed hierarchical porous MIL-100 (Fe) by sizeselective partial etching using H_2SO_4 and H_3PO_4 , these acids attacked the framework through the accessible hexagonal windows. Further reported a complete crystal destruction with a smaller molecule, HCl (Koo et al., 2017). The investigation of Ye et al. proves that Fe-2D MOFs exhibit superior photoelectron- Fento property towards the degradation of organic micropollutants under UVA and visible light. Nonetheless, it could not be considered as a catalyst due to structural degradation, amorphization and iron leaching. 18 wt% of iron leaching and 30% reduction in performance are reported after first use at pH 3. Fig. 18a shows the amount of iron leached at different experimental pH (Ye et al., 2020). Taha et al. reported severe iron leaching from MIL-101 during the Fenton reaction within 15 min of the first reaction cycle (Taha, 2020).

Metal-carboxylate coordinative bonds are more prone to degradation



Fig. 18. a) The mechanism of photoelectro-Fenton treatment of organic micropollutants by using Fe-based MOF under UV and visible light irradiation, and the representation of dissolved iron concentration and final pH after 90 min of reaction. Reprinted with permission from (Ye et al., 2020). **b)** The effect of different activation strategies on the activity of MIL-53(Fe) as a dark-Fenton catalyst for Rhodamine 6G (Rh6G) degradation, and SEM images of (I) as-synthesized MIL-53(Fe), solid obtained after activation using (II) distilled water, (III) H_2O_2 and (IV) methanol. Reprinted with permission from (Ortega Moreno et al., 2020). **c**) schematic representation of Fe₃-µ₃-oxo cluster, ligand flipping, and the structural transformation due to ligand flipping under mechanical stress. Reprinted with permission from (Yuan et al., 2017).

in basic medium. PCN-600 is an example of Fe-MOF stable in basic medium (K. Wang et al., 2014). MIL-101(Fe) shows severe metal core leaching at pH 11.15.35 mg/L iron leached within 60 min in the course of catalytic degradation of organophosphate (Hu et al., 2019a). Chávez observed and reported the massive release of ligand trimesic acid (TMA) from the MIL-100(Fe) structural backbone. Leached TMA from structure coordination sites was detected in the reaction system even at neutral pH and increased with pH, resulting in complete structural collapse and formation of amorphous ferrihydrite at basic pH. Hence, pristine MIL-100(Fe) is not recommended for water depollution (Chávez et al., 2021). Similarly, the anions commonly present in the real water system such as carbonate/bicarbonate, phosphate, chloride and organic matter have detrimental effect on Fe-MOFs. The most sever complication is raised by phosphate anions, it could lead to the dissolution and hydration of MOFs at the entire pH range, especially in basic pH (Feng et al., 2020). MIL-100 (Fe) and MIL-101(Fe) have been proved structurally weak in the presence of PO₄³⁺. Compared to microparticles, nanoparticles of Fe-MOF degraded rapidly in phosphate buffer. Microparticles maintained their reticular structure in moderate phosphate concentration (X. Li et al., 2017) (Taylor-Pashow et al., 2009). The concentration of oxidizing agent employed in AOPs also play a crucial role in maintaining structural framework. Excessive concentration of $\rm H_2O_2$ and $\rm O_3$ retards the catalytic reaction and expedites ligand and $\rm Fe^{+3}$ leaching. The reaction condition employed in AOP is a deciding factor of catalyst's liability, H2O2/photoradiation and O3/dark reaction could harm the M-L coordinative bond but the crosswise combination is comparatively harmless (Chávez et al., 2021).

6.2. Mechanical instability

The well-known tunability and porosity possessed by MOFs naturally reduce its mechanical stability. The mechanical stability of MOFs is inferior compared to their industrial competitor zeolites. Depending on the magnitude of mechanical force and direction, a partial collapse, phase change or complete amorphization could be observed. This instability is more pronounced during the design of compact industrially appropriate forms like pellets, and during the solvent/guest molecule desorption due to the internal capillary force generated (Howarth et al., 2016). Mesoporous MOFs are likely vulnerable to mechanical destruction. Chemically robust mesoporous Fe MOF completely loses its enormous surface area and porous framework when subjected to removal of guest molecules by classical thermal activation (Q. Liu et al., 2016). Supercritical CO₂ activation is preferred, which is a hurdle towards its commercialization. Fateeva et al. compared the theoretical and experimental surface area of MIL-141(Fe), a decline of 2000 m^2/g is reported for Fe⁺² based MOF. In this work they summarized that Fe⁺³ based MIL-141 is stable towards traditional activation in contrast Fe^{+2} based sample, which underwent extreme structural destruction even with supercritical CO₂ (Fateeva et al., 2015). The characteristic properties of the guest/solvent molecules present in the pores is a determinative factor of mechanical stability. Ortega Moreno et al. showed the solvent used during activation could alter the activity, iron leaching, and even particle size of MIL-53(Fe). The difference in particle size of MIL-53(Fe) obtained with respect to solvents used is shown in Fig. 18b. Solvent exchange to low boiling point methanol induces fast deterioration of MOF structure and converts it as fragile and catalytically weak toward dark Fenton degradation of Rhodamine 6G (Rh6G) (Ortega Moreno et al., 2020).

MOF-based engineered materials are a great leap towards the industrialization of MOFs. However, extreme caution is required not to damage the crystal structure. Yuan and co-workers reported a structural transformation in PCN -250 while subjected to mechanical pressure during pelletization. A phase transformation from lower symmetry to denser phase is triggered by flipping of N=N bond in ABTC linkers (ABTC = 3,30,5,50-azobenzene-tetra carboxylate) and by Fe–O bond bending (Fig. 18c). In this work they showed that desolvated samples

show inferior resistance towards mechanical compression compared to solvated samples (Yuan et al., 2017).

6.3. Thermal and photolytic instability

Thermal stability is indispensable for high-temperature catalytic reactions and for achieving the absolute theoretically predicted surface area through activation. Fe-MOFs exhibited inferior thermal stability compared to the isostructural Al and Cr-based MOFs (Yuan et al., 2018). Likewise, MIL-88B-NH2 (Fe) (250 °C) is more susceptible towards thermal degradation compare to its Cr analog, MIL-88B-NH₂ (Cr) (350 °C) (Hsuan-lan Wang et al., 2018). Trinuclear SBU, MIL-101(Fe) units decompose rapidly (300 °C) compared to 1D-chain MIL-53(Fe), Still lower temperature degradation is observed for the triiron acetate framework (PCN-250 -225 °C)) (Feng et al., 2020). These observations pinpoint the influence of SBUs on thermal stability. Even variation in synthesis and experimental conditions could alter the thermal stability, Bezverkhyy et al. showed that HF-free synthesis leads to a thermally inferior framework. Fluoride-free MIL-100(Fe) and MIL-53(Fe) exhibit partial degradation at 100 °C, and at pH 7 a complete framework destruction is observed even at room temperature, which is unsatisfactory in comparison to parent MOF (Bezverkhyv et al., 2016).

The recent boom in the number of research dealt with photocatalytic degradation using Fe-MOFs ensures the catalytic efficiency and their ability to take advantage of visible light spectra. Regardless of novel catalytic activity, the stability of this material is creating obstacles towards fully-fledged utilization, which is rarely investigated. The destabilization upon irradiation starts either from the photo labile functional group or by complete framework degradation due to increased light intensity. Mateo et al. examined the photostability of a series of terephthalate MOFs under irradiation of UV/visible radiation for a prolonged period. The MOF structures subjected to the investigation were UiO-66(Zr), UiO66 Zr-NO2, MIL-101(Fe), MIL-125 Ti-NH2, MIL-101 Cr, and MIL-101 Cr(Pt). The result indicates that the prolonged irradiation results in the decarboxylation of the terephthalate ligand and significant evolution of CO2. Among the studied MOFs, CO2 generated is highest for MIL-101(Fe) and indicates the poor ligand to metal charge transfer. Through these studies authors, pinpoint the need for a new tool to quantify the structural integrity of MOF structure. The conventional techniques such as XRD, BET, TGA, and UV/Vis absorption spectra failed to prove the instability generated due to decarboxylation of the ligands (Mateo et al., 2019). Likewise, instability of MIL-100(Fe) under-stimulated solar radiation had been reported. Trimesic acid occluded in the pores leached in the first photocatalytic cycle and the decoordination of structural trimeric acid was observed after the fifth catalytic cycle (Chávez et al., 2021).

6.4. Advances towards structural stability

Recently, researchers are devoting massive efforts to tackle the restrictions generated by structural instability. The strategies adopted could be sub-categorize as given below.

6.4.1. Isomorphic metal substitution and compositional modification

Postsynthetic metal substitution technique is employed commonly to modify the SBU and thus enhance the framework stability without affecting the intrinsic catalytic activity of the Fe-center. Predominantly used substituents are chromium (III), manganese (II), cobalt (II), and nickel (II). Kirchon et al. investigate the activity of PCN-250(Fe) towards the degradation of methylene blue by substituting one Fe atom from the trimeric SBU with divalent Mn^{+2} , Co^{+2} , and Ni^{+2} . The results proved that the metal (II) substituted MOF performed better than the parent MOF, PCN -250(Fe₂Co) is highly stable even in glacial acetic acid and from pH = 1 to pH = 11 for 24 h, compared to PCN-250(Fe₃) (Kirchon et al., 2020). Photocatalytic degradation of rhodamine using bimetallic Al/Fe-MOF also proves the betterment in the stability achieved without affecting the catalytic rate of reaction (Nguyen et al., 2020). Likewise, improved chemical stability is achieved for Al-doped Fe-MOF, with superior adsorption capacity towards oxyanion selenite (Wang et al., 2019).

6.4.2. Polymer- MOF composites and derived materials

Polymer-metal-organic framework composites are emerging as a new novel technique to enhance stability without affecting their characteristic targeted performance (Yang et al., 2021). The most evident enhancement in chemical stability was reported for MIL-100(Fe) @PDA-SF composite, prepared by coating polydopamine to the surface followed by Michael addition reaction with 1H,1H,2H,2H-perfluorodecanethiol (HSF) (Fig. 19a). The introduced hydrophobic group impart the chemical stability to the framework, which is visible from the structural properties preserved for composites obtained after soaking in acidic solution with pH 0-3 and basic pH 11-13 (Queen, 2019). Fe-BTC -Poly (p-phenylenediamine) (Fe-BTC/PpPDA) composite was used for the extraction of gold particles from complex water samples. The monomers were introduced into the pores of the MOF, followed polymerization step facilitated the generation of Fe⁺² by reducing structural Fe^{+3} . The redox-active polymer in the MOF accelerates the reduction of Au^{+3} to Au, combinedly this system achieves equilibrium within 5 min with a removal rate of 99%. The structural stability and catalytic performance are maintained in a pH range of 2-10, a 1% reduction in performance was reported at pH 11.98% removal efficiency was maintained up to 5 cycles and decreased to 81% after 10 cycles (Daniel T Sun et al., 2018). Fe- MOF polymer composite, Fe-BTC-polydopamine (PDA) is a promising material to selectively remove 99.8% Pb²⁺ and Hg²⁺ from real water samples with a 1 ppm pollutant concentration. The superior adsorption capacity is attributed to the accessible metal-scavenging catechols in the pores formed from the polymer introduced. This system ensures consistent performance and rapid regeneration with cycling. For the industrial real flowing water system application, Fe-BTC- PDA bead was designed by reacting MOF with sodium alginate and applied for the removal of Pb²⁺. 10 L of continuously flowing water with 600 ppb Pb²⁺could be treated with 1 g of Fe-BTC- PDA (Daniel T. Sun et al., 2018).

MOF-derived materials are excellent catalysts with adequate stability for their application in extreme water decontamination treatments. Thermal instability of the Fe-MOF material could be tackled by the utilization of its pyrolysis products. Magnetic carbon nanocomposites derived by the pyrolysis of Fe -MOFs between a temperature of 400-600 °C yielded a chemically stable catalyst with exceptional high catalytic activity towards the degradation of 4-nitrophenol even at pH 2.2 (Chen et al., 2017). Fe₃O₄ nanoparticle encapsulated in mesoporous carbon shows high catalytic degradation of methylene blue and exhibit opportunity for recyclability with only 2% iron leaching after 5 catalytic cycles. This catalytically active stable structure was synthesized by the carbonization of MOF derived from Fe²⁺ and 1,4,5,8-naphthalene tetracarboxylic dianhydride at 725 °C under N2 atmosphere followed by air treatment at 300 °C (Angamuthu et al., 2017). Similar to the superior property exhibited by the bimetallic MOF the mesoporous carbon derived from bimetallic MOF also exhibit superior properties. The synergistic effect of the complimentary metal present in the system along



Fig. 19. a) Schematic representation of a hydrophobic modification of MOF using polydopamine (PDA) and 1H, 1H, 2H, 2H-perfluorodecanethiol (HSF) (Queen, 2019), and **b**) hierarchical mesoporous MOF structure obtained by selective etching through hexagonal pores using H_3PO_4 . Reprinted with permission from (Koo et al., 2017).

with Fe promotes higher pollutant degradation rates (Fan et al., 2020). Recent researches on Fe-MOF derived materials for water treatment are summarized in Table 7.

6.4.3. Defects to application

MOF instability could be utilized to achieve hierarchical structures and superior selective properties otherwise unachievable. Defects indicate the disruption of periodic structural arrangement in crystalline MOFs either by selectively removing structural entities or by using sizeable ligands.

By exploiting the thermal and vacuum instability of Fe-MOFs, defective large pore Fe(BDC)(DMF, F) with superior stability has been synthesized using monocarboxylic acid as a modulator. The defects generated during the removal of the modulator from the MOF structure by heat and vacuum treatment lead to the formation of large pores and new catalytically active unsaturated cites. The overall catalytic activity of the defective structure towards the activation of persulfate is higher than the typical MOF structure, and the amount of iron leaching is negligible (Huang et al., 2020). Defect formation achieved through acid etching is an easy method to obtain mesoporous structure by preserving the crystal framework. The properties of the final product could be tuned using wisely choosing the molecular size of acid. Koo et al. reported mesoporous hierarchical MIL-100(Fe) obtained by phosphoric acid etching through the hexagonal window leaving the pentagonal window intact and thus maintaining the structural integrity (Fig. 19b) (Koo et al., 2017). Through these methods, we could achieve highly efficient Fe-MOF structures for water treatment.

7. Conclusions and perspectives

Through this review, we have presented the current advances in the synthesis techniques and explained the complicated reticular structural aspects of Fe-MOFs in detail. Among the various synthesis techniques, the solvothermal method has been used primarily, but the microwave and ultrasound-assisted synthesis is gaining more priority being fast and energy-efficient. The structure of the MOFs depends on the strength, flexibility, length, and symmetry of the ligands. Variation in any of these parameters could result in a wide range of topologies with different architecture and functional performances. In this decade, a plethora of research activities has been published regarding the catalytic activities and aqueous phase removal of contaminants using Fe-based MOFs. The highly active SBUs invariably show improved degradation capacities,

kinetics and recyclability compared to conventional adsorbents and other members of the MOF family. Fe-based MOFs attain special attention because they could be used efficiently in almost all depolluting techniques such as adsorbent, environmental photocatalyst, heterogeneous catalyst, and catalyst in AOPs. Also, Fe-MOFs mediated heterogeneous Fenton and Fenton-like processes are efficient. Currently, there is a growing interest in using heterobimetallic MOFs, MOF-derived porous materials, metal/metal composite nanoparticles doped MOF structures to improve the water stability of these fascinating materials for real water system applications.

Despite the remarkable dominance in water remediation, the number of Fe-MOFs applicable for largescale real world applications are still scarce and this is mainly limited due to poor stability, especially in alkaline/acidic pH. Additionally, these novel materials also experience structural disintegration while subjected to extreme experimental conditions. Moreover, still there is a large void in research regarding many aspects of this porous crystalline frameworks. These could be listed as 1) Functionalization and investigation are concentrated mostly on carboxylate ligands, an expanded spectrum of organic ligands must be employed for the development of versatile frameworks. 2) In the modification and composite formation of Fe-MOFs dispersion and quantifications are extremely difficult and require further attention. 3) In bimetallic MOFs and metal nanoparticle doped MOFs, precious elements such as Pt, Au, and Ag are mostly used thus the overall cost of the treatment shoots up therefore cheaper alternatives should be developed. 4) The prominent contaminants such as biologically active pollutants and radioactive pollutants are inferiorly considered. 5) The investigation on production of the hazardous intermediate is mostly ignored and should be addressed. 6) More research should be focused on real water samples, especially in photocatalyic studies.7) The multifunctional application of MOFs must be exploited to treat chemically different pollutants. 8) The structure of MOFs should be adjusted to get a more environmental friendly enzymatic type degradation pathway. 9) Functionalization or structural modification methods should be developed to enhance the stability and to reduce the leaching of the metal ion. Lastly, more research should be done to uncoil the structural aspects of MOF and the factors disturbing the framework integrity by employing the principles of simulation and computational chemistry.

Declaration of competing interest

The authors declare that they have no known competing financial

Table 7

Fe-MOF-derived materials utilized in water remediation process.

MOF precursor	MOF derived nanomaterial	Pollutant	Method	Efficiency/stability	Reference
MIL-53(Fe) Co/Fe-MOF MIL-101(Fe) [Cu/Fe]-BTC MIL-100(Fe)	carbon-αFe/Fe ₃ C CoP/Fe ₂ P@mC Fe ₃ O ₄ /C CuFe ₂ O ₄ /Cu@C Nitrogen-doped graphene	Tetracycline Rhodamine B Methylene blue Methylene blue Phenol	Adsorption Photocatalytic degradation Fenton degradation Fenton- degradation Catalytic degradation	511.0 mg/g, 5 cycle 97.0%, 5 cycle 100.0%, 10 cycle 100.0%, 10 cycle 100.0%, 3 cycle	(Xiong et al., 2019b) (Hu et al., 2018) Li et al. (2018) (Bao et al., 2015) (Sun and Wang, 2017)
Fe(Hbidc)	Fe@C	Sulfamethoxazole	Catalytic degradation	98.3%,4 cycle	(Pu et al., 2021)
FeyCo1y-Co PBA MIL-53(Fe) MOFs(Fe)	Fe _{0.8} CO ₂₋₂ O ₄ Hollow mesoporous carbon P–Fe ₂ O ₃	Bisphenol A Ibuprofen Cr(VI) Pb(II) Cu(II) Co(II)	Catalytic degradation Adsorption Adsorption	95%, 4 cycle 206.5 mg/g, 5 cycle 175.5 mg/g 97.8 mg/g 66.2 mg/g 60.4 mg/g	(Li et al., 2016) Tran et al. (2019b) (Li et al., 2018)
MIL-88(Fe)	γ-Fe ₂ O ₃ /C	Phenol	Catalytic degradation	98.23%	(Li et al., 2020)
MIL-100(Fe)	CMIL-100@PCM	Napropamide	Electro-Fenton	82.3%, 4 cycle	(Liu et al., 2019)
Ti–Fe-MOF	4% Au-Fe ₂ O ₃ /TiO ₂	2,4-dichlorophenol 4-bromophenol	Photocatalysis	95% 97%, 5 cycle	(Li et al., 2021)
Fe-BDC	α-Fe/Fe ₃ C	Tetracycline hy-drochloride	Adsorption	652.0 mg/g, 5 cycle	(Jung et al., 2020)
MIL-53(Fe)	Fe ₃ O ₄ -carbon	Methyl red Methylene blue Phenol	Adsorption	134 mg/g 74 mg/g 445 mg/g	(Banerjee et al., 2012)
Fe-NTCDA Zn/Fe-MIL-88B	FeMCNA-300 MC-800	Methylene blue Chlortetracycline	Catalytic degradation Adsorption	84% 1158.0 mg/g 5 cycle	Angamuthu et al. (2017) Fan et al. (2020)

interests or personal relationships that could have appeared to influence the work reported in this paper.

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