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Application of MOFs on Removal of Emerging Water Contaminants

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Abbreviated list

AC	**Activated carbon**
AOPs	**Advanced oxidation processes**
FO	**Forward osmosis**
MF	**Microfiltration**
MOFs	**Metal–organic frameworks**
NF	**Nanofiltration**
PPCPs	**Pharmaceuticals and personal care products**
RO	**Reverse osmosis**
UF	**Ultrafiltration**
WWTPs	**Wastewater treatment plants**

1.1 Introduction

1.1.1 Sources of Emerging Water Contaminants

Water is an essential factor that can define the properties of all living species, and there is no doubt that our Earth cannot exist without water. With the rapid development of human society and the economic sector, the types of contaminants are

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becoming increasingly hard to control. One of the particular concerns is called "emerging contaminants".

Emerging contaminants can be defined as contaminants that have new sources and new pathways to the human body, with novel adverse effects on human health, the environment, and the ecological system. Emerging contaminants are common chemical substances, and modern analytical techniques can detect them. They can be classified depending on their nature, origin, potential effects, or the possible fate of the contaminants. For example, the NORMAN database classified the emerging contaminant into 21 groups with over 700 counted compounds: PPCPs, organic dyes, herbicides and pesticides, industrial compounds/by-products, and nanomaterials [1–5]. These contaminants have been dispersed in wastewater and sewage water via different routes, and lots of them can even be found where they have never been used. Emerging contaminants enter the water environment from different sources, and the origin of the emerging contaminants in the water is often difficult to detect.

One of the primary sources of emerging water contaminants is wastewater treatment plants (WWTPs). Humans use PPCPs, nanomaterials, and food additives in their daily life, and produce a tremendous amount of waste or wastewater, then wastewater moves to WWTPs. It should be mentioned that most emerging contaminants are outside the scope of regulation, or they are not regulated. Besides, current WWTPs are not designed to treat emerging contaminants due to their low concentration. The biosolids obtained after WWTPs are another source of these contaminants.

Other remarkable sources of emerging water contaminants are agriculture and livestock. In modern agriculture, pesticides, herbicides, antibiotics, hormones, etc., are used frequently, introducing the residue chemicals to the environment, including air, soil, and water. The contaminants can be transported between different phases of the environment by spreading, leaching, and runoff.

The landfill, which is the final destination of waste from everywhere, is another source of emerging contaminants. The components of waste are very complex. The leachate from landfill sites consists of emerging contaminants that can come into the groundwater, streams, or WWTPs, leading to adverse environmental and human health effects.

1.1.2 Emerging Water Contaminants Treatment Methods

Identifying the treatment methods for removing emerging contaminants in the water is a priority that must be concentrated on the best practices for ensuring the use of safe water for the community. Recently, many studies have investigated new processes to eliminate emerging contaminants from water, including membrane technology, adsorption, biodegradation, advanced oxidation processes (AOPs), and so on (Table 1.1).

i) Membrane technology

The membrane process is a phase-changing process that can be applied for emerging water contaminant treatment. The membrane can be made from many different materials (e.g., carbon nanotubes, polyurethane, polysulfone, and polyvinylidene), and the contaminant that can be retained or passed through can be decided based

Table 1.1 Summary of advanced treatment technologies for organic pollutant removal.

Technology	Target emerging contaminant	Removal efficiency	Note	Ref.
1) Membrane				
a) IF				
Polysulfone- and polyvinylidene UF membranes	Bisphenol A (BPA) and 17β-estradiol (E2)	75–98%	Polysulfone from Koch Membrane Systems	[6]
b) NF				
NF-200 and NF-90	Acetaminophen	18–81%		[7]
	Phenacetin	70–78%		
	Caffeine	62–93%		
c) FO				
FO: Hydration Innovations (HTI, Albany)	1,4-dioxane	55–68%		[8]
	Acetaminophen	45–89%		
	Metronidazole	70–99%		
	Phenazone	85–99%		
	Caffeine	80–99%		
	Bisphenol A	40–99%		
	Carbamazepine	65–99%		
	17α-ethinylestradiol	85–99%		
d) RO				
RO: Aromatic polyamide membrane (Midland, MI)	Ibuprofen	90–99%		[8]
	Naproxen	95–99%		
	Fenoprofen	95–99%		
	Gemfibrozil	95–99%		
	Ketoprofen	95–99%		
	Acetaminophen	100%		
2) Adsorption				
a) Activated carbon				
Commercial AC (PB 170, PB 170–400, PC 1000, WP 235, Carbsorb 28, Cyclecarb 305, W 35, SA Super, LP 39, MP 25 and Hydro XP 17)	Atrazine, Diuron (pesticides)	40–75%	Wastewater with an average DOC of 5.6 ± 0.9 mgC/l, C_0 of 6 and 57 ng/l, AC doses of 10 mg/l	[9]
Polymer-based spherical activated carbon particles	Estradiol (hormone)	96–99%	In combination with UF	[10]

(Continued)

Table 1.1 (Continued)

Technology	Target emerging contaminant	Removal efficiency	Note	Ref.
Granular activated carbon	NO_3^--N Metoprolol and diclofenac (PPCPs)	95% for NO_3^--N 80% for PPCPs	Integrate with solid-phase denitrification (SPD) with biodegradable polymer poly-3-hydroxybutyrate-co-hydroxyvalerate (PHBV)	[11]
b) Biochar				
Tea-waste biochar	Caffeine in aqueous media (PPCPs)	15.4 mg/g^{-1}	Pyrolyzed at 700°C using steam activation (TWBC-SA)	
Magnetic porous biochar obtained from a biomass garlic skin	Paraben, metronidazole, and oxytetracycline (PPCPs)	415, 287, and 822 mg/g^{-1} for paraben, metronidazole, and oxytetracycline, respectively		[12]
Biochar (BC) and biomass carbon quantum dots (CQDs) from reed straw	Carbamazepine (PPCPs)	96.43%	BC and CQDs for the modification $MgIn_2S_4$/BiOCl (MB) heterojunction photocatalyst with Z-scheme structure	[13]
c) CNTs				
Multiwall carbon nanotube (MWCNT)	Ciprofloxacin hydrochloride (PPCPs)	1.7446 mg·g^{-1} or >88%	Initial ciprofloxacin hydrochloride concentration of 4 ppm	[14]
Commercial multi-walled carbon nanotubes	Chloramphenicol, thiamphenicol, florfenicol, sulfadiazine, sulfapyridine, sulfamethoxazole, sulfathiazole, sulfamerazine, sulfamethzine, sulfaquinoxaline, ibuprofen, carbamazepine and diclofenac	Freundlich constant (KF) values were 353–2814 $mmol^{1-n}$ Ln/kg, 571–618 $mmol^{1-n}$ Ln/kg, and 317–1522 $mmol^{1-n}$ Ln/kg for sulfonamides, chloramphenicol, and non-antibiotic pharmaceuticals, respectively		[15]

Table 1.1 (Continued)

Technology	Target emerging contaminant	Removal efficiency	Note	Ref.
Multi-walled carbon nanotubes	Tetracycline antibiotics	253.38 mg/g^{-1}	CNTs were synthesized in the CH_4/H_2 mixture at 700 ^{0}C by a chemical vapor deposition method using Co-Mo particles as catalysts	[16]
3) Biodegradation				
Activated Sludge	Estrone 17β-Estradiol Estriol Estrone-3-Sulfate 17β-Ethinyl estradiol 4-Nonylphenol mono- and ethoxylated nonylphenol polyethoxylated nonylphenols	79% 0% 45% 36% 34% 0% 88% 66%	Aerobic and anaerobic WWTP in the UK	[17]
Soil Filtration	Estrogens 17β-Estradiol 17β-Ethinyl estradiol Triclosan Ibuprofen	26% 99% 27% 90% 18%	Aerobic	[18]
4) AOPs				
Photocatalyst ZnO rod in coupling with activated carbon fiber	Tetracycline	Removal capacity of over 99%	The initial concentration of 40 mg/L	[19]
N-Cu co-doped TiO_2@CNTs	Sulfamethoxazole	93% of COD and 89% of TOC	Sono-photocatalytic degradation eliminated within 180 min	[20]
UV/H_2O_2 treatment	Meprobamate Carbamazepine Dilantin Atenolol Primidone Trimethoprim	> 90%		[21]

(Continued)

on the properties of pore size, surface charge, hydrophobicity, oleophobicity, etc., of the membrane. Membrane technology can be classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), forward osmosis (FO), and reverse osmosis (RO). MF cannot remove contaminants with a size lower than 1μm; therefore, it is not capable of removing emerging contaminants. UF, NF, FO, and RO have smaller pore sizes than MF, and they have been used to remove emerging contaminants in water. When the pore size decreases, emerging contaminant removal efficiency improves significantly.

Due to pore blocking and pore restricting, membrane fouling may be the main obstacle to the application of the filtration process, which generally causes high costs for the operation and maintenance of the system.

ii) Adsorption

Similar to membrane technology, the adsorption process can transfer the contaminants from one phase (i.e., in water) to another phase (i.e., in solid), and it has been widely reported on for the removal of different emerging contaminants. Activated carbon (AC) is the most popular material for the conventional adsorption treatment of contaminants in water due to its high porosity and high surface area. AC can be made from different raw materials, such as wood and coconut shells AC's adsorption can be integrated with other treatment processes, such as UF, coagulation, and AOPs in order to improve the total removal capacity. Biochar is also an adsorption material that can be applied to emerging contaminants in water. Biochar is a charcoal-based material that is made by heating biomass via a pyrolysis process at high temperatures in conditions without oxygen. The feedstock for biochar synthesis may come from agriculture by-products such as straw, rice husk, and corn husk. Carbon nanotubes (CNTs) with very high surface area are also popular materials that can be applied to emerging water contaminants.

The structure of the adsorbent material plays a significant role in the process's efficiency, and it is required to count on the treatment parameter, such as pH and temperature, to achieve the best performance of the materials. Besides, the key disadvantage of this kind of material is related to the sustainability of the production process; scaling up can lead to high energy consumption, and the carbon footprint is too large to consider the biochar or AC as an effective material to treat environmental problems.

iii) Biodegradation

Depending on the type of pollutants, some biological processes can be applied in different conditions: aerobic and anaerobic. Activated sludge seems to be the most common, and other systems using biological filtration and membrane bioreactors have also been investigated. Removal levels can range from low to nearly complete removal, and biological processes may not eliminate some common biodegradable contaminants under any conditions. Another research direction developed recently is the combining of the biological process with the adsorption or electrical process.

It should be noted that the biggest disadvantage of this method is managing and treating the biosolid produced during and after application. Another area for improvement is the need for analytical methods to identify and quantify the compounds in a very complex matrix. However, it can also be an excellent opportunity for further research related to biodegradation for emerging contaminants in the water environment.

iv) AOPs

AOPs gained much attention from researchers because of their high capacity in the removal of pollutants in water as compared with other processes. Emerging contaminants in water can be treated using photocatalysis, UV photolysis, Fenton, sono-chemical oxidation, or ozone in combination with hydrogen peroxide. By the activities of free hydroxyl radicals (•OH), AOPs can help deal with complex and durable emerging pollutants when other processes seem not to work. AOPs are considered a highly effective, novel, and green process for environmental treatment in general and emerging contaminants in particular.

However, a gap exists when discussing AOPs, and it is about how to scale up the process and apply it to the industrial system.

1.1.3 MOFs as Exceptional Materials for Water Remediation

MOFs are porous structures prepared from metal ions and organic linkers or bridging ligands via the formation of coordination bonds. Recently, MOFs have been considered a promising material that can effectively deal with the issues related to water pollution due to (i) large surface area, (ii) stability in water, (iii) ease of functionalization, and (iv) capacity to produce on a large scale. Interestingly, MOFs can work as selective adsorbents, the catalytic material, and a combination of them. MOFs and the composite of MOFs with other components have been proven by several studies to successfully remove a wide range of contaminations, such as dye, PPCPs, pesticides, and herbicides [22–25].

The first research on MOF was published in 1995, opening a new direction for adsorption materials with a much better surface area, high porosity, and high accessibility to contact the adsorption site. MOFs also have advantageous properties compared to conventional porous materials because the porosity of MOFs can be turned through a reticular approach through inorganic nodes and organic linkers. MOFs are new for removing emerging contaminants in water, and there is an increased interest in it. The following sections of this chapter will discuss detailed strategies and examples for applying MOFs in water remediation.

1.2 MOFs Strategies in Water Remediation

Three important strategies related to MOFs have recently been applied to water remediation: (i) adsorption of emerging water contaminants by MOFs, (ii) catalytic oxidation of emerging water contaminants by MOFs, and (iii) a combination of adsorption and catalysis for the mitigation of emerging water contaminants by MOFs.

1.2.1 Adsorption

Compared to other water remediation technologies, which have many drawbacks such as low efficiency, high sludge production, and expensive disposal, adsorption is a popular, attractive, and versatile treatment method due to its effectiveness, economic benefits, simple and easy operation, and potential reversibility [26, 27]. Adsorption refers to the process in which molecular or ionic compounds in the liquid or gaseous phase are kept on the rigid surface of solids. Adsorption has been commonly used in environment-related fields such as sewage treatment and removal of toxic gases due to its low price and easy operation [28–31]. Various factors can strongly impact the efficiency of the adsorption process, including the fate and concentration of contaminants, the types and physicochemical characteristics of adsorbents, and operation parameters such as temperature, pH, and adsorption time. Some current adsorbents such as zeolite, silica, etc., face problems with slow adsorption rate and low adsorption capacity [32, 33]. Unlike these, MOFs possess a large surface area, high porosity, and varied pore properties, which makes it possible for them to become competitive adsorbents for the mitigation of different species such as organic dyes, heavy metals, PPCP, herbicides, pesticides, etc. [34–38]. For instance, Ji et al. developed a MOF-based carboxyl adsorbent (MIL-121) for the selective removal of Cu^{2+}, Pb^{2+}, and Ni^{2+} ions from aqueous solutions [39]. More than 99% of the heavy metals were removed from the water in the presence of co-existing 10 000 mg/L of Na^{+} ions. When applied to a real electroplating wastewater sample, the adsorbent could produce 3000 mL of clean water per gram material. Similarly, selective adsorption of Cr^{3+} in a solution containing other co-existing ions such as Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Cr^{3+} was reported on formic acid and amino-modified MOFs Form-UiO-66-NH_2 [40]. The modified MOFs were fabricated via formic acid modification and were used as adsorbents for selective adsorption of Cr^{6+}. After modification, the material exhibited a higher specific surface area (919 m^2/g), total pore volume (0.49 cm^3/g), and pore diameter (2.14 nm) than the unmodified material, whose specific surface area, total pore volume, and pore diameter were 879 m^2/g, 0.34 cm^3/g, and 1.86 nm, respectively. The good texture of Form-UiO-66-NH_2 enabled its outstanding Cr^{6+} adsorption capacity (338.98 mg/g), which was ten times higher than that of the unmodified MOFs [40].

The adsorption of Cr (VI) over MOFs was also reported by Valadi et al. [41]. In their study, they synthesized a variety of zirconium-based MOF and chitosan composites, namely MOF 808/chitosan, and used them as efficient adsorbents for homogenous adsorption of Cr (VI). The MOF 808/chitosan had the maximum adsorption capacity of 320 mg/g and could be reused after six successive adsorption cycles. For the remediation of Cu (II), Hg (II), As (III), and Pb (II), a magnetic Fe-BTC MOF composite was synthesized as an adsorbent by a solvothermal method [42]. The maximum adsorption capacity was found to be 55 mg/g, 57 mg/g, 147 mg/g, and 155 mg/g for Cu (II), As (III), Pb (II), and Hg (II), respectively. The Langmuir isotherm model was best fitted to the adsorption of Cu (II), Pb (II), and As (III), while the Temkin isotherm model was best fitted to that of Hg (II). The MOF composite also showed the selective adsorption of those heavy metals in their mixture.

In addition, many authors have reported using MOF-based materials as adsorbents for the removal of organic dyes. Ahmadijokani et al. used the zirconium-based MOF, namely UiO-66, to selectively adsorb different organic dyes, including cationic dyes (malachite green and methylene blue) and anionic dyes (methyl red and methyl orange) [43]. The adsorption capacities of UiO-66 for anionic dyes were higher than those for cationic dyes. The excellent adsorption capacities of UiO-66 were the consequences of its large specific surface area (1276 m^2/g) recorded on a gas adsorption system. In an attempt to control the specific surface area and charge of the MOF framework, Li et al. introduced a mixture of ligands containing 1,4-benzenedicarboxylic acid (BDC) and 1,2,4,5- benzenetetracarboxylic acid (BTC) with different stoichiometry in order to construct multivariate MOFs denoted as UiO-66-n$(COOH)_2$ MOFs ('n' represents the molar fraction of BTC, n = 0.25, 0.5, 0.75, 1.0) [44]. It can be deduced from their study that the decrease of specific surface area (from 1620 to 179 cm^3/g) and the zeta potential (from 36.11 to -29.78 mV) indicated that the surface charge of the zirconium-based MOFs changed from positively charged to negatively charged. Thereby, their adsorption behaviors toward interested dye molecules can be easily regulated.

While the pristine UiO-66 only showed its ability to adsorb anionic dyes, the multivariate MOFs could adsorb cationic dyes selectively. The adsorption selectivity of the MOFs was attributed to their high surface area and the electrostatic interaction between their charged surface and the dyes. With the introduction of Fe_3O_4 and covalent organic frameworks (COFs) to the structure of MOFs (M = Ti, Fe, Zr) via a facile solvothermal method, Wang et al. were able to fabricate magnetic and porous Fe_3O_4@MOF (M = Ti, Fe, Zr)@COFs hybrid composites with good recyclability for effective azo dye adsorption [45].

For the adsorptive removal of sewage containing a pharmaceutical-like sulfanilamide, Jia et al. developed a novel hierarchical porous starch-chitosan-UiO-66-COOH composite in which the UiO-66-COOH-type carboxylic zirconium metal-organic framework was nearly immobilized within porous starch using a one-pot chitosan-adhesive route [46]. Due to the high affinity between the Zr-O bond within UiO-66-COOH and the sulfonic atoms, sulfanilamide could adsorb on the composite. The adsorption obeyed the pseudo-second-order kinetic and Langmuir models and was considered homogeneous monolayer chemisorption.

By grafting UiO-66 into polymerized chitosan with the aid of epichlorohydrin as a linking agent, Chen et al. successfully prepared porous chitosan / UiO-66 composite foams [47]. The materials were successfully applied to the effective adsorption of ketoprofen. The maximum adsorption capacity of the porous chitosan / UiO-66 composite foams was 209.7 mg/g, which outweighed most reported adsorbents. Also, working on zirconium metal-organic frameworks, Zhao et al. could achieve a magnetic Zr-MOF structure by loading Fe_3O_4 nanoparticles on MOF-525 via a secondary-growth approach [48]. The material improved the removal of pharmaceuticals such as tetracycline and diclofenac sodium with maximum adsorption capacities of 745 and 277 mg/g for diclofenac sodium and tetracycline, respectively. Different kinds of interaction, such as hydrogen bonding, electrostatic interaction, π-π interaction and anion -π interaction, were found to be involved in the adsorption process. Similarly, electrostatic interaction, hydrogen bonding and π-π interaction also played major roles in the adsorption of two popular pharmaceuticals such as clofibric acid and carbamazepine on the rigid MIL-101(Cr) and flexible MIL-53(Cr) reported by Gao et al. [49].

When it comes to the removal of herbicides and pesticides by MOFs, several studies have reported them. For example, a recent study discussed the ability of a new hollow NiO/Co@C magnetic MOF to be used as a solid-phase extraction adsorbent for the effective adsorption of organic nitrogen pesticides [50]. The results showed that the hollow NiO/Co@C magnetic MOF is a promising candidate for water purification and removal of hazardous organic nitrogen pesticides. Moreover, the role of MIL-53 MOFs in the effective adsorption of metolachlor herbicide was emphasized in the study conducted by Hamza et al. [51].

In general, the physicochemical properties of MOFs determine their pollutant adsorption behavior. High porosity, surface area, selectivity, mechanical stability, and ease of functionalization are the critical features of MOFs [34]. The higher the surface area that MOFs have, the more adsorption sites they have. Their active sites and surface charge are tunable for the accumulation of a specific pollutant and can be functionalized by surface modification. The accumulation of various functional groups on the surface of MOFs and their unique structures make it possible for them to adsorb emerging pollutants effectively. The adsorption efficiency of MOFs can be enhanced by using large organic linkers, creating defects in MOF structures, introducing functionalities in metal nodes and the organic linkers, and fabricating various MOF-based composites [52]. Understanding the adsorption mechanism is pivotal because it enables us to design different MOF materials for future applications. Plausible adsorption mechanisms of emerging contaminants on MOFs are acid-based, hydrophobic, electrostatic, hydrogen bonding, or π-π interactions or a combination of these interactions.

1.2.2 Catalyst

Unlike adsorption, which only transfers pollutants from a solution to the surface of an adsorbent, requires costly posttreatment for the elimination of recalcitrant pollutants, and may cause toxic secondary pollutants, catalytic oxidation using various catalysts can completely degrade or convert water contaminants into biodegradable, less toxic, and benign substances. Recently, AOPs have received much interest in wastewater treatment due to their excellent reproducibility and simplicity [53].

In AOPs, the oxidative degradation is driven by free radicals such as $\bullet OH$, $O_2\bullet^-$, and/or $SO_4\bullet^-$, which have high oxidation power (e.g., 1.8–2.7 V for $^{\cdot}OH$, 2.5–3.1 V for $SO_4\bullet^-$) and can oxidize organic compounds to harmless and benign substances, such as CO_2 and H_2O, under appropriate conditions [53, 54]. AOPs include photocatalysis, Fenton reactions, Fenton-like reactions (electro-Fenton, photo-Fenton, and photo-electro-Fenton), and sulfate radical-based oxidations. Photocatalysis is the AOP in which photo-active materials or semiconductors such as ZnO, TiO_2, CdS, WO_3, etc., are used as homo- or heterogeneous photocatalysts and are capable of generating photo-induced charge carriers (electrons and holes) under irradiation of

UV or visible light [55]. Those charge carriers can then react with adsorbed O_2 and H_2O molecules on the catalyst's surface to generate $O_2\bullet^-$ and $\bullet OH$ radicals, respectively. Meanwhile, Fenton and Fenton-like processes refer to the AOPs in which ferrous ions catalyze the decomposition of H_2O_2 (Fe II) to generate $\bullet OH$ and peroxide radicals capable of oxidizing organic molecules [56].

In contrast, sulfate radical-based oxidations are alternative approaches to Fenton reactions and are driven by highly reactive sulfate radicals ($SO_4\bullet^-$) produced by successful activation of certain oxidants, such as persulfate (PS) and peroxymonosulfate (PMS), by UV, heat, alkaline pH, sonication, and transition metals. In the last decade, many studies have emphasized the role of MOFs as heterogeneous catalysts in different AOP reactions to remove emerging water contaminants. MOFs can act as semiconductors under light irradiation because their organic ligands can absorb light to activate their metal sites through a ligand-to-metal charge transfer mechanism [57]. For example, Khosroshahi et al. introduced the nanocomposites of MOF-808 and $NiFe_2O_4$ as photocatalysts for effective photocatalytic degradation of meropenem and photocatalytic reduction of Cr (VI). The synthesized materials have low bandgap energies and were active under visible light irradiation [58]. In another study, Khodkar et al. explored the photocatalytic degradation of paraquat, a popular herbicide for killing weeds in agriculture, using a magnetic MOF composite α-Fe_2O_3@MIL-101(Cr)@TiO_2 [59]. The effects of experimental parameters such as the dosage of catalyst, pH, the initial concentration of paraquat, and reaction time on the paraquat degradation efficiency were also investigated in their study. The results showed that the maximum photocatalytic degradation efficiency could reach 87.46% after 45 min under the optimal conditions: catalyst dosage = 0.2 g/L, pH = 7, and initial paraquat concentration = 20 mg/L [59].

Moreover, the role of MOFs as heterogeneous catalysts for the removal of emerging water contaminants was also found in studies of Fenton and Fenton-like processes. For example, in the study of an ultrasound-assisted heterogeneous Fenton system, Geng et al. provided new insights into the catalytic performance of environmentally friendly Fe-based MOFs (MIL-53, MIL-88B, and MIL-101) in the degradation of tetracycline hydrochloride, a universal therapeutic medicine [60]. The active coordination sites of metals of MOFs were responsible for their catalytic performance. MIL-88B showed the best catalytic performance owing to its great Lewis acid sites, representing the most coordinated active sites in the structure of MIL-88B [60]. Recently, in Ye et al.'s work, they have reported the role of Fe-bpydc MOF (bpydc is short for 2,2′-bipyridine-5,5′–dicarboxylate) as a highly active catalyst showing excellent catalytic performance in the heterogeneous photo-electro-Fenton degradation of the lipid regulator bezafibrate [61]. Its excellent catalytic performance can be explained by the enhanced mass transport and charge transfer, the reduction of H_2O_2 to $\bullet OH$ and of Fe (III) to Fe (II), and the excitation of Fe-O clusters. In addition, the use of MOFs as catalysts in sulfate radical-based oxidations has been known in the last decade. A recent study reported using B,N-doped carbocatalyst (Fe@BPC-XBN) as an effective peroxymonosulfate activator for bisphenol A degradation [62]. The catalyst was synthesized from the iron-based MOF, boric acid, and boron nitride, providing it with more catalytic centers and helping it improve its stability.

1.2.3 Synergistic Effect of Adsorption and Photocatalyst

Developing MOFs with desirable adsorption and catalytic degradation performance is another strategy for removing emerging water contaminants. This strategy is based on the fact that adsorption and catalysis are not independent. Obviously, the immobilization of the contaminants on the surface of MOFs is one of the requirements for their excellent catalytic performance. Therefore, combining adsorption and catalytic degradation of pollutants by MOFs will open the door to efficiently removing emerging water contaminants. For example, by using titanium metal-organic frameworks (Ti-MOFs) and COFs in combination with triazine frameworks through covalent bonding, Yang et al. were able to construct a composite material that has high adsorption capacity and good photocatalytic activity for the removal of bisphenol A (BPA) [63]. The efficient synergistic adsorption and degradation of BPA (100 ppm) by the covalent-integrated Ti-MOFs@COFs could be achieved within ten minutes, which is more preeminent than other materials.

Similarly, in another study, Zhao et al. introduced a series of nanosheet-structured manganese-carbon (MnO_x@C) composites obtained from the calcination of 2D manganese-1,4 benzenedicarboxylic acid-based MOFs under different temperatures [64]. The composites could adsorb and degrade 4-aminobenzoic acid ethyl ester (ABEE) through the PMS activation. The MnO_x@C calcined at 900 ^oC exhibited outstanding ABEE adsorption (27.0%) and degradation performance (91.3%).

1.3 Emerging Water Contaminants by MOFs

Recently, due to (i) large surface area, (ii) stability in water, (iii) ease of functionalization, and (iv) capacity to produce on a large scale, MOFs are widely utilized for the removal of pollutants in aqueous solutions.

1.3.1 Organic Dyes

In recent years, synthetic dyes have been widely utilized in medicine, printing and dyeing, and cosmetics industries due to the development of the dye industry. Therefore, a massive amount of dye wastewater was released into the environment. The dye wastewater composition is complex; most are refractory organic matter, high chroma, and continuous solid pollution. Nowadays, there is much-advanced research on the removal of organic dyes based on MOF materials. MOFs removed organic dyes through adsorption and the photocatalytic process.

1.3.2 Adsorption

PEI-modified Cu-BTC was used to adsorb congo red and acid blue with high concentrations (1200 and 100 mg/L^{-1}) [65]. The adsorption capacity for the two dyes mentioned above of PEI-modified Cu-BTC is 2578 and 132 mg/g, respectively. Not only does it have excellent processing efficiency, but the reusability of PEI-modified Cu-BTC is also highly effective, with the ability to be reused six times.

Li et al. successfully synthesized MIL-53 (Al) with the adding amine functional group and applied this material to adsorb methylene blue and malachite green [66]. The results showed that the removal capacity of MIL-53 (Al)-NH_2 was superior to that of MIL-53 (Al), while the adsorption capacity of MIL-53 (Al)-NH_2 for methylene blue and malachite green only reached 45.2 and 37.8 mg/g, respectively. In contrast, the adsorption capacity of MIL-53 (Al) is only 3.6 and 2.9 mg/g.

Hamedi et al. [67] successfully synthesized composite material MIL-101(Fe)@PDopa@Fe_3O_4 by solvothermal method and used it for the adsorption of two dyes: methyl red and malachite green. The results show that the processing ability of MIL-101(Fe)@PDopa@Fe_3O_4 is excellent, with high processing efficiency. Through experiments, the adsorption capacity of MIL-101(Fe)@PDopa@Fe_3O_4 for methyl red and malachite green was determined to be 833 and 1250 mg/g.

Activated carbon is a normal adsorbent used to treat common industrial colorants. The activated carbon-enhanced HKUST-1-MOF derived from copper salts is established by Azad et al. [68] with the treatment of 10 mg/L^{-1} of three dyes including crystal violet, disulfide blue, and quinoline yellow. At optimum values of pH 4, 0.02 g adsorbent was very effective with the adsorption capacity of Ac-HKUST-1 for respectively 133, 130, and 65 mg/g.

1.3.3 Photocatalytic and Electrostatic Activities

Wang et al. proposed a new carbon material—CQD—which was used to modify NH_2-MIL-125(Ti) [69]. The results show that the modified material has a smaller specific surface area than NH_2-MIL-125(Ti) ($198\ m^2/g < 478\ m^2/g$) but the visible light treatment efficiency for Rhodamine B of CQD/ NH_2-MIL-125(Ti) is better than that of NH_2-MIL-125(Ti). The reusability of the two materials is also remarkable, as the two materials can be reused seven times.

After adding the NH_2 group to enhance the electrostatic interaction in the framework, MOF-199-NH_2 was denatured with $BaWO_4$ [70]. UV-Vis measurement results show that the band gap of the modified material is smaller than that of MOF-199-NH_2 ($3eV < 3.2eV$). The band gap is reduced, so the photocatalytic ability of the modified material is also better than that of the original material ($98\% > 38\%$). Although the photocatalytic treatment results are positive, the light of the photocatalyst must be in the ultraviolet region.

1.3.4 PPCPs

PPCPs have attracted much attention from scientists as newly emerging water pollutants. These products mainly include analgesics, antibiotics, fungicides, etc. The amount of PPCPs has increased significantly every year due to human demand. PPCPs are persistent in bioaccumulation and toxicity and will release into the water many ways after use, causing severe environmental issues. Therefore, MOFs are considered safe and effective materials to degrade/remove PPCPs.

1.3.5 Adsorption

Cheng et al. [71] enhanced the sulfamethoxazole (SMX) adsorption rate of only ten minutes with a maximum adsorption capacity of up to 284.7 mg/g^{-1} by imprinting the molecular polymers (MIPs) on the surface of UIO-66. The received MIP-IL@ UiO-66 exposed superior identification toward SMX based on both π-π and/or electrostatic interactions, hydrogen bonds, and molecular structure. The material could be applied as a commercial solid-phase extraction (SPE) adsorbent when it can be cycled five times.

The metal-organic frameworks had high adsorption for tetracycline or/and norfloxacin based on the ferric fabricated benzenetricarboxylic (Fe-BTC) material [72]. The pollutant adsorption capacity in the isolation system for each antibiotic tetracycline and norfloxacin was 714.3 and 334.6 mg/g^{-1} and the effect of norfloxacin is significant in a binary system. The dominant adsorption mechanisms are coordination bond, π-π interaction most attributed to norfloxacin, and pore diffusion, an active site for tetracycline.

Fe_3O_4@Cd-MOF@CS microspheres were prepared through facile coating and applied to amoxicillin removal. The adsorbed microspheres showed the best removal efficiency at a pH of 8.1. The hydrogen bonding, electrostatic interaction, and π-π stacking were the three main factors for the adsorption of amoxicillin when the highest adsorption capacity was found at 103.09 mg/g^{-1}, respectively. After five reused cycles where the material was washed with 40% methanol solution, the Fe_3O_4@Cd-MOF@CS microspheres showed good amoxicillin removal efficiency with a slight change from 73.92% to 62.07% [73].

A composite of MIL101(Cr) combined with magnetite nanoparticles was successfully synthesized for the selective extraction of parabens (preservative) through an adsorption process reached from hydrogen bonding, hydrophobic, and π-π interactions. The synthesized composite showed good stability and accuracy and achieved high extraction recoveries [80–96%] [74].

Copper mixed-two multivariate triazole frameworks (CuMtz) [75] were fabricated employing a solid solution approach to use for the adsorption of triclosan (disinfectant). The material contains 22% doping ligand, giving the best adsorption capacity as 743.2 mg/g^{-1} even even after four reuses. The motivating force is the hydrogen bonding accompanied by the anion exchange under the basic environment between anionic and BF_4^- of copper precursor.

1.3.6 Photocatalytic Activities

In the modulation of Fe(II)-MOF using different organic acids, Chen et al. [76] indicated that citric acid can regulate the release rate of Fe through chelation and improve the degree of crystallinity and porosity. In comparison with adding other modulators, Fe(II)-MOF-CA showed ideal catalytic activity: the SMX degradation increased from 40.4% to achieve the highest rate of 91.7% within 120 min.

The extracted lecithin from the yolk was used as an auxiliary for $LiY(MoO_4)_2$ quantum dots bond to 1,3,5-Benzenetricarboxylic acid throughout the hydrothermal process. The formed $LiY(MoO_4)_2QD$/BioMOFs is an eco-friendly photocatalyst that has ibuprofen removal higher than 99% after one hour under UV irradiation. The morphology of $LiY(MoO_4)_2QD$/BioMOFs is coral-like with radius <10 nm, and it shows super-radiant photoluminescence (SRP) properties that can be utilized for drug delivery systems in anti-cancer drugs [77].

A novel photocatalyst material was synthesized by the hybridization of graphitic carbon nitride (g-C_3N_4) and titanium-MOF (NH_2-MIL-125) [78]. The synthesized material has a near band gap with the pristine MOF. At the same time, the reduced electron-holes recombination rate led to a higher photocatalytic performance that completed the removal of 10 mg/L^{-1} diclofenac in 2h under LED irradiation. The detected by-products include short-chain carboxylic acids, such as oxalic and formic acid, and chloride and nitrite give the primary avenue of the diclofenac degradation pathway.

1.3.7 Herbicides and Pesticides

Herbicides and pesticides are toxic chemicals widely used in agricultural crop production. However, due to its difficult biodegradability, the remaining herbicides and pesticides in the soil after use will move to the water environment, causing environmental problems [79]. Therefore, removing herbicides and pesticides by MOFs is a better choice for scientists. Herbicides and pesticides can be removed from the water environment via adsorption or photocatalysis.

1.3.8 Adsorption

HKUST-1(Cu) was a metal-organic framework efficiently synthesized at room temperature, similar to ZrO_2@HKUST-1, an easily composited material from HKUST-1. These two materials had large pore size and surface area, which makes both have better adsorption capacity for cyhalothrin. The results showed the adsorption capacity of HKUST-1(Cu) and ZrO_2@HKUST-1 for cyhalithrin was 140 and 138 mg/g after 120 min, respectively [80].

UiO-67(Zr) metal-organic framework was a popular metal-organic framework synthesized by many methods such as hydrothermal and solvothermal. With a large surface area, UiO-67(Zr) was a suitable material for the adsorption of herbicides. In 2018, UiO-67(Zr) was utilized for the removal of the herbicide atrazine and showed entirely satisfactory results with UiO-67(Zr), although the adsorption capacity of UiO-67(Zr) for atrazine was only 12 mg/g [81].

MIL-53(Cr) was evaluated to remove 2,4-dichlorophenoxyacetic acid (2,4-D) in the aqueous solution [82]. MIL-53(Cr) showed fast adsorption (within 1 h) with high adsorption capacity (556 mg/g), followed by its simple reusability by washing the used MOF with water/ethanol.

MIL-101(Cr) is a fairly common MOF material synthesized by the hydrothermal method. The MIL-101(Cr) was applied to adsorb diazinon with a treatment time of about 45 minutes. The adsorption capacity of the MIL-101(Cr) carbon metal frame is 158 mg/g [83]. In the other study, the modification of Cr-MIL-101 by 3,5-Bis (trifluoromethyl) phenyl isocyanate (BTP) metal-organic framework was fabricated to adsorb acetochlor with an adsorption capacity of 322 mg/g. Cr-MIL-101-BTP can treat acetochlor with high concentration and the regeneration ability is extremely promising, with the ability to be used six times [84].

An ionic liquid modified chitosan used to dominate with UiO-66 is also a promising composite material with an adsorption capacity up to 893 mg/g when applied to treat high concentrations of 2,4-dichlorophenoxyacetic acid (up to 500 mg/L^{-1}) for one hour [85]. H-bond and electrostatic interaction mechanisms explain why this has such a good adsorption capacity.

1.3.9 Photocatalytic Activities

Khodkar et al. used α-Fe_2O_3@ MIL-101(Cr) magnetic MOF to reduce bipyridine concentration in an aqueous medium [59]. Under strict control conditions on pH and dosage, the α-Fe_2O_3@ MIL-101(Cr) material had reduced only 45% of contaminants. The combination of pristine material with TiO_2 raised the efficiency of bipyridine removal up to 90% in the first solution with a concentration of 20 mg/L^{-1} [59].

MIL-100(Fe)@ZnO was obtained by Ahmad et al. [86] and fabricated for application as a photocatalyst to treat the herbicide atrazine. MIL-100(Fe)@ZnO synthesized by the solvothermal method had a specific surface area of 654 m^2/g and a band gap energy of 2.63 eV. Under visible light for 120 minutes, 79% of 20 mg/L^{-1} atrazine solution was reduced by the MIL-100(Fe)@ZnO material. The reusability of the material is also entirely satisfactory with five reuses, showing the material's potential.

Fe_3O_4@MOF-2 is a modified magnetic material developed by Sajjadi et al. for diazinon insecticide treatment application [87]. Under visible light, the photocatalytic ability of Fe_3O_4@MOF-2 was demonstrated through a treatment efficiency of up to 99% for 30 mg/L^{-1} of diazinon insecticide within 30 minutes. Not only that, the regenerative ability of this magnetic organic metal frame material is also surprising, with 15 reuse times.

Metal-organic frameworks can be synthesized relatively easily by conventional methods. In their study, Oladipo et al. [88] fabricated AgIO3/MIL-53(Fe) material under room temperature conditions. The AgIO3/MIL-53(Fe) material has a small band gap energy of 2.4 eV and is suitable for photocatalysts to treat malathion and chlorpyrifos. The results showed that, under sunlight, its ability to handle these two pesticides was excellent, reaching more than 90% efficiency with 120 minutes of lighting and a concentration of pesticide solution of 20 mg/L^{-1}.

Zr-MOF@WO_3/graphene oxide is also a metal-organic framework composite material with good photocatalytic ability [89]. Fakhri et al. [89] used this photocatalyst material to reduce the concentration of malathion in water. Within 70 minutes, under visible light, 20 mg/L^{-1} malathion solution was treated quite effectively with an efficiency of up to 83%. The Zr-MOF@WO_3/graphene oxide can be reused with four cycles.

1.3.10 Industrial Compounds/By-products

Various organic pollutants have also been removed from water by MOFs and MOF-based adsorbents or photocatalysts to form by-products or unharmful products [79, 90, 91].

1.3.11 Adsorption

A synthesized MOF-177 had a BET surface area of 2970 m^2/g applied to the adsorption of VOCs compounds. The main results showed the adsorbed amount of benzene was 800 mg/g^{-1} and toluene was 585 mg/g^{-1}. Even at high humidity, the water became the competitor, but the adsorption capacity was still relatively high. However, MOF-177 could be pre-drying to avoid the decomposition of the MOF-177 framework structure [79].

The industrial surfactant perfluorooctane sulfonate (PFOS) has been removed with an adsorption capacity reaching 939 mg/g^{-1} at acidic pH using a novel MOF-808 metal-organic framework. This material has a high specific surface area of 1610 m^2/g with good pore size and abundant active adsorption sites that offer stability in solution under different pH conditions for 7 days. The PFOS adsorption recorded was an endothermic and spontaneous process that related to the electrostatic interaction between the cationic central cluster $((Zr_6O_4(OH)_4)^{12+})$ of MOF-808 and PFOS anion [90].

1.3.12 Photocatalytic Activities

The bi-functional composite $Bi_{12}O_{17}Cl_{12}$/MIL-100(Fe) (BM200) was synthesized to explore the degradation of bisphenol A (BPA). Under white-light irradiation, the photodegradation of BPA reached 100% after 60 min with the addition of persulfate. The BPA was degraded by $\cdot SO_4^-$ and ·OH radicals to form intermediate products such as short-chain aliphatic acids and mineralized products of CO_2 and H_2O [91].

1.4 Challenges and Perspective in Using MOFs for the Removal of Emerging Water Contaminants

Facing contaminants has become one of the main issues of the last few decades, and MOFs, as a new group of porous materials with several advantages over conventional adsorbents, are the outstanding candidate to help humans deal with these related issues. The potential applications using MOFs have been broadened recently for all types of environments, which prominently include emerging water contaminants [92–94]. However, stability under different conditions is a crucial challenge when being discussed in relation to MOFs. Most MOFs are water-labile or unstable at different levels due to water molecules' gradual replacement of metal-coordinated linkers. Thus, many efforts have been made to improve this issue. For example, selecting MOF constituents is a feasible approach to fabricating water-stable MOFs via de novo synthesis [95, 96]. Besides de novo synthesis, many postsynthetic methods have been researched to improve the water stability of MOFs: functional group modification, ion-exchange, hydrophobic surface treatment, and material compositization[97, 98]. Another issue is that many MOFs are built up from toxic metals such as cobalt, cadmium, chromium, and/or noxious organic moieties – even molecules that are themselves considered emerging pollutants that can be released to the environment. Choosing safe components to make greener materials is also a priority that needs to be considered to deal with issues such as toxicity, life cycle assessment studies, cost-effectiveness. Further, the behavior of MOFs as adsorbents, catalysts, or synergetics is still under discussion.

Overall, there is no doubt that MOFs are a great porous material that can effectively be applied to remove emerging water pollutants. The ability to control pore size and nature, access mesoporosity, utilize reticular chemistry, and incorporate active sites in porous compounds as per demand has resulted in MOFs commanding research interest across other areas as well.

1.5 Conclusion

Recently, a group of emerging contaminants has been recognized as significant water pollutants that adversely affect human and wildlife endocrine systems. Natural attenuation and conventional treatment processes cannot remove these micropollutants, which are reported to bioaccumulate in macroinvertebrates, other organisms in the aquatic food web, and humans. With high surface area, stability, and modular composition, MOFs are a potential candidate for environmental treatment in general and emerging water contaminants (organic dyes, PPCPs, herbicides, and pesticides). For the long-term outlook, MOFs have recently been one of the most attractive research directions. The challenges and perspectives in this field illustrate this material's increased interest and vast future.

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