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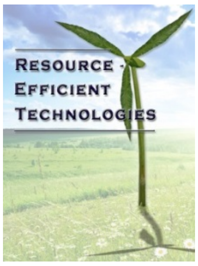

Review article

METAL-ORGANIC FRAMEWORKS APPLIED FOR WATER PURIFICATION

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Abstract

Metal-organic frameworks (MOFs) which are materials constructed from metal ions/clusters bridged with organic linkers have emerged as an important family of porous materials for widely varying applications. The purification of water polluted with both of organic and inorganic contaminants is a potentially promising application of MOFs since the chemical and thermal properties of the porous materials are easily tunable, e.g. ligand modification, different metal, etc. The demonstration of alignment and the obtained insights facilitate the direction of designing ideal MOF materials with improved water stability for application in water purification. This review gives a brief overview and will be beneficial to the design, functionalization, and promotion of the development of MOFs as adsorbent materials for applications in water purification.

Keywords: metal-organic frameworks, water purification, water pollution, adsorbent.

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1. Introduction

Water contamination is one of the severe pollutions of urban life. This problem mainly occurs during rapid urbanization and the steady increase of the world population. Moreover, improving the human living-conditions also requires all kinds of different products, which during the production process generate by-products and/or hazardous contaminated wastewater. Recently, various contaminants such as pharmaceuticals and personal care products (PPCPs) [1], herbicides/pesticides [2], dyes [3], spilled oil [4], and aromatics/organics [5] have been detected in different natural surface water sources. It is necessary to treat or recover the contamination from the water before exposing the water to natural sources and thus

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protecting the environment and human health. Several innovative technologies and processes have been developed to solve water contamination or treatment of wastewater, such as coagulation, chemical precipitation, ion exchange, filtration, etc. [6–9]. Among different techniques, the adsorption on porous materials is the most promising approach since a high surface area (active sites) can be exposed to attach the contaminating compounds (adsorbed). Consequently, porous materials such as zeolite, activated carbon, silica, polymeric materials, as well as hybrid materials are excellent candidates to be used as an adsorbent for contaminant removal from wastewater. However, a higher efficiency, lower production and operation cost, and easier maintenance are still desirable. The strong interaction and/or a higher number of active sites on a high surface area of porous materials are mainly concept ideas to take into consideration to enhance the efficiency of wastewater treatment.

Due to the large porosity, numerous active sites, tunable structure, etc. of metal-organic frameworks (MOFs) or coordination polymers, these porous materials have a huge potential which is attractive for several applications including adsorption and/or separation of in-/organic compounds [10]. Due to the high flexibility and tunable physicochemical properties of MOFs, they are arising to be one of the most promising adsorbents for water purification [11]. For water purification applications, the main properties required as an adsorbent is water stability and resistance to polluting compounds [12]. In consideration of the structure design, some strategies and methods have been developed to construct functionalized MOFs and expand their applications by means of pore functionalization, pore size regulation and surface modification. In this review a series of MOFs are explored with a potential for water purification or removal of contaminants. The overview is apportioned in three parts; (1) the construction of MOFs which are stable in water, (2) reported MOFs applied for the removal of contaminants (metal ions, in-/organic compounds) from water, (3) strategies for tuning the MOF structure to improve the water stability and adsorption efficiency. The aim of this review is to help or guide the scientist to be able to select and tune or develop MOFs in the future, which is suitable for water purification applications.

2. Metal-Organic Frameworks construction

MOFs are crystalline porous materials with network structures of metal ions/clusters (SBUs) bridged by organic ligands containing O- or N donors (linker) generating a 2D or 3D structure, which offers a high degree of structural flexibility for design and functional adjustability.

2.1. Stability of MOFs in the presence of water

The MOFs stability in water must be considered first before using these materials for water purification applications. The study of the water-stability of MOFs has been investigated by two procedures, namely by exposure to humid vapors and by contact with aqueous phases. Low and co-workers reported the comparison of molecular modeling results with experimental data of the stability of some well-known MOFs (Fig. 1) [13]. They also investigated the nature or the basics of how framework dimensionality can govern the relative stabilities of MOFs in water. They concluded that the key factor is the strength of the bonding or coordination between metal-ligand that plays a crucial role in the water stability of these materials, more than the metal geometry, valence of the metal cation, or flexibility of the framework, etc. Matzger and co-workers investigated various MOFs immersed in pure water or in wet dimethylformamide (DMF) from hours to months [14].

UMCM-150 remained stable in a mixture of water and DMF for hours (ratio water/DMF; 9:2) and for a month at ratio 3:40. Whereas, the copper paddlewheel MOFs (MOF-505 and HKUST-1) started to degrade in pure water after 24 hours. In contrast to the copper paddlewheel MOFs, MIL-101 (Cr) and ZIF-8 revealed a stability for a month in pure water conditions, moreover, the XRD pattern of ZIF-8 or SIM-1 retained after treatment in boiling water up to 24 hours [11, 15].

Degradation mechanisms of MOFs exposed to water have been investigated via computational chemistry and confirmed experimentally. The degradation can be explained in two steps: (1) ligand displacement and

(2) hydrolysis [13]. A water molecule inserts into the M–O metal-ligand bond via displacement of a ligand in the framework. It results in the formation of a hydrated cation and to the release of a free ligand:

$$M^{n+}\text{—}L^{n-} + H_2O \longrightarrow M^{n+}\text{—}(OH_2)\cdots\cdots L^{n-} \tag{1}$$

Whereas after the metal-ligand bond is broken, the water molecule dissociates to form a hydroxylated cation and a free protonated ligand:

$$M^{n+}\text{—}L^{n-} + H_2O \longrightarrow M^{n+}\text{—}(OH)^{-} + HL^{(n-1)-} \tag{2}$$

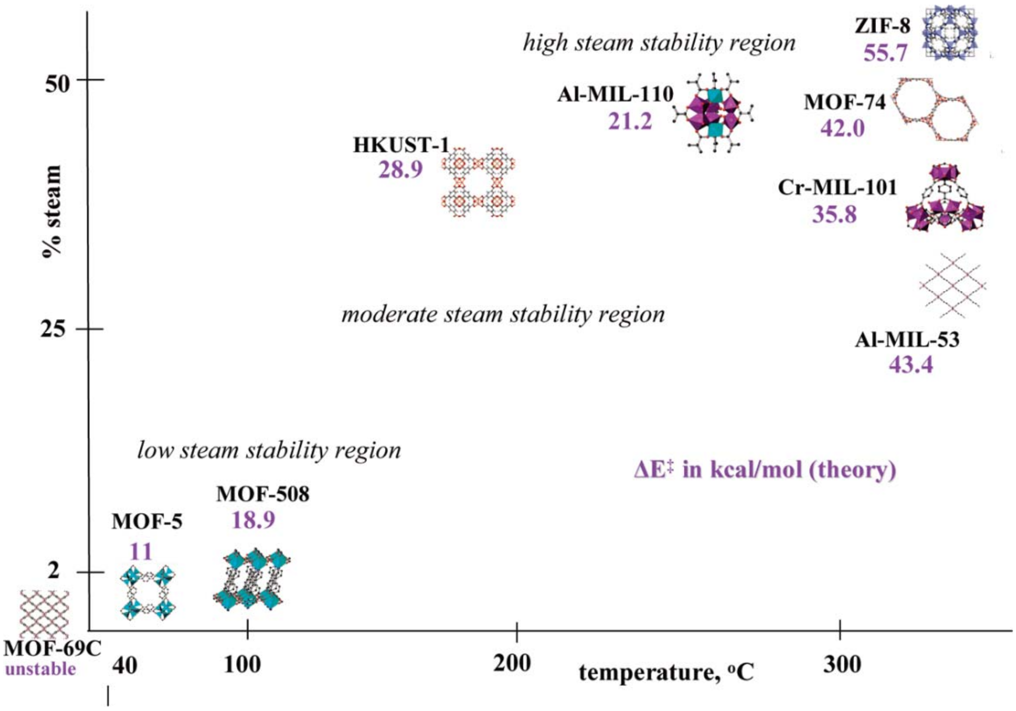

Fig. 1. Steam stability map of MOFs. The position of the structure for a given MOF represents its maximum structural stability as probed by XRD measurements, while the energy of activation for ligand displacement by a water molecule as determined by molecular modeling is represented by the magenta numbers (in kcal·mol^{-1}), (Reproduced with permission from ref. 13)

A ligand displacement mechanism was proposed to explain the structural breakdown of various MOFs in the presence of moisture or water. The isoreticular series of $M_2(BDC)_2(DABCO)$ containing either Cu, Zn, Co or Ni cations were also investigated under humid conditions [16]. According to DFT calculations in combination with experimental data a different degradation was observed depending on the cation (metal). The Cu-O bond was found to undergo hydrolysis to form hydroxide species while the ligand displacement occurs to break Zn/Co–O bonds. Furthermore, the Ni-cation based MOF ($Ni_2(BDC)_2(DABCO)$) exhibited a lower reactivity meaning a high stability in the presence of water compared to the other metal ions (Cu, Zn, Co) in this MOFs series.

2.2. Construction of water-stable MOFs

MOFs are porous materials of which their advantages can be exploited in a variety of applications, such as gas storage, separation and catalysis, including, the removal of organic and/or inorganic compounds via adsorption. As reported before, it is of major importance to determine the stability of MOFs. The stability can greatly impedes their practical applications because during the degradation of the MOF a dramatic drop of the surface area is observed and hence, detrimental for the removal of impurities from water via adsorption. A strong metal-ligand coordination is an indication that the MOF will be able to prevent the coordination of water molecules and thus preventing the degradation of these materials [17]. Therefore, the metal nodes coordination in the frameworks plays a key role to stabilize MOFs in water. This is confirmed by a study of a IRMOF-1 type series with three different metal nodes (Zn, Mg and Be) in which the Be-based MOF was more stable than Mg or Zn-based MOFs due to the stronger coordination between ligand and metal. Born–Oppenheimer Molecular Dynamics were used to determine their behavior in liquid water and could be used to explain the observed tendency. The metals Zn, and Mg generated penta- and hexa-coordination spheres combined with the flexibility of the M_4O core and the weaker metal-oxide bonds [18]. Furthermore, the Mg structures exhibited a structure degradation different compared with the Zn analogues due to the larger rigidity of their core and the strong Mg–O coordination. This would prevent further water coordination to the metal, in contrast to Zn-IRMOF-1 in which Zn clusters are more flexible and open up more easily. The hydrothermal resistance of Be-IRMOF-1 is due to the very high activation energy required for the metal-ligand dissociation leading to the hydrated Be–terephthalate compound from Be-IRMOF-1. A similar behavior was found also in the case of UiO-types, and MIL-100/-101 MOFs of which the high stability of these materials was related to the strong coordination of the metal centres [19–21]. Indeed, upon water adsorption up to 90 % RH, the 8-coordinated zirconium-based UiO-66 was the only one to retain both its crystallinity and porosity compared to Mg-MOF-74, DMOF-1, HKUST-1, and UMCM-1 [12].

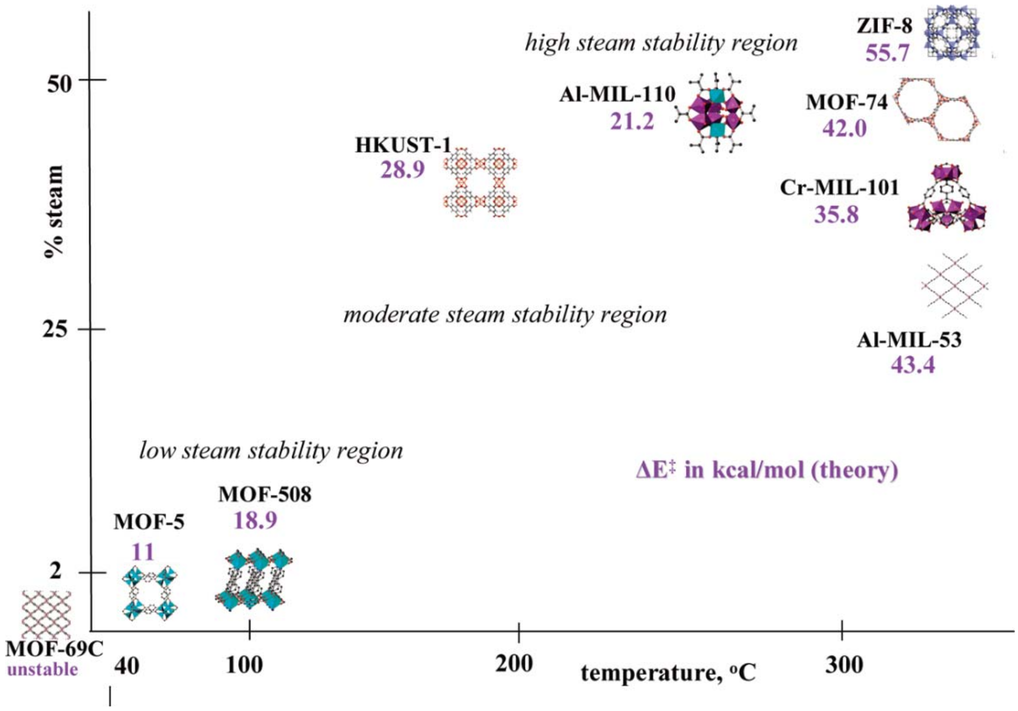

Fig. 1. Steam stability map of MOFs. The position of the structure for a given MOF represents its maximum structural stability as probed by XRD measurements, while the energy of activation for ligand displacement by a water molecule as determined by molecular modeling is represented by the magenta numbers (in $kcal \cdot mol^{-1}$), (Reproduced with permission from ref. 13)

The high valence state metals such as V^{3+}, Fe^{3+}, Al^{3+}, Eu^{3+}, Tb^{3+}, Ti^{4+} and Y^{3+} etc., usually show a remarkable higher stability in a high humid environment or aqueous solution. The MIL series was an example of MOFs with a remarkable stability in aqueous media within a wide pH range. MIL-101(Cr) constructed of chromium (III) and carboxylate forming a hexagonal window of 16Å an inner free cage diameter of 34 Å exhibits a high surface area (4100 $m^2 \cdot g^{-1}$ and 5900 $m^2 \cdot g^{-1}$ of BET and Langmuir, respectively) [22]. The stability of MIL-101(Cr) could be partly attributed to Cr^{3+} cation that can be considered as a hard Lewis acid and is easy to bond with carboxylate, which can effectively slow down the metal-ligand bond dissociation process. Additionally, MIL-125, a Ti^{4+}-based MOF, is stable in water and acidic gases as well [23]. The relative strength of the M-O bond is another factor of robustness of MOFs. For example, MIL-53(Al^{3+}) shows a higher stability toward water vapor relative to MIL-53(Cr^{3+}) by comparing the calculated stability of the isostructural MIL-53(Al^{3+}) and MIL-53(Cr^{3+}), since the Al-O bond is stronger than the Cr-O bond in these MOFs [24]. So, Al^{3+}-containing MOFs will generally be more stable than Cr^{3+}-containing MOFs. More impressively, zirconium (Zr) metal based MOFs exhibit a remarkable high-level of chemical and thermal stability due to the high affinity of zirconium for hard oxygen donor ligands [25]. For instance, UiO-66 using $ZrCl_4$ as a metal precursor bridged with 1,4-benzenedicarboxylate (H_2BDC) as a linker to construct an ultra-stable MOF of which the Zr-octahedron ($Zr_6O_4(OH)_4$) is coordinated with 12-organic ligands (BDC) [19]. Furthermore, the isoreticular UiO-67 and UiO-68 in which BDC is substituted 4,4-biphenyl-dicarboxylate (BPDC) and terphenyl dicarboxylate (TPDC) respectively, were investigated as well on their stability. Also these two MOFs are stable in most common solvents (water, benzene, acetone, ethanol, and DMF etc.), acid (HCl) and base (NaOH), moreover, from thermal studies a stability up to 375°C was observed [26]. The surface area property which is crucial for their practical application, also exhibit large number such as 1187 $m^2{\cdot}g^{-1}$, 3000 $m^2{\cdot}g^{-1}$, 4170 $m^2{\cdot}g^{-1}$ for the Langmuir surface of UiO-66, UiO-67 and UiO-68, respectively. Further investigation of their high-stable structure revealed that the main reason was found to be the crowding coordination of the building unit between metal with ligand and the enhanced strength of metal-ligand bond preventing the water molecules to coordination near the metal. Other series of MOFs using a similar idea were constructed such as PCN-224 [27], PCN-777 [28], MOF-525, MOF-535 [29], MOF-535, NU-1100, etc [30]. All these MOFs presented a high-level of chemical and thermal stability.

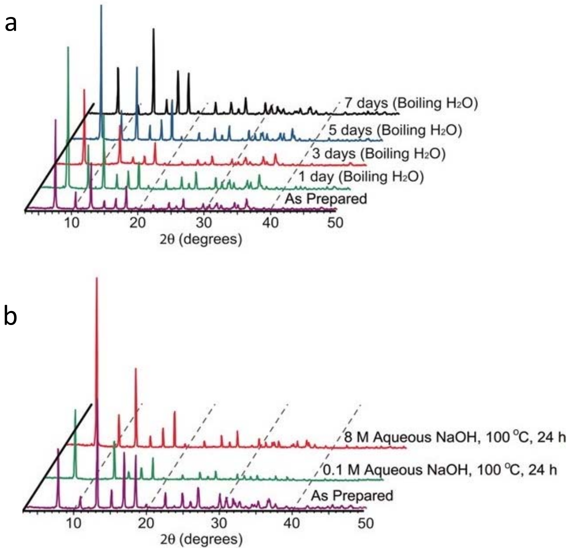

Fig. 2. The PXRD patterns for ZIF-8 in refluxing water at 100°C for up to 7 days (a) and in refluxing aqueous NaOH solution for up to 1 day (b) (Reproduced with permission from ref. 11)

The organic ligand or linker is the other component to build a framework structure of MOFs, which impacts the stability of materials due to the strength of metal-ligand coordination. The pK_a value of organic ligands could be an indicator or used to predict the stability of the synthesized MOF material. As reported for the synthesis of a series of stable pyrazolate-ligand MOFs, highly stable MOFs could be obtained by using ligands having a high pK_a value (pyrazolate ligand, $pK_a = 19.8$) [31]. Imidazole ligands (IM) with a high pK_a value (more than 18.6) were used to construct a series of zeolitic imidazole frameworks (ZIFs) of which the obtained structure is highly thermal and chemical stable. ZIF-8 and ZIF-11 are examples of the ZIF family of which the structure can be retained chemical even in refluxing benzene, methanol, water, and aqueous sodium hydroxide, etc. (Fig. 2). A thermal stability up to 300 °C for ZIF-11 and 500 °C for ZIF-8 are reported [11]. The key factor to make materials with outstanding stability properties is the very strong coordination or interaction of IM (with high pK_a value) with the metal unit (metal-ligand bond). An azolate-based MOF constructed of polyazolate-bridging frameworks was obtained with a stable structure such as $[Mn(DMF)_6]_3[(Mn_4Cl)_3(BTT)_8(H_2O)_{12}]_2{\cdot}42DMF{\cdot}11H_2O{\cdot}20CH_3OH$, in which Mn^{2+}-ions bridge with a tritopic ligand (1,3,5-benzenetristetrazolate with tetrazole having a $pK_b = 4.9$). The ability of promoting the self-assembly of highly symmetric and stable frameworks, including a thermal stability retained up to 200 °C under N_2 flow was demonstrated [32]. Furthermore, Long et al. developed a series of pyrazolate-bridged MOFs $M_2(BTP)_2{\cdot}$xsolvent (M = Ni, Cu, Zn, Co) by using the tritopic pyrazole-based ligand 1,3,5-tris(1H-pyrazol-4-yl)benzene (H_3BTP) (Fig. 3) [31]. These materials obtained permanent porosity from 930 up to

1860 $m^2 \cdot g^{-1}$ and their structure remained after immersing in boiling aqueous solutions from pH 2 to 14 for 2 weeks.

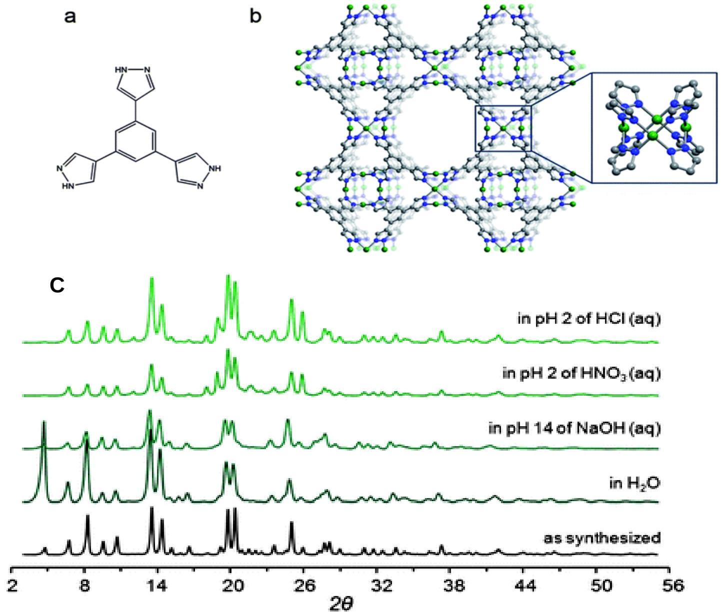

Fig. 3. (a) The pyrazole-based ligand 1,3,5-tris(1H-pyrazol-4-yl)benzene, H_3BTP. (b) The structure of $Ni_3(BTP)_2 \cdot 3CH_3OH \cdot 10H_2O$. Color scheme: Ni (green); N (blue); C (gray); H atoms and solvent molecules are omitted for clarity. (c) X-Ray diffraction patterns of $Ni_3(BTP)_2 \cdot 3CH_3OH \cdot 10H_2O$ after treatment in water, acid or base for two weeks at 100°C (Reproduced with permission from ref. 31)

Table 1. Summary of water-stable MOFs and their properties

MOFs	Metals	Linkers	Surface area ($m^2 \cdot g^{-1}$)	Pore diameter (nm)	Pore volume ($cm^3 \cdot g^{-1}$)	Uptake* ($cm^3 \cdot g^{-1}$)	ref.
CAU-10	Al	1,3-H_2BDC	635	0.7	0.25	0.31	33
CAU-10-H	Al	1,3-H_2BDC	635	n.d.	0.5	0.382	33
CAU-10-NH_2	Al	5-H_2BDC-NH_2	n.d.	n.d.	n.d.	0.19	33
CAU-10-NO_2	Al	5-H_2BDC-NO_2	440	n.d.	0.18	0.15	33
CAU-10-OCH_3	Al	5-methoxyiso-phthalic acid	n.d.	n.d.	n.d.	0.07	33
CAU-10-OH	Al	5- H_2BDC-OH	n.d.	n.d.	n.d.	0.27	33
CAU-6	Al	BDC- NH_2	620	n.d.	0.25	0.485	34
DUT-4	Al	H_2NDC	1360	n.d.	0.79	0.28	35
DUT-67	Zr	H_2TDC	1560	1.66/0.88	0.60	0.625	36
MIL-100	Cr	H_3BTC	1517	2.5/2.9	n.d.	0.41	21
MIL-100	Fe	H_2BDC	1549	n.d.	0.82	0.81	35
			1917	2.5/2.9	1.0	0.77	37
MIL-100	Al	H_3BTC	1814	2.5/2.9	1.14	0.50	37
MIL-100	Cr	H_3BTC	1330	2.5/2.9	0.77	0.40	38
			2059	2.9/3.4	1.103	1.01	20
			3017	n.d.	1.61	1.28	35
			3124	2.9/3.4	1.58	1.40	39
MIL-100-DEG	Cr	H_3BTC	580	1.2/1.5/1.9	0.50	0.33	38
MIL-100-EG	Cr	H_3BTC	710	1.2/1.5/1.9	0.47	0.43	38
MIL-101-NH_2	Cr	H_2BDC	2509	<2.9/3.4	1.27	0.90	39
			2690	<2.9/3.4	1.60	1.06	40
MIL-101-NO_2	Cr	H_2BDC	2146	<2.9/3.4	1.19	1.08	39
			1245	<2.9/3.4	0.7	0.44	40
MIL-101-pNH_2	Cr	H_2BDC	2495	<2.9/3.4	1.44	1.05	40
MIL-101-pNO_2	Cr	H_2BDC	2195	<2.9/3.4	1.11	0.6	40
MIL-125	Ti	H_2BDC	1160	0.6/1.1	0.47	0.36	41
MIL-125-NH_2	Ti	H_2BDC-NH_2	830	0.6/1.1	0.35	0.36	41
			1220	0.6/1.26	0.55	0.37	42

MOFs	Metals	Linkers	Surface area ($m^2\cdot g^{-1}$)	Pore diameter (nm)	Pore volume ($cm^3\cdot g^{-1}$)	Uptake* ($cm^3\cdot g^{-1}$)	ref.
MIL-53	Al	H_2BDC	1040	0.7-1.3	0.51	0.09	41
			n.d.	n.d.	n.d.	0.09	43
MIL-53-NH_2	Al	H_2BDC-NH_2	940	0.7-1.3	0.37	0.05	41
			n.d.	n.d.	n.d.	0.09	43
MIL-53-OH	Al	H_2BDC-OH	n.d.	n.d.	n.d.	0.40	43
MIL-53	Ga	H_2BDC	1230	0.8-2	0.47	0.05	41
MIL-53-NH_2	Ga	H_2BDC-NH_2	210	0.8-2	n.d.	0.02	41
MIL-53-$(COOH)_2$	Fe	H_2BDC-$(COOH)_2$	n.d.	n.d.	n.d.	0.16	43
MIL-68	In	H_2BDC	1100	0.6/1.6	0.42	0.32	41
MIL-68-NH_2	In	H_2BDC-NH_2	850	0.6/1.6	0.302	0.32	41
MOF(NDI-SEt)	Zn	Pyrazole ligands	888	n.d.	1.6	0.25	44
MOF(NDI-SO_2Et)	Zn	Pyrazole ligands	764	n.d.	<1.6	0.25	44
MOF(NDI-SOEt)	Zn	Pyrazole ligands	927	n.d.	<1.6	0.30	44
MOF-199	Cu	H_3BTC	1340	n.d.	0.72	0.55	35
			921	2.1	0.492	0.64	45
			1270	0.9,0.6	0.62	0.49	12
MOF-74	Co	DOT	1130	1.11	0.49	0.63	36
MOF-74	Mg	DOT	1250	1.11	0.53	0.75	36
			1400	1.1	0.65	0.62	12
MOF-74	Ni	DOT	1040	1.11	0.46	0.615	36
			639	2.3	0.362	0.48	45
MOF-801-P	Zr	Fumaric acid	990	0.74,0.56,0.48	0.45	0.450	36
MOF-801-SC	Zr	Fumaric acid	690	0.74,0.56,0.48	0.27	0.35	36
MOF-802	Zr	PZDC	1290	0.84,0.74	0.49	0.11	36
MOF-804	Zr	DOT	1145	0.72,0.68	0.46	0.29	36
MOF-805	Zr	NDC-$(OH)_2$	1230	0.95,0.86	0.48	0.415	36
MOF-806	Zr	BPDC-$(OH)_2$	2220	1.26,1.01	0.85	0.425	36
MOF-808	Zr	BTC	2060	1.84	0.84	0.735	36
MOF-841	Zr	H_4MTB	1390	0.92	0.53	0.640	36
PIZOF-2	Zr	PEDB-$(OMe)_2$	2080	1.76	0.88	0.850	36
SIM-1	Zn	4-methyl-5-imidazolecarboxaldehyde	570	0.65	0.303	0.14	41
UiO-66	Zr	H_2BDC	1290	0.84,0.74	0.49	0.535	36
			1032	0.75/1.2	0.77	0.40	42
			1105		0.55	0.39	46
			1160	0.6	0.52	0.37	12
UiO-66-1,4-Naphyl	Zr	1,4-Naphyl	757	n.d.	0.42	0.26	46
UiO-66-2,5-$(OMe)_2$	Zr	2,5-$(OMe)_2$	868	n.d.	0.38	0.42	46
UiO-66-NH_2	Zr	H_2BDC-NH_2	1328	0.75/1.2	0.70	0.38	42
			1123	<0.75/1.2	0.52	0.34	46
			1040	0.6	0.57	0.37	12
UiO-66-NO_2	Zr	H_2BDC-NO_2	792	<0.75/1.2	0.40	0.37	46
UiO-67	Zr	H_2BPDC	2064	1.2/1.6	0.97	0.18	42
ZIF-8	Zn	2-MIM	1255	n.d.	0.64	0.02	35
			1530	1.1	0.485	0.01	41

*Water adsorption properties measured at 298 K at nearly saturated vapor pressure ($P/P_0 \approx 1$),

n.d. = no data.

Ligand abbreviation: 1,3-H_2BDC = 1,3-Benzenedicarboxylic acid / 1,4-Naphyl = 1,4-naphthalenedicarboxylic acid / 2,5-$(OMe)_2$ = 2,5-dimethoxy-terephthalic acid / 2-MIM = 2-methylimidazole / 5- H_2BDC-NH_2 = 5-aminoisophthalic acid / 5- H_2BDC-NO_2 = 5-nitroisophthalic acid / 5- H_2BDC-OH = 5-hydroxyisophthalic acid / DEG = diethylene glycol / DOT or H_2BDC-$(OH)_2$= 2,5-dihydroxy-1,4-benzenedicarboxylic acid / EN = Ethylenediamine / H_2BDC = 1,4-Benzenedicarboxylic acid / H_2BDC-$(COOH)_2$ = 1,2,4,5-benzenetetracarboxylic acid / H_2BDC-NH_2= 2-aminoterephthalic acid / H_2BDC-NO_2= 2-nitro-terephthalic acid / H_2BDC-OH = 2-hydroxyterephthalic acid / H_2BPDC = Biphenyl-4,4′-dicarboxylic acid / H_2BPDC-$(OH)_2$= 3,3'-dihydroxy-4,4'-biphenyldicarboxylic acid / H_2NDC-$(OH)_2$ =1,5-Dihydroxynaphthalene-2,6-dicarboxylic acid / H_2-PEDB-$(OMe)_2$= 4,4'-[(2,5-Dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl)]dibenzoic acid / H_2PZDC = 1H-pyrazole-3,5-dicarboxylic acid / H_2TDC = Thiophene-2,5-dicarboxylic acid / H_3BTC = 1,3,5-benzenetricarboxylic acid / H_4MTB = 4,4',4'',4'''-Methanetetrayltetrabenzoicacid.

3. MOFs applied in water purification

Applying MOFs for water purifications one has to investigate the water stability which is the first priority. The adsorption capacity efficiency, the interaction, and regeneration of materials are considered in a later stage of the research. Herein, an overview of the different MOFs utilized for water purification for the removal of inorganic (such as arsenic, selenium, fluoride, mercury, chromium, etc.) and organic (such as organoarsenic, aromatics, dyes, phenols, sugars, pharmaceuticals, personal care products and herbicides/pesticides) contaminants is given in Table 2.

Table 2. An overview of different MOFs applied for contaminant removal in water purification

Adsorbent (MOFs)	Surface area (m^2/g)	Pore volume (cm^3/g)	Contaminant compound	Capacities (mg/g)	Initial concentration, adsorption condition	ref.
CAU-6	n.d.	n.d.	Fluoride	24.22	40 mg/L, 30°C, pH 6.8	47
	n.d.	n.d.	As(V)	33	10 mg/L, 25°C, pH 10	48
HKUST-1	1492	0.83	Hg(II)	714.29	1431mg/L, 25°C	49
MIL-100(Cr)	1760	0.75	Methyl orange	211.8	30ppm, 30°C, pH 5	50
	1760	0.75	Methylene blue	645.3	30ppm, 30°C, pH 5	50
MIL-100(Fe)	1794	1.12	*p*-arsanilic acid	120	25 mg/L, 25°C, pH 4.3	51
	1794	1.12	Roxarsone	235	25 mg/L, 25°C, pH 4.7	51
	1770	0.76	Methyl orange	1045.2	30ppm, 30°C, pH 5	50
	1770	0.76	Methylene blue	736.2	30ppm, 30°C, pH 5	50
	1626	0.79	Malachite green	266	ppm, 30°C, pH	52
	1626	0.79	Malachite green	485	ppm, 30°C, pH	52
MIL-101(Cr)	3574	1.91	*p*-arsanilic acid	18	25 ppm, 25°C, pH 4.3	51
	3574	1.91	Roxarsone	80	25 ppm, 25°C, pH 4.7	51
	3200	1.35	As (III)	29	10 mg/L, 25°C, pH 7	48
	3200	1.35	As(V)	78	10 mg/L, 25°C, pH 7	48
	n.d.	n.d.	Benzene	1302.6	-	53
	3980	1.85	Toluene	1096	0.55P/P_0, 25°C	54
	3980	1.85	Ethylbenzene	1105	0.55P/P_0, 25°C	54
	3980	1.85	m-Xylene	727	0.55P/P_0, 25°C	54
	3980	1.85	o-Xylene	0.866	0.55P/P_0, 25°C	54
	3980	1.85	p-Xylene	1.246	0.55P/P_0, 25°C	54
	3873	1.7	Methyl orange	114	200ppm, 25°C	10
	846	n.d.	Methyl orange	21	-	55
ED-MIL-101(Cr)	3491	1.37	Methyl orange	160	200 ppm, 25°C	10
PED-MIL-101(Cr)	3296	1.18	Methyl orange	194	200ppm, 25°C	10
Fe_3O_4@MIL-101(Cr)	2270	1.04	As (III)	121	10 mg/L, 25°C, pH 7	48
Fe_3O_4@MIL-101(Cr)	n.d.	n.d.	As (III)	111	10 mg/L, 25°C, pH 10	48
MIL-47(V)	1049	0.36	Benzothiophene	215	1000ppm, 25°C	56
	930	0.36	Ehylbenzene	35wt%	0.035bar, 130°C	57
	930	0.36	m-Xylene	37wt%	0.030bar, 130°C	57
	930	0.36	o-Xylene	36wt%	0.028bar, 130°C	57
	930	0.36	p-Xylene	40wt%	0.035bar, 130°C	57
MIL-53(Al)	920	n.d.	As(V)	105.6	2.428 mg/L, 25°C, pH 8	58
	1282	0.47	Benzothiophene	34	1000ppm, 25°C	56
	1002	0.03	Malachite green	34.9	ppm, 30°C, pH	52
MIL-53(Cr)	n.d.	n.d.	Fluoride	10.3	10mg/L, 30°C, pH 6.8	47
	1510	0.98	*p*-arsanilic acid	23	25 ppm, 25°C, pH 4.3	59
	1510	0.98	Roxarsone	75	25 ppm, 25°C, pH 4.7	51
	1419	0.50	Benzothiophene	80	1000ppm, 25°C	56
	1438	0.55	Methyl orange	57.9	200ppm, 25°C	10
MIL-53(Fe)	14	0.012	As(V)	21.27	5 mg/L, 25°C, pH 5	60
	n.d.	n.d.	Fluoride	16.96	10mg/L, 30°C, pH 6.8	47
MIL-96(Al)	272	n.d.	Fluoride	21.18	5 mg/L, 25°C, pH 7	61
MIL-96(Fe)	n.d.	n.d.	As(V)	12.29	5 mg/L, 25°C, pH 2-10	62
MOF-235	n.d.	n.d.	Methyl orange	477	40ppm, 25°C	63
	n.d.	n.d.	Methylene blue	187	40ppm, 25°C	63

Adsorbent (MOFs)	Surface area (m^2/g)	Pore volume (cm^3/g)	Contaminant compound	Capacities (mg/g)	Initial concentration, adsorption condition	ref.
MOF-74	632	0.39	Sulfur dioxide	194	1%SO_2/N_2, 25°C	64
	632	0.39	Ammonia	93	0.99%$NH_3/N_{2,}$25°C	64
	632	0.39	Chloride	-	4%Cl_2/N_2, 25°C	64
	632	0.39	Tetrahydrothiophene	90	1240ppm, 25°C	64
	632	0.39	Benzene	96	440ppm, 25°C	64
	632	0.39	Dichlomethane	32	-	64
MOF-808	n.d.	n.d.	As(V)	24.83	10 mg/L, room temp.	65
NU-1000	1035	n.d.	Selenite	95	100mg/L, 25°C	66
	1035	n.d.	Selenate	85	100mg/L, 25°C	66
UiO-66(Hf)	n.d.	n.d.	Fluoride	33.35	40 mg/L, 30°C, pH 6.8	47
	n.d.	n.d.	As (V)	80	10 mg/L, 25°C, pH 7	48
UiO-66(Zr)	569	n.d.	As(V)	147.7	50 mg/L, 25°C, pH 7	67
	569	n.d.	As(V)	303.3	50 mg/L, 25°C, pH 2	67
	569	n.d.	As(V)	52	50 mg/L, 25°C, pH 11	67
	n.d.	n.d.	Fluoride	40.09	40 mg/L, 30°C, pH 6.8	47
ZIF-7	n.d.	n.d.	Fluoride	2.57	40mg/L, 30°C, pH 6.8	47
ZIF-8	1063	0.57	As(III)	49.49	20 mg/L, 25°C, pH 7	68
	1063	0.57	As(V)	60.03	20 mg/L, 25°C, pH 7	68
	1388	0.78	As(V)	106.7	5 mg/L, 25°C, pH 7	69
	1258	0.64	As(V)	72.33	5 mg/L, 25°C,	70
	587	0.38	As(V)	50.50	5 mg/L, 25°C,	70
	876	0.55	As(V)	72.67	5 mg/L, 25°C,	70
	1021	0.72	As(V)	74.08	5 mg/L, 25°C,	70
	1167	1.03	As(V)	90.92	5 mg/L, 25°C,	70
ZIF-9	n.d.	n.d.	Fluoride	1.70	40 mg/L, 30°C, pH 6.8	47

n.d.= no data

4. Modification of MOFs for water purification applications

The chemical functionalization of linkers is an option to enhance the stability of MOFs and thus is beneficial for the materials to be used in ambient conditions such as water purification applications. Introduction of a hydrophobic functional group such as alkyl or fluorinated groups and so on, into the framework channels of MOFs enhances the hydrophobic properties of the material resulting in an increased water stability [71]. Incorporation of a methyl group in the sensitive MOF-5 through a solvothermal route generated CH_3MOF-5 and DiCH_3MOF-5 of which the topology was similar to the original MOF-5. The modified MOFs (CH_3MOF-5 and DiCH_3MOF-5) can retain the structure after exposure to ambient air for four days while for the original material (MOF-5) degradation was observed (decrease of intensity in crystal analysis, XRD) after exposure to ambient air for 1 h followed by a completely phase change yielding another structure [72]. Other examples are reported, e.g. Zn-BDC based MOFs (BDC is 1,4-benzenedicarboxylate) bridged with bipyridine ligands (second ligand in MOFs structure) generated the series of MOF-508 (P_1 = 4,4'-bipyridine) SUCTC-18 (P_2 = 2,2'-dimethyl-4,4'-bipyridine), and SCUTC-19 (P_3 = 3,3'-dimethyl-4,4'-bipyridine) [73]. MOF-508 was reported to be unstable in ambient air and the structure fully collapsed after exposing for one week, whereas the SCUTC-19 and SCUTC-18 retained the original structure (up to 7 days for SCUTC-19 and a month for SCUTC-19) after being treated using the same conditions. This work demonstrated that the coordination of a nitrogen atom in the *ortho*-position and a methyl group on the 4,4'-bipyridine linker, improved the water stability.

The ligand-functionalization strategy was designed to investigate the water-resistant TKL-MOFs. The MOFs are constructed from Ni(II) anions with 2,4,6-tri(4-pyridinyl)-1,3,5-triazine (tpt) and o-phthalic acid (OPA) bearing different functional groups (-NH_2, -NO_2, and –F denote as TKL-105, TKL-106 and TKL-107, respectively). The different MOFs of the TKL series all possess a similar structure (isostructural), high crystallinity and showed an enhanced stability of the fluorine-decorated frameworks (Fig. 4). Within the series of fluorine decorated frameworks, the functionalization of OPA at 3-position with F is much more efficient for structure stabilization than that at the 4-position and F atoms play a key role in improving the framework stability, as evidenced by the theoretical study and nitrogen gas adsorption experiments [74]. A similar design was applied on Zr-based MOFs, UiO-66, via substitution of the BDC ligand with different functional groups such as –NH_2, –Br, –NO_2, –Naph, etc [75]. A thermal analysis revealed that UiO-66–Br and UiO-66–1,4–Naph exhibit a higher thermal stability compared to UiO-66, while the nitro-functionalized UiO-66 analogues showed a significant retained crystalline structure in NaOH solution (pH=14). Walton et al. as well, illustrated the effect of polar functional groups (nitro, bromo, hydroxyl, etc.) using the pillared MOF structure $[Zn(L)(Lx)_{0.5}]$ (L= functionalized 1,4-benzenedicarboxylic acid, L_1 = 4,4'-bipyridine, x = 1, L_2 = 4-diazabicyclo[2.2.2]octane, x = 2) [76]. The authors demonstrated that the polar functional groups on the dicarboxylate linker could impact the kinetic/thermodynamic stability of these MOFs, which make them unstable in water, compared with the parent MOFs. This instability effect was generated by a negative shielding effect, accelerating the hydrolysis of metal-ligand bonds. Moreover, the same authors further investigated the water stability and found out that the water stability of the MOFs can be improved through incorporation of hydrophobic/nonpolar functional groups on the BDC ligand.

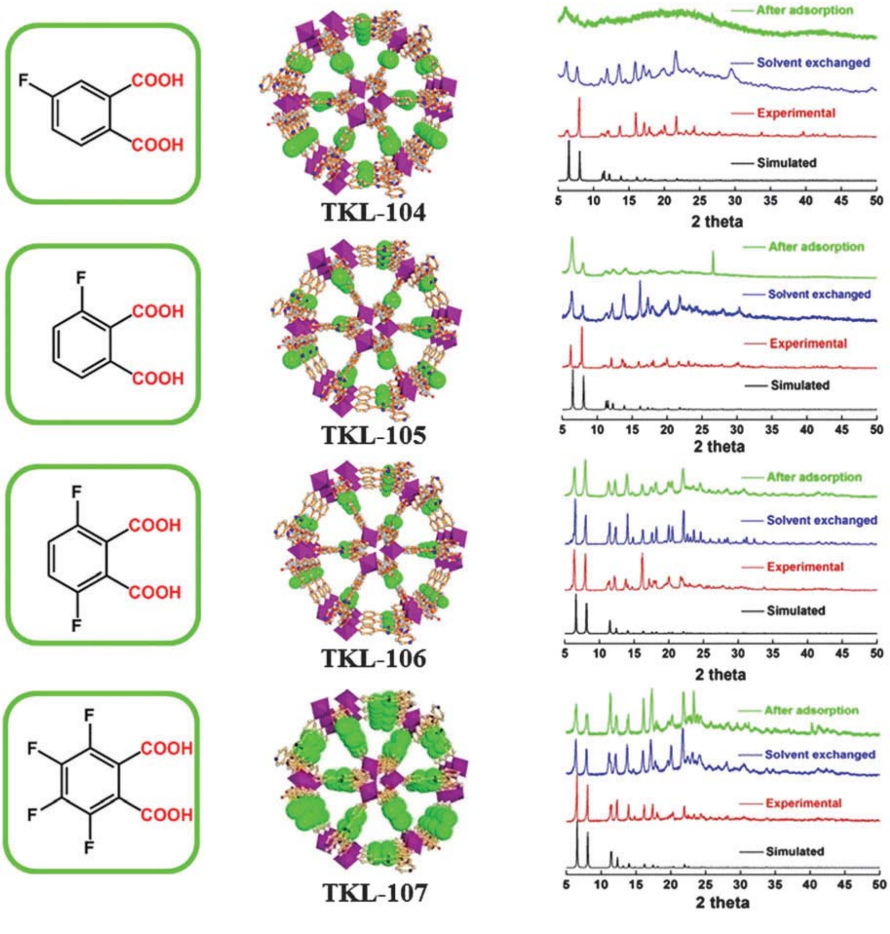

Fig. 4. The fluorine decorated ligands (Left). View of crystal structure of TKL-104 to 107 along the c axis (Center). PXRD patterns of TKL-104 to 107 (Right) (Reproduced with permission from ref. 71)

Surface modification has been adopted to improve the water stability of MOFs. The utilization of hydrophobic functional groups can enhance their stability, and even push forward their practical applications. For instance, IRMOF-3 after using a surfactant-assisted drying technique demonstrated a stable structure in ambient moisture for at least one month [77]. A heat treatment method was applied to IRMOF-1 combined with a carbon-coating technique [78]. For the original IRMOF-1, the results from the characterization indicated that IRMOF-1 had a different XRD pattern and new peaks were found after exposure to air for three days indicating the emergence of hydrolysis of the structure. Whereas the pattern of IRMOF-1 after the carbon coating, no changes were observed indicating that structure remained stable even after fourteen days. Additionally, the surface analysis confirmed the stability of carbon-coated IRMOF-1 since the surface porosity after exposure to air for fourteen days retained, while a sharp decrease from 3450 to 960 $m^2 \cdot g^{-1}$ of IRMOF-1 (untreated) after exposure in the same condition was observed. Surface coating with polydimethysiloxane (PDMS) has been developed to enhance the water stability of MOFs [72]. This strategy is different from other modified materials and improves the stability keeping the porosity intact and preserving good performances in gas adsorption/storage and catalysis. All PDMS-coated samples not only remained their unaltered frameworks and crystallinity for three months or even longer (Fig. 5). The BET for pristine and coated MOF-5 is retained after one day treatment in 55 % humidity.

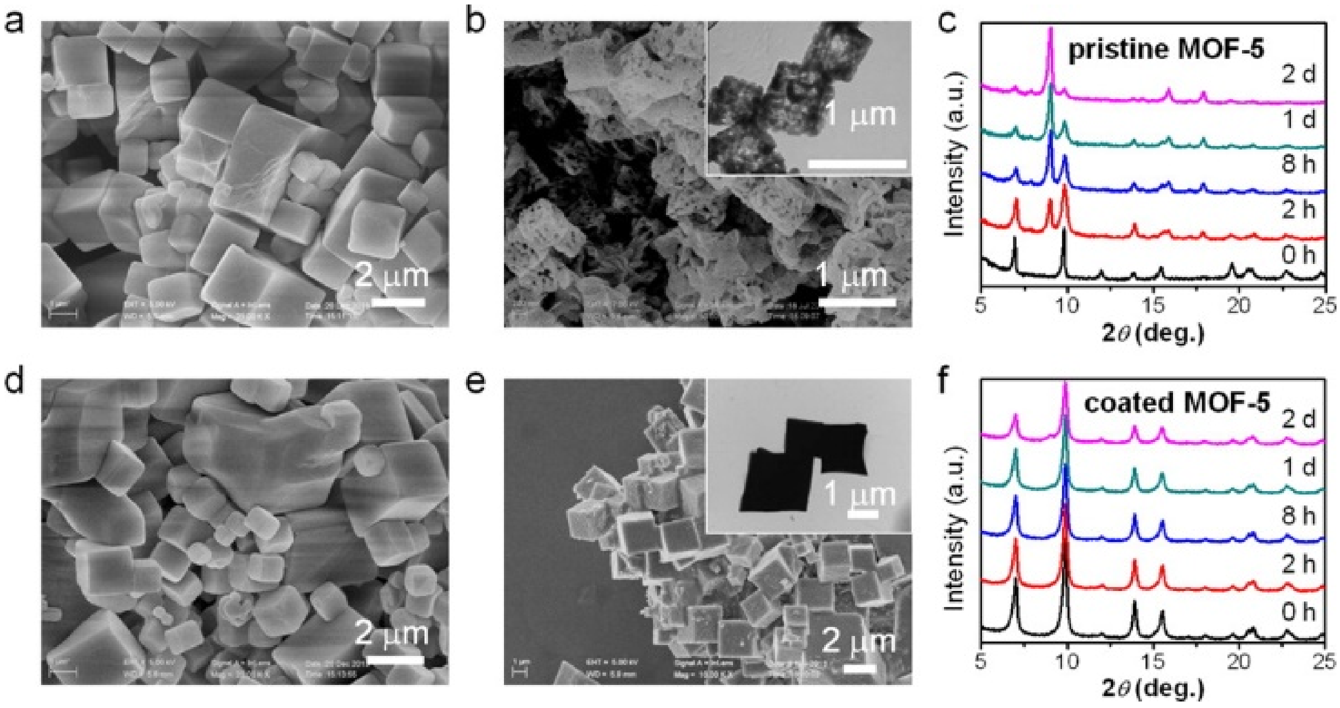

Fig. 5. (a–b) SEM and TEM images of pristine MOF-5. (d–e) SEM and TEM images of PDMS-coated MOF-5. (c–f) Powder XRD patterns of pristine MOF-5 and PDMS-coated MOF-5 exposure to humidity for different times (Reproduced with permission from ref. 67)

5. Conclusion and perspective

Applying MOFs as an adsorbent material for contaminant removal via water purification, the stability of the applied MOF in water and contaminated water should be considered first. The different structures and topologies of MOFs can affect the stability performance of the materials. Generally, the selected metal ion/cluster should exist of highly charged cations, such as Cr^{3+}, V^{3+}, Fe^{3+}, Al^{3+}, Eu^{3+}, Tb^{3+}, $Ti^{4+}$and Y^{3+}, to construct MOF frameworks that possess a good to excellent thermal and water stability. The MOFs from the MIL-family, e. g. MIL-53, MIL-100, MIL-101, MIL-125 etc., are stable in water and acidic gases. While based on the reported mechanisms of the framework decomposition of MOFs, the interaction between metal and linker is the next decisive factor for MOFs design. Compared with the above factors, tuning of structural features within the framework, strengthening of the framework and functionalizing frameworks or framework surface, *etc*., could also be a unique method for the development of water stable MOFs. Up to now, the design and modification for MOFs having excellent water stability are still continuously under investigation since it is important to extend the versatility of MOFs.

Metal-organic frameworks could serve as prospective alternative adsorbent materials for water purification due to their outstanding properties such as high surface area, more sites of metal ions or organic linkers to coordinate contaminant compounds, recyclability of adsorbent after saturation, etc. However, due to the specific circumstances such as acid/base and anion/cation of the wastewater, case-by-case investigations are required. Including, the understanding of the interaction and/or mechanisms between contaminant and MOFs that could guide scientist for new strategies in design or functionalization of MOFs.

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Conflict of interest

The authors declare no conflict of interest.

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