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Review

Removal of contaminants of emerging concern by metal-organic framework nanoadsorbents: A review

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HIGHLIGHTS

- Removal of contaminants of emerging concern by MOF nanoadsorbents was comprehensively reviewed.
- Comprehensively information was provided for applications of MOF nanoadsorbents in water industry.
- Areas of future research for the removal of various contaminants in MOF nanoadsorbents were suggested.

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ABSTRACT

Over the last two decades, various contaminants of emerging concern (CECs), such as endocrine disrupting compounds, along with pharmaceuticals and personal care products (PPCPs), have been of interest to the water industry because of their incomplete removal during the typical water and wastewater treatment processes. Recently, the potential environmental applications of metal-organic frameworks (MOFs) and MOF-based nanoadsorbents (MOF-NAs) have been widely studied. In particular, the use of these nanoadsorbents for CECs in water and wastewater treatment processes has been a rapidly growing area of interest in the recent literature due to their unique physicochemical properties. Therefore, it is necessary to understand the adsorption phenomena of various CECs by MOF-NAs, particularly because the physicochemical properties of various CECs create unique challenges for the removal of these compounds from water. In addition, the adsorption of CECs on MOF-NAs is significantly influenced by the physicochemical properties of the MOF-NAs and the water quality conditions. Therefore, this review provides a comprehensive assessment of recent studies on the removal of various CECs (*e.g.*, analgesics, antibiotics, antiepileptics, antiseptics, and etc.) with different physicochemical properties by various MOF-NAs under various water quality conditions (*e.g.*, pH, background ions/ionic strength, natural organic matter, and temperature). In addition, this review briefly discusses the recent literature on the synthesis of MOF-NAs, regeneration of MOF-NAs, and removal of CECs during water and wastewater treatment processes.

1. Introduction

Over the last two decades, various contaminants of emerging concern (CECs), such as endocrine-disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs), have been a major issue in the water industry [1,2]. Numerous CECs, including analgesics, antibiotics, antiepileptics, antiseptics, hormones, plasticizers, stimulants, and sunscreens, have frequently been detected in wastewater treatment plant effluents, indicating that these micropollutants are inadequately removed during the typical wastewater treatment processes [3]. Although some difficulty exists in explicitly defining the term "EDCs," exogenous agents that inhibit the behavior of natural hormones in the body are generally classified as EDCs by the United States Environmental Protection Agency [4]. Stumm-Zollinger

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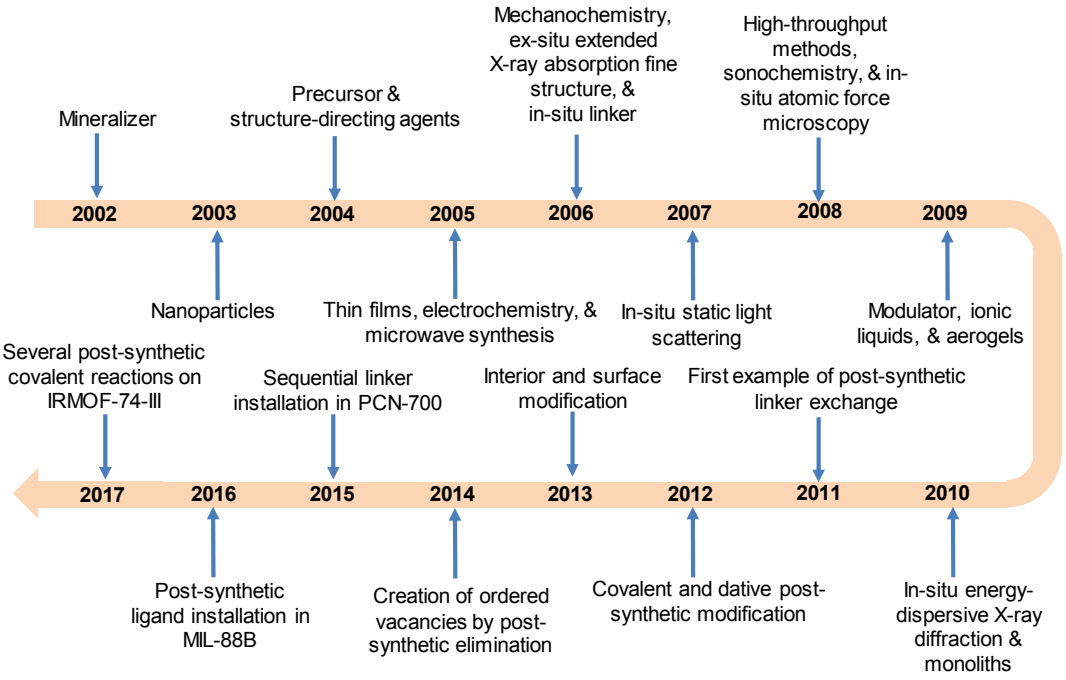

Fig. 1. Historical developments in the synthesis of various MOFs modified from [51,54].

and Fair (1965) and Tabak and Bunch (1970) raised the first alarms regarding the possible adverse effects of various pharmaceuticals in municipal wastewater [1,5–9].

Numerous studies have examined the fate and transport of EDCs and PPCPs in water and wastewater treatment processes because several of these compounds have been detected in drinking water sources and wastewater effluents [3,10–19]. The fate and transport of EDCs and PPCPs vary greatly depending on the treatment processes that are used, including coagulation-flocculation-sedimentation-filtration [20,21], activated carbon treatment [22], ozonation [23], chlorination [24], sonodegradation [25,26], and biodegradation [27,28]. Among these commonly used technologies, adsorption is typically considered the most promising method for drinking water and wastewater treatment due to its adaptability, extensive applicability, and cost-effectiveness [29]. While granular or powdered activated carbon is commonly used in water and wastewater treatment, relatively new adsorbents such as carbon nanotubes, graphenes or graphene-based adsorbents, and metal-organic frameworks (MOFs) have been investigated recently for the removal of EDCs/PPCPs [30–32].

MOFs are an emerging class of porous materials fabricated from metal-containing nodes and organic linkers [33]. Over the past two decades, several hundred different MOFs have been studied for different applications, including gas purification, gas separation, gas storage, energy storage, and environmental applications (*e.g.*, adsorption, membrane preparation, and catalysis) [34–38]. Particularly in the environmental area, MOFs and MOF-based nanoadsorbents (MOF-NAs), such as Zr-benzenedicarboxylate (UiO-66), Zr-biphenyldicarboxylate (UiO-67), metal-benzenetricarboxylate (MIL-100; metal = Fe^{3+}, Cr^{3+}, or Al^{3+}), metal-benzenetricarboxylate (MIL-96; metal = Al^{3+}, Cr^{3+}, Ga^{3+}, or In^{3+}), Zn-2-methylimidazolate (ZIF-8), MIL-101-graphene oxide (GO), UiO-67/GO, Fe_3O_4@MIL-100(Fe), and urea-MIL-101(Cr), have been widely studied for the removal of various EDCs and PPCPs in water [37,39–44]. In addition, due to the unique physicochemical properties of MOF-NAs, the use of these nanoadsorbents for EDCs and PPCPs in water and wastewater treatment processes has been an area of rapidly growing interest in the recent literature. While a few recent review studies have documented the removal of organics and heavy metals using various MOFs [45,46], it remains critical to develop an understanding of the adsorption phenomena of various EDCs and PPCPs by MOF-NAs because their physicochemical properties create unique challenges for the removal of these compounds in water. In particular, it is essential to develop an understanding of the mechanisms of removal, such as by electrostatic interactions, metal effects, acid-base interactions, π- π interactions, and H-bonding. Additionally, the adsorption of EDCs and PPCPs on MOF-NAs is significantly influenced by the physicochemical properties of the compounds (*e.g.*, size/shape, hydrophobicity, functional group, and charge), as well as the physicochemical properties of the adsorbent itself (*e.g.*, surface area, hydrophobicity, charge, and functional group) and water quality properties (*e.g.*, pH, temperature, solute concentration, natural organic matter (NOM), and background anions/cations). It is very important to understand the problems that we have been faced for the potential use of MOF-NAs in the adsorptive removal of various EDCs and PPCPs from aqueous systems.

Therefore, the primary goal of this review is to provide a comprehensive assessment of the removal of various EDCs and PPCPs that have different physicochemical properties by various MOF-NAs under different water quality conditions. To accomplish this goal, this review briefly surveys recent literature on the synthesis of MOFs, regeneration of MOF-NAs, and removal of EDCs and PPCPs during water and wastewater treatment processes.

2. Synthesis of MOFs

Tomic (1965) first introduced materials that have metal–organic polymers or supramolecular structures, which are currently called MOFs [47]; however, the term “MOF” was widely disseminated by Yaghi et al. in 1995 [48]. Detailed historical developments in the synthesis of MOFs are described in Fig. 1. Since both nonflexible and flexible porous MOFs (*i.e.*, MIL-47 and MIL-53) were first reported in 2002 [49,50], studies have shown that the synthesis of MOFs coupled with functionalization (*i.e.*, post-synthetic modification) may be an effective and practical tool for the modification of their structure and other properties [51]. Bi- and trivalent aromatic carboxylic acids have already been employed for fabrication of frameworks with Al, Fe, Ni, U, Th, and Zn, resulting in interesting features, such as high metal content and thermal stability [52]. For various applications, the main purpose of MOF fabrication is to determine the optimal synthesis conditions to

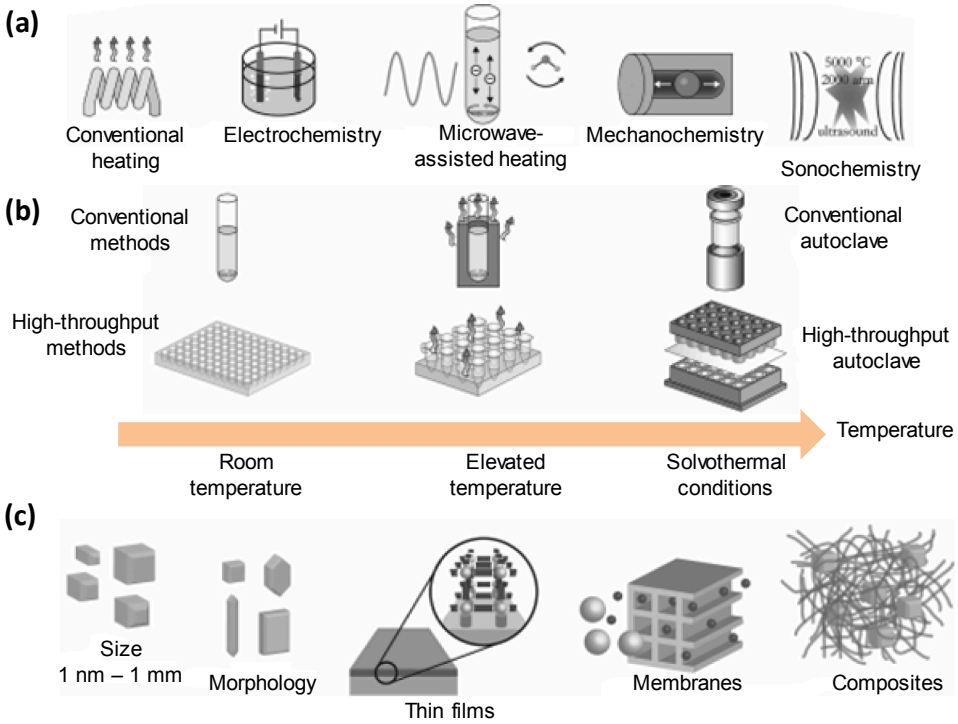

Fig. 2. Overview of (a) synthesis methods, (b) possible reaction temperatures, and (c) final reaction products in MOF synthesis. Reproduced with permission from Ref. [54], © American Chemistry Society 2011.

result in distinct inorganic building blocks without decay of the organic linker, while the kinetics of crystallization must be suitable to permit nucleation and growth of the desired phase [53]. Fig. 2 provides an overview of synthesis methods (*e.g.*, conventional heating, electrochemistry, microwave-assisted heating, mechanochemistry, and sonochemistry), possible reaction temperatures (*e.g.*, room temperature, elevated temperatures, and solvothermal conditions), and final reaction products (*e.g.*, thin films, membranes, and composites) of MOF synthesis based on the various synthesis methods that have been applied in the last two decades [54]. While conventional synthesis includes reactions associated with conventional electric heating, excluding any parallelization of reactions, the two temperature ranges that include the solvothermal and non-solvothermal are generally distinguished from these [55]. Solvothermal reactions occur above the boiling point of the solvent at autogenous pressure in closed vessels, whereas non-solvothermal reactions take place below the boiling point of the solvent at room or elevated temperatures [56].

Systematic examination of the synthesis of MOFs is important because the properties of MOFs are greatly influenced by the synthetic methods employed. Detailed descriptions of these synthetic methods have been published previously [51,54]. Briefly, a high-throughput method was first employed in the late 1990s for zeolites using solvothermal synthesis [57]. This method is a powerful tool that enables the use of solvothermal synthesis to accelerate the discovery of new MOFs and to enhance synthesis procedures [58]. Optimal conditions by which new compounds are fabricated can be determined by time-resolved examination of MOF crystallization, which can be used to detect crystalline intermediates, determine reaction parameters (*i.e.*, reaction rate constants and activation energies), and provide insight into the mechanisms of crystallization [59]. Different measurement methods are used in *ex situ* and *in situ* studies of MOF crystallization: Extended X-ray absorption fine structure, electron spray ionization-mass spectrometry, and X-ray powder diffraction are commonly used for *ex situ* studies, whereas energy-dispersive X-ray diffraction, atomic force microscopy, small-angle X-ray scattering, wide-angle X-ray scattering, static light scattering, and surface plasmon resonance are commonly employed for *in situ* studies [54]. The degree of MOF crystallization varies depending on the *ex situ* and *in situ* methods. In the *ex situ* method, the reaction is allowed to proceed for limited time intervals, which can result in changes in the composition of the sample and non-reliable outcomes; however, this method is advantageous because it can be conducted in a laboratory using relatively easy and uncomplicated methods [60]. In the *in situ* method, specific equipment and synchrotron radiation are often required to monitor the reactions continuously; however, this results in relatively better time-resolution data [61]. Overall, it is important to examine the mode of synthesis when comparing results because different methods of synthesis can affect the adsorption properties of MOFs.

3. Removal of CECs in conventional and advanced wastewater and water treatment processes

3.1. Removal in wastewater treatment processes

Numerous studies have described the occurrence of various EDCs and PPCPs at different stages during wastewater treatment processes, which implies that the effectiveness of the removal of these micro-contaminants is significantly influenced by the physicochemical properties of the contaminants (*e.g.*, p*K*a, functional groups, and hydrophilicity) and the type of wastewater treatment method employed (*e.g.*, methods involving biological treatment, dilution of wastewater effluent or combined sewer overflow, or variations in rainfall or temperature) [62–64]. However, it is difficult to determine the exact transport and fate mechanisms of various EDCs and PPCPs during the processes of biodegradation (anaerobic/anoxic/aerobic), sorption to sludge, or oxidative degradation by chlorine or ozone [3]. Ryu *et al.* found that the approximate degradation rates of four antibiotics during wastewater treatment processes were as follows: triclocarban (85%) > sulfamethoxazole (70%) ≥ triclosan (65%) > trimethoprim (20%) [3]. Different degradation mechanisms can be employed. For example, for triclocarban and triclosan, sorption to sludge is a main method of degradation due to the relatively high hydrophobicity of these compounds

(log K_{OW} = 4.90 and 4.76, respectively) [65], whereas biodegradation of these chemicals is relatively difficult [66]. During the degradation processes, some degree of removal may also result from oxidation of these compounds by chlorine [23]. In particular, relatively high removal efficiency was observed for hydrophilic sulfamethoxazole (log K_{OW} = 0.89), probably due to the oxidation of the compound during chlorination [67]. However, hydrophilic trimethoprim (log K_{OW} = 0.91) demonstrated a very low degree of removal due to its low biodegradability [68] and limited adsorption to sludge [69], whereas oxidation by chlorine may have an insignificant influence [23].

The removal efficiencies of analgesics and anti-inflammatories can be elucidated by investigating the various mechanisms by which they are degraded, such as biodegradation, sorption to sludge, and oxidation [3]. Diclofenac was significantly removed during chlorination [70] but exhibited minimal biodegradability and adsorption to sludge [71,72]. A separate study revealed that compounds such as diclofenac, sulfamethoxazole, and trimethoprim, which contain primary or secondary amines, can be significantly oxidized by chlorine, which mainly occurs when the amines form heterocyclic ring structures [23]. In addition, chlorine was found to enhance naproxen removal, whereas removal of ibuprofen was relatively insignificant, presumably due to the electron-capturing functional group on its aromatic ring [23]. High concentrations of artificial sweeteners (sucralose and acesulfame) were detected in raw wastewater at levels of approximately 5300 and 3900 ng/L, respectively, and relatively low removal of these compounds (< 25%) was achieved during wastewater treatment processes [3]. Similarly, it was found that degradation of these compounds through both aerobic and anaerobic biological processes was insignificant [73,74]. Sucralose and acesulfame also appeared to be poorly oxidized by chlorine under typical wastewater treatment plant operating conditions and demonstrated negligible partition coefficients in activated sludge due to their high hydrophilicity (log K_{OW} = −1.00 for sucralose and −1.33 for acesulfame) [3]. Table 1 describes the degree of removal for selected CECs in wastewater treatment plants under dry-weather conditions using a representative sample of the existing literature regarding biodegradability, along with trends concerning adsorption to sludge and oxidation by chlorination.

3.2. Removal in water treatment processes

The majority of the population of the United States (approximately 95%) has access to drinking water from community water systems that employ conventional water treatment processes (coagulation-flocculation, sedimentation, filtration, and disinfection) [75]. However, numerous studies focusing on various CECs, such as EDCs, PPCPs, herbicides, pesticides, and polyaromatic hydrocarbons, have shown that conventional processes can remove these compounds at only minimal levels [1,76]. The potential fate and transport of EDCs/PPCPs in conventional drinking water treatment processes are described in Fig. 3. Aluminum- or iron-based salts are commonly used to precipitate compounds as metal hydroxides during the chemical coagulation processes used in drinking water treatment. Westerhoff et al. reported that 26 of 28 EDCs and PPCPs exhibited < 20% removal during coagulation using aluminum sulfate, whereas slightly more removal (> 20%) was achieved for herbicides, pesticides, and polyaromatic hydrocarbons (10 of 25 compounds) [23]. This is presumably because the compounds with higher removal efficiencies are considered relatively hydrophobic (based on their log octanol-water partition coefficients; log K_{OW} = 2.16–6.13) and partitioned either onto particulate matter or onto precipitated solids that contained adsorbed NOM during removal.

Adsorption with activated carbon has been widely used to remove various organic and inorganic contaminants in aqueous solutions [77].

Table 1
Removal efficiencies of selected CECs at wastewater treatment plant under dry weather conditions with examples of previously published literature related to biodegradability, tendency of adsorption to sludge, and tendency of oxidation by chlorination.

Compound	Use	MW (g/mol)	pK_a[b]	Log K_{OW}[c]	Inf. (ng/L)	Eff. (ng/L)	Rem. (%)	Bio.	Ads.	Oxi.	Ref.
Acesulfame	Sugar substitute	201.2	2.0	−1.33	3863	3705	4	L	L	L	[73]^{B,A}; [161]^{O}
Atrazine	Herbicide	215.1	< 2 (1.6)	2.61	ND	ND	NA	L	M	L	[162]^{B,A}; [163]^{O}
Atenolol	Oral beta blocker	266.3	9.6	−0.03	1040	529	49	M	L	L	[164]^{B,A}; [144]^{O}
Benzophenone	Ultraviolet blocker	182.2	< 2	3.18	88	47	47	L	M	L	[165]^{B}; [166]^{A}; [167]^{O}
Benzotriazole	Heterocyclic	119.2	8.2	1.44	88	47	47	M	L	L	[168]^{B,A}; [169]^{O}
Caffeine	Stimulant	194.2	6.1	−0.07	8810	236	97	H	H	M	[162]^{B}; [170]^{A}; [23]^{O}
Carbamazepine	Analgesic	236.3	< 2	2.45	188	156	17	L	L	H	[171]^{B}; [72]^{A}; [23]^{O}
DEET	Insect repellent	191.3	< 2	2.18	47	46	2	M	L	L	[162]^{B,A}; [23]^{O}
Diltiazem	Calcium channel blockers	414.5	12.9	2.79	ND	ND	NA	M	M	L	[172]^{B}; [170]^{A}; [144]^{O}
Diclofenac	Arthritis	318.1	(4.2)	0.7	6897	359	95	L	L	H	[71]^{B}; [72]^{A}; [23]^{O}
Diphenhy dramine	Antihistamine	255.5	9.0	3.27	171	142	17	L	M	NF	[173]^{B}; [65]^{A}
E1	Steroid	270.4	10.3	3.13	ND	ND	NA	H	M	H	[162]^{B,A}; [23]^{O}
Gemfibrozil	Anticholesterol	250.2	4.7	4.72	45	33	27	H	M	H	[162]^{B,A}; [23]^{O}
Ibuprofen	Analgesic	206.1	4.5 (4.9)	3.97	2724	241	91	H	M	M	[174]^{B}; [72]^{A}; [163]^{O}
Iohexol	Contrast agent	821. 1	11.7	−3.05	14,432	16,008	−11	L	L	L	[175]^{B,A}
Iopamidol	Contrast agent	777.1	10.7	−2.42	8518	10,091	−18	L	L	NF	[175]^{B,A}
Iopromide	Contrast agent	790.9	< 2 and > 13	−2.10	11,133	12,895	−16	L	L	L	[162]^{B,A}; [163]^{O}
Meprobamate	Anti-anxiety	218.3	< 2	0.70	ND	ND	NA	M	L	L	[162]^{B,A}; [163]^{O}
Naproxen	Analgesic	230.1	4.5 (4.2)	3.18	5113	482	91	M	M	H	[162]^{B}; [65]^{A}; [163]^{O}
Primidone	Anticonvulsant	218.3	11.5	0.73	100	40	60	M	L	H	[176]^{B}; [177]^{A}; [144]^{O}
Propylparaben	Preservative	180.2	8.5	3.04	520	7	99	H	H	H	[165]^{B,A}; [178]^{O}
Simazine	Herbicide	201.7	1.62	2.18	ND	ND	NA	H	M	M	[164]^{B,A}; [179]^{O}
Sucralose	Sweetener	397.6	NA	−1.00	5289	4043	24	L	L	L	[74]^{B,A,O}
Sulfamethoxazole	Antibiotic	253.1	2.1 & < 2 (5.7)	0.89	400	117	71	L	H	H	[162]^{B,A}; [23]^{O}
TCEP	Fire retardant	285.5	NA	1.44	439	348	21	L	M	L	[180]^{B,A}; [162]^{A}; [163]^{O}
Triclocarban	Antibiotic	315.6	NA	4.90	198	33	83	L	H	NF	[66]^{B}; [65]^{A}
Triclosan	Antibiotic	289.6	8 (7.9)	4.76	190	63	67	L	H	H	[162]^{B,A}; [23]^{O}
Trimethoprim	Antibiotic	290.1	6.3, 4.0, < 2 (7.1)	0.91	150	118	21	L	L	H	[68]^{B}; [69]^{A}; [23]^{O}

Source: Modified from [3].
Inf. = influent; Eff. = effluent; Rem. = overall removal; Bio. = biodegradation (^{B}); Ads. = adsorption to sludge (^{A}); Oxi. = oxidation by chlorine (^{O}); Ref. = references; H = high; M = medium; L = low; ND = not determined because under detection limit (ND values = 15 ng/L for E1, 50 ng/L for diltiazem, 5 ng/L for atrazine, 1.5 ng/L for simazine, and 0.5 ng/L for meprobamate) ; NA = not available or not applicable; NF = not found.

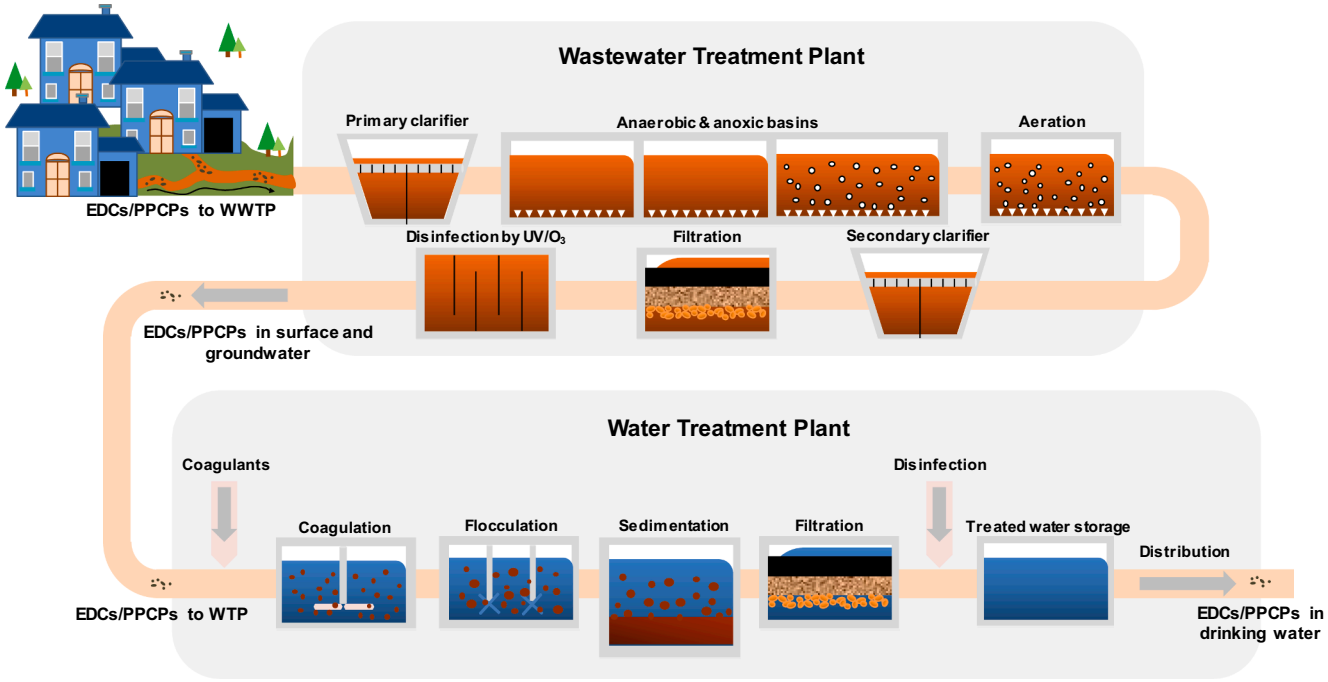

Fig. 3. Possible fate and removal of EDCs and PPCPs in conventional wastewater treatment and drinking water treatment processes modified from [160].

Activated carbon treatment is a cost-effective process, and activated carbon is a popular adsorbent for water treatment due to its strong interactions, particularly with hydrophobic organic contaminants. However, the physicochemical properties of activated carbon, including its pore size, shape, and charge, prevent the adsorption of large molecules [78]. Jung et al. showed that the degree of adsorption of three EDCs and four active pharmaceutical compounds was in the following order: ibuprofen > EE2 > atrazine > bisphenol A > carbamazepine > sulfamethoxazole > diclofenac; this order is presumably due to varying degrees of competitive adsorption, particularly based on π–π bonding and hydro-bonding interactions in the mixture [79]. A separate study conducted a linear regression analysis to assess the adsorption of 22 EDCs and PPCPs by a commercially available powdered activated carbon, arriving at the following equation: [percentage removal] = 15 × [log K_{OW}] + 27% (n = 22; R^2 = 0.88) [23]. Overall, the findings implied that protonated bases are substantially removed by powdered activated carbon, whereas EDCs and PPCPs with relatively low log K_{OW} values or deprotonated acid functional groups were the most challenging to remove with powdered activated carbon.

Membrane processes such as forward osmosis, reverse osmosis, nanofiltration, and ultrafiltration have been widely used in water and wastewater treatment processes [80–83]. However, the removal of EDCs and PPCPs using these membranes varies depending on their physicochemical properties (*e.g.*, solute size/shape, pK_a, and hydrophilicity), water quality conditions (*e.g.*, pH, temperature, background anions/cations, and NOM), and membrane properties (*e.g.*, membrane pore size/density, porosity, charge, hydrophobicity) [84]. Heo et al. reported the removal of several selected organic compounds by forward osmosis: sulfamethoxazole (65–90%) ≈ carbamazepine (65–85%) > > atrazine (35–50%) > 4-chloraphenol (30–40%) > phenol (20%) [85]. The forward osmosis process uses an osmotic pressure difference produced by a concentrated draw solution to transport water from a feed solution to the draw solution through a membrane [86]. Conversely, reverse osmosis, nanofiltration, and ultrafiltration processes use hydraulic pressure difference as the main driving force to permeate water through a semipermeable membrane [87]. Removal by reverse osmosis exhibited different retention trends compared to those observed with forward osmosis for selected organic compounds, as follows: 4-chloraphenol (94%) > EE2 (90%) > > phenol (70%) > atrazine (55%) > carbamazepine (32%) > > sulfamethoxazole (6.2%) [85]. In a separate study, removal of neutrally charged carbamazepine (p*K*a = 2.3) by two nanofiltration membranes (NF-90 and NF-270) was fairly constant because removal is governed completely by steric exclusion in the absence of charged functional groups [88]. The removal of seven different pharmaceuticals using an ultrafiltration membrane was relatively low (< 50%) in a pilot-scale municipal wastewater reclamation system, although the findings indicated that molecular weight, log D, and the charge of the molecules were key factors influencing their retention [89].

In drinking water treatment systems, the addition of free chlorine and ozone causes oxidation of reduced metals and organic compounds, as well as the inactivation of microorganisms [90,91]. In addition, the presence of nucleophilic sites (*e.g.*, carbon-carbon double bonds), the electron density degree of functional groups, and the amount of protonation influence the reactivity of organic matter with these oxidants [92]. For instance, free chlorine reacts quickly with phenolic compounds, primarily through the reaction between hypochlorous acid and the deprotonated phenolate anion, which causes repeated addition of chlorine to the aromatic ring, followed by ring cleavage [93]. This reactivity of the phenolic functional group is likely the mechanism of the oxidation that occurs during chlorination of various estrogenic hormones that contain phenolic moieties (*e.g.*, ethynylestradiol, estriol, estradiol, and estrone) [94]. Of approximately 60 EDCs and PPCPs, the concentrations of some residual EDCs and PPCPs (*e.g.*, sulfamethoxazole, diclofenac, estradiol, ethynylestradiol, estriol, naproxen, estrone, acetaminophen, oxybenzone, triclosan, and several polyaromatic hydrocarbons) were below the detection limit of 10 ng/L, demonstrating a high degree of oxidation with chlorine, whereas ozone had much stronger oxidation reactivity with these compounds [23]. In particular, steroids containing phenolic moieties (*e.g.*, estradiol, ethynylestradiol, and estrone) were oxidized more effectively by ozone compared to those without benzene or phenolic moieties (*e.g.*, androstenedione, progesterone, and testosterone). This is presumably because the OH functional groups lose electrons to the benzene rings, which leads to increased reactivity with ozone compared to non-aromatic ring structures or conjugated bonds with COOH functional groups [95]. Table 2 summarizes the expected performances of various technologies used in

Table 2
Unit processes and operations used for CEC removal.

Group	Classification	AC	BAC	MOFs/MOF-NAs	O_3/AOPs	UV	Cl_2/ClO_2	Coagulation/flocculation	Softening/metal oxides	NF	RO	Degradation {B/P/AS}*
EDCs	Pesticides	E	E	F - E	L - E	E	P - E	P	G	G	E	E {P}
	Industrial chemicals	E	E	F - E	F - G	E	P	P - L	P - L	E	E	G - E {B}
	Steroids	E	E	F - E	E	E	E	P	P - L	G	E	L - E {B}
	Metals	G	G	F - E	P	P	P	F - G	F - G	G	E	P {B}, E {AS}
	Inorganics	P - L	F	F - E	P	P	P	P	G	G	E	P - L
PhACs	Antibiotics	F - G	E	F - E	L - E	F - G	P - G	P - L	P - L	E	E	E {B}G - E {P}
	Antidepressants	G - E	G - E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	G - E
	Anti-inflammatories	E	G - E	F - E	E	E	P - F	P	P - L	G - E	E	E {B}
	Lipid regulators	E	E	F - E	E	F - G	P - F	P	P - L	G - E	E	P {B}
	X-Ray contrast media	G - E	G - E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	E {B and P}
	Psychiatric control	G - E	G - E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	G - E
PCPs	Synthetic scents	G - E	G - E	F - E	L - E	E	P - F	P - L	P - L	G - E	E	E {B}
	Sunscreens	G - E	G - E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	G - E
	Antimicrobials	G - E	G - E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	F {P}
	Surfactants/detergents	E	E	F - E	F - G	F - G	P	P - L	P - L	E	E	L - E {B}

Source: Modified from [76].
PhACs = pharmaceuticals; PCPs = personal care products; BAC = biological activated carbon; AOPs = advanced oxidation processes; UV = ultraviolet NF = nanofiltration; RO = reverse osmosis; *B = biodegradation, P = photodegradation (solar); E = excellent (> 90%), G = good (70–90%), F = fair (40–70%), L = low (20–40%), P = poor (< 20%).

both water and wastewater treatment plants based on literature reports characterizing particular classes of compounds or their similarities to other EDCs and PPCPs that have been investigated in detail (See Table 3).

4. Removal mechanisms of various CECs by MOF-NAs

4.1. Removal influenced by the adsorption properties of MOF-NAs

4.1.1. MOF-NA properties

The physicochemical properties of MOF-NAs can significantly influence removal of EDCs and PPCPs [96–98]. The porosity structure of MOF-NAs is one of the main factors affecting the adsorption performance, particularly when no specific adsorption mechanism exists, excluding van der Waals interactions [99]. For example, a Cu–benzene-1,3,5-tricarboxylic acid-cotton composite was reported to have a high sorption capacity for ethion insecticide due to the accessible binding sites on the cellulose in the composite [96], which are particularly associated with chemical interactions and physical adsorption. Two factors may contribute to this effect. First, the physical adsorption can be significant because the pores of Cu–benzene-1,3,5-tricarboxylic acid may act as binding sites for the target molecules. Second, the anticipated chemical interactions between the solute and the composite may occur by H-bonding between cellulose functional groups and the oxygen of ethion. In a separate study, nitrogen-doped porous carbons were prepared from MOF (ZIP-8) combined with ionic liquid via a ship-in-bottle method [100]. While ionic liquid@MOF-derived carbons are less porous than MOF-derived carbons, the ionic liquid@MOF-derived carbons showed better adsorption performance than the MOF-derived carbons. This finding indicates that ionic liquid loading in ZIF-8 combined with the increased nitrogen content of carbonaceous materials significantly influences adsorption. Fig. 4 illustrates a plausible adsorption mechanism for six different compounds (atrazine, dibenzothiophene, sodium diclofenac, diuron, indole, and quinoline) over ionic liquid@MOF-derived carbons. Of three different major forms of doped nitrogen on the surface of the material (N-6, N-5, or N-Q) [101], N-6 and N-5, which are primarily observed at the edge of the graphite sheet, are the most chemically active nitrogen sites [102]. In addition, H-bonding and acid-base interactions readily occur at the N-6 and N-5 nitrogen sites due to basic and H-bonding functionality [103].

Pyrolysis temperature was found to be a significant factor influencing the porosity, surface area, and pore volume of MOF-derived carbons. For example, highly porous MOF-derived carbons at 1000 °C (total pore volume = 1.32 cm^3/g) showed approximately 2.5 times higher porosity than that of the pristine MOF (ZIF-8; total pore volume = 0.51 cm^3/g) employed to fabricate it, and thus the adsorption capacity of MOF-derived carbons was almost twenty times greater than that of the pristine ZIF-8 for the pharmaceutical compound sulfamethoxazole [104]. Three MOFs (ZIF-8, UiO-66, and UiO-67) that have different properties showed different adsorptive removal trends for atrazine [105]. The removal efficiencies of atrazine aqueous solution at pH 6.9 using the MOFs were as follows (mg atrazine/g adsorbent): UiO-67 (11.0) > ZIF-8 (6.78) > UiO-66 (2.57). These findings can be explained by their pore size, pore volume, and surface area: the higher adsorption capacity of UiO-67 is presumably due to its larger total pore volume (1.249 cm^3/g) and surface area (2345 m^2/g) than those of ZIF-8 (0.714 cm^3/g and 1875 m^2/g, respectively) and UiO-66 (0.656 cm^3/g and 1640 m^2/g, respectively). The relatively small pore size of UiO-66 compared to that of UiO-67 may make it difficult for atrazine to access its pores, and while ZIF-8 also has relatively small pore size, almost all atrazine is still removed by ZIF-8, presumably due to the relatively high hydrophobic attraction between the hydrophobic ZIF-8 [106] and atrazine (log K_{OW} = 2.67). However, the less hydrophobic UiO-66 does not enable effective adsorption of atrazine from aqueous solution even by surface interactions [107].

The adsorption performance for several CECs was compared between metal-azolate frameworks, porous carbon-derived metal-azolate frameworks, and commercial activated carbon [98]. The findings for the CECs revealed that adsorption values on these adsorbents were partly reliant on the adsorbents' surface areas when few specific interaction sites existed. Overall, the porous carbon-derived metal-azolate frameworks had greater adsorption capacities than did the metal-azolate frameworks. This was presumably because adsorption over metal-azolate frameworks occurs mainly due to simple filling resulting from hydrophobic interactions, π-π interactions, and van der Waals interactions [108]. However, additional mechanisms, such as electrostatic attraction, acid-base interactions, and H-bonding, which occur in porous carbon-derived metal-azolate frameworks, could enhance adsorption [109]. Moreover, further study of the detailed mechanisms is necessary due to the complex chemistry of adsorption and the numerous functional groups of different CECs [45].

Table 3
Summary of the removal of selected CECs by MOFs and MOF-NAs.

CEC class	Adsorbent	Surface area (m^2/g)	Co (mg/L)	q_m(mg/g)	Main finding	Ref.
Analgesics						
Diclofenac	CDM6-K1000	3123	50	503	The porosity and pore size of the carbons derived from metal azolate framework-6 increased remarkably on adding KOH before pyrolysis.	[142]
	UiO-66	NA	20	189	The adsorptive removal of Alizarin Red S. from aqueous solutions has a record adsorption capacity of 400 mg/g in acidic conditions.	[40]
	UiO-66	902	1–50	189	The functionalization of UiO-66 with SO_3H groups resulted in an increase of approximately 40% in the diclofena adsorption capacity.	[145]
	SO_3H-UiO-66	910		263		
Ibuprofen	CDM6-K1000	3123	50	408	The adsorption of ibuprofen could be explained by van der Waals and hydrophobic interactions.	[142]
Ketoprofen	MIL-101-$(OH)_3$	1838	50	80	H-bonding is a plausible interaction mechanism for adsorption.	[151]
Ketorolac tromethamine	UiO-66	1139	10–100	833	The adsorption process obeys the pseudo-second order kinetic model and could be fitted with the Langmuir isotherm.	[181]
Naproxen	MIL-101	3014	10–50	132	Lower solution pH is proved to be more favorable for the adsorption of naproxen over MIL-101.	[37]
	MIL-100-Fe	1492		115		
	MIL-101	3014	10–18	131	The adsorption of naproxen over ED-MIL-101 was shown to be less favorable at both low and high pH conditions, due to protonation and deprotonation of the adsorbents & adsorbates, respectively.	[182]
	AMSA-MIL-101	2322		93		
	ED-MIL-101	2555		154		
	MIL-101	3066	10–50	112	The adsorbent could be easily regenerated after adsorption of NAP by ethanol treatment without severe degradation.	[43]
	MIL-101-GO	3259		155		
	MIL-101	3030	100	114	The MIL-101s with –OH and $–NH_2$ groups were effective for naproxen adsorption, while MIL-101-NO_2 was very poor at adsorption.	[141]
	MIL-101-OH	2170		185		
Antibiotics						
Chloramphenicol	PCN-222	2917	5–110	370	The finding indicates that H-bond and electrostatic interaction as well as the special pore structure of PCN-222 can play positive effect on the adsorption.	[183]
Ciprofloxacin	MIL-101/Fe_3O_4	764	1–15	80.7	The increasing temperature caused a decrease in both adsorption and desorption efficiencies.	[97]
	ZIP-8 derived carbons	750	10	417	The adsorption rate of ciprofloxacin on the MOF can be satisfactorily fitted by pseudo-second-order kinetic model.	[124]
	ZIF-67 derived hollow Co_3S_4	NA	10	472	The hollow Co_3S_4 could be efficiently regenerated and reused for Ciprofloxacin adsorption over five recycle steps.	[41]
	MOF-235(Fe)	974	250	217	The sorption kinetics of CIP by Fe_3O_4@MIL-100(Fe) was found to fit the Elovich model and the pseudo-second-order model, indicating that sorption is both chemisorption and physical adsorption.	[42]
	MIL-100(Fe)	2800		303		
	Fe_3O_4@MOF-235(Fe)	NA		256		
	Fe_3O_4@MIL-100(Fe)	NA		322		
Doxycycline	MIL-35(Fe)/Fe_3O_4	75.5	20–300	477	Regeneration of the used adsorbent was performed for six regeneration cycles and the regenerated adsorbent retained most of its initial capacity.	[184]
Gatifloxacin	PCN-224	1,900	300	1233 (298 K) 1163 (308 K) 892 (328 K)	This result suggested that electrostatic competition occurs and plays a certain role during adsorption.	[120]
Nitroimidazole	Urea-MIL-101(Cr)	1970	10	185 (dimetridazole) 188 (metronidazole)	The adsorption mechanism was suggested as H-bonding between the $-NO_2$ of the nitroimidazole antibiotics and $-NH_2$ of the modified MOFs.	[44]
Oxytetracycline	ZIF-8	1745	10–40	28.3	The highest removal rate of 60% for the 10 mg/L concentration was reached after 200 min.	[185]
	MIL-101	3588	10–80	149	The adsorption of oxytetracycline over ethylenediamine -MIL-101 is favorable at the pH values located in a range of 4–10 due to the favorable electrostatic interaction.	[186]
	Ethylenediamine-MIL-101	1834		455		
Sulfachloropyridazine	HKUST-1	1700	20–40	365 (298 K) 429 (308 K) 501 (328 K)	Electrostatic interactions, π–π interactions, and hydrogen bonding, are the main factors in sulfachloropyridazine removal.	[113]

(*continued on next page*)

Table 3 (*continued*)

CEC class	Adsorbent	Surface area (m^2/g)	Co (mg/L)	q_m(mg/g)	Main finding	Ref.
	Activated UiO-66	1155	5–45	403 (298 K) 339 (308 K) 312 (328 K)	The pH effect on adsorption showed that the contribution from electrostatic interactions is accounting for only 20%.	[159]
Sulfamethoxazole	ZIF-8 ZIF-8 derived carbons	968 1855	100	22 435	Pyrolysis temperature was found to exert a significant effect on the characteristics of the prepared MOF-derived carbons, particularly the porosity.	[104]
	MOF-5 derived carbons	1731	10–100	625	The surface area and pore structure of carbonaceous adsorbents should be of particular importance in removal of contaminants from aqueous solution.	[187]
Tetracycline	UiO-66	592	10–100	23.1 (298 K) 31.0 (308 K) 46.4 (318 K)	The adsorption behaviors of tetracycline on UiO-66 were studied with adsorption isotherms/dynamics, the effect of temperature, solution pH, humic acid and cations, as well as the competitive adsorption.	[130]
	MIL-53 MWCNT/MIL-53(Fe)	137 60.2	1–200	298 364	The adsorption mechanisms were also ascribed to pore/size-selective adsorption and influence of framework metal ions in adsorption.	[188]
Antiepileptics						
Carbamazepine	UiO-67	1640 2344	0.2–5	18.9[c]	Carbamazepine adsorption was found to be independent of pH, indicating that the electrostatic interaction is a dominant removal mechanism.	[39]
	UiO-66	592	10–100	37.2 (298 K) 42.2 (308 K) 60.1 (318 K)	The characterization of UiO-66 before/after adsorption of carbamazepine indicate that the adsorption on UiO-66 is mainly a physisorption.	[130]
Antiseptics						
Triclosan	MIL-53(Al) MIL-53(Al)-1	1030 1270	50	447 488	The adsorption of the both adsorbents showed favorable stability under different water chemistry; pH (4–9) and ionic strength (up to 40 mM).	[158]
	IL@AIPCP	2084	10–50	326	The efficiency of the recycled adsorbent for triclosan adsorption did not diminish severely with an increasing number of recycles.	[189]
	UiO-66-NH-CO-COOH	762	10–50	402	The remarkable adsorption over UiO-66-NH-CO-COOH can be explained in terms of H-bonding.	[116]
Perchlorate	Amino sulfonic acid-Cu-4,4′-bipyridyl	NA	100	134	The thermodynamic parameters, negative values of Gibbs free energy and enthalpy, indicated the spontaneous and exothermic nature of the process	[131]
	$Cu_2(4,4'\text{-bipy})_2(O_3SCH_2CH_2SO_3)$		100	120	The perchlorate ions preliminarily gathered on the surface of MOFs, and then exchanged with sulfonic acid group within interlayer.	[121]
Pesticides/herbicides/insecticides						
Atrazine	Ionic liqid@ZIF-8 derived carbons ZIF-8 derived carbons	1421 1889	20	208 168	The pyridinic (N-6) or pyrrolic (N-5) nitrogen content of ionic liqid@ZIF-8 derived carbon increased with increasing the introduced ionic liqid content in MOF (before pyrolysis) or decreasing the pyrolysis temperature.	[100]
	UiO-66 UiO-67 ZIF-8	1640 2345 1875	2–25	1.71–2.69 10.04–11.87 6.19–6.78	Regenerated UiO-67 maintained most of its atrazine adsorption capacity after the third use.	[105]
2,4-dichlorophenoxy-acetic acid	MIL-53	1434	25–150	556	The reusability of MIL-53, after simple washing of the used MOF with water/ethanol, for the adsorption of 2,4-dichlorophenoxy acetic acid was also noticeable.	[190]
Diuron	Ionic liqid@ZIF-8 Ionic liqid@ZIF-8 derived carbons	1889 1468	10–20	224 284	The remarkable adsorption capacity with faster adsorption kinetics may be explained by H-bonding with minor contributions from hydrophobic and π - π interactions.	[136]
Ethion	Cu-BTC@cotton	NA	25–125	3.21 (cotton) 10.4 (5% Cu-BTC@cotton) 12.8 (10% Cu-BTC@cotton)	Feasibility studies of ethion adsorption onto composite suggest that binding sites of composite represented in reactive groups and Cu of cellulose and MOF, respectively, bound ethion via sulfur.	[96]
Glufosinate	UiO-67	2172	5–68	537	The abundant active adsorbent anchorages, high specific surface area as well as the adequate pore size, lead to the remarkably enhanced adsorption capacities.	[107]

(*continued on next page*)

Table 3 (*continued*)

CEC class	Adsorbent	Surface area (m^2/g)	Co (mg/L)	q_m(mg/g)	Main finding	Ref.
Glyphosate	NH_2-MIL-101(Cr)	NA	5–300	64.3	The structural and electrical properties change of functional MOFs could meet specific requirements, which plays an important role in practice.	[191]
	UiO-67/GO	NA	40	483	The dominant mechanisms of glyphosate adsorption mechanism are verified to form surface/inner-complexation with functional groups ofUiO-67/GO.	[137]
Mecoprop	UiO-66	982	20–170	370	The reusability of UiO-66, after simple washing of the used MOF with water/ethanol, for the adsorption of MCPP was also confirmed.	[147]
Plasticizer						
Bisphenol A	Bio-MOF-1-derived porous carbons	1078–1365	100	390–710	Hydrophobic and π-π interactions also play an important role in bisphenol A adsorption, especially at pH > pKa.	[132]
	MOF-5 derived carbons	1731	10–100	757	The important contribution of electrostatic interaction in the adsorption of bisphenol A on the adsorbent.	[187]
Stimulant						
Caffeine	UiO-66	1391	500–3000	24.3	The adsorption of caffeine was significantly influenced by the properties of adsorbents including pore volume, pore diameter, and surface area.	[192]
	UiO-66-NH_2	973		14.4		
	MIL-125-NH_2	1484		11.1		
Sunscreen						
Oxybenzone	MAFs-4 to 6 CDMs-4 to 6	938–1642	10–50	65–440	H-bonding (H-donors mainly from adsorbates) was proposed as the principal mechanism for the adsorption over me azolate framework-6 derived carbons.	[98]
Sweetener						
Saccharin	MDC-4h	1502	10–50	93.3	MDC-6h is the most remarkable adsorbent for saccharin due to its high concentration of functional groups, especially phenolic groups.	[193]
	MDC-6h	1525		99.2		
	MDC-12h	1610		94.5		
	MIL-101	3030	10	53.4	Third, the very favorable adsorption over urea-MIL-101 and melamine-MIL-101 could be explained by H-bonding, and the direction of the H-bonding.	[38]
	Urea-MIL-101	1970		86.4		
	Meamine-MIL-101	1350		70.1		
	O_2N-MIL-101	1620		18.7		

C_o = EDC/PPCP initial concentration; NA = not available; q_m = maximum sorption capacity; ^cK_F = capacity factor (μg/g)/(m^3/mg) for the Freundlich model; CDM6-K1000, MAFs-4 to 6, and CDMs-4 to 6 = metal azolate framework-6-derived porous carbon; ZIF-8 = Zn-[2-methylimidazolate] frameworks; IL@AIPCP = ionic liquid-loaded Al-based porous coordination polymers; MDC = metal azolate framework-6 derived porous carbons; MWCNT = multi-walled carbon nanotube; GO = graphene oxide.

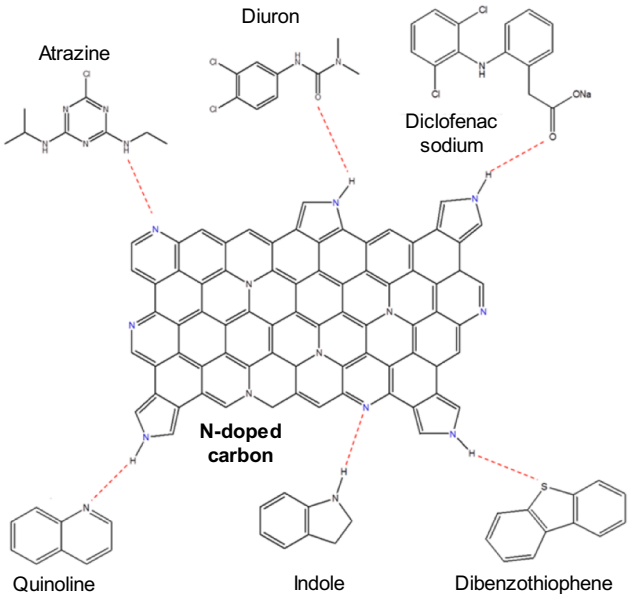

Fig. 4. Plausible adsorption mechanism of the six adsorbates over ionic liquid@MOF-derived carbons through H-bonding (dotted lines). Reproduced with permission from Ref. [100] © American Chemistry Society 2017.

4.1.2. Environmental parameters that influence MOF-NA adsorption properties

4.1.2.1. Influence of pH. One of the most important parameters that affects adsorption capacity is solution pH, because both inorganic/organic speciation and adsorbent surface functional groups vary depending on solution pH [110]. Adsorption of sulfamethoxazole on porous MOF-derived carbons varies within a wide range of pH values, from 2 to 12 [104], which can be explained by the electrostatic interactions between the solute and adsorbent (pH point of zero charge, pH_{pzc} = 4.9) [46]. At pH < 1.6, the sulfamethoxazole is positively charged, whereas at pH > 5.7 it is negatively charged due to its two pK_a values associated with the protonated $–NH_3^+$ and acidic NH groups [111]. Therefore, at pH > 5.7, where the acidic –NH group of the sulfamethoxazole molecule becomes deprotonated, electrostatic repulsion is expected because, at pH > 4.9, the surface charge of the adsorbent also becomes negative [104]. In a separate study, the adsorption of atrazine on different MOFs was found to be insignificantly influenced by solution pH, because the electrostatic interactions that occur between the MOFs and the neutral form of atrazine are negligible (i.e., the neutral form is dominant over the protonate form in water) [112]. A copper-based MOF demonstrated varying adsorption trends for sulfonamide antibiotics under different pH conditions [113]. Sulfonamide exists in cationic and neutral forms at pH < 5.5 and in an anionic form at pH > 5.5 due to its pK_a value of 5.5 [114], whereas the copper-based MOF is positively charged at pH < 4 and negatively charged at pH > 4 [115]. In general, the adsorption capacity of the copper-based MOF decreased with increasing solution pH (ranging from 3.5 to 11.5). The highest adsorption was achieved at pH 3.5, at which a cationic form of sulfonamide is more likely to be dominant based on the protonation of heterocyclic nitrogen (in the strongest basic form of the sulfonamide molecule, sulfonamide$^+$). Therefore, the greater adsorption capacity of sulfonamide at this pH is due mainly to electrostatic attraction associated with H-bonding and π-π interactions [113].

Sarker et al. reported that triclosan adsorption was significantly influenced by carboxylic-acid-functionalized UiO-66-NH_2 at different pH conditions in aqueous solutions [116]. Of various adsorption mechanisms, such as electrostatic interactions, acid-base interactions, coordination, π-π interactions, and hydrophobic interactions, electrostatic interactions were irrelevant as a possible main mechanism at pH < 8.1. The adsorption of triclosan is expected to be very low because triclosan is neutral under this pH condition, and thus no electrostatic interactions could occur with any species. However, a relatively high adsorption capacity (approximately 120–140 mg/g) was achieved at pH 2–8, mainly due to H-bonding interactions between triclosan and the functionalized MOF, which had positive ($–NH_2^+$) and negative ($–COO^-$) ions in its structure [116]. The adsorption capacity for triclosan increased with increasing pH from 2 to 8 and decreased rapidly with further increases in solution pH (from 8 to 12). Thus, the H-bond interactions might occur between triclosan (H-bond donor = H of the phenolic group) and the MOF (H-bond acceptor = O and N species). The increase in adsorption capacity with increasing pH (from 2 to 8) could be because the ability of the $–NH_2^+$–CO-COO^- group to act as an H-bond acceptor is greater than that of $–NH_2^+$–CO–COOH. While the H-bond accepting ability of –NH–CO–COO^- (i.e., the group produced on the MOF at a high pH) is high, no hydrogen (H-bond donor) is present on the phenolic group of triclosan at pH > 8.1 due to deprotonation [116].

It should be noted that the choice of pH during adsorption from water might result in severe degradation of certain MOF structures, sometimes to the point of complete destruction or transformation of the original phase and resulting in loss of most if not all adsorption capacity. For instance, Bezverkhyy et al. found that the structural stability of iron-containing MOFs, MIL-100(Fe) and MIL-53(Fe) that were synthesized under fluoride-free conditions is severely degraded when these materials are exposed to water and the pH was brought to neutral using buffer solutions [117]. This process yields hydrated iron oxide species and, therefore, a structural collapse in both MOFs. In general, the check for stability of a specific MOF to acidic or alkaline conditions should be considered paramount prior to considering it effective for water purification. In acidic conditions, the degradation may be driven by competition of a proton and a metal ion for the coordination with the ligand, while in alkaline conditions decomposition may take place due to replacement of linkers by hydroxide [118]. This should be considered guidance and not certainty since there are other factors that may inhibit these processes to take place. In fact, there are several ways to improve stability of MOFs under certain pH conditions, some even capable of eliminating any detrimental effects on the structure [119].

4.1.2.2. Influence of background ions and ionic strength. Porous carbon derived from metal azolate framework-6 demonstrated various degrees of adsorption for different CECs, such as bisphenol-A, clofibric acid, sodium diclofenac, oxybenzone, and salicylic acid [98]. The presence of background ions (NaCl, 0–40 mM) had almost no effect on the adsorption of these CECs by the MOF, indicating that the MOF would be usable in the presence of various salts. Chen *et al.* reported the effects of ionic strength based on NaCl on the adsorption of the antibiotic gatifloxacin on Zr(IV)-based porphyrinic MOFs [120]. The adsorption was found to be enhanced with increasing NaCl concentration (from 0 to 0.75 mol/L). This increase is presumably due to the decrease in gatifloxacin solubility by the salting out effect, which may impel the diffusion of gatifloxacin onto the hydrophobic surface of the MOF and increase the adsorption capacity. However, different results were observed for the removal of ciprofloxacin by ZIF-67-derived hollow $C_{O3}S_4$, particularly in the presence of $CaCl_2$ [41]. The adsorption capacity of ciprofloxacin decreased from 118 to 83.2 mg/g and 118 to 18.6 mg/g with increasing NaCl and $CaCl_2$ concentrations (0–1 mol/L), respectively. This finding is presumed to be attributed to the competition of Na^+ or Ca^{2+} with ciprofloxacin for the active adsorptive sites, while the presence of salt also negatively influenced electrostatic interactions for adsorption between ciprofloxacin and the MOF [41].

Zhang et al. employed two-tailed cationic MOFs (*i.e.*, α,β-ethanebbbdisulfonic-Cu-(4,4′-bipy)$_2$ and sulfamic-Cu-(4,4′-bipy)$_2$) to remove ClO_4^- in the presence of co-existing anions in aqueous solution

[121]. For the removal of ClO_4^-, two potential mechanisms were investigated: electrostatic attraction and ion exchange. SO_3H groups on these MOFs were found to act as selective anion displacers in solutions containing ClO_4^- and/or PO_4^{3-}, and the receptors exhibited favorable selection of tetrahedron oxoanions. Therefore, the MOFs were capable of trapping both ClO_4^- and PO_4^{3-} due to interactions with the cationic MOFs and exchange with SO_4^{2-} groups. Anions with properties comparable to SO_3H groups can be removed using cationic MOFs. These findings are consistent with previous research for the removal of arsenic by MOFs, in which the mechanism of removal was found to operate primarily due to electrostatic interactions and ion-exchange [122]. Additionally, the free-energy change (ΔG^0) of ClO_4^- was lower than the ΔG^0 values of PO_4^{3-} and the mixture of ClO_4^- and PO_4^{3-}, which also indicates that ClO_4^- may be more favorably adsorbed onto MOFs than PO_4^{3-} and the mixture of ClO_4^- and PO_4^{3-}. Although as an anionic species, SO_4^{2-} has similar physicochemical properties to those of ClO_4^- and PO_4^{3-}, the R-SO_4, which is the main functional group of the MOFs, may create difficulties for the direct swap of ClO_4^- and PO_4^{3-} with SO_4^{2-} [121].

4.1.2.3. Influence of NOM. Various types of NOM are found widely in natural water and wastewater at different levels. It is therefore necessary to evaluate the effects of NOM on the removal of CECs by MOF-NAs. Liang et al. examined the effects of humic acid (0–30 mg/L) on ciprofloxacin removal by ZIF-67-derived hollow $C_{O3}S_4$ at an initial concentration of 10 mg/L at pH 7 [41]. The results revealed that the adsorption capacity of the MOF-NA for ciprofloxacin was barely influenced by the presence of humic acid, whereas the presence of humic acid decreased adsorption for the removal of ciprofloxacin by a magnetic carbon composite [123]. Nanoporous carbons derived from carbonization of zeolitic imidazolate framework-8 were employed to remove ciprofloxacin in the presence of humic acid in water [124]. The results did not support the original assumption that adsorption of ciprofloxacin would decrease in the presence of humic acid due to competition between ciprofloxacin and humic acid for the adsorption sites of the MOF-NA. The findings instead revealed that adsorption of ciprofloxacin on the MOF-NA was enhanced as humic acid concentration increased (from 0 to 5 mg/L), and then remained nearly constant at high humic acid levels (5–40 mg/L), presumably due to various interactions between humic acid, ciprofloxacin, and MOF. The initial enhancement in the degree of adsorption may be due to adsorption of humic acid on MOF-NA carbon materials [125], which may provide additional adsorption sites by creating hydrogen bonds between multiple hydroxyl groups and the amine of ciprofloxacin. However, due to the limitation of the adsorption capacity of carbon materials for humic acid [126], the additional increase in humic acid concentration would be unfavorable to the adsorption behavior of the MOF-NA, particularly under the more neutral pH condition (pH 6) [124].

4.1.2.4. Influence of temperature. Thermodynamic assessments in terms of ΔG^0, the standard enthalpy change (ΔH^0), and the standard entropy change (ΔS^0) provide detailed information on the internal energy variations associated with adsorption [127]. A copper-based MOF was reported to demonstrate different adsorption capacities for sulfonamide at varying solution temperatures [113]. In that study, a linear relationship was observed between ln ΔG^0 and 1/temperature for the ΔH^0 and ΔS^0 calculations at various temperatures (from 298 to 318 K), indicating that the positive ΔH^0 (4.0 kJ/mol) and ΔS^0 (110.3 J/mol·K) values imply an endothermic process and increased randomness for the adsorption of sulfonamide, respectively. Additionally, the ΔH^0 and ΔS^0 values imply negligible desorption of pre-adsorbed H_2O molecules [128]. This finding also provides support for the presence of unsaturated metal sites in the copper-based MOF that occur as a result of the removal of H_2O molecules [129]. Chen et al. observed that the adsorption capacities of both carbamazepine and tetracycline hydrochloride increase with increasing temperature, indicating that endothermic reactions are dominant for the process of adsorption [130]. During the adsorption process of ClO_4^- onto the cationic MOF, the negative value of ΔH^0 (−38.2 kJ/mol) indicated that the adsorption on MOF is exothermic, while the negative entropy change ΔS^0 (−0.113 J/mol·K) indicated that the free energy was reduced at the solid-solution interface throughout the adsorption process [131]. In addition, the decreasingly negative ΔG^0 values (from −6.29 to −1.67 kJ/mol) with increasing temperature (from 283 to 323 K) indicate that the adsorption is unfavorable at high temperatures and occurs spontaneously.

4.2. Removal of selected CECs by MOF-NAs

4.2.1. Edcs

4.2.1.1. Bisphenols. Bisphenol A is an EDC. Bhadra et al. synthesized Bio-MOF-1-derived carbons that were employed as an adsorbent to remove bisphenol A [132]. The adsorption results implied that an important parameter in the adsorption of bisphenol A is the porosity or surface area of the adsorbent. Electrostatic interactions may be minimal between neutral bisphenol A at pH < its pK_a and Bio-MOF-1-derived carbons (pH_{pzc} = 4.3) [104]. H-bonding interactions may be the applicable adsorption mechanism, because the Bio-MOF-1-derived carbons have some acidic functional groups, as well as N-containing basic groups, and bisphenol A has two –OH groups, providing H-bond donors and acceptors [133]. Two findings support the conclusion that the H atom of the phenol group of Bio-MOF-1-derived carbons also acts as an H donor for the oxygen atom of bisphenol A at pH < 9.6: the variation in the total concentrations of nitrogen and oxygen between different Bio-MOF-1-derived carbons was minimal, even when the adsorption rates were very different; and the phenol groups of both bisphenol A and the MOF should be similar in terms of chemical properties [132].

4.2.1.2. Pesticides and herbicides. Organophosphate pesticides are commonly used to control various pests in different crops by preventing acetyl cholinesterase enzyme activity [134]. Several billion United States dollars are spent every year on these types of pesticides, indicating that an enormous quantity of pesticide is used [135]. Over 97% of ethion (an insecticide, maximum adsorption capacity = 182 mg/g) was removed by adsorption to the stable and readily recyclable Cu–benzene-1,3,5-tricarboxylic acid that was effectively composited with cotton materials [96]. Sarker et al. employed ion liquid@ZIF-8 adsorbent to remove two herbicides (diuron and 2,4-dichlorophenoxyacetic acid (2,4-D)) [136]. Their removal phenomena were described as having occurred mainly through the mechanism of H-bonding. While electrostatic attraction was considered a factor in the removal, the influence of these interactions appeared to be minimal based on their properties (ion liquid@ZIF-8, pH_{pzc} = approximately 3.0; 2,4-D, pK_a = 2.7–2.8). For the removal of diuron and 2,4-D by liquid@ZIF-8, H-bonding was found to be very strong between target compounds having a polar nature and the adsorbent, which possesses several surface functional groups (lactonic, carboxylic, and phenolic groups) along with its surface pyridinic and pyrrolic species [100]. While the adsorbents and adsorbates may contribute as H-bond donors or acceptors, the degree of H-bonding varies depending on the pH conditions. For example, the adsorption of diuron was relatively constant between pH 4 and 7, while it decreased at pH < 4 and pH > 7, which can be explained by the influence of electrostatic interactions (*i.e.*, repulsion) between protonated diuron and the positively charged liquid@ZIF-8 surface (pH < 3) and a reducing contribution of H-bonding caused by protonated diuron when the compound acts as an H-acceptor [136].

Yang et al. fabricated a UiO-67/graphene oxide hybrid nanocomposite, which was employed to remove glyphosate in water [137]. The dominant mechanisms of glyphosate adsorption on UiO-67/

graphene oxide were revealed through Fourier-transform infrared (FTIR) spectroscopy analysis to be the formation of surface/inner-complexes between the various functional groups and the UiO-67/graphene oxide surface. The FTIR analysis data revealed that the spectra of UiO-67/graphene oxide had clear differences in bonds before and after glyphosate adsorption due to interactions between the target compound and the adsorption sites of UiO-67/graphene oxide [137]. In particular, the glyphosate adsorption exhibited a new transmittance band at 941 cm^{-1} based on the spectrum of UiO-67/graphene oxide, which indicates a Zr-O-P stretching vibration [138]. Additionally, new bands were observed at 1157 and 1075 cm^{-1}, which appeared to be P═O and P− O bonds, respectively, indicating that the Zr-OH of UiO-67/graphene oxide may be an active node for the binding of the target compound molecules, thus enhancing the removal efficiency of glyphosate. Moreover, after the adsorption of glyphosate, the vibration intensity of C-O-Zr (1500–1650 cm^{-1}) reduces significantly due to the influences of the generation of C-O-Zr-O-P, which implies that chemical integration is the key parameter affecting glyphosate removal by UiO-67/graphene oxide [137].

4.2.1.3. Perchlorate. Perchlorate (ClO_4^-) is an EDC [139]. Colinas et al. reported removal of a high concentration of ClO_4^- (initial concentration = 35 mg/L) through complete anion exchange using cationic MOF (silver 4,4′-bipyridine nitrate, adsorption capacity = 354 mg/g, with a contact time of 90 min). In a separate study, a cationic MOF based on amino sulfonic acid ligand linked with Cu-4,4′-bipyridyl chains was fabricated using the solvothermal method and was used as an adsorbent for efficient removal of ClO_4^- in water [131]. The findings demonstrated that the maximum sorption amount of ClO_4^- was approximately 135 mg/g at pH 7 and that the ClO_4^- could be removed effectively at a wide range of pH values (2–11). For ClO_4^- removal, one of the primary mechanisms is ion exchange, presumably because SO_3^- groups in the MOF are exchanged with ClO_4^- after adsorption [140]. In addition, electrostatic adsorption cannot be ignored because the stretching vibration of N–H in the $–NH_2$ groups was not present after the adsorption process, indicating that the $–NH_2$ groups may be surrounded by ClO_4^- due to its positive charge [131].

4.2.2. Ppcps

4.2.2.1. Analgesics. H-bonding and electrostatic interactions were previously discussed to describe the adsorption of organic compounds on MOF-NAs [99,141]. However, recent findings have revealed that the adsorption of carbamazepine on UiO-67 is not significantly influenced by electrostatic interactions at varying pH conditions, and the influence of H-bonding is anticipated to be minimal [39]. Unlike H-bonding and electrostatic interactions, the study observed that the hydrophobic and π-π interactions between the benzene rings of carbamazepine molecule and the MOF linkers were dominant mechanisms of the adsorption. The benzene rings of carbamazepine, which have a strong electron-donating group (*i.e.*, $–NH_2$; π donor), can form a strong bond with the oxygen-containing functional group on the surface of the UiO-67 (electron acceptor; π acceptor) [39]. An et al. observed that porous metal azolate framework-6 carbon (a subclass of MOFs; q_{max} = 408 mg/L) was significantly more effective for removal of ibuprofen than commercially available activated carbon (q_{max} = 168 mg/L) [142]. This is presumably because hydrophobic interactions play an important role in the adsorption between the hydrophobic adsorbate (ibuprofen, log K_{OW} = 3.97) and the hydrophobic adsorbent, i.e., the hydrophobicity of metal azolate framework-6 carbon is much higher than that of activated carbon [143]). Additionally, π-π interactions should also be considered for adsorption, because the ibuprofen and metal azolate framework-6 carbon have an aromatic benzene ring and a graphitic layer, respectively [142].

Diclofenac is one of the most commonly detected pharmaceuticals in drinking water sources [144]. Zr-based functionalized MOFs (UiO-66/SO_3H-NH_2) were tested to remove diclofenac in aqueous solutions [145]. The removal mechanisms can be explained based on the properties of diclofenac and UiO-66/SO_3H-NH_2. For example, at a pH of approximately 4–5.5, electrostatic attraction is expected to be favorable between negatively charged diclofenac (pH_{pzc} = 4 [146]) and positively charged UiO-66/SO_3H-NH_2 (pH_{pzc} = 5.5 [147]). However, both diclofenac and UiO-66/SO_3H-NH_2 exist in negatively charged states at a pH > 5.5, resulting in a rapid decrease in diclofenac adsorption with pristine UiO-66. Thus, the influence of electrostatic interactions would be minimal under high-pH conditions. A similar influence of pH was observed in adsorption of *p*-arsanilic acid and phthalic acid [148,149]. The adsorption of diclofenac at varying pH conditions (4.5, 7.5, and 10.5) may be due to π–π stacking between the diclofenac benzene rings and the pristine UiO-66 [150].

4.2.2.2. Antibiotics. For various hazardous compounds, one of the main adsorption mechanisms is H-bonding [151]. Ahmed et al. observed that the extraordinary adsorption of sulfamethoxazole on highly porous MOF-derived carbons was due mainly to H-bonding because the MOF-NA has several acidic groups, such as carboxylic and phenolic groups, that engage in H-bonding [104]. The findings also indicated that both sulfamethoxazole and MOF-NA act as H-bonding donors and acceptors. Increased attention has been given to ciprofloxacin (a second-generation fluoroquinolone antibiotic) due to its extensive use in both humans and animals [152]. Liang et al. demonstrated the effective adsorption performance of ZIF-67-derived hollow $C_{O3}S_4$ for the removal of ciprofloxacin [41]. Of four different kinetic models (intra-particle diffusion, liquid-film diffusion, pseudo-first-order kinetic, and pseudo-second-order kinetic), the fitted results exhibited the highest correlation coefficient (0.999) when using a pseudo-second-order kinetic model. In addition, the findings indicated chemisorption behavior of ciprofloxacin on the hollow $C_{O3}S_4$ on the ZIF-67 surface, which was verified by FTIR measurements. After adsorption by the MOF, two bands shift to 1269 and 1710 cm^{-1} (assigned to stretching of C—O and O—H deformation of the carboxyl group, and C—O stretching in the carboxyl group, respectively [153]) and their peaks are reduced. This phenomenon is presumably due to surface complexation between the –COOH of ciprofloxacin and the hollow $C_{O3}S_4$ on the ZIF-67 surface [154].

Seo et al. reported removal of nitroimidazole by MIL-101(Cr) modified with urea, melamine, and O_2N [44]. While electrostatic interactions were considered as a potential mechanism for the removal of nitroimidazole, they do not appear to be the main mechanism for the effective adsorption of nitroimidazole by these modified MOF-NAs. The adsorption capacity values for nitroimidazole by the MOF-NAs are in the following order: MIL-101-urea > MIL-101-melamine > MIL-101 > MIL-101-O_2N; however, the surface area values of each adsorbent are as follows: MIL-101 (3030 m^2/g) > MIL-101-urea (1970 m^2/g) > MIL-101-O_2N (1620 m^2/g) > MIL-101-melamine (1350 m^2/g). The results suggest that the influence of the $–NH_2$ group (in melamine and urea) on the adsorption of nitroimidazole needs to be evaluated to verify the adsorption mechanisms. H-bonding interactions between MIL-101 and nitroimidazole can be considered as a possible mechanism due to their $–NH_2$ and $–NO_2$ groups, respectively [133]. In particular, effective H-bonding through the solid six-membered ring takes place between the $–NO_2$ and $–NH_2$ groups, which is comparable to the interactions between sweeteners and the $–NH_2$ group on MIL-101 [38]. MIL-101-O_2N demonstrated unfavorable adsorption of nitroimidazole, presumably due to the lack of possible H-bonding between the two $–NO_2$ groups in MIL-101 and nitroimidazole. Thus, the $–NO_2$ on nitroimidazole and the $–NH_2$ groups on MIL-101-urea or MIL-101-melamine would be the H-acceptor and H-donor, respectively [44].

4.2.2.3. Antiepileptics. Several possible mechanisms were evaluated for the adsorption of carbamazepine by UiO-66 [130]. Adsorption due to hydrophobic interactions can be explained mainly by the hydrophobicity of carbamazepine (log K_{OW} = 2.77); however, the

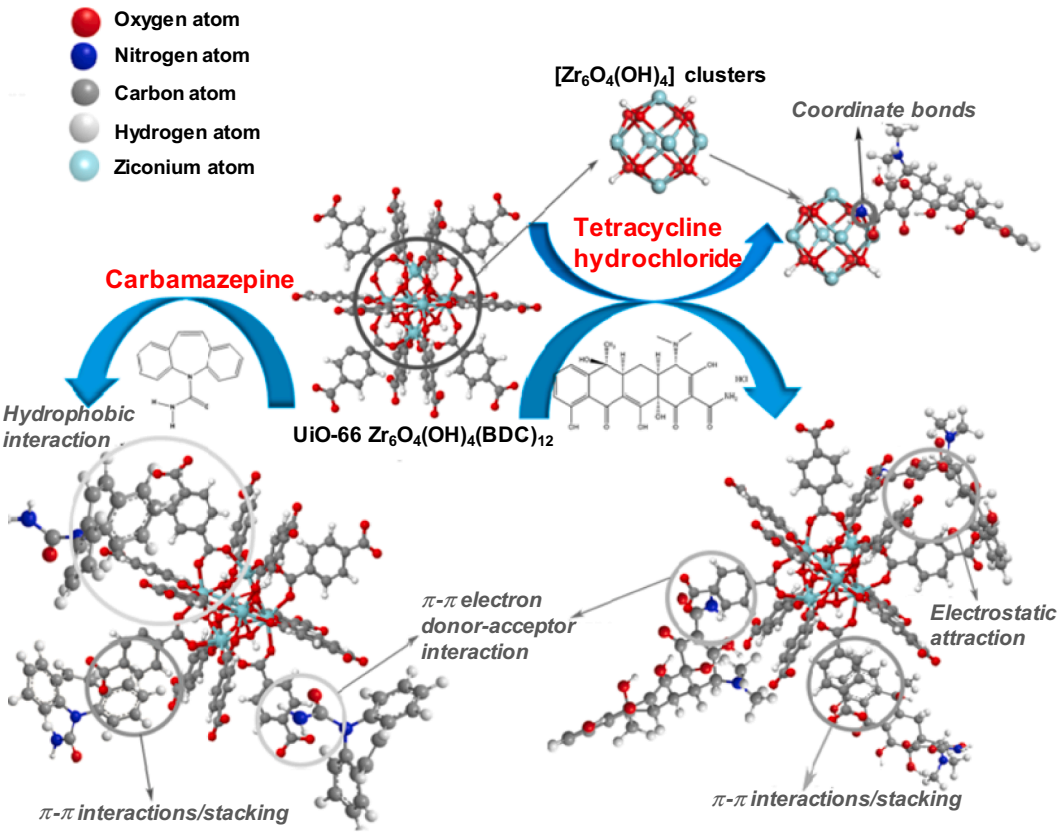

Fig. 5. Schematic illustration adsorption mechanism between zirconium MOF UiO-66 and carbamazepine/tetracycline hydrochloride. Reproduced with permission from Ref. [130], © American Chemical Society 2017.

influences of electrostatic attraction and π-π interactions/stacking should also be considered. The intermolecular electrostatic attraction between carbamazepine and UiO-66 is relatively weak because both are negatively charged at pH > 5 based on their pH_{pzc} values (4.81 for UiO-66 and 2.45 for carbamazepine). π-π interactions/stacking are commonly found in the absence of electrons or in electron-rich chemicals [45]. π-π electron donor-acceptor interactions readily occur between carbamazepine, which possesses NH_2 groups (i.e., electron donor), and UiO-66, which possesses a benzene ring (i.e., electron acceptor) [155]. Moreover, π-π stacking (aromatic-aromatic interactions) was found to occur between the benzene rings in carbamazepine and in the organic ligands of UiO-66 [130]. Fig. 5 describes the potential adsorption mechanisms that occur with carbamazepine and tetracycline hydrochloride. Akpinar and Yazaydin compared the removal efficiencies of carbamazepine with UiO-67 and commercial activated carbon (F400) [39]. Significant removal of carbamazepine was demonstrated by UiO-67 (95%), whereas F400 removed only 35% of the compound within a contact time of 2 min, which may have been due to UiO-67's relatively small particle size/pore volume and the very active adsorption sites generated by the missing-linker defects. Twelve linkers are found in defect-free samples of UiO-67 nodes, while binding around the node can be changed to have less than twelve carboxylates. The sites that are missing carboxylate are covered with –OH and H_2O groups. Thus, carbamazepine may create particular interactions with these functional groups on nodes [39]. In addition, some missing-linker defects result in improved porosity, which may expedite quicker adsorption and higher adsorption capacity [156].

4.2.2.4. Antiseptics. Triclosan is a broad-spectrum bacteriostatic germicide that is used widely in a number of PPCPs [157]. Structure-directing agent-modified mesoporous MIL-53(Al) was examined for removal of triclosan at various initial concentrations (0–60 mg/L) [158]. The modified MOF with relatively high meso-porosity and total pore volume demonstrated greater adsorption capacity (488 mg/g) than that of microporous MIL-53(Al) (447 mg/g), and the triclosan adsorption was approximately 4.5 times faster with the modified MOF. In addition, the adsorption capacity values for different compounds by the modified mesoporous MIL-53(Al) were in the following order: triclosan > bisphenol A > 1-naphthol > phenol, which was proportional to their hydrophobicity (log K_{OW} = 4.84, 2.84, 2.76, and 1.46, respectively). This implies that higher selectivity for triclosan adsorption on the modified MOF occurs in the presence of coexisting compounds with relatively low hydrophobicity. FTIR measurements provide more insights into the interactions between triclosan and the MOF. Bands were observed at 3660 and 995 cm^{-1}, which were assigned to the asymmetric/symmetric stretching of the hydroxyl groups of $AlO_4(OH)_2$. The band at 3660 cm^{-1} moved to a lower frequency and an extra vibrational band at 3540 cm^{-1} was detected after triclosan adsorption, implying H-bond interactions between triclosan and $AlO_4(OH)_2$ groups, which indicates that H-bond interactions are an additional parameter affecting triclosan adsorption. Additionally, adsorption of triclosan on the modified MOF was confirmed by the presence of both a vibrational band at 660 cm^{-1} (–C–Cl) and small stretching bands at 1025–1245 cm^{-1} (aromatic C–O–C) [158]. Sarker et al. reported effective adsorption performance for the removal of triclosan by carboxylic-acid-functionalized UiO-66-NH_2 [116]. While UiO-66-NH-CO-COOH has the smallest porosity (0.37 cm^3/g) of the tested adsorbents, including activated carbon, UiO-66, UiO-66-NH_2 (0.56, 0.53, and 0.48 cm^3/g, respectively), it demonstrated better adsorption performance for triclosan compared to the other adsorbents, implying that the functional groups on the MOF may play an important role in the adsorption of triclosan. The potential mechanisms that may be important for the adsorption of CECs on MOF-

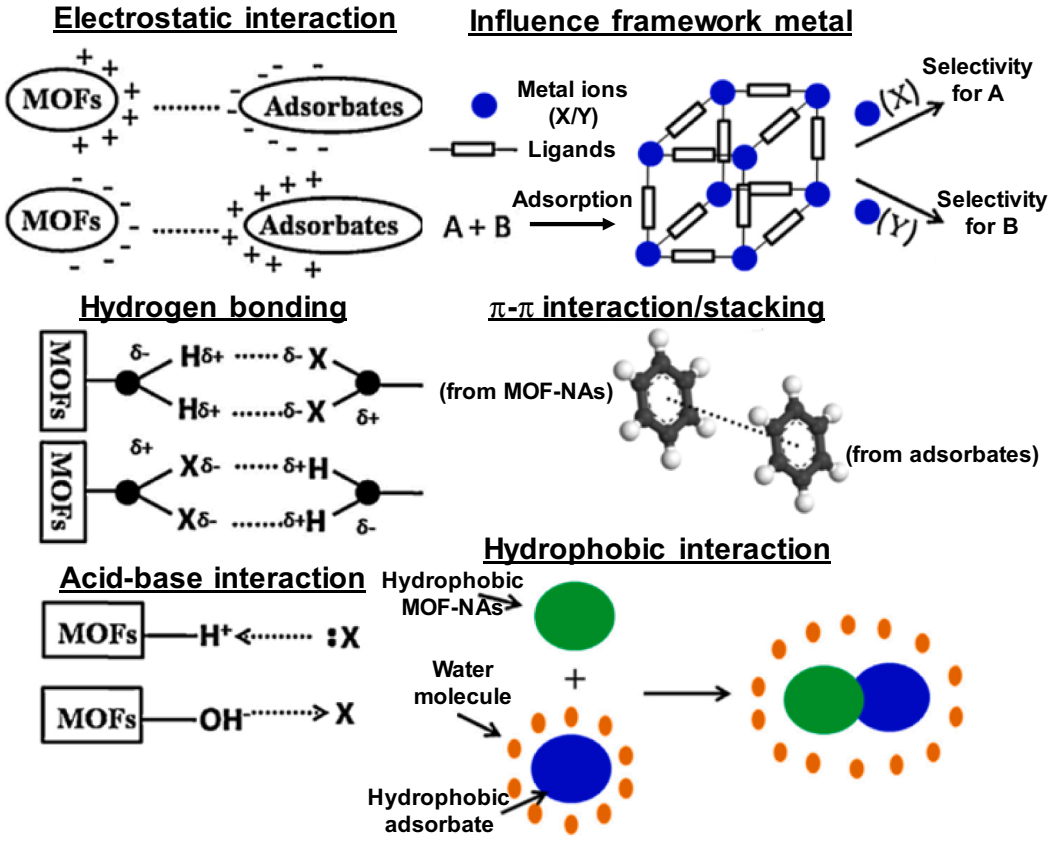

Fig. 6. Schematic diagram of possible mechanisms for adsorptive removal of CECs on MOFs or MOF-NAs. Reproduced with permission from Ref. [45], © Elsevier B.V. 2015.

NAs are summarized in Fig. 6.

5. Regeneration of MOF-NAs

The regeneration capacity of MOF-NAs is a factor of concern because extraordinary reusability may result in improved environmental sustainability and cost efficiency in the treatment of various CECs. The desorption degree of the CECs during regeneration of MOF-NAs is an essential parameter for evaluation of the reusability of the MOF-NAs. Successful regeneration was achieved for a Cu–benzene-1,3,5-tricarboxylic acid/cotton composite, because ethion is well-dissolved in a solvent (*i.e.*, acetonitrile) [96]. An effective removal efficiency (> 85%) of ethion was observed during a consecutive regeneration/reuse (desorption/adsorption) process after five cycles. Ahmed *et al.* observed that the adsorption capacity of atrazine by ionic liquid@MOF-derived carbons was not significantly reduced even after four cycles of washing with ethanol [100]. Acetone was employed to regenerate MOF (UiO-67) after the adsorption of carbamazepine [39]. During the regeneration process, the used MOF was shaken at room temperature and reactivated under vacuum at 90 °C; it demonstrated a minor reduction in adsorption capacity after five recycles. After sulfonamide adsorption, the regeneration capacity of an MOF (UiO-66) was evaluated with NaOH (0.01 M) [159]. While the MOF retained greater than approximately 80% removal efficiency after three cycles, the N_2 adsorption-desorption isotherm was not significantly affected by the adsorption of sulfonamide, which indicates that the structure of the MOF was stable after adsorption. Bhadra *et al.* used simple solvent washing (water (v):methanol (v)) under ultrasonic irradiation to regenerate used Bio-MOF-1-derived carbons after bisphenol A adsorption [132]. After four cycles, almost no reduction in the porosity of the recycled adsorbent occurred compared to the pristine one. In a separate study, used MOF (UiO-66) after adsorption of carbamazepine and tetracycline hydrochloride was regenerated by soaking in chloroform for 24 h to desorb the target compounds [130], washing with methanol, and drying at 80 °C for 24 h. While the regeneration was relatively unsuccessful, the findings are useful because they indicate that the adsorption of carbamazepine on UiO-66 is primarily physical adsorption, and that the absorbed carbamazepine in the micropores of the MOF was desorbed only during the degassing process. However, after the adsorption of tetracycline hydrochloride, the BET surface area and total pore volume of the MOF reduced significantly from 592 to 285 m^2/g and from 0.323 to 0.183 cm^3/g, respectively, which indicates that tetracycline hydrochloride may be adapted to the micropore inner surface by strong interactions, including H or chemical bonding [130].

In a separate study, ethanol washing was employed for regeneration of used liquid@ZIF-8 after diuron adsorption [136]. The FTIR spectra revealed peaks at 1740 and 1291 cm^{-1} for fresh liquid@ZIF-8, pure diuron, diuron-adsorbed liquid@ZIF-8, and recycled liquid@ZIF-8; the stretching bands were detected for both diuron and diuron-adsorbed liquid@ZIF-8, implying the presence of adsorbed diuron on liquid@ZIF-8. The disappearance of these bands in the recycled liquid@ZIF-8 confirmed that it was effectively regenerated by ethanol washing [136]. After the adsorption of ciprofloxacin on ZIF-67-derived hollow $C_{O3}S_4$, ethanol was employed as a washing agent to desorb ciprofloxacin and regenerate the hollow $C_{O3}S_4$ MOF [41]. However, ethanol removed only a limited amount of ciprofloxacin (approximately 5%) from the MOF. An additional cleaning agent (HCl, 0.1 mol/L) was therefore used for desorption of ciprofloxacin from the used MOF. Consequently, a mixture of ethanol and HCl was adopted as the cleaning agent. While the adsorption capacity was slightly reduced after the first use of the MOF, the removal efficiency for ciprofloxacin was retained at > 80% after five regeneration cycles, implying that the ZIF-67-derived hollow $C_{O3}S_4$ MOF has high adsorption capacity for ciprofloxacin and is readily regenerated for acceptable reusability [41]. The maximum regeneration

performance for used structure-directing agent-modified mesoporous MIL-53(Al) was using 90% methanol at pH 11 [158]. This was presumably because triclosan entirely dissociates into ionized forms at high pH conditions, disturbing each part of the adsorption process by splitting the H-bonds between $(AlO_4)OH_2$ and triclosan species adsorbed on the modified MOF, which reduces the triclosan hydrophobicity and enhances the solvation of triclosan molecules in water, therefore resulting in more favorable desorption of triclosan from the modified MOFs [158]. It is strongly recommended that in addition to adsorption and desorption performance, the stability of MOF-NAs should also be monitored throughout reusability/regeneration studies over prolonged periods

6. Conclusions and areas of future study

Over the last two decades, several hundred different MOFs and MOF-NAs have been studied for different applications, including gas purification, gas separation, gas storage, energy storage, and environmental applications. Of the various environmental applications, numerous recent studies have reported that MOF-NAs are effective for removal of organics and heavy metals, including different CECs. These findings have shown that the removal/adsorption efficiency of CECs by MOF-NAs is significantly influenced by the properties of the CECs and MOF-NAs, as well as the water quality conditions. The porosity volume and structure of MOF-NAs appears to be a major factor in adsorption performance, particularly when no specific adsorption mechanism excluding van der Waals interactions exists. However, once MOF-NAs are modified with different functional groups, the removal may be explained by more complex mechanisms, such as electrostatic interactions, metal effects, acid-base interactions, π-π interactions/stacking, hydrophobic interactions, and H-bonding, which also vary greatly depending on water chemistry conditions. In general, one of the most important parameters affecting adsorption capacity is pH, because both the speciation of CECs and the functional groups of MOF-NAs vary depending on solution pH. Significant electrostatic interactions can occur only when CECs and MOF-NAs have different negative/positive charges. Moreover, the adsorption of CECs may vary depending on the type and concentration of background anions and cations. Unlike activated carbon, NOM appears to enhance the adsorption of some CECs as a result of various interactions among NOM, CECs, and MOF-NAs. The increased adsorption is presumably due to adsorption of NOM on the surface of MOF-NAs, which may provide additional adsorption sites.

The research has shown that it is relatively difficult to determine common trends for the effects of CEC properties on their removal by MOF-NAs, because CECs have varying physicochemical properties. However, of the potential mechanisms for the selected CECs and MOF-NAs, the dominant mechanisms are influential in the following order: electrostatic interactions > H-bonding > π-π interactions/stacking > hydrophobic interactions ≈ acid-base interactions ≈ metal effects; however, these factors may vary depending on water chemistry conditions. In the adsorption processes, one of the main concerns for environmental sustainability is the regeneration capacity of the MOF-NAs, because extraordinary reusability may improve their cost efficiency in the treatment of various CECs. The findings demonstrate that most MOF-NAs can be regenerated effectively using different solvents, such as acetonitrile, acetone, NaOH, methanol, ethanol, and HCl. Regeneration capacity can be enhanced by combined use of these cleaning agents.

More comprehensive assessments of different synthesis methods for MOF-NAs are necessary because the physicochemical properties of MOF-NAs can vary significantly depending on the reaction time used, particle size, and morphology, particularly for their application in large-scale processes. Additionally, the adsorption of different CECs varies significantly depending on the physicochemical properties of the compounds, the physicochemical properties of the MOF-NAs themselves, and the water quality; this might require almost unlimited experiments to identify the adsorption properties all CECs. Therefore, quantitative structure-activity relationship studies may be needed to elucidate the adsorption mechanisms for CECs on different MOF-NAs, which may be useful in understanding interactions between the functional groups in the CEC molecules with the highest activity. Overall, to be competitive with other types of adsorbents that are currently used in water and wastewater treatment processes, MOF-NAs must be practical in terms of cost. While these emerging MOF-NAs are promising due to their high-performance adsorption, many challenges must still be overcome to develop homogeneous pores, structures, and functional groups with long-term stability. In addition, more research is needed to provide comprehensive life-cycle analyses and ecotoxicological assessments of MOF-NAs, particularly when considering its disposal. However, the use of MOFs and MOF-NAs for the adsorption of CECs remains a very promising avenue of research.

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